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PETRUCCI HERRING MADURA BISSONNETTE

solutions to b) exercises and even-numbered problems (student) PHYSICAL CHEWISTRY Thermodynamics, Structure, and Change Tenth Edition Peter Atkins [Julio de Paula Foundations A Matter 132.98 19 K 223) 21 H3 JIIB4 108 4 10 A 223 19 H3 K 223 1 St 223 2 IIA 3 IIB4 108 5 VB 6 VIB 7 VIB 8 VIB 6 VIB 6 VIB 7 VIB 8 VIB 6 VIB 6 VIB 7 VIB 8 200 0 C 72.59 50 Sn 118.7 82 Pb 207.2 7 N 14.01 15 P 30.97 33 As 74.92 51 Sb 121.8 38 12 02.0 8 0 16.00 16 5 32.07 34 Se 78.96 52 Te 127.6 84 Pc (29) 9 F 19.00 17 Cl 35.45 35 Br 79.90 53 1 126.9 85 Pr 127.6 84 Pr 102.9 7 Tr 129.2 58 C 140.1 90 Th 22.2 05 Pr 140.9 91 Pr 23.95 36 Kr 83.90 54 Yr 140.9 21 Pr 23 Pr 140.9 91 Pr 23.95 36 Kr 83.90 54 Yr 140.2 91 Pr 23.95 36 Kr 83.90 54 Yr 140.9 21 Pr 24.9 20 Pr 24.9 20 Pr 24.9 197 Pr 24.9 21 Pr

predicted by drawing the Lewis structure and applying the concepts of VSEPR theory. (i) H2O2 Lewis structure: H O O H Orientations caused by repulsions between two lone pair and two bonding pair around each oxygen atom: H O O H Molecular shape around each oxygen atom: bent (or angular) with bond angles somewhat smaller than 109.5^o (ii) FSO3- Lewis structure: (Formal charge is circled.) O S O F O Orientations around the sulfur are caused by repulsions between one lone pair, one double bond, and two single bonds: O F S O O Molecular shape around the sulfur atom is trigonal pyramidal with bond angles somewhat smaller than 109.5^o while the shape around the oxygen to which fluorine is attached is bent (or angular) with a bond angle somewhat smaller than 109.5^o. (iii) KrF2 Lewis structure: F Kr F Orientations caused by repulsions between three lone pair and two bonding pair: F Kr F Molecular shape: linear with a 180° bond angle. (iv) Cl PCl4+ Lewis structure: (Formal charge is shown in a circle.) Cl P Cl Cl Orientations caused by repulsions between four bonding pair (no lone pair): Cl Cl P Molecular shape: tetrahedral and bond angles of 109.5° Cl A.7(b) (i) C (ii) P Nonpolar or weakly polar toward the slightly more electronegative carbon. H δ+ δ- S Cl (c) δ+ N δ- Cl A.8(b) (i) O3 is a bent molecule that has a small dipole as indicated by consideration of electron densities and formal charge distributions. (ii) XeF2 is a linear, nonpolar molecule. (iv) C6H14 is a nonpolar molecule. (iv) C6H14 is a nonpolar molecule that has a small dipole moment $XeF2 \sim C6H14$, NO2, O3 A.10(b) (i) Pressure is an intensive property. (ii) Specific heat capacity is an intensive property. (iii) Weight is an extensive property. (iii) $(6.0221 \times 1023 \text{ molecules}) 22\ 0.028\ mol = 1.7 \times 10\ molecules A\ mol / A.12(b) (0.028\ mol) = 1.7 \times 10\ molecules A\ mol / A.12(b) (0.028\ molecules A\ mol) = 1.7 \times 10\ molecules A\ mol / A.12(b) (0.028\ molecules A\ m$ mol [A.3] (i) (78.11 g) = m n = M 10.0 mol = |781. g (mol) [A.3] (ii) = weight F = m g Mars gravity on Mars (1 kg) - 2 = (781. g) × (3.72 m s - 2) × | = 2.91 kg m s = 2.91 N 1000 g () = p A.13(b) F mg = A A (60 kg) × (9.81 m s - 2) (1 cm 2) (1 30 bar A.14(b) (1 atm) ± 10 bar) | 30 atm ± 10 atm = 10.1325 bar A.15(b) (i) (1.01325 bar A.1 relationship 1 °F / 1 °R (given in the exercise) and knowing the scaling ratios 5 °C / 9 °F and 1 K / 1 °C, we find the scaling factor between the Kelvin and Rankine scale and the value of the scaling relationship implies that: $T/K = 5 \times (\theta R / \circ R) 9 \text{ or } \theta R / \circ R = 95 \times (T/K)$ Normal freezing point of water: $\theta R / \circ R = 95 \times (T/K) = 491.67 \circ R (1 \text{ mol}) (8.314 \text{ J K} - 1 \text{ mol} - 1) (293.15 \text{ K}) (2.00 \text{ dm dm} 3) = -33$ $10 \text{ m}/3 = 1.96 \times 104 \text{ Pa} = 19.6 \text{ kPa}$ mRT M A.19(b) = pV nRT = [A.5] M = mRT \rho RT = pV p where ρ is the mass density [A.2] (0.6388 kg m)(8.314 J K - 3 = mol - 1) (373.15 K) kg mol - 1 = 0.124 = 16.0 \times 103 \text{ Pa} - 1 The molecular mass is four times as large as the atomic mass of phosphorus (30.97 g mol - 1) so the molecular formula is P4. (1 mol) 7.05 g × | 0.220 mol [A.3] n = | 32.00 g / (0.220 mol) (8.314 J K - 1 mol - 1) (373.15.15 K) (cm3) nRT [A.5] = p = | -63 | V 100. cm3 \langle 10 m | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle 10 m | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 6.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (0.25 mol) (8.314 J K - 1 mol - 1) (283.15 K) (100. cm3 \langle ma | A.20(b) = 0.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = pO2 nO2 RT [A.5] = V (100. cm3 \langle ma | A.20(b) = 0.83 \times 106 Pa = 6.83 MPa = nO2 0.25 = mole and nCO2 0.034 mole A.21(b) = 5.9 MPa (10 m) Since the ratio of CO2 moles to O2 moles to O2 moles is 0.034/0.25, we may scale the oxygen partial pressure by this ratio to find the partial pressure of CO2. (0.034) 0.80 MPa pCO2 = | × (5.9 MPa) = (0.25) B p = pO2 + pCO2 [1.6] = 6.7 MPa Energy Answers to discussion questions B.2 All objects in motion have the ability to do work during the process of slowing. That is, they have energy, or, more precisely, the energy possessed by a body because of its motion is its kinetic energy of an object equals the work done on the object in order to change its motion from an initial (i) state of vi = 0 to a final (f) state of vf = v. For an object of mass m travelling at a speed v, Ek = 1.2 mv 2 [B.8]. The potential energy is = = V (h) mgh [B.11] where g 9.81 m s -2 Eqn B.11 assigned to the surface of the Earth, the gravitational potential energy is = = V (h) mgh [B.11] where g 9.81 m s -2 Eqn B.11 assigned to the surface of the Earth, the gravitational potential energy is = V (h) mgh [B.11] where g 9.81 m s -2 Eqn B.11 assigned to the surface of the Earth is position. the gravitational potential energy at the surface of the Earth, V(0), a value equal zero and g is called the acceleration of free fall. The Coulomb potential energy describes the particularly important electrostatic interaction between two point charges Q1 and Q2 separated by the distance r: V (r) = Q1Q2 in a vacuum [B.14, ε 0 is the vacuum permittivity] $4\pi\epsilon 0 r V (r) = Q1Q2$ in a medium that has the relative permittivity ϵr (formerly, dielectric constant) $4\pi\epsilon r \epsilon 0 r$ and Eqn B.14 assigns the Coulomb potential energy when the interaction is attractive and a positive value when it is repulsive. The Coulomb potential energy and the force acting on the charges are related by the expression F = -dV/dr. B.4 Quantized energies are videst apart—for particles of small mass confined to small regions of space. Consequently, quantization is important for the electronic states of atoms and molecules and for both the rotational states of molecules. B.6 The Maxwell distribution of speeds indicates that few molecules have either very low or very high speeds. Furthermore, the distribution peaks at lower speeds when either the temperature is high or the molecular mass is low. Solutions to exercises B.1(b) a = dv/dt = g of the Mars. $\int v(t) dv = \int t = t v 0 = t 0 = s 0$ dv = g dt. The acceleration of free fall is constant near the surface g dt v (t) = g Mars t (i) s (3.72 m s) × (1.0 = mv = (0.0010 kg) × (3.72 m s) × (3.0 = mv = 63 m] = (0.0010 kg) × (11.2 m s) = s) v (3.0 = Ek 1 - 2212 - 1 - 122 B.2(b) The terminal velocity occurs when there is a balance between the force exerted by the pull of gravity, mg = Vparticlepg = $4/3\pi R3\rho g$, and the force of frictional drag, $6\pi\eta Rs$. It will be in the direction of the gravitational pull and have the magnitude sterminal 3 sterminal = $2R2\rho g$ 9 η B.3(b) The harmonic oscillator solution x(t) = A sin(ωt) has been the force of frictional drag, $6\pi\eta Rs$. It will be in the direction of the gravitational pull and have the magnitude sterminal 3 sterminal = $2R2\rho g$ 9 η B.3(b) The harmonic oscillator solution x(t) = A sin(ωt) has been the force of frictional drag. the characteristics that $dx = A\omega \cos(\omega t) dt$ t) v(= 2 kf where = $\omega (kf/m)1/2$ or m ω = xmin = x(t=n $\frac{1}{2}$) π/ω , n=0,1,2...) = 0 and
xmax = x(t=(n+\frac{1}{2})\pi/\omega, n=0,1,2...) = 0 and xmax = x(t=(n+\frac{1}{2})\pi/\omega. equal zero while kinetic energy, Ek, is a maximum. As kinetic energy causes movement away from xmin, kinetic energy continually converts to potential energy causes movement away from xmin, kinetic energy causes mo E = Ek + V = Ek, max, by deriving the expression for the harmonic potential energy. $dV = -Fx dx [B.10] = k f x dx \int V(x) 0 x dV = \int k f x dx 0 V(x) = 12 k f x 2$ Thus, V = 12 k f x 2 Thus, V = 12 k f $ze\Delta \varphi$ or where m = M / NA (2 × 2 × (1.6022 × 10-19 C) × (20 × 103 V) | v = -1 - 23 | ((0.07603 kg mol)/(6.022 × 10 mol) 1/2) | | / 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | | kg | 1/2 (CV) = 3.2 × 105 | infinity is identical to the Coulomb potential drop that occurs when the two ions are brought from an infinite separation, where the interaction potential equals zero, to a separation of r. In a vacuum: $(2e) \times (-2e) = 12 | [B.14] = -1 | [B$ m 2 -1 C) 2) × (250 × 10 - 12 = 3.69 × 10 - 12 = 3.69 × 10 - 18 J m) In water: ((2e) × (-2e) e 2 (QQ) [B.15] where $\varepsilon r = 78$ for water at 25°C w = -V = - | 12 | = - | = | 4\pi\varepsilon r (4\pi\varepsilon r) (250 × 10 - 12 = m) 4.73 × 10 - 20 J B.7(b) We will model a solution by assuming that the NaCl pair consists of the two point charge ions Na+ and Cl-. The electric potential will be calculated along the line of the ions. (-e) e e (11) [B.16] = $\varphi = \varphi Na + \varphi Cl$ [2.17] = + - $|4\pi\epsilon 0 rCl 4\pi\epsilon 0|$ (rNa rCl ||+-+-+- When rNa = rCl |+-+-+-| when rNa = rCl |+-+-+--| when rNa = rCl |+-+-+----| when rNa = rCl |+-+-+---------|the line perpendicular to the internuclear line and crossing the internuclear line at the mid-point so electric potential equals zero at every point on that perpendicular line. $+ - + - B.8(b) \Delta U$ ethanol = energy dissipated by the electric circuit = I $\Delta \phi \Delta t$ [B.20] = 2.41 × 103 C s -1 V s = 2.41 × I03 C s -1 V)ethanol [B.21] ΔU ethanol = (nC) ethanol = ΔT ΔU ethanol 2.41 × 103 J = (mC / M) ethanol (150 g) × (111.5 J K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C C 5.77 kJ K - 1 mol - 1) / (46.07 g mol - 1) = 6.64 K = 6.64 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K or 8.67 °C ΔU 50.0 kJ = [B.21] = 8.67 K (10.0 K) (= 417 J B.11(b) 1 mol) Cs = Cm / M = 1.228 J K - 1 g - 1 (28.24 J K - 1 mol - 1) × (1 22.99 \models g) B.12(b) G Cm = Cs M = 24.4 J K - 1 mol - 1 (0.384 J K - 1 g - 1) × (1 63.55 \models mol / B.13(b) H m - Um = pVm [B.23] = pM \rho = (1.00 × 10 Pa) × (18.02 g mol - 1) (10-6 m3) - 1 | = 1.81 J mol 3 0.997 g cm - 3 cm / / 5 B.14(b) SH O(l) > SH O(s) 2 2 B.15(b) SH O(l, 100 °C) > SH O(l, 0 °C) 2 2 B.16(b) In a state of static equilibrium there is no net force or torque acting on the object in a steady position above the ground, there is a balance between the downward gravitational force pulling on the object downward and the upward force of the hold. Release the object and it falls. A movable, but non-moving, piston within a cylinder may be at equilibrium because of equal pressures on each side of the piston. Increase the pressure on one side of the piston and it moves away from that side. In the Bohr atomic model of 1913 there is a balance between the electron steadily lose kinetic energy, it spirals into the nucleus. Ni – ($\epsilon i - \epsilon j$) / kT – $\Delta\epsilon$ / kT = e = e ij [B.25a] B.17(b) Nj (i) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19 J eV -1) / {(1.381×10-23 J K -1)×(200 K)} N2 = e = 4.2 × 10-51 N1 (ii) – (2.0 eV)×(1.602×10-19) (ii) – (2.0 eV)×(1.602 2.0 eV)×(1.602×10-19 J eV -1)/{(1.381×10-23 J K
-1)×(2000 K)} N2 = e = 9.2 × 10-6 N1 (N) upper -0 B.18(b) Tlim = e = 1 (e - \Delta \epsilon / kT) [B.25a] | Tlim → ∞ N → ∞ (lower / In the limit of the infinite temperature both the upper and the lower state are equally occupied. B.19(b) $\Delta \epsilon = \epsilon$ upper - ϵ lower = h $\nu = (6.626 \times 10-34 J s)(10.0 \times 109 s)$ -1) = 6.63 × 10 - 24 J N upper - (6.63 × 10 - 24 J) / {(1.381 × 10 - 23 J K - 1) × (293 K)} - \Delta \epsilon / klT [B.25a] e = e = N lower 0.998 The ratio Nupper/Nlower indicates that the two states are equally populated. A large fraction of gasphase molecules will be in excited rotational states. B.20(b) Rates of chemical reaction typically increase with increasing temperature because more molecules have the requisite speed and corresponding kinetic energy to promote excitation and bond breakage during collisions at the high temperatures. B.21(b) vmean (303 K) (203 K) (2031/2 1/2 B.22(b) vmean (M 2) = vmean (M 2) = vmean (M 1) (T/M 2) = 1/2 (T/M 1) 1/2 1/2 (M 1) (V/M 2) = 1/2 (T/M 1) 1/2 1/2 (M 1) 1/2 (M Consequently, the equipartition theorem assigns a mean energy of 3 Um = 2 kT to each atom. The molar internal energy is N A kT = 3 2 3 2 3 2 RT = U nU mM -1 = Um = m (8.3145 J mol-1 (1 mol) (3.78 kJ mol-1 (1 mol degrees of freedom (the components of vibrational motion in the x, y, and z directions). Its potential energy also has a quadratic form in each direction because the atoms have no translational or rotational motion. Consequently, the equipartition theorem assigns a mean energy of 6 2 kT = 3kT to each atom. This is the law of Dulong and Petit. The molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U nU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | B.25(b) See exercise B.23(b) for the description of the molar internal energy is U m 3 = N A kT 3RT = 3 (8.3145 J mol-1 U mU mM -1 = Um = = m (1 mol)(7.31 kJ) = | 0.353 kJ (207.2 g) (mol)(10.0 g) | 0.353 kJ (207.2 g) (mol)(10.0 g) | 0.3 of helium. $CV = m \partial U m \partial (32 \text{ RT}) = = \partial T \partial T = R 3 2 3 2 (8.3145 \text{ J mol} - 1 \text{ K} - =) 12.47 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T 24.94 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T 24.94 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T 24.94 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T 24.94 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T = R 3 (8.3145 \text{ J mol} - 1 \text{ K} - =) \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial T \partial T 24.94 \text{ J mol} - = \partial$ sound wave of displaced air molecules that propagates away from the collision with intensity, defined to be the power transferred by the watt per meter squared (W m -2) and 'loudness' increases with increasing intensity. The 'bang' creates a shell of compressed air molecules that propagates away from the source as a shell of higher pressure shell into the adjacent, lower pressure shell into the adjacent, lower pressure shell and the effective propagation of the high density shell. The regions over which pressure and density variations are of the mean free path. Solutions to exercises C.1(b) cbenzene = 3.00×108 ms -1 c [C.4] = 1.97×108 ms -1 rr 1.521ν (106 µm) 1 = |-1| 3600 cm (102 cm) c 3.00×108 ms -1 c $(2.5) = \lambda = 2.78 \mu$ m $\nu = [C.1] = 1.08 \times 1014$ s $-1 = \lambda 2.78 \times 10-6$ m Integrated activities F.2 The plots of Problem F.1 indicate that as temperature increases the peak of the Maxwell- Boltzmann distribution shifts to higher speeds with a decrease in the fraction of molecules that have low speeds and an increase in the fraction that have low speeds and an increase in the fraction that have low speeds and an increase in the fraction that have low speeds with a decrease in the fraction that have low speeds and an increase in the fraction that have low speeds and the frac property because molecular speed is a positive quantity', 'the absolute temperature of 0 K is unobtainable because the area under the plots of Problem F.1 must equal 1'. 1 The
properties of gases 1A The perfect gas Answers to discussion questions 1A.2 The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. Dalton's law because it holds exactly only under conditions where the gases have no effect upon each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation. Solutions to exercises 1A.1(b) The perfect gas law [1A.5] is pV = nRT, implying that the pressure would be nRT p = V All quantities on the right are given to us except n, which can be computed from the given mass of Ar. 25 g $n = 0.626 \text{ mol} - 1.39.95 \text{ g mol} (0.626 \text{ mol}) \times (8.31 \text{ mol})$ × 10-2 dm 3 bar K -1 mol-1) × (30 + 273) K = 10.5 bar 1.5 dm 3 So no, the sample would not exert a pressure of 2.0 bar. so p=1A.2(b) Boyle's law [1.4 dm 3) (i) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (i) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = f f = Vi (2.14 + 1.80) dm 3 (ii) The original pressure in Torr is (1 atm) (760 + 2.14 dm 3) (ii) = 1.07 bar pi = 1.07 bar Torr = 803 Torr \times pi = (1.07 bar) $\times |$ (1.013 bar || (1 atm || 1.013 bar || (1 atm || 1. perfect gas law [1.8], one can compute the amount of gas from pressure, temperature, and volume. $pV = nRT pV (1.00 atm) \times (1.013 \times 105 Pa atm -1) \times (20 + 273)K$ Once this is done, the mass of the gas can be computed from the amount and the molar mass: so $n = -1 m = (1.66 \times 105 mol RT (8.3145 J K - 1mol - 1) \times (20 + 273)K$ Once this is done, the mass of the gas can be computed from the amount and the molar mass: so $n = -1 m = (1.66 \times 105 mol RT (8.3145 J K - 1mol - 1) \times (20 + 273)K$ $105 \text{ mol} \times (16.04 \text{ g mol}) = 2.67 \times 106 \text{ g} = 2.67 \times 103 \text{ kg}$ 1A.5(b) The total pressure is the external pressure at the top of the straw and p the pressure on the surface of the liquid (atmospheric pressure). Thus the pressure difference is $3.1 \text{ kg} (1.5 \text{ mol}) \times (16.04 \text{ g mol}) = 2.67 \times 106 \text{ g} = 2.67 \times 103 \text{ kg}$ $cm p - pex = \rho gh = (1.0 g cm) \times 3 \times |-2| \times (9.81 m s - 2) \times (0.15m) 10 g (10 m) - 3 = 1.5 \times 104 Pa \times (103 g || (10-2 m || \rho gh = 13.55 g))$ cm -3 × | p = 1.013 × 105 Pa + 1.33 × 104 Pa = 1.146 × 105 Pa = 1.146 × 10 $= \rho V p p$ The best value of M is obtained from an extrapolation of ρ/p versus p to zero pressure; the intercept is M/RT. Draw up the following table: Rearrange the perfect gas equation [1A.5] to give R = p/atm 0.750 000 (pVm/T)/(dm3 atm K-1 mol-1) 0.082 0014 0.082 0227 0.082 0414 (ρ/p)/(g dm-3 atm-1) 1.428 59 1.428 22 1.427 From Figure 1A.1(a), R = lim | m | = 0.082 062 dm 3 atm K - 1 mol - 1 p $\rightarrow 0$ (T) Figure 1A.1 (a) 2 (b) (ρ) From Figure 1A.1(b), lim | = 1.427 55 g dm - 3 atm K - 1 mol - 1) $\rightarrow 0$ (p) = 31.9988 g mol - 1 The value obtained for R deviates from the accepted value by 0.005 per cent, better than can be expected from a linear extrapolation from three data points. 1A.8(b) The mass density ρ is related to the molar mass. Putting this relation into the perfect gas law [1A.5] yields pM pVm = RT so = RT ρ Rearranging this result gives an expression for M; once we know the molar mass, we can divide by the molar mass of phosphorus atoms to determine the number of atoms per gas molecule. $-1 M = RT \rho (8.3145 Pa m 3 mol) \times [(100 + 273) K] \times (0.6388 kg m - 3) = p 1.60 \times 104 Pa = 0.124 kg mol - 1 31.0 g mol$ -1 = 4.00 suggesting a formula of P4. 1A.9(b) Use the perfect gas equation [1A.5] to compute the amount; then convert to mass. pV n = pV = nRT so RT We need the partial pressure of water, which is 53 per cent of the equilibrium vapour pressure at the given temperature and standard pressure. (We must look it up in a handbook like the CRC or other resource such as the NIST Chemistry WebBook.) $p = (0.53) \times (2.81 \times 103 \text{ Pa}) = 1.49 \times 103 \text{ Pa} = 1.49 \times 103 \text{ Pa} = 2.72 \text{ kg} - 1 \text{ 1A.10(b)}$ (i) The volume occupied by each gas is the same, since each completely fills the container. Thus solving for V we have (assuming a perfect gas, eqn. 1A.5) n RT V = J pJ We have the pressure of neon, so we focus on it 0.225 g = $1.115 \times 10-2$ mol $\times 8.3145$ Pa m 3 K -1 mol -1×300 K = $3.14 \times 10-3$ m 3 = 3.14 dm 3 8.87×103 Pa (ii) The total pressure is determined from the total amount of gas, n = nCH + nAr + nNe. V = 40.175 g 0.320 g $= 4.38 \times 10-3$ mol $nCH = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol () $n = 1.995 \times 10-2$ mol nAr = -1.439.95 g mol-1.16.04 g mol nArexercise uses the formula, $M = \rho RT$, which was developed and used in Exercise p 1A.8(b). First the density must first be calculated. 33.5 × 10-3 g (103 cm 3) × $\rho = = 0.134$ g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (298 K) = 16.4 g mol -1 152 torr 1A.12(b) This exercise is similar to Exercise 1.12(a) in (0.134 g dm -3) × (62.36 dm 3 torr K mol -1) × (62.36 d that it uses the definition of absolute zero as that temperatures. The solution uses the experimental fact that the volume is a linear function of the Celsius temperature: where V0 = 20.00 dm3 and $\alpha = 0.0741 \text{ dm}3^\circ\text{C}-1$. $V = V0 + \alpha\theta$ At absolute zero, $V = 0 = V0 + \alpha \theta V 20.00 \text{ dm} 3$ so θ (abs.zero) = $-0 = -= 6270^{\circ}C \alpha 0.0741 \text{ dm} 3$; C-1 which is close to the accepted value of -273C. 1A.13(b) (i) Mole fractions are n 2.5 mol xN = N [1A.9] = = 0.63 (2.5 + 1.5) mol ntotal Similarly, $xH = 0.37 \text{ According to the perfect gas law ptotV} = \text{ntotRT 4 ptot} = \text{so ntot RT (4.0 mol)} \times (0.08206 \text{ dm})$ $3 \text{ atm mol}-1 \text{ K} - 1 \times (273.15 \text{ K}) = 4.0 \text{ atm} = V 22.4 \text{ dm} 3$ (ii) The partial pressures are pN = xN ptot = (0.63) × (4.0 \text{ atm}) = 2.5 \text{ atm and pH} = (0.37) × (4.0 \text{ atm}) = 1.5 \text{ atm} (iii) p = pH + pN [1A.10] = (2.5 + 1.5) \text{ atm} = 4.0 \text{ atm} Solutions to problems 1A.2 Solving for n from the perfect gas equation [1A.5] yields n = pV . From the definition of RT Mp Rearrangement yields the desired
relation, namely molar mass n = m, hence $\rho = m = M V RT$. p = ρRT . M Therefore, for ideal gases, find the zero-pressure p/ ρ M by plotting it against p. Draw up the following table. 12.223 0.225 25.20 0.456 36.97 0.664 60.37 $1.062\ 85.23\ 1.468\ 101.3\ 1.734\ 54.3\ 55.3\ 55.7\ 56.8\ 58.1\ 58.4\ Bear$ in mind that 1 kPa = 103 kg m-1 s-2. p is plotted in Figure 1A.2. A straight line fits the data rather well. The extrapolation to p = 0 ρ yields an intercept of 54.0×103 m2 s-2 . Then M= RT (8.3145 J K -1 mol-1) × (298.15 K) = 5.40 × 104 m 2 s -2 = 0.0459 kg mol-1 = 45.9 g mol Figure 1A.2 5 -1 Comment. This method of the determination of the molar masses of gaseous compounds is due to Cannizarro who presented it at the Karlsruhe Congress of 1860. That conference had been called to resolve the problem of the molar masses of gaseous compounds is due to Cannizarro who presented it at the Karlsruhe Congress of 1860. of compounds. 1A.4 The mass of displaced gas is ρV , where V is the volume of the bulb and ρ is the density of the displaced gas. The balance condition for the two gases is m(bulb) = $\rho V(bulb) m(bulb) = \rho V(bulb) m(bulb)$ relation is valid in the limit of zero pressure (for a gas behaving perfectly). In experiment 1, p = 423.22 Torr, p' = 327.10 Torr; 423.22 Torr, p' = 293.22 experiments one should reduce the pressure (e.g. by adjusting the balanced weight). Experiment 1, so it is more likely to be close to the true value: and M \sim 102 g mol-1. Comment. The substantial difference in molar mass between the two experiments ought to make us wary of confidently accepting the result of Experiment 2, even if it is the more likely estimate. 1A.6 We assume that no H2 remains after the reaction has gone to completion. The balanced equation is $N_2 + 3 H_2 \rightarrow 2 NH_3$. We can draw up the following table N2 H2 NH3 Total Initial amount n 0 n' n + n' 2 n - 13 n'n + 13 n'n' 0 Final amount 3 Specifically 0.33 mol 0 1.33 mol 1.66 mol Mole fraction 0.20 0 0.80 1.00 3 ((0.08206 dm atm mol-1 K - 1) × (273.15 K) nRT = (1.66 atm V 22.4 dm 3 ()p(H2) = x(H2)p = 0 p(N2) = x(H2)p = x(H2 is $pV = nRT n = so pV RT At mid-latitudes (1.00 atm) \times \{(1.00 dm 2) \times (250 \times 10-3 cm) / 10 cm dm -1\} = 1.12 \times 10-3 mol (0.08206 dm 3 atm K - 1mol - 1) \times (273 K) The corresponding concentrations$ are n = $6 \ 1.12 \times 10 - 3 \ \text{mol}\ n = 2.8 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{dm}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{mol}\ -3 = 2 \ \text{V}\ (1.00 \ \text{dm}\ \text{m}\ -1)\ \text{n}\ 4.46 \times 10 - 4 \ \text{mol}\ = = 1.1 \times 10 - 9 \ \text{mol}\ \text{mol}\ -3 \ \text{mol}\$ $n = (a) (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ K} - 1) \times (298 \text{ K})$ (b) The mass that the balloon can lift is the difference between the mass of the balloon. We assume that the mass of the balloon is essentially that of the gas it encloses: The volume \times (2.02 g mol) = 9.33 × 103 g - 3 Mass of displaced air = (113 m 3) × (1.22 kg m) = 1.38 × 102 kg (c) For helium, m = nM (He) = (4.62 × 103 mol) × (4.00 g mol - 1) = 18 kg The maximum payload is now 138 kg - 18 kg = 1.2 × 102 kg (1.22 kg m) = 1.38 × 1 states that equal volumes of gases contain equal amounts (moles) of the gases, so the volume mixing ratio is equal to the mole fraction. The definition of partial pressures is pJ = xJp. The perfect gas law is x p p nJ = J = J pV = nRT so $RT RT V n(CCl3 F) (261 \times 10-12) \times (1.0 atm) (a) = 1.1 \times 10-11 mol dm - 3 = V (0.08206 dm 3 atm K - 1mol - 1) \times (1.0 atm) (a) = 1.1 \times 10-12$ (10 + 273) K and n(CCl2 F2) (509 × 10-12) × (1.0 atm) = = $2.2 \times 10-11$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (200 K) and n(CCl2 F2) (509 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) K (b) n(CCl3 F) (261 × 10-12) × (0.050 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm K - 1mol - 1) × (10 + 273) mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.08206 dm 3 atm) = $1.6 \times 10-12$ mol dm -3 V (0.0820 K - 1 mol - 1) × (200 K) 1B The kinetic model Answers to discussion questions 1B.2 The formula for the mean free path [eqn 1B.13] is kT $\lambda = \sigma p$ In a container of constant volume, the mean free path is directly proportional to temperature and inversely proportional to temperatu molecules travel, the farther on average they go between collisions. The latter also makes sense in that the lower the pressure, the less frequent are collisions, 7 and therefore the further the average distance between collisions. The latter also makes sense in that the lower the pressure, the ratio T/p is directly proportional to the size of the container holding a set number of gas molecules. Finally, the mean free path is inversely proportional to the size of the container holding a set number of gas molecules. square of the molecules' radius). Solutions to exercises 1B.1(b) The mean speed is [1B.8] 1/2 (8RT) when $= | (\pi M) |$ The mean translational kinetic energy is 3kT m (3RT) [1B.3] = 22 | (M) | The mean translational kinetic energy is 3kT m (3RT) [1B.3] = 22 | (M) | The mean translational kinetic energy is 3kT m (3RT) [1B.3] = 22 | (M) | The mean translational kinetic energy is 3kT m (3RT) [1B.3] = 22 | (M) | The mean translational kinetic energy is 3kT m (3RT) [1B.3] = 22 | (M) |vmean,Hg (200.6) = (4.003 || 1 2 2 mvrms = Ek 1 Ek 2 = 1 1/2 = 7.079 (ii) The mean translational kinetic energy is independent of molecular mass and dependent of molecular mass and dependent of mean translational kinetic energy is independent with translating kinetic energy is temperature always equals 1. 1B.2(b) The root mean square speed [1B.3] is 1/2 (3RT) vrms = | M | For CO2 the molar mass is M = (12.011 + 2×15.9994)×10-3 kg mol-1 = 44.010×10-3 kg kg mol -1 = 408 m s -1 For He 1B.3(b) = 1.35 × 103 m s -1 = 1.35 km s -1 The Maxwell-Boltzmann distribution of speeds [1B.4] is 3/2 2 (M) v 2 e - Mv / 2 RT f (v) = 4\pi | || 2\pi RT | and the fraction of molecules that have a speed in the range between v1 and v2 is, therefore, $\int v^2 v^1 f(v) dv$. If the range is relatively small, however, such that f(v) is nearly constant over that range, the integral may be approximated by $f(v)\Delta v$, where f(v) is evaluated anywhere within the range and $\Delta v = v^2 - v^1$. Thus, we have, with $M = 44.010 \times 10-3 \text{ kg mol} - 1 \text{ (v)} dv \approx f(v)\Delta v$, where $f(v) \Delta v = 4\pi | |-1|$ $-1 (2\pi (8.3145 \text{ J K mol})(400 \text{ K}) / 8 3/2 (402.5 \text{ m s} - 1) 2 (44.010 \times 10 - 3 \text{ kg mol} - 1)(402.5 \text{ m s} - 1) 2 - 1 \times \exp | - | \times (405 - 400) \text{ m s} - 1 - 1 2(8.3145 \text{ J K mol})(400 \text{ K}) | = 0.0107$, just over 1% 1B.4(b) The most probable, mean, and mean relative speeds are, respectively 1/2 (8RT)(2RT)(1B.9) vmp = | vmean = | || \pi M || M / The temperature is T = (20+273) K = 293 K. so (2(8.3145 J K - 1 mol - 1)(293 K) wrea = $| (\pi \mu | / 1/2 [1B.8] (8RT)$ vrel = $| (\pi \mu | / 1/2 [1B.10b] 1/2 = 1.55 \times 103 \text{ m s} - 1 -
3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K})$ wreas = $| = 1.75 \times 103 \text{ m s} - 1 - 3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K})$ wreas = $| = 1.75 \times 103 \text{ m s} - 1 - 3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K})$ wreas = $| = 1.75 \times 103 \text{ m s} - 1 - 3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K})$ wreas = $| = 1.75 \times 103 \text{ m s} - 1 - 3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K})$ wreas = $| = 1.75 \times 103 \text{ m s} - 1 - 3 - 1 | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10 \text{ kg mol}) (1/2 \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10^{10} \text{ mol} - 1)(293 \text{ K}) | \pi (2 \times 1.008 \times 10^{10} \text{ mol}) (1/2 \text{ mol} - 1)(293 \text$ with an average molar mass of 29.0 g mol-1. In that case, the reduced molar mass [1B.10b] is MA MB (29.0 g mol-1) = 1.88 g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ = MA + MB (29.0 + 2 × 1.008) g mol-1 = μ mass of air just as one computes the average molar mass of an isotopically mixed element, namely by taking an average of the species that have different masses weighted by their abundances. Comment. Note that vrel and vmean are very nearly equal. This is because the reduced mass between two very dissimilar species is nearly equal to the mass of the lighter species (in this case, H2). and 1B.5(b) $1/2 (8(8.3145 \text{ J K} - 1 \text{ mol} - 1)(298 \text{ K}) - 1 \text{ (i) } \text{ mean free path } [1B.13] \text{ is } \text{ kT kT} (1.381 \times 10 - 23 \text{ J K} - 1) / (298 \text{ K}) 1 \text{ Torr } \lambda = = = \times 2 - 12 2 - 9 \sigma \text{ p n d p n} (395 \times 10 \text{ m}) (1 \times 10 \text{ Torr}) 133.3 \text{ Pa} (8RT) = | \pi M | / 1/2 = 6.3 \times 104 \text{ m}$ = 63 km The mean free path is much larger than the dimensions of the pumping apparatus used to generate the very low pressure. (iii) The collision frequency is related to the mean free path and relative mean speed by [1B.12] 1B.6(b) vrel 21/2 vmean λ = vrel so z z = 21/2 (475 m s - 1) = 1.1 × 10 - 2 s - 1.6.3 × 104 m z = λ = λ [1B.10a] The collision diameter is related to the collision cross section by $\sigma = \pi d2$ so $d = (\sigma/\pi)1/2 = (0.36 \text{ nm}2/\pi)1/2 = 0.34 \text{ nm}$. The mean free path [1B.13] is $kT \lambda = \sigma p$ Solve this expression for the pressure and set $\lambda = 3.3 \times 106 \text{ Jm} - 3 = 3.3 \text{ MPa} \sigma \lambda = 0.36 \times (10-9 \text{ m})2 (10 \times 0.34 \times 10-9 \text{ m})$ Comment. This pressure works out to 33 bar (about 33 atm), conditions under which the assumption of perfect gas behavior and kinetic model applicability at least begins to come into question. p= 1B.7(b) kT = The mean free path [1B.13] is $\lambda = kT (1.381 \times 10-23 \text{ J K} - 1)(217 \text{ K}) = 5.8 \times 10-7 \text{ m } \sigma \text{ p } 0.43 \times (10-9 \text{ m})2 (12.1 \times 103 \text{ Pa atm } -1)$ Solutions to problems 1B.2 The number of molecules that escape in unit time is the number per unit time that would have collided with a wall section of area A equal to the area of the small hole. This quantity is readily expressed in terms of ZW, the collisions per unit time with a unit area), given in eqn 19A.6. That is, - Ap dN = -Z W A = dt (2 m kT) 1/2 where p is the (constant) vapour pressure of the solid. The change in the number of molecules inside the cell in an interval Δt is therefore $\Delta N = -Z W A \Delta t$, and so the mass loss is $1/2 1/2 (M)(m) \Delta t \Delta t = -Ap | \Delta w = m\Delta N = -Ap | (2\pi RT || (2\pi RT$ dvxdvy in the circular shell of radius v. The sum of the area elements is the area of the circular shell of radius v and thickness dv which is $\pi(v+dv)^2 - \pi v^2 = 2\pi v dv$. Therefore, $2(M) - Mv^2/2 RT(m)v ef(v) = ||ve - mv/2kT e|| RT || kT ||$ 0 0 | kT | Using integral G.3 from the Resource Section yields (m) ($\pi 1/2$) (2kT) vmean = | |×| × | kT || (4 || || (m || 1B.6 3/2 (πkT) = | (2m kT || 2m kT || (2m kT) $0 3/2 \int vrms 0 v 2 e - Mv 2/2 RT dv Defining a \equiv R/2RT$, $(a)P = 4\pi | ||\pi|/3/2 \int vrms 0 (a) dv = -4\pi | ||\pi|/3/2 \int vrms 0 (a) dv = -4\pi | ||\pi|/3/2 \int vrms 0 (a) dv = -4\pi | ||\pi|/3/2 \int vrms a1/2 0 2 e - \chi d\chi 3/2 dvrms - av2 dv e da f0 } (0) (0) 3/2 vrms a1/2 2 || 1 1 e - \chi d\chi + 1 ||- \int 0 2 a a || Then we use the error function$ [Integral G.6]: $(a) = -4\pi \left[\frac{1}{2} 0 \frac{3}{2} (2 \frac{1}{2} \frac{$ $2vrms a1/2 / \pi 1/2 e Now (3RT) vrms = | (M || and P = erf || (| 1/2 (3RT) vrms a1/2 = | (M || so) 1/2 (M) × | (2RT || 1/2 3 = 0.61 2 || || (\pi || (Therefore, (a) 1 - P = 39\% have a speed less than the root mean square speed. (b) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed less than the root mean square speed. (c) P = 61\% of the molecules have a speed less than the root mean square speed less thave square speed less thave$ root mean square speed. (c) For the proportions in terms of the mean speed vmean, replace vrms by (vmean = $\frac{8kT}{\pi}$) + (e (= erf $2/\pi 1/2$) - (4/ π) = $-\frac{4}{\pi}$ vmean $\frac{1}{2}$) - 2vmean $\frac{1}{2}$ (2 (vrms)) = $-\frac{8kT}{\pi}$ (c) For the proportions in terms of the mean speed vmean, replace vrms by (vmean = $\frac{8kT}{\pi}$) + (e (= erf $2/\pi 1/2$) - (4/ π) = $-\frac{4}{\pi}$ vmean $\frac{1}{2}$ (vrms) = $-\frac{8kT}{\pi}$ (c) For the proportions in terms of the molecules have a speed less than the mean, and 47% have a speed greater than the mean. 1B.8 The average is obtained by substituting the distribution (eqn 1B.4) into eqn 1B.7: $(M) = 4\pi | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+1)! (2RT) | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+1)! (2RT) | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int
\infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 \int \infty 0 v n+2 e - Mv (n+2) | 2 | (n+4) | (2\pi RT | 3/2 3/2 f) | (n+4) | (2\pi RT | 3/2 3/2 f) | (n+4) | (2\pi RT | 3/2 3/2 f) | (n+4) | (2\pi RT | 3/2 f) | ($ $(n+1)!! = 1 \times 3 \times 5 \dots \times (n+1) 1/2 \text{ Thus vn } 1/n \left[\left(RT \right) \right] = \{(n+1)!! \mid (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid n/2 \mid n/2 \mid n/2 \mid | (M \mid | dv 1/2 \mid n/2 \mid n/2$ $v = \{ 1/2 \mid = \} \pi (M \mid \mid \mid \pi 1/2n \mid (M \mid \mid \mid \mid \pi 1/2n \mid (M \mid \mid \mid \mid)]$ Question. Show that these expressions reduce to vmean and vrms for n = 1 and 2 respectively. n 1B.10 1/n Dry atmospheric air is 78.08% N2, 20.95% O2, 0.93% Ar, 0.04% CO2, plus traces of other gases. Nitrogen, oxygen, and carbon dioxide contribute 99.06% of the molecules in a volume with each molecule contributing an average rotational energy equal to kT. (Linear molecules can rotate in two dimensions, contributing two "quadratic terms" of rotational energy, or kT by the equipartition theorem [Topic B.3(b)]. The rotational energy density is given by 0.9906N ε E 0.9906NkT = 0.9906 p = ρ R = R = V V V = 0.9906(1.013 × 105 Pa) = 1.004 \times 105 J m -3 = 0.1004 J cm -3 The total energy density is translational plus rotational (vibrational energy contributing negligibly): R ptot = ρ T + ρ R = 0.15 J cm -3 = 0.25 J cm approximated by a sum over a discrete set of velocity values. For convenience, let the velocities vi be evenly spaced within the interval software, make a column of velocity values and then a column for f(v) [1B.4] at 300 K and at 1000 K. Figure 1B.1 shows f(v)plotted against v for these two temperatures. Each curve is labeled with the numerical value of T/K, and each is shaded under the curve between v = a and v = b. One should take some care to avoid double counting at the edges of the interval, that is, not including both endpoints of the interval with full weight. example, beginning the sum with the area under the curve at those speeds. Using a spreadsheet that evaluates f(v) at 5-m s-1 intervals, and including points at both 100 and 200 m s-1, 200 m s-1, 200 m s-1, 200 m s-1) ≈ 0.281 at 300 K and 0.066 at 1000 K. Figure 1B.1 12 1C Real gases Answers to discussion questions 1C.2 The critical constants represent the state of a system at which the distinction between the liquid and vapour phases can no longer coexist, though supercritical fluids have both liquid and vapour characteristics. 1C.4 The van der Waals equation in the volume, V. Every cubic equation in the volume, V. Every cubic equation in the volume, V. Every cubic equation in the volume of real roots passes from three to one. In fact, any equation of state of odd degree n > 1 can in principle account for critical behavior because for equations of odd degree in V there are necessarily some values of V converge from n to 1 as the temperature approaches the critical temperature. This mathematical result is consistent with passing from a two phase region (more than one volume for a given T and p) to a one phase region (only one V for a given T and p), and this corresponds to the observed experimental result as the critical point is reached. Solutions to exercises 1C.1(b) The van der Waals equation [1C.5a] is 2 an p = nRT - 2 V - nb V From Table 1C.3 for H2S, a = 4.484 dm6 atm mol-1 and b = 0.0434 dm3 mol-1. (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (273.15 K) (i) p = 22.414 dm 3 - (1.0 mol) × (4.34 × 10-2 dm 3 mol-1) - (ii) p = -1C.2(b) (4.484 dm 6 atm mol-2) × (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (500 K) 0.150 dm 3 - (1.0 mol) × (4.34 × 10-2 dm 3 mol-1) - (ii) p = -1C.2(b) (4.484 dm 6 atm mol-2) × (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (500 K) 0.150 dm 3 - (1.0 mol) × (4.34 × 10-2 dm 3 mol-1) - (ii) p = -1C.2(b) (4.484 dm 6 atm mol-2) × (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (500 K) 0.150 dm 3 - (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (500 K) 0.150 dm 3 - (1.0 mol) × (0.08206 dm 3 atm mol-1) - (ii) p = -1C.2(b) (4.484 dm 6 atm mol-2) × (1.0 mol) × (0.08206 dm 3 atm mol-1 K - 1) × (500 K) 0.150 dm 3 - (1.0 mol) × (0.08206 dm 3 atm mol-1) - (ii) p = -1C.2(b) (4.484 dm 6 atm mol-2) × (1.0 mol) × (0.08206 dm 3 atm mol-1) × (0.08206 dm 3 atm mo $(4.484 \text{ dm 3 atm mol}-1) \times (1.0 \text{ mol})2 = 190 \text{ atm} (2 \text{ sig. figures}) (0.150 \text{ dm 3})2$ The conversions needed are as follows: 1 atm = 1.013 × 105 Pa, 1 Pa = 1 kg m - 1 s - 2 10 - 6 m 6 × 1 atm dm 6 = 1.34 × 10 - 1 kg m 5 s - 2 mol - 2 and 2 mol - 2 and 2 mol - 2 mol - 2 and 2 mol - 2 mol $1C.3(b) b = 0.0426 dm 3 mol - 1 \times 10 - 3 m 3 = 4.26 \times 10 - 5 m 3 mol - 1 dm 3 The compression factor Z is [1C.1] V pVm Z = m^{\circ} = RT Vm (i) Because Vm = Vmo + 0.12 Vmo = (1.12) Vmo = ($ mol 12 atm | Since Vm > Vmo repulsive forces dominate. 1C.4(b) (i) According to the perfect gas law 3 RT (8.3145 J K - 1 mol - 1) × (298.15 K) (1 dm $| \times | -1 | = 0.124$ dm 3 mol - 1 = V = -1 p $| 10 \text{ m} | (200 \text{ bar}) \times (105 \text{ Pa bar})$ (ii) The van der Waals equation [1C.5b] is a cubic equation in Vm. Cubic equations can be solved analytically. However this approach is cumbersome, so we proceed as in Example 1C.1. The van der Waals equation is rearranged to the cubic form (RT)2 (a) ab with x = Vm/(dm3 mol-1). x3 - |b + |p / p(p) t will be convenient to have the pressure in atm: 1 atm 200 bar x = 197.4 atm 1.013 bar The coefficients in the equation are RT (0.08206 dm 3 atm mol-1 K - 1) × (298.15 K) b + = (3.183 × 10-2 dm 3 mol-1) + p 197.4 atm or = (3.183 × 10-2 + 0.1239) dm 3 mol-1) + p 197.4 atm or = (3.183 × 10-2 dm 3 mol-1) + p 197.4 atm or = \times 10-4 dm 9 mol-3 p 197.4 atm Thus, the equation to be solved is x 3 - 0.1558x 2 + (6.89 \times 10-3)x - (2.193 \times 10-4) = 0. Calculators and computer software for the solution of polynomials are readily available. In this case we find x = 0.112 dm3 mol-1. The perfect-gas value is about 15 percent greater than the van der Waals result. 1C.5(b) The molar volume is obtained by solving Z = Vm = pVm [1C.2], for Vm, which yields RT ZRT (0.86) × (0.08206 dm 3 atm mol-1 K - 1) × (300 K) = 1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm
= (8.2 × 10-3 mol) × (1.06 dm 3 mol-1 = p 20 atm V = nVm = (8.2 × 10-3 mol) × (1.06 truncation of the series expansion after the second term, B/Vm, in the series. Then, $pV = 1 = Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = (1.06 \text{ dm 3 mol} - 1) \times (0.86 - 1) = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \setminus RT = -0.15 \text{ dm 3 mol} - 1 + Vm \times (Z - 1) \times$ $49.3 \text{ cm } 3 \text{ mol} - 1 = 0.0493 \text{ dm } 3 \text{ mol} - 1 3 14 - 2 \text{ and } a = 3 \times (0.148 \text{ dm } 3 \text{ mol} - 1)2 \times (48.20 \text{ atm}) = 3.17 \text{ dm } 6 \text{ atm mol} \text{ mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ atm mol} - 1 \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ along with } 27 \text{ RbTc } 9 \text{ RVcTc } a = 8 8 9 (0.08206 \text{ dm } 3 \text{ atm mol} - 1 \text{ k} \text{ same value of } b \text{ atm mol} - 1 \text{ same value of } b \text{ atm mo$ -1)(0.148 dm 3 mol-1)(305.4 K) = 8 6 -2 = 4.17 dm atm mol Or we could use Tc along with pc. In that case, we can solve the pair of equations for a equal to each other: 27BTc a = 27b2 pc = 8 Solving the resulting equation for b yields RTc (0.08206 dm 3 atm mol-1 K -1)(305.4 K) = = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 K - 1)(305.4 K) = 0.06499 dm 3 atm mol-1 mol-1 b= 8(48.20 atm) 8 pc and then a = 27(0.06499 dm3 mol-1)2(48.20 atm) = 5.497 dm6 atm mol-2 3.17 4.17 5.497 b/dm3 mol-1 0.0493 0.06499 One way of selecting best values for these parameters would be to take the mean of the three determinations, namely a = 4.28 dm6 atm mol-2 and b = 0.0546 dm3 mol-1. By interpreting b as the excluded volume of a mole of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e., twice their radius); that volume times the Avogadro constant is the molar excluded volume b (4π (2r)3) b = NA 3 ||(1 (3b) so r = |2 (4π NA ||1 (3(0.0546 dm 3 mol-1)) r= |2 (4π NA ||1 (3(0.0546 dm 3 mol-1)) r= |2 (4π ($6.022 \times 1023 mol-1$) ||1C.7(b) 1/3 1/3 = 1.39 × 10-9 dm = 0.139 nm The Boyle temperature, TB, is the temperature at which the virial coefficient B = 0. In order to express TB in terms of a and b, the van der Waals equation [1C.5b] must be recast into the form of the virial equation. a RT - 2 p = Vm - b Vm a || RT || 1 Factoring out RT yields p = - | Vm Vm || 1 - b / Vm RTVm || So long as b/Vm < 1, the first term inside the brackets can be expanded using (1-x)-1 = 1 + x + x2 + ..., which gives $|a \rangle (1)$ RT || (|x| + L) p = 1+ b - RT / Vm / Vm / Vm / Vm | (|) a We can now identify the second virial coefficient as B = b - RT 15 At the Boyle temperature 27Tc a a so TB = = bR 8 RTB 6 - 2 (i) From Table 1C.3, a = 4.484 dm atm mol and b = 0.0434 dm 3 mol - 1. Therefore, B = 0 = b - (4.484 dm 6
atm mol - 2) = 1259 K (0.08206 L atm mol - 1 K - 1) × (0.0434 dm 3 mol - 1) (ii)As in Exercise 1C.6(b), TB = $(4\pi (2r)3)$ b = NA $3 \parallel (1 (3b) \text{ so } r = |2 (4\pi \text{ N A } || (3(0.0434 \text{ dm 3 mol}-1))r = |2 (4\pi (6.022 \times 10-9 \text{ dm } = 0.129 \text{ nm } 1C.8(b) \text{ States that have the same reduced pressure, temperature, and volume } [1C.8] are said to correspond. The reduced pressure and$ temperature for N2 at 1.0 atm and 25°C are [Table 1C.2] p 1.0 atm T (25 + 273) K = = 0.030 and Tr = = 2.36 (304.2 K) = 718 K p = 2.36(304.2 K) = 718 K p = 2.36(373.3 K) = 881 K p = 0.030(89.7 atm) = 2.67 atm (ii) For CO2 T = 2.36(304.2 K) = 718 K p = 2.36(373.3 K) = 881 K p = 0.030(89.7 atm) = 2.67 atm (iii) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iii) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 2.36(304.2 K) = 718 K p = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm) = 2.67 atm (iv) For CO2 T = 0.030(89.7 atm)0.030(72.9 atm) = 2.2 atm (iii) For Ar T = 2.36(150.7 K) = 356 K p = 0.030(48.0 atm) = 1.4 atm 1C.9(b) The van der Waals equation [1C.5b] is a RT - 2 p = Vm - b Vm which can be solved for b RT (8.3145 J K - 1 mol - 1) × (288 K) b = Vm - = $4.00 \times 10 - 4 \text{ m 3 mol} - 1 - a (0.76 \text{ m 6 Pa mol} - 2) p + 24.0 \times 106 \text{ Pa} + | \text{ Vm} | (4.00 \times 10 - 4 \text{ m 3 mol} - 1) 2$ $||= 1.3 \times 10-4 \text{ m 3 mol}-1$ The compression factor is pVm (4.0 × 106 Pa) × (4.00 × 10-4 \text{ m 3 mol}-1) = 0.67 Z= [1C.2] = RT (8.3145 J K -1 mol-1) × (288 K) Solutions to problems 1C.2 From the definition of Z [1C.1] and the virial equation [1C.3b], Z may be expressed in virial form as 2 (1) (1) Z = 1 + B | + C | + L (Vm) (Vm) 16 p Since Vm = RT (by assumption of approximate perfect gas behavior), 1 = ; hence upon Vm RT p () substitution, and dropping terms beyond the second power of |1| (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / p) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | / (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | (Vm / (P) (p) + C | Z = 1 + B | (RT | $-1.3 (0.08206 \text{ dm atm mol K}) \times (273K)$ ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 = 1 - 0.0968 + 0.0239 = 0.927 (RT) Vm = (0.927) ||2 =Since B'(TB) = 0 at the Boyle temperature [Topic 1.3b]: B'(TB) = a + be - c/TB2 = 0 1/2 Solving for TB: 1C.6 [$-cT = \{B \mid ln - a \ b \mid () 1/2 \} = 5.0 \times 10 \ K - 1 \mid ln (-(-0.1993bar)) \mid |U| (0.2002 \ bar - 1) \mid |U| (1) (2aR), pc = |X| 3 \mid |U| ($ an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e., twice their radius); that volume times the Avogadro constant is the molar excluded volume b ($4\pi(2r)3$) b = NA | 3 || (1(3b)) so $r = | 2 (<math>4\pi N A ||) 1(160 \text{ cm } 3 \text{ mol} - 1 r = | 23 - 1 | 2 (<math>4\pi(6.022 \times 10^{-1} \text{ mol} + 1$ mol) $\int 1C.8 \frac{1}{3} \frac{1}{V} \left[\text{Exercise 1C.6(b)} \right] = |c|^2 \left(\frac{4\pi N A}{1} \frac{1}{3} \frac{1}{3} = 1.38 \times 10 - 8 \text{ cm} = 0.138 \text{ nm} \text{ Substitute the van der Waals equation [1C.5b] into the definition of the compression factor [1C.2] 17 Z = pVm 1 [Exercise 1C.7(a)] = -a RTVm RT (b | 1 - V | (m) - 12 (c) (which upon expansion of | 1 - b | = +1 b + | b | + yields VV (Vm) m / m 2$ 1 when 1C.10 The Dieterici equation is -a/RTV m RTe [Table 1C.4] Vm - b At the critical point the derivatives of p with respect to Vm equal zero along the isotherm defined by T = Tc. This means that $(\partial p / \partial Vm) T = 0$ and $(\partial 2 p / \partial Vm2) T = 0$ at the critical point. $p = \int |aVm - ab - RTVm2| (\partial p) = p \langle 2 \rangle |\partial V| (m / T | Vm (Vm - b)(RT))|$ and -2aVm2 + 4Vm ab + RTVm3 - 2ab 2) ($\partial 2 p$) ∂p $\partial aVm - ab - RTVm2$ = $+ p | 2 || | 2 Vm3 || (Vm - b) (RT) || (<math>\partial Vm /T | \partial Vm /T | \partial Vm /T | 0 Vm - b)$ (RT) || ($\partial Vm /T | \partial Vm /T | 0 Vm /T | 0 Vm - b)$ (RT) || ($\partial Vm /T | 0 Vm /T$ - RTcVc2 = 0 - 2aVc2 + 4Vc ab + RTcVc3 - 2ab2 = 0 Solving the middle equation for Tc, substitution of the result into the last equation, and solving for Vc yields the result b = Vc / 2 Vc = 2b into the middle equation and solving for Tc gives the result or a = 2RTcVc Tc = a / 4bR Substitution of Vc = 2b and Tc = a / 4bR into the first equation for Vc, Tc, pc are substituted into the equation for Vc = 2RTcVc Tc = a / 4bR Substituted into the equation for Vc = 2RTcVc Tc = a / 4bR Substituted into the first equation for Vc = 2RTcVc Tc = a / 4bR Substituted into the equation for Vc = 2RTcVc Tc the critical compression factor that is predicted by the van der Waals equation: Zc (vdW) = pcVc / RTc = 3 / 8 = 0.3750. Experimental values for Zc are pc = 18 summarized in Table 1C.2 where it is seen that the Dieterici equation prediction is often
better. 1C.12 pVm = 1 + B 'p + C 'p 2 + [1C.3a] RT pVm 1 B + C2 + [1C.3b] = + RT Vm Vm Thus B 'p + C 'p 2 + [1C.3a] RT pVm 1 B + C2 + [1C.3b] = + RT Vm Vm Thus B 'p + C 'p 2 + [1C.3a] RT pVm 1 B + C2 + [1C.3b] = + RT Vm Vm Thus B 'p + C 'p + C 'p + (1C.3b] = + RT Vm Vm Thus B 'p + C 'p + (1C.3b] = + RT Vm Vm Thus B 'p + (1C.3b) + + C'p 2 + = B + C2 + Vm Vm Multiply through by Vm, replace pVm by RT{1+(B/Vm) + ...}, and equate coefficients of powers of 1/Vm: 2 2 B'RT + BB'RT + C'R T + = B + C + Vm Vm Hence, B'RT = B, implying that B' = 1C.14 B RT Also BB'RT + C'R2T2 = C = B2 + C'R2T2, implying that C' = Write (∂V)(∂V)Vm = f(T, p); then dVm = | m | dT + $|m|dp \partial T \langle \partial p|T \langle \partial p|T \langle \partial p|T \rangle = -|\partial p|x| \langle \partial T|| = -|\partial p|x|$ $RVm + b(\partial p)bR|(\partial T|) = V + V 2 = V 2 m V m m m Substituting ()(RVm + b)(\partial Vm)Vm 3 RVm 2 + bVm = = |||| \partial T || || P | Vm RT + 2(a + bT) || Vm 2 || P | Vm RT + 2(a + bT) || Vm 2 || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2(a + bT) || P | Vm RT + 2($ where $Vm^\circ =$ the molar volume of a perfect gas $Vm = b + = b + Vm \circ p$ For Vm = 10b = = 1.11 9b 9 1C.18 The virial equation is () B C + 2 + |[1C.3b] pVm = RT | 1 + Vm Vm 2 (a) If we assume that the series may be truncated after the B term, then a plot of pVm vs 1 RT Vm will have B as its slope and 1 as its y-intercept. Transforming the data gives p/MPa Vm/(dm3 mol-1) (1/Vm)/(mol dm-3) pVm/RT 0.4000 6.2208 0.1608 0.9976 0.5000 4.1423 0.2414 0.9964 0.8000 3.1031 0.3223 0.9952 1.000 2.4795 0.4033 0.9941 1.500 1.6483 $0.6067\ 0.9912\ 2.000\ 1.2328\ 0.8112\ 0.9885\ 2.500\ 0.98357\ 1.017\ 0.9858\ 3.000\ 0.81746\ 1.223\ 0.9832\ 4.000\ 0.60998\ 1.639\ 0.9782$ Figure 1C.1(a). The data are plotted in Figure 1C.1(a). The data fit a straight line reasonably well, and the yintercept is very close to 1. The regression yields B = -1.324 \times 10-2\ dm3\ mol-1. (b) A quadratic function fits the data somewhat better (Figure 1C.1(b)) with a slightly better correlation coefficient and a y-intercept closer to 1. This fit implies that truncation of the virial series after the term with C is more accurate than after just the B term. The regression then yields 20 Figure 1C.1(b) B = $-1.503 \times 10-2$ dm3 mol-1 1C.20 and C = $-1.06 \times 10-3$ dm6 mol-2 The perfect gas equation [1A.5] gives RT (8.3145 J K -1 mol-1)(250 K) = = 0.0139 m 3 = 13.9 dm 3 p 150 × 103 Pa The van der Waals equation in Vm. Cubic equati Vm = (ab RT) 2 (a x + |x - with x = Vm/(dm3 mol-1)) = 0 x3 - |b + p xp // It will be convenient to have the pressure in atm: 1 atm 150 kPa × = 1.48 1 atm 101.3 kPa The coefficients in the equation are RT (0.08206 dm 3 atm mol-1 K - 1) × (250 K) b+ = (5.42 × 10-2 dm 3 =0 V + V - Vm3 - 1 h +mol-1) + p 1.48 1 atm or = (5.42 × 10-2 + 13.85) dm 3 mol-1 = 13.9 1 dm 3 mol-1 = 13.9 1 dm 3 mol-2 = 4.23 dm 6 mol-2 p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3 = p 1.48 1 atm mol-2) × (5.42 × 10-2 dm 9 mol-3) = 0. Calculators and computer software for the solution of polynomials are readily available. In this case we find x = 13.6 and Vm = 13.6 dm3 mol-1. Taking the van der Waals result to be more accurate, the error in the perfect-gas value is 13.9 - 13.6 × 100% = 2% 13.6 21 Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K. 2 The First Law 2A Internal energy Answers to discussion questions 2A.2 Work is a precisely defined mechanical concept. It is produced from the application of a force through a distance. The technical definition is based on the realization that both force and displacement are vector quantities and it is the component of the force through a distance. acting in the direction of the displacement that is used in the calculation of the amount of work, that is, work is the scalar product of the two vectors. In vector notation $w = -F \cdot d = -fd \cos \theta$, where θ is the angle between the force and the displacement. The negative sign is inserted to conform to the standard thermodynamic convention. Heat is associated with a non-adiabatic process and is defined as the difference between the adiabatic work associated with the same change in state of the system. This is the formal (and best) definition of heat and is based on the definition of heat as the formal (and best) definition of heat and is based on the definition of heat as the difference between the adiabatic work associated with the same change in state of the system. that is transferred between bodies in thermal contact with each other by virtue of a difference in temperature. The interpretations of heat and work in terms of energy levels and populations is based upon the change in the populations of those levels as explained more fully in Chapter 15 of this text. The statistical thermodynamics of Chapter 15 allows us to express the change in total energy of a system in a reversible, isothermal expansion can be identified with the second term on the right of this expression, since there is no change in the populations of the levels which depend only on temperature; hence, the first term on the right is zero. Because the influx of energy as heat does not change the energy levels of a system, but does result in a change in temperature; hence, the first term on the right of the above equation is zero and the heat associated with the process (a constant volume process, with no additional work) can be identified with the first term. The change in temperature, which redistributes the molecules over the fixed energy levels. Solutions to exercises 2A.1(b) See the solution to Exercise 2A.1(a) where we introduced the following equation based on the material of Chapter 15. CV .m = 12 (3 + vR* + 2vV*) R with a mode active if T > θ M (where M is T. R. or V). (i) O3 : CV .m = 12 (3 + 3 + 0)R = 3R [experimental = 3.7R] E = 3 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E
= 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 J K -1 mol -1 × 298.15 K = 7.436 kJ mol -1 (ii) C2 H 6 : CV .m = 12 (3 + 3 + 2 × 1)R = 4R [experimental = 6.3R] E = 4 RT = 4 × 8.314 H (experimental = 8.3R] E = 4 RT = 4 × 8.314 H (experimental = 8.3R] E = 4 RT = 4 × 8.314 H (experimental = 8.3R] E = 4 RT = 4 × 8.314 H (experimental = 8.3R] E = 4 RT = 4 × 8.314 H (experimental = 8.3R] E = 4 RT = 4 × 8.314 H (ex $K - 1 \text{ mol} - 1 \times 298.15 \text{ K} = 9.915 \text{ k} \text{ mol} - 1 2:1$ (iii) SO 2 : CV, m = 1 2 (3 + 3 + 0) R = 3R [experimental = 3.8R] E = 3RT = 3 \times 8.314 \text{ J} K - 1 \text{ mol} - 1 \times 298.15 \text{ K} = 7.436 \text{ k} \text{ mol} - 1 \text{ Consultation of Herzberg}, Molecular spectra and Molecular spectr among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in C2H6, corresponding to the "internal rotation" of CH3 groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity—albeit not to the full equipartition value—that our estimates have classified as inactive. 2A.2(b) (i) volume, (iii) internal energy, and (iv) density are state functions. 2A.3(b) This is an expansion against a constant external pressure; hence $w = -pex \Delta V$ [2A.6] The change in volume is the cross-sectional area times the linear displacement: 3 ($1m -3 3 \Delta V = (75.0 \text{ cm } 2) \times (25.0 \text{ cm}) \times |$ $| = 1.87 \times 10 \text{ m} \setminus 100 \text{ cm} / 3 \text{ w} = -(150 \times 103 \text{ Pa}) \times (1.87 \times 10 - 3 \text{ m} 3) = -281 \text{ as } 1 \text{ Pa } \text{m} = 1 \text{ J so } 2A.4(b)$ For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. From the definition of enthalpy, H = U + pV, so $\Delta H = \Delta U + \Delta (pV) = \Delta U + \Delta (nRT)$ (perfect gas). $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas. $\Delta U = \Delta H = 0$ (i) $V = -nRT \ln |f| [2A.9] Vi = -(2.00 \text{ mol}) \times (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times 273K \times \ln 20.0 \text{ dm} 3 \text{ q} = -w = 6.29 \times 103 \text{ J } \Delta U = \Delta H = 0$ (ii) $w = -pex \Delta V [2A.6]$ where pex in this case can be computed from the perfect gas law $pV = nRT (2.00 \text{ mol}) \times (2.00$ × (8.3145 JK - 1 mol - 1) × 273K so p = × (10 dm m - 1) = 2.22 × 105 Pa 20.0 dm 3 – $(2.22 \times 105 \text{ Pa})$ × (20.0 - 5.0) dm 3 and w = = $-3.34 \times 103 \text{ J}$ (iii) $\Delta U = \Delta H = 0$ w = 0 [free expansion] q = $\Delta U - w = 0 - 0 = 0$ Comment. An isothermal free expansion of a perfect gas is also adiabatic. 2:2 2A.5(b) The perfect gas law leads to p1V nRT1 = p2V nRT2 or p2 = p1T2 (111k Pa) × (356 K) = 143k Pa 277 K T1 There is no change in volume, so w = 0. The heat flow is $q = \int CV dT \approx CV \Delta T = (2.5) \times (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (2.5 \text{ mol}) \times (356 \text{ K}) = -19 \text{ J} (10 \text{ mol}) \times (356 \text{ mol}) \times (356 \text{ K}) = -143k Pa 277 \text{ K} \text{ T1}$ There is no change in volume, so w = 0. The heat flow is $q = \int CV dT \approx CV \Delta T = (2.5) \times (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (2.5 \text{ mol}) \times (356 \text{ mol}$ dm m -1)3 (V) w = - nRT ln | f | [2A.9] (Vi) () (2.5 + 18.5) dm3 6.56 g -1 -1 w = 8.3145 J K mol 305 K ln - | × × × ()) -1 | (18.5 dm3 (39.95 g mol) = -52.8 J Solutions to problems w = - pex ΔV [2A.6] 2A.2 Hence Vf = nRT >> Vi ; so $\Delta V \approx Vf pex (nRT) - 1 - 1 w \approx (- pex) \times | = -nRT = (-1.0 mol) \times (8.314 J K mol) \times (1073K) p (ex) w \approx -$ 8.9 kJ Even if there is no physical piston, the gas drives back the atmosphere, so the work is also w ≈ -8.9 kJ 2A.4 V2 dV dV + n2 a $\int V1 V 2 V1 V 1 - nb \int V2 V1 V 1 V - nb \int V2 V 1 V 1 V + nb \int V2 V 1 V 1 V + nb \int V2 V 1 V 1 V + nb \int V2 V 1 V V + nb \int V2 V V + nb \int V2 V V + nb V V + nb V$ $2 \sqrt{V} \sqrt{T} \ln c = -nR \times \frac{|Tc \times ln|}{c \times c - c} \sqrt{1} \ln b || \sqrt{c} || \sqrt{1} \sqrt{Tc} || - || \sqrt{c} \sqrt{c} 2:3 T \sqrt{Tr} = \sqrt{c} + \sqrt{c} \sqrt{2} \ln c + \sqrt{c} \sqrt$, then w = and 3b a (V - 1/3)(181) wr = $-nTr \ln |r, 2 - |-n| |9 (Vr, 1 - 1/3) (Vr, 2Vr, 1)$ Along the critical isotherm, Tr = 1, Vr, 1 = 1, and Vr, 2 = x. Hence wr 8 (3x - 1)1 - +1 = - ln |9 (2) x n 2A.6 One obvious limitation is that the model treats only displacements along the chain, not displacements that take an end away from the chain. (See Fig. 2A.2 in the Student's Solutions Manual) (a) The displacement is twice the persistence length, so x = 2l, n = 2, $\nu = n/N = 2/200 = 1/100$ and $F = (1 + \nu)(1.381 \times 10 - 23 \text{ K} - 1)(298 \text{ K})(1.01) \text{ kT} = 9.1 \times 10 - 16 \text{ N} \ln l = \ln |2| (0.99 ||1 - \nu||2 \times 45 \times 10 - 9 \text{ m}$ Figure 2A.1 5 4 3 2 force 1 Hooke 0 1-D model -1 -2 -3 -4 -5 -1 -0.8 -0.6 -0.4 -0.2 0 0.2 0.4 0.6 0.8 1 displacement (b) Fig. 2A.1 displays a plot of force vs. displacements, the magnitude of the force in the one-dimensional model grows much faster. In fact, in the one-dimensional freely jointed chain. For small displacements, the magnitude of the force vs. displacement for Hooke's law and for the one-dimensional freely jointed chain. model, the magnitude of the force approaches infinity for a finite displacement, 2:4 namely a displacement the size of the chain itself ($|\nu| = 1$). (For Hooke's law, the force approaches infinity only for infinitely large displacement, 2:4 namely a displacement.) (c) Work is dw = -F dx = (1 + v)(1 + $1+\nu$ kNT kNT dv = ln $22(1-\nu)$ by f $[\ln(1+\nu) - \ln(1-\nu)]d\nu$ f kNT $[(1+\nu) - \ln(1-\nu)]d\nu$ f kNT $[(1+\nu) + (1-\nu)]d\nu$ f kNT $[(1+\nu)]d\nu$ f $[(1+\nu)]d\nu$ f $[(1+\nu)]d\nu$ f kNT $[(1+\nu)]d\nu$ f $[(1+\nu)]d\nu$ f [(1+expression above is indeterminate at these points. In particular, for expansion to the full length of the chain kNT $[(1 + \nu) + (1 - \nu)] 2 kNT [kNT [ln(1 - \nu)] - 1] 2 [2] w = \lim \nu \rightarrow 1 (1 - \nu)] (1 + 1) + \lim(1 - \nu)] (1$ ratio in order to apply l'Hospital's rule. Focusing on the problematic limit and taking the required derivatives of numerator and denominator yields: $-(1 - \nu) - 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu)
= \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_{\nu \to 1} (1 - \nu) + 1 \ln(1 - \nu) = \lim_$ the text. There are two related reasons that can be given as to why Cp is greater than CV. For ideal gases Cp - CV = nR. For other gases that can be considered roughly ideal the difference is still approximately nR. Upon examination of figure 2B.3, we see that the slope of the curve of enthalpy against temperature is in most cases greater that the $+ 273 \text{ K} [20.17 + (0.4001)\text{T} / \text{K}] dT \text{ J} \text{ K} - 1 373 \text{ K} [(T2)] 1 \text{ J} \text{ K} - 1 = |(20.17) \text{ K}| (173 - 298) + (0.4001) \times (373 - 298) + (0.4001) \times (373$ of a perfect gas depend on temperature alone. Thus, 11.0 kJ, as above. At constant volume, w = 0 and $\Delta U = q = +11.0$ kJ and $\Delta U = +11.0$ kJ and $\Delta U = +10.0$ kJ and $\Delta U = +10$ $= 2.0 \times 10$ J mol $- (2.0 \text{ mol}) \times (8.3145]$ K - 1 mol - 1) $\times (277 - 250)$ K $3 = 1.6 \times 103$ J mol - 1 Solutions to problems 2B.2 In order to explore which of the two proposed equations are given in the following table. parameters a b/10-3 K-1 c/105 K2 values 28.796 27.89 -1.490 std dev of parameter 0.820 0.91 0.6480 The correlation coefficient is 0.99947. The parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggested alternate equation are as follows: parameters and their standard deviations obtained with the fitting process to the suggest and their standard deviations are as follows: parameters are as follows: parameters are as follows: parameters are as follows: parameters are as follows: paramet parameter 0.437 1.45 1.106 2:6 The correlation coefficient is 0.99986. It appears that the alternate form for the heat capacity equation fits the data slightly better, but there is very little difference. $(\partial U) (\partial (\partial U)) (\partial$ a substance is the pure substance at a pressure of 1 bar and a specified temperature. The term reference state generally refers to elements and is the thermodynamically most stable state of the element at the temperature of interest. elements that can exist in more than one form at a specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature. So an element can have more than one standard state, one for each form that exists at the specified temperature. mol) × (8.3145 J K -1 mol-1) × (260 K) w = -3.78 × 103 J = -3.78 kJ $\Delta U = w + q = -3.78 + 76.1 = 72.3 kJ 2:7$ Comment. Because the vapor is treated as a perfect gas, the specific value of the external pressure provided in the statement of the external pressure provided in the external preserved in the external preserved in th \rightarrow 6 CO 2 (g) + 3 H 2 O(1) Δ c H O = 6 Δ f H O (CO 2) + 3 Δ f H O (H 2 O) - Δ f H O (C6 H 5 OH) - 7 Δ f H O (O 2) = [6(-393.51) + 3(-285.83) - (-165.0) - 7(0)] k mol-1 = -3053.6 k mol- $\{\text{reaction}(2)\} + 3 \times \Delta r \text{ H O} \{\text{reaction}(3)\} - \Delta r \text{ H O} \{\text{reaction}(3)\} - \Delta r \text{ H O} \{\text{reaction}(3)\} - (-2036)\} \text{ kJ mol} - 1 = +36.6 \text{ kJ mol}$ $2(g) + 5H 2 O(l) 2 2 \Delta c U O = \Delta c H O - \Delta ng RT [2B.4], \Delta ng = -5 mol 2 (5) \Delta c U O = -7061 kJ mol - 1 (-1 - × 8.3 × 10 - 3 kJ K - 1 mol - 1 × 298 K || 2 | = -7055 kJ mol - 1 (-1 × 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || (-1 + 298 K || 2 | = -7055 kJ mol - 1) || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1 || -1$ $5OH(s) + 15O(2)(g) \rightarrow 6CO(2)(g) + 3H(2)O(l)(2)\Delta c H O = -3054 \text{ kJ mol} - 1 \text{ [Table 2C, 1]} \Delta c U = \Delta c H - \Delta ng RT$, $\Delta ng = -32 - 13 = (-3054 \text{ kJ mol} - 1) \times (298 \text{ K}) = -3050 \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (375 \text{ kJ mol} - 1) \times (298 \text{ K}) = -3050 \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ kJ mol} - 1 (135 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10
- 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.314 \times 10 - 3) \text{ g} + (2) \times (8.$ (a) reaction(3) = $(-2) \times \text{reaction}(1) + \text{reaction}(2)$ and $\Delta ng = -1$ The enthalpies of reactions are combined in the same manner as the equations (Hess's law). $\Delta r H O (3) = (-2) \times \Delta r H O ($ (298 K) = -589.56 kJ mol - 1 + 7.43 kJ mol - 1 = -582.13 kJ mol - 1 (b) $\Delta f H O$ refers to the formation of one mole of the compound, so $O(HI) \Delta f H = 1 \text{ mol} - 1$) ($52.96 \text{ kJ} = 226.48 \text{ kJ} \text{ mol} - 1 + (5) \times (8.3145 \times 10 - 3 \text{ kJ} \text{ K} - 1)$ mol-1) × (298 K) = -760.3 kJ mol-1 2C.8(b) The hydrogenation reaction is (1) C2 H 2 (g) + H 2 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 2 (g) + H 2 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 2 (g) + H 2 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 2 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 2 (g) \rightarrow C2 H 2 (g) \rightarrow C2 H 4 (g) \rightarrow C2 H 2 (g) \rightarrow C2 (g $2CO_2(g) \Delta c H O(3) = -1411kJ mol - 1(4) C2 H 2(g) + 5 O(g) \rightarrow H 2 O(l) + 2CO_2(g) \Delta c H O(4) = -1300 kJ mol - 1 2 2 reaction (1) = reaction (2) - reaction (3) + reaction (4) Hence, at 298 K; (i) \Delta r H O = \Delta c H O(3) + A c H O(4) = -175kJ mol - 1 \Delta r U O = \Delta r H O - \Delta ng RT [2B.4]; \Delta$ $= -1 = -175 \text{ kJ mol} - 1 - (-1) \times (2.48 \text{ kJ mol} - 1) = -173 \text{ kJ mol} - 1 \text{ (ii) At } 427 \text{ K} \cdot \Delta r \text{ H O} (427 \text{ K}) = \Delta r \text{ H O} (298 \text{ K}) + \Delta r \text{ C pO} (427 \text{ K} - 298 \text{ K}) 2:9 [Example 2C.2] = \Delta r \text{ C pO}, m (C 2 \text{ H } 4, g) - C \text{ pO}, m (C 2 \text{ H } 4, g) - C$ H O (427 K) = $-(175 \text{ kJ mol}-1) - (29.19 \times 10-3 \text{ kJ K} - 1 \text{ mol}-1) \times (129 \text{ K}) = -171 \text{ kJ mol}-1 2C.9(b)$ For the reaction C10 H 8 (l) + 120 2 (g) $\rightarrow 10CO 2$ (g) + 4H 2 O(g) O Δr H = 10 × Δf H O (C0 2, g) + 4 × Δf H O (C0 2, g) + 4 × Δf H O (C0 2, g) + 4 × Δf H O (C10 H 8, l) In order to calculate the enthalpy of reaction at 478 K we first calculate its value at 298 K using data in Tables 2C.1 and 2C.2. Note at 298 K naphthalene is a solid. It melts at 80.2 °C = 353.4 K. $-1 \Delta r H (298 \text{ K}) = 10 \times (-241.82 \text{ kJ mol}) + 4 \times (-241.82 \text{ kJ mol}) = -4980.91 \text{ kJ mol}) + 4 \times (-241.82 \text{ kJ mol}) + 4 \times (-241.82 \text{ kJ mol}) = -4980.91 \text{ kJ mol}) = \Delta H$, of each substance as the temperature increases from 298 K to 478 K. The enthalpy of reaction at 478 K can be obtained by adding all these enthalpy of reaction at 478 K. This process is shown below: $\Delta r H (478 \text{ K}) = \Delta r H (298 \text{ K}) + 10 \times \Delta H (CO 2, g) - \Delta H (C10 H 8) - 12 \times \Delta H (O 2, g) O O For$ H2O(g), CO2(g), and O2(g) we have $\Delta f H O (478 \text{ K}) = \Delta f H O (298 \text{ K}) + \int 478 \text{ K} 298 \text{ K} O \text{ C} \text{ p}$, m dT For naphthalene we have to take into account the change in state from solid to liquid at 80.2 °C = 353.4 K. Then $\Delta f H O (478 \text{ K}) = \Delta f H O (478 \text{ K}) + \int 478 \text{ K} 298 \text{ K} O \text{ C} \text{ p}$, m dT For naphthalene we have to take into account the change in state from solid to liquid at 80.2 °C = 353.4 K. Then $\Delta f H O (478 \text{ K}) = \Delta f H O (478 \text{ K}) + \int 478 \text{ K} 298 \text{ K} O \text{ C} \text{ p}$, m dT For naphthalene we have to take into account the change in state from solid to liquid at 80.2 °C = 353.4 K. Then $\Delta f H O (478 \text{ K}) = \Delta f H O (478 \text{$

dependence of the heat capacities in the form of the equation given in Problem 2C.7 because data for the heat capacities of the substances in the form of the equation of Table 2B.1. We use C p , $m = \alpha + \beta T + \gamma T 2 O$ For H2O(g), CO2(g), and O2(g), α , β , and γ values are given in Problem 2C.7. For naphthalene, solid and liquid, γ is zero and the two forms of the heat capacity equation are then identical and we take $\alpha = a$ and $\beta = b$ from Table 2B.1. 19.01 kJ mol-1 Δ fus H O (C10 H8) = Using the data given in Problem 2C.7. For naphthalene, solid and liquid, γ is zero and the two forms of the heat capacity equation are then identical and we take $\alpha = a$ and $\beta = b$ from Table 2B.1. 19.01 kJ mol-1 Δ fus H O (C10 H8) = Using the data given in Problem 2C.7. and ΔH (O=, g) 5.430 kJ mol-1 2 2 2 Using the data from Table 2C.1 we calculate for naphthalene 55.36 kJ mol-1 ΔH (C10 H8) = Collecting all these enthalpy changes we have $\Delta H r 2C.10(b) O (478 \text{ K}) = O - 1 - 5023.77 \text{ kJ mol} - 1 \Delta H (298 \text{ K}) + (10 \times 5.299 + 4 \times 6.168 - 55.36 - 12 \times 5.430) \text{kJ mol} = r$ The cycle is shown in Fig. 2C.1. Figure 2C.1 $2:10 - \Delta$ hyd H O (Ca 2 +) = $-\Delta$ soln H O (CaBr2) - Δ f H O (CaBr2), s) + Δ sub H O (Ca) + Δ vap H O (Br2) + Δ diss H O (Br2) + Δ diss H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + Δ ion H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ hyd H O (Ca +) + 2Δ eg H O (Br) + 2Δ eg H O (B $-1684 \text{ kJ mol} - 1 \text{ Solutions to problems } 2C.2 \text{ Cr}(C6 \text{ H } 6)2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2C6 \text{ H } 6(\text{g}) \Delta \text{ng} = +2 \text{ mol} \Delta \text{r H } O = \Delta \text{ r U } O + 2 \text{ RT}, \text{ from}[2B.4] = (8.0 \text{ kJ mol} - 1) + (2) \times (8.314 \text{ J K} - 1 \text{ mol} - 1) \times (583K) = +17.7 \text{ kJ mol} - 1 \text{ In terms of enthalpies of formation } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) - \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = \Delta \text{ r U } O + 2 \text{ RT}, \text{ from}[2B.4] = (8.0 \text{ kJ mol} - 1) + (2) \times (8.314 \text{ J K} - 1 \text{ mol} - 1) \times (583K) = +17.7 \text{ kJ mol} - 1 \text{ In terms of enthalpies of formation } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) = +17.7 \text{ kJ mol} - 1 \text{ In terms of enthalpies of formation } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) = +17.7 \text{ kJ mol} - 1 \text{ In terms of enthalpies of formation } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) = +17.7 \text{ kJ mol} - 1 \text{ In terms of enthalpies of formation } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O (\text{metallocene}, 583K) \text{ or } \Delta \text{ r H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f H } O = (2) \times \Delta \text{ f$ 2Δ f H O (benzene, 583K) - 17.7 kJ mol-1 The enthalpy of formation of benzene gas at 583 K is related to its value at 298 K by Δ f H O (benzene, 583K) = Δ f H O (benzene, 298 K) C p,m (l) + Δ vap H O + (583K - 298 K)C p,m (gr) - 3 × (583K - 298 K)C p,m (H 2, g) where Tb is the boiling temperature of benzene (353 K). We shall assume that the heat capacities of graphite and hydrogen are approximately constant in the range of interest and use their values from Tables 2B.1 and 2B.2. 2:11 Δ f H O (benzene, 583K) = (49.0 kJ mol-1) + (353 - 298) K × (136.1J K - 1 mol-1) + (353 - 298) K × (136.1J K - 1 mol-1) + (30.8 kJ mol-1) + (30.8 298) K × (8.53J K - 1 mol - 1) - (3) × (583 - 298) K × (28.82 J K - 1 mol - 1) = {(49.0) + (7.49) + (18.78) + (30.8) - (24.64)}kJ mol - 1 = +66.8 kJ mol - 1 = +66.8 number of moles of gas, $\Delta r H = \Delta r U [2B.4]$. Therefore $\Delta c H O = -25968 \text{ kJ} \text{ mol} - 1$ (-36.0334 kJ g - 1) × (60 × 12.011 g mol - 1) = Now relate the enthalpy of combustion to enthalpies of formation and solve for that of C60. $\Delta c H O = 60\Delta f H O (C02) - \Delta f H O (C02) - 60\Delta f H O (C02) -$ O = [60(-393.51) - 60(0) - (-25968)] k mol - 1 = 2357 k mol - 1 = 2357 k mol - 1 = 2357 k mol - 1 = 240 k moprotein's unfolding we need to determine the area under the plot of Cp,ex at T1, the start of the process, to the baseline value of Cp,ex at T1, the start of the process, to the baseline value of Cp,ex at T1, the start of the process at T1, the start of the process. We are provided with an illustration that shows the plot, but no numerical values can be extracted from the plot and $\int T^2$ then the value of the integral $\Delta H = C p$, ex dT can be obtained by numerical evaluation of the area T1 under the curve, the last column gives the approximate area under the curve. The first two columns in the table below show the data estimated from the curve, the last column gives the approximate area under the curve. kJ mol-1, is the enthalpy of unfolding of the protein. The four significant figures shown are not really justified because of the imprecise estimation process involved. 2:12 θ /°C C p, ex/kJ K-1 mol-1 Δ H /kJ mol 20 23 26 28 33 40 46 52 58 63 70 80 89 90 85 80 68 60 52 47 41 37 36 0 215 460 567 626 663 706 755 810 870 937 1011 1096 1141 1185 1267 $1342 1405 1461 1511 1598 1676 1889 30 40 50 54 56 57 58 59 60 61 62 63 64 64.5 65 66 67 68 69 70 72 74 80 2C.10 - 1 (a) qV = -n\Delta cU O;$ hence (ii) $\Delta cU O = - = -2802 kJ mol - 1 0.3212 g - qV - C\Delta T - MC\Delta T = =$ where m is sample mass and M molar mass n m n (i) The complete aerobic oxidation is C6 H12 O6 (s) + 60 2 (g) \rightarrow 6CO 2 (g) + 6H 2 O(l) Since there is no change in the number of moles of gas, $\Delta r H = \Delta r U [2.21]$ and $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = \Delta c U O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c
H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 1 (iii) $\Delta c H O = -2802$ kJ mol - 2 (iii) $\Delta c H O = -2802$ kJ mol - 2 (ii) $\Delta c H O$ $f H O (O 2,g) - \Delta c H O \Delta f H O (C6 H12 O6 + 2CH 3CH(OH)COOH \Delta r H O = 2\Delta f H O (actic acid) - \Delta f H O (actic ac$ exothermic by 2688 kJ mol-1 than glycolysis. 2:13 2D State functions and exact differentials Answers to discussion questions 2D.2 An inversion temperature is the temperature at which the Joule-Thomson coefficient, μ , changes sign from negative to positive or vice-versa. For a perfect gas μ is always zero, thus it cannot have an inversion temperature As explained in detail in Section 2D.3, the existence of the Joule-Thomson effect depends upon intermolecular attractions and repulsions. A perfect gas has by definition no intermolecular attractions and repulsions. A perfect gas has by definition no intermolecular attractions and repulsions. The internal pressure of a van der Waals gas is = $Vm \pi T = a / Vm^2$. The molar volume can be estimated from the perfect gas equation: RT 0.08206 dm3 atm K - 1 mol-1 × 298 K = = 24.76 dm3 mol-1) 2 2D.2(b) The dm3 mol-1 dVm Vm2 = - a Vm a a 29.00a = - + = -1 -1 3 3 30.00 dm mol 1.00 dm mol 1.00 dm 3 mol-1 30.00 dm3 mol-1 1.00 dm3 mol-1 = 0.9667 a dm -3 mol From Table 1C.3, a = 1.337 dm6 atm mol-1 Δ U m = (0.9667 mol dm3) × (1.337 atm dm 6 mol-2) (1m3) = (1.2924 atm dm3 mol-1) × (1.01325 × 105 Pa atm -1) × 3 3 || 10 dm $= 131.0 = Pa m 3 mol - 1 131.0 J mol - 1 w = - \int p dVm where p = a RT - 2 for a van der Waals gas. Hence, Vm - b Vm (RT) a w = - \int | dVm + \int V 2 dVm = -q + \Delta U m (Vm - b) m Thus 2:14 = q \int 30.00 dm 3 mol - 1 3 1.00 dm mol - 1 3 0.00 dm 3 mol - 1 (RT) dVm RT ln(Vm - b) | 1.00 dm 3 mol - 1 | = (Vm - b) 30.00 - 3.20 \times 10 - 2 | = +8.505 k$ $mol-1 - 2 \parallel 1.00 - 3.20 \times 10 \parallel j \parallel = (8.314 \text{ J K} - 1 \text{ mol} - 1) \times (298 \text{ K}) \times ln \parallel$ and $w = -q + \Delta U m = -(8505 \text{ J mol} - 1) + (131 \text{ J mol} - 1) = -8374 \text{ J mol} - 1 = -8.37 \text{ kJ mol} - 1 =$ $\times 10-4 (T/K) + 1.52 \times 10-6 (T/K)2 = [3.7 \times 10-4 + 2 \times 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 + 3.7 \times 10-4 (310) + 1.52 \times 10-6 (310)] K - 1 = 1.27 \times 10-3 K - 10.77 \times 10^{-3} \times 10^{$ be applied is $\Delta p = 2D.5(b) \ 0.0010 = 2.21 \times 10-6$ atm $-1 \ 4.5 \times 102$ atm The isothermal Joule-Thomson coefficient is constant in an isothermal Joule-Thomson experiment, then the heat which must be supplied to maintain constant temperature is ΔH in the following relationship $\Delta H / n = -41.2 \text{ J}$ atm -1 mol - 1 so $\Delta H = -(41.2 \text{ J} \text{ atm} - 1 \text{ mol} - 1) \times (10.0 \text{ mol}) \times (-75 \text{ atm}) = 30.9 \times 103 \text{ J}$ Solutions to problems ($\gamma \text{ RT}$) cs = $|\langle M \rangle / 2D.2 \rangle$ (a) 12, $\gamma = C \text{ p,m} \text{ CV}$, m + R CV, m = 12 R(3 + $\nu \text{ R} + 2\nu \text{ V} \times) = 12 \text{ R}(3 + 2) = 52 \text{ R C p,m} = 0.9 \times 103 \text{ J}$ Solutions to problems ($\gamma \text{ RT}$) cs = $|\langle M \rangle / 2D.2 \rangle$ (a) 12, $\gamma = C \text{ p,m} \text{ CV}$, m + R CV, m = 12 R(3 + $\nu \text{ R} \times + 2\nu \text{ V} \times) = 12 \text{ R}(3 + 2) = 52 \text{ R C p,m} = 0.9 \times 103 \text{ J}$ Solutions to problems ($\gamma \text{ RT}$) cs = $|\langle M \rangle / 2D.2 \rangle$ (a) 12, $\gamma = C \text{ p,m} \text{ CV}$, m + R CV, m = 12 R(3 + $\nu \text{ R} \times + 2\nu \text{ V} \times) = 12 \text{ R}(3 + 2) = 52 \text{ R C p,m} = 0.9 \times 103 \text{ J}$ Solutions to problems ($\gamma \text{ RT}$) cs = $|\langle M \rangle / 2D.2 \rangle$ (b) $|\langle M \rangle / 2D.2 \rangle$ (c) $2D.4 \left(\frac{\partial V}{\partial V} \right) \left(\frac{$ $p d ln p = Likewise 1 \left(\frac{\partial p}{\partial p} dV + | | dT = | p (\frac{\partial T}{V} p (\frac{\partial V}{\partial T}) p (\frac{\partial V}{\partial T}) p (\frac{\partial V}{\partial p}) T | (\frac{\partial V}{\partial p}) T |$ identity] $V = -1 \times V = (-nRT) 2 (V - nb) 1$ [Problem 2D.5] (2n 2 a) + 3 | V V 2 (V - nb) 2 RTV 3 - 2n 2 a (V - nb) 2 RTV 3 - 2n 2 RT[Euler chain relation] $\partial p / V - nb = [Problem 2D.5], nR \alpha (V - nb) \kappa TR = n Hence, \kappa TR = \alpha (Vm - b) () (\mu = |\partial T| = -1 |\partial H| [Justification 2D.2] (\partial p / T 2D.8 [|(\partial V)]| - V] [See the section below for a derivation of this result] {T | ||(<math>\partial T / p |) \partial V = nR V$ [nRT - nb] = -V] = { C p C p [p p] C p c [p p] C p c [A D] C p c [A D] C p c [A D] C p c c c clude that for this gas $\mu < 0$ or A T < 0. This says that when the A D = 0 and C p > 0, we conclude that for this gas $\mu < 0$ or A T < 0. This says that when the A D = 0 and C p > 0, we conclude that for this gas $\mu < 0$ or A T < 0. This says that when the A D = 0. This says that when the A D = 0. $\int \left(\frac{\partial V}{\partial v} \right)^{-1} \left(\frac{\partial V}{\partial v} \right)$ $+= \int \partial T \sqrt{\partial p} / T - T \partial T \partial V () + V [chain relation] p () + V [chain relation] p () + V [reciprocal identity] = -T \partial V \partial T 2D.10 p (a) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1 \text{ MPa} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1 \text{ MPa} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1 \text{ MPa} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p)
(\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1 \text{ MPa} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1 \text{ MPa} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1) / (110.0 \text{ J K} - 1 \text{ mol} - 1) = 29.9 \text{ K MPa} - 1 (b) The Joule-Thomson coefficient is related to the given data by <math>\mu = -(1 / C p) (\partial H / \partial p) T = -(-3.29 \times 103 \text{ J mol} - 1) / (110.0 \text{ J K} - 1) / (110.0 \text{ J K$ Assuming that the expansion is a Joule-Thomson constant-enthalpy process, we have $\Delta T = \mu \Delta p = (29.9 \text{ K MPa} - 1) \times [(0.5 - 1.5) \times 10 - 1 \text{ MPa}] = -2.99 \text{ K 2E}$ Adiabatic changes Answers to discussion questions 2E.2 See Figure 2E.2 of the text and the Interactivity associated with that figure. For an adiabatic change, $\pi T dV + CV dT = -\text{pex dV} [2A.6]$ 2D.5]. Thus we see that the heat capacity enters into the dU = dw = calculation of the change in energy of the system that occurs during an adiabatic expansion. For a perfect γ Cp (V). Again the heat capacity plays a gas Eqn 2E.3 of the text can be written as pf = | i | pi with γ = CV (Vf / role. Solutions to exercises 2E.1(b) 1 2 R for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, Cp,m = R + CV,m. So for CO2 The equipartition to molar heat capacity of 2:18 With vibrations CV, m / R = 3(12) + 2(12) +1.15 6.5 3.5 = 1.40 2.5 γ = 37.11 J mol-1K -1 1.29 = (37.11 - 8.3145) J mol-1K -1 Experimental result is closer to that obtained by neglected entirely. (6.626 × 10-34 J s) × (2.998 × 1010 cm s -1) × (0.39 cm -1) hcB = = 0.56 K 0, for all spontaneous processes. In this case, S tot 10 J K -1 > 0, so the process may be spontaneous. $\Delta = 3A.2(b)$ Efficiency, η , is work performed w 0.71 kJ = = 0.262. For an ideal heat absorbed qh 2.71 kJ T T h 273.16 K c Heat engine we have η rev = 1 - c [3A.10] = 0.262 = 1 - obtain Tc = 201.6 K as the temperature of the organic liquid. F12:1. Solving for Tc, we 3A.3(b) Assume that the block is so large that its temperature does not change significantly as a result of the heat transfer. Then f dg f q rev = $\Delta S = [3A.2] 1$ fi dqrev [constant = T] rev T T T i 250 × 103 J 250 × 103 J 250 × 103 J (a) $\Delta S = 853$ J K $-1 = (b) \Delta S = 670$ J because Δ Sfus and Δ S vap are greater for CO2(g). 3A.5(b) We use (V) nR ln | f | [3A.14] Δ S = (Vi) (4.00 g) (750) -1 -1 -1 = | × 8.314 J K mol × ln | = |0.482 J K 28.0 g/mol 500 (//)3A.6(b) Trouton's rule in the form Δ vap H O = Tb × 85 J K -1 mol -1 can be used to obtain approximate enthalpies of vaporization. For cyclohexane Δ vap H O = Tb × 85 J K -1 mol -1 can be used to obtain approximate enthalpies of vaporization. $(273.2 + 80.7)K \times 85 J K - 1 mol - 1 = 30.1 kJ/mol - 1 3A.7(b) At 250 K$, the entropy at 298 K plus ΔS where CV, m dT dqrev T $\Delta S = = CV$, m ln f T T Ti $\int so \int S = 154.84 J K - 1 mol - 1 + [(20.786 - 8.3145) J K - 1 mol - 1] \times ln 250 K 298 K S = 152.65 J K - 1 mol - 1 = 30.1 kJ/mol - 1 3A.8(b) No matter how the change occurred, <math>\Delta S$ has the same value as if the change happened by reversible heating at constant pressure (step 1) followed by reversible isothermal compression (step 2) $\Delta S = \Delta S1 + \Delta S2$ For the first step $\Delta S1 = \int dqrev = T \int C p, m dT T$ () = C p, m dT T () = C p, m d $= \Delta S2 = TTpV$ where qrev $= -w = pdV = nRT ln f = nRT ln i Vi pf \int so \Delta S2 = nR ln pi = (2.00 mol) \times (8.3145 JK - 1 mol - 1) \times ln 1.50 atm = -25.6 JK - 1 pf 7.00 atm \Delta S = (18.3 - 25.6) JK - 1 = -7.3 JK - 1 3:2$ The heat lost in step 2 was more than the heat gained in step 1, resulting in a net loss of entropy. Or the ordering represented by confining the sample to a smaller volume in step 2 overcame the disordering represented by the temperature rise in step 1. A negative entropy elsewhere results in ΔS total > 0. 3A.9(b) Since the masses are equal and the heat capacity is assumed constant, the final temperature will be the average of the two initial temperatures, 1 Tf = (100 C + 25 C) = 62.5 C 2 The heat capacity of each block is C = mCs where Cs is the specific heat capacity. So, ΔH (individual) = mCs $\Delta T = 10.0 \times 103 \text{ g} \times 0.449 \text{ J} \text{ K} - 1 \text{ g} - 1 \times (\pm 37.5 \text{ K}) = \pm 168 \text{ kJ}$ These two enthalpy changes add up to zero: ΔH tot = 0 (T) ΔS = mCs ln | f |; 100 C = 373.2 K; 25 C $= 298.2 \text{ K}; 62.5 \text{ C} = 335.7 \text{ K} \text{ Ti } (335.7) - 1 \Delta \text{S1} = (10.0 \times 103 \text{ g}) \times (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | = 532 \text{ J} \text{ K} 298 2 . () 335 7 . () - 1 \Delta \text{S} 2 = (10.0 \times 103 \text{ g}) \times (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | = -475 \text{ J} \text{ K} (373.2) \Delta \text{S} \text{ total} = \Delta \text{S1} + \Delta \text{S2} = 57 \text{ J} \text{ K} - 1 3\text{ A}.10(\text{b}) (\text{ Vf}) () 21\text{ g} 4.60 \text{ dm3} = \Delta \text{S} (\text{gas}) \text{ nR} \ln | = \times (8.314 \text{ J} \text{ K} - 1 \text{ mol} - 1) \ln | [3A.14] | -1 | 1.20 \text{ dm3} (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | = -475 \text{ J} \text{ K} (373.2) \Delta \text{S} \text{ total} = \Delta \text{S1} + \Delta \text{S2} = 57 \text{ J} \text{ K} - 1
3\text{ A}.10(\text{b}) (\text{ Vf}) () 21\text{ g} 4.60 \text{ dm3} = \Delta \text{S} (\text{gas}) \text{ nR} \ln | = \times (8.314 \text{ J} \text{ K} - 1 \text{ mol} - 1) \ln | [3A.14] | -1 | 1.20 \text{ dm3} (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | = -475 \text{ J} \text{ K} (373.2) \Delta \text{S} \text{ total} = \Delta \text{S1} + \Delta \text{S2} = 57 \text{ J} \text{ K} - 1 3\text{ A}.10(\text{b}) (\text{ Vf}) () 21\text{ g} 4.60 \text{ dm3} = \Delta \text{S} (\text{gas}) \text{ nR} \ln | = \times (8.314 \text{ J} \text{ K} - 1 \text{ mol} - 1) \ln | [3A.14] | -1 | 1.20 \text{ dm3} | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | = -475 \text{ J} \text{ K} (373.2) \Delta \text{S} \text{ total} = \Delta \text{S1} + \Delta \text{S2} = 57 \text{ J} \text{ K} - 1 3\text{ A}.10(\text{b}) (\text{ Vf}) () 21\text{ g} 4.60 \text{ dm3} = \Delta \text{S} (\text{gas}) \text{ nR} \ln | = \times (8.314 \text{ J} \text{ K} - 1 \text{ mol} - 1) \ln | [3A.14] | -1 | 1.20 \text{ dm3} | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J} \text{ K} - 1 \text{ g} - 1) \times \ln | (0.449 \text{ J}$ 39.95 mol /(i) $Vi = 5.873 = J K - 1 5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] <math>\Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state function) \Delta S(surroundings) = 0 [No heat is transferred to the surroundings] \Delta S(total) = +5.9 J K - 1 (Sis a state functi$ 0 3A.11(b) (i) (ii) Δ vap H 35.27 × 103 J mol-1 = +104.58 J K -1 = 104.6 J K -1 (64.1 + 273.15) K Tb If vaporization occurs reversibly, as is generally assumed Δ vap S = = Δ Ssys + Δ Ssur = 0 so Δ Ssur = -104.6 J K -1 Comment. This calculation has been based on the assumption that the heat capacities remain constant over the range of temperatures involved and that the enthalpy of vaporization at 298.15 K given in Table 3A.2 can be applied to the vaporization at 373.15 K. Neither one of these assumptions are strictly valid. Therefore, the calculated value is only approximate. F12:3 3A.12(b) Δ S nCp (H 2 O,s)ln = n = Tf Ti + n Δ fus H + nCp (H 2 O,l)ln Tfus Tf Ti + n Δ vap H Tvap nCp (H 2 O,g)ln Tf Ti 15.0 g 0.832 mol = 18.02 g mol - 1 = Δ S 0.832 mol × 38.02 J K - 1 + 0.832 mol × 75.291 J K + 0.832 mol × mol - 1 - 1 mol 40.657 kJ/mol × ln - 1 273.15 × ln - 1 273.15 × ln - 1 273.15 K 378.15 373.15 × ln - 1 273.15 × ln - 1 273.1 calculation was based on the assumption that heat capacities were constant over the range of temperatures involved. This assumption is not strictly valid. Therefore the calculated value is only approximate. Problems 3A.2 The Otto cycle is represented in Fig. 3.1. Assume one mole of air. Figure 3A.1 η= | w | cycle [3A.8] | q2 | wcycle = w1 + w3 = ΔU + $\Delta U 3 [q1 = q3 = 0] = CV (TB - TA) + CV (TD - TC) q2 = \Delta U 2 = CV (TC - TB) |TB - TA + TD - TC| (T - T) = 1 - |DA| |TC - TB| (VA ||1/c and Since VB = VC and VA = VD, TD (VC) = TC || (VD ||1/c [2E.2a] TT TA TD =, or TD = A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TC 3:4 Then TATC - TA 1/c T T (V) = \eta = 1 - B 1 - A C TB TC 3:4 TB T$ or $\eta = 1 - |B|TC - TB TB |VA|$ Given that Cp, m = 7/2R, we have CV, m = 5/2R [2D.11] and c = 252/5 VA 1 For 10, $\eta = 1 - 0.47 = VB 10$ () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$, $m \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$ ($M \ln |C| |TB| / (T) (p) At$ constant volume |C| = 1 - 0.47 = VB 10 () $\Delta S1 = \Delta Ssur, 3 = 0$ [adiabatic reversible steps] (T) $\Delta S2 = CV$ ($M \ln |C| |TB| / (T) (p) At$ ($M \ln |TB$ +33J K -1 Δ Ssur,2 = $-\Delta$ S2 = -33J K -1 T T Δ S4 = $-\Delta$ S2 | C = B | = -33J K -1 T T A \perp D Δ Ssur,4 = $-\Delta$ S4 = +33J K -1 3A.4 (a) As suggested, relate the work to the temperature-dependent coefficient of performance : dw = dqc c C p dT = (T)[T - T](h) = Cp Th dT - dT T Integrating yields w = C p Th \int Tf Ti dT + T \int Tf Ti dT = C p Th ln () Tf Ti dT = C p Th ln
() Tf Ti dT = C p Th ln (freezing temperature. For this isothermal process, the coefficient of performance does not change, so q $(T - Tc)\Delta$ fus H w freeze = c = Δ fus H | h | c (Tc)|T - T| (h c = 6.008 × 103 J mol-1 × (293 - 273)250 g = 6113 J × | -1 (273) (J = 6.86 × 103 J = 6.86 kJ) = 6.86 kJ At the rate of 100 W = 100 J s-1, the refrigerator would freeze the water in t = 6.86×103 J = 68.6×1 $\rightarrow H 2 O(s, -5 C) Thus \Delta trs S (l \rightarrow s, -5 C) = \Delta Sl + \Delta trs S (l \rightarrow s, 0 C) + \Delta Ss$, where C p, m (l) ln ΔSl = and Tf -5 C] [3A.20; $\theta f = 0 C$, $\theta = T T \Delta Ss = C p, m$ (s) ln Tf $\Delta Sl + \Delta Ss = -\Delta C p ln$ Thus, T Tf with $\Delta C p = C p, m$ (l) -C p, m (s) = +37.3] K $-1 mol-1 \Delta trs S(l \rightarrow s, Tf) = -\Delta fus H [3A.17]$ Tf $\Delta trs S(l \rightarrow s, T) = -\Delta fus H T - \Delta C p ln$ Tf Tf $\Delta = \operatorname{trs} S(l \rightarrow s, -5^{\circ}C) 268 - 6.01 \times 103 \text{ J} \text{ mol} - 1 - (37.3] \text{ K} - 1 \text{ mol} - 1) \times \ln 273 \text{ K} 273 = -21.3 \text{ K} + 1 \text{ mol} - 1 \wedge fus \text{ H} (T) = \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) = -\Delta \operatorname{fus} H(T) - \Delta \operatorname{fus} H(T) - \Delta$ -273 6.01kJ mol + (37.3] K -1 mol-1) × $\Delta Ssur = 268$ K 268 $\Delta Ssur = 268$ K 268 $\Delta Ssur = +21.7$ J K -1 mol-1 ΔS total = $\Delta Ssur + \Delta S = (21.7 - 21.3)$ J K -1 mol-1 = +0.4 J K -1 mol-1 transformation here is to the high temperature state (vapour) from the low temperature state (liquid), which is the opposite of part (a), we can expect that the analogous equations will occur with a change of sign. T Δ trs S(1 \rightarrow g, T) = Δ $40.7 \text{ kJ mol} - 1 - (41.9 \text{ J K} - 1 \text{ mol} - 1) \times \ln | 373 \text{ K} \langle 373 || = +109.7 \text{ J K} - 1 \text{ mol} - 1 = -1.5 \text{ J K} - 1 \text{ mol} - 1 = -1.5 \text{ K} - 1 \text{ mol} - 1 = -1.5 \text{ K} + 1 \text{ mol} - 1 = -1.5 \text{ mol} + 1 \text{ mol} - 1 = -1.5 \text{ mol} + 1 \text{$ transition, $g \rightarrow l$, is spontaneous at 95°C. 3A.8 (a) q(total) = q(H 2 O) + q(Cu) = 0, hence $-q(H 2 O) = n(-\Delta vap H) + nC p,m$ (H 2 O) $= n(-\Delta vap H) + n(-\Delta$ vap H) - nC p,m (H 2 O, l) × (θ - 100°C) = mCs θ Solving for θ yields: n{ Δ vap H + C p, m (H 2 O, l) × 100°C} θ = mCs + nC p, m (H 2 O, l) × 100°C θ = mCs + nC p, m (H 2 O, l) × 100°C θ = mCs + nC p, m (H 2 O, l) × 100°C θ = mCs + nC p, m (H 2 O, l) × (θ - 100°C) = mCs θ = mCs + nC p, m (H 2 O, l) × 100°C θ $K = 4.39 \times 104 \text{ J} = 43.9 \text{ kJ} \text{ q} (H 2 \text{ O}) = -43.9 \text{ kJ} \Delta \text{S}(\text{total}) = \Delta \text{S}(H 2 \text{ O}) + \Delta \text{S}(\text{Cu}) \text{ S} (H 2 \text{ O}) \Delta = -n\Delta \text{ vap } H(T)[3A.17] + nC \text{ p}, \text{ m ln} \text{ f} [3A.20] \text{ Tb} \langle 330.2 \text{ K} \rangle + (1.00 \text{ mol}) \times (40.656 \times 103 \text{ J} \text{ mol} - 1) \times \text{ln} | \langle 373.2 \text{ K} \rangle = -108.9 \text{ J} \text{ K} - 1 - 9.22 \text{ J} \text{ K} - 1 = -118.1 \text{ J} \text{ K} - 1 \Delta \text{S}(\text{Cu}) = \text{mCs ln
Tf} (330.2 \text{ K}) = -108.9 \text{ J} \text{ K} + 1 - 9.22 \text{ J} \text{ K} - 1 = -118.1 \text{ J} \text{ K} - 1 \Delta \text{S}(\text{Cu}) = \text{mCs ln Tf} (330.2 \text{ K}) = -108.9 \text{ J} \text{ K} + 1 - 9.22 \text{ J$ $(2.00 \times 103 \text{ g}) \times (0.385 \text{ K} - 1 \text{ g} - 1) \times \ln | (273.2 \text{ K} |)$ Ti = 145.9 J K - 1 + 145.9 J K - 1 + 145.9 J K - 1 = 28 J K - 1 This process is spontaneous since $\Delta S(\text{surroundings})$ is zero and, hence, $\Delta S(\text{universe}) = \Delta S(\text{total}) > 0$ (b) The volume of the container may be calculated from the perfect gas law. nRT (1.00 mol) × (0.08206 dm 3 atm K - 1 mol - 1) × (373.2 K) V = = 30.6 dm 3 1.00 atm p At 57°C the vapor pressure of water is 130 Torr (Handbook of Chemistry and Physics, 81st edition). The amount of water vapor present at equilibrium is then F12:7 (1atm) × (30.6 dm3) (130 Torr) × 760 Torr || pV| = 0.193 mol n = RT (0.08206 dm 3 atm K - 1 mol - 1) × (330.2 K) This is a substantial fraction of the original amount of water and cannot be ignored. Consequently the calculation needs to be redone taking into account the fact that only a part, nl, of the vapor condenses into a liquid while the remainder (1.00 mol - nl) remains gaseous. The heat flow involving water, then, becomes q(H 2 O) = -n1\Delta vap H + n1C p,m (H 2 C) $O, I)\Delta T (H 2 O) + (1.00 mol - n1)C p, m (H 2 O, g)\Delta T (H 2 O)$ Because nl depends on the equilibrium temperature through pV, where p is the vapor pressure of water, we will have two unknowns (p and T) in n1 = 1.00 mol - RT the equation -q(H 2 O) = q(Cu). There are two ways out of this dilemma: (1) p may be expressed as a function of T by use of the Clapeyron equation, or (2) by use of successive approximations. Redoing the calculation yields: $\theta = nL \Delta vap H + nC p,m$ (H 2 O, I) × 100°C + (1.00 - nl)C p,m (H 2 O, q) × 100°C + (1.00 - nl)C p,m (H 2 O, $47.2^{\circ}C$. At this temperature, the vapor pressure of water is 80.41 Torr, corresponding to n1 = (1.00 mol) - (0.123 mol) = 0.877 mol This leads to $\theta = 50.8^{\circ}C$. The successive approximations eventually converge to yield a value of the final temperature. (At this temperature, the vapor pressure is 0.123 bar.) Using this value of the final temperature, the heat transferred and the various entropies are calculated as in part (a). $q(Cu) = (2.00 \times 103 \text{ g}) \times (0.385 \text{ K} - 1 \text{ g} - 1) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(H 2 \text{ O}) \Delta S(H 2 \text{ O}) = -n\Delta \text{ vap } H \text{ Tb} \Delta S(Cu) = mCs \ln (T) + nC \text{ p,m} \ln |f| = -119.8 \text{ J} \text{ K} - 1 \text{ g} - 1) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(H 2 \text{ O}) \Delta S(H 2 \text{ O}) = -n\Delta \text{ vap } H \text{ Tb} \Delta S(Cu) = mCs \ln (T) + nC \text{ p,m} \ln |f| = -119.8 \text{ J} \text{ K} - 1 \text{ g} - 1) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(H 2 \text{ O}) \Delta S(H 2 \text{ O}) = -n\Delta \text{ vap } H \text{ Tb} \Delta S(Cu) = mCs \ln (T) + nC \text{ p,m} \ln |f| = -119.8 \text{ J} \text{ K} - 1 \text{ g} - 1) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(H 2 \text{ O}) \Delta S(H 2 \text{ O}) = -n\Delta \text{ vap } H \text{ Tb} \Delta S(Cu) = mCs \ln (T) + nC \text{ p,m} \ln |f| = -119.8 \text{ J} \text{ K} - 1 \text{ g} - 1) \times (49.9 \text{ K}) = 38.4 \text{ kJ} = -q(H 2 \text{ O}) \Delta S(H 2 \text{ O}) = -n\Delta \text{ vap } H \text{ Tb} \Delta S(Cu) = mCs \ln (T) + nC \text{ p,m} \ln |f| = -119.8 \text{ J} \text{ K} - 1 \text{ g} - 1 \text{ g}$ ln ΔS depends on only the initial and final states, so we can use $\Delta S = Since q = nC p,m$ (If – Ti), Tf = Ti + Tf [3A.20] Ti I 2 Rt q [q = ItV = I 2 Rt] = Ti + nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω) × (15.0 s)) $\Delta S = (7.87 mol) × (24.4 J K - 1 mol-1) × ln | 1 + | nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω) × (15.0 s)) <math>\Delta S = (7.87 mol) × (24.4 J K - 1 mol-1) × ln | 1 + | nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω) × (15.0 s)) <math>\Delta S = (7.87 mol) × (24.4 J K - 1 mol-1) × ln | 1 + | nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω)) × (15.0 s)) <math>\Delta S = (7.87 mol) × (24.4 J K - 1 mol-1) × ln | 1 + | nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω)) × (15.0 s)) <math>\Delta S = (7.87 mol) × (24.4 J K - 1 mol-1) × ln | 1 + | nC p,m Ti / Since n = 500 g = 7.87 mol 63.5 g mol-1 ((1.00 A) 2 × (1000 Ω)) × (15.0 s))$ $-1 (7.87) \times (24.4 \text{ J K}) \times (293 \text{ K}) / (192 \text{ J K} - 1) \times (\ln 1.27) = +45.4 \text{ J K} - 1 3:8 [1 \text{ J} = 1 \text{ AVs} = 1 \text{ A 2 } \Omega \text{ s}]$ For the second experiment, no change in state occurs for the water, considered as a large heat sink q I 2 Rt (1.00 A) 2 × (1000 Ω) × (15.0 s) Δ S (water) = = = +51.2 \text{ J K} - 1 \text{ T T 293 K 3A.12 Le}^{-1} us write Newton's law of cooling as follows: dT = -A(T - Ts) dt Where A is a constant characteristic of the system and TS is the temperature of the system and TS i Let Ti be the initial temperature of the system when t = 0, then $K = \ln(Ti - TS)$ Introducing this expression for T, we obtain $dS = -CA \ln(Ti - TS)$. Substituting ln t we obtain $dS = -CA \ln(Ti - TS)$. Substituting ln t we obtain $dS = -CA \ln(Ti - TS)$. TS), where now Ti can be interpreted as any temperature T during the dt course of the cooling process. 3B The measurement of entropy Solutions to exercises 3B.1(b) Use Sm = R ln s, where s is the number of orientations of about equal energy that the molecule can adopt. Draw up the following table: n: s 0 1 1 6 2 3 4 o m p 6 6 3 6 6 2 6 $6 3 \text{ Sm/R } 0 1.8 1.8 1.8 1.1 1.8 1.8 1.1 1.8 1.8 0.7 6 6 1 1.8 1.8 1.1 1.8 \text{ isomer, b the } 1,2,3 \text{ isomer, b the$ SmO (C12 H 22 O11,s) - 12SmO (O 2, g) = $\left[(12 \times 213.74) + (11 \times 69.91) - 360.2 - (12 \times 205.14) \right] K - 1 \text{ mol} - 1 \text{ (ii)} = +512.0 \text{ J K} - 1 \text{ mol} - 1 \text{ mol}$ (primitively) by counting squares. Area A = 38.28 J K-1 mol-1. Area B up to $0^{\circ}\text{C} = 25.60 J K-1 mol-1$; area B up to $25^{\circ}\text{C} = 27.80 J K-1 mol-1$ (b) Sm (298 K) = Sm (0) + 66.08 J K -1 mol-1 Sm
(T) = Sm (0) + 63.88 J K -1 mol-1. plotting C p,m / T against T and determining the area under the curve. Draw up the following table. (The last two columns come from determining areas under the curves described below.) T/K 0.00 10.00 20.00 30.00 40.00 50.00 60.00 70.00 80.00 90.00 100.00 110.00 150.00 160.00 170.00 180.00 190.00 200.00 C p.m C p.m T SmO - SmO (0) H mO - H mO (0) J K -1 mol-1 0.00 2.09 14.43 36.44 62.55 87.03 111.00 131.40 149.40 165.30 179.60 192.80 237.60 247.30 256.50 265.10 273.00 280.30 J K -2 mol-1 0.00 0.21 0.72 1.21 1.56 1.74 1.85 1.88 1.87 1.84 1.80 1.75 1.58 1.55 1.51 1.47 1.44 1.40 J K -1 mol-1 kJ mol-1 0.00 0.80 5.61 15.60 29.83 46.56 64.62 83.29 102.07 120.60 138.72 $156.42\ 222.91\ 238.54\ 253.79\ 268.68\ 283.21\ 297.38\ 0.00\ 0.01\ 0.09\ 0.34\ 0.85\ 1.61\ 2.62\ 3.84\ 5.26\ 6.84\ 8.57\ 10.44\ 19.09\ 21.52\ 24.05\ 26.66\ 29.35\ 32.13\ Plot\ Cp,m\ =\ aT3\ fitted\ to\ the\ point\ at\ T\ =\ 10\ K,\ which\ gives\ a\ =\ 2.09\ m]\ K\ -\ 2\ m]\$ Sm against T (Fig. 3B.2(b)). Figure 3B.2 (a) Fig. 3.3(a) 2.0 (Cp/T)(J/K^2·mol) 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 0 50 100 150 200 T/K The molar enthalpy is determined in a similar manner from a plot of Cp,m against T by determining the area under the curve (Fig. 3.4) H mO (200 K) – H mO (0) = $\int 200 \text{ K} 0 \text{ C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 150 100 50 0 0 50 100 150 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 150 100 50 0 0 50 100 150 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 150 100 50 0 0 50 100 150 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 150 100 50 0 0 50 100 150 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 300 Cp/(J/K·mol) 250 200 T/K 3B.6 The entropy at 200 K is calculated from Sm O (200 K) = Sm O (100 K) + $\int 200 \text{ K C p,m} dT = 32.1 \text{ kJ}$ mol-1 Figure 3B.3 Fig. 3.4 mol-1 Fig appear below. The numerical integration can be carried out by a standard procedure such as the trapezoid rule (taking the integration are readily available for personal computers. Many graphing calculators will also perform this numerical integration. T/K C p,m / (J K - 1 mol - 1) C p,m T (J K - 2 mol - 1) 100 23.00 120 23.74 140 24.25 150 24.44 160 24.61 180 24.89 200 25.11 0.230 0.1732 0.1629 0.1538 0.1256 Integration by the trapezoid rule yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 = 46.60 J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant yields Sm O (200 K) = (29.79 + 16.81) J K - 1 mol - 1 3:12 Taking Cp,m constant $O(200 \text{ K}) = \text{Sm } O(100 \text{ K}) + \text{C p,m ln}(200 \text{ K} / 100 \text{ K}) = [29.79 + 24.44 \ln(200 / 100 \text{ K})] \text{ K} - 1 \text{ mol} - 1 = 46.60 \text{ J K} - 1 \text{ mol} - 1 \text{ mol} - 1 = 46.60 \text{ J K} - 1 \text{ mol} - 1 \text{ mol} - 1 = 46.60 \text{ J K} - 1 \text{ mol} - 1 \text{ mol} - 1 = 46.60 \text{ J K} - 1 \text{ mol} - 1 \text{ mo$ depends on what comparison is made. Multiply the answer by Avogadro's number to obtain the molar residual entropy, 5.76×109 J K-1 mol-1, surely a large number—but then DNA is a macromolecule. The residual entropy per mole of base pairs may be a more reasonable quantity to compare to molar residual entropy. that answer, divide the molecule's entropy by the number of base pairs before multiplying by NA. The result is 11.5 J K-1 mol-1, a quantity more in line with examples discussed in Exercises 3B.1(a) and (b). 3C Concentrating on the system that we have encountered, U, H, S, A, and G can be used as the criteria for the spontaneity of a process under specific conditions. The criteria for the fundamental relation of the first and second laws, namely $-dU - pext dV + dwnon-pV + TdS \ge 0$ The inequality sign gives the criteria for the spontaneity of a process, the equality gives the criteria for equilibrium. The specific conditions we are interested in and the criteria that follow from inserting these conditions into the fundamental relation are the following: (1) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and P, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and P, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V, no work at all dSU $V \ge 0$ (2) Constant S and V $V \ge 0$ (2) Constant all dH S, $p \le 0$ (4) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, no non-pV (8) Constant T and p, no non-pV (8) Constant T and p, no non-pV (8) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, no non-pV (8) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, no non-pV (8) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, p = pext dGT, $p \le 0$ (7) Constant T and p, $p \le 0$ $kJ mol - 1 = -218.66 kJ mol - 1 \Delta r G O = -218.66 kJ mol - 1 - (298.15 K) \times (-21.0 J K - 1 mol - 1) = -212.40 kJ mol - 1 \Delta r G O = -5645 kJ mol - 1 \Delta r G O = -5645 kJ mol - 1 \Delta r G O = -5645 kJ mol - 1 - (298.15 K) \times (512.0 J K - 1 mol - 1) = -5798 kJ mol - 1 \Delta r G O = -5645 kJ mol - 1 \Delta r G O = -5645
kJ mol - 1 \Delta r G O = -5645 kJ mol - 1 - (298.15 K) \times (512.0 J K - 1 mol - 1) = -5798 kJ mol - 1 \Delta r G O = -5645 kJ mol -$ Reactants = $-510.7 \text{ kJ} \text{ mol} - 1 - (-277.69 \text{ kJ} \text{ mol} - 1) - (-110.53 \text{ kJ} \text{ mol} - 1) = -122.5 \text{ kJ} \text{ mol} - 1 \text{ O} \Delta = \text{rS} \Sigma \text{ vS} \text{ O} \text{ m} - \text{Products} \Sigma \text{ vS} \text{ O} \text{ m} (3B.2) \text{ Reactants} = 191.0 \text{ J} \text{ K} - 1 \text{ mol} - 1 - 197.67 \text{$ 3C.3(b) C3 H 8 (g) + 50 2 (g) $\rightarrow 3CO 2$ (g) + 4H 2 O(l) Δ r G O = 3Δ f G O (CO 2, g) + 4A f G O (H 2 O, l) - Δ f G O (Zn 2+, aq) - Δ f O (Zn 2+, aq) - Δ f O (Zn $O(Cu 2 + ,aq) = -147.06 - 65.49 \text{ kJ mol} - 1 = -212.55 \text{ kJ mol} - 1 \Delta r G O = 12\Delta f G O(CO 2, g) + 11\Delta f G O(H 2 O, l) - \Delta f G O(CO 2, g) = [12 \times (-394.36) + 11 \times (-237.13) - (-1543) - 12 \times 0] \text{ kJ mol} - 1 = -5798 \text{ kJ m$ Exercise 3C.1(b). 3C.5(b) The formation reaction of glycine is $1 \ 2 \ 5 \ 2 \ 2C(gr) + O \ 2(g) + H \ 2(g) \rightarrow NH \ 2 \ CH \ 2 \ COOH(s) + F \ 2 \ OOH(s) + F$ $COOH(s) = 2\Delta f H O (CO 2, g) + \Delta f H O (H 2 O, 1) - \Delta c H (NH 2 CH 2 COOH(s)) 5 2 = -2 \times 393.51 \text{ kJ mol} - 1 + () \times (-285.83 \text{ kJ mol} - 1) = -532.6 \text{ kJ mol} - 1 = -53$ $-(205.138 \text{ J K} - 1 \text{ mol} - 1) - 1 - 1 \times 191.61 \text{ J K 2 mol} - 1 - 5 - 1 \times (130.684 \text{ J K 2 mol} - 1) = -535.63 \text{ J K} - 1 \text{ mol} - 1 \wedge f \text{ G O} = \Delta f \text{ H O} - T \Delta f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ S O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ s O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ s O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ s O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 \wedge f \text{ s O} = -532.6 \text{ kJ mol} - 1 - (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ K}) \times (-535.63 \text{ J K} - 1 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15 \text{ mol} - 1) = -373 \text{ kJ mol} - 1 + (298.15$ 1 - e The molar internal energy, molar entropy, and molar Helmholtz energy are obtained from the partition function as follows: $U - U(0) = -S = N\omega e - x N\omega N(\partial q) d = x = -N(1 - e - x) + nR \ln q = -x T 1 - e)(x - \ln(1 - e - x)) = Nk |x|/(e - 1A - A(0)) = -Nk |x|/(e - 1A - A(0$ $G - G(0) = -nRT \ln q = NkT \ln(1 - e - x)$ The functions are plotted in Fig. 3C.1. F12:15 Figure 3C.1 3D Combining the First and Second Laws Answers to discussion questions 3D.2 The relation ($\partial G / \partial p$)T = V, eqn 3D.8, shows that the Gibbs function of a system increases with p at constant T in proportion to the magnitude of its volume. This makes good sense when one considers the definition of G, which is G = U + pV - TS. Hence, G is expected to increase with p in proportion to V when T is constant. Solutions to exercises (p) (V) = $\Delta G nRT = \ln |f| [3D.14] nRT \ln |i| [Boyle's law] 3D.1(b) p (i) (Vf) (52) \Delta G = (6.0 \times 10 - 3 mol) \times (8.314 J K - 1 mol - 1) \times (298 K) \times \ln |i| = -13 J (122)$ $3D.2(b)\left(\partial G \right)\left(\partial G$ pressures given and that, therefore, equation 3D.13 which applies to incompressible substances can be used to solve this exercise. The change in Gibbs energy for this sample is then given by $\Delta G = nVm \Delta p [3D.13] = V \Delta p 3:16 (1m3) \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40 \text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ In order to calculate the change in Gibbs energy per this sample is then given by } \Delta G = nVm \Delta p [3D.13] = V \Delta p 3:16 (1m3) \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40
\text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ In order to calculate the change in Gibbs energy per this sample is then given by } \Delta G = nVm \Delta p [3D.13] = V \Delta p 3:16 (1m3) \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40 \text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ In order to calculate the change in Gibbs energy per this sample is then given by } \Delta G = nVm \Delta p [3D.13] = V \Delta p 3:16 (1m3) \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40 \text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ In order to calculate the change in Gibbs energy per this sample is then given by } \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40 \text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ In order to calculate the change in Gibbs energy per this sample is then given by } \Delta G = (100 \text{ cm} 3) \times | 6 \times 400 \text{ kPa} = 40 \text{ Pa} \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{ J} 3 | 10 \text{ cm} () \text{ m} 3 = +40 \text{$ mole we calculate the molar volume M 18.02 g mol -1 10 -6 m 3 = x = Vm = 1.81 × 10 -5 m 3 mol -1 , then -3 3 ρ (density) 0.997 g cm cm Δ Gm = RT ln | f |=(8.314 J K -1 mol-1) × (500 K) × ln | | 50.0 kPa | pi | 3D.4(b) = +2.88 kJ mol-1Solutions to problems 3D.2 The Gibbs-Helmholtz equation [3D.9] may be recast into an analogous equation involving ΔG and ΔH , since $\left(\frac{\partial \Delta G}{\partial G}\right)\left(\frac{\partial G T}{\partial G}\right)$ and $\Delta H = H f - H i$ Thus, $\left(\frac{\partial \Delta G O}{\partial G}\right)\left(\frac{\partial G T}{\partial G}\right)\left(\frac{\partial G T}{\partial G}\right)$ $= - \left(T \right) T \Delta r H O dT Tc T 2 \int \approx -\Delta r H O Tc T 2 \int \approx -\Delta r H O Tc T 2 \int \tau C dT = \Delta H O r T 2 \left(1 \right) O T - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r G O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O (Tc) + 1 - T \right] \Delta r H O (Tc) + 1 - T \left[\Delta r H O ($ $2NH 3 (g) \Delta r G O = 2\Delta f G O (NH 3, g) (a) so At 500 K, \tau = 500 = 1.678, 298 \Delta r G O (500 K) = {(1.678) \times 2 \times (-16.45) + (1 - 1.678) \times 2 \times (-46.11)} Jmol - 1 = -7 kJmol - 1 = -7 kJmol$ [Table 3D.1] $\partial V |T| \partial T || V || \partial T || V m - b$ $\partial V |T$ so we can simply compare (∂S) expressions for the three gases. For a perfect gas, ($\partial V |T| = (\partial S) = (\partial p) = R (\partial V) T || \partial T || V m V n RT RT so = V Vm (\partial S)$ is certainly greater for a van der Waals gas than for a perfect gas, for the denominator is ($\partial V |T| = (\partial S) = (\partial p) = R (\partial V) T || \partial T || V m V n RT RT so = V Vm (\partial S)$ is certainly greater for a van der Waals gas to the Dieterici gas is $\partial V / T$, Die always less than 1. Clearly (1+x)e-x < 1 for large x, for then the exponential dominates. But (1+x)e-x < 1 even for small x, as can be seen by using the power series expansion for the exponential. $\partial V / T$, $\partial V / T$, and ΔS vdW > ΔS perfect The comparison between a perfect gas and a Dieterici gas depends on particular values of the constants a and b and on the physical conditions. 3D.6 (a) (V) (∂T) 1 × ∂V ; $\alpha = p()(() T \kappa T = -1 \times |\partial V| (\partial P) | (\partial V | = | (\partial T | (Maxwell relation] T V () () (\partial P) | (\partial P) |$ numerator: $(\partial S) - \partial V$ [Maxwell relation] = $-\alpha V$ | = $\partial T p (\partial p) \Gamma$ () As for the denominator, at constant $p(\partial S) dS = | dT and (\partial T) p ()$ Therefore, $\partial S \partial T (2) = p Cp T dS = (\partial \partial VS) and dqrev dH C p dT = T T = p [dq p = dH] \alpha TV Cp (\partial T) (\partial P) || <math>\partial S || = -| (\partial V | S (\partial S) (\partial V) || || (\partial T) P (\partial S) (\partial V) || || (\partial T) P (\partial T) (\partial P) || = \partial T P (\partial P) (\partial S) (\partial V) || = \partial T P (\partial P) (\partial S) (\partial V) || = \partial T P (\partial P) (\partial S) (\partial V) || = \partial T P (\partial P) (\partial S) (\partial S) (\partial V) || = \partial T P (\partial P) (\partial S) (\partial P) (\partial S) (\partial P) || = \partial T P (\partial P) (\partial S) (\partial P) (\partial$ \mathcal{N} ∂S \mathcal{T} ($\partial \partial VS$) ($\partial \partial TS$) T [reciprocal] V () () () (∂p ∂V (∂p -| || ∂T $|| \partial V$ \mathcal{T} ∂T p \mathcal{N} [Maxwell relation] [Euler chain relation] = $\partial S \partial U \partial S \partial U \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V)
\partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V)$ (∂U) $\partial T \partial S = (\partial V) \partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V) (\partial U \partial T V = ()$ () $-(\partial V \partial U \partial V = ()$ () $-(\partial V \partial U \partial V = ()$ () $-(\partial V \partial U \partial T V = ()$ () $-(\partial V \partial U \partial V = ()$ () $(= = \partial V)(\partial T)\partial V(\partial U)(\partial p) = -(\partial U)[reciprocal identity] = p - T | [3D.6]\partial V(\partial T)\mu] = (b) V U V T T V F12:19(\partial p) - 1[Euler chain] = |(\partial T)| = (\partial V)(\partial V)p|(\partial p)|T = \alpha \kappa T Therefore, \mu] CV = p - \alpha T \kappa T(\partial p) 3D.8 = \pi T T | - p[3D.6](\partial T)V - kT \ln Q[Chapter 15] A = (\partial A)[\partial \ln Q]p = kT | - | = kT | = kT | - | = kT | - | = kT | - | = kT | =$ so f d ArG T O = - f O O = A r G220 A r G190 A r G2 T2 O = A r G1 T1 O - Ar H T2 O AT A r G190 O A r G220 O Ar H O d T and = + Ar H O T2 T190 T220 T190 + Ar H O T2 T190 T220 T190 + Ar H O T220 (11) | T - T | (190 220) (T190) | 1 - T | (220) For the monohydrate (190 K) (190 K) O (+ (127 kJ mol - 1) × | 1 - = (46.2 kJ mol - 1) × | A r G190 | 220 K | (120 K) | (220 K $\Delta r G190 = 57.2 \text{ kJ mol} - 1$ For the dihydrate (190 K) (190 K) O + (188 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69.4 \text{ kJ mol} - 1) × | 1 - , = (69 3.2 For a thorough discussion of the relationship between the thermodynamic and statistical definitions of entropy, see Section 3A. We will not repeat all of that discussion here and will merely summarize the main points. dq The thermodynamic entropy is defined in terms of the quantity dS = rev where dqrev is the T infinitesimal quantity of energy supplied as heat to the system reversibly at a temperature T. The statistical entropy is defined in terms of the Boltzmann formula for the entropy: S = k ln W where k is the Boltzmann constant and W is the number of microstates, the total number of the system can be arranged to achieve the same total energy of the system. These two definitions turn out to be equivalent provided the thermodynamic entropy is taken to be zero at T = 0. The concept of the number of microstates makes quantitative the ill-defined qualitative concepts of 'disorderly' that are used widely to introduce the concept of entropy: a more 'disorderly' distribution of energy and matter corresponds to a greater number of microstates associated with the same total energy. The more molecules that can participate in the distribution of energy and the greater the entropy than when the energy is confined to a smaller number of molecules. The molecular interpretation of entropy given by the Boltzmann formula also suggests the thermodynamic definition. At high temperatures where the molecules of a system can occupy a large number of accessible energy levels, whereas at low temperatures the transfer of the same quantity of heat will increase the number of accessible energy levels and microstates significantly. Hence, the change in entropy should be greater when the energy is transferred to a cold body than when it is transferred to a cold body
than inversely proportional to the temperature at which the transfer takes place as in indicated in the thermodynamic definition. F12:21 4 Physical transformations of pure substances 4A Phase diagrams pV term within the Gibbs energy (part of the definition of enthalpy); the product changes when the pressure changes. Physically, an incompressible gas); however, it can transmit energy is it does in a hydraulic cylinder. Furthermore, an incompressible system under pressure is under stress at a molecular level. Its bonds or intermolecular repulsive forces resist external forces without contraction. Finally, one can observe changes in phases in equilibrium with incompressible liquids (the pressure of their vapours, for example) when pressure is applied to the liquid; see Topic 4B.1(c). 4A.4 Figure 4A.1 Refer to Figure 4A.1. Starting at point A and continuing clockwise on path p(T) toward point B, we see a gaseous phase only within the container with water at pressures and temperatures p(T). Upon reaching point B on the vapour pressure curve, liquid appears on the bottom of the container with water at pressures and temperatures p(T). gas above it. The liquid and gaseous phases are at equilibrium at this point. Proceeding clockwise away from the vapour pressure curve the meniscus disappears and the system becomes wholly liquid. Continuing along p(T) to point C at the critical temperature no abrupt changes are observed in the isotropic fluid. Before point C is reached, it is possible to return to the vapour pressure curve and a liquid-gas equilibrium by reducing the pressure is othermally. Continuing clockwise from point C along path p(T) back to point A, no phase boundary is observed even though we now consider the water to have returned to the gaseous state. point after point C, it is impossible to return to a liquid-gas equilibrium. When the path p(T) is chosen to be very close to the critical conditions, densities and refractive indices of both the liquid and gas phases are nearly identical. Furthermore, molecular fluctuations of densities and refractive indices of both the liquid and gas phases are nearly identical. and refractive indices on a scale large enough to strongly scatter visible light. This is called critical opalescence. Solutions to Exercises 4A.1(b) The phase rule (eqn 4A.1) relates the number of phases (P), components (C), and degrees of freedom (F) of a thermodynamic system: 1 F=C-P+2. Restricting to pure substances (C=1) and rearranging for phases gives P=3-F. Areas in the phase diagram have two degrees of freedom; one can vary pressure and temperature independently (within limits) and stay within the area. Thus, F = 2 and P = 1 in areas. Lines have one degree of freedom; one can vary pressure or temperature independently (within limits) and stay within the area. Thus, F = 1 and P = 2 on lines. Points on the phase diagram have zero degrees of freedom; one can vary neither pressure nor temperature and on a given points. (a) is in an area, so there is a single phase. (b) and (c) are points, so there are three phases present. (d) is on a line, so there are two phases present. (d) is on a line, so there is a single phase. (b) and (c) are points, so there are three phases present. (d) is on a line, so there are two phases present. (d) is on a line, so there are two phases present. (d) is on a line, so there is a single phase. (b) and (c) are points, so there are three phases present. (d) is on a line, so there are two phases present. 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(for a line, so there are three phases present. (for a line, so there are three phases present. (for a line, so there are three phases present. (for a line, so there are three phases phases phases phases present. (for a line, so there are three phases ph For pure substances (one-component systems), the chemical potential is the molar Gibbs energy: $dG = (\mu 2 - \mu 1)n = (-8.3 \text{ kJ mol}-1)(0.15 \times 10-3 \text{ mol}) = +1.2 \times 10-3 \text{ kJ} = 1.2 \text{ J}$. 4A.3(b) Use the phase rule (eqn 4A.1) F=C-P+2 to solve for the number of phases: P=C-F+2=4-F+2=6-F \le 6. The maximum number of phases in equilibrium occurs when the number of degrees of freedom is at a minimum, namely zero; that number is six. 4B Phase diagrams of pure substances Answers to discussion questions 4B.2 See Topic 4B.1(b). The mathematical reason can be seen in eqn 4B.2, ($\partial \mu$)|| ∂p || = Vm T Because Vm > 0 for all pure substances, the slope of the change in chemical potential with respect to change in pressure is positive: chemical potential increases with increasing pressure. See also the answer to Discussion question 4A.2, which addresses why the chemical potential increases with increasing pressure. the first derivative of the Gibbs energy with respect to temperature. They are recognized by finite discontinuities in plots of H, U, S, and V against temperature and by an infinite discontinuities in the second derivatives of the Gibbs energy with respect to temperature, but the first derivatives are continuous. The second-order transitions are recognized by kinks in plots of H, U, S, and V against temperature, but most easily by a finite discontinuity in a plot of Cp against temperature. A λ -transition shows characteristics of both first and second-order transitions and, hence, is difficult to classify by the Ehrenfest scheme. It resembles a firstorder transition in a plot of Cp against T, but appears to be a higher-order transition with respect to other properties. At the molecular level first-order transitions are associated with discontinuous changes in the interaction energies between the atoms or molecules constituting the system and in the volume they occupy. One kind of second-order transition may involve only a continuous change in the arrangement of the atoms from one crystal structure (symmetry) to another while preserving their orderly arrangement. In one kind of λ-transition, called an orderdisorder transition, called an orderdisorder transition, called an orderdisorder transition to the atomic arrangement. Exercises 4B.1(b) The difference between the definition of normal and standard transition temperatures is the pressure at which the transition temperatures is the pressure at which tempera equilibrium, so their chemical potentials are equal: μ liquid(Tstd,pstd) = μ gas(Tstd,pstd) The same can be said at the normal boiling temperature and pressure: μ liquid(Tnorm,pnorm) = μ gas(Tnorm,pnorm) Equations 4B.1 and 4B.2 show how the chemical potential changes with temperature and pressure, so for small changes we can write ($\partial \mu$)($\partial \mu$ $d\mu = | |dT + | |dp = -Sm dT + Vm dp | \partial p | T | \partial T | p$ Assuming that the differences between standard and normal boiling point are small enough, we can equate the differences in the chemical potentials of the two phases: $\Delta \mu gas = -Sm, gas \Delta T + Vm, gas \Delta p = -Sm, dT + Vm, dp | \partial p | T | \partial T | p$ Assuming that the differences between standard and normal boiling point are small enough, we can equate the differences between standard and normal boiling point are small enough. isolate ΔT : (Sm,liquid-Sm,gas) $\Delta T = (Vm,liquid-Vm,gas)\Delta p \approx -Vm,gas\Delta p$ Use the ideal gas law to find the molar volume of the gas. Also, we need to find $\Delta vapS$ or to use Trouton's rule (eqn 3A.17): Vm,gas $\Delta p \approx -Vm,gas\Delta p \otimes T = (Vm,liquid-Vm,gas)\Delta p \otimes T = (V$ $(40.656 \times 103 \text{ J}) = 0.38 \text{ K}$ That is, the normal boiling temperature is 0.38 \text{ K} higher than the standard boiling temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature is 0.38 K higher than the standard boiling temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with
temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with temperature. 4B.2(b) Equation 4B.1 shows how the chemical potential changes with tem 4B.3(b) Equation 4B.2 shows how the chemical potential changes with pressure ($\partial \mu$) M d μ = | |dp = Vm dp = d $p \wedge \Delta p$ = 78.11 g mol-1 + 0.088 kJ mol-1 vapour pressure of a change in applied external pressure on a liquid is given by eqn 4B.3: p = p * e m For liquid naphthalene, the molar volume is V (l) $\Delta P/RT$ Vm = 4B.5(b) M = $\rho = 118.16$ g mol-1 = 122.8 cm 3 mo 368 K and p = p *e Vm (1) $\Delta P/RT = (2.0 \text{ kPa})e0.598 = 3.6 \text{ kPa}$. Use the Clapeyron equation (eqn 4B.5a) dp Δ trs S = dT Δ trs V 3 Assume that Δ fusS and Δ fusS = (152.6 cm 3 mol-1) × (1.2 × 106 Pa - 1.01 × 105 Pa) 429.26 K - 427.15 K $1m 3 = (10.6 \text{ cm } 3 \text{ mol}-1) \times | 63| \times (5.21 \times 105 \text{ Pa } \text{K}-1) (10 \text{ cm }) = 5.52 \text{ Pa } \text{m } 3 \text{ K}-1 \text{ mol}-1 = +5.5 \text{ K} \times (5.52 \text{ J } \text{ K}-1 \text{ mol}-1) = +2.4 \text{ kJ} \text{ mol}-1 + 8.6(b) \text{ On the assumption that the vapour is a perfect gas and that } \Delta \text{ vapH is independent of temperature}, we may write [4B.11]$ $(\Delta vap H)(11)p*x$, $\ln - \chi p = p*e - \chi$, $\chi = |||*|p(R)(TT)p*R11 \ln = *+\Delta vap HTTp(58.0)18.3145 JK - 1 mol - 1 = 3.378 \times 10 - 3 K - 1 \times ln| + 3 - 1.293.2 K 32.7 \times 10 J mol(66.0)| = Hence T = 4B.7(b) 1 = 296 K = 23^{\circ}C 3.378 \times 10 - 3 K - 1 \times ln| + 3 - 1.293.2 K 32.7 \times 10 J mol(66.0)|$ f d ln p = f RT 2 dT Δ vap H so ln p = constant - RT Therefore, Δ vap H = 3036.8 K × R = 8.3145 J K -1 mol-1 × (3036.8 K) = +25.25kJ mol-1 4B.8(b) (i) The indefinitely integrated form of eqn 4B.10 is used as in Exercise 4B.7(b). Δ vap H Δ vap H h p = constant - RT 2.303 RT Thus Δ vap H = 1625 K × R × 2.303 = 1625 K × 8.3145 J K -1 mol-1 × 2.303 = 31.11kJ mol-1 (ii) The normal boiling point corresponds to p = 1.000 atm = 760 Torr, 1625 K so log 760 = 8.750 - T 1625 K s point is Tf = (273.15 - 3.65) K = 269.50 K at a pressure of 1 atm, which is about 0.1 MPa. Thus, to the nearest MPa, $\Delta p = 100$ MPa = 1.00×108 Pa $(\Delta T \approx)$ 1 269.50 K × 46.1 g mol-1 × $(1.00 \times 108$ Pa) $(\times | -3 - 1 - 3 - 3 | 0.789$ g cm 0.801g cm $/ 8.68 \times 10$ J mol ≈ 2.7 K Therefore, at 100 MPa, Tf = (269.50 + 2.7) K = 272.2 K or -1.0° C. 4B.10(b) The rate of loss of mass of water may be expressed as dm d q = (nM) where $n = dt dt \Delta vap H$ Thus dn d $q dt (0.87 \times 103 \text{ J mol}-1 \text{ and } dm = (200 \text{ mol } \text{ s} -1) \times (18.02 \text{ g} \text{ mol}-1) = 3.6 \text{ kg } \text{ s} -1 \text{ dt } 4B.11(b)$ The equilibrium vapour pressure of ice at -5° C is 0.40 kPa Therefore, the frost would sublime. A partial pressure of 0.40 kPa or more would ensure that the frost remains. 4B.12(b) (i) According to Trouton's rule (eqn 3A.17) Δ vap H \approx 85J K -1 mol-1 \times Tb = 85J K -1 mol-1 \times 342.2 K = 29.1 kJ mol-1 (ii) Use the integrated form of the Clausius-Clapeyron equation (eqn 4B.11) rearranged to (p) Δ vap H (11) \times | - $\ln | 2 | = R$ $(T1 T2 | p1 | At T1 = 342.2 \text{ K}, p1 = 1.000 \text{ atm} [normal boiling point]; thus at 25^{\circ}C () (2.91 \times 104 \text{ J mol}-1)(p2 1) 1 \ln | - = -1.51 \times | = -1.-1 | 298.2 \text{ K} | 342.2 \text{ K} 1.000 \text{ atm} | (1.000 \text$ $(273.15 \text{ K}) \times 9.9 \times 106 \text{ Pa} \times 18.0 \text{ g mol} - 1)\Delta T = |6.01 \times 103 \text{ J mol} - 1) |0.01 \times 103 \text{ J mol} - 1 |0.01$ e-0.276 atm = 0.76 atm. and $4B.13(b) \Delta T = Tf (10 \text{ MPa}) - Tf (0.1 \text{ MPa}) = Tf \Delta pM (1) [Exercise 4B.9(b)] \Delta \Delta fus H | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1) | (1)$ $\Delta vap(pV) = 43.5 \text{ kJ mol} - 1 \Delta vap(pV) = p\Delta vapV = p(Vgas - Vliq) \approx pVgas = RT [perfect gas] \Delta vap(pV) \approx (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (352 \text{ K}) = 2.93 \times 103 \text{ J mol} - 1 \text{ Fraction} = = 0.0673 = 6.73 \text{ per cent } \Delta vap \text{ H} 43.5 \text{ kJ mol} - 1 \text{ Solutions to problems 4B.2 Use the definite integral form of the Clausius-Clapeyron equation [Exercise]}$ 4B.12(b)]. (p) Δ vap H (11) × | - |ln| 2 |= R (T1 T2) (p1) At T1 = (273.15 - 29.2) K = 244.0 K (normal boiling point), p1 = 1.000 atm ; thus at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm
Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (p2 11) = 2.205 ln | - ||=| × (1.000 atm × e2.205 = 9.07 atm Comment. Three significant figures at 40°C 5 () (20.25 × 103 J mol-1) (20.25 × 103 J mol-1) (20.25 × 10 are not really warranted in this answer because of the approximations employed. 4B.4 (a) $-\Delta$ fus H ($\partial\mu$ (b) ($\partial T \parallel - | (\partial T \parallel - Sm (l) + Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (l) + Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - | (\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1mol-1 273.15 K $-\Delta$ vap H ($\partial\mu$ (c) ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1 ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01×103 J mol-1 = -22.0 J K -1 ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01 \times 103 J mol-1 = -22.0 J K -1 ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01 \times 103 J mol-1 = -22.0 J K -1 ($\partial T \parallel - Sm (s) = -\Delta$ fus S = T f p p = (b) -6.01 \times 103 J mol $-1 = -2.01 \times 103$ J mol $-1 = -2.01 \times 10$ $-108.8 \text{ J K} - 1 \text{ mol} - 1 373.15 \text{ K } \mu(l, -5^{\circ}\text{C}) - \mu(s, -5^{\circ}\text{C}) = \mu(l, 0^{\circ}\text{C}) + \mu(s, -5^{\circ}\text{C}) = \mu(s, 0^{\circ}\text{C}) + \mu(s, -5^{\circ}\text{C}) - \mu(s, -5^{\circ}\text{C}) = \mu(s, 0^{\circ}\text{C}) + \mu(s, -5^{\circ}\text{C}) = \mu(s, -5^{\circ$ $5^{\circ}C$ - $\mu(l,0^{\circ}C)$ - $\mu(s,-5^{\circ}C) - \mu(s,0^{\circ}C)$ = $-\Delta fus S \Delta T \mu(l,-5^{\circ}C) - \mu(s,-5^{\circ}C)$ = $-(+22.0 \text{ J K} - 1 \text{ mol} - 1) \times (-5 \text{ K}) = +110 \text{ J mol} - 1$ Since $\mu(l,-5^{\circ}C) - \mu(s,-5^{\circ}C)$, there is a thermodynamic tendency to freeze. $\Delta H dp \Delta fus S [4B.6] [4B.5a] = fus = dT \Delta fus V dp$. $\Delta fus V dp \Delta fus S [4B.6] = -\Delta fus V dp$. = $\int p bot p top Tm \Delta fusV T \Delta V d p = m fus \Delta p [assuming the integrand is constant] \Delta fus H \Delta p = pbot - ptop = \rho gh; T \rho gh \Delta fusV \Delta T = m \Delta fus H (234.3K) \times (13.6 g cm - 3) \times (9.81m s - 2) \times (10.0 m) \times (0.517 cm 3 mol - 1) 1 kg \times 3 10 g 2.292 \times 103 J mol - 1 = 0.071 K = Therefore, the freezing point changes to 234.4 K 4B.8 Integrating the$ Clausius-Clapeyron eqation [4B.10] yields an expression for ln p: Δ vap H ln p = constant - RT Therefore, plot ln p against 1/T and identify - Δ vapH/R as the slope of the plot. Construct the following table 0 20 40 50 70 80 90 100 θ /°C T/K 273 293 313 323 343 353 363 373 1000 K / T 3.66 3.41 3.19 3.10 2.92 2.83 2.75 2.68 ln (p / kPa) 0.652 1.85 2.87 3.32 4.13 4.49 4.83 5.14 6 Figure 4B.1 The points are plotted in Figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. 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The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, which from the figure 4B.1. The slope is -4569 K, so $-\Delta$ vap H = +38.0 kJ mol-1 R The normal boiling point occurs at p = 1 atm = 101.3 kPa, or at ln(p/kPa) = 4.618, w 4B.10 The slope of the solid-vapour coexistence curve is given by Δ H dp dp = sub [analogous to 4B.9] so Δ sub H = T Δ subV dT Figure 4B.2. linear fit to the transformed data. The fit equation is $p/Pa = 2.659 \times 10 - 10 \ e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times e0.1687T/K 7 \ dp = (2.659 \times 10 - 10 \ Pa) \times (0.1687 \ K - 1) \times (0.1687 \ K - 1)$ H O = (150 K) × (47.7 m 3) × 4.41Pa K -1 = 3.16 × 104 J mol - 1 = 31.6 kJ mol - 1 dH = CpdT + V dp implies $d\Delta H = \Delta CpdT + \Delta V dp$, where Δ signifies a difference between phases. Along a phase boundary dp and dT are related by dp $\Delta H [4B.6 \text{ or } 4B.9] = dT T \Delta V$ Therefore, $(\Delta H \Delta H) \Delta H dT = |\Delta Cp + dV \times = \Delta Cp + \Delta V \times = \Delta Cp + \Delta V \times = \Delta Cp + \Delta V = \Delta Cp + \Delta V dp$. hydrostatic pressure of the liquid overlying the depth d: $\Delta P = \rho gd$ The molar volume of the liquid is Vm(l) = M / ρ Substituting into eqn. 4B.3 yields $p = p^*eMgd/RT$ For a 10-m column of water at 25°C, V (l) $\Delta P / RT$ Mgd (18.02 × 10-3 kg mol-1) × (298 K) so $-4p = e7.1 \times 10 = 4P$ (8.3145 J K -1 mol-1) × (298 K) so $-4p = e7.1 \times 10 = 4P$ $7.1 \times 10-4 \times p$ That is, the fractional increase in vapor pressure is $7.1 \times 10-4$ or 0.071 per cent. 4B.16 In each phase the slopes of curves of chemical potential plotted against temperature are $(\partial \mu) || \partial T || = -Sm [4.1] p$ The
curvatures of the graphs are given by $(\partial Sm) (\partial 2\mu) || \partial T 2 || = -|| \partial T || p$ To evaluate this derivative, consider dS at constant p: C p,m $(\partial S)(\partial 2\mu)$ dq dH C p dT so dS = rev = = - | m | = - | 2 | T T T ($\partial T / 0$ p Since Cp,m is necessarily positive, the curvatures in all states of matter are necessarily negative. Cp,m is often largest for the liquid state, though not always. In any event, it is the 8 ratio Cp,m/T that determines the magnitude of the curvature, so no general answer can be given for the state with the greatest curvature. It depends upon the substance. 4B.18 $\hat{S} = S(T,p) \left(\frac{\partial S}{\partial S} \right) dS = | |dT + | |dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV \times aV = C p dT - T (\partial V) dp (\partial T / p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | = C p - TV \alpha | | = C p - aV + A = C p dT + C p (\partial P / CS = | = C p - A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P / CS = A = C p dT + C p (\partial P /$ trs [4B.6] Δ trsV (∂ T /S (∂ T /S Integrated activities 4.2 (a) The phase diagram is shown in Figure I4.1. Figure I4.1 (b) The standard melting point is the temperature at which solid and liquid are in equilibrium at 1 bar. That temperature can be found by solving the equation of the solid-liquid coexistence curve for the temperature: 1 = p3/bar + 1000(5.60+11.727x)x. Put the equation into standard form: $11727x2 + 5600x + (4.362 \times 10-7 - 1) = 0$ The quadratic formula yields (×11727 × (-1)] $2 = x = 11727 2 \times (1727 - 1 \pm 1 + 45600 - 5600 \pm {(5600) 1/2}) 1/2 {}$ The square root is rewritten to make it clear that the square root is of the form 1 + a () 12, with a = 1; thus the numerator is approximately -1 + 1 + 12 a = 12 a, and the whole expression reduces to $x \approx 1/5600 = 1.79 \times 10-4$. Thus, the melting point is the temperature at which the liquid and vapour are in equilibrium at 1 bar. That temperature can be found by solving the equation of the liquid-vapour coexistence curve for the temperature. This equation is too complicated to solve 9 analytically, but not difficult to solve 9 analytically, but not difficult to solve 9 analytically, but not difficult to solve 9 analytically with a spreadsheet. The calculated answer is $y = 0.6459 \times 593.95 \text{ K} = 383.6 \text{ K}$. (d) The slope of the liquid-vapour coexistence curve is given by Δ vap H dp dp = [4B.9] so Δ vap H = T Δ vap V dT T he slope can be obtained by differentiating the equation for the coexistence curve. d ln p dy d ln p dp = p = p dy dT dT dT dT dp $(10.413 = | -15.996 + 2(14.015) y - 3(5.0120) y 2 - (1.70) \times (4.7224) \times (1 - y)0.70 | 2 dT (y)(p) \times | | Tc | Substituting the value of y at the boiling point yields, dp = 2.848 \times 10^{-10}$ 10-2 bar K -1 = 2.848 kPa K -1 = 2.848 kPa K -1 dT ((30.3 -0.12) dm 3 mol-1) -1 -1 and Δ vap H = (383.6 K) × | × (2.848 kPa K) = 33.0 kJ mol 1000 dm 3 m -3 / 4.4 (a) The phase boundary is plotted in Figure I4.2. Figure I4.2 (b) The standard boiling point is the temperature at which the liquid is in equilibrium with the standard pressure of 1 bar (0.1 MPa). Interpolation of the plotted points gives Tb = 112 K. (c) The slope of the liquid-vapor coexistence curve is given by Δ vap H dp (4B.9] so Δ vap H = (T Δ vapV) = dT dT T Δ vapV (8.89 - 0.0380) dm 3 mol - 1 - 1 = 0.000 coexistence curve is given by Δ vap H dp (4B.9] so Δ vap H dp (4B.9] so Δ vap H dp (4B.9] so Δ vap H = (T Δ vapV) and (2.89 - 0.0380) dm 3 mol - 1 - 1 = 0.000 coexistence curve is given by Δ vap H dp (4B.9] so Δ vap H dp (4B.9] so Δ vap H dp (4B.9) so Δ vap H vap H = $(112 \text{ K}) \times | | | \times (8.14 \text{ kPa K}) = 8.07 \text{ kJ mol} (1000 \text{ dm } 3 \text{ m} - 3 10 5 \text{ Simple mixtures 5A The thermodynamic description of mixtures 5A.1(b), dG = dwadd, max (where wadd stands for additional (non-expansion) work) for systems at constant temperature and pressure. Therefore [5A.8]$ dwadd,max = μ AdnA + μ BdnB + ... Thus non-expansion work can arise from the changing composition of a system. Physically, it should not be surprising that at least energy can be changed by changing composition, by a chemical reaction transforming a species into one that is more or less favored energetically. In an electrochemical cell, where the reaction takes place at two distinct sites, the electrical work of transporting charge between the electrodes can be traced to changes in composition as products are formed from reactants. 5A.4 See Topic 5A.3(a). In both cases, the vapor pressure of a component in a solution is proportional to its concentration (mole fraction) in the solution, at least in the limit of low concentration: p J x J If the proportionality constant is the component's vapor pressure as a pure substance, then Raoult's law into eqn 5A.22: $\mu A = \mu A^* + RT \ln xA$ If Raoult's law applies to both or all components of a mixture over a large range of composition, then we call the solution ideal. If, on the other hand, only the solvent obeys Raoult's law, and it may only obey it in the limit of mole fractions close to 1, we call the solution ideal-dilute if the solution ideal-dilute if the solution ideal-dilute if the solution of Henry's law [5A.23]. Substitution of Henry's law into eqn 5A.20 for solutes yields eqn 5E.8: K where μ BO = μ B* + RT $\ln *B [5E.7] \mu B = \mu BO + RT \ln xB pB Solutions to exercises 5A.1(b) The partial molar volume is (\partial V) (dv) ($ + 1.13784 x + 0.03069 x 2 + 0.00936 x 3) cm3 mol - 1 5A.2(b) Let A stand for water and B for MgSO4(aq) $(\partial V)(\partial x)[5A.1] = |||V] = |||V| = ||V| = ||V|$ mol kg-1 (x = 0.050), recalling that the original expression for v applies for 1.000 kg of water (i.e., for nAMA = 1.000 kg). The result is VB = -1.4 cm3 mol-1. The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.000 kg (55.49 mol) water is V = 1.001.21 + 34.69 × (0.050-0.070)2 = 1001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.21 + 34.69 × (0.050-0.070)2 = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.21 + 34.69 × (0.050-0.070)2 = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.23 cm3 · 1 The total volume is also equal to V = VAnA + 1.000 kg (55.49 mol) water is V = 1.001.23 cm3 · 1 The total volume is also equal to V = 1.001.23 cm3 · 1 The total volume is also equal to V = 1.001.23 cm3 · 1 The total volume is also equal to V = 1.001.23 cm3 · 1 The total volume is also equal to V
= 1.001.23 cm3 · 1 The total volume is also equal to V = 1.001.23 cm3 · 1 The total volume is also equal to V = 1.001.23 c VBnB [5A.3]. V – VB nB 1001.21 cm 3 – (-1.4 cm 3) × (0.050 mol) Therefore, VA = = 18.04 cm 3 mol-1 55.49 mol nA Question. VA is essentially the molar volume of pure solid MgSO4. What meaning can be ascribed to a negative partial molar volume? 5A.3(b) Use the Gibbs-Duhem equation [5A.13], replacing infinitesimal changes in chemical potential (dµ]) with small finite changes ($\delta\mu$]) n 0.22nB $\delta\mu$ B \approx - A $\delta\mu$ A = - × (-15 J mol-1) = +3.3 J mol-1 nB nB 5A.4(b) The Gibbs energy of mixing perfect gases is Δ mixG = nRT(xA ln xA + xB ln xB) [5A.16] = pV(xA ln xA + xB ln xB) [perfect gase law] Because the compartments are of equal size, each contains half of the gas; therefore, $(pV) \times 1 \ln 1 + 1 \ln 1 = \Delta \min G = -pV \ln 2 2 2 2 (1m3) - 17.3 Pa m3 = -17.3 J = -(100 \times 103 Pa) \times (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (\Delta \min S = -nR(xA \ln xA + xB \ln xB) [5A.17] = 5A.5(b) - \Delta \min G = -pV \ln 2 2 2 2 2 (1m3) - 17.3 Pa m3 = -17.3 J = -(100 \times 103 Pa) \times (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (\Delta \min S = -nR(xA \ln xA + xB \ln xB) [5A.17] = 5A.5(b) - \Delta \min G = -pV \ln 2 2 2 2 2 (1m3) - 17.3 Pa m3 = -17.3 J = -(100 \times 103 Pa) \times (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (\Delta \min S = -nR(xA \ln xA + xB \ln xB) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (\Delta \min S = -nR(xA \ln xA + xB \ln xB) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (\Delta \min S = -nR(xA \ln xA + xB \ln xB) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 6 \times \ln 2 = 3 | 10 cm (1) (250 cm3) | 10 cm3) | 10 cm (1) (250 cm3) | 10 cm3$ J We need mole fractions: $n x J = J \sum n J J$ Since we have mass percentages, 100.0 g is a convenient sample size. The amounts of each component are 1 mol = 2.696 mol nN = 75.52 g × 2 2 × 14.007 g nO = 23.15 g × 2 nAr = 1.28 g × 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.0200 mol 39.95 g nCO = 0.046 g × 2 1 mol = 0.00105 mol (12.011 + 2 × 15.999 g 1 mol = 0.00105 mol (12.011 + 2 × 1 15.999) g The mole fractions are nN 2.696 mol 2 = 0.7809 = xN = 2 (2.696 + 0.7235 + 0.0320 + 0.00105) mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096, xAr = 0.00928, and xCO = $0.00030 \cdot 2$ 2 Once we have mole fractions, the convenient sample size is for a total of one mole of gas: Δ mix S = $-R\sum xJ \ln xJ = -R\{(0.7809\ln 0.7809) + 0.00105\}$ mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096, xAr = 0.00928, and xCO = $0.00030 \cdot 2$ 2 Once we have mole fractions, the convenient sample size is for a total of one mole of gas: Δ mix S = $-R\sum xJ \ln xJ = -R\{(0.7809\ln 0.7809) + 0.00105\}$ mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096, xAr = 0.00928, and xCO = $0.00030 \cdot 2$ 2 Once we have mole fractions, the convenient sample size is for a total of one mole of gas: Δ mix S = $-R\sum xJ \ln xJ = -R\{(0.7809\ln 0.7809) + 0.00105\}$ mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096, xAr = 0.00928, and xCO = $0.00030 \cdot 2$ 2 Once we have mole fractions, the convenient sample size is for a total of one mole of gas: Δ mix S = $-R\sum xJ \ln xJ = -R\{(0.7809\ln 0.7809) + 0.00105\}$ mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096, xAr = $0.00030 \cdot 2$ 2 Once we have mole fractions, the convenient sample size is for a total of one mole of gas: Δ mix S = $-R\sum xJ \ln xJ = -R\{(0.7809\ln 0.7809) + 0.00105\}$ mol nN + nO + nAr + nCO 2 2 2 Similarly, xO = 0.2096. $(0.2096\ln 0.2096)$ J + $(0.00928\ln 0.00928)$ + $(0.00030\ln 0.00030)$ = 0.5665R = +4.70 J K -1 mol-1 From the data in Exercise 5A.5(a), the entropy of mixing was Δ mix S = - R Σ xJ ln xJ J = - R{ $(0.781\ln 0.781)$ + $(0.210\ln 0.210)$ + $(0.0094\ln 0.0094)$ = 0.565R = +4.70 J K -1 mol-1 2 So the difference is Δ mix S (a) = 0.0015 R = +0.012 J K -1 mol-1 Comment. We can readily see that the data in this exercise (b) includes the CO2 term, which contributes -R(0.00030 ln 0.00030) = 0.0025R to the entropy of mixing—more than the total difference. The fact that the mole fractions of the other components are slightly smaller in part (b) to make room for the small amount of CO2 partly offsets the direct CO2 term itself. 5A.6(b) Let 12 refer to 1,2-dimethylbenzene and 13 to 1,3-dimethylbenzene. Because the two components are structurally similar, we assume Raoult's Law [5A.21] applies. ptotal = p12 + p13 = x12p12* + x13p13* = (0.500)(20 + 18) kPa = 19 kPa. The mole fractions in the vapor phase are the ratios of partial to total pressure: $x_{12} p_{12} (0.500)(20 \text{ kPa}) p_{12} and x_{vap}, 13 = 0.47 x_{12}, vap = = = 0.53 19 \text{ kPa ptotal ptotal 5A.7(b)}$ Total volume V = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), where n = nA + nB Total mass m = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = nAVA + nBVB = n(xAVA + xBVB), n = n(x(198.2 g mol-1) V = n(xAVA + xBVB) and = (4.670 mol) × {(0.3713) × (188.2) + (1 - 0.3713) × (176.14)} cm 3 mol-1 = 843.5 cm 3 5A.8(b) Let W denote water and E ethanol. The total volume of the solution is V = n W V W + n EV E We are given VE, we need to determine nW and nE in order to solve for VW, for V - nEVE VW = nW 3 Take 100 cm of solution as a convenient sample. The mass of this sample is $m = \rho V = (0.9687 \text{ g cm}-3) \times (100 \text{ cm}3) = 96.87 \text{ g}$. 80 per cent of this mass water and 20 per cent of this mass wate $-(0.42 \text{ mol}) \times (52.2 \text{ cm } 3 \text{ mol} - 1) = 18 \text{ cm } 3 \text{ mol} - 1 = 4.3 \text{ mol} \text{ nW}$ Henry's law is [5A.23] pB = xBKB, so check whether pB / xB is equal to a constant (KB) x 0.010 0.015 0.020 p/kPa 82.0 122.0 166.1 (p/kPa) / x 8.2 × 103 8.1 × 103 8.3 × 103 Hence, KB = p / x = 8.2 × 103 kPa (average value). 5A.10(b) Refer to Brief Illustration 5A.4 and use the Henry's Law constant from Table 5A.1. Henry's law in terms of molal concentration is pB = bBKB. So the molal solubility of methane in benzene at 25°C in equilibrium with 1.0 bar of methane is pCH 100 kPa 4 bCH = = = 2.25 \times 10-3 mol kg -1.3 - 1.4 K CH 44.4×10 kPa kg mol 4
To find the molar solubility, we assume that the density of the solution is the same as that of pure benzene, given at a nearby temperature (20°C) in Table 0.1: [CH 4] = bCH ρ benzene = 2.25 × 10-3 mol kg -1 × 0.879 kg dm -3 = 2.0 × 0.879 kg $p_{total} = 1$ atm = 101.3 kPa For N2, K = 1.56 × 105 kPa kg mol-1 [Table 5A.1] 0.78 × 101.3 kPa b = 5.1 × 10-4 mol kg -1 1.56 × 105 kPa kg mol-1 [Table 5A.1] 0.21 × 101.3 kPa b = 2.7 × 10-4 mol kg -1 7.92 × 104 kPa kg mol-1 5A.12(b) As in Exercise 5A.11(b), we have p 2.0 × 101.3 kPa b = 8 = 0.067 mol kg -1 K 3.01 \times 103 kPa kg mol-1 Hence, the molality of the solution is about 0.067 mol kg-1. Since molalities and molar concentrations (molarities) for dilute aqueous solutions are numerically approximately equal, the molar concentrations (molarities) for dilute aqueous solutions are numerically approximately equal, the molar concentration is about 0.067 mol kg-1. Solutions to problems 5A.2 C = 1; hence, according to the phase rule (eqn 4A.1) F = C - P + 2 = 3 - P Since the tube is sealed there will always be some gaseous compound in equilibrium with the condensed phases. Thus when liquid begins to form upon melting, P = 3 (s, l, and g) and F = 0. 5A.4 Letting B stand for CuSO4(aq), the partial molar volume of the dissolved salt is $(\partial V)VB = | [5A.1] (\partial nB / nA We will determine VB by plotting V against nB while holding nA constant. We can find the volume from the density: m + mB m + mB so . <math>\rho = A V = A V \rho$ The data include the composition of the solution expressed as mass percent. (That is, m(CuSO4)/g, the mass in grams of B dissolved in 100 g solution, is numerically equal to w, defined as mass of B over total solution mass expressed as a percent). For our plot, we need nB per fixed amount of A. Let us choose that fixed quantity to be mA = 1 kg exactly, so nB is numerically equal to the molal concentration. So m nB = B MB mB × 100 = w. mA + mB Solve for mB: wmA mB = . 100 - w Draw up the following table of values of mB, nB, and V at each data point, using mA = 1000 g. W 5 10 15 20 - 3 1.051 1.107 1.167 1.23 ρ /(g cm) mB/g 52.6 111.1 176.5 250.0 nB/mol 0.330 0.696 1.106 1.566 V/cm3 1001.6 1003.7 1008.1 1016.3 VB/(cm3 mol-1) 2.91 8.21 14.13 20.78 A plot V against nB

is shown in Figure 5A.1. such that 4 Figure 5A.1 To find the partial molar volume, draw tangent lines to the curve at each of the data points and measure the slope of each tangent. Alternatively, fit the curve to a polynomial and differentiate the fit equation. A quadratic equation fits the data quite well V/cm3 = 7.226(nB/mol)2 - 1.851(nB/mol) + 1001.4 $(\partial V/cm 3)$ so VB / cm 3 = | = 2 × 7.226 × (nB / mol) - 1.851 ∂nB / mol) n A Comment. Selecting mA = 1000 g is arbitrary. If you chose a different values for mB, nB, and V; however, you should arrive at the same values for WB. 5A.6 From Example 5A.1, we have VE/(cm3 mol-1) = 54.6664 - 0.72788x + 0.728 0.084468x2, where x = nE/mol mixed with 1.000 kg water. Thus, x is also equal to the numerical value of the molality. To find the minimum in VE, differentiate it and set the derivative equal to zero: dVE (cm 3 mol-1) = $-0.72788 + 2 \times 0.084468x = 0$ dx 0.72788 Thus so b = 4.3086 mol kg-1 $x = 4.3086 2 \times 0.084468$ This value is consistent with Figure 5A.3 of the main text. 5B The properties of solutions Answers to discussion question 5B.2 All of the colligative properties result from the solute. This reduction takes the form $\mu A = \mu A^* + RT \ln aA$, depending on whether or not the solution can be considered ideal. The lowering of the chemical potential results in a freezing point depression and a boiling point depressi molecules, reducing their escaping tendency. Solutions to exercise 5B.1(b) In Exercise 5B.1(b) In Exercise 5A.10(b), the Henry's law constant was determined for concentrations; KB = 8.2×103 kPa. Thus the concentration must be converted from molality to mole fractions; KB = 8.2×103 kPa. Thus the concentration must be converted from molality to mole fractions; KB = 8.2×103 kPa. Thus the concentration must be converted from mole fractions; KB = 8.2×103 kPa. mol - 1 = 13.50 mol 0.25 mol = 0.018 (0.25 mol) + (13.50 mol) The pressure is pB = KBxB [5A.23] = (0.018) × (8.2 × 103 kPa) = 1.5 × 102 kPa . 5B.2(b) We assume that the solvent, 2-propanol, is ideal and obeys Raoult's law [5A.21]. p 49.62 xA (solvent) = * = 0.9924 50.00 p Since MA(C3H8O) = 60.096 g mol - 1, 250 g nA = = 4.16 mol 60.096 g where $bB = \Delta T$ [5B.13] Kf mB K f (5.00 g) × (6.94 K kg mol-1) = 178 g mol-1 mA ΔT (0.250 kg) × (0.780 K) From the concentration to the van't Hoff equation [5B.16], the osmotic pressure is n $\Pi \Pi = [B]RT$ so = B [B] = RT Vsoln The expression for freezing point depression [5B.13] includes the molality b rather than the molarity [B]. In dilute solutions, the two concentration measures are readily related: nB n [B] $\Pi = b = B \approx mA$ Vsoln psoln RT psoln The density of a dilute aqueous solution is approximately that of water: $\rho \approx 1.0 \text{ g cm} - 3 = 1.0 \times 103 \text{ kg m} - 3 = -1.0 \times 103 \text{ kg m} - 3$ (8.3145 J K -1 mol - 1) × (288 K) × (103 kg m) Therefore, the solution will freeze at about -0.077° C. 5B.5(b) $\Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } [5A.16] \text{ and } \text{J} \Delta \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x ln x } \text{J } (100 \text{ mix } \text{G} = - \text{nR} \Sigma \text{ x l$ xheptane = 0.500 Therefore, $\Delta \min G = (2.00 \text{ mol}) \times (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (298 \text{ K}) \times 2 \times (0.500 \ln 0.500) = -3.43 \times 103 \text{ J} = -3.43 \text{ k} \text{ J} - \Delta \min G + 3.43 \times 103 \text{ J} = -3.43 \text{ k} \text{ J} - \Delta \min G + 7 \Delta \min G + 3.43 \times 103 \text{ J} = -3.43 \text{ k} \text{ J} - \Delta \min G + 7 \Delta \min G = (2.00 \text{ mol}) \times (2.00 \text$ $\Delta \min G + T \mid T \mid \text{and 5B.6(b)} \Delta \min S = (i)$ Benzene and ethylbenzene form nearly ideal solutions, so. $\Delta \min S = -nRT(xA \ln xA + xB \ln xB)$ [5A.17] We need to differentiate $\Delta \min S = -nRT(xA \ln xA + xB \ln xB)$ [5A.17] We need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate $\Delta \min S = -nRT(xA \ln xA + xB \ln xB)$ [5A.17] We need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA and look for the value of xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA at which the derivative is zero. Since xB = 1 -xA, we need to differentiate eqn 5A.17 with respect to xA at which the derivative is zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we need to zero. Since xB = 1 -xA, we nead to zero. Since xB = 1 -xA, we need to zero. Since gives (using d ln x = 1) (x) dx x d Δ mix S = -nR{ln xA + 1 - ln(1 - xA) - 1} = -nR ln A dxA 1 - xA which is zero when xA = 1. Hence, the maximum entropy of mixing is maximized when nE = nB (changing to notations) specific to Benzene and Ethylbenzene) m mE = B ME MB This makes the mass ratio mB M B 78.11 g mol-1 = 0.7357 = mE M E 106.17 g mol-1 5B.7(b) The ideal solubility in terms of mole fraction is given by eqn 5B.15: $\Delta H (\ln xPb = fus \times |1 - 1| R (Tf T) (5.2 \times 103 \text{ J mol} - 1) (1) = -1 | = -0.089 \times |-1| (1) = -1 | = -1 | = -0.089 \times |-1| (1) = -1 | = -1 | = -0.089 \times |-1| (1) = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1 | = -1$ kg of lead and 1 kg of bismuth would normally be regarded as a solution of bismuth in lead, not the other way around. It is unlikely that such a mixture could be regarded as an ideal dilute solution of bismuth in lead, not the other way around. It is unlikely that such a mixture could be regarded
as a solution of bismuth. molar mass is obtained from values of the data extrapolated to zero concentration, since it is under this condition that the van't Hoff equation (5B.16) applies. 7 $\Pi V = nBRT \Pi = mRT = cRT$ where c = m/V. so M MV But the osmotic pressure is also equal to the hydrostatic pressure is also equal to thydrostatic pressure i against c and identify the slope as RT. Figure 5B.1 shows the plot of the ρ gM data. The slope of the line is 1.78 cm /(g dm-3), so RT 1.78 cm = 1.78 cm /(g dm-3), so RT 1.78 cm = 1.78 cm /(g dm-3), so RT 1.78 cm = 1.78 cm /(g dm-3), so RT 1.78 cm = 1.78 cm /(g dm-3), so RT 1.78 cm / (g dm-3), so RT $(1.78 \times 10-2 \text{ m 4 kg} - 1) = 14.0 \text{ kg mol-1}$ In an ideal dilute solution the solvent (CCl4, A) obeys Raoult's law [5A.23]; hence pA = xA p* = (0.934) × (23 kPa) = 21.5 kPa pB = xBKB = (0.066) × (73 kPa) = 4.8 kPa ptotal = (21.5 + 4.8) kPa = 26.3 kPa The composition of the vapour in equilibrium with the liquid is p p and vA = A = 21.5 kPa = 0.82 yB = B = 4.8 kPa = 0.18 ptotal 23.3 kPa ptotal 23.3 kPa 5B.10(b) Let subscript 12 denote the 1,2 isomer and 13 the 1,3 isomer. Assume that the structurally similar liquids obey Raoult's law [5A.21]. The partial pressures of the two liquids sum to 19 kPa. p13 + p12 = p = x13p13* + x12p12* + x13p13* + x12p12* = x13p13* + x12p12* + x13p13* (1-x13)p12* Solve for x13: p-p*(19-20) kPa x13 = *12* = 0.5 (18 - 20) kPa p13 - p12 and x12 = 1 - 0.5 = 0.5. The vapour phase mole fractions are given by eqn 1A.8: 8 and y13 = $p13 x13 p13*(0.5) \times 18$ kPa = = 0.47 19 kPa p $p y12 = x12 p12*(0.5) \times 20.0$ kPa = $= 0.53 \cdot 50.7$ kPa p 5B.11(b) The partial vapour pressures are given by Raoult's law [5A.21]: and pB = xBpB* = (1-xB)pB* . pA = xApA* Eqn 1A.8 relates these vapour pressures to the vapour-phase mole fractions: p xA pA* yA = A = ptotal xA pA* + (1 - xA) pB* Solve for xA: xA pA* + (1 - xA) pB* = xA pA* yA (p*)xA | pA* - pB* - A | = -pB* yA / pB* xA = pB* + * A p - pA* yA = 82.1 kPa = 0.662 (68.8 kPa - 68.8 kPa 82.1 + |||| 0.621 and xB = 1 - xA = 1 - 0.662 = 0.338. The total vapour pressure is ptotal = $xApA^* + xBpB^* = 0.662 \times 68.8$ kPa + 0.338×82.1 kPa = 73.3 kPa . 5B.12(b) (i) If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]: $pA^\circ = xApA^* = 0.4217 \times 110.1$ kPa = 46.4 kPa and $pB^\circ = xBpB^* = (1-xB)pB^* = (1$ 0.4217) × 76.5 kPa = 44.2 kPa. (Note the use of the symbol ° to emphasize that these are idealized quantities; we do not yet know if they are the actual partial vapour pressures.) At the normal boiling temperature, the partial vapour pressures must add up to 1 atm (101.3 kPa). These ideal partial vapour pressures add up to only 90.7 kPa, so the solution is not ideal. (ii) We actually do not have enough information to compute the initial composition of the vapour pressures. We know only that the actual vapour pressures must sum to 101.3 kPa. We can make a further assumption that the proportions of the vapours are the same as given by Raoult's law. That is, we assume that $pA \circ 46.4 \text{ kPa} = 0.512 = yA = pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.512 = yA = yA \circ = pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. = $pA \circ + pB \circ (46.4 + 44.2) \text{ kPa} = 0.488$. 0.488×101.3 kPa = 49.4 kPa . To find the activity coefficients, note that p p 49.4 kPa and = 1.117 yA = A* = A = 44.2 kPa and yB = yB ° = Comment. Assuming that the actual proportions of the vapours are the same as the ideal proportions begs the question (i.e., arrives at the answer by assumption) rather than calculation). The assumption is not unreasonable, though. It is equivalent to assuming that the activity coefficients of the two components are equal (when in principle they could be different). The facts that the difference between ideal and actual total pressure is relatively small (on the order of 10%), that non-ideal behavior is due to the interaction of the two components, and that the two components are present in comparable quantities combine to suggest that the error we make in making this assumption is fairly small. 9 5B.13(b) (i) If the solution is ideal, then the partial vapour pressures are given by Raoult's law [5A.21]: $pB = xBpB^* = 0.50 \times 9.9$ kPa = 4.95 kPa pT = $xTpT^* = 1.000 \text{ m}$ 0.50×2.9 kPa = 1.45 kPa The total pressure is ptotal = pB + pT = (4.95 + 1.45) kPa = 6.4 kPa ptotal (ii) When only a few drops of liquid remain, the equimolar mixture is almost entirely vapour. Thus yB = yT = 0.50, which implies that $pB = xBpB^* = pT = xTpT^* = (1-xB)pT^*$. Solving for xB yields $p^* 2.9 kPa = T^* = 0.23$ (9.9 + 2.9) kPa $pB = xBpB^* = 0.23 \times 9.9 kPa = 2.24 kPa = pT$ [vapour mixture is equimolar] = ptotal/2. The total pressure is ptotal = 2pB = 4.5 kPa. Comment. Notice that an equimolar liquid mixture yields a vapour composition directly proportional to the vapour pressures of the pure liquids. Conversely, an equimolar vapour mixture implies a liquid composition inversely proportional to those vapour pressures. Solutions to problems 5B.2 The apparent molality is 0.0703 K ΔT = 0.0378 mol kg -1 [5B.13] = bapp = Kf 1.86 K/(mol kg -1) Since the solution molality is nominally 0.0096 mol kg-1 in Th(NO3)4, each formula unit supplies 0.0378 ≈ 4 ions.) 5B.4 (a) Let V1* be the molar volume of pure propionic acid and V1 be its partial molar volume in the mixture (and V2* and V2 the analogous quantities for oxane) The volume of an ideal mixture is additive Videal = $n1V1^* + n2V2^*$, so the volume of a real mixture is V = Videal + VE. We have an expression for the excess volume as a function of moles a (n - n2) nn (VE = (n1 + n2)VmE = 12 a a0 + 11 n1 + n2 ||n1 + n2 ||n1a1 (x1 - 3x2)x12 = V2* + $|2 3 \partial n$ (n1 + n2) (n1 + n2) (1 + n2) (2 n 1 10 (b) We need the molar volumes of the pure liquids M 74.08 g mol-1 = 76.23 cm 3 mol-1 P2 0.86398 g cm - 3 In an equimolar mixture, the partial molar volume of propionic acid is V1 = 76.23 + (-2.4697) × (0.5)2 + (-2.4697) × (0.5) $(0.0608) \times \{3(0.5) - 0.5\} \times (0.5)2 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp}.63 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp}.63 \text{ sp}.63 \text{ sp} + (-2.4697) \times (0.5)2 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp}.63 \text{ sp} + (-2.4697) \times (0.5)2 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp}.63 \text{ sp} + (-2.4697) \times (0.5)2 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp} + (-2.4697) \times (0.5)2 \text{ cm } 3 \text{ mol} - 1 \text{ sp}.63 \text{ sp} + (-2.4697) \times (0.5)2 \text{ sp$ $\Delta mixG = \Delta mixGideal + nGE = nRT(xA \ln xA + xB \ln xB) + nGE [5B.5 and 5A.16] \Delta mixG = nRT(0.250 \ln 0.250 + 0.750 \ln 0.750) + 0.1021nRT = -0.460 \times 4.00 mol \times 8.3145 J mol-1 K-1 \times 303.15 K = -4.64 kJ mol-1 . ()() \mu A = | \partial G | [5A.4] = \mu Aideal + | \partial (nG E) | [5B.5] where \mu Aideal = \mu A^* + RT \ln xA
[5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nGE [5B.5] where \mu Aideal = \mu A^* + RT \ln xA [5A.22] (\partial nA / n (\partial nA / n B) + nG (\partial n$ After expanding and collecting terms, we arrive at ($\partial nG E$)2 | ∂n |= gRT (1 - xA) = gRTxB()A n B Therefore, μA = μA^* + RT ln xA + gRTxB2 This function is plotted for several values of the parameter g in Figure 5B.2. Figure 5B.2 11 5B.10 By the van't Hoff equation [5B.16] Π = [B]RT = cRT M Division by the standard acceleration of free fall, g gives $\Pi = c(R / g)T M g$ (a) This expression may be written in the form $\Pi' = cR'T M$ which has the same form as the van't Hoff equation, but the unit of osmotic pressure (Π') is now force / area (mass length / time 2 would have the units of R/g. energy K - 1 mol - 1 (mass length 2 / time 2) K - 1 mol - 1 = mass length K - 1 mol - 1 = mass length / time 2 l following we will drop the primes giving $\Pi = cRT M$ and use the Π units of g cm-2 and the R units g cm K-1 mol-1. (b) By extrapolating the low concentration plot of Π / c versus c (Figure 5B.3(a)) to c = 0 we find the intercept 230 g cm-2/(g cm-3). In this limit the van't Hoff equation is valid so Figure 5B.3(a) RT = intercept M or M = RT intercept 12 $M = (84\ 784.0\ g\ cm\ K\ -1\ mol\ -1\)\ \times\ (298.15\ K)\ RT = 1.1\ \times\ 105\ g\ mol\ -1\ =\ intercept\ (230\ g\ cm\ -2\)\ (g\ -2\)\ (g\ cm\ -2\)\ (g\ cm\ -2\)\ (g\ cm$ analogue to the van't Hoff equation (eqn. 5B.18) rearranges to $\Pi / c = (RT / M)(1 + B'c + C'c 2)$ Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M)(1 + B'c + C'c 2) Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M)(1 + B'c + C'c 2) Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M)(1 + B'c + C'c 2) Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M)(1 + B'c + C'c 2) Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M)(1 + B'c + C'c 2) Since RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M has been determined in part (b) by extrapolation to c = 0, it is best to determine the second and third virial coefficients with the linear regression fit (Π / c) / (RT / M has been cm3 g-1. C' = 211 cm6 g-2; standard deviation = 15 cm6 g-2. (e) Using 1/4 for g and neglecting terms beyond the second power, we may write () () (1/2) 1/2 Π RT = 1 + 1 B 'c c M 2 We can solve for B', then g(B')2 = C'. (Π c) (RTM) 1/2 1/2 - 1 = 1 B 'c 2 RT / M has been determined above as 230 g cm-2/(g cm-3). We may analytically solve for B' from one of the data points, say, $\Pi / c = 430$ g cm -2/g cm -3 it c = 0.033 g cm -3 if a = 0.033 g cm B' and C' can be obtained by plotting Π c M shown in Figure 5B.3(c). The slope is 14 cm3 g-1. B' = 2 × slope = 28 cm3 g-1. C' is then 196 cm 6 g -2. The intercept of this plot should theoretically be 1.00, but it is in fact 0.916 with a standard deviation of 0.066. The overall consistency of the values of the parameters confirms that g is roughly 1/4 as assumed. Figure 5B.3(c) 5B.12 The Gibbs energy of mixing an ideal solution is [5A.16] Δ mixG = nRT(xA ln xA + xB ln xB) The molar Gibbs energy of mixing is plotted against composition for several temperatures in Fig. 5B.4. The legend shows the temperature in Kelvins. Figure 5B.4 The composition at which the temperature dependence is strongest temperature for various values of the enthalpy of fusion and the freezing temperature. The dependence on the freezing temperature is relatively uninteresting, though, since it enters into a factor that is independence on the freezing temperature and simply plot dxB/dT with this factor divided out. That is, in Figure 5B.5, we plot f(T) vs. T for several values of Δ fusH between 1 and 10 kJ mol-1, where $(\Delta H)(\Delta H) f(T) = \exp |-fus| \times |f(T)|$ for several values of Δ fusH between 1 and 10 kJ mol-1, where $(\Delta H)(\Delta H) f(T) = \exp |-fus| \times |f(T)|$ plotted over a temperature range that extended back to T = 0. The function has a maximum because the exponential factor increases toward zero. The higher the value of Δ fush. the higher the temperature at which f(T) is maximal and the lower the value of that maximum value. For $\Delta fusH = 1$ or 2 kJ mol-1, the maximum occurs at temperatures lower than those shown and for $\Delta fusH = 10$ kJ mol-1 it occurs at a higher temperature lower than those shown. 5C Phase diagrams of binary systems Answers to discussion question 5C.2 A low-boiling azeotrope has a boiling temperature lower than that of either component, so it is easier to get the molecules into the vapor phase than in a "normal" (non-azeotropic) mixture, a sign that the components are less attracted to each other in the liquid phase than to molecules of their own kind. These intermolecular interactions are determined by factors such as dipole moment (polarity) and hydrogen bonding. Conversely, a highboiling azeotrope has a boiling temperature higher than that of either components that have more favorable intermolecular interactions with each other in the liquid phase than with molecules of their own kind. The concepts of ideal 15 mixtures of liquids (in Topic 5A) and deviations from ideal behavior of "normal" (ideal) mixtures. Solutions to exercises 5C.1(b) Add the boiling point of A to the table at xA = yA = 1 and the boiling point of B at xB = yB = 0. Plot the boiling temperatures against liquid mole fractions and the same boiling temperatures against vapour mole fractions on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is yA = 0.82. (ii) Find xA = 0.67 (i.e., xB = 0.33) on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is yA = 0.91 (i.e., yB = 0.09). 5C.2(b) The phase diagram is shown in Figure 5C.2. Figure 5C.2 16 5C.3(b) Refer to the figure given with the exercise. At the lowest temperature shown on the phase diagram, there are two liquid phases, a water-rich phase (xB = 0.07) and a methylpropanolrich phase (xB = 0.07) and increasing significantly in methylpropanol and the methylpropanol-rich phase more gradually increasing in water. (Note how the composition of the left side of the diagram changes more with temperature than the right.) The relative proportions of the phases continue to be given by the lever rule. Just before the isopleth intersects the phase boundary, the methylpropanol-rich phase (xB = 0.84) is in equilibrium with a vanishingly small waterrich phase (xB = 0.3). Then the phases merge, and the single-phase region is encountered with xB = 0.3. 5C.4(b) The feature that indicates incongruent melting (Topic 5C.4(c)) is circled in Figure 5C.3. The incongruent melting point is marked as T1 The composition of the eutectic is xB \approx 0.58 and its melting point is labeled T2. Figure 5C.4(a) are shown in Figure 5C.4(b). Note the breaks (abrupt change in slope) at temperatures corresponding to the phase diagram
in Figure 5C.4(b). Note the breaks (abrupt change in slope) at temperatures corresponding to the phase diagram in Figure 5C.4(b). Note the breaks (abrupt change in slope) at temperatures corresponding to the phase diagram in Figure 5C.4(b). 5C.4 5C.6(b) Refer to Figure 5C.5. Dotted horizontal lines have been drawn at the relevant temperatures. 17 Figure 5C.5 (i) At 300°C, the phase at all compositions, so B is soluble in A in all proportions. (ii) At 390°C, solid B exists in equilibrium with a liquid whose composition is circled and labeled x1 on Figure 5C.5 (i) At 500°C, the phase diagram shows a single liquid phase at all compositions, so B is soluble in A in all proportions. 5.11. That composition is xB = x1 = 0.63. (iii) At point x2, two phases coexist: solid AB2 and a liquid mixture of A and B with mole fraction xB = x2 = 0.41. Although the liquid does not contain any AB2 units, we can think of the liquid as a mixture of dissociated AB2 in A. Call the amount (moles) of the compound nc and that of free A na. Thus, the amount of A (regardless of whether free or in the compound) is nA = na + nc, and the amount of B is 2nc 2nc nB = xB = x2 = nA + nB (na + nc) + 2nc na + 3nc Rearrange this relationship, collecting terms in nc on one side and na on the other: $nax^2 = nc(2-3x^2)$. The mole ratio of compound to free A is given by nc x2 0.41 = 0.53. = = na $2 - 3x2 2 - 3 \times 0.41$ 5C.7(b) The phase diagram is shown in Figure 5C.6. Point symbols are plotted at the given data points. The solid solution with x(ZrF4) = 0.27 appears. The solid solution x(Zr 0.40 at 830°C. At that temperature and below, the entire sample is solid. 5C.8(b) The phase diagram for this system (Figure 5C.7) is very similar to that for the system methyl ethyl ether and diborane of 0.80. Followship ethyl ethyl ether and below, the entire sample is solid. 5C.8(b) The phase diagram for this system (Figure 5C.7) is very similar to that for the system methyl ethyl ether and below, the entire sample is solid. 5C.8(b) The phase diagram for this system (Figure 5C.7) is very similar to that for the system methyl ethyl e this isopleth down to see that crystallization begins at about 123 K. The liquid in equilibrium with the solid becomes progressively richer in diborane until the liquid compound and solid diborane. Figure 5C.7 5C.9(b) The cooling curves are sketched in Figure 5C.8. Note the breaks and halts. The breaks correspond to changes in the rate of cooling due to the freezing out of a solid which releases its heat of fusion and thus slows down the cooling process. The halts correspond to the existence of three phases and hence no variance until one of the phases disappears. Figure 5C.8 19 5C.10(b) The phase diagram is sketched in Figure 5C.9. Figure 5C.9 (i) When xA falls to 0.47, a second liquid phase appears. The amount of new phase increases as xA falls and the amount of new phase increases as xA diagram is shown in Figure 5C.10. Figure 5C.10 20 (b) We need not interpolate data, for 296.0 K is a temperature for which we have experimental data. The mole fraction of N, N-dimethylacetamide in the heptane-rich phase (call the point α , at the left of the tie line) is 0.168 and in the acetamide-rich phase (β , at right) 0.804. The proportions of the two phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is $n\alpha / n\beta = l\beta / l\alpha = (0.804 - 0.750) / (0.750 - 0.168) = 0.093$ The smooth curve through the data crosses x = 0.750 at 302.5 K, the temperature at which the heptane-rich phase will vanish. 5C.4 Figure 5C.11 displays the phase diagram. A compound with probable formula A3B exists. It melts incongruently at 700 °C, undergoing the peritectic reaction A 3 B(s) \rightarrow A(s) + (A + B, l) The proportions of A and B in the product are dependent upon the overall composition and the temperature. A eutectic exists at 400°C and xB = 0.83. Figure 5C.11 5C.6 The information has been used to construct the phase diagram in Figure 5C.12(a). In MgCu2 the mass percentage of Mg is 21 24.3 = 16 24.3+127 and in Mg2Cu it is 48.6 (100) \times = 43 . 48.6 + 63.5 The initial point is a1, corresponding to a single-phase liquid system. At a2 (at 720°C) MgCu2 begins to come out of solution and the liquid becomes richer in Mg, moving toward e2. At a3 there is solid MgCu2 + liquid of composition e2 (33 per cent by mass of Mg). This solution freezes without further change. The cooling curve will resemble that shown in Figure 5C.12 (b). (100) × Figure 5C.12 (c). (100) × Fig until the temperature reaches $351^{\circ}C$, at which point KFeCl3(s) also appears. Below $351^{\circ}C$ the system is a mixture of K2FeCl4(s) and KFeCl3(s). Figure 5C.13 5C.10 Equation 5C.5 is $22 p = pA^* pB^* pA^* + (pB^* - pA^*) yA$ First divide both sides by pA^* to express the pressure in units of pA^* . Next, divide both numerator and denominator by pB^* to see if the right hand side can be expressed as a function of the ratio pA* / pB* rather than of each vapor pressure separately: p / pA* = 1 p / p + (1 - pA* / pB*) yA* A* B The plot of p / pA* vs. yA at several values of the vapor pressure ratio is shown in Figure 5C.4 of the main text. 5C.12 Equation 5C.7 is The simplest way to construct a plot of ξ vs. xA is to isolate ξ : A plot based on this equation is shown in Figure 5C.14(a). Figure 5C.14(a). Figure 5C.14(a). Figure 5C.14(b). Here the left-hand side of eqn 5C.7 is plotted as the bold curve, and the lighter lines are the right-hand side for $\xi = 1, 2, 3$, and 5. Small squares are placed where the curve intersects one of the lines. Note that the curve intersects every line at $xA = \frac{1}{2}$, the composition at which HE is maximized. For values of $\xi > 2$, that is the only point of intersection; for values of $\xi > 2$, there are two additional points of intersection arranged at equal distance from $xA = \frac{1}{2}$. 23 Figure as can be seen in Figure 5C.18 of the main text. However, in the equation obtained by isolating ξ , $xA = \frac{1}{2}$ leads only to $\xi = 2$. That equation yields an indeterminate form for $xA = \frac{1}{2}$, but application of L'Hospital's rule yields $x \ln A x - 1 - (-xA) - 12 + 21 - xA \ln xA - \ln(1 - xA) = \lim 1 = \lim 1 = \lim 1 = \lim 1 = 2 \lim 1 =$ One method of numerical solution is illustrated by the following cells from a spreadsheet. Set up one column to represent xA, one for the left-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the left-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the left-hand side of eqn 5C.7, and one for the right-hand side of
eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of eqn 5C.7, and one for the right-hand side of e sides were equal lies somewhere between 0.9985 and 0.9990, or, to three decimal places, at 0.999. Therefore, a root of eqn 5C.7 when $\xi = 7$ is xA = 0.999. x ln(x/(1-x)) 7(2x-1) 0.998 6.213 6.972 0.9985 6.501 6.979 0.999 6.907 6.986 5D Phase diagrams of ternary systems Answers to discussion question 5D.2 The lever rule [5C.6] applies in a ternary system, but with an important caveat. The tie lines along which the rule applies are experimentally determined, not necessarily horizontal lines or lines parallel to any edge of the triangular diagram. Thus the lever rule applies, but as a practical matter it can be used only in the vicinity of plotted tie lines. (By contrast, recall that the lever rule applies, but as a practical matter it can be used only in the vicinity of plotted tie lines. binary phase diagram could be applied within a two-phase region simply by drawing a horizontal line to the appropriate phase boundaries.) See Topic 5D.2(a) and Figure 5D.1. The vertices of the triangular phase diagram are labeled for the component that is pure at that vertex. For example, the top of the diagram is pure A: (1, 0, 0). As a reminder, at the edge opposite a labeled vertex, that 24 component's mole fraction is zero. For example, the base of the diagram represents compositions (0, xB, xC). Figure 5D.1 5D.2(b) Note that the compositions are given in mass percentages, not mole percentages, so we simply convert to moles before plotting. Assume a convenient sample size, such as 100 g, making the numerical values of the mass percentages equal to masses in grams: 1 mol = 0.102 mol 32 .21 g 1 mol = 0.102 mol 3 these amounts by the total amount of 2.55 mol: 0.565 mol = 0.22 x(NaCl) = 2.55 mol x(H2O) = 0.74 x (Na2SO4·10H2O) = 0.040 This composition is point a in Figure 5D.2. (ii) We want to plot a line representing equal masses of salt with varying amounts of water. Compute the mole fractions that correspond to the amounts of salt computed in part (a) with no water. In that case, the total amount is: ntotal = (0.565 + 0.102) mol = 0.667 mol 34 g × H2O: 0.565 mol and x (Na2SO4·10H2O) = 0.15 = 0.85 0.667 mol Plot this point on the edge opposite the vertex labeled H2O. The other extreme has the salts in the same proportions, but in amounts negligible compared to that of water, so the other end of this line lies at the vertex labeled H2O. The line is labeled b on Figure 5D.2, and note that it goes through point (a) as it must. so x(NaCl) = Figure 5D.2 25 5D.3(b) First convert to moles and find composition by mole fraction. 1 mol H2O (W): = 3.05 mol 55.0 g × 18.016 g CHCl3 (C): 8.8 g × 1 mol = 0.074 mol 119.4 g 1 mol = 0.062 mol 60.05 g To get mole fractions, divide these amounts by the total amount of 3.19 mol: 3.05 mol x C = 0.023 xA = 0.019 = 0.958 xW = 3.19 mol This point is plotted in Figure 5D.3; it is very close to the label W in the original Figure 5D.4 of the main text. One phase is present, since our point lies outside the phaseboundary arc (to the left of it). (i) If water is added to our mixture, the composition changes from our point along the very short line connecting it to the vertex labeled W. The system remains in a single phase. (ii) If acetic acid is added to our mixture, the composition changes from our point along the very short line connecting it to the vertex labeled A. The system remains in a single phase. Figure 5D.4 (a) is in a two-phase region and point (b) in a three-phase region; that is, it is on the border between a single-phase and a two-phase region, so there would be a vanishingly small amount of a second phase present. Finally, point (d), for which all three components are present in nearly equal amounts, is in a three-phase region (although very near the border with a two-phase region). 5D.5(b) (i) Note the line in Figure 5D. 5 that runs from the water-NH4Cl edge near x(NH4Cl) = 0.2 (the point that represents a saturated aqueous solution of NH4Cl) to the (NH4)2SO4 to a saturated aqueous solution of NH4Cl. Note that it traverses the single-phase region at first. That is, the added (NH4)2SO4 dissolves and does not cause NH4Cl to precipitate out. If one starts with saturated aqueous NH4Cl in excess, then the starting point is a bit further down on the water-NH4Cl edge, for example at x(NH4Cl) = 0.3. Adding (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point is a bit further down on the water-NH4Cl edge, for example at x(NH4Cl) = 0.3. Adding (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point is a bit further down on the water-NH4Cl edge, for example at x(NH4Cl) = 0.3. Adding (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point is a bit further down on the water-NH4Cl edge, for example at x(NH4Cl) = 0.3. Adding (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from that point to the (NH4)2SO4 to such a solution would take one from the take one from but eventually a single-phase region is reached. Note that the line intersects the single-phase region at a higher NH4Cl velative to water at that intersection point, but NH4Cl is a larger fraction of the saturated threecomponent solution than it was in the saturated twocomponent system of water and NH4Cl.) So here too, the effect of adding (NH4)2SO4 is to make additional NH4Cl dissolve, at least at first. Figure 5D.5 (ii) First convert to moles for a convenient sample size, such as 100 g, and find composition by mole fraction. 1 mol NH4Cl: 25 g × = 0.467 mol 53.49 g 1 mol = 0.568 mol 132.15 g To get mole fractions, divide these amounts by the total amount of 1.03 mol 27 (NH4)2SO4) = 0.55 x(NH 4Cl) = 0.457 mol x((NH4)2SO4) = 0.557 mol x((N as water is introduced, a third (saturated aqueous) phase is formed in equilibrium with two solid phases. As more water is added, one of the solid phases consist of a saturated aqueous phase and a solid rich in (NH4)2SO4. Eventually, as still more water is added, that solid phases and a solid rich in (NH4)2SO4. single aqueous phase at $x(H2O) \ge 0.63$. Solutions to problem 5D.2 (i) The phase diagram is shown in Figure 5D.6. Figure 5D.6. Figure 5D.6. Figure 5D.6 (ii) Lines from the baseline (the CO2-nitroethane edge) to the DEC vertex represent compositions obtained by adding DEC to a CO2-nitroethane mixture. Such lines that avoid two-phase regions represent compositions of CO2-nitroethane edge) to the DEC vertex represent compositions obtained by adding DEC to a CO2-nitroethane mixture. and nitroethane to which addition of DEC can cause no phase separation. The range of such CO2-nitroethane compositions can be found by drawing lines are tangent to the two-phase regions, and they intersect the baseline at x = 0.2 and x = 0.4 (where x is mole fraction of nitroethane). So binary CO2nitroethane compositions between these would show no phase separation if DEC is added to them in any amount. (Keep in mind, though, that the phase boundaries here are sketched, not plotted, so the tangent lines are only approximate.) 5E Activities Answers to discussion question 5E.2 Raoult's law [5A.21] assumes that the vapor pressure of a solvent in solution (or of a liquid in a mixture of liquids) is simply its pure-substance vapor pressure multiplied by its mole fraction in the mixture. That is, it assumes that the intermolecular interactions that produce equilibrium between pure liquid and vapor are unchanged except for the fact that only a fraction of the molecules in the liquid are molecules of the species of interest. In effect, Raoult's law predicts vapor pressure and composition (mole fraction): pA = pA*xA For real solutions, on the other hand, we modify Raoult's law to say, in effect, whatever the vapor pressure really is, let us use that to define an "effective" mole fraction. Raoult's law implies $pA = xA pA^*$ We modify this relationship to define activity: 28 pA = aA [5E.2] $= 0.9701 \ 0.02239 \ atm aA = A^*$ [5E.2] $= 0.9701 \ 0.02308 \ atm pA$ solutions to exercises 5E.1(b) Let A = water and B = solute. $p \ 0.02239 \ atm aA = A^*$ [5E.2] $= 0.9701 \ 0.02308 \ atm pA$ solutions to exercises 5E.1(b) Let A = water and B = solute. $p \ 0.02239 \ atm aA = A^*$ [5E.2] $= 0.9701 \ 0.02308 \ atm pA$ solutions to exercises 5E.1(b) Let A = water and B = solute. $p \ 0.02239 \ atm aA = A^*$ [5E.2] $= 0.9701 \ 0.02308 \ atm pA$ solutions to exercise 5E.1(b) Let A = water and B = solute. $p \ 0.02239 \ atm aA = A^*$ [5E.2] $= 0.9701 \ 0.02308 \ atm pA$ solutions to exercise 5E.1(b) Let A = water and B = solute. $= 51.1 = 0.990 51.1 + 0.506 122 \text{ g} = 0.506 \text{ mol} 241 \text{ g} \text{ mol} - 1 \text{ and } \gamma \text{ A} = 0.9701 = 0.980 0.990 \text{ From eqn } 1A.8 \text{ (partial pressures)} \text{ and } pA = pB = 101.3 \text{ kPa} = 31.8 \text{
kPa} = 69.5 \text{ kPa p} 31.8 \text{ kPa} = 0.436 \text{ and } aA = A * [5E.2] = 73.0 \text{ kPa}$ $pA \gamma A = 5E.3(b) nB = aA 0.436 = 1.98 [5E.4] = 0.220 xA aB = and \gamma B = pB 69.5 kPa = 0.755 = 0.967 = xB 0.780 The biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies aH + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies a H + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies a H + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies a H + = 10-7. All other activities in the biological standard state is defined as pH 7, which implies a H + = 10-7. All other activities in the biologi$ + = 1 = 100 as well (which implies pH 0). As a result, the biological standard molar Gibbs function for H+ is lower than that of the chemical standard by 7 RT ln 10 [5E.16], which is equal to 39.96 kJ mol-1 at 25°C [Brief illustration 5E.3]. For the given reaction, the standard Gibbs energy is $\Delta G O = \Delta f G O (B) + 4\Delta f G O (H +) - 2\Delta f G O (A)$ The biological standard is $\Delta G \oplus = \Delta f G \oplus (B) + 4\Delta f G O (B) + 4\Delta f G O (B) + 4 \Delta f O (B) +$ sum of the two partial pressures. The vapor-pressure diagram is plotted in Figure 5E.1 29 Comment. The physical interpretation given in Topic 5E.3: negative ξ corresponds to exothermic mixing, reflecting favorable interactions between the components. Solutions to problems 5E.2 $\varphi = -\ln aA xA \ln aA = -r xB$ (a) Therefore, $d\varphi = -1 d \ln aA + 12 \ln aA dr - rd\varphi$. r Now the Gibbs-Duhem equation [5A.12a], implies xAdµA + $xBd\mu B = 0$. Since $\mu = \mu^* + RT \ln a$, $xA d \ln aA + xB d \ln aB = 0$. $x d \ln aA = - - A d \ln aB = - A d \ln aA = - - 12 \ln aA dr + d\phi$ [from (b)] $xB r r \phi$ (b) = $dr + d\phi r Subtract d \ln r + d\phi r Subtract d \ln r + d\phi r Subtract d \ln r + d\phi$. an arbitrary composition: a $(\varphi - 1) \int d\ln rB = \int r \, dr + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln \ln |B| = \lim \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln \ln |B| = \lim \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln \ln |B| = \lim \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln \ln |B| = \lim \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower limit of the left-hand integral is: $(\gamma x)(a) \ln |\varphi| + \int d\varphi$ The lower lintegral is: $(\varphi x)(a) \ln |\varphi| + \int$ 5E.19, is ξ (1-x) 2 pA / pA* = xAe A For small xA, this becomes approximately [5E.20] pA / pA* ≈ xAeξ 30 Certainly one would not expect this expression to hold over the entire range of compositions. In fact, the two equations differ pretty quickly, particularly for relatively large values of ξ. These two equations are plotted against xA in Figure 5E.2. Figure 5E.2 At xA > 0.019, eqn 5E.20 exceeds 5E.19 by more than 10 per cent. 5F The activities of ions Answers to discussion question 5F.2 The Debye-Hückel theory of electrolyte solutions from ideal behavior (essentially, deviations due to electrolyte solutions from ideal behavior (essentially, deviations due to electrolyte) in terms of the work of charging the ions. The assumption is that the solute particles would behave ideally if they were not charged, and the difference in chemical potential between real and ideal behavior amounts to the work of putting electrical charges onto the ions. (Recall [Topic 3C.1(e)] that the Gibbs function is associated with maximum non-expansion work.) To find the work of charging, the distribution of ions must be found, and that is done using the shielded Coulomb potential [5F.15], which takes into account the ionic strength of the solutions are found in Topic 5F.2 (particularly in the Justifications). The Debye-Hückel limiting law [5F.19b] (valid only for dilute solutions because of some truncated series expansions) gives a mean ionic activity coefficient that depends on the charges of the ions involved, the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b isometry coefficient that depends on the charges of the ionic strength is 1 (b) I = Σ | Oi | zi2 [5F.9] 2 i \b | and if b Thus, for this mixture I = I(K 3 [Fe(CN)6]) + I(KCl) + I(NaBr) I = (b(K 3 [Fe(CN)6]) + b(KCl) + (0.030) +
(0.030) + (0.030)solution, as in the solution to this exercise, by summing the product | Oi |zi2 for each 2(b /individual ion as in the definition of I [5F.9]. Question. Can you establish that the comment holds for this exercise? Note that the term for K+ in a sum over ions includes ions from two different salts. 5F.2(b) The original KNO3 solution has an ionic strength of 0.110. (For compounds of monovalent ions, the ionic strength is numerically equal to the molal concentration, as shown in Exercise 5F.1(b).) Therefore, the ionic strength is numerically equal to the added is therefore (0.500 kg) × $(0.890 \text{ mol kg-1}) \times (101.11 \text{ g mol-1}) = 45.0 \text{ g}$. (b) (b) 1 (ii) For Ba(NO3)2 I = (1 \times 22 + 2 \times 12) | O |[5F.9] = 3| O |2 (b) (b) -1 Therefore, the solution should be made 0.890 mol kg /3 = 0.297 mol kg-1) × (261.32 \text{ g mol-1}) = 38.8 \text{ g}. 5F.3(b) The solution is dilute, so use the Debye-Hückel limiting law. log $y \pm = -|z+z|$ AI1/2 [5F.8] I = 1 1 (bi) 2 z [5F.9] = {(0.020 \times 12) + (0.035 \times 22) + (2 \times 0.035 \times 12)} $\sum 2 2 i | b O | i = 0.125$ For NaCl: log $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180$ so $y \pm = -1 \times 1 \times 0.509 \times (0.125)1/2 = -0.180 \times (0.125)1/2 = -$ 0.020 = 0.013 Question: What are the activity coefficients and activities of Ca(NO3)2 in the same solution? 5F.4(b) The extended Debye-Hückel law [5F.11a] is A | z + z - | 1/2 log y ± = -1 + BI 1/2 Solving for B. ((1 A | z + z - | 0.509) 1 B = -| 1/2 + + = -| | 0.1/2 log y ± | | (b / b) | I Draw up the following table b / (mol kg-1) 5.0×10-3 $10.0 \times 10-3$ 50.0 × 10-3 $\gamma \pm 0.927$ 0.902 0.816 B 1.32 1.36 1.29 The values of B are reasonably constant, illustrating that the extended law fits these activity coefficients with B = 1.3 . 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. 32 Solutions to problem 5F.2 Specialized to 1,1 electrolytes, the Davies equation with C = 0 and Debye-Hückel limiting law are, respectively AI 1/2 [5F.11b] and log $\gamma \pm = 1.3$. $-1 + BI \frac{1}{2} \frac{1}{2} (b) -0.509 I \frac{1}{2} [5F.8] = -0.509 | O| [5F.9] \log y \pm = (b) \frac{1}{2} F.1(a)$ shows a plot of log $\gamma \pm vs.$ I for both equations. Figure 5F.1(a) It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted are log $\gamma \pm vs.$ I for both equations. Figure 5F.1(a) It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure 5F.1(a) It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure 5F.1(a) It is clear that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; however, note that the values plotted differ by about 50% at the right side of the figure; how by a bout 50% at the right side of the figure; how by a bout 50% at the right side of the figure; how by a bout 50% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at the right side of the figure; how by a bout 50\% at t both equations. Toward the right side of this graph, one can see that the values plotted differ by about 10%. To be exact, for I < 0.086, the limiting law predicts activity coefficients within 10% of those predicted by the extended law. Figure 5F.1(b) Integrated activities 5.2 The data are plotted in Figure 15.1. The dotted lines correspond to Henry's law vapour pressures and the dashed lines to Raoult's law; the solid curves represent the experimental data. Figure I5.1 33 On a Raoult's law * xp p p [5E.2] and a = γx [5E.4], so $\gamma = *$. On a Henry's law * xp p p [5E.10], so $\gamma = *$. On a Henry's law * xp p p [5E.2] and a = γx [5E.4], so $\gamma = *$. On a Henry's law * xp p p [5E.2] and a = γx [5E.4], so $\gamma = *$. experimental data to obtain $p^*A = 7.3$ kPa and $p^*B = 35.6$ kPa. The Henry's law constant for acetic acid can also be determined by extrapolating the low-A data to xA = 1) The values obtained are KB = 68.1 kPa and KA = 30.3 kPa. Then draw up the following table based on the partial pressures given in the data. xA 0.016 0.0439 0.0835 0.1138 0.1714 pA/kPa 0.484 0.967 1.535 1.89
2.45 pA/kPa 0.484 0.967 1.535 1.53 1.048 [pB/xBp*B] yB(R) aB(H) 0.515 0.504 0.489 0.479 0.454 [pB/KB] 0.523 0.527 0.533 0.541 0.548 [pB/xBKB] yB(H) basis, a = xA pA/kPa pA/kPa aA(R) aB(H) yB(H) 0.2973 3.31 28.16 0.453 0.791 1.525 1.126 0.414 0.588 0.3696 3.83 26.08 0.525 0.733 1.420 1.162 0.383 0.607 0.5834 4.84 20.42 0.663 0.574 1.136 1.377 0.300 $0.720\ 0.6604\ 5.36\ 18.01\ 0.734\ 0.506\ 1.112\ 1.490\ 0.264\ 0.779\ 0.8437\ 6.76\ 10\ 0.926\ 0.281\ 1.098\ 1.797\ 0.147\ 0.999\ 0.013\ 1.006\ 1.913\ 0.007\ 1.000\ GE$ is defined [5B.5] as $G E = \Delta \min G - \Delta \min G$ ideal = nRT (xA ln xA + xB ln xB) and with a = yx $GE = nRT(xA \ln yA + xB \ln yB)$. For n = 1, we can draw up the following table from the information above and RT = 8.3145 J mol-1 K-1 × 323 K = $2.69 \times 103 \text{ J}$ mol-1 = 2.69 kJ mol-1 = 2.69 kJ mol-1 = 2.69 kJ mol-1 = $2.69 \times 103 \text{ J}$ mol-1 = 2.69 kJ mol-1 = 2.69 kJ mol-1 = 2.69 kJ mol-1 = $2.69 \times 103 \text{ J}$ mol-1 = 2.69 kJ mol-1 = 2.69 kJ mol-1 = $2.69 \times 103 \text{ J}$ mol-1 = 2.69×1 $0.9931\ 0.125\ 0.129\ 0.075\ 0.070\ 0.079\ 0.006\ xA\ ln\ yA\ 0.083\ 0.095\ 0.133\ 0.135\ 0.092\ 0.004\ xb\ ln\ yB\ as\ a\ solvents,$ but only B as a solute. Extend the table by including a row for yA(H). 5.4 pA = aA pA* [5E.2] = yAxApA* [5E.4] p y p so y A = A* = A * xA pA xA pA Sample calculation at 80 K: 0.11×100 kPa (760 Torr) = 1.079 y (O 2) = $\times 0.34 \times 225$ Torr (101.325kPa |) Summary T/K 77.3 78 80 82 84 86 88 90.2 0.877 1.079 1.039 0.995 0.993 0.995 0.995 0.993 0.995 0.995 0.993 0.995 0.995 0.993 0.995 nonideality; however, the larger relative uncertainty in y(O2) is probably the origin of the low value. A temperature-composition diagram is shown in Figure 15.2(a). The liquid line is essentially a straight line as predicted for an ideal solution. Figure I5.2(a) Figure I5.2(b) 35 5.6 The Gibbs-Duhem equation applies to any partial molar quantity, so we start, as in Example 5A.2, with nA dVA + nB dVB = $-\int VB(xA, xB) n VB(0,1) = \int V VA(0,1) VB(0,1) VB(0,1) VB(0,1) = \int V VA(0,1) VB(0,1) VB(0,1) VB(0,1) VB(0,1) VB(0,1) = \int V VA(0,1) VB(0,1) VB(0,$ - xA) A (0,1) nB The notation VB* means the molar volume of B when xB = 1. Therefore, VA (xA, xB) = VB* - $\int VA(0,1) 1 - xA$ We must now plot xA/(1 - xA) against VA and estimate the integral. That means we must first find the partial molar volumes of chloroform (VA) that corresponds to various chloroform mole fractions (xA). At constant temperature and pressure, $(\partial V)(\partial (nVm)) = VA = |[5A.1]|$ where n = nA + nB is the total number of moles. $(\partial nA) n (\partial (nxA)) = VA | = |[5A.1]|$ draw up a table of V, n, and nA values using the Vm, xA data given and the relationship n nA xA = A = . n nA + 1 mol Solving for nA yields xA Vm/(cm3 mol-1) nA/mol n/mol V/cm3 nA = 0 73.99 vA 1 - xA 0.194 75.29 0.241 1.241 93.41 × 1 mol 0.385 76.5 0.626 1.6 4.717 373.0 0.889 79.82 8.009 9.009 719.1 1 80.67 In Figure I5.3(a), we plot V against nA. Both linear and quadratic fits to the data are shown. The data fit a straight line is constant, which would imply VA is constant (at 80.54 cm3 mol-1) over this range of compositions. We require some variation in VA so we use the quadratic fit, V/cm3 = 0.0252(nA/mol) + 74.03, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 × 0.0252(nA/mol) + 74.03}, which leads to (∂V) 3 -1 VA = | = {2 we integrate up to VA(0.5,0.5) = 84.39 cm3 mol-1. Figure I5.3(b) The points are plotted in Figure I5.3(b), and the area required is 0.025 cm3 mol-1 = 73.96 cm3 mol-1 = 73. component given that of the other. In this case, the data given were overall molar volumes, from which we had to compute VB directly in the same way we compute VB. In such a case, it would have been easier to compute VB directly in the same way we compute VB. In such a case, it would have been easier to compute VB directly in the same way we compute VB. In such a case, it would have been easier to compute VB. mass of N 2 = pN × mass of H 2 O × K N 2 2 37 (1) At pN = 0.78×4.0 atm = 3.1 atm 2
mass of N 2 = 3.1 atm 2 mass of N 2 = 1.4μ g N 2 2 (3) In fatty tissue the increase in N2 concentration from 1 atm to 4 atm is $4 \times (56 - 14) \mu$ g N 2 = $1.7 \times 102 \mu$ g N 2 5.10 (a) The sum has just one term, so v NK 4.0 × 107 dm 3 mol-1 40 dm 3 μ mol-1 = = 7 3 -1 [A]out 1 + (1.0 × 10 dm mol)[A]out 1 + (1.0 × 10 dm mol)[A]o) × [A]out 1 + (2 × 106 dm 3 mol-1) × [A]out 4 dm 3 μ mol-1 + -1 3 1 + (0.1 dm μ mol) × [A]out 1 + (2 dm 3 μ mol-1) × [A]out The plot is shown in Figure I5.4(b). = Figure I5.4(b) 5.12 Kevlar is a polyaromatic amide. peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces 38 partial double bond character between the carbon and nitrogen atoms. There is a substantial energy barrier preventing free rotation about the CN bond. The two bulky phenyl groups on the ends of an amide group are trans because steric hinderance makes the cis conformation unfavourable. See Figure 15.5(a). Figure 15.5(a) The flatness of the Kevlar polymeric molecules with parallel alignment form highly ordered, untangled crystal bundles. The alignment makes possible both considerable van der Waals attractions between adjacent molecules and for strong hydrogen bonding between the polar amide groups on adjacent molecules. These bonding forces create the high thermal stability and mechanical strength observed in Kevlar. See Figure 15.5(b). Figure 15.5(b). a speeding bullet, through hydrogen bond breakage and the transition to the cis conformation. 39 6 Chemical Equilibrium 6A The equilibrium constant Answers to discussion questions 6A.2 Eqn 5E.9, in the form of the following expression, provides the general definition of the activity for species J, aJ: = $\mu J \mu J O + RT \ln aJ$ [5E.9] where $\mu J O$ is the value of the chemical potential of J in the standard state, i.e., the standard state for which aJ = 1. In fact, the standard state of a substance that is a either a pure solid (e.g., copper, sodium chloride, naphthalene) or a pure liquid (e.g., bromine, water, methanol) equals 1 at, say, 25°C. Since the activity coefficients are generally used to address questions that concern real, non-ideal mixtures. It is well worth remembering several useful activity forms. Of course, both activities, aJ, and activity coefficients, yJ, of non-ideal mixtures are dimensionless and related by eqns that have the general form aJ = $yJ \times$ (concentration of J). Perfect Gas: aJ = pJ/p O (μ J O depends upon T alone; p O = 1 bar.) Real Gas: Ideal-dilute solutions: Ideal-dilute solu $/p O (\mu J O depends upon T alone.) a J = xJ a B = [B]/c O where c O \equiv 1 mol dm-3 a A = \gamma AxA a B = \gamma B[B]/c O Solutions to exercises 6A.1(b) 2 A \rightarrow B nJ = nJ(0) + vJ\Delta\xi$ where ξ is the extent of reactants and positive for reactants and $B \Delta rG = -2.41 \text{ kJ mol} - 1 \left(\frac{\partial G}{\Delta rG} = [6A.1] \right| \left(\frac{\partial F}{\partial p}, T \left(\frac{\partial G}{\Delta G} \right) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = (-4.73 \text{ kJ mol} - 1) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right) \times (+0.051 \text{ mol}) = -0.12 \text{ kJ } 6A.3(b) 2 \text{ NO2}(g) \rightarrow \text{N2O4}(g) \Delta rG = -4.73 \text{ kJ mol} - 1 \right)$ mol-1) × ln Q at 298.15 K The above equation is used to calculate ΔrG values at the given Q values in the following table. Part (i) (ii) (ii) (iv) Q 0.10 1.0 100 lnQ -2.303 0 2.303 4.605 ΔrG / kJ mol-1 -10.44 -4.73 +0.979 +6.69 The above equation also indicates that a plot of lnQ against ΔrG should be linear so points ii and iii, which straddle ΔrG = 0, can be used to perform a linear interpolation to find K from our equilibrium knowledge that $\ln Q = \ln Q = \ln Q = 1$ ($\Delta r G - \Delta r G = 0$) $\Delta r G = 0 + || - (-4.73) || \times | -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || -1 || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 - (-4.73) || 0.979 + 4.73 | -1 | kJ mol | Thus, ln = K 0.4034 \times (0 + 4.73) = 1.908 1.908 6.74$ from a two-point interpolation = K e = The two-point interpolation = K e = The two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - $\Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74$ from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - $\Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74$ from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - $\Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74$ from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - $\Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74$ from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point interpolation is in agreement with the result given by eqn 6A.8: K = e - \Delta r G O / RT [6A.8] + (0 + 4.73) = 1.908 1.908 6.74 from a two-point given by eqn 6A. K = aJvJ | [6A.13] | [] (p] /ulibrium table (Example 6A.2). Amount at equilibrium Mole fraction Partial pressure N2O4(g) NO2(g) $(1 - \alpha)n 2\alpha n 1 - \alpha 1 + \alpha (1 - \alpha)p 1 + \alpha 2\alpha 1 + \alpha 2\alpha p 1 + \alpha v J$ $\alpha = 0.201$ at eq uilibrium We draw up the following e (0) (perfect gas assumption) = $\prod (j)$ equilibrium (j) DNU2 / 1 $pNO2(1 + \alpha) = pN 2O4/pOpN2O4pO((1 - \alpha)p)O(p(1 + \alpha)2 = (O) 222(|)| (0.201)\alpha 24p(|)| 4 = \{ \} \} Op || (1 - \alpha) \times (1 + \alpha)| \} || (1 - 0.201) \times (1 + 0.201) || = 0.168 T = 1600 K, p = 1 bar = pO, \alpha = 0.24 at equilibrium 6A.5(b) (i) Br2 (g) 2 Br(g) We draw up the following equilibrium table (Example 6A.2). Amount at$ equilibrium Mole fraction Partial pressure Br2(g) Br(g) $(1 - \alpha)$ n 2α n $1 -
\alpha 1 + \alpha (1 - \alpha)$ p $1 + \alpha 2\alpha$ p $1 + \alpha v$)) $(prfect gas assumption) = \prod (J)$ equilibrium (J) $p O O 2 2 Br 4 p | [\alpha 2 |] = \{ O p | [(1 - \alpha) \times (1 + \alpha) |] = 0.244 at 1600 K (ii) ln K 2 = ln K1 - \Delta r H O R (1 1) | - | [6A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta r H O (1 1) - | [A.22] (T2 T1] \Delta$ the temperature increase causes a shift to the right when the reaction is endothermic. 6A.6(b) CH 4 (g) + 3 Cl2 (g) CHCl3 (l) + 3 HCl(g) (i) Using data tables of the text Resource section at 25°C, we find Δ r G O = Δ f G O (CHCl3 , l) + 3 Δ f $-308.84 \text{ kJ mol} - 1 \Delta r \text{ H O} = \Delta f \text{ H O} (\text{CHCl3}, l) + 3 \Delta f \text{ H O} (\text{HCl}, g) - \Delta f \text{ H O} (\text{CH } 4, g) = (-134.47 \text{ kJ mol} - 1) - (-74.81 \text{ kJ mol} - 1)$ (ii) $\Delta r H O R (11) | - | [6A.22] (T2 T1) \Delta r H O (11) - | R (323.15 K 298.15 K) (-336.59 \times 103 J mol - 1) (11) = ln (1.30 \times 1054) - | x - | = 114.1 - 1 - 1 || (8.3145 J K mol) (323.15 K 298.15 K) ln K 50°C = ln K 25°C - 1 K = e114. = 3.57 \times 1049 50° C As expected, the temperature increase causes a shift to the left when the reaction is$ exothermic. $\Delta rGO = -RT \ln K [6A.14] \Delta r G50O °C = -(8.3145 J K - 1 mol - 1) × (323.15 K) \ln (3.57 × 1049) = -307 kJ mol - 1 For this gas phase reaction <math>\Delta v = \sum vJ = 2 - 3 - 1 = -2 6A.7(b) 3 N2(g) + H2(g) \rightarrow 2 HN3(g) J v vJ) () ((vJ) O K = aJvJ | [6A.13] |] = = (vJ pJ / p O) J |] |] | [vJ |] | [vJ |] |] (vJ) (J) equilibrium (J) equilibri$ p and K p | Π + γ K b (J = γ K b ($\prod (c RT/p) | (J equilibrium (J equilibrium (J equilibrium v) \Delta v (OOK = where Kc | \prod ([J]/cO) | c (c RT/p) (J equilibrium K = Kc \times (c ORT/pO) - 2 because \Delta v = -2 for this reaction - 1 Since c R/p = 0.0831451 K, this expression may be written in the form O = KO (144.653 K) \times K2 c/T 2 Anhydrous hydrogen azide, HN3, boils at$ 36°C and decomposes explosively. A dilute solution can be handled safely. 6A.8(b) Draw up the following table for the reaction equation: A + B C + 2 D. A B C D Initial amounts / mol 1.21 0.79 4.58 Mole fractions 0.1163 0.1782 $0.0309 \ 0.6745$ (i) Mole fractions are given in the table. (ii) K x = $\prod x\nu J J T$ otal 6.00 6.79 0.9999 (0.1163) × (0.6745) 2 K x = (iii) = 9.61 (0.1782) × (0.0309) pJ = xJ p . Assuming the gases are perfect, aJ = pJ / p O , so (pC / p O) × (pD / p O) 2 (p) = Kx | O | = Kx O O (pA / p) × (pB $K = -(8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (298 \text{ K}) \times \ln(9.61) = -5.61 \text{ kJ mol} - 1 6A.9(b)$ The formation reaction is: $U(s) + 3/2 \text{ H}(g) 2 (pO) | || pH || 2/3/2 = aU(s) aUH pH2/pO.) (= 1 \text{ and, assuming perfect gas behavior, } a = H 2 (g) 3 (s) 3/2 (105 \text{ Pa}) 4 = | = 1.93 \times 10 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O = -RT \ln K [6A.14] = -(8.3145 \text{ J K} - 1) 139 \text{ Pa} (J\Delta rG O =$ mol-1) × (500 K) × ln (1.93 × 104) = -41.0 kJ mol - 1 6A.10(b) P(s,wh) + 3/2 H2(g) \rightarrow PH3(g) $\Delta f G O = +13.4 kJ mol - 1 \Delta f G = \Delta f G O + RT ln PH3 / p O (pH2 = / pO) 3 [Perfect gas assumption] 2 (+13.4 kJ mol) + (8.3145 × 10 - 1 - 3 (0.60) kJ K - 1 mol - 1) × (298.15 K) × ln 3 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12
| 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 12 || 1$ = +12.1 kJ mol-1 Since Δ f G > 0, the spontaneous direction of reaction is toward the elements in their standard states. 6A.11(b) PbI 2 (s) PbI 2 (ag) K s = 1.4 × 10-8 \Deltar G O = - RT ln K s = -(8.3145 J K -1 mol-1) × (298.15 K) × ln (1.4 × 10-8) = +44.8 kJ mol-1 = Δ f G O (PbI 2, ag) $-\Delta$ f G O (PbI 2, ag) = Δ r G O + Δ f G O $(PbI 2, s) = -128.8 \text{ kJ mol} - 1 (44.8 - 173.64) \text{ kJ mol} - 1 = Solutions to problems 6A.2 \Delta r G O (H 2 CO, l) + \Delta vap G O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = 1 bar \Delta vap G O = - RT ln p O (H 2 CO, l) + \Delta vap G O (H 2 CO, l) + \Delta vap G O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln K (vap) = - RT ln p O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O where p = 1500 Torr = 2.000 bar and p O = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = p O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(l) H 2 CO(g), K (vap) = - RT ln P O (H 2 CO, l) + 28.95 \text{ kJ mol} - 1 For H 2 CO(g), K$ -1 mol-1) × (298 K) × ln 2.000 bar = -1.72 kJ mol-1 1 bar Therefore, for the reaction CO(g) + H 2 (g) H 2 CO(g), $\Delta r G O = \{(+28.95) + (-1.72)\} \text{ kJ} \text{ mol}-1$) × (298 K) Hence, K = $(-27.23 \times 10 = -10.99 = 1.69 \times 10 - 5 \cdot 6A.4 \pm A \text{ reaction proceeds spontaneously if its reaction Gibbs function is}$ negative. $\Delta r G = \Delta r G O + RT \ln Q [6A.10]$ Note that under the given conditions, $RT = 1.58 \text{ k} \text{ mol} - 1 = 23.6 - 1.58 \ln (1.3 \times 10 - 7) (ii) \Delta r G / (k] \text{ mol} = +1.5 - 1) = \{\Delta G (ii) - RT \ln p P\} / (k] \text{ mol} = +1.5 - 1) = \{\Delta G (ii) - R$ -10 } $\Delta r G / (kJ mol - 1) = \Delta r G O (iii) - RT ln pH2 O 2 pHNO3 / (kJ mol - 1) - 72 = -85.6 - 1.58ln[(1.3 × 10 - 10)] = -1.3 (iv) {} \Delta r G / (kJ mol - 1) = -1.3 (iv) {}$ vapour. Does one convert spontaneously into the other? Consider the reaction (iv) - $\Delta r G$ (iv (at least of the four we considered). 6B The response to equilibria to the conditions Answers to discussion questions 6B.2 (1) Response to change as the total pressure, but the individual partial pressure, but the individual partial pressure change in pressure. The equilibria to the conditions Answers to discussion questions 6B.2 (1) Response to change in pressure. difference, Δv , between the sums of the number of moles of gases on the product and reactant sides of the balanced chemical reactant gases = = The requirement of an
unchanged equilibrium constant implies that the side with the smaller number of moles of gas be favored as pressure increases. To see this, we examine the general reaction equation $0 = \sum vJ J$ [6A.9] in the J special case for which all reactants and products are perfect gases. In this case the activities equal the partial pressure of the gaseous species and, therefore, aJ(gas) = pJ/p O = xJp/p O where xJ is the mole fraction of gaseous species J. Substitution into equa 6A.13 and simplification yields a useful equation. vJ $((y | O K) = aJvJ | = \prod | \prod xJ (p / p) | J equilibrium (J equilibrium$ reactant concentration factors that has a form analogous to the equilibrium constant K. However, whereas K depends upon temperature and pressure. Solving for Kx provides an equation that directly indicates its pressure dependence. Kx = K (p / p O) - Δv This equation indicates that, if $\Delta v = 0$ (an equal number of gas moles on both sides of the balanced reaction equation), Kx = K and the concentration ratio has no pressure dependence. An increase in pressure causes no change in Kx and no shift in the concentration equilibrium is observed upon a change in pressure. However this equation indicates that, if $\Delta v < 0$ (fewer moles of gas on the product side of the balanced reaction equation), K x = K (p / p O) Δv. Because p is raised to a positive power in this case, an increase while the denominator concentrations (products) must increase in pressure causes Kx to increase. The concentrations shift to the product side to reestablish equilibrium when an increase in pressure has stressed the reaction equilibrium. Similarly, if $\Delta v > 0$ (fewer moles of gas on the reactant side to reestablish equilibrium. equilibrium when an increase in pressure has stressed the reaction equilibrium. d ln K Δ r H O = [6B.2(a)], shows that K dT RT 2 decreases with increasing temperature. The van 't Hoff equation, the left. The opposite occurs in endothermic reactions (i.e., $\Delta r H O > 0$). See text Section 6B.2 for a more detailed discussion. Solutions to exercises 6B.1(b) At 1120 K, $\Delta r G O = +22 \times 103$ J mol-1) ln K1 (1120K) = [6A.14] = -r - = -2.363 RT (8.3145 J K -1 mol-1) × (1120 K) K e -2.363 = 9.41 × 10 - 2 \Delta r H O (11) | - |[6B.4] R (T2 T1 / Solve for T2 at ln K2 = 0 (K2 = 1). 1 1 R ln K1 1 (8.3145 J K - 1 mol - 1) × (-2.363) = + = + = 7.36 × 10 - 4 T2 1120 K (125 × 103 J mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where $\Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where <math>\Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where \Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where \Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where \Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) \Delta r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = A + B + C3 T T At 450 K: A = -2.04, B = -1176 K, and C = 2.1 × 107 K 3 where \Delta rG O = -RT ln K [6A.14] = RT × (|A + B + C3)|T T | 7 3) (= -(8.3145 J K - 1 mol - 1) A r H O T1 ln K 2 = ln K1 - T2 1.4 × 103 K = 6B.2(b) ln K = -1176 K (A + B + C3) |T T | 1 + 10 K |$ -1 mol-1) × (450 K) × $|-2.04 - 1176 \text{ K} + 2.1 \times 10 \text{ K3} | 450 \text{ K} (450 \text{ K}) | -1 = +16.6 \text{ kJ mol} d \ln \text{ K} [6B.2(b)] \Delta r H O = -R d(1/T) = -R d(1/T) = -R d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | (|73) | = -R \times |B+2| d(1/T) | T | T | (|73) | = -R \times |B+2| d(1/T) | T | (|73) | = -R \times |B+2| d(1/T) | T | (|73) | = -R \times |B+2| d(1/T) | T | (|73) | = -R \times |B+2| d(1/T) | = -R \times |B+2$ $O 7.19 \text{ kJ mol} - 1 - 16.6 \text{ kJ mol} - 1 - 20.9 \text{ J K} - 1 \text{ mol} - 1 \Delta r \text{ S O} = r = = T 450 \text{ K 6B.3(b) CH3OH(g)} + \text{NOCl(g)} \rightarrow \text{HCl(g)} + \text{CH3NO2(g)} = v \text{ For this gas phase reaction } \Delta v \Sigma = J 0 \text{ J v vJ} \left(\int (v \text{ J} \circ V \text{ J}) \int (v \text{ J} \circ$ $\prod = \text{ and } K p \mid \prod (pJ/pO) \mid = K = \gamma K p (J/equilibrium (J/eq$ |= K = x (p/p) (J) equilibrium For this reaction: $K = Kx \times (p/p O) = Kx 0$ because $\Delta v = 0 K$ is independent of pressure so we conclude by the above eqn that for this reaction: $K = Kx \times (p/p O) = Kx 0$ because $\Delta v = 0 K$ is independent of pressure. Thus, the percentage change in Kx upon changing the pressure equals zero for this reaction. $6B.4(b) N 2 (g) + O 2 (g) 2NO(g) K = 1.69 \times 10^{-10} M C$ 10-3 at 2300 K Initial modes: nN2 = 5.0 g 0.1785 mol = 28.013 g mol-1 Initial moles:= nO2 2.0 g = $6.250 \times 10-2$ mol 32.00 g mol-1 N2 nO2 = 0.0625 0 n = 0.2410) 2z/n 1 (n (=) (2) (n $-z/n N2 \Delta v z = Total nN2 = 0.1785$ (p) K K x | O |= K x (Because $\Delta v = \sqrt{p}$ $(2 z) 2 K = nN2 - z \times nO2 - z (1 - K) z NO Initial amount/mol Mole fractions 4 O2 v \Sigma = J O2 - z/n 0 for this reaction. See Exercise 6B.3(a) or (b)) J - nz + nN2 nO2 = 0 n \pm n 2 - 4 (1 - 4 K) nN2 nO2 2 (1 - 4 K) 0.2410 \pm 0.24102 - 4 (1 - 2 (1 - 2 - 2.223 \times 10 = 2.121 \times 10 - 3 - 3 4 4 or 2.121 \times 10 1.69 \times 10 - 3 1.69 \times 10^{-3} \times 10^{-3$ because the negative value is non-physical. $2z (2.121 \times 10-3) = 1.8 \times 10-2$ xNO = = n 0.24 1 6B.5(b) ln K2 Δ HO (11) = -r - [6B.4] K1 R | (T2 T1 |) - 1 (11) (K) Δ r H O = R × | - | × ln | 2 | (T1 (K1) 2 |) (1 - 11) (K2) H O (b) $-1 \ln (2.00) (55.85 \text{ kJ mol}) \times = K2/K1 = 0.500 - 1.38.71 \text{ kJ mol} - 1 (55.85 \text{ kJ mol} - 1) \times \ln (0.500) = 6B.6(b)$ The reaction is CuSO 4 \cdot 5H 2 O(g). For the purposes of this exercise we may assume that the required temperature is that temperature at which K = 1 at a pressure of 1 bar. For K = 1, $\ln K = 0$, and $\Delta r G O = 0$. $\Delta r G O = 0$. $\Delta r G O = 0$, $\Delta r G O = 0$. $\Delta r G O = 0$, $\Delta r G O = 0$. $\Delta r G O = 0$, $\Delta r G O =$ $\sum v \int \Delta f_{J} H O = J \sum v S = \{(109) + (5) \times (188.83) - (300.4)\} J K \Delta r S = O O J - 1 J 1 mol - 278 C = 608 kPa and 6B.7(b) NH 4 Cl(s) NH 3 (q) + (5) \times (188.83) - (300.4)\} J K \Delta r S = O O J - 1 J 1 mol - 2752.8 J K - 1 mol - 1 J 299.2 \times 103 J mol - 1 = 397 K 752.8 J K - 1 mol - 1 J 299.2 \times 103 J mol - 1 J 299.2 \times$ HCl(g) 1 p. The gases originate from the dissociation of
the solid alone so p = p = 2 NH3 HCl (i) Equilibrium constants = K pNH3 / p O × pHCl / p O ((= 1 = 1 4 2 p / pO (p/ p 1 [Perfect gas assumption] O 2 2 = 9.24 4 (608 kPa / 100 kPa) = K 427°C 1 = K 459°C 1 (ii) O) ()×(p / p) 2 = 31.08 4 (1115 kPa / 100 kPa) 2 Δ GO = - RT ln K [6A.14] O Δ $r G 4 27 - (8.3145] K - 1 mol - 1) \times (700.15 K) \times ln (9.24) = -12.9 k mol - 1$ °C = (iii) ln K2 Δ HO (11) = $-r - [6B.4] K1 R | (T2 T1 | | -1(11)(K) \Delta r H O = R \times | -| \times ln | 2 | TT | K1 / 2 | (18.3145] K = -1 - 1(11() 31.08 - mol) \times | | \times ln 9.24 700.15 K 732.15 K | | -1) = 162 k mol - 1$ (iv) Δ HO $-\Delta$ r GO (162 k mol - 1) - (-12.9 k mol - 1) - (-12.9 k mol - 1) \times | | \times ln 9.24 700.15 K 732.15 K | | -1) = 162 k mol - 1 (iv) Δ HO $-\Delta$ r GO (162 k mol - 1) - (-12.9 k mol - 1) + (-12.9 k mol - 1) \times | | \times ln 9.24 700.15 K 732.15 K | | -1) = 162 k mol - 1 (iv) Δ HO $-\Delta$ r GO (162 k mol - 1) - (-12.9 k mol - 1) + (-12.9 k mol - 1) \times | | \times ln 9.24 700.15 K 732.15 K | | -1) = 162 k mol - 1) +250 J K -1 mol -1 Δ r S O = r = = T 700.15 K Solutions to problems 6B.2 U(s) + 3 2 H 2 (g) UH 3 (s) p459°C = 1115 kPa - 3/2 = K a = (pH2/p O) -3/2 [perfect gas] H2 = (= p/p O) -3/2 [perfect gas] H2 = (= p $(K) = -32 \text{ RT } 2 - 32 \text{ RT } 2 - 32 \text{ RT } 2 \times |2 + |(T/dT/T \text{ RT } 2 \Delta f \text{ H } \text{ O} = 3 \text{ R} \times \text{ B} - \text{CT} = () 2 \text{ where } \text{B} = -1.464 \times 104 \text{ K} \text{ and } \text{C} = -5.65 \text{ d} (\Delta f \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ applied to chemical reactions, } 2C.7(a)] \text{ or } (\partial \Delta \text{ H } \text{ O}) = \Delta r \text{ CpO} \text{ dT} [\text{from eqn } 2B.6(a) \text{ dT} \text{ dT} (A) \text{ d$ RT ln p +78 kJ mol-1 K = and Δ r H O = pO p pO (1.71 kPa)O = -(8.3145 J K - 1 mol-1) × (400 K) × ln | 1 bar = 100.0 kPa] | [p = \ 100.0 kPa] | $470 \text{ K}, \text{T} (T)(-1 - 1 \Delta r \text{G} \text{ O} = (\text{T}) | \times (13.5 \text{ kJ mol}) + (78 \text{ kJ mol}) + (78 \text{ kJ mol}) \times | 1 - |400\text{ K} 400 \text{ K} / (13.5 - 78) \text{ kJ mol} - 1) + (8 \text{ kJ mol} - 1) = 78 - 0.161 \times (\text{T K})$. 6B.6 The equilibrium we need to consider is I 2 (g) 2 I(g) (MI = 126.90 \text{ g mol} - 1). It is convenient to express the equilibrium constant in terms of α , the degree of dissociation of I2, which is the predominant species at low temperatures. Recognizing that the data nI2 is related to the total iodine mass, mI, by nI2 = mI / M I2 we draw the following table. Equilibrium amounts Mole fraction Partial pressure The equilibrium constant for the dissociation is I 2 α nI2 I2 (1 - α)nI2 2 α 1+ α 2 α $p 1 + \alpha 1 - \alpha 1 + \alpha (1 - \alpha)$ | $p (1 + \alpha) nI2 T p (p K = I / pO) 2 = 4\alpha 2 (p / pO) pI2 = pI2 pO 1 - \alpha 2 pI 2 / pO We also know that <math>pV = ntotal RT = (1 + \alpha) nI2 RT mplying that = \alpha pV - 1$ where V = 342.68 cm3. The provided data along with calculated values of α and K(T) nI2 RT are summarized in the following table. T/K p / atm 104 nI2 / $p = 12 pO T - \alpha 2 pI 2 / pO We also know that <math>pV = ntotal RT = (1 + \alpha) nI2 RT mplying that = \alpha pV - 1$ where V = 342.68 cm3. The provided data along with calculated values of α and K(T) nI2 RT are summarized in the following table. T/K p / atm 104 nI2 / $p = 12 pO T - \alpha 2 pI 2 / pO We also know that <math>pV = ntotal RT = (1 + \alpha) nI2 RT mplying that = \alpha pV - 1$ where V = 342.68 cm3. mol α K Since Δr H O 973 0.06244 2.4709 0.08459 1.82×10-3 1073 0.07500 2.4555 0.1887 1.12×10-2 1173 0.09181 2.4366 0.3415 4.91×10-2 is expected to be approximately a constant over this temperature range and since (d ln K) O Δr H O = -R | [6B.2(b)], a plot of lnK against 1/T should be linear with slope = $-\Delta r$ H / R. The linear (d(1/T) of the description of) /regression fit to the plot is found to be lnK = 13.027 – (18809 K)/T with R2 = 0.999969. Thus, $\Delta r H O = -(-18809 K) R = +156 kJ mol-1 at 298.15 K Let the temperatures of interest be T1 = 298.15 K and T2. <math>\Delta fG(T2)$ at 1 bar can be calculated from the reaction thermodynamic properties at T1 with the following relations. $\Delta r H (T2) = \Delta r B (T1) + \int \Delta r C p(T) dT [2 C.7(a) and (b); \Delta r C p(T) + \int T2 \Delta r$

function capability and numeric integrations of either the scientific calculator or a computer software package. The following is a Mathcad Prime 2 worksheet also makes it Thus, with numerical integrations we have found that Δ f G O = very easy to examine, even plot, changes in the reaction thermodynamic properties. The following worksheet plot shows the variation of the formation of the shows a decrease with temperature in a near-linear manner. Can you explain why? 6C Electrochemical cells Answers to discussion questions 6C.2 A salt bridge connecting two half-cells is usually a U-tube filled with potassium chloride in agar jelly. It provides the mobile electrolyte for completing the circuit of an electrochemical cell. In its absence, the cell cannot generate an electrochemical cell. In electrochemical cell. In its absence, the cell cannot generate an electrochemical cell. In electrochemical cell or enter either half-cell, because this act would cause the net electronic charge of the half-cell to be non-zero. The strong electrostatic force prevents this from happening and causes macroscopic objects to normally have a zero net electrical charge. However, a salt bridge provides an anion to the anodic half-cell for every electron that leaves while simultaneously providing a cation to the cathodic half-cell for every electron that enters. This is a "closed" electrical circuit in which the net charge of each half-cell remains zero but an electric current can be generated. 6C.4 When a current is being drawn from an electrochemical cell, the cell potential is altered by the formation of charge double layers at the surface of electrodes and by the formation of solution chemical potentials between dissimilar materials both external and external to the cell may occur and junction specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined. For the calculation of the standard electrode potentials from data tables. cell EO (i) R: L: Ag 2 CrO 4 (s) + 2 e \rightarrow 2 Ag(s) + CrO 24 - (aq) - +0.45 V - Cl2 (g) + 2 e - $2 \text{ Cl}(aq) + 1.36 \text{ V} - 2 - 4 \text{ Overall}(R - L): \text{ Ag } 2 \text{ Cro } 4(s) + 2 \text{ Cl}(aq) \rightarrow 2 \text{ Ag}(s) + \text{ Cro }(aq) + 2 \text{ e} \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ e} \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 2 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}(aq) \rightarrow \text{ Sn } 3 + (aq) + 2 \text{ Fe } 3 + -0.62 \text{ V}($ H 2 O(1) Cu 2+ (aq) + 2 e - + 1.23 V \rightarrow Cu (s) + 0.34 V + Overall (R - L) : Cu (s) + MnO 2 (s) + 4 H (aq) \rightarrow Cu 2+ (aq) + Mn 2+ (aq) + 2H 2 O(1) + 0.89 V Comment. Those cells for which Ecell > 0 may operate as spontaneous galvanic cells under standard conditions. O O O Those for which Ecell informs us of the < 0 may operate as nonspontaneous electrolytic cells. Recall that Ecell spontaneity of a cell under standard conditions only. For other conditions (concentrations, etc.) under which these reactions occur are not given. For the purposes of this exercise we assume standard conditions. The specification of the right and left electrodes is determined by the direction of the reaction as written. As always, in combining half-reactions to form an overall cell reaction we must write half-reactions, and then set up the corresponding cell. EO - - (i) R: 2 H 2 O(1) + 2 e \rightarrow 2 OH (aq) + H 2 (g) - $0.83 \text{ V} - 2.71 \text{ V} \text{ L}: 2 \text{ Na} + (aq) + 2 \text{ e} \rightarrow 2 \text{ Na(s)}$ and the cell is Na(s) NaOH (aq) H 2 (g) Pt (ii) R: +1.88 \text{ V} I 2 (s) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) + 2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 \text{ e} \rightarrow 4 2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq) +2 (g) Pt (ii) +0.54 \text{ V} R: 2 \text{ H} + (aq - (aq) H + (aq) H 2 (g) Pt -0.83 V +0.83 V O Comment. All of these cells have Ecell > 0, corresponding to a spontaneous cell reaction would have been the reverse of the one given, with the right and left electrodes of the cell also reversed. 6C.2(b) Pt|H 2 $(g, p, O) \mid HCl(aq, 0.010 \text{ mol } kg - 1) \mid AgCl(s) \mid Ag(i) R: AgCl(s) + e \rightarrow Ag(s) + Cl-(aq) L: HCl(aq) + e \rightarrow \frac{1}{2} H2(g) \rightarrow 2 Ag(s) + 2 HCl(aq) E O = +0.22 V E O = +$ for the above cell reaction is: RT O E = Ecell $-\ln Q$ [6C.4] cell vF (aHCl/b O) = $-\nu$ FEcell = $-2 \times (9.6485 \times 10^{-1} + 10^{-1})$ (bHCl/b O) = $-2 \times (9.6485 \times 10^{-1})$ (bHCl/b O) $- F O \Delta r G O = -\nu$ FEcell = $-2 \times (9.6485 \times 10^{-1})$ (bHCl/b O) $- F O \Delta r G O = -\nu$ FEcell = $-2 \times (9.6485 \times 10^{-1})$ $104 \text{ C mol} - 1 \times (0.22 \text{ V}) = -42 \text{ kJ mol} - 1 \text{ (iii)}$ The ionic strength and mean activity coefficient are: I = $12 \sum z (b/b) [5F.9] = \{1(0.010) + 1(.010)\} = 2 \text{ i } 0.12 \text{ i } 0.010 \text{ i } \log y \pm = -z + z - \text{ AI } 1/2 [5F.8] = -1 \times (0.509) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = 0.889$ Therefore,
$\{ \} 2 \text{ RT ln } y \pm (b \text{ HCl} / b \text{ O}) \text{ F } 2 \times (8.3145 \text{ J mol} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = -z + z - \text{ AI } 1/2 [5F.8] = -1 \times (0.509) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = -z + z - \text{ AI } 1/2 [5F.8] = -1 \times (0.509) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = -z + z - \text{ AI } 1/2 [5F.8] = -1 \times (0.509) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = 0.889$ Therefore, $\{ \} 2 \text{ RT ln } y \pm (b \text{ HCl} / b \text{ O}) \text{ F } 2 \times (8.3145 \text{ J mol} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = 0.889 \text{ Therefore}, \{ \} 2 \text{ RT ln } y \pm (b \text{ HCl} / b \text{ O}) \text{ F } 2 \times (8.3145 \text{ J mol} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ y} \pm = -2 \text{ K} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm = -2 \text{ K} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm = -2 \text{ K} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm = -2 \text{ K} - 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 = -0.0509 \text{ g} \pm 1 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.010) 1/2 \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.899) \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.889) \times (0.899) \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.89) \times (0.899) \times (0.899) \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.89) \times (0.899) \times (0.899) \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.89) \times (0.899) \times (0.899) \text{ K} - 1) \times (298.15 \text{ K}) \ln \{(0.89) \times (0.899) \times (0.899)$ (0.010) = 0.22 V + 0.24 V = 0.22 V - 9.6485 × 105 C mol-1 = +0.46 V O - E = Ecell cell Solutions to problems Ecell = +0.190 V 6C.2 Cell: Hg|Hg2Cl2(s)|HCl(aq)|Q·QH2|Au The electrode half-reactions and their standard potentials are and v=2 EO R : Q(aq) + 2 H + (aq) + 2 e - \rightarrow 2 Hg(l) + 2 Cl- (aq) 0.6994 V 0.2676 V Overall (R - L): Q(aq) + 2 H + (aq) + 2 Hq(l) + 2 Cl - (aq) \rightarrow QH 2 (aq) + Hg 2 Cl 2 (s) 0.4318 V The reaction quotient is directly related to the pH, a relation bH+ = bCl- while for the Q·QH2 equimolecular complex of quinone bQ = bQH2. Q = aQH2 aQ aH2 + aCl2 - The Debye-Hückel limiting law makes use of the mean activity coefficient for the compound MpXq defined by aJ = $\gamma \pm bJ$. Thus, aQH2 / aQ = 1, aH + = aCl - , and the reaction quotient. ln (aH +) ln (Q) pH = $-\log(aH +) = - \text{ or } = - \ln(10) \ln(10$ $4 \ln (10)$ pH The Nernst equation [6C.4] at 25 °C is now used to relate cell potentials to the pH. O - E = Ecell - 25.693 × 10-3 V v ln Q (4 ln (10) pH) v (EcellO - Ecell - 25.693 × 10-3 V v (EcellO - Ecell - 25.693 × 10-3 V v (EcellO - Ecell - 25 solution can in principle be measured with any electrode having an emf that is sensitive to H+(ag) concentration (activity). In principle, the hydrogen electrode being the right-hand electrode with known potential as the left-hand electrode. A common choice is the saturated calomel electrode is not convenient to use, so in practice glass electrodes are used because of ease of handling (see Impact I6.2). Solutions to exercises 6D.1(b) In each case the equilibrium constant is calculated with the expression $\ln K = (i) Sn(s) + CuSO 4 (aq) R : Cu 2 + 2 e - \rightarrow Cu(s) 2 + - L : Sn (aq) + 2 e - Sn(s) = \ln K + 0.34 V |] O Ecell = +0.48 V - 0.14 V |] O vFEcell (2) × (0.48 V) = [6C.5] = 37.4 RT 25.693 mV = = 1.7 × 1016 K e37.4 O vFEcell RT [6C.5] . (ii) Cu(s) + Cu 2 + (aq) 2 Cu + ($ $(ag) + 0.16 V | 0 | Ecell = -0.36 V + 0.52 V | R : Cu 2 + e - \rightarrow Cu + (ag) - L : Cu (ag) + e \rightarrow Cu(s) + ln K = O v Ecell RT (1) \times (-0.36 V) = -14.0 25.693 mV [6C.5] = = Ke - 14.0 = 8.3 \times 10 - 7 6D.2(b) Bi|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3(s)|Bi2S3$ Bi 2S3 (s) R: 2 Bi (i) = ln K - 3 + O ν FEcell = [6C.5] RT EO +0.20 V -0.76 V +0.96 V v=6 6 (0.96 V) = 224 (25.693 × 10-3 V) K = e 224 = 1.9 × 1097 The solubility product of Bi2S3(s) is Ksp = K-1 = 1 / 1.9 × 1097 = 5.3 × 10-98 . (ii) The solubility product of Bi2S3(s) is very small. Consequently, the molar solubility, s, of Bi2S3(s) must also be very low and we can reasonably take the activity coefficients of the aqueous ions to equal 1. $\frac{1}{2}$ Bi 2+= 2 5 3 2 s) (3s) / (c) (= 2 3 0 5 108 (s / c 0) 5 1.4 × 10-20 mol dm -3 s= (Ksp / 108) c 0 = (5.3 × 10-98 / 108) mol dm -3 = 1 1 5 5 Solutions to problems 6D.2 The method of the solution is first to determine Δ r G O, Δ r H O, and Δ r S O at 25 °C for the cell reaction 1 H (g) + AgCl(s) \rightarrow Ag(s) + HCl(aq) v=1 2 2 and then, from the values of Δ f G O, Δ r H O, and S O, for all the species other than Cl- (aq), to calculate Δ f G O, Δ f H O , and S O for Cl- (aq). O O O O Ecell EAgCl/Ag,Cl EHO+ / H EAgCl/Ag,Cl = EAgCl/Ag,Cl Since = - = -0 -, we have (R.G. Bates and V.E. Bowers, J. Res. Nat. 2 Bur. Stand., 53, 283 (1954)): O /V = 0.236 59 - 4.8564 × 10-4 (θ /°C) - 3.4205 × 10-6 (θ /°C)2 + 5.869 × 10-9 (θ /°C)2 + 5.869 × 10-9 (θ /°C)3 Ecell and we proceed with the calculation of the electrochemical and thermodynamic reaction properties at 25 °C. EcOell / V = $(0.23659) - (4.8564 \times 10 - 4) \times (25.00) - (3.4205 \times 10 - 6) \times (25.00) = -1 \times (96.485 \text{ kC mol} - 1) \times (0.22240 \text{ V}) = -21.46 \text{ kJ mol} - 1 \text{ O } (\partial \Delta G \text{ O }) \nu \nu F F \Delta r S \text{ O } = -| r = [6C.6] | | | | | (\partial T) p (\partial T)$ $\partial \theta \mid p \in vF \{(-4.8564 \times 10 - 4() \mid
d\theta \circ C = dT K \mid (\circ C) - 2 \times 3.4205 \times 10 - 6 \theta (\circ C) + 3 \times 5.869 \times 10 - 9 \theta 2 (\circ C) 2 \mid (-4.8564 \times 10 - 4) - 2 \times (3.4205 \times 10 - 6) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times \{ \} 2 - 9 \mid +3 \times (5.869 \times 10) \times (25) \mid V = x 1 (96.485 \text{ kC mol} - 1) \times (25) \mid V = x 1 (96.48$ (-62.30 J K -1 mol-1) = -40.03 kJ mol-1 The cell reaction Gibb's energy is related to formation Gibb's energies by Δ r G O = Δ f G O (Cl-) - Δ f G O (Cl-) = Δ r G O + Δ f G O (AgCl) = (-21.46 - 109.79) kJ mol-1 = -131.25 kJ mol-1 () Similarly, $\Delta f H O Cl = \Delta r H O + \Delta f H O (AqCl) = (-40.03 - 127.07) k mol - 1 = -167.10 k mol - 1 = -16$ (130.68) + (96.2) JK - 1 mol - 1 = +56.7 JK - 1 mol - 1 = +56.7 JK - 1 mol - 1 Integrated activities 6.3 (a) 1 (b) 2 (b) 1 = 4 O (1.0 × 10-3) = 4.0 × 10-3 For ZnSO4, I = (4) × (3.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± = - |z+z-|AI|/2 [5F.8] log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (4.0 × 10-3) = 1.2 × 10-2 (b) log \gamma ± (CuSO 4) = -(4) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.509) × (0.50 10-3 $1/2 = -0.1288 \gamma \pm (CuSO 4) = 0.74 \log \gamma \pm (ZnSO 4) = -(4) \times (0.509) \times (1.2 \times 10-2) 1/2 = -0.2230 \gamma \pm (ZnSO 4) = 0.60$ (c) The reaction in the Daniell cell is Cu 2 + (aq) + SO 24 - (aq) + SO 24 -(x + b) = b(x + b) = $(2nSO 4)(0.60) 2 \times (3.0 \times 10-3) 2 = = 5.92 = Q \gamma \pm 2 (CuSO 4) b 2 (CuSO 4) b 2 (CuSO 4) (0.74) 2 \times (1.0 \times 10-3) 2 (d) (e) 5.9 \Delta GO - (-212.7 \times 103 J mol-1) O Ecell = Ecell ln Q = -(1.102 V) - ||ln(5.92) 2 v|| = (1.102 V) - (0.023 V) = +1.079 V$ $6.4 \text{ Pt}|\text{H 2 (g, p O)}|\text{NaOH (aq, 0.01000 mol kg - 1)}, \text{NaCl (aq, 0.01125 mol kg - 1)}|\text{AgCl(s)}|\text{Ag(s)} + 2 \text{ Cl} - (\text{aq}) + 2 \text{ AgCl(s)} \rightarrow 2 \text$ EcellT -/ KEcell |-0.05115| $|=(5039.75 V) \times |ET -/ KE - 1 cell O cell Using information of the data tables, we find that O Ecell = ERO - ELO = EO (AgCl, Ag) - EO (H + /H 2) = +0.22 V - 0 = +0.22 V - 0 = +0.22 V$. This value does not have the precision needed for computations with the high precision data of this problem. Consequently, we will use the more precise value found in the CRC Handbook of Chemistry and Physics(71st ed): O Ecell / V 20.0 1.04942 pK w 14.14 13.92 13.70 Inspection of the table reveals that for each 5 K increase in temperature the value of pKw decreases by 0.22 and, consequently, d(pKw)/dT = -0.22/5.0 K = -0.044 K - 1. Thus, at 25°C: $d \ln K w \Delta w H O = [6B.2(a)] dT RT 2 d \ln K w d \log K w d pK w \Delta w H O = = - \ln 10 \times (7.3 \text{ K}) + (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (298.15 \text{ K}) \times (-0.044 \text{ K} - 1) \times (-0.044 \text{ K} - 1)$ $\Delta wG O \Delta w S O = = -15.4 J K - 1 mol - 1 T 6.5 \ddagger Electrochemical Cell Equation: 1 2 H 2 (g, 1 bar) + AgCl(s) H + (aq) + Cl - (aq) + Ag(s) with a (H = 1 = bar p O and = aCl - yCl - b . 2) Weak acid Equilibrium: BH + B + H + with bBH = b + B () = K a a = yBba = / yBH + b yB aH + / aBH + H + Thus, aH + = yBH + K a / yB . I Ionic$ strength (neglect bH+ because bH+ 0) O C ψ 3 = f ψ O - g ψ C + h ψ N N C O C ψ 2 = d ψ O - e ψ N N C O C N ψ 1 = a ψ O + b ψ C + c ψ N C (b) This arrangement only works if the entire peptide link is coplanar. For starters, the O, C, and N atoms in the peptide link must be in the same plane (call it the xy plane) if all three atoms are to contribute unhybridized p orbitals (pz orbitals) to make the three MOs sketched in Figure 10.15(a). And if the peptide C atoms must also lie in the xy plane. Hence the peptide C atoms bound to the peptide C and N atoms must also lie in the xy plane. That is, the entire peptide linkage plus the ends of the carbon chains that they connect. 28 O O - + C C C N N H H (c) The energy order of the orbitals and their occupancy are shown in Figure 10.15(a). There are four electrons to be distributed. If we look at the neutral representation of the peptide link (on the left side of the resonance structures shown here), the two electrons represented by the C=O π bond are obviously part of the σ system. Turning now to the Lewis octet of electrons around the N atom, we must assign two electrons to each of the σ bonds involving N; clearly they cannot be part of the π system. That leaves the lone pair on N, which must occupy the other orbital that N contributes to the molecule, namely the pz orbital with respect to C and O, and ψ6 is antibonding with respect to C and O, and ψ6 is antibonding with respect to C and O. to C and O. ψ 5 is non-bonding orbital. C Figure I10.2(b) Energy (a,..,g > 0) O C ψ 6 = f ψ O - g ψ C N C O C ψ 5 = e ψ N N C O C N ψ 4 = a ψ O + b ψ C C (e) This system cannot be planar. As before, the end of the chain connected to the peptide C must be in the xy plane. As before, the atoms bound to N must be in a plane perpendicular to the orbital that N contributes to this system, which is itself in the xy plane. Only one of the N atom's σ bonds can be in both the xy plane and a plane perpendicular to the orbital that N contributes to this system. Thus,
the bonding partners of N other than the peptide C are forced out of the xy plane. (f) The bonding MO ψ 4, for ψ 1 is bonding (stabilizing) with respect to all three atoms, while ψ 4 is bonding with respect to all three atoms, while ψ 4 is bonding MO ψ 4, for ψ 1 must have a higher energy than the antibonding MO ψ 6, for ψ 3 is antibonding (destabilizing) with respect to all three atoms pairwise, while ψ 6 is antibonding only with respect to two of them. The non-bonding MOs ψ 2 and ψ 5 must have similar energies, not much different than the parameter α , for there is no significant constructive or destructive interference between adjacent atoms in either one. (g) Because bonding orbital ψ 1 has a lower energy than ψ 4, the planar arrangement has a lower energy than the non-planar one. The total energy of the planar arrangement is Eplanar = 2E1 + 2E2 = Eplanar. The fact that E3 > E6 is immaterial, for neither of those orbitals is occupied. ψ trial = Ne $-\alpha$ r 10.4 2 We must find the expectation value of the hydrogenic hamiltonian: 2 (2 2 e 2) $-\alpha$ r 2 ∇ $-\tau$ Etrial Ne $-\alpha$ r | $- = H = \psi$ trial * H[^] ψ trial d = |N e d τ 4 π e 0 r / 2μ f f The laplacian operator is $\partial 2 2 \partial 1 2 \nabla = + + \Lambda 2 \partial r 2 r \partial r 2 r \partial r 2$. Because $\Lambda 2$ contains derivatives with respect to angles only, we can ignore it in applying the laplacian to our trial function, which is independent of angles. Applying the kinetic energy operator to our trial function yields $(\partial 2 2 \partial) - \alpha r 2 2 \alpha N (\partial 2) - \alpha r 2 2 \alpha N (\partial 2) - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 2 \alpha N (\partial 2) - \alpha r 2 2 \alpha N (\partial 2) - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 2 \alpha N \mu (3 - 2\alpha r 2) e - \alpha r 2 \alpha N \mu (3 - 2\alpha r 2$ Inserting this into the energy expectation yields: $2\ 2\ 2\ 2\ \alpha$ ne 2 Ne $-\alpha$ r | $d\tau 4\pi\epsilon 0$ r / $\mu \int$ To actually evaluate the integrating over the angles yields 4 π . Thus the integral becomes $2 2 \propto 2 (3 \alpha r 2 2 \alpha 2 r 4 e^2 r)$ Etrial = $4\pi N 2 e^{-2\alpha r} - dr 0 4\pi e^{-2\alpha r} - dr 0 4\pi e^{-2\alpha r}$ (2n - 1)! = $1 \times 3 \times 5 \times ... \times (2n - 1) 0 2 n + 1 a n$ (a)/Apply these to the appropriate terms in the integral table in the regral table in the Resource section to find [G.7 and G.8] $\propto 2 n! \times 2n + 1e^{-2\alpha r} - dr 0 4\pi e^{-2\alpha r}$ (2n - 1)! = $1 \times 3 \times 5 \times ... \times (2n - 1) 0 2 n + 1 a n$ (a)/Apply these to the appropriate terms in the integral table in the integral table in the Resource section to find [G.7 and G.8] $\propto 2 n! \times 2n + 1e^{-2\alpha r} + 10 2a \int \int 1/2 (2n - 1)! (\pi)(2n - 1)! (\pi$ to obtain ($3 2\alpha 1$) $e 2 3\pi 1/2 2 2\alpha 2\pi 1/2 \times - \times 3 - \times 2$ Etrial = $4\pi N 2 | 5/2 3/2 4\pi \epsilon 0 2(2\alpha) | \mu 2 (2\alpha) 2 (2\alpha) | \mu 2 (2\alpha) 2 (2\alpha)$ r 2 4π N 2 = or 27/2 α 3/2 π 1/2 27/2 α 3/2 π 1/2 e2 3 2α e2α 1/2 . - - = 2μ π 1/2 | 29/2 α 1/2 μ 16πε 0α | 21/2 π 3/2ε 0 The variation principle says that the minimum energy is obtained by taking the derivative of the trial energy with respect to adjustable parameters, setting it equal to zero, and solving for the parameters: dEtrial 3 2 e2 = -= 1/2 µ e4 µ e4 - µ e4 = 32 π 2 ε 02 2 for 3 ε 02 2 12 π 3 ε 02 2 12 π 3 ε 02 2 12 π 3 ε 02 2 Notice that the above expression indicates that V = -2 Ek in accord with the virial -1 theorem for a potential that goes as r. Also, compare the above result to the actual hydrogenic energy: - µ e4 EH = 32 π 2 ε 02 2 Etrial has 12 π in the denominator where the true energy has 32. Thus, the trial energy is greater than (not as negative as) the true energy, consistent with the variation principle. 10.6 The equations for studying the amplitudes of the 1σ and $2\sigma^*$ dihydrogen ion states are found in eqn. 10B2 and Brief Illustration 10B.1. This approximate method uses a linear combination of atomic 1s orbitals of the hydrogen atoms, which are label A and B. Atom A is placed at the point (x,y,z) = (0,0,0) with atom B at (x,y,z) = (0,0,R). Both LCAOs have cylindrical symmetrical around the internuclear z-axis so we examine amplitudes as they vary with z along a cylinder that is the perpendicular distance r from the z-axis where $r^2 = x^2 + y^2$. Calculations will be setup so that the user can select any desired r/a0 ratio. Identical results are obtained should you wish to assign x and/or y to arbitrary values. A Mathcad Prime 2TM setup and amplitude plots are shown below. Be sure to explore changes in the coefficients of both R and r and explain the observed effects. The antibonding orbital vanishes halfway between the nuclei, so we see antibonding associated with low internuclear electron density. Similarly, the bonding orbital is substantially non-zero between the nuclei (although not as large in value as at each nucleus), so we see bonding associated with high internuclear electron density. 31 32 11 Molecular Symmetry 11A Symmetry Elements Answers to discussion questions 11A.2 Symmetry operation Symmetry, in-fold improper rotation n-fold improper rotation n-fold axis of symmetry, in-fold improper rotation axis, Sn There are three kinds of mirror plane, σv, is parallel to the principal axis while the principal ax horizontal mirror plane, σh , is perpendicular to the principal axis. A mirror plane that bisects the angle between two C2 axes is called a dihedral plane, σd . A vertical mirror plane that bisects bonds is also given the σd designation. 11A.4 A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation Sn. An improper rotation is a rotation followed by a reflection and this combination of operations always converts a right-handed object into a left-handed object and vice-versa; hence an Sn axis guarantees that a molecule cannot exist in chiral forms. When discussing optical activity, it is helpful to remember that: (a) the presence of both a Cn and a of his equivalent to an Sn. (b) i = S2. (c) σ = S1. Thus, a molecule cannot be optically active if it possesses a centre of symmetry or a mirror plane. Solutions to exercises 11A.1(b) CCl4 belongs to the point group Td. It has 4 C3 axes (he same as the C2 axes), and 6 dihedral mirror planes. Figure 11A.2 11A.3(b) Sketch a figure of the object, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the group assignment. (i) Sharpened pencil: (ii) Propellor: E, Co , σ v ; therefore C3 (iii) Square table: E, C4 , 4σ v ; therefore C4v ; Rectangular table: E, C2 , 2σ v ; therefore C2v (iv) Person with left-right symmetry: E, σ ; therefore Cs 2 11A.4(b) Make a sketch of the molecule, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the point group assignment. (i) furan: E, C2, σv , $\sigma v'$; C2v (ii) γ -pyran: E, C2, σv , $\sigma v'$; C2v (iii) 1,2,5-trichlorobenzene:
E, σh ; Cs 11A.3(b) Make a sketch of the molecule, identify symmetry elements, and use the flow diagram in Figure 11A.7 of the text when it simplifies the point group assignment. (i) HF: linear, no i, so Cov (ii) IF7: pentagonal bipyramidal, E, C5, 5C2, S5, oh, ov; D5h (iii) XeO2F2: see-saw, E, C2, ov, ov (i) Fe2(CO)9: E, C3, 2C2, 3C2', S3, oh, ov; D3h (v) Cubane (C8H8): E, 8C3, 6C2, 6C4, i, 6S4, 8S6, 3oh, 6od; Oh (vi) Tetrafluorocubane: E, 8C3, 3C2, 6S4, 6od; Td 11A.4(b) Only molecules belonging to Cs, Cn, and Cnv groups may be polar, so ... (i) CH 3Cl (C3v) polar along the C-Cl bond HW2 (CO)10 (D4h) not polar (ii) SnCl 4 (Td) not polar (ii) 11A.5(b) The parent of the dichloroanthracene isomers is shown to the right. Care must be taken when determining possible isomers because anthracene is a flat molecule that belongs to the point group D2h as discussed in Exercise C1 C9 C8 C2 C7 C3 C6 C4 C10 C5 11A.2(b). It has an inversion centre, mirror planes, and rotational axes that cause superficially distinct visual images to actually be the same the following table. 7:3 Isomers and Point Groups of m,n-Dichloroanthracene m,n 1,2 1,3 1,4 1,5 1,6 1,7 1,8 Point Group Cs Cs C2v 2,9 Cs 2,10 Cs 9,10 D2h 11A.6(b) A molecule cannot be chiral if it has an axis of improper rotation. The point group Td has S 4 axes and mirror planes (= S1), which preclude chirality. The Th group has, in addition, a centre of inversion (= S2). Therefore, molecules belonging to these point groups cannot be chiral and cannot be chiral and cannot be optically active. Solutions to problems 11A.2‡ (a) We work through the flow diagram in the text (Fig. 11A.7) first noting that this complex with freely rotating CF3 groups is not linear, no Cn axes with n > 2. It does have three mutually perpendicular C2 axes and each has a perpendicular mirror plane. Therefore, the point groups each have a CF bond in the plane. (i) If the CF3 groups are staggered, then the Ag-CN axis is an S2 axis The Ag-CF3 axis is also an S2 axis, which means that the Ag atom is at an inversion centre. There is a C2 axes perpendicular to the plane of the molecule and the plane of the molecule and the plane of the Ag bonds is no longer a C2 axis; however, the Ag- CN axis is a C2 axis. There is no of but there are two ov planes (the plane shown and the plane perpendicular to it and through the Ag-CN bond). So the point group is C2v. S2 F F F C NC Ag F F C i CN NC S2 Ag CN C2 C2 C of F F F ov (i) Staggered form, C2h F F C F (ii) Eclipsed form, C2v Figure 11A.4 11B Group theory Answers to discussion questions 11B.2 A representation is reducible when matrices of the set can be transformed and a one-dimensional representation is denoted symbolically by writing $\Gamma(3) = \Gamma(2) + \Gamma(1)$. One-dimensional representations $\Gamma(1)$ are necessarily irreducible. An irreducible representation cannot be transformed into matrices that are a direct sum of representations of smaller dimension. The sums of their diagonal elements (the traces) are the characters of the representation symmetry operations. The set of characters for an irreducible representation is called the symmetry species of that representation is called the symmetry operations. The set of pz orbitals are perpendicular to the molecular plane, we recognize that the set of pz orbitals on each atom of BF3 experience the C3 change (p B , p F1, p F2, p F3) D (C3) = (p B, p F3, p F1, p F2). Consequently, we find by inspection that $(1 \mid 0 \mid 0 \mid 0 \mid 0 \mid 1 \mid 0) \mid 11B.2(b)$ The matrix representations of the operations of the operations of the second in Exercises 11B.1(a) and 11B.1(b). According to the precepts of group theory, the successive application of these operations yields another member of the D3h group to which BF3 belongs and, in fact, by definition the operation C3 σ h should yield the S3 symmetry operation. The matrix representation of S3 can be found by matrix multiplication of the component operation. The matrix representation of S3 can be found by matrix multiplication of the C3 belongs and, in fact, by definition the operation. (0 0 - 1)(-1 0 0)| (0 - 1 0 || = D (S3)| 0 0 - 1 || || 0 - 1 0 0 || = D (S3)| 0 0 - 1 || || 0 - 1 0 0 || 0 - 1 0 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 || 0 - 1 0 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 || 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 0 - 1 0 || = D (S3)| 0 - 1 || = D (S3)|planes belong to the same class if there it a member S of the group such that $\sigma v' = S-1 \sigma v C2''$, an operator for which S-1 = C2''. By comparison of the action of $\sigma v'$ upon the same vector we can determine whether or not the equality of eqn. 11B.1 holds. If it does, σv and $\sigma v'$ mirror belong to the Dichlorobenzene belongs to the D2h point group. Because the largest character is 1 in the column headed E in the D2h character table, we know that the orbitals are nondegenerate of C2 on ohP is to generate the point C2ohP. The same point is generated from P by the inversion i, so C2ohP = iP for all points P. Hence, C2o h = i, and i must be a member of the group affect lz = xpy - ypx when applied to it. The transformation of x, y, and z, and by analogy px, py, and pz components of momentum, are as follows (see Fig. 11B.3). Figure 11B.3 7:7 E (x, y, z) \rightarrow (z, y, z) (z, y, z) \rightarrow (z, y, z) \rightarrow (z, y, z) (z, y, z) (z, y, z) \rightarrow (z, y, z) (z, y, hence we need consider only one operation in each class. Elz = xp y - ypx = lz σ vlz = -xp y + ypx = -lz [(x, y, z) \rightarrow (-12 3 x - 12 y) \times (-12 3 y - 12 3 y) - (-12 3 x - 12 y) \times (-12 3 y - 12 3 y) = 14 (3 xpx + xp y - 3 ypx - 3 $y - ypx = lz + The representatives of E, \sigma v, and C3 are therefore all one-dimensional matrices with characters 1, -1, 1, respectively. It follows that lz is a basis for A2 (see the C3v character table). 11B.6 Using the symbolism defined in the solution for Problem 11B.5, we find: <math>(1 \mid 0 + -C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \setminus 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \mid D (= |0| \mid 0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0| \mid D (= |0| \mid D (= |0| \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0 + + S 4AB) D (C3A) \mid D (= |0 | |0 (0 \mid 0$ matrices, o. 11C Applications of symmetry Answers to discussion questions 11C.2 Molecular orbitals of specified symmetry can be generated from an arbitrary basis or set of atomic orbitals by the application of group theory. The technique involves generating symmetry-adapted linear combinations (SALCs), which serve as building blocks of LCAO molecular orbitals. The method makes use of a projection operator, $P(\Gamma)$, an operator that takes one of the basis orbitals and generates from it an SALC of the symmetry species Γ : P(I) = To perform the projection: ••••1 () (R,R) for $m
= P(I) \circ [11C, 5] h R$ Write each basis orbital at the head of a column and in successive rows show the effect of each operation R on each orbital. Treat each operation individually. Multiply each member of the column with the factors as determined in (2). Divide the sum by the order of the group, h. Text Example 11C.4 illustrates the construction method. We provide a further example by constructing the E symmetry-adapted linear combinations of H1s orbitals for NH3, which belongs to the C3v point group. From the following table with each row showing the effect of the operation shown on the left. sN sA sB sC E sN sA sB sC C3+ sN sB sC c3+ sN sC sA sB ov sN sA sC sB $\sigma v'$ sN sB sA sC $\sigma v'$ sN sC sB sA To generate an E combination, we take the characters for E (2,-1,-1,0,0,0); then multiplication by the column under sC leads to a combination. that is a linear combination of the previous two so it gives no further information. Notice that the first SALC minus the second gives $\psi \propto sA - sB$ can be chosen as the doubly degenerate e orbitals as shown in text Figure 11B.1. Solutions to exercises 11C.1(b) The px orbital spans E' of the D3h point group while z and pz span A2". Following the Section 11C.1(a) procedure for deducing the symmetry species spanned by the product f1f2 and hence to see whether it does indeed span A1, we write a table of the characters of each function and multiply the rows. 7:9 D3h E of 2C3 2S3 3C2' 3ov px z pz pxzpz 2 1 1 2 2 -1 -1 2 -1 1 1 -1 -1 -1 -1 1 -1 0 -1 -1 0 0 1 1 0 The characters of the product pxzpz are those of E' alone, so the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integrand does not span A1. It follows that the integral must be zero. $A1g \rightarrow E2u$ transition. By inspection of the direct product to be: E2u × E1u × A1g = B1g + B2g + E1g. Since it does not span A1, the x and y components of the transition integral must be zero. Consequently, the z component of the transition integral must also equal zero and we conclude that the transition integrand and multiply. Here is the table for the x and y components of the dipole moment: A1 correspond to the functions of the transition integrand and multiply. E2u (x, y) Integrand E 2C6 2C3 C2 3C2 3C=(4) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) + 3(0) + 2(-1) + 2(1) + (-4) + 3(0) + 3(0) = 0 Since the species A1g is absent, the transition is forbidden for x- or y-polarized light. A similar analysis leads to the conclusion that A1g is absent, the transition is forbidden for x- or y-polarized light. A similar analysis leads to the conclusion that A1g is absent from the product A1gE2uz; therefore the transition is forbidden. 11C.3(b) The classes of operations for D2 are: E, C2(x), C2(y), and C2(z). How does the function xyz behave under each kind of operation? E leaves it unchanged. C2(y) and C2(z) have similar effects, leaving one axis unchanged and taking the other two into their negatives. These observations are summarized. as follows. xyz E 1 C2(x) 1 C2(y) 1 C2 the view of simple molecular orbital theory. With three O atoms providing valence pz orbitals (perpendicular to the molecular plane) in the combination. Furthermore, only the valence pz orbital of N may possibly have a nonzero overlap with this O combination. Furthermore, only the pz, the dxz and the dyz orbitals of S may possibly have nonzero overlap in this π system. To see this, look for nonzero overlap between pz(O) and px(N) orbitals in Fig. 11C.1(a). (The orbital has a positive lobes (constructive interference) is exactly cancelled by the overlap of a negative lobe with a positive lobe (destructive interference) to give a net zero overlap shown in Fig. 11C.1(b). The pz/dxz overlap shown in Fig. 11C.1(c) yields a net nonzero overlap because both the overlap of positive lobes and the overlap of negative lobes results in constructive interference. 10 (b)p/d overlap (c) pz/dxz overlap Figure 11C.1 Now, consider the non-normalized combination of oxygen pz orbitals to be: pz,comb × pz (N) $d\tau = \int \{a \times pz\}$ $(A) + b \times p z (B) + c \times p z (R) d\tau = a \times \int p z (A) \times p z (N) d\tau = \int p z (B) \times p z (N) d\tau = \int p z (A) \times p z (N) d\tau = \int p$ + c = 0 (as in this exercise, which has a + b + c = 2 - 1 - 1 = 0) { $\neq 0$ if a + b + c $\neq 2$ Thus, the overlap integral is generally nonzero but it is zero for the very specific combination 2pz(A) - pz(B) - pz(C) because the AO's are in the specific ratio +2:-1:-1. We conclude that no orbital of the central N atom can have a nonzero overlap with the combination 2pz(A) - pz(B) - pz(C) of the three O atoms but that the dxz and dyz orbitals of S may possibly have nonzero overlap in this π system. We now turn to the application of group theory and the use of symmetry-adapted linear combinations (SALCs) to gain a understanding of origin and symmetry species of the 2pz(A) - pz(B) - pz(C) combination. The symmetry species spanned by the oxygen (pz(A),pz(B),pz(C)) basis is easily found with use of these quick rules for determining the character of the basis set under each symmetry operation of the group D3h: Count zero each time a basis function is changed by the operation but count 1 each time a basis function is left unchanged by the operation, because only these functions give a nonzero entry on the diagonal of the matrix representative. In some cases there is a sign change, $(...-f ...) \leftarrow (... f ...)$; then -1 occurs on the diagonal of the matrix representative. In some cases there is a sign change, $(...-f ...) \leftarrow (... f ...)$; then -1 occurs on the diagonal of the matrix representative. used to evaluate the effect of the operations on the oxygen (pz(A), pz(B), pz(C)) basis. B A N C Figure 11C.2 Here is a tabulated summary of the characters: D3h (pz(A), pz(B), pz(C)) basis spans A "2 + E" because the sum of the A "2 and E " characters yields those of the above table. Further inspection of the D3h character table reveals that z belongs to A "2 and byz orbitals of the central atom may possibly have nonzero overlap with symmetryadapted basis formed from (pz(A), pz(B), pz(C)). We continue by finding the second of text Section 11C.2(b). In the process we find why the specific combination 2pz(A) - pz(C) has been introduced in this exercise. We use the D3 subgroup for convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience
and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on members of the convenience and the following table summarizes the effect of point group operations on the convenience and the following table summarizes the effect of point group operations on the convenience and the following table summarizes the effect of point group operations of the convenience and the following table summarizes the effect of point group operations of the convenience and the following table summarizes the effect of point group operations of the convenience and the following table summarizes table summarizes the effect of point group operations of table summarizes table sum $(p_z(A), p_z(B), p_z(C))$ basis. D3, h = 6 E C3+ pz(A) pz(C) pz(B) pz(A) pz(C) pz(B) pz(A) pz(C) pz(B) -pz(A) -pz(C) -pz(B) -pz(A) -pz(C) -pz(B) -pz(A) -pz(C) -pz(B) -pz(A) -p and divide by 6. This gives the totally symmetric combination. pz, comb 1 = $\frac{1}{3} \times (pz(A) + pz(B) + pz(C)) A''_2$: To generate the E combinations, sum terms for each, and divide each by 6. This gives three SALCs. pz, comb 2 = $\frac{1}{6} \times (2pz(A) - pz(B) - pz(C)) B''_2$: pz, comb 3 = $1/6 \times (2pz(B) - pz(A) - pz(C))$ pz,comb 4 = $1/6 \times (2pz(C) - pz(B) - pz(A))$ pz,comb 4 is a linear combination of the previous two, pz,comb 4 = -(pz,comb 2 + pz,comb 3), so we discard it and are left with the double degenerate, orthogonal pair pz,comb 2 and pz,comb 3. In the process we have shown that the combination of the exercise, pz, comb 2, belongs to the E " symmetry species of D3h. Finally, inspection of the D3h character table tells us that pz(N) belongs to the A "2 symmetry A" = E'. The integrand does not span the totally symmetric species A1' so the overlap integral is the symmetry A "2 × E" = E'. necessarily zero. 11C.4(b) The product Γ f × Γ (μ) × Γ i must contain A1 (Example 11C.5 of text). Then, since Γ i = B1 and Γ (μ) = Γ (y) = B2 of the C2v character table, we can draw up the following table of characters. E C2 $\sigma v \sigma' v B2 B1 B1 \times B2 111 - 1 - 11 Hence$, the upper state is A 2, because A2 × A2 = A1. 11C.5(b) D2, h = 4 A1 B1 B2 E 11 $-1 \times = 0$ } {1(1 × 6) + 1(-1 × (-2)) + 1(-1 × 0) + 1(1 × = 1 4 2 4 2 Thus, this set of basis functions spans A1 + B1 + 2B2 + 2B3 . 11C.6(b) (i) Anthracene belongs to the D2h point group. The components of μ span B3u(x), B2u(y), and B1u(z). The totally symmetric ground state is Ag. Since Ag × $\Gamma = \Gamma$ in this group, the accessible upper terms are B3u (x-polarized), B2u (y-polarized), and B1u (z-polarized). (ii) Coronene, like benzene, belongs to the D6h group. The integrand of the transitions from the ground state is A1gqf, where q is x, y, or z and f is the symmetry species. That integrand of the transitions from the ground state is A1gqf. ground state is already totally symmetry. Such combinations include zA2u, xE1u, and yE1u. Therefore, we conclude that transitions are allowed to states with A 2u or E1u symmetry. 11C.8(b) The Cs character table indicates that x and y are invariant under the oh symmetry operation while the character of z is -1 under oh. Thus, the z-axis is perpendicular to the oh plane, the x and y axes are in the plane. The character table also indicates that x2 belongs to the A' irrep so we surmise that $x \times x^2 = x^3$ also belongs to A' (because A'×A' = A') and that any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any polynomial in x must belong to the totally symmetric A' irrep. Thus, the integral of any z×(3z2-1). Being perpendicular to the σh plane, the z dimension can exhibit a symmetrical integration interval from one side of the plane. The Cs character table indicates that z belongs to A'' while z2 belongs to the totally symmetric A' irrep. Thus, the function z×(3z2-1). belongs to A'×A'' = A'' and, since it does not span the totally symmetric irrep, integration of the function over a symmetric interval around z = 0 is necessarily zero: I f1 z f 2 z dz 2 3 z 2 1 dz 0 a a a Solutions to problems 11C.2 (a) In C3v symmetry the H1s orbitals span the same irreducible representations as in NH3, which is A1 + 7:13 A1 + E There is an additional A1 orbital because a fourth H atom lies on the C3 axis. In C3v, the d orbitals span A1 + E + E [see the final column of the C3v character table]. Therefore, all five d orbitals may contribute to the bonding. (b) In C2v symmetry the H1s orbitals span the same irreducible representations as in H2O, but one "H2O" fragment is rotated by 90° with respect to the other. Therefore, whereas in H2O the H1s orbitals span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 + A1 + B1 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 + A1 + B1 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in the distorted CH4 molecule they span A1 + B2 [H1 + H2, H1 - H2], in t Note: The method used to solve Problem 11C.1 also works nicely. 11C.4‡ (a) For a photon to induce a spectroscopic transition moment is the integral y *f μψ i dτ , where the dipole moment operator has components proportional to the Cartesian coordinates. The integral vanishes unless the integrand, or at least some part of it, belongs to the totally symmetric representation of the molecule's point group. We can answer the first part of the integrand under inversion. Each component of u has u character, but each state has g character; the integrand is g × g × u = u, so the integral vanishes and the transition is not allowed. (b) However, if a vibration breaks the inversion symmetry, a look at the I character of the integrand, we multiply together the character so f its factors. For the transition to T1: E 12C52 12C5 20C3 15C2 A1 μ (T1) 1 3 1 2 1 (1 + 5) 1 2 1 (1 - 5) 1 0 1 -1 T1 3 1 2 (1 + 5) 1 2 (1 - 5) 0 -1 Integrand 9 1 2 (3 + 5) 1 2 (3 - 5) 0 1 The decomposition of the irreducible representations is difficult to do by
inspection, but when accomplished it is seen to contain A1. Therefore the transition to T1 would become allowed. It is easier to use the eqn. 11C.2 to determine the coefficient of A1 in the integrand: 1 (A1) n (A1) = h $\Sigma \chi$ (R) χ (R) R = {9 + 12[12(3 + 5)] + 12[12(3 + 5)] + 12[12(3 - 5)] + 20(0) + 15(1)} = / 601 So the integrand contains A1, and the transition to T1 would become allowed. For the transition to G: E A1 μ (T1) G Integrand 1 3 4 12 12C52 12C5 1 2 1 (2 - 5)] + 20(0) + 15(1) + 5) - 1 - (1 + 5) 1 2 1 2 1 (1 - 5) - 1 - (1 - 5) 1 2 20C3 15C2 1 0 1 - 1 1 0 0 0 Eqn. 11C.2, the little orthogonality theorem, gives the coefficient of A1 in the integrand as 14 n (A1) = 1 χ () (R) χ (R) Σ h A1 R = {12 + 12[-12 (1 + 5)] + 20(0) + 15(0)} / 60 = 0 So the integrand does not contain A1, and the transition to G would still be forbidden. 11C.6 Can the Eu excited state be reached by a dipole transition from the A1q ground state? Only if the representation of the products we must consider are Eu×A2u×A1g and Eu×Eu×A1g. For z-polarized transitions, the relevant characters are: Eu A2u A1g EuA2uA1g E 2C4 C2 2C2' 2C2'' i 2S4 oh 2ov 2od 2 1 1 2 0 1 1 0 0 -1 1 0 2 -1 1 2 0 -1 1 0 0 -1 1 0 2 -1 1 2 0 -1 1 0 0 -1 1 0 0 -1 1 0 2 -1 1 -2 0 1 1 0 0 -1 1 0 0 -1 1 0 2 -1 1 2 0 -1 1 0 0 -1 0 0 -1 0 0 -1 0 the characters of A1g, sum those products, and divide the sum by the order h of the group; since the characters of A1g are all 1, we can simply sum the charact of nuclides are listed in Table 0.2 of the Resource section. 12A General features of molecular spectroscopy Answers to discussion questions are moving towards or away from the detecting device. Molecules have a wide range of speeds in all directions in a gas and the temperature of the experiment; hence the line broadens as the temperature is increased because the molecules acquire a wider and higher range of speeds. Doppler broadening. The Doppler broadening is significant in gas-phase samples, but lifetime broadening occurs in all states of matter. This kind of broadening is a quantum mechanical effect related to the uncertainty principle in the form $\delta E \approx \hbar/\tau$ (eqn 12A.19) and is due to the finite, the energy of the states is smeared out and hence the transitions. When τ is finite, the energy of the states is smeared out and hence the transition frequency is broadened. The rates of spontaneous emission cannot be changed; hence it is a natural limit to the breadth of a spectral line. Pressure broadening or collisional broadening or collisional broadening. Collisional broadening or collisional broadening or collisional broadening. state. Lowering the pressure can reduce this rate. For a gas phase collisional lifetime of τ col, the mean time between collision frequency, the kinetic model of gases implies that z is proportional to the pressure and that linewidths are proportional to the gas pressure. Thus, gas phase linewidths can be reduced by decreasing the pressure has little effect upon liquid density and kinetic energy, we expect pressure to have little effect upon the linewidth of liquid samples. Estimating that a liquid-phase molecule experiences a deactivating collision in the period of a vibration, the collisional linewidth is something like δ Ecol ~ / τ col ~ / (1.0 × 10-21 J or ~53 cm-1/(τ/ps) [12A.19] as a wavenumber. Solutions to exercises 12A.1(b) The ratio of Einstein coefficients A/B is (i) 8π ($6.626 \times 10-34$ Js) × (500×106 s -1) A $8\pi hv 3 [12A.9] = = 3 B c 3 (2.998 \times 108 m s - 1)$ (ii) $v = 37.73 \times 10 - 32 J m - 3s - 34 c A 8\pi h 8\pi (6.626 \times 10 J s)$ so $= = 3.9 \times 10 - 28 J m - 3 s 3 - 2 B \lambda \lambda 3 (3.0 \times 10 m) 12:1 12A.2(b) log I I = -log 0 = -\varepsilon [J]L [12 A.13 and 12A.14] I0 I = (-227 dm 3 mol - 1 cm - 1) \times (2.52 \times 10 - 3 mol dm - 3) \times (0.200 cm) = -0.114 I 0.114 0.769$, and the reduction in intensity is 23.1 per cent. Hence, = $10 - = I0 II = -log 0 = -\epsilon [J]L [12 A.13 and 12A.14] I0 I \epsilon = -1 log I [J]L I0 12A.3(b) log - log 0.615 = 1.2 \times 103 dm3 mol - 1 cm - 1 (7.17 \times 10 - 4 mol dm - 3) \times (0.25 cm) = 1.2 \times 106 cm3 mol - 1 cm - 1 [1dm = 10 cm] = = 1.2 \times 106 cm 2 mol - 1 12A.4(b) log T = -A = -\epsilon [J]L [12 A.12-14] 1 - log (1 - 1) [12 A.12-14] 1 - log (1 - 1) [12 A.12-14] 1 - log (1 - 1) [12 A.13 and 12A.14] I0 I \epsilon = -1 log I [J]L [12 A.13 and 12A.14] I0 I \epsilon = -1 log I [J]L [12 A.13 and 12A.14] I0 I \epsilon = -1 log I [J]L [12 A.12-14] 1 - log (1 - 1) [12 A.13 and 12A.14] I0 I \epsilon = -1 log I [J]L [12 A.13 and 12A.1$ 0.483 [J] = log T = 3 - ϵ
L (423 dm mol-1 cm -1) × (0.650 cm) = 1.04 mmol dm -3 1 I 12A.5(b) ϵ = log [12 A.13 and 12A.14] with L = 0.20 cm - [J]L IO We use this formula to draw up the following table. [dye] / mol dm-3 I / IO ϵ / (dm-3 mol-1 cm-1) 0.0010 0.68 670 0.0050 0.18 596 0.0100 0.037 573 0.0500 1.03 × 10-7 559 The table indicates that as the dye concentration increases the molar absorption coefficient does not remain constant. Rather, it significantly decreases. The reason for this is not entirely evident but we may hypothesize that the dye molecules become associated at the higher concentrations and that the associated at the higher concentration increases the molecules become associated at the higher concentration increases at the unassociated dye molecule. Should this hypothesis be correct, the molar absorption coefficient at the low concentration, 670 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.13, 12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.12-14] I0 = 10(12A.14) = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.14] = log (0.29) = 58 dm3 mol-1 cm -1 -3 []]L I0 (0.0185 mol dm) × (0.500 cm) T = I = 10-[]]E L [12A.14] = log (0.29) = 10(12A.14) = $-0.0185 \text{ mol dm } 12A.7(b) \log -3) \times (58 \text{ dm } 3 \text{ mol} - 1 \text{ cm } -1) \times (0.250 \text{ cm}) = 10 - 0.27 = 0.54, \text{ or } 54 \text{ per cent I } 1 \text{ I } [12A.13 \text{ and } 12A.14] = -\varepsilon [J]L \text{ so } L [J] = - \log I0 \text{ I0} \varepsilon (i) 1 1 L [J] = - \times \log = 0.010 \text{ mol dm } -3 \text{ cm } 3 - 1 - 1 2 30 \text{ dm mol cm } (ii) 1 - \times \log (0.10) = L [J] = 0.033 \text{ mol dm } -3 \text{ cm } 3 - 1 - 1 30 \text{ dm mol cm } 12:2 12A.8(b) \text{ A parabolic lineshape}$ shown in Fig. 12.1 of the text, is symmetrical, extending an equal distance on either side of its peak. It is well known, and proven in the note below, that the area under a parabola equals 2/3 × base width × height. Let vi and vf be the initial and final wavenumbers of the absorption band. Then, the base of the band has the width $\Delta v = vf - vi$ and the integrated absorption coefficient is the area given by $A = \nu f [12A.15] = \int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v) dv = 23 \times (vf - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below.) $\int \varepsilon (v - vi) \times \varepsilon max$ (See note below $4 \text{ cm} - 1 - 3.64 \times 104 \text{ cm} - 1 \times 3.35 \times 104 \text{ dm} 3 \text{ mol} - 1 \text{ cm} - 1 \text{ A} =)$ () 3 (= 6.19 × 108 dm3 mol - 1 cm - 2 Note: The formula for the area of a parabola (see Fig. 12.1 of the text): { ε (v - vmax) 2 } The symmetry of the parabola means that vmax = vi + 1 2 Δv = vf - 1 2 Δv . Because $\varepsilon = (vi) \varepsilon = (vf) 0$, the constant κ is easily determined by examination of the parabola equation at either $\varepsilon (vi)$ or $\varepsilon (vf) \cdot \{ \} \{ \} 0 = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi -
vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax) = \varepsilon \max 1 - \kappa (vi - vmax$ $| dv = \varepsilon \max | v - vv() \max 2 | vi | \Delta v | 3\Delta v | v = vi 4 4 | 3|3 | = \varepsilon \max | vf - v - vmax) | 2 (f 2 (i 3\Delta v 3\Delta v | | | | | 3|3 | | 4 | v - (vf - 1 2 \Delta v)) | | = \varepsilon \max | vf - 2 (f 2 (i 3\Delta v 3\Delta v | | | | | | | \Delta v | | \Delta v | | \Delta v | | + | | = 6 | | 6 | | | 2 3 \times \Delta v \times \varepsilon \max 12A.9(b) The integrated$ absorption coefficient is the area under an absorption peak $A = \int \varepsilon (v) dv [12A.15]$ band We are told that ε is a Gaussian function, i.e. a function of the peak. The integrated absorption coefficient, then, $\varepsilon = \varepsilon \max \exp |$ where $x = v - v \max is \infty (-x^2) = \varepsilon \exp \int -\infty \max i | dx \varepsilon |$ max a π We must relate a to the half-width at half-height, x1/2 . = A (-x12/2) - x12/2 1 1 = = $\epsilon \epsilon \exp so \ln and a$ | max 2 max 2 2 a 2 (a) So, A = $\epsilon \max x1/2$ (ln $\pi 2$) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -1) × (4233 cm -1) × (12.3 (ln $\pi 2$) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -1) × (4233 cm -1) × (4233 cm -1) × (12.3 (ln $\pi 2) + 1/2 \ln 2) = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -1) × (4233 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) 1/2 x1/2 ln 2 = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -1) × (12.3 (ln \pi 2) + 1/2 ln 2) = (1.54 × 104 dm3 mol-1 cm -2) (1 + s/c) (1$ $\int ||1 + s/c| v [12A.16a] 1/2 \text{ or } \lambda \text{ approach} = | \text{ Solve for s. } (\lambda/\lambda s = (\lambda/\lambda \text{ approach approach}) 2 - 1 2 + 1 \lambda c = 2.9979 \times 108 \text{ m s} - 1 = 1.0793 \times 109 \text{ km h} - 1 \text{ where } (680/530) 2 + 1 || For this very large Doppler-shift the traffic light must be approached at 24.4% the speed of light in a vacuum. 12A.11(b) \delta E$ $\approx h/\tau$ so, since E = hv, $\delta v = (2\pi\tau)$. Solving for $\tau: -1()(i) \tau = (2\pi\delta v) = 2\pi (200 \times 106 \text{ s} - 1)(i) \tau = (2\pi\delta v) = 2\pi (2.9979 \times 1010 \text{ cm s} - 1) \times (2.45 \text{ cm} - 1) - 1 - 1 - 1 = 0.796 \text{ ns}(hv, \delta v 12A.12(b) \delta E \approx h/\tau \text{ so, since } E = 2\pi\tau)(= -1) - 1 = 2.17 \text{ ps deactivation rate}[i.e., \tau 1 / deactivation rate] = 2\pi 1.0 \times 109 \text{ s} - 1 = 159 \text{ MHz} 2\pi 1.0$ \times 109 s -1 δv = 16 MHz (ii) = 2 π × 10 δv = (i) Solutions to problems 12A.2 Solutions that have identical transmittance must have identical values of the absorbance [12A.13] and identical values of the absorbance [12A.14]. Consequently, [1] cell 1 / Lcell 2 = 25 μ g dm -3 × (1.55 cm) / (1.18 cm) = 33 μ g dm -3 12A.4 The absorbance's A1 and A2 at wavelengths $\lambda 1$ and $\lambda 2$ are the sum of the individual absorbance's in the mixture of A and B. = A1 ϵ A1 L[A] + ϵ B1 L[B] (i) = A2 ϵ A2 L[A] + ϵ B1 L[B] (ii) ϵ A1 L Substitution of (iii) into (ii) and solving for [B] gives (A - ϵ L[B] A2 ϵ A2 L A = ϵ E ϵ A1 ϵ B1 L[B] (ii) = A2 ϵ A2 L[A] + ϵ B1 L[B] (ii) ϵ A1 L Substitution of (iii) into (iii) and solving for [B] gives (A - ϵ L[B] A2 ϵ A2 L A = ϵ E ϵ L[B] $[B] + -A1 2 A2 1 A2 B1 [B] = \varepsilon A1 A2 - \varepsilon A2 \varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1 \varepsilon B2 - \varepsilon A2\varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L (iv) Substitution of (iv) into (iii) and simplifying gives 12:4 | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$ | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$) L | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon B1$ | $\varepsilon A1\varepsilon B2 - \varepsilon A2\varepsilon$ A2 ϵ B1) ϵ B2 A1 - ϵ B1 A2 (ϵ A1 ϵ B2 - ϵ A2 ϵ B1) L (v) Equations (iv) and (v) are the desired results. 12A.6 \ddagger The integrated absorption coefficient is A = $\int \epsilon (v) dv [12 A.15] band$ If we can express ϵ as an analytical function of v, we can express ϵ as an analytical function of v, we can express ϵ as an analytical function of v. which means that a plot of $\ln \varepsilon$ versus v ought to be a ε m v + b, then straight line. So, if $\ln = \varepsilon = \exp(m v) = \exp(m v)$ and A (e b / m) {exp(m vi)} We draw up the following table, find the best-fit line, and make the plot of Fig. 12A.1. The linear regression fit yields the values of m and b for the computation of the integrated absorption coefficient. /nm 292.0 296.3 300.8 305.4 310.1 315.0 320.0 ϵ /(dm3 mol-1 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.28 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.88 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 3.54 2.92 2.92 1.61 0.912 Figure 12A.1 ‡ These problems were supplied by Charles Trapp and Carmen Giunta. 12:5 So A (1.26 × 10-3 cm -1) 4.69 4.13 0.912 Figure 12A.1 ‡ These problems were s $(1.26 \times 10-3 \text{ cm})$ $3-1-1 \text{ e} -38.383 - \exp \exp | | | | | dm \text{ mol cm} -7 1.26 \times 10-3 \text{ cm} | 20 \times 10-7 \text{ cm} | 320 \times 10 \text{ cm} | 32$ and solving for $v - \mu$
gives ϵ) ($v - \mu = \pm | 2 \ln \max | \sigma \epsilon | 1/2$ The width of the distribution at half-height, $\Delta v1/2$, equals $2v - \mu$ evaluated at $\epsilon = \epsilon \max/2$. Thus, 2)1/2 σ or $\sigma = \Delta v1/2$ 2(2 ln = $\Delta v1/2$ 2(2 ln = $-\frac{1}{2}x = \sigma \sigma \infty$ Then = A ε dv [40.10] $\int = 1(\pi) | \varepsilon \max \Delta v 1/2 2 \ln 2 - \infty \infty \varepsilon \max = \sigma \int e^{-\frac{1}{2}x} dx 2 - \infty 1/2$ (2π) $\varepsilon \max \Delta v 1/2 2 \ln 2 - \infty \infty \varepsilon \max = \sigma \int e^{-\frac{1}{2}x} dx 2 - \infty 1/2$ (2π) $\varepsilon \max \Delta v 1/2 2 \ln 2 - \infty \infty \varepsilon \max = \sigma \int e^{-\frac{1}{2}x} dx 2 - \infty 1/2$ (2π) $\varepsilon \max \Delta v 1/2 2 \ln 2 - \infty \infty \varepsilon \max = \sigma \int e^{-\frac{1}{2}x} dx 2 - \infty 1/2$ have this symmetry. It appears to be a skewed slightly toward the higher wavenumbers. Never the less, we estimate A by assuming that it can be approximated as a single Gaussian characterized by $\epsilon \max \Delta = v1/2 \ 1.064467 \ \epsilon \max \Delta = v1/2 \ 1.064467 \ 1.0647 \ 1.$ 5.4×103 cm -1) = 5.7×104 dm³ mol-1 cm -2 Let us now suppose that the slightly non-Gaussian shape exhibited by text Fig. 12.2 results from two separate absorption coefficient that is the sum of two independent Gaussians each characterized by an amplitude A, a mean value μ, and a standard deviation σ. That's a total of 6 parameters to be adjusted to fit the data of the figure. We label the 3 parameters to be adjusted to fit the data of the figure. labeled with a '2'. A lot of (v, c) data pairs are needed to determine precise values of the parameters so we expanded text Fig. 12.2 and used Photoshop to read a total of 20 data pairs, several of which are displayed in the following Mathcad Prime 2 worksheet. parameters to calculate the difference cobs - Gsum at each of the 20 vobs, the difference is squared and summed over all data pairs, which the worksheet calls the 'sum of the squared errors' SSE. The idea is to systematically adjust the 6 parameters so as to minimize SSE. Mathcad performs the minimization process with the 'minerr()' function within a solve block. The symbol 'v' is used to represent wavenumber within the worksheet. 12:7 The plot shows that the sum of two Gaussians with adjusted parameters are listed just above the plot. The following worksheet section uses the fitted function to calculate the integrated absorption coefficient with eqn 12A.15. The earlier, coarse estimate is seen to be rather close to the more precise calculation. 12A.8‡ (a) The integrated absorption coefficient is (specializing to a triangular lineshape) = ϵ dv $\frac{1}{2} \epsilon$ max Δv A \int = band = $\frac{1}{2}$ (150 dm3 mol-1 cm -1) × (34 483 - 31250) cm -1 = 2.42 × 105 dm3 mol-1 cm -2 (b) The concentration of gas under these conditions is n p 2.4 Torr [CH 3 I]total = = = $1.03 \times 10-4$ mol dm -3 V RT (62.364 Torr dm3 mol-1 K -1) × (373K) Over 99% of these gas molecules are monomers, so we take this concentration to be that of CH3I (If 1 of every 100 of the original monomers turned to dimers, each produces 0.5 dimers; remaining monomers represent 99 of 99.5 molecules.) Beer's law states $A = \epsilon$ [CH 3 I]L = (150 dm3 mol - 1 cm - 1) × (1.03 × 10 - 4 mol dm - 3) × (12.0 cm) = 0.185. (c) The concentration of gas under these conditions is 12:8 n p 100 Torr [CH 3 I]total = = = = 4.30 × 10 - 3 mol dm - 3 V RT (62.364 Torr dm3 mol - 1 K - 1) × (373K) Because 18% of these CH3I units are in dimers (forming 9% as many molecules as were originally present as monomers), the monomer concentration is only 82/91 of this value or $3.87 \times 10-3$ mol dm -3) × (12=.0 cm) 3 I]L 6.97 If this absorbance were measured, the molar absorption coefficient inferred from it without consideration of the dimerization would be $\varepsilon = A / ([CH 3 I]L) = 6.97 / ((4.30 \times 10 - 1 \text{ mol dm} - 3) \times (12.0 \text{ cm})) = 135 \text{ dm}^3 \text{ mol} - 1 \text{ cm} - 1 \text{ an apparent drop of } 10\% \text{ compared to the low-pressure value} = vf where f = ||1 + s/c||This can be rearranged to yield: 1 - 1 + 10\% \text{ cm}^2 \text{ mol} + 10\% \text{ cm}^2 \text{ mol} + 12\% \text{ mol}^2 \text{$ f = c. 1 + f = 0.9260, f = c. 1 + f = 0.92602 The broadening of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature of the line is due to local events (collisions) in the distant star. It is temperature dependent and hence yields the surface temperature dependent star. It is temperature dependent and hence yields the surface temperature dependent star. It is temperature dep star. Eqn 12A.17 relates the observed linewidth to temperature: $1/2 \text{ m } 2 \text{ m$ collision deactivates the molecule we may write $1 = \tau \operatorname{col} \approx z 1/2 1/2 \operatorname{kT}(\operatorname{nm}) \operatorname{kT}(\operatorname{nm}) = || | 4\sigma p (\operatorname{kT}/4\sigma p (\operatorname{RT}/For HCl, with MHCl = 36 \operatorname{g} \operatorname{mol}-1) \times || | -18 - 1 - 125 (4) \times (0.30 \times 10 \operatorname{m}) \times (1.013 \times 10 \operatorname{Pa}) / (8.315 \operatorname{JK} \operatorname{mol}) \times (298 \operatorname{K}) = 2.3 \times 10 - 10 \operatorname{s} = \delta \operatorname{E}$ $h = \delta v \tau$ The width of the collision-broadened line is therefore approximately 12:9 1 1 = $\approx 700 \text{ MHz} 2\pi \tau \text{ col}(2\pi) \times (2.3 \times 10 - 10 \text{ s})$ To calculate the Doppler width we need the relation $\delta v \text{ col} = 1/2 \delta v (2 \text{ RT ln } 2) - 1 = | | | | | | 40.12, \text{ M HCl} \approx 36 \text{ g mol}] c | m / c | M / (2 \times (8.315 \text{ J K} - 1 \text{ mol} - 1) \times (298 \text{ K}) \times \ln (2)) | = \times 10^{-10} \text{ s}$ $36 \times 10-3$ kg mol-1 (2.998 × 108 m s-1) || $/-6 = 2.1 \times 10$ v 1/2 2 v HCl exhibits a microwave, rotational transition at $\lambda \approx 0.016$ cm (v $\approx 1.9 \times 1012$ Hz) so the Doppler width is proportional to p [$\delta \nu \propto 1/\tau$ and $\tau \propto 1/p$] and, the pressure must be reduced by a factor of about 4.0/700 = 0.006 before Doppler broadening begins to dominate collision broadening. Hence, the pressure 5 Torr must be reduced to below (0.006) × (760 Torr) = 12A.14 Our study uses the discrete forms of eqns 12A.21 and 12A.22 for the signal and Fourier transformation. These are described in text Example 12A.2. Here's a Mathcad Prime 2 worksheet that is suitable for the study. 12:10 By changing the values of the signal wavenumbers and intensities it is found that the Fourier transform of the interferometer number of p values, N, is set too low (try 20), the Fourier transform becomes a very bad distortion of the original signal and spurious peaks appear. 12B Molecular rotation; label them a, b, and c. The corresponding moments of inertia are Ia, Ib, and Ic. A prolate symmetric rotor has I a \neq I b = I c with I a = I < I b = I c = I \perp . An oblate symmetric rotor has I = I b \neq I c with I a = I b = I \perp < I c = I. An American football and a cigar a are prolate symmetric rotors, a discus and pancake are oblate. Solutions to exercises 12B.1(b) PH3 is a symmetric rotor similar to NH3; we use 12:11 = I $2mH(1 - \cos\theta) R 2$ [Table 12B.1] = 2 ×1.0079 mu × 1.66054 × 10-27 kg/mu × (1 - cos 93.5) × (1.42 × 10-10) 2 = 7.161 × 10-47 kg m 2 The corresponding rotational constant is = A 1.05447 × 10-34 J s = 390.9 m - 1 3.909 cm - 1 4 \pi cI 4 \pi × 2.998 × 108 m s - 1 × 7.161 × 10-47 kg m 2 12B.2(b) In order to conform to the symbols used in the first symmetric rotor figure of Table 12B.1, we will use the molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear
axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the internuclear axis, the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the unique AB bond, and I \perp is perpendicular to both I and a molecular formula BA4. I is along the unique AB bond, and I \perp is perpendicular to both I and I mC = mA and = tetra (109.471°). You can demonstrate that $\cos(\theta \text{ tetra}) = -13$ and, using the definition $\rho R = RAB'/R$, = AB/RAB the equations of Table 12B.1 simplify to 8 I / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - $\cos\theta$ tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + m + m I \perp / mA R 2 = 2 (1 - \cos\theta tetra) = 3 4 + does not depend upon either atomic masses or bond lengths. It is a constant 8/3 for all symmetric rotors with tetrahedral angles. However, the I \perp / mA R 2 moment of inertia ratio does have a specific atomic mass dependence for CH4, an important fuel and powerful greenhouse gas. The computational equation is I \perp / mAR2 = 7748 + (15 ρ + 2) ρ /16 and its plot is found in Fig. 12B.1. As ρ increases, the atom on the axis of I moves away from the axis of I \perp , thereby, increasing the moment of inertia around this axis. 5.5 5.0 I \perp for CH 4 4.5 I / mAR 2 4.0 3.5 I all BA 4 molecules 3.0 2.5 1 1.2 1.4 1.6 ρ Figure 12B.1 12:12 1.8 2 12B.3(b)(i) asymmetric, (ii) oblate symmetric, (iii) asymmetric, (iv) linear 12B.4(b) This exercise is analogous to Exercise 12B.4(a), but here our solution will employ a slightly different 16 algebraic technique. Let = R ROC = , R' R = = O, C 12 C. CS, O I = [See the comment in the solution to Exercise 12B.4(a)] 4π B 1.05457 × 10-34 J s = 1.3799 × 10-45 kg m 2 = I (OC32S) = 1.3799 × $8,3101 \times 10 - 19$ mu m 2 (4π) × (6.0815×109 s -1) 1.05457 × 10 -34 J s I (OC34S) = = 1.4145 × 10 -45 kg m 2 = 8.5184 × 10 -19 mu m 2 9 -1 π 4 × 5.9328 × 10 s () () The expression for the moment of inertia given in Table 12B.1 may be rearranged as follows. Im = mA mR 2 + mC mR 2 -1 mA R - mC R') 2 = mA mR 2 + mC mR 2 -1 mA real rearranged as follows. Im = mA mR 2 + mC mR 2 -1 mA mR 2 + mC2 + 2mA mC RR' - mC2 R'2 = mA(mB + mC) R 2 + mC(mA + mB) R'2 + 2mA mC RR' mC mC'(b) Subtracting Im I'm' -= mC mC'[(mA)] 2 (mA) || |(mB + mC) - || (mB + m mC') |R'|| | mC / || mC / || mC / Solving for R2()() Im I'm 'mC' Im - mC I'm 'm C - mC' = [mmA(mB + mC) - mmA'(mB + mC')] mB mA(mC' -mC) C | C] R2 = () = mA m = m = m32S, and = mC' m34S Substituting the masses, with O, mB C, mC m (15.9949 12.0000 31.9721) mu 59.9670 mu m (15.9949 12.0000 33.9679) mu 61.9628 mu R2 (33.9679 mu) (8.31011019 mu m 2) (59.9670 mu) (12.0000 mu) (15.9949 mu) (33.9679 mu 31.9721 mu) (33 expression for R2 involves the difference between two rather large numbers of nearly the same magnitude, the number of significant figures in the answer for R, either equation (a) or (b) above can be solved for R. The result is R 1.5591010 m 155.9 pm RCS 12B.5(b) The centrifugal distortion constant is given by B 4 DJ = 23ν = DJ J \propto B D 3 [12B.17, also see Integrated Activity I12.2] 4×(0.0809 cm -1)2 \propto B 1 2.028×10-8 cm -1 I \propto mBr [Table 12B.1] I (81 Br) m793 (78.9183 mu)3 D 1 Br = = Therefore, D J \propto 3 and 0.9277 J (79 Br) m813 m (80.9163 m)3 D Br Br u We have assumed that the internuclear distance remains constant upon substitution. Solutions to problems 12B.2 Figure 12B.2 Atom A Atom C Atom B Let us assume atom C is the most massive. Then the center of mass, CM, will be located at a distance, D, from atom B. In the notation of Table 12B.1, we must have the relation mA (R + D) + mB D = mC (R' - D), which may be rearranged into D(mA + mB + mC) = mCR' - mAR 12:14 Solving for D, we obtain D = mCR' - mAR, where m = mA + mB + mC. Expanding $mI = \sum mi ri 2 [12B.1]$ gives i I = mAR 2 + mAD 2 + 2 RDmA + mB D 2 + mCR' 2 + mCD 2 - 2 R'DmC = mAR 2 + mCR' 2 + D 2 (mA + mB + mC) + 2 D(mAR - mCR') After substituting the above

formula for D, and using m = mA + mB + mC we obtain 2 (mR' - mAR) 2 mR' - mR' + mCR' + mCR'spectroscopy Answers to discussion questions 12C.2 (1) Rotational Raman spectroscopy. The gross selection rule is that the molecule must be anisotropically polarizable, which is to say that its polarizability, α, depends upon the direction of the electric field relative to the molecule. symmetric rotors are rotationally Raman active. (2) Vibrational Raman spectroscopy. The gross selection rule is that the polarizability of the molecules swell and contract during a vibration, the control of the nuclei over the electrons varies, and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active, In polyatomic molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 12D.5 and demonstrated in Brief Illustration 12D.5. 12C.4 Hydrogen molecules can exist in two forms: the para-form has antiparallel nuclear spins and the orthoform has parallel nuclear spins. Because of these arrangements of the nuclear spins the ortho-form must have rotational wavefunctions restricted to odd J values only as discussed in detail in Section 12C.3. Orthohydrogen cannot exist in the J = 0 state. Hence, the lowest energy level of ortho-hydrogen has J = 1 and therefore a zero-point energy. The conversion between the two forms is very slow. 12:15 Solutions to Exercises 12C.1(b) Polar molecules show a pure rotational absorption spectrum. Therefore, select the polar molecules based on their well-known structures. Alternatively, determine the point groups of the molecules belonging to Cn, Cnv, and Cs may be polar, and in the case of Cn and Cnv, that dipole must lie along the rotation axis. Hence all are polar molecules. Their point group symmetries are (i) H 2 O, C2v, (ii) H 2 O 2, C2, (iii) NH 3, C3v, (iv) N 2 O, Cv All show a pure rotational constant by =hcB [J (J + 1) - (J - 1)J] = 2hcBJ hv = ΔE =hc ΔF where J here refers to the upper state (J = 2). The rotational constant by =hcB [J (J + 1) - (J - 1)J] = 2hcBJ hv = ΔE =hc ΔF where J here refers to the upper state (J = 2). The rotational constant by =hcB [J (J + 1) - (J - 1)J] = 2hcBJ hv = \Delta E constant is related to molecular structure by $B = 4\pi cI 4\pi$ cmeff R 2 where I is moment of inertia, meff is effective mass, and R is the bond length. Putting these expressions together yields = $v 2 = cBJ 2\pi$ meff R 2 where I is moment of inertia, meff is effective mass is -1 = mC - 1 + mO - 1 = meff = So v (12mu) - 1 + (15.9949mu) $(8.78348 \times 10 = 8.78348 \times 1025 \text{ kg} - 1 \text{ kg} - 1) \times (1.0546 \times 10 - 34 \text{ J s}) \times (2) = 22\pi (112.81 \times 10 - 12 \text{ m}) 252.3169 \times 1011 \text{ s} - 1$ When centrifugal distortion is taken into account the frequency decreases as can be seen by considering eqn. 12C.8b. 12C.3(b) The wavenumber of the transition is related to the rotational constant by =hcB [J (J + 1) - 12m] (J + 1) - 12m (112.81 \times 10 - 12m) (252.3169 \times 1011 \text{ s} - 1) \times (252.3169 \times 1011 \text{ s} - 1) (J-1)J = 2hcBJ hcv = ΔE = hc ΔF where J refers to the upper state (J = 1). The rotational constant is related to molecular structure by = B 4π cI where I is moment of inertia. Putting these expressions together yields BJ ν 2 = (1.0546 × 10-34 J s) × (1) J J I so = 2\pi cI 2π c ν 2π (2.998 × 1010 cm s - 1) × (16.93 cm - 1) = I 3.307 × 10-47 kg m 2 The moment of inertia is related to the bond length by $(I)^2 = Im = eff R so R | (m) eff 12 12:16 - 1 - 1 = mH - 1 + mBr = meff (1.0078 mu) + (80.9163 mu) - 1 1.66054 \times 10 - 27 kg mu - 1 {(6.0494 \times 1026 kg - 1 kg - 1) \times (3.307 \times 10 - 47 kg m 2)} 12 26 1.414 \times 10 - 10 m = 141.4 pm = 12C.4(b) The wavenumber of the$ transition is related to the rotational constant by =hcB [J(J + 1) – (J - 1)J] = 2hcBJ hcv = ΔE = hc ΔF where J refers to the upper states differ by 1) differ by = $\Delta v = 2$ B so I = 2π cl 2π c Δv where I is the moment of inertia, meff is the effective mass, and R is the bond length. So $I = (1.0546 \times 10 (2\pi 2.9979 \times 10 \text{ cm s } 10 - 34 - 1 \text{ Js}) = \times 1.033 \text{ cm } - 1)() 5.420 \times 10 - 46 \text{ kg m } 2 \text{ The moment of inertia is related to the bond length by} (I) = I \text{ m} = \text{eff R so } R || \text{ m} || \text{ eff } 12 2 - 1 = \text{mF} - 1 + \text{mCl} - 1 = \text{meff and} = R (18.9984 \text{ mu}) - 1 + (34.9688 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 {(4.89196 \times 1025 \text{ kg} - 1 + \text{mCl} - 1)} = \text{meff and} = R (18.9984 \text{ mu}) - 1 = 4.89196 \times 1025 \text{ kg} - 1 \text{ meff} - 1 \text{ meff}$) × (5.420 × 10-46 kg m 2) 12 = 1.628 × 10-10 m = 162.8 pm 12C.5(b) See eqn 12C.9 and problem 12C.9. The most highly populated rotational level is given by J max $\frac{1}{2}$ (KT) 1 ≈ | -2 0.2328 (J(i) At 25°C = 298.15 K, J max $\frac{1}{2}$ (28.15 K, J max $\frac{1}{2}$ (28.15 K) = 1.628 × 10-10 m = 1.628 × /K $\approx |$ $-2 (0.2328)/2 \approx 36 (373.15 / K) 1 | -2 (0.2328)/2 \approx 36 (373.15 / K) 1 | -2 (0.2328)/(ii)$ At 100°C = 373.15 K, J max $\approx |$ Answers are rounded off to the nearest integer. 12:17 ≈ 40 12C.6(b) A molecule must be anisotropically polarizable to show a rotational Raman spectrum; all molecules except spherical rotors have this property. So (i)CH 2 CI 2, (ii)CH 3 CH 3, and (iv)N 2 O can display rotational Raman spectra; SF6 cannot. 12C.7(b) The wavenumber of a Stokes line in rotational Raman is v Stokes v i 2B(2 J 3) [12C.15] where J is the initial (lower) rotational state. So v Stokes 20623 cm1 2(1.4457 cm1) [2(2) 3] 20603 cm1 , so B 1 (3.5312 cm1) 0.88280 cm1 The separation of lines is 4B 4 12C.8(b) Then we use R 4π meff cB 12 [Exercise 12C.8(a)] with meff 12 m 19 F 12 (18.9984 mu) (1.66051027 kg mu 1) 1.577342 1026 kg 1.05461034 J s R 26 1 1 10 4π (1.57734210 kg) (2.99810 cm s) (0.88280 cm) 12 1.41785 1010 m = 141.78 pm For 12C32S2, all nuclei are spin-0. The symmetry considerations are identical to those of 12C16O2 discussed in the text; only even values of J are permissible. For 13C32S2, the symmetry of the molecule is unchanged, so again only even values of J are permissible. 12C.9(b) Solutions to problems 12C.2 The separations between neighbouring lines are 20.81, 20.60, 20.64, 20.52, 20.34, 20.37, 20.26 mean:20.51cm -1 = B 10.26cm -1 and (1) × (20.51cm -1) $= 2 \ 1.05457 \times 10 - 34 \ Js = = = I \ (4\pi) \times (2.99793 \times 1010 \ cm \ s^{-1}) \times (10.26 \ cm^{-1}) 4\pi \ cB \ 2.728 \times 10 - 47 \ kg \ m^{-2}) = = 129.5 \ pm^{-27} \ (1.6266 \times 10 \ kg^{-27} \ (1.6266 \times 1$ and not by just taking a simple average would result in a more accurate value. Alternatively, the effect of centrifugal distortion could be minimized by plotting them to a smooth curve, and a 1 and I are m, B a 1. Hence, the corresponding lines in extrapolating that curve to J = 0. Since B eff I meff 2 H 35 Cl will lie at a factor 12:18 meff (1 H 35 Cl) 1.6266 = = 0.5144 meff (2 H 35 Cl) 3.1622 to low frequency of 1 H 35 Cl lines. Therefore, we expect lines at 42.23, 52.79, 63.34, 73.90, 84.46, 95.02, and 105.57 cm -1 . 1/2 12C.4 () R = | (4 \pi \mu cB) ((J + 1) [12C.8a, with v = and v = 2cB cv] (63.55) × (79.91) mu = 35.40 mu (63.55) + (79.91) and draw up the following table: J 13 14 15 We use μ (CuBr) \approx v / MHz 84421.34 90449.25 96476.72 / cm -1 B 0.10057 0.10057 0.10057 0.10057 0.10057 ($1.05457 \times 10-34$ Js Hence, R = | -27 ($(4\pi) \times (35.40) \times (1.6605 \times 10 \text{ kg}) \times (2.9979 \times 1010 \text{ cm s} -1) \times (0.10057 \text{ cm} -1)$ | 1/2 = 218 pm 12C.6 The data given is analyzed in the Excel® worksheet below in which a linear regression is performed on the left hand side of the equation provided in the problem. See Fig. 12C.1 below: J (J+1) (J slope $-1.2257 \times 10-5 \text{ cm-1}$ gives The intercept 1.9225287 cm-1 is the value of the rotational constant B. Therefore D = $6.1285 \times 10-6 \text{ cm-1}$. The equilibrium bond length is calculated from -2 D J J 1/2 () $R = | | (4\pi \mu \text{ cB})$. We use $\mu (12 \text{ C16 O}) = (12.0000) \times (15.9949) \text{ mu} = 6.8562 \text{ mu} (12.0000) + (15.9949) = 1.13850 \times 10 - 26 \text{ kg } 1/2$ () $1.05457 \times 10-26 \text{ kg } 1/2$ () $1.05457 \times 10-26 \text{ kg } 1/2$ () $1.05457 \times 10-26 \text{ kg} 1/2$ () $1.0547 \times 10-26 \text{ kg} 1/2$ () $1.0547 \times 10-26 \text{ kg} 1/2$ () $\times 10-34$ Js Hence, R = |-26-1-1|10 (4) (1.13850 10 kg) (2.99793 10 cm s) (1.9225287 cm) $\pi \times \times \times \times \times (1 = 113.09$ pm Comment: these values for the rotational constant are slightly different from the values
for the rotational terms given in the problem we obtain for the frequencies of the allowed transitions the expression ν J + 1, K \leftarrow J, K = F (J + 1, K) – F (J , K = (J + 1) – 4 D (J + 1)3 – 2 D (J + 1) K 2 ν J + 1, K \leftarrow J, K = F) 2B J K To work with the latter expression one must convert the data given in frequency units to wavenumbers. Here we solve the problem in frequency units using the former expression for the transition frequency units to wavenumbers. Here we solve that the identification of the transitions as shown in the table below can be made. transition 1 2 3 4 5 transition frequency, ν /GHz 51.0718 102.1426 102.1408 153.2103 153.2076 12:20 transition frequency expression 2 B - 4 DJ 4 B - 32 DJ 4 B - 32 DJ 4 B - 32 DJ - 4 DJK 6 B - 108DJ 6 B - 108DJ 6 B - 108DJ - 6 DJK Examination of these expressions reveals that the difference in transitions 5 and 2 and also from simultaneous solution of the equations for transitions 1 and 2 and also from transitions 2 and 4. The average value of DJ obtained in this way is DJ = 56 kHz. The value of B obtained from transition 1 is then B = 25.5360 GHz. If desired, these results in frequency units, Hz, can be converted to units of cm s-1. 12C.10 The question of whether to use CN or CH within the interstellar cloud of constellation Ophiuchus for the determination of the temperature of the cosmic background radiation of 2.726 K. Given B rotational constant that is needed for the comparative analysis may be calculated from the 226.9 GHz -1 12 14 spectral line of the CN bond length (117.4 pm), the CN rotational constant is calculated as follows. $0 B = B / c \nu \nu = 2c(J + 1) 4c = 1.892 \text{ cm} - 1$ Blackbody radiation at 2.726 K may be plotted against radiation wavenumber with suitable transformation of the equation for $\rho(\lambda, T)$ in section 7A.2(b) $\rho(\nu) =$ Spectral absorption lines of 8π hcv3 e hcv/kT - 1 12 C14 N and (J + 1) $\nu(J + 1 \leftarrow = J)$ 2B 12 C1H are calculated with eqn 12C.8a. J = 0, 1, 2, 3..... The cosmic background radiation and molecular absorption lines are shown in the graph, Fig. 12C.2. It is evident that only CN spans the background radiation. Figure 12C.2 12:21 12C.12 Rotation of the pseudolinear molecule in Fig. 12.3(a) about the x-axis in the figure. Figure 12C.3(a) The data allow for a determination of RC and RH(D) which may be decomposed into RCC and RCH(D) = I H 4mH RH2 + 4mC RC2 = 147.59 × 10-47 kg m 2 I D = 4mD RD2 + 4mC RC2 = 178.45 × 10-47 kg m 2 I D = 4mD RD2 + 4mC RC2 = 10-47 kg m 2 RH2 = × 4.6169 10-20 m 2 RC2 = RH = 2.149 × 10-10 m (147.59 × 10-47 kg m 2) - (4mH RH2) 4mC = (147.59 × 10-47 kg m 2) - (4) × (1.66054 × 10-27 kg m u - 1) × (4.6169 × 10the relation between RH, RC, RCC, and RCH. Figure 12C.3(b) 12:22 R 1.209 \times 10-10 m RCC = C = 1.396 \times 10-10 m e139.6 pm 0.8660 cos 30 R - RC 0.940 \times 10-10 m e139.6 pm 0.940 \times 1 Spectra and Electronic Structure of Polyatomic Molecules, p 666, which are 139.7 and 108.4 pm respectively. 12D Vibrational ground states are smaller than in the vibrational ground state and continue to get smaller as the vibrational level increases. Any anharmonicity in the vibration causes a slight extension of the bond length in the excited state. This results in an increase in the moment of inertia, and a consequent decrease in the moment of inertia, and a consequent decrease in the moment of inertia. e - a (v + 1), where B 2 v is the rotational constant in level v. e is a constant and B B 12D.4 Isotopic substitution can change the spin of the nuclear spin of the n change rotational spectra. See Section 12C.3 and Brief Illustration 12C.2. Vibrational frequencies are determined by the effective masses, isotopic substitution changes the effective masses of the molecule; hence, in general, the vibrational frequencies are changed and the vibrational spectrum will be (slightly) different. But not all vibrational frequencies are necessarily changed by isotopic substitution. For example, since the mass of 12C, in general we expect that vibrational frequencies
would be slightly different in 13CO2. However, in the symmetric stretch of CO2, the C atom is stationary, and the effective mass of the mode depends only on the O atoms. Consequently we expect that the vibrational frequency is k ω f $2\pi\nu$ m 12 so kf $(2\pi\nu)$ 2 m (2π) 2 (3.0 s1) 2 (3.0 s1) 2 $(2.0103 \text{ kg}) \text{ kf } 0.71 \text{ N} \text{ m1} 12\text{ D.2(b)} \text{ k} \omega \text{ fm} \text{ eff} 12 12 2 \text{ H} 37 \text{ CI}$ The force constant, k, is assumed to be the same for both molecules. The fractional difference is $\omega \omega \omega \text{ k} \text{ fm} \text{ eff} 12 1 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} \text{ eff} 12 \text{ m} 12 12 \text{ m} 12 \text{ m$ 2 1 mH mCl meff ω (m2 m37) 12 12 H Cl H Cl 12 (1.0078 m) (34.9688 m) (2.0140 mu) + (36.9651 mu) u 1 (1.0078 mu) + (34.9688 mu) (2.0140 mu) + (34.9688 mu) (2.0140 mu) + (34.9688 mu) (2.0140 mu) (36.9651 mu) 0.284 Thus the difference is 28.4 per cent 12D.3(b) The fundamental vibrational frequency is k ω f m $2\pi\nu$ 2π c ν eff 12 so kf (2π c ν) 2 meff We need the effective mass meff1 m11 m21 (78.9183 mu)1 (80.9163 mu)1 (0.0250298 mu 1 kf [2 π (2.9981010 cm s1) (323.2 cm1)]2 (1.660541027 kg mu 1) 0.0250298 mu 1 245.9 N m1 12D.4(b) The relation between vibrational frequency and wavenumber is (k ω | = (m 12 12)1 (k) v π v 2π cv so = = ||= 2 = 2 c || meff || π eff (km) -1 1 2 eff 2π c The reduced masses of the hydrogen halides are very similar, but not identical -1 m = mD - 1 + mX - 1 eff We assume that the force constants as calculated in Exercise 12D.4(a) are identical for the deuterium halide and the hydrogen halide. For DF 12:24 (2.0140mu) + (18.9984 mu) = 3.3071 \times 1026 \text{ kg} - 1 1.66054 \times 10 - 27 \text{ kg mu} - 1 - 1 = \text{meff} $\{(3.3071 \times 10 - 1 - 1 \} \text{kg} - 1) \times (967.04 \text{kg} \text{s} - 2) = 3002.3 \text{cm} - 12\pi (2.9979 \times 1010 \text{ cm} \text{s} - 1) = \nu 1/2 26 \text{ For DCl}(2.0140 \text{ mu}) + (34.9688 \text{mu}) = 3.1624 \times 10-27 \text{ kg} \text{ mu} - 1 - 1 \text{ meff} \{(3.1624 \times 10 - 1 - 1 \text{ kg} - 1) \times (515.59 \text{ kg} \text{s} - 2)\} = 2\pi (2.9979 \times 1010 \text{ cm} \text{s} - 1) \nu = 12 26 2143.7 \text{ cm} - 1 \text{ For DBr}(2.0140 \text{ mu}) + (34.9688 \text{ mu}) = 3.1624 \times 10-27 \text{ kg} \text{ mu} - 1 - 1 \text{ meff} \{(3.1624 \times 10 - 27 \text{ kg} \text{ mu} - 1 - 1 \text{ meff} \{(3.1624 \times 10 - 27 \text{ kg} \text{ mu} - 1 - 1 \text{ kg} - 1) \times (515.59 \text{ kg} \text{ s} - 2)\}$ $(80.9163 \text{mu}) - 1 = 3.0646 \times 1026 \text{kg} - 1.66054 \times 10 - 27 \text{kg} \text{mu} - 1 - 1 = \text{meff} \{(3.0646 \times 10 \text{kg} - 1) \times (411.75 \text{kg} \text{s} - 2)\} = 1885.8 \text{cm} - 1.2\pi (2.9979 \times 1010 \text{ cm} \text{s} - 1) \nu = 12.26 \text{ For DI} (2.0140 \text{ mu}) - 1 + (126.9045 \text{mu}) - 1 = 3.0376 \times 1026 \text{kg} - 1.66054 \times 10 - 27 \text{kg} \text{mu} - 1 - 1 = \text{meff} \{(3.0376 \times 10 \text{kg}) \times (314.21 \text{kg} \text{s})\} \{= 26 \nu 12D.5(b) - 1 - 212.6 \text{kg} - 1.26054 \times 10 - 27 \text{kg} \text{mu} - 1 - 1 = \text{meff} (3.0376 \times 10 \text{kg}) \times (314.21 \text{kg} \text{s})\} \{= 26 \nu 12D.5(b) - 1 - 212.6 \text{kg} - 1.26054 \times 10 - 27 \text{kg} \text{mu} - 1 - 1 = \text{meff} (3.0376 \times 10 \text{kg}) \times (314.21 \text{kg} \text{s})\}$ $2\pi(2.9979 \times 1010 \text{ cm s} - 1) 1640.1 \text{ cm s} - 1) 1640.1 \text{ cm s} - 1) \times (321 \text{ cm } - 1) \times (321 \text{ c$ 2.998×1010 cm s -1) × (321 cm -1) × ($= 2\nu - 6\nu x = 4631.20 \text{ cm} - 1 \text{ [12D.15]} \Delta G \text{ e Multiply the first equation by 3, then subtract the second. } \nu = (3) \times (2329.91 \text{ cm} - 1) - (4631.20 \text{ cm} - 1) = 2358.53 \text{ cm} - 1) + (2358.53 \text{ cm} - 1) + (2358.53$ 14.31 cm -1 (v = 3 \leftarrow 0) = 3 ν - 12vx = (3) × (2358.53 cm -1) - (12) × (14.31 cm -1) \Delta G e = 6903.87 cm -1 Very close to the given experimental value. 12D.7(b) v + 1 2 = v + 1 2 = (v + 1) - G (v) \Delta G \nu - 2(v + 1) xe ν [12D.14] where ΔG G Therefore, since v + 1 2 = ΔG (1 - 2 xe) ν - 2vxe ν a plot of $\Delta G \nu$ + 1 2 against v should give a straight line which gives (1 - 2 xe)v from the intercept at v = 0 and -2xev from the slope. We draw up the following table $v \ 0\ 1\ 2\ 3\ 4$ (v) cm $-1\ G\ 1230.07\ 2150.61\ 2071.15\ 1991.69$ The points are plotted in Fig. 12D.1. Figure 12D.1 The intercept lies at 2230.51 and the slope = -76.65 cm -1; hence $xev = 39.83 \text{ cm} - 1\ 2230.51 \text{ cm} - 1\ \text{it}$ follows that $v = 2310.16 \text{ cm} - 2\ xev = \text{The dissociation energy may be obtained by assuming that a Morse potential describes the molecule and in the expression for the potential describes the molecule and <math>v = 2310.16 \text{ cm} - 2\ xev = \text{The dissociation energy may be obtained by assuming that a Morse potential}$ $cm - 1 = 4.15 \text{ eV D} = 4 \text{ xe } 4 \text{ xe } (4) \times (39.83 \text{ cm} - 1) 2$ However, the depth of the potential well De differs from D0, the dissociation energy of the bond, by the zero-point energy; hence $12:26 = D - 1 \nu = (33.50 \times 103 \text{ cm} - 1) - (1) \times (2310.16 \text{ cm} - 1) D = 202 = 3.235 \times 104 \text{ cm} - 1 = 4.01 \text{ eV Solutions to problems } 12D.2$ In order to plot this potential function define the variable $y \equiv x / a$ and rewrite the potential function as v(y) = V(zero and the force constant is zero. There is no restoring force for small displacements from the equilibrium position. The particle cannot undergo simple harmonic motion. 12D.4 1 = $-\nu$ (with ν = $\{(1494.9) - () \times (52.05)\}$, cm 1 4 -1 = 1481.8 cm -1, or 0.184 eV = 5.33 - 0.18 = 5.15 eV = 5.33 - 0.18 = 5.15 eV = 5.33 - 0.18 = 5.15 eV = $\{(1494.9) - () \times (52.05)\}$, cm 1 4 -1 = 1481.8 cm -1, or 0.184 eV = 5.33 - 0.18 = 5.15 eV = 5.33 - 0.18 = 5.15Hence, D 0 12:27 (b) 2 HCl: ν 2 \propto 2 2meff ω xe 1 = ν ; so as a is a constant. We also have D = a 2 [12D.12], so ν xe α e meff 4 xe ν 1 1, implying $\nu \propto 1/2$. Reduced masses were calculated in Exercises 12D.4(a) and 12D.4(b), meff meff and we can write 1/2 (m (1 HCl) 1 (0.7172) \times (2989.7 cm -1) = 2144.2 cm -1 $\times \nu$ (HCl) = 2 m (HCl) eff eff ν (2 HCl) = $\int (m(1 \text{ HCl}) 1 - 1 - 1 \text{ xev} (2 \text{ HCl}) = (5.33 - 0.132) \text{ eV} = 5.20 \text{ eV}$ Hence, D 0 12D.6 (a) In the harmonic approximation -D = +1 v so v = D D 2 (D e e 2 0 0 2(1.51 × (2.144.2) - () × (2. $10-23 \text{ J} - 2 \times 10-26 \text{ J} = 152 \text{ m} - 1$ (6.626 × 10-34 J s) × (2.998 × 108 m s - 1) The force constant is related to the vibrational frequency by v 12 (k) = 2 = ω | f |[12D.7] π v 2 π cv so = kf (2 π cv) 2 meff m (eff / The effective mass is meff = 12 m = 12 (4.003 mu) × (1.66 × $10-27 \text{ kg} \text{ mu} - 1) = 3.32 \times 10-27 \text{ kg} 2 \text{ kf} / 2\pi$ (2.998 × 108 ms - 1) × (1.66 × $10-27 \text{ kg} \text{ mu} - 1) = 3.32 \times 10-27 \text{ kg} 2 \text{ kf} / 2\pi$ (2.998 × 108 ms - 1) × (1.66 × $10-27 \text{ kg} \text{ mu} - 1) = 3.32 \times 10-27 \text{ kg} 2 \text{ kf} / 2\pi$ (2.998 × $108 \text{ ms} - 1) × (1.66 \times 10-27 \text{ kg} \text{ mu} - 1) = 3.32 \times 10-27 \text{ kg} 2 \text{ kf} / 2\pi$ (2.998 × $108 \text{ ms} - 1) \times 10^{-27} \text{ kg} = 2 \times 10^{-27} \text{ kg} - 10^{-27} \text{ kg} + 10^{-27} \text{ kg$ (152 m - 1) $(3.32 \times 10 - 27 \text{ kg}) = 2.72 \times 10 - 4 \text{ kg m } 2$ The moment of inertia is I = meff Re2 = $(3.32 \times 10 - 27 \text{ kg}) \times (297 \times 10 - 12 \text{ m}) 2 = 2.93 \times 10 - 46 \text{ kg m } 2$ (b) In the Morse potential v = D + 1
(1 - 1 x) v = D + 1 (1 - 1 x)(1 - v)|v xe = and De || e 0 0 | 2 2 2 | 2 || 8 D 4 D e e |This rearranges to a quadratic equation in v 1 v 2 - D = 0 so = v - v + D = 0 16 D $| -1 2(16 D e 12:28 e () | 1 - D 0 || v 4 D = e || De || (4(1.51 \times 10 - 23 J) 2 \times 10 - 26 J)| |1 - (6.626 \times 10 - 34 J s) \times (2.998 \times 108 m s - 1) || 1.51 \times 10 - 23 J || = 293 m$ -1 and xe (293 m -1) × (6.626 × 10-34 J s) × (2.998 × 108 m s -1) = 4(1.51 × 10-23 J) 0.96 (v) = 12D.8 See Fig. 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.14] against v + 1. Figure 12D.3 for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.15] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.16] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.17] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.18] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v + 1) xe\nu$ [12D.19] for a plot of $\Delta G \nu - 2(v$ provided; yet we have four distances to calculate: R(CC), for both C2H2 and C2D2, R(CH), and R(CD). Consequently we must make some reasonable approximations in order to solve this problem. We will assume that the CC and CH distances are the same in both molecules. Our procedure will be first to calculate the moments of inertia of the molecules from the given rotational constants and then from the moments of inertia and the known masses of the atoms to calculate the interatomic distances. = B = hence I 4π cl 4π cl 4(eqn 2) where a is the distance from the center of mass to the C atom, which is half the CC interatomic distance, and b is the distance from the center of mass to the H or D atom. 2.352 cm -1 1.696 cm -1 -1 B(C2 H 2) = 1.176 cm and = B(C2 D 2) = 0.848 cm -1 = 2.2 Therefore, = 2.3804 \times 10-46 kg m 2 and -1 4 \pi c \times 1.176 cm I (C = 3.3010 m + 1.696 cm - 1 - 1.696 cm - 1.696 cm - 1 - 1.696 cm - $\times 10-46$ kg m 2 2 D2) -14π c $\times 0.848$ cm I (C = 2H2) The masses are mC = 12.0000 u, mH = 1.0078 u, and mD = 2.0140 u; u is the atomic mass unit. Substituting these values into eqns. 1 and 2 above and solving the equations simultaneously for distances a and b we obtain: a = 0.6049 $\times 10-10$ m and b = 1.6598 $\times 10-10$ m R(CC) = 2a = 1.2098 x = 10 - 10 m = 121.0 pm and R(CH) = R (CD) = b - a = 1.055 $\times 10 - 10 \text{ m} = 105.5 \text{ pm} = 120.12 \text{ Here we make use of results that have been obtained in Chapter 8 for the average value of x = R - Re and 2 x = (R - Re) 2 . x = 0 2 \text{ Consider first } 1/Rx 2 = (v + 12)$. We need to evaluate [8B.12a & b] (mk) $\frac{1}{2}$ R . R = Re + x [Re is a constant] = Re + x = Re + 0 = Re 2 1/R = 1/Re 2 Next consider 1/R 2 = (Re + x) 1/R 2 2 2. We need to evaluate $R = \text{Re } 2 + 2 \text{ Re } + x 2 = 2 2 = R + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x 2 + 2 x \text{Re } + x 2 + 2 x \text{Re } + x 2 = R + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x 2 + 2 x \text{Re } + x 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } 2 + 2 x \text{Re } + x e 1/(1 + x 2 / \text{Re } + x e 1/(1 + x 2 / \text{Re$ 11 = 2 R (Re + x) 2 1 (Re 2 || 1 + (x) | e| x) |Re || = 2) 1 (x x 2 | || 1 2 3 ... + + |Re Re 2|| Re 2 || 2 3 ... + + |Re Re 2|| Re 2 || 1 2 3 ... + + |Re Re 2|| Re x . Re || 1 1 1 > > . 2 2 2 R R resultsshows that e = 0.27971 cm-1 and a = 0.187 m-1 = 0.00187 cm-1. Values for B 0 and B 1 12D.14 For IF, the rotational constant B 1 v = B e - 1 a = 0.27971 cm - 1 - 1 (0.00187 cm - 1) = B 2 2 3 3 - 1 B e - a = 0.27971 cm - (0.00187 cm - 1) = 2 2 The wavenumbers of the 12D.18 & 12D.19 a. $0.278775 \text{ cm} - 1 \ 0.276905 \text{ cm} - 1$ $-2 \times v = 610.258 \text{ cm} - 1 - 2 \times 3.141 \text{ cm} - 1 = 603.976 \text{ cm} - 1 \Delta G \text{ e For the P branch J} = J = 4$, and for the R branch J' = J = 2. Substituting all of these values into eqns 12D.18 & 12D.19 a we obtain (v) - (B1 + B 0)J = \Delta G 601.723 \text{ cm} - 1 P (v) + (B1 + B 0)(J + 1) + (B1 - B 0)(J + 1) = 605.626 \text{ cm} - 1 vR (J) = 200.18 \text{ cm} + 1 \text{ cm} + ΔG = The dissociation energy of the IF molecule may be obtained from D e = D D e 0 - 11 v + 4 xev 2 v 2 [12D.12] and the relation 4 xev if a Morse potential energy is assumed. Substituting the values given for v and v xe we obtain = D = 29641 cm - 1 e 0 12D.16 We work with eqns. 12D.22 which give the transition energies for the S and O branches of the vibrational Raman spectra. Transitions having $\nu S(J-2)$ and $\nu O(J+2)$ have a common upper state; hence the corresponding combination difference, $\Delta 0$, is a function of B1 only. Using eqns. 12D.22 we obtain 12:31 0 $(J-2) - 6 B \nu S (J-2) = \nu i - \nu - 4 B 0 (J+2) - 2 B 0 \nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu - 4 B 0 (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking
the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu i - \nu + 4 B 0$ Taking the difference between $\nu O (J+2) = \nu +$ Vibrational spectroscopy of polyatomic molecules Answers to discussion questions 12E.2 The gross selection rule is that the polarizability of the molecules satisfy this condition as the molecules satisfy this condition as the molecules and the molecular polarizability changes. Hence both homonuclear and heteronuclear diatomics are vibrationally Raman active. In polyatomic molecule is anisotropically polarizable; hence group theoretical methods are relied on for judging the Raman activity of the various normal modes of vibration. The procedure is discussed in Section 12E.4 and demonstrated in the Brief Illustration in that section. Solutions to exercises 12E.1(b) See Section 12E.2. Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The infrared active 3(12) - 6 = 30 normal modes. (ii) C6 H 6 CH 3 has 3(16) - 6 = 42 normal modes. (iii) HC = C - C = CH is linear; it has 3(6) - 5 = 13 normal modes is 3N-5. N = 36 in this case; therefore, the number of vibrational modes is $103 \cdot 12:32 \frac{1}{2} 1 (kq) \nu q = ||[12E.1] 2\pi c || mq || 1 q$ (v) = (v +)vq G 12E.4(b) 2 The lowest energy term is 2 corresponding to the normal mode for bending. For this mode the sulfur atom may be considered to remain stationary and the effective mass is approximately mq = 2mO mS . 2mO + mS For the other modes the effective mass expression is more complicated and is beyond the scope of this text SO2, like H2O, is a bent molecule so it has three normal modes (3N - 6 = 3) that have the same motions as the normal modes of H2O shown in text Fig. 12E.3. However, because of differences in bond strengths and effective masses, the wavenumbers of the two molecules differences in bond strengths and effective masses, the wavenumbers of the two molecules differences in bond strengths and effective masses. H2O, the ground vibrational term of SO2 is the sum of eqn. 12E.1 normal mode terms: 2(0) + G = 3(0 + G = 1(0) + G = 1(0determining the characters of the reducible representation of the molecule formed from all 12 displacements and then subtracters of the characters of the reducible representation. This latter information is directly available in the characters are the characters of the reducible representation of the vibrations. This representation can be reduced to the symmetry species of the vibration) 3 10 - 2 - 11 Unmoved atoms $4 4 1 1 2 2 12 4 0 - 2 - 22 \chi$ (rotation) $3 - 102 - 1 - 1 \chi$ (vibration) $6 4 0 - 202 \chi$ (total, product) χ (vibration) corresponds to A1' + A''2 + 2E'. Again referring to the character table of D3h, we see that E' corresponds to x and y, A ''2 to z; hence A''2 and E' are Raman active. (ii) A trigonal pyramidal AB3 molecule belongs to the group C3v. In a manner similar to the analysis in part (i) we obtain C3V χ (total) χ (vibration) 2C3 3σ V 12 0 2 6 -2 2 E 12:33 χ (vibration) corresponds to 2A1 + 2E . We see from the character table that A1 and E are IR active and that A1 + E are also Raman active. Thus all modes are observable in both the IR and the Raman spectra. 12E.6(b) (i) The boat-like bending of a benzene ring clearly changes the dipole moment of the ring, for the moving of the C—H bonds out of the plane will give rise to a non-cancelling component of their dipole moments. So the vibration is IR active. (ii) Since benzene has a centre of inversion, the exclusion rule applies: a mode which is IR active (such as this one) must be Raman inactive. 12E.7(b) The displacements span A1g + 2A1u + 2E1u + E1g . The rotations span E1g , and the translations span E1u + A1u . So the vibrations span E1g , and the translations span A1g + A1u + E1u 12E.8(b) CS2 is a linear AB2 molecule similar to CO2; therefore (see the solution to Exercise 12E.5(a)); the symmetric stretch, A1g, is infrared inactive but Raman active. The antisymmetric stretch, A1u, is infrared active, and (by the exclusion rule) Raman inactive. The two bending modes, E1u, are infrared active and therefore Raman inactive. The two bending modes, E1u, are infrared active and therefore Raman inactive. the modes is consistent with the rule of mutual exclusion; none is both infrared and Raman active. These transitions may be compared to those for CO2 (Fig. 12E.2 of the text) and are consistent with them. The Raman active mode at 1400 cm-1 is due to a symmetric stretch (v1), that at 2360 cm-1 to the antisymmetric stretch (v3) and that at 540 cm-1 to the two perpendicular bending modes (v2). There is a combination band, v1 + v3 = 3760 cm-1 \approx 3735 cm-1, which shows a weak intensity in the infrared. 12E.4 Summarize the six observed vibrations according to their wavenumbers (v / cm - 1): IR 870 1370 2869 3417 Raman 877 1408 1435 3407. (i) If H 2 O 2 were linear, it would have 3 N - 5 = 7 vibrational modes. (ii) Follow the flow chart in Fig. 11.7. Structure 1 is not linear, there is only one Cn axis (a C2), no σ h, but two σ v; the point group is C2v. Structure 2 is not linear, there is only one Cn axis (a C2), no σ h, no σ v; the point group is C2 . 12:34 (iii) The exclusion rule applies to structure 1 because it has a center of inversion: no vibrational modes of structure 2 span 3A1 + A 2 + 2B2 . (The full basis of 12 cartesian coordinates spans 4A1 + 2A 2 + 2B1 + 4B2 remove translations and rotations.) The C2v character table says that five of these modes are IR active (3A1 + 2B2) and all are Raman active. (A look at the character table shows that both symmetry species are IR and Raman active, so determining the symmetry species of the normal modes does not help here.) Both structures 2 and 3 have more active modes than were observed under experimental group theory can only tell us whether the transition moment is sufficiently strong to be observed under experimental conditions. Integrated activities 12.2 Because the centrifugal force and the restoring force balance, kf (rc -= re 1 - meff ω 2 / kf Classically, then, the energy would be the rotational energy plus the energy of the stretched bond: J 2 kf (rc -= re 1 - meff ω 2 / kf Classically, then, the energy would be the rotational energy plus the energy of the stretched bond: J 2 kf (rc -= re 1 - meff ω 2 / kf Classically, then, the energy would be the rotational energy plus the energy plus the energy of the stretched bond: J 2 kf (rc -= re 1 - meff ω 2 / kf Classically, then, the energy would be the rotational energy plus the energy be a stretched bond e re) 2 J 2 kf 2 (rc - re) 2 J 2 (meff ω 2 rc) 2 E = + = + = + . 2I 2 2I 2k 2I 2k How is the energy different form the rigid-rotor energy? Besides the energy? Besides the energy of stretching of the bond, the larger moment of inertia alters the strictly rotational piece of the energy. 2 / kf) 2 meff 2 ω 4 re2 + . 2meff re2 2kf (1 - meff ω 2 / kf) 2 Assuming that meff ω 2/kf is small (a reasonable assumption for most molecules), we can expand the expression and discard squares or higher powers of meff ω 2/kf even before squaring and expanding the denominator, so we discard all terms of that expansion after the first.) Begin to clean up the expression by using classical definitions of angular momentum: = J I = ω meff r 2 ω so = ω J / meff re , 2 which allows us to substitute expressions involving J for all ω s: E \approx J2 J4 J4 - + . 2 6 6 meff 2 re kf 2meff 2meff 2 re kf 2meff 2 r re (At the same time, we have expanded the first term, part of which we can now combine with the last term.) Continue to clean up the expression over to its quantum mechanical equivalent by substituting J (J + 1) 2 for J2: 12:35 $E \approx J 2 J 4$ meff J (J + 1) 2 J 2 (J + 1) 2 4 meff - 3 = $E \approx - .2 I$ 2 I kf 2I 2 I 3 kf (J): Dividing by hc gives the rotational term, F 2 2 4 2 2 3 2 (J) \approx J (J + 1) - J (J + 1) meff = J (J + 1) - J (J + 1) meff = J (J + 1) - J (J + 1) meff = J (J + 1) - J (J + 1) meff = J (J + 1) -
J (J + 1) meff. \Rightarrow F $4\pi CI$ kf Finally, use the relationship between the force constant and vibrational wavenumber: $1/2(kf)2\pi v 2\pi cv so = | = \omega = vib(meff)meff = 2.2 kf 4\pi cv 3.2 (J) \approx BJ (J + 1) - D JJ2 (J + 1) = (J$ profile for each of the hydrogen halides. Calculations are performed with Spartan '10 using the MP2 method with the 6-311++G** basis set. In a 6311G basis set functions. Valence orbitals are split into three basis set functions consisting of three, one, and one Gaussians. The 6-311++G basis set adds both an s-type diffuse functions for each atom other than hydrogen and one s-type diffuse functions for each atom other than hydrogen atom. The 6-311++G** basis set adds a set of five d-type polarization functions for each atom other than hydrogen atom. hydrogen atom. The plot clearly shows that in going down the halogens from HI to HBr to HCl to HF the equilibrium bond length decreases and the depth of the potential well decreases. The equilibrium properties of each molecule are summarized in the following table. The calculated bond lengths and enthalpies of formation are in excellent agreement with experimental values. The dipole moments of HCl, HBr, and HI are surprisingly high. Equilibrium Properties of Hydrogen Halides Calculated with Spartan '10 using MP2/6-311++G** HF HCl HBr Re / pm 91.7 127.3 141.3 Re(exp) / pm 91.680 127.45 141.44 -1 4198.162 3086.560 2729.302 / cm v ELUMO / eV 1.16 1.09 1.14 EHOMO R / pm Figure I12.1 (b) The calculated fundamental vibrational wavenumbers, reported in the above table, increase in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HBr to HCl to HF. 12.6 These in going down the halogens from HI to HCl to HF. 12.6 These in going down the halogens from HI to HCl to HF. 12.6 These in calculations were performed with Spartan '06 using the both MP2 and DFT(B3LYP) methods with both 6-31G* and 6-311G* basis sets). (a) and (b) The following tables summarize the calculated equilibrium properties of H2O and CO2 and present experimental values for comparison. H2O Ground State MP2/6-311G* DFT/6-31G* 24 19 95.7 96.8 -2074.5 -2074.6 106.58 103.72 3858.00 3731.72 Basis fns R / pm E0 / eV Angle / ° v1 / cm-1 MP2/6-31G* 45 118.0 -5118.7 180.00 1332.82 v2 / cm-1 636.22 657.60 641.47 666.39 667 v3 / cm µ/D 2446.78 n.s. 2456.16 n.s. 2438.17 0.0000 2437.85 0.0000 2349 0 -1 DFT/6-311G* 24 96.3 -2079.9 105.91 3764.70 104.45 3652 1709.79 1705.47 1595 3853.53 2.0950 3877.60 2.2621 3756 1.854 DFT/6-311G* 24 96.3 -2079.9 105.91 3764.70 104.45 3652 1709.79 1705.47 1595 3853.53 2.0950 3877.60 2.2621 3756 1.854 DFT/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 24 96.3 -2079.9 105.91 3764.70 104.45 3652 1709.79 1705.47 1595 3853.53 2.0950 3877.60 2.2621 3756 1.854 DFT/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. CO2 Ground State MP2/6-311G* 54 116.0 -5133.2 180.00 1376.55 Exp. DFT/6-31G* 54 45 116.9 116.9 -5121.2 -5131.6 180.00 1341.46 1373.05 Exp. 95.8 116.3 180 1388 (c) Except for the dipole moment, all calculations are typically within a reasonable 1-3% of the experimental value. 12:37 The dipole moment, all calculations are typically within a reasonable 1-3% of the experimental value. moment calculations and the experimental dipole moment may indicate that the computation methods do not adequately account for charge distribution in the very polar water molecule. 12.8 1) ($(J + 1) [12 \text{ D.18}] S (v, J) = |v + |v + B] 2 | O (2J - 1) [\Delta v = 1, \Delta J = -2] \Delta S J = v - 2 B S (2J + 3) \Delta S J = v + 2 B [\Delta v = 1, \Delta J = +2]$ The transition of maximum intensity corresponds, approximately, to the transition with the most probable value of J, which was calculated in Problem 12C.9. $(kT)Jmax| = ||(2hcB 1/2 - 12 The peak-to-peak separation is then SO(2J+3) - \{-2B(2J-1)\} = 8B(J+1)\Delta S = \Delta SJmax - \Delta SJmax = 2Bmax max max 212 || 2 (32 BkT (kT) = 8 B||)$ $2 = hc(\Delta S) B 32kT = and convert to a bond length using B 1/2 () R = | 8 \pi cm B ||X| / nc\Delta S ||mX| We can now draw up the following table. HgCl2 HgBr2 HgI2 T/K 555 565 565 mX / u 35.45$ 79.1 126.90 Δ S / cm-1 23.8 15.2 11.4 R / pm 227.6 240.7 253.4 Hence, the three bond lengths are approximately 230, 240, and 250 pm . 12:38 13 Electronic transitions 13A.2 The Franck-Condon principle states that because electrons are so much lighter than nuclei, an electronic transition occurs so rapidly compared to vibrational motions that the internuclear distance is relatively unchanged as a result of the transition. This implies that the most probable transition. This vertical line (Fig. 13A.7) will, however, intersect any number of vibrational levels vf in the upper electronic state. Hence transitions to many vibrational states of the excited state will occur with transition probabilities proportional to the verlap integral of the wavefunctions of the initial and final vibrational states. This creates the band structure, a progression of vibrational transitions that is
observed in electronic spectra. The band shape is determined by the relative horizontal positions are those to excited vibrational states with wavefunctions having a large amplitude at the internuclear position Re . 13A.4 Color can arise by emission, absorption, or scattering of electromagnetic radiation by an object. Many molecules have electronic transitions that have wavelengths in the visible portion of the emitted radiation, and it may be an additive color resulting from the emission of more than one wavelength of radiation. When a substance absorbs radiation its color is determined by the subtraction of those wavelengths from white light. For example, absorption of red light results in the object being perceived as green. Scattering, including the diffraction that occurs when light falls on a materia with a grid of variation in texture or refractive index having dimensions comparable to the wavelength of light (for example, a bird's plumage) may also form color. Solutions to exercises 13A.1(b) The 1σg21σu21πu21πg2 valence configuration has four unpaired electrons because both the 1π u and 1π g levels are doubly degenerate (see text Figure 13C.11); each with two electrons. Although Hund's rule does not apply to excited states, we examine the state of maximum spin multiplicity. Thus, $S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$ and the spin multiplicity is given by 2S + 1 = 2(2) + 1 = 5. Because $u \times u = g$ and $g \times g = g$, the net parity of two electrons paired in an orbital is always gerade. Consequently, the overall parity is found by multiplying the parity of unpaired electrons. For this configuration, $u \times u \times g \times g = g$. 13A.2(b) The electronic spectrum selection rules concerned with changes in angular momentum are (eqn 13A.4): = $\Delta \Lambda 0$, $\pm 1 \Delta S = 0 \Delta \Sigma = 0 \Delta \Omega = 0$, ± 1 where $\Omega = \Lambda + \Sigma$. A gives the total orbital angular momentum about the internuclear axis and Σ gives the total spin angular momentum about the internuclear axis. The ± superscript selection rule for reflection rule for reflection rule states that for a centrosymmetric molecule (those with a center of inversion) the only allowed transitions are transitions that are accompanied by a change of parity: $u \leftrightarrow g$. $\Lambda 0$, $\Delta S = 0$, $\Delta \Sigma = 0$, $\Delta \Omega = 0$, $u \leftrightarrow g$, and $+ \leftrightarrow +$ so the transition (i) The changes in the transition $3\Sigma g + \leftrightarrow 3\Sigma + u$ are $\Delta =$ is allowed. (iii) The transition $\pi^* \leftrightarrow n$ is forbidden. For example, in a carbonyl group, where the non-bonding orbital of the lone pair on the oxygen does not change sign (-), the + \leftrightarrow - transition is forbidden. 13A.3(b) We begin by evaluating the normalization constants N0 and Nvv. 13:1 1/2 N 02 = 1 (2a) = $|\infty - 2 \text{ ax } 2 \int e dx \left(\pi \right) - \infty \text{ Likewise} = \text{Nv} 1 2 \int \infty x^2 e^{-\infty 1/4} \left(2a \right) \text{N0} \left| (\text{standard integral}); = \left(\pi \right) (2b) (2b); \text{Nv} = 1/2 = \Gamma (3/2) \pi / 2 3/2 = 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) \left| 1/2 \sqrt{2} \right| 1/2 \sqrt{2} \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2 b (x - x0) 3/2 \left(2(2b) 3/2 \right) | 1/2 \sqrt{2} + 2 dx - 2$ dz Then, the vibration overlap integral between the vibrational wavefunction in the upper and lower electronic states is: $S (= v, 0) = \infty \infty - b x - x | 0 N 0 N v \int xe - ax e(= dx N 0 N v \int xe - ax e(= dx N 0 N v \int xe - ax e(= dx N 0 N v \int xe - ax e(= dx N 0 N v \int xe - ax e(= dx N 0 N v f xe) = 220 - \infty N 0 N v f xe - ax e(= dx N 0 N v f xe) = 220 - \infty N 0 N v f xe =$ $-ab x 02 | [bx0 \{ 1/2 |](a+b) \int \infty - \infty \infty 22 |]e - z dz + \int z e - z dz \} - \infty | x 02 | [(\pi)1/2 |]w - z2 \{ bx0 |] + \int -\infty z e dz \} | [(a+b)] | The integral of the above expression is necessarily zero because on the z axis the function z has ungerade symmetry. Thus, u × g = u and v = u$ the integral over the complete z axis of an ungerade function equals zero. 2 - ab x02 N 0 Nv bx0 e a + b (π)(2a)S(v, 0) = = $|||a+b|a+b||\pi/2|/4(2(2b)3/2||\pi/2|/4/4a+b)|$ = |a| x0 e $\int \frac{1}{2} \int \frac{$ $L 2 \int L \int L \int L \int ab x 02 bx 0 e^{a} + b \int \pi \int ab x 02 bx 0 e^{a} + b \int \pi \int ab x 02 bx 0 e^{a} + b \int \pi \int ab x 02 bx 0 e^{a} + b \int \pi \int ab x 02 bx 0 e^{a} + b \int ab x 0 e^{a} + b \int ab x$ $2\pi x/L - \pi/2$ $|-|L| 4\pi/L |x/2 L = = L/2 1 = - [sin (3\pi/2) - sin (\pi/2)] 2\pi 1 = \pi$ The Franck-Condon factor is S (v, 0) = 2 1 $\pi 2$ () () 2 +1) : vR (J) = v + B + B (J + 1) + B - B (J + 1) lines of the R branch appear at successively increasing energies as J increases, begin to converge, go through a head at Jhead, begin to decrease with increasing J, and become smaller than v when (J + 1) > B '+ B / B '- B (see () () Section 13A.1(d) and Discussion question 13A.3; the quadratic shape of the vP against J curve is called the Fortrat parabola). This means that vR (J) is a maximum when J = Jhead. It is reasonable to deduce that Jhead is the closest integer to 1 2 (B'+B)/(B'-B) - 1 because it takes twice as many J values to reach the maximum line of the R branch and to return to v. We can also find Jhead by finding the maximum of the Fortrat parabola: = dvR / dJ 0 = when J $bead \cdot dvR d = v + B + B (J + 1) - B - B (J + 1) = + B + B - 2 B - B (J + 1) dJ dJ B + B - 2 B - B (J + 1) = 0 \{ ((= J head)) ()) () + B + B - 2 B - B (J + 1) = 0 \{ ((= J head)) ()) () \} () () head (B + B) - 1 2 (B - B) 13A.6(b) Since B + B - 2 B - B (J + 1) = 0 \}$ (10.470 + 10.308) = 2 (B' - B) 2 (10.470 - 10.308) 64.2 J head = 64 13 A.7(b) When the P branch has a head, Jhead is the closest integer to 1 2 (B' + B) / (B' - B) (see Exercise 13A.5(a)). Thus, if we are only given that Jhead = 25 and B = 5.437 cm - 1, we know only that 24.5 < 1 2 B' + B / B - B < 25.5 () (because the fractional value of a) 1 2(B'+B)/(B'-B) calculation must be rounded-off to give the integer value J Algebraic manipulation of the inequality yields 13:3 head. {2(24.5) + 1} B > B' > {2(25.5) + 1} B > B' > {2(25.5) + 1} B > B' > 1.040 B 5.665 cm -1 > B' > 5.654 cm -1 When B' > B, the bond length in the electronically excited state is shorter than that in
the ground state. Below is an alternative solution that gives the same answer with insight into the band head concept: At the head of a P band, vJ head +1 > vJ head < y head -1 where vJ head -1 is the transition J head $-2 \leftarrow J = J$ head -1. Substitution of eqn. 13A.8(a) into this inequality B ' < J head B /(J head -1). Yields the relationship $1 = 32.8 \times 103$ cm $-1 \cdot \lambda$ 305 nm The cyano ligand (CN-) is a strong ligand field splitter, so we expect the d5 electrons of Fe3+ to have the t 52g low spin ground state configuration in the octahedral [Fe(CN)6]3- complex. The d-orbital electron spins are expected to be paired in two of the orbital electron spins are expected to be paired in two of the orbital. where P is the energy of repulsion for pairing two electrons in an orbital. 13A.8(b) The transition to the t 42g e1g octahedral excited state with S = 1/2 and 2S + 1 = 2 is expected to be parity forbidden and, therefore, have a small molar absorption coefficient. This transition requires the energy ΔO and releases the energy P because the excited electron will come from a t2g orbital that has paired electrons in the ground state. Thus, v = $\Delta O - P$ and $\Delta O = v + P$. Using the typical value P ~ 28 × 103 cm-1 yields the estimate $\Delta O \sim 63 \times 103$ cm-1. See F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th ed., (New York: WileyInterscience Publishers, 1980), p. 646, for electron-pairing energies. This ΔO value is much too large so we conclude that this transition is unlikely to be a satisfactory description of the cN- ligands and the t2g orbitals of Fe3+ to produce complex. wide MOs that drastically reduce the electron pairing energy. Assuming that CN- has a ground electronic configuration that is similar to that of N2, 1σ22σ*21π42σ21π*0 (see text Fig. 10C.12), we see that the cyanide ligand has an antibonding 1π* MO LUMO that has the correct symmetry to form a π bond with an Fe3+ t2g orbital. This possibility is depicted in Fig. 13A.1 with the LUMO polarized toward the carbon as expected for an antibonding MO. Fig. 13A.2 depicts a reasonable energy level diagram for the Fe3+-CN- π bond. Fe C N - dxy π* LUMO of CN Figure 13A.1 13:4 π* T e 3+ 2σ eg C N- eg Δ t 2g O π Figure 13A.2 Since the Fe3+-CN- π bond electron pair are more dispersed than either a t2g electron or a 2 σ ligand electron, it now seems reasonable to assume that the electron pairing energy is small enough to ignore yielding the estimate $\Delta O \sim 33 \times 103$ cm-1. This value seems acceptable. 13A.9(b) The normalized wavefunctions are: $1/2(1) = \psi i | ||a|$ for $0 \le x \le a$ and 0 elsewhere. $1/2(1) = \psi f | ||a - ca|$ for $ca \le x \le a$ a and 0 elsewhere; $0 \le c < 1 \frac{1}{2} \frac{1}{2}$ 13A.10(b) The normalized wavefunctions are: $1/2(1) = \psi i | || a \pi | e - x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $1/2(2) = \psi f | || a \pi | e - x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot x 2/2 a 2$ for $-\infty \le x \le \infty$ and width a $-2 \cdot (21/2) \infty - 5 \cdot (21/2) \infty$ gerade symmetry. Because $u \times g = u$, the integral of an ungerade symmetric interval equals zero). 13A.11(b) The weak absorption at 320 nm is typical of a carbonyl chromophore of an enol. The assignment is $\pi^* \leftarrow n$ where a non-bonding electron om one of the two lone pair of the oxygen valence. The two lone pair of oxygen are in sp2 hybrid orbitals, which define the xy plane. There is little overlap between the n and π* orbitals, thereby, producing a low value for the dipole transition integral and a low molar absorption coefficient. 13:5 The strong absorption at 213 nm has the π*-π transition of the absorption at 213 nm has the π*-π transition of the absorption at 213 nm has the π*-π transition of propanone (190 nm). This shift can be understood in terms of the simple Hückel theory of π molecular orbitals using the butadiene π energy model shown in text Fig. 10E.2 and the simple MO energy levels becomes smaller as the number of adjacent, overlapping orbitals becomes larger. 165 nm pz(C) pz(C) 213 nm 320 nm 190 nm sp2(O) sp2(O) C=C C=C-C=O pz(C) pz(C) pz(O) C=C C=C-C=O pz(C) pz(C) pz(O) C=C C=C-C=O pz(C) pz(C) pz(O) C=C C=C-C=O pz(C) pz(O) pz(transitions between different electronic states. Question: What is the percentage change in v 00 if the anharmonicity constants xe v, 12.0730 cm-1 and 8.002 cm-1 for the ground and excited states, respectively, are included in the analysis? 13:6 Figure 13A.4 13A.4 The ionization is HBr \rightarrow HBr+ + e- with the accompanying electronic energy change given by the equation = hv 1 2 mev 2 + I i + $\Delta E \upsilon$ ' $\leftarrow \upsilon = 0$. This modified form of eqn 10C.6 accounts for the possibility of an excitation change in the vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of an excitation change in the vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start, to the ionized electronic vibrational state vv = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecules start v = 0, in which a majority of molecu vv'=0-vv=0 is called an adiabatic transition. Fig. 13A.5 shows the potential energy + H + Br Io HBr + In HBr Internuclear Separation Figure 13A.5 (a) The photoelectron spectrum band between 15.2 eV and 16.2 eV is the σ electron of HBr (see text Fig. 13.1). Loss of this electron reduces the bond order from 1 to $\frac{1}{2}$, reduces the mag itude of the bond force constant, and lengthens the equilibrium bond length of the ionized molecule. The electronic transition is labeled as Ισ in Fig. 13A.5. The longer bond length of the ionized state cause th Franck-Condon factor for the adiabatic transition ($vv'=0 \leftarrow vv=0$) to be small. This is the lowest energy transitions indicates that these vertical transitions have successively larger Franck-Condon factors. The separation of lines (~0.162 eV) corresponds to an ionized vibrational wavenumber of about 1300 cm-1, which is considerably lower than the 2648.98 cm-1 of the neutral ground state. The presence of one unpaired electron in the bonding σ orbital means that the ionized molecule is in a 2 + Σ state. (b) The lines between 11.6 eV and 12.3 eV involve transitions of a non-bonding electron of the chlorine p valence
subshell to two very closely spaced electronic states of the ionized molecule. The ionized state makes it a doublet with spin-orbit coupling producing $j = |1 + \frac{1}{2}|, |1 - \frac{1}{2}| = 3/2, 1/2$. Consequently, the term symbols of these states are 2 II/ 2 and 2 II 3 / 2 is lowest in energy because the subshell is more than halffilled. Excitation of a non-bonding electron does not affect the bonding force constant or the equilibrium bond length. Only the vertical, adiabatic transitioned is more than halffilled. $(vv'=0 \leftarrow vv=0)$ has an appreciable Franck-Condon factor. The transition $vv'=1 \leftarrow vv=0$ of the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 3 / 2 transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 4 diabatic transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 4 diabatic transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 4 diabatic transition has a very small vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 4 diabatic transition vertical, vibrational overlap integral; it cannot be seen in the spectrum because it lies below the 2 Π 4 diabatic transition vertical. overlap integral and it is located at 12.3 eV. The 0.3 eV line separation corresponds to an ionized vibrational wavenumber of about 2400 cm-1. This is consistent with the vibrational wavenumber of about 2400 cm-1. This is consistent with the vibrational wavenumber of about 2400 cm-1. gives the peak and half-height points: $-1 = \epsilon$ peak 250 dm3 mol-1 cm = , λ peak 284 = nm (v 35200 cm -1) = = $\epsilon 1/2$ 125 dm3 mol-1 = cm (v 37700 cm -1)) and $\lambda 1/2$ 265 We estimate that the wavenumber band has a normal Gaussian shape: 13:8 = $\epsilon \epsilon$ max e = A (-v - vpeak) 2 / a2 where a is a constant related to the half-width $\Delta v_1 = 2 \infty - (v - v \text{ peak}) = \int \varepsilon(v) dv [12 \text{ A.15}] \varepsilon \max \int e^{-\infty} 2/a^2 (37700 - 32800) - 1 \text{ cm} = 4900 \text{ cm} - 1 \text{ dv}$ band = $\varepsilon \max a \pi$ (standard integral) The relationship between the half-width and a is found by evaluation of the line shape at $\varepsilon(v_1/2) = \varepsilon \max (2 - v \varepsilon \max / 2 - v \varepsilon$ vpeak) / a 2 ln(1/2) = 2 v - v) (= ($\Delta v 2 = a 2 a = 1/2 peak ln(2)/2$) ln(2) 2 1/2 $\Delta v 1/2 \epsilon max \pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = A = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$) $\pi / ln(2) = 1.0645 \Delta v 1/2 \epsilon max 2 - 1 3 - 1 1 A = cm - 1$ A1, B1, and B2 terms are allowed. 13A.8 Modeling levels of the π electrons in a linear box yields non-degenerate energy En = n2 h2 [8A.7b] 8me L2 The molecule has six π electrons, so the lowest energy transition is from n = 3 to n = 4. The length of the box is 5 times the C - C bond distance R. So (42 - 33) h2 Δ Elinear = 8me (5 R) 2 Modeling the π electrons of benzene as free electrons on a ring of radius R yields energy levels are doubly degenerate, except for the non-degenerate ml = 0. The six π electrons fill the ml = 0 and 1 levels, so the lowest-energy transition is from ml = 1 to ml = 2 (22 - 12) 2 (22 - 12) 2 (22 - 12) 2 (22 - 12) A = Ering (h2) 2 (22 - 12) A = Ering (h2) 2 (8me R 2) a = \Delta Elinear = | | < \Delta Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2) | 2 | 8me R 2 / \pi 2 \Delta = Ering (h2 show the characteristic absorption of a phenyl group at about 280 nm. Cysteine (Cys) and glycine (Gly) lack the phenyl group as is evident from their spectra. 13:9 13B Decay of excited states Answers to discussion questions 13B.2 The characteristics of fluorescence which are consistent with the accepted mechanism are: (1) it ceases as soon as the source of illumination is removed; (2) the time scale of fluorescence, ~10-9 s, is typical of a process in which the rate determining step is a spontaneous radiative transition, but faster than phosphorescence; (3) it occurs at longer wavelength (lower frequency) than the inducing radiation; (4) its vibrational structure is characteristic of the ground vibrational level of the excited electronic state; and (5) the observed shifting and in some instances quenching of the fluorescence spectrum by interactions with the solvent. Solutions to exercises 13B.1(b) After some vibrational decay the benzophenone (which does absorb near 360 nm) can transfer its energy to naphthalene. The latter then emits the energy radiatively. 13B.2(b) When the steeply repulsive section of the H2 potential energy curve for the
excited state lies slightly toward the short side of the equilibrium bond length and the minimum of the excited state lies to the longer side (as shown in text Fig. 13B.7), a great many excited vibrational states overlap with the lowest energy vibration of the ground state thereby making the Franck-Condon factor appreciable for many vertical transitions (see text Fig. 13A.7). This, combined with continuous absorption above the dissociation limit, yields a relatively broad absorption band. Furthermore, predissociation to the unbound 1 Σ +u state shortens the lifetime of excited vibrational states. This causes the high resolution limit, yields a relatively broad absorption band. Furthermore, predissociation to the unbound 1 Σ +u state shortens the lifetime of excited vibrational states. This causes the high resolution limit, yields a relatively broad absorption band. 13C.2 Strong and short radiation pulses from a Q-switched or mode-locked laser can be used to study ultrafast chemical reactions by promoting a molecule B to form an intermediate species AB. AB may even be an activated complex. A second pulse of radiation that is synchronized to pass through the sample at a specific time after the excitation pulse is used to monitor the appearance of the various species. Reaction progress and rates on the nanosecond-topicosecond scale can be examined by varying the time delay between the excitation pulse is used to monitor pulse. Text 13C.10 is a schematic of a time-resolved absorption spectrometer. A beamsplitter directs a portion of the excitation beam to a continuum generator, which converts the monochromatic laser pulse to a wide-frequency pulse suitable for monitoring reaction species. The time delay is selected by changing the position of the motorized stage in the directions shown by the double arrow. The monitor pulse is directed through the sample to the monochromator along a path, which avoids coincidence with the intense excitation pulse, to the monochromator and detector. Solutions to exercises 13C.1(b) Only an integral number of half-wavelengths fit into the cavity. These are the resonant modes. $\lambda = 2 L / n [13C.1]$ where n is an integer and L is the length of the cavity. 13:10 The resonant frequencies are given by= v c= / λ nc / 2 L. The lowest energy resonant modes (n = 1) in a 3.0 m cavity are λ = 6.0 m (v = 50.0 MHz). 13C.2(b) Referring to Example 13C.1, we have Ppeak = Epulse/tpulse and Paverage = Etotal/t = Epulse × vrepetition is the pulse repetition rate. 20 µJ / Ppeak = tpulse = 200 ps 100 kW 0.40 mW = vrepetition Paverage = / Epulse = 20 Hz 20.0 µJ Solutions to problems 13C.2 This Mathcad Prime 2 worksheet simulates the output of a mode-locked laser. The radiation intensity is analyzed in text Justification 13C.1 and we take the constant of proportionality to equal 1 (see eqn 13C.3). The worksheet plots for N = 5, 20, and 75 demonstrate that the superposition of many modes creates very narrow spikes separated by t = 2L/c = 2 nm. Integrated activities 13.2 (a) Ethene (ethylene) belongs to D2h. In this group the x, y, and z components of the dipole moment transform as B3u, B2u, and B1u respectively. The π orbital is B1u (like z, the axis perpendicular to the plane) and π^* is B3g. Since B3g × B1u = B2u and B2u × B2u = A1g, the transition is allowed (and is y-polarized). 13:11 (b) Regard the CO group with its attached groups as locally C2v. The dipole moment has components that transform as A1(z), B1(x), and B2(y), with the z-axis along the C==O direction and x perpendicular to the R2CO plane. The n orbital is py (in the R2CO plane), and hence transforms as B1. Since $\Gamma f \times \Gamma i = B1 \times B2 = A2$, but no component of the dipole moment transforms as A2, the transition is forbidden. 13.4 EHOMO calculations, performed with Spartan '10 using the DFT/B3LYP/6-31G* method, are reported in the following table along with the energy of experimentally determined I2-aromatic hydrocarbon charge transfer bands. Figure 13.1 is a plot of the charge transfer bands. -6.70 Biphenyl 3.654 -5.91 Naphthalene 3.452 -5.78 Phenanthrene 3.288 -5.73 Pyrene 2.989 -5.33 Anthracene 2.890 -5.23 Hydrocarbon The plot shows a clear correlation between the energy of charge transfer decreases. The correlation appears to be linear and the correlation coefficient (R = 0.988) indicates that about 98.8% of the variation is explained by the linear correlation. This supports the hypothesis that for π -donor hydrocarbons hvmax = ELUMO(I2) - EHOMO(π). -5 EHOMO / eV -5.5 -6 y = -1.0912x - 2.0594 R² = 0.9755 -6.5 -7 2.5 3 3.5 hvmax / eV Figure 13.1 13:12 4 4.5 14 Magnetic Resonance 14A General principles Answers to discussion questions D14A.2 The magnetogyric ratio of the electron is much larger in magnetogyric ratio of the electron is much larger than the magnetogyric ratio of the electron is much larger in magnetogyric ratio of the electron is much larger in magnetogyric ratio of the electron is much larger than the magnetogyric ratio of the electr Hence the energy of interaction of an electron with a magnetic field is much greater than the energies of interaction of nuclei with a magnetic field, on the order of magnitude by a factor of 1000. Solutions to exercises μ N E14A.1(b) Since= e / = 2mp 5.051×10-27 J T -1 and knowing the SI base units of e, , and mp , we can solve for the units of T in terms of the base units of the SI system. In terms of units, the above equation for μ N can be written (A s J s)/kg = (J T-1). Or T = kg s-2 A-1. In the solution to E47.1(a) it is shown that therefore, γ N = s -1T -1; γ N = A s kg -1 E14A.2(b) The magnitude of the angular momentum is given by Magnitude = {I (I + 1)}/2. For a 14 N nucleus I = 1, hence = $2 \, 1.491 \times 10 - 34$ J s. The components along the z - axis are 0, ± = 0, ± $1.055 \times 10 - 34$ J s. The angles that the projections of the angular momentum make with the z-axis are = 0, ± 0.7854 rad = 0, \pm 0.7854 rad = 0, ± 0.7854 rad = 0, \pm 0.7854 rad = 0, ± 0.7854 rad = 0, \pm 0.78544 rad = 0, \pm 0.78544 rad = 0, \pm 0.78544 rad = 0, \pm 0. $(5.0508 \times 10 - 27 \text{ J} \text{ T} - 1) \times (17.17) = h (6.626 \times 10 - 34 \text{ J} \text{ s}) = 6.85 \times 108 \text{ s} - 1 = 685 \text{ MHz g I } \mu \text{ N}] - \gamma \text{ N} 0 \text{ mI} = - \text{g I } \mu \text{ N} 0 \text{ mI} = - \text{g I } \mu \text{ N} 0 \text{ mI} = - \text{g I } \mu \text{ N} 0 \text{ mI} = - (0.404) \times (5.0508 \times 10 - 27 \text{ J} \text{ T} - 1) \times (10.50 \text{ T})\text{mI I } () = - 2.1425 \times 10 - 26 \text{ J} \text{ mI} = -2.14 \times 10 - 26 \text{ J} \text{ mI} = -2.14 \times 10 - 26 \text{ J} \text{ mI} = -2.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 -
26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J} \text{ mI} = -9.14 \times 10 - 26 \text{ J}$ between the two levels is $\Delta = E h\nu \nu$ where = $\gamma N 0$ (1.93 × 107 T - 1 s - 1) × (14.4 T) = $2\pi 2\pi = 4.42 \times 107$ s - 1 = 44.2 MHz E14A.6(b) A 600 MHz is the resonance field for protons for which the magnetic field is 14.1 T. In high-field NMR it is the field, not the frequency, that is fixed. (i) A N nucleus has three energy states in a magnetic field corresponding to mI = +1, 0, -1. But 14 ΔE (+1 \rightarrow 0) = ΔE (0 \rightarrow -1) ΔE = EmI - EmI = -y N 0 mI' - (-y N 0 mI) = -y N 0 mI' - (-y N 0 mI' - (-y N 0 mI) = -y N 0 mI' - (-y N 0 mI' - (-y N 0 mI) = -y N 0 mI' - (-y N 0 mI' - (-y N 0 mI) = -y N 0 mI' - (-y N 0 mI)) = -y N 0 mI' - (-y assume that the electron g-value in the radical is equal to the free electron g-value, ge = 2.0023. Then $\Delta E = h\nu = g e \mu B 0 [14A.12] = (2.0023) \times (9.274 \times 10 - 24 J T - 1) \times (0.300 T) = 5.57 \times 10 - 24 J T - 1) \times 10 + 24 J T - 1) \times 10 + 24 J T - 1$ spectrometer, despite the fact that NMR spectrometers normally operate at much higher magnetic fields. E14A.7(b) The relative population difference for spin $\delta N \propto -N \beta \gamma 0 q I \mu N 0 = \approx = N N \alpha + N \beta 2kT 2kT = (i)$ For 0.50 T (ii) For 0.50 T (iii) For 0.50 T 10-27 J T - 1) 0 = 8.62 × 10-7 (0/T) 2 (1.381 × 10-23 JK - 1) × (298 K) \delta N = (8.62 × 10-7) × (0.50) = 4.3 × 10-7 N \delta N = (8.62 × 10-7) × (15.5) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (60 MHz) This ratio is 10-27 J T - 1) = 1.34 × 10-5 N Ng I \mu N 0 Nhv [Exercises 14A.7(a) & (b)] = 2kT 2kT Thus, \delta N \alpha v \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (450 MHz) 450 MHz = 7.5 60 MHz \delta N (450 MHz) 450 MHz not dependent on the nuclide as long as the approximation ΔE kT holds. (Exercise 14A.7(a)) 14:2 = 0 E14A.9(b) hv hc = ge μB ge $\mu B \lambda$ (6.626 × 10-34 J s) × (2.998 × 108 m s -1) 1.3 T = (2.0023) × (9.274 × 10-24 J T -1) × (8 × 10-3 m) Solutions to problems $\mu = g I \mu N | I | [\mu N = 5.05079 × 10-27 JT -1]$ P14A.2 (a) Using the formulas $\lceil \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (a) Using the formulas $\lceil \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (a) Using the formulas $\lceil \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (b) $\mu h c = ge \mu B ge \mu B \lambda (6.626 \times 10-34 J s) \times (9.274 \times 10-24 JT -1) \times (8 \times 10-3 m)$ Solutions to problems $\mu = g I \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (b) $\mu h c = ge \mu B ge \mu B \lambda (6.626 \times 10-34 J s) \times (9.274 \times 10-24 JT -1) \times (8 \times 10-3 m)$ Solutions to problem $\mu = g I \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (b) $\mu h c = ge \mu B ge \mu B \lambda (6.626 \times 10-34 J s) \times (9.274 \times 10-24 JT -1) \times (8 \times 10-3 m)$ Solutions to problem $\mu = g I \mu N | I | [\mu N = 5.05079 \times 10-27 JT -1]$ P14A.2 (b) $\mu h c = ge \mu B ge \mu B \lambda (6.626 \times 10-34 J s) \times (9.274 \times 10-24 JT -1) \times (8 \times 10-34 J s) \times (9.274 \times 10-24 JT -1) \times (8 \times 10-34 Js)$ (nuclide) Rv (nuc2.62835 0.941 0.83350 31 P 1 2 1.1317 0.405 0.06654 H 1 2 2.79285 H 13 C 14 1 (b) μ N Spin I = μ Y = g I μ N | I | N I Hence Y N = μ I At constant between the nuclei] Thus Sensitivity ratio(v) = Rv (1 + 1) μ (nuclide) μ N $| \Gamma \mu$ (nuclide) | 2 2 (I + 1) | (I + 1) | = $| = 3 3 1 1 \lfloor \mu$ (I + 1) | = $| = 3 3 1 1 \lfloor \mu$ (I + 1) μ (μ (N = μ) (I + 1) μ (μ (nuclide) μ N $| \Gamma \mu$ (nuclide) | 2 2 (I + 1) | (I + 1) | = $| = 3 3 1 1 \lfloor \mu$ (I + 1) μ (I + 1) μ (I + 1) μ (μ (N = μ) (I + 1) μ (I $(H) \downarrow \mu$ (H) μ N as above. Substituting $\omega 0 = \gamma$ N B0 and γ N = RB $\propto \mu$ I, $\omega 0 = (I + 1)\mu$ 3 B02 I2 14:3 μ B0 I so R (nuclide) = Sensitivity ratio() = R (1 H) 1 6 (I + 1) [μ (nuclide) / μ N] = 16 | 2 || 1 (I) μ (H) / μ N 3 3 as in part (a). 14B Features of NMR spectra Answers to discussion questions D14B.2 Detailed discussions of the origins of the local, neighbouring group, and solvent contributions to the shielding constant can be found in Sections 14B.2(a). (b), and (c) as well as books on NMR. Here we will merely summarize the major features. The local contribution is essentially the contribution of the electrons in the atom that
contains the nucleus being observed. It can be expressed as a sum of a diamagnetic parts, that is σ (local) = $\sigma d + \sigma p$. The diamagnetic part arises because the applied field generates a magnetic field. The direction of this field can be found through Lenz's law which states that the induced magnetic field must be opposite in direction to the field producing it. Thus it shields the nucleus. The diamagnetic contribution for closed shell free atoms and for distributions of charge that have spherical or cylindrical symmetry. The local paramagnetic contribution is somewhat harder to visualize since there is no simple and basic principle analogous to Lenz's law that can be used to explain the effect. The applied field adds a term to the hamiltonian of the effect requires detailed knowledge of the excited state wave functions. It is to be noted that the paramagnetic contributions arise in a induced field in the same direction as the applied field. The neighbouring group contributions arise in a manner similar to the local contributions. Both diamagnetic and paramagnetic currents are induced in the neighbouring atoms and these currents result in shielding contributions to the nucleus of the atom being observed. However, there are some differences: The magnitude of the effect is much smaller because the induced currents in neighbouring atoms are much farther away. It also depends on the anisotropy of the magnetic susceptibilities result in a contribution. Solvents can influence the local field in many different ways. Detailed theoretical calculations of the effect are difficult due to

the complex nature of the solute-solvent interaction. Polar solvent-polar solute interactions are an electric field effect that usually causes deshielding, for example, for solutes in benzene solution. In addition, there are a variety of specific chemical interactions are an electric field effect that usually causes deshielding of the solute protons. between solvent and solute that can affect the chemical shift. D14B.4 See Section 14B.3(d) for a detailed discussion of chemical and magnetic equivalence as applied to NMR and the distinction between them. Here we will summarize the basic concepts. Two nuclei are chemical shift. Symmetrically equivalent nuclei will have the same resonance frequency, i.e. the same chemical shift. Examples are the protons in benzene and the protons are related by a C6 operation (as well as others) and in para-nitrophenol. In benzene and the protons are related by a plane of symmetry and a C2 operation. Two nuclei are magnetically equivalence in the molecule. Examples are CH2CF2 and 1,2,3-trichlorobenzene. Chemical equivalence does not imply magnetic equivalence. In the case of para-nitrophenol, the protons H-2 and H-6, though chemically equivalent, are 14:4 not magnetically equivalent because the coupling of H-2 to H-3 is different from the coupling of H-2 to H-3 is different from the coupling of H-2 to H-3 is different from the coupling of H-6 to H3. Solutions to exercise 14B.1(b) See the solution to Exercise 14B.1(c) See chemical shift is $(450 \text{ MHz}) = (60 \text{ MHz}) \nu - \nu^{\circ} (450 \text{ MHz}) = \nu - \nu^{\circ} (60 \text{ MHz}) 7.5 \text{ loc} = (1 - \sigma)0 \text{ E}14B.2(b) |\Delta \text{loc}| = (2.20 \times 10 - 6) \times (1.9 \text{ T}) = (ii) 0 = 16.5\text{T}, \text{ E}14B.3(b) 4.2 \times 10 - 6 \text{ T} |\Delta \text{loc}| = (2.20 \times 10 - 6) \times (16.5\text{T}) = 3.63 \times 10 - 5 \text{ T} \text{ v}$ $v^{\circ} = v^{\circ}\delta \times 10-6 \mid \Delta \nu \mid \equiv (\nu - \nu^{\circ})(CH 2) - (\nu - \nu^{\circ})(CH 2) - (\nu - \nu^{\circ})(CH 2) - \nu (CH 3) = v^{\circ}(\delta (CH 2) - \delta (CH 3)] \times 10-6 = (3.36 - 1.16) \times 10-6\nu^{\circ}(i) \nu^{\circ} = 650 \text{ MHz} \mid \Delta \nu \mid = (2.20 \times 10-6) \times (650 \text{ MHz}) = 1.43 \text{ kHz}$ Figure 14B.1 At 650 MHz, the spin-spin splitting remains the same at 6.97 Hz, but as Δν has increased to 1.43 kHz, the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for the splitting appears narrower on the δ scale E14B.4(b) See section 14B.3 of the text for text fo 1:6:15:20:15:6:1. See Fig. 14B.2. 14:5 Figure 14B.2 δA E14B.5(b) $\nu =$ Hence, g I μ N 0 h [Solution to exercises 14A.3(a) & (b)] v(31 P) = v(1 H) g (1 H) 2.2634 or ν (31 P) = v(1 H) 2.2634 o 1:4:6:4:1 (Pascal's triangle for four equivalent spin 1 2 nuclei, Section 5.5857 = 2.47 times greater in the phosphorus region than the proton 2.2634 region. The spectrum is sketched in Fig. 14B.3. 48.3). The lines are spaced Figure 14B.3 E14B.6(b) See Section 14B.3(a), Example 14B.3 and Figs. 14B.12 and 14B.13 for the approach to the solution to this exercise. Also see Example 14D.1 and Figs. 14D.4 and 14D.5. That latter example and those figures are applied specifically to EPR spectra, but the process of determining the intensity pattern in the fine structure of an NMR spectrum is the same. See the table below for the version of Pascal's triangle for up to 3 spin-5/2 nuclei. Each number in the table is the sum of the six (I = 5/2, 2I + 1 = 6) numbers above it (3 to the left). 14:6 1 1 1 3 6 2 1 3 10 4 15 21 1 5 25 1 6 27 1 5 27 1 4 25 3 21 2 15 1 10 6 3 E14B.7(b) Look first at A and M, since they have the largest splitting. The A resonance will be split into a widely spaced triplet (by the two M protons); each peak of that triplet will be split into a less widely spaced triplet (by the five X protons). The X resonance will be split into a widely spaced triplet (by the two A protons); each peak of that triplet will be split into a narrowly spaced triplet (by the two M protons). (See Fig. 14B.4.) Only the splitting of the central peak of Fig. 14B.4(a) is shown in Fig. 14B.4(b). Figure 14B.4 E14B.8(b) (i) Since all JHF are equal in this molecule (the CH2 group), the H and F nuclei are both chemically and magnetically equivalent. (ii) Rapid rotation of the PH3 groups about the Mo-P axes makes the P and H nuclei chemically and magnetically equivalient in both the cis- and trans-forms. E14B.9(b) $\tau \approx 2 [4B.16, with \delta v written as \Delta v] \pi \Delta v \Delta = v v^{\varrho} (\delta' - \delta) \times 10 - 6 [Exercise 14B.3(a)] \tau \approx Then \approx 2 \pi v 0 (\delta' - \delta) \times 10 - 6 2 \approx 9.9 \times 10 - 4 s (\pi) \times (350 \times 10 Hz) \times (5.5 - 6)$ $4.2) \times 10-6$ 6 Therefore, the signals merge when the lifetime of each isomer is less than about 0.99 ms, corresponding to a conversion rate of about 1.0 × 103 s -1 Solutions to problems 14:7 1 P14B.2 See Figures 14B.5(a), 14B.5(b), and 14B.5(c). In Figure 14B.5(c), 14B.5(c) values of the parameters A, B, and C. For J2 in the figure, we have changed C to +6.0 Hz. We see that a small change in J, but the overall shape of the curve remains similar; the crossover point remains at $\pi/2$. In Figure 14B.5(b), we have changed B from its initial value of -1 Hz to -2 Hz. This curve is shown in the figure as J3. There is not a large change in J and the shape remains the same, as does the crossover point. In Figure 14B.5(c), we have change as J4. Here we see that a small change in A eliminates the crossover of the curves, although again the general shape of the curve is similar. Figure 14B.5(a) Figure 14B.5(b) 14:8 Figure 14B.5(c) P14B.4 (a) The Karplus equation for 3 J HH is a linear equation in 3 J HH . In general, if F (f) is linear in f, and if f (x) is linear in x, then F (x) is linear. So we expect demonstrated in (b). (b) 3 3 J SnSn to be linear in $\cos \varphi$ and $\cos 2\varphi$. This is J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) +
27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn /Hz = 78.86(3 J HH /Hz) + 27.84 Inserting the Karplus equation for 3 J SnSn 14B.6 (c) A staggered configuration (Fig.14B.7) with the SnMe3 groups trans to each other is the preferred configuration. The SnMe3 repulsions are then at a minimum. Figure 14B.7 P14B.6 Equation 14B.15 may be written nuc = k (1 - 3cos 2 θ) where k is a constant independent of angle. Thus $\pi 2\pi 0.0$ (nuc) $\propto \int (1 - 3cos 2 \theta) \sin \theta \, d\theta \int d\phi - 1 \propto \int (1 - 3cos 2 \theta) \sin^2\theta \, d\theta$ $(1 - 3x 2) dx \times 2\pi [x = \cos \theta, dx = -\sin \theta d\theta] 1 \propto (x - x3) - 11 = 0.14:10.14$ CPulse techniques in NMR Answers to discussion questions D14C.2 Both spin-lattice and spin-spin relaxation are caused by fluctuating magnetic and electric fields at the nucleus in question and these fields result from the random thermal motions present in the solution or other form of matter. These random motions can be a result of a number of processes and it is hard to summarize all that could be important. In theory every known nuclear interaction coupled with every type of motion can contribute to relaxation and detailed treatments can be exceedingly complex. However, they all depend on the other service and it is hard to summarize all that could be important. magnetogyric ratio of the atom in question and the magnetic fields caused by the presence of neighboring magnetic nuclei will be greater, and the relaxation will be greater, and the relaxation time for protons Another consideration is the structure of compounds containing carbon and hydrogen. Typically the C atoms are in the interior of the molecule bonded to other C atoms, 99% of which are nonmagnetic, so the primary relaxation effects are due to bonded to other C atoms are in the interior of the molecule bonded to other C atoms. hence faster relaxation. D14C.4 In the nuclear Overhauser effect (NOE) in NMR, spin relaxation processes are used to transfer the population difference typical of one species of nucleus X to another nucleus A, thereby enhancing the intensity of the signal enhancement is given by IA $\gamma = 1 + 1$ $\eta = 1 + X 0$ IA 2y A NOE can be used to determine interproton distances in biopolymers. This application makes use of the fact that when the dipole-dipole mechanism, the NOE is given by IA T1 y = 1 + $\eta = 1 + X \times 0$ IA 2y A T1, dip-dip where T1 is the total relaxation time and T1, dip-dip is the relaxation time due to the dipole-dipole mechanism. Here A and X are both protons. The enhancement depends on the separation, r, of the two spins, for the strength and therefore on 1/r6. This sharp dependence on separation is used to build up a picture of the conformation of the biopolymer by using NOE to identify which protons can be regarded as neighbors. Solutions to exercises E14C.1(b) Analogous to precession of the magnetization vector in the laboratory frame due to the presence of 1, namely N N 1 or $\omega \gamma = N \ 1 \ 1 \ 2\pi$ Since ω is an angular frequency, the angle through which the magnetization vector rotates is $\nu L = 14:11 = \theta \gamma = N \ 1t \ g \ I \ \mu N \ 1t \ (\pi / 2) \times (1.0546 \times 10 - 34 \ J \ s) = 1.08 \times 10 - 34 \ J \ s) = 1.08 \times 10 - 34 \ J \ s) = 1.08 \times 10 - 34 \ J \ s)$ time is given by $T2^* = 11 [14C.7] = 0.027 \text{ s} = \pi \Delta \nu \frac{1}{2} \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ The maximum enhancement is given by $= \eta \gamma 1H 26.752 \times 107 \text{ T} - 1 \text{ s} - 1 \text{ E}_{14C.3}(b)$ and $H(C\alpha)$ protons are expected to show coupling. This results in a simple COSY spectrum with only two off-diagonals, one at (8.25 ppm, 4.35 ppm) and the other at (4.35 ppm, 1.39 ppm). CBH δ C α H NH δ Figure 14C.1 14:12 Solutions to problems P14C.2 The FID signals from the three nuclei are all of the form of eqn 14C.1 unit we will assume that all T2 values are the same at 1.0 s j and that the maximum signal intensity S0j is the same for each nucleus. No information is given, so again for simplicity we will assume only one nucleus corresponds to each value of δ . The total FID can then be expressed as F (t) = S0 \sum cos(2 $\pi\nu$ Lj t) e - t/T2 j The solution is contained in the following MathCad® worksheet. Definitions: 6 12 MHz := 10 · Hz N := 2 m := 0 , 1 .. N - 1 Time domain: t max := 10 · s Relaxation time: T2 := 1 · s Chemical shifts: $\delta 1 := 3.2$ Larmor frequencies: m := $\delta 2 := 4.1$ S2 := 1 S1 := 1 (| $\nu 1 := | 1 + S3 := 1)$ | $\nu 6 | 0 10] \delta 1$ $\nu 2 := \delta \left(1 + 2 + \nu 6 \right) \left$ ||(1 + 3 + 2)||(1 + 3 + 2)||(1 + 3 + 2)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3)||(1 + 3Fourier transformation of the FIDs from the time domain to the frequency domain. Increasing the frequency of the spectrometer from 200 MHz to 800 MHz to higher and higher frequencies. Increasing the frequency (and hence the field) allows for greater resolution of spin-spin splittings in the spectrum as the chemical shift (vL - v0) increases. That would not be obvious in this example because no information is given about spin-spin splittings. As an example of this problem in a real substance, ethanol, where spin-spin splittings occur, examine Figures 14C.7 and 14B.2 of the text P14C.4 (a) The Lorentzian function in terms of angular frequencies is I L (ω) = S0T2 1 + T ($\omega - \omega 0$) 2 2 2 The maximum in this function occurs when $\omega = \omega 0$. Hence IL,max = S0T2 and I L ($\Delta \omega 1/2$) = where $\Delta \omega = \Delta \omega \frac{1}{2}$; 1 2 I L,max 2 hence = S0T2 S0T2 S0T2 S0T2 = 2 2 2 + T2 (ω 1/2 - ω 0) 1 + T22 ($\Delta\omega$) 2 2 2 = 1 + T22 ($\Delta\omega$) 2 and $\Delta\omega$ = 1/T2. Therefore I G,max 2 = 2 2 2 2 S0T2 = -T2 ($\omega - \omega 0$) 2 2 The maximum in this function occurs when $\omega = \omega 0$. Hence IG,max = S0T2 and I G ($\Delta\omega$ 1/2) = where $\Delta\omega = \Delta\omega \frac{1}{2}$; 1 2 Therefore I G,max 2 = 2 2 2 2 S0T2 = -T2 ($\omega - \omega 0$) 2 2 The maximum in this function occurs when $\omega = \omega 0$. Solve $-T2(\omega / 2 - \omega 0) = Solve -T2(\Delta \omega) 2$ hence $\ln 2 = T2 2(\Delta \omega) 2$ and $\Delta \omega =
(\ln 2) / 2 / T2 2(\ln 2) / 2 \Delta \omega = 1/2 T2 (c)$ If we choose the same values of S0, T2, and $\omega 0$ for both functions we may rewrite them as 2.1 and I G (ω) = I L (ω) = L(x) $\propto G(x) \propto e - x$ where $x = T2(\omega - \omega 0) 2.1 + x$ These functions are plotted against x in the following Mathcad worksheet. Note that the Lorentzian function is slightly sharper in the center, although this is difficult to discern with the scale of x used in the figure are not normalized but are matched at their peak amplitude in order to more clearly display the differences in their shapes. If the curves had been normalized the areas under the two curves would be lower than the Gaussian peak height. 14:15 Figure 14C.3 x := -5, -4.95.. 51 L(x) := G(x) := e 2 2 - x 1 + x 1 L(x) G(x) 0.50 6 4 2 0 2 4 6 x P14C.6 We have seen (Problem 14C.5) that if G $\propto \cos \omega 0 t$, then I (ω) $\propto 1$ which peaks at $\omega \approx \omega 0$. [1 + ($\omega 0 - \omega$) 2 $\tau 2$] [] Therefore, if G (t) $\propto a \cos \omega 1 t + b \cos \omega 2 t$ we can anticipate that I (ω) $\propto a b + 221 + (\omega 1 - \omega) \tau 1 + (\omega 2 - \omega) 2 \tau 2$ and explicit calculation shows this to be so. Therefore, I(ω) consists of two absorption lines, one peaking at $\omega \approx \omega 1$ and the other at $\omega \approx \omega 2$. 14:16 P14C.8 Methionine residue may lay between them as represented in figure 14C.4 Figu tryptophan residue 14D Electron paramagnetic resonance Answers to discussion questions D14D.2 The hyperfine parameter a due to a nucleus in an aromatic radical, as illustrated in Fig. 14D.3 of the textbook, for the benzene anion radical, can be related to the spin density ρ of the unpaired electron on the nuclei in the aromatic radical. For the hyperfine splitting due to protons in aromatic systems, the relationship required is the McConnell equation, eqn. 14D.5. The process of obtaining ρ from the McConnell equation is illustrated in Brief Illustra other than protons in aromatic radicals similar, although more complicated equations arise; but in all cases the spin densities can be related to the unpaired electron. Solutions to exercises E14D.1(b) The g factor is given by $h\nu$ g = ; μ B 0 = g 6.62608 × 10-34 J s = = $7.1448 \times 10-11$ T Hz -1 = 71.448 mT GHz -1μ B 9.2740 $\times 10-24$ J T -1 h 71.448 mT GHz -1×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT, the difference between adjacent lines in the spectrum. The g value is given by 14:17 g = E14D.3(b) (71.448 mT GHz -1×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.02 mT 2.0022 E14D.2(b) The hyperfine coupling constant for each proton is 2.2 mT and 1.2×9.2482 GHz = 330.22 mT 2.0022 E14D.2(b) T $1.992\ 334.7\ \text{mT}\ \mu\text{B}\ 0$ If the spectrometer has sufficient resolution, it will see a signal split into eight equal parts at $\pm 1.445\ \pm\ 1.435\ \pm\$ with intensity ratios of 1:1:2:2:1:1. The four central peaks of the more highly resolved spectrum would be the two central peaks of the less resolved spectrum. E14D.4(b) (i) If the CH2 protons have the larger splitting there will be a triplet (1:2:1) of quartets (1:3:3:1). Altogether there will be a triplet (1:2:1) of quartets (1:3:3:1). lines), and 6(2 lines). Their positions in the spectrum will be determined by the magnitudes of the two proton splittings which are not given. (ii) If the CD2 deuterons have the larger splitting there will be 35 lines), 3(6 lines), 7(2 lines), 7(lines), 9(2 lines), 12(4 lines), 14(2 lines), 14(2 lines), 14(2 lines), and 21(1 line). Their positions in the spectrum will determined by the magnitude of the two deuteron splittings which are not given. E14D.5(b) The g value is given by $g = h\nu h\nu h = so 0 = 71.448 \text{ mT GHz} - 1 \mu B 0 \mu B g \mu B$ (i) $0 = (71.448 \text{ mT GHz} - 1) \times (9.501 \text{ GHz} (71.448 \text{ mT GHz} - 1) \times (34.77 \text{ GHz}) = 1241 \text{ mT } 2.0024 \text{ E14D.6(b)}$ Two nuclei of spin I = 1 give five lines in the intensity. Three H nuclei split each into a 1:2:3:2:1 (Fig. 14D.1). Figure 10D.1 E14D.7(b) The X nucleus produces four lines of equal intensity. Three H nuclei split each into a 1:2:3:2:1 (Fig. 14D.1). Figure 10D.1 E14D.7(b) The X nucleus produces four lines of equal intensity. 1:3:6:7:6:3:1 (see Exercise 14D.4(a). (see Fig. 14D.2.) 14:18 Figure 10D.2 Solutions to problems P14D.2 = g hv (7.14478 × 10-11 T) × (9.302 × 109) 0.6646 1 = . 2 002 g \perp = 0.33364 0.6646 1 = . 2 002 g \perp = 0.33194 P14D.4 Construct the spectrum by taking into account first the two equivalent 14 N splitting (producing a 1:2:3:2:1 quintet) and then the splitting of each of these lines into a 1:4:6:4:1 quintet due to the qquintet due to the quint protons. Figure 10D.3 14:19 P14D.6 Write P = (N2s) P (= N2pz) 5.7mT = 55.2mT 0.10 (10 percent of its time). (a) P(N) = 0.38 = 3.8 P(N2s)0.10 The unpaired electron therefore occupies an orbital that resembles an sp3 hybrid on N, in accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. From the discussion in Section 10A we can write $a^2 = 1 + \cos \varphi + 2 = 1$ accord with the radical's nonlinear shape. 131° Integrated activities I14.2 (a) The first figure displays spin densities computed by molecular modeling software (ab initio, density functional theory, Gaussian 98TM). 14:20 (b) First, note that the software assigned slightly different values to the two protons ortho to the oxygen. This is undoubtedly a computational artifact, a result of the minimum-energy structure having one methyl proton in the plane of the ring slightly non-equivalent. (See second figure.) In fact, fast internal rotation makes the two halves of the ring slightly non-equivalent. We will take the spin density at the ortho carbons to be 0.285 and those of the meta carbons to be -0.132. Predict the form of the spectrum by using the McConnell equation (14D.5) for the splitting 0.285×2.25 mT = 0.64 mT; these will in turn be split by the two meta protons into 1:2:1 triplets with splitting 0.132×2.25 mT = 0.297 mT = 0.297 mT And finally, these lines will be seen to be further split by the three methyl protons into 1:3:3:1 quartets with splittings, but the software generates them directly from calculated spin densities on the methyl hydrogens. The computed splittings agree well with experiment at the ortho positions (0.60 mT) and at the methyl hydrogens (1.19 mT) but less well at the meta positions (0.145 mT). I14.4 The desired result is the linear equation: = [I]0 [E]0 Δν δν - K, not K as K is defined in the problem statement.] Our first task is to express quantities in terms of [I]0, [E], $\Delta\nu$, $\delta\nu$, and K, eliminating terms such as [I], [E], $\nu 1$, νEI , and ν . [Note: symbolic mathematical software is helpful here.] Begin with v: = $\nu [I]0 - [EI][I] + [EI] + [EI][I] + [EI][I] + [EI] +$ than [EI]: [I]0 (v - vI) [I]0 $\delta v = , \Delta v v EI - vI = [EI]$ where in the second equality we notice that the frequency differences that appear are the ones defined in the problem. Now take the equilibrium constant: = K [E][I] = [EI] ([E]0 - [EI]) ([I]0 - [EI]) ([I] condition that [1]0 [E]0), so it must also be much greater than [EI], even if all E binds I. Now solve this for [E]0: [E]0 $= (K + [I]0) (K + [I]0) (K + [I]0) (V / The expression contains the desired terms and only those terms. Solving for [I]0 yields: 14:21 = [I]0 [E]0
<math>\Delta v (I]0 / (L + [I]0) (K + [I]0) (V - K \delta v)$ with slope [E]0 $\Delta \nu$ and y-intercept -K if one plots [I]0 against 1/ $\delta \nu$. 14:22 15 Statistical thermodynamics 15A.2 The principle of equal a priori probabilities is the assumption that the population of any physical state depends only on its energy is distributed. For example, a state in which the molecule's energy ε is all in translational motion or in any combination of these modes of motion—provided, of course, that the distribution is consistent with the molecule's quantized energy levels. 15A.4 Because the Boltzmann distribution gives the ratio of populations of states of different energy as a function of temperature, it accounts for the temperature dependence of many physical and chemical phenomena. In this chapter, reference was made to the intensities of spectral transitions (Topics 12A and 14A) as one phenomenon governed by the Boltzmann distribution. Chemical equilibrium is governed by the Boltzmann distribution of reactant and product species is determined by a single Boltzmann distribution of molecular speeds in the kinetic model of gases is an application of the Boltzmann distribution to translational motion (Topic 1B). Collision theory explains the temperature dependence of reaction rates through the Boltzmann distribution (Topic 1B). 6!0!5!0!4!0!3!0!2!0!0!1!15A.2(b) (i) $10! = 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 3628800$ exactly. (ii) According to Stirling's better approximation [15A.2a], $x! \approx (2\pi)1/2xx + 1/2e - x$ so $10! \approx (2\pi)1/21010.5e - 10 = 13.026$ and $10! \approx 10 \ln 10 + 10 \ln 10$ $3.60 \times 106\ 15A.3(b)$ For two non-degenerate levels, N 2 e - $\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ 21 = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ 21 = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ 21 = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ 21 = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 1 \mid -\beta(\epsilon - \epsilon) = e\ -\beta\epsilon 2 \mid 2 - \beta$ ($\epsilon - \epsilon$) = $e^2 1 = e^{-\beta \Delta \epsilon} = e^{-\Delta \epsilon}/kT = N1 e^{-\beta \epsilon 1}$ so ln N2 $\Delta \epsilon = -N1 kT$ Thus T = $-and T = -\begin{bmatrix} 1 \end{bmatrix} | 15A.7a$ with $\beta = kT | \rfloor | \Delta \epsilon N k \ln 2 N1 6.626 \times 10 - 34 J s \times 2.998 \times 1010$ cm s -1×300 cm $-1 = 623 K 1.381 \times 10 - 23 J K - 1 \times ln(1/2) 1 15A.5(b)$ See Example 15A.1. The ratio of populations of a particular state at the J = 5 level to the population of the non-degenerate J = 0 level is N 2 e - $\beta\epsilon$ 2 | 1 | - β ($\epsilon - \epsilon$) = - $\beta\epsilon$ = e 2 1 = e - $\beta\delta\epsilon$ = e - $\Delta\epsilon$ /kT 15A.7a with β = | 1 kT || N1 e | Because all of the states of a degenerate level are equally likely, the ratio of populations of a particular level is - $\beta\epsilon$ N 5 g5e 5 g5 - (ϵ 5 - ϵ 0)/kT = = e N 0 g0 e - $\beta\epsilon$ 0 g0 The degeneracy of spherical rotor energy levels are gI = (2J+1)2, and its energy levels are [12B.8] $(J + 1) = \varepsilon J hcBJ$ Thus, using kT/hc = 207.224 cm-1 = e = e N0 g0 (2 × 0 + 1) 2 = 81.7 . 15A.6(b) In fact there are two upper states, but one upper level. And of course the answer is different if the question asks when 15% of the molecules are in the upper level, or if it asks when 15% of the molecules are in each upper state. The solution below assumes the former. If the levels were non-degenerate, then N 2 e - $\beta \epsilon 2 \lceil 1 \rceil - \beta (\epsilon - \epsilon) = = e 2 1 = e - \Delta \epsilon / kT \lceil 15A.7a]$ equally likely, the population ratio of the levels is $-\beta \epsilon$ N 2 g 2e 2 g = [15A.7b] = 2 e $-\Delta \epsilon$ /kT $-\beta \epsilon$ 1 N1 g1e g1 Assuming that other states (if any) are negligibly populated, g N $\Delta \epsilon$ and ln 2 = ln 2 -T = -N g N1 g1 kT k ln 2 1 g 2 N1 Thus T = $-6.626 \times 10-34$ J s $\times 2.998 \times 1010$ cm s -1×360 cm -1 = 213 K /(15 $\times 1 - 1 - 23$ 1.381 $\times 10$ J K \times ln (100 - 15) × 2 || Solutions to problems 15A.2 For a configuration to resemble an exponential decay, populations of successively higher states must be no greater than the previous state. In this entire list, the only configuration to resemble an exponential decay, populations of successively higher states must be no greater than the previous state. In this entire list, the only configuration that meets this criterion is {4,2,2,1,0,0,0,0,0,0,0}. This is the configuration to resemble an exponential decay, populations of successively higher states must be no greater than the previous state. $\{4,2,2,1,0,0,0,0,0,0\}$, is the most likely: 9! N! = 3780 [15A.1] = W = 4!2!2!1! N 0 !N1 !N 2 ! … 15A.4 If the electronic states were in thermal equilibrium with the translational states, then the temperature would be the same for both. The ratio of electronic states at 300 K would be $-\varepsilon/kT$ $-\Delta \epsilon /kT = 2e - hc\nu /kT = 2e - kc\nu /kT = 2e - \{(1.4388 \times 450)/300\} = 0.23 = 2 \text{ N 0 g0e} - \epsilon 0 /kT$ The observed ratio is 0.30 = 0.43. Hence the populations are not at equilibrium. $0.70 \ 15A.6$ (a) The probability of finding a molecule in state j is N j e $-\beta \epsilon j = pj = [15A.6] q \text{ N In the systems under consideration}$, ϵ is both the mean energy and the energy difference between adjacent levels, so e - j\beta in plies that pj = -j\beta = ln Nj - ln N + ln q and ln N j = ln N - lnq - j\beta = ln Thus, a plot of ln Nj against j should be a straight line with slope -\varepsilon/kT. We draw up the following table using the information in Problem 15A.2 3 N j\varepsilon - q kT j 0 1 2 3 Nj 4 2 2 1 ln Nj 1.39 0.69 0.69 0 [most probable configuration] These are points plotted in Figure 15A.1 (full line). The slope is -0.416, and since $\varepsilon = 50 \text{ cm} - 1$, the slope corresponds to a temperature hc T = (50 cm - 1) × (6.626 × 10 - 34 J s) = 163 K (0.416) × (1.381 × 10 - 23 J K - 1) Figure 15A.1 (b) Choose one of the weight 2520 configurations and one of the weight 504 configurations, and draw up the following table W = 2520 W = 504 J 0 1 2 3 4 Nj 4 3 1 0 1 ln Nj 1.39 1.10 0 - ∞ 0 Nj 6 0 1 1 1 ln Nj 1.79 - ∞ 0 0 0 Inspection confirms that these data give very crooked lines—even without considering the points represented by the unoccupied states. 15A.8 If the atmosphere were at equilibrium, then the Boltzmann distribution would apply, so the relative populations per unit volume would be N i $e - \beta \epsilon i [1] - (\epsilon - \epsilon)/kT = -\epsilon j i [15A.7a with \beta = kT | N j e - \beta \epsilon j]$ What distinguishes the states and energies of molecules in a planet's gravitational field is the distance r from the center of the planet. The energy is gravitational, measured from the ground-state energy $(1 \ 1) \epsilon$ (r) = V (r) - V (r0) = -GMm | - || r r0 |Note that the ground-state energy is literally the energy at the ground-or more precisely at the planet, we have $(1 \ GMm \lim \epsilon (r) = -GMm | 0 - | = r \rightarrow \infty r0 r0 ||$ so N (r) -GMm/r0 kT = e N (r0) Hence, i the atmosphere were at equilibrium, the farther one ventured
from the planet, the concentration of molecules would tend toward a non-zero fraction of the concentration at the surface. This is obviously not the current distribution for planetary atmospheres where the corresponding limit is zero. Consequently, we may conclude that no planet's atmosphere, including Earth's, is at equilibrium. and lim $r \rightarrow \infty$ 15B Molecular partition functions Answers to discussion questions 15B.2 For two non-degenerate levels, see Brief Illustration 53.1. The mean energy is $\epsilon = \epsilon 1 + e \beta \epsilon$ where ϵ is the energy of the upper level (and zero the energy of the lower level). At low temperatures, the e $\beta \epsilon$ in the denominator makes the denominator very large and the average energy levels off at a value of ε/2 as the e βε term comes down to approach 1. 15B.4. The symmetry number, σ, of a molecule is the number of its indistinguishable orientations. See Table 15B.2, Justification 15B.4, and Brief illustration 15B.4. We can think of including the symmetry number in the calculation of partition functions as a way of avoiding "double counting," because one divides by σ . But double counting is not, strictly speaking, what is prevented. Indistinguishable configurations rule out certain rotational states because of the Pauli principle. (See Topic 12C.3.) The symmetry number need not be included in calculation of the rotational partition function by direct summation over states, as long as only allowed states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the sum; furthermore, using the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to correct a direct summation over states are included in the symmetry number to co expression for the partition function is a good approximation, though, the inclusion of the symmetry number in that expression is also a good approximation. Solutions to exercises 15B.1(b) (i) The thermal wavelength is [15B.7b] h Λ= (2π mkT)1/2 We need the molecular mass, not the molar mass: 20.18 × 10-26 kg 6.022 × 10-26 kg 6 $1023 \text{ mol}-16.626 \times 10-34 \text{ J} \text{ s} 3.886 \times 10-10 \text{ m} = -26 - 23 1/2 - 1 (2\pi \times 3.351 \times 10 \text{ J} \text{ K} \times \text{T}) (\text{T} / \text{K})1/2 \text{ m} = 300 \text{ K} \times \text{T} = 3000 \text{ K} \times \text{T} = 3000 \text{ K} \times \text{T} = 3000 \text{ K} \times \text{T}$ T = 300 K: qT = $(1.00 \times 10 - 2 \text{ m})3 = 8.86 \times 1025$ (2.243×10-11 m)3 T = 3000 K: qT = $(1.00 \times 10 - 2 \text{ m})3 = 2.80 \times 1027$ (7.094×10-12 m)3 q (Λ) A V T 15B.2(b) However, $\Lambda = 1$ h [52.7b] $\propto 1/2$ so (2π mkT) 1/2 m q (39.95) Therefore, Ar = | q Ne (20.18 || 3 q (m) = q' | (m' || 3/2 3/2 = 2.785 15B.3(b) The high-temperature expression for the rotational partition function of a linear molecule is kT I μ R 2 [Table 12B.1] = qR = , B = [15B.13b] [12B.7], cI π 4 σ hcB 8 π 2 kTI 8 π 2 kT μ R 2 = σ h2 σ h2 For N2, μ = 12 m(N) = 12 × 14.007 mu = 7.00 mu , and σ = 2; therefore Hence q = q = (8 π 2)×(1.381×10-23 J K -1)×(300 K)×(7.00×1.6605×10-27) kg)×(1.0975×10-10 m)2 (2)×(6.626×10-34 J s)2 = 52.2 15B.4(b) The high-temperature expression for the rotational partition function of a non-linear molecule is [15B.14] 1 (kT)q = $|\sigma (hc || R 3/2 (\pi) || (ABC / 1/2 () 1.381 \times 10-23 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 - 1 || (6.626 \times 10 J s \times 2.998 \times 10 cm s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 J s / = 0.01676 \times (T / K)3/2$ (i) At 25°C, 3/2 $\pi () | -32 J K - 1 \times T = | 10 - 34 J s / = 0.01676 \times (T / K)3/2$ $(27.877 \times 14.512 \times 9.285 \text{ cm}) 1/2 \text{ q R} = 0.01676 \times (298)3/2 = 86.2 \text{ (ii) At } 100^{\circ}\text{C}, \text{ q R} = 0.01676 \times (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ J} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ q R} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ q R} + 1)e - \text{hcBJ} (373)3/2 = 121 158.5 \text{ (b) The rotational partition function of a nonsymmetrical linear molecule is } 1 \text{ q R} = \sum (2 \text{ q R} + 1)e - 128.5 \text{ q R} = 23.5 \text{ q R} = 123.5 \text{ q R$ 10-23 J K -1 so q R = $\sum (2J + 1)e -9.366$ K \times J (J +1)/T J Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms of the sum and terms of the sum an expression reaches 95% of the explicit sum at 62 K. Figure 15B.1 15B.6(b) The rotational partition function of a spherical rotor molecule, ignoring nuclear statistics, is $\Sigma g = qR e - \epsilon J/kT [12B.8] J 6.626 \times 10-34 J s \times 2.998 \times 1010 cm s - 1 \times 0.0572 cm - 1 0.0823 K = 1.381 \times 10-23 J K$ are compared in Figure 15B.2. The hightemperature expression reaches 95% of the explicit sum at 0.4 K. Figure 15B.2 15B.7(b) The rotational partition function of a symmetric rotor molecule, ignoring nuclear statistics, is J (2) - ϵ R / kT qR = g J , K e J , K [15B.1b] = (2 J + 1)e - hcBJ (J + 1)/kT | 1 + 2 > e - hc (A - B) K / kT] [12B.13] > 2 = J , K J $0 = K 1 \sqrt{7} hcB 6.626 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = 13.585 K}$, and $k 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.626 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times (6.196 - 9.444) cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 l(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = 13.585 K$, and $k 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.626 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times (6.196 - 9.444) cm - 1 =
-4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 2.998 \times 1010 cm s - 1 \times 9.444 cm - 1 = -4.672 Kk 1.381 \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 JK - 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10 - 23 Jk + 1 hc(A - B) 6.26 \times 10 - 34 Js \times 10$ computer program or use other mathematical software to evaluate the terms of the sum and to sum the terms until they converge. Nested sums are straightforward to program in languages such as BASIC or FORTRAN, whereas spreadsheets are more unwieldy. with $B = C : (\pi)(kT) 1$ qR = | || || A || hc /B The explicit and high-temperature expressions are compared in Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95\% of the explicit sum at 55 K. 1/2 3/2 Figure 15B.3. The hightemperature expression reaches 95\% is the order of the rotational subgroup of the group to which a molecule belongs (except for linear molecules, for which $\sigma = 2$ if the molecule has inversion symmetry and 1 otherwise). The rotational subgroup C2; hence $\sigma = 2$ (ii) O3: Full group L2 is the molecule has inversion symmetry and 1 otherwise). C2v; subgroup C2; $\sigma = 2$ (iii) SO3: Full group D3h; subgroup D3h; subgroup C2; $\sigma = 6$ (iv) SF6: Full group D2d; subgroup Oh; subgroup D2d; [15B.14] qR = 1 (kT) σ || hc || 3/2 (π) || (ABC)1/2)1 ($1.381 \times 10-23$ JK -1 × 298.15 K = | 10 - 34 - 1 | 2 (6.626×10 Js × 2.998 × 10 cm s)3/2 π ()| -3 || ($0.2014 \times 0.1936 \times 0.0987$ cm)= 4.26×104 15B.10(b) The partition function for a mode of molecular vibration is 1 [15B.15 with β = 1/kT] e - vhcv / kT = qV Σ = - hcv / kT 1 - e v 8 1/2 $hcv \ k \ 6.626 \times 10-34 \ J \ s \times 2.998 \times 1010 \ cm \ s - 1 \times 214.5 \ cm - 1 = 308.5 \ K \ 1.381 \times 10-23 \ J \ K - 1 \ 1 \ so \ e - vhcv \ / \ kT = qV \ \Sigma = -308.5 \ K \ / \ T \ 1 - e \ v \ The \ high-temperature \ expressions \ are \ compared \ in \ Figure \ 15B.4.$ explicit sum at 3000 K. Use Figure 15B.4 15B.11(b) The partition function is 1 [15B.15 with $\beta = 1/kT$] qV = 1 - e - hcv / kT and the overall vibration function is the product of the partition function for a mode of the partition function is the product of the partition function for a mode of the partition function for a mode of the partition function is 1 [15B.15 with $\beta = 1/kT$] qV = 1 - e - hcv / kT and the overall vibration function is 1 [15B.15 with $\beta = 1/kT$] qV = 1 - e - hcv / kT and the overall vibration function for a mode of the partition function for a mode of the partition function for a mode of the partition function is 1 [15B.15 with $\beta = 1/kT$] qV = 1 - e - hcv / kT and the overall vibration function for a mode of the partition function function for a mode of the partition for a mode of the partition function for a mode of the partition for a mode of the partition for a qV mode 1 3311 2 712 3 712 4 2097 5.292 1.005 1.138 1.472 1.138 1.472 1.138 1.472 3.352 1.036 The overall vibrational partition function is 1 [15B.15 with $\beta = 1/kT$] qV = 1 - e - hcv / kT and the overall vibrational partition function is the product of the partition functions of the individual modes. (See Example 15B.2.) We draw up the following table, including the degeneracy of each level: mode 1 2 3 -1.178 90 555 ν / cm gmode 1 2 3 0.512 0.259 1.597 hc ν / kT V q mode 2.50 4.381.254 The overall vibrational partition function is qVmode = $2.50 \times 4.382 \times 1.2543 \times 3.313 = 3.43 \times 10394$ 125 $3 0.360 3.31 q = \sum g j e - \beta \epsilon j [15B.1b] = \sum g j e - 15B.13(b)$ levels where hcv j kT Therefore, hcv j / kT = 4 + e - hcv 1 / kT + 2e - hcv 2 / kT levels $6.626 \times 10 - 34 J s \times 2.998 \times 1010$ cm s $-1 \times v j = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 - 4 \times (v j / cm - 1) - 4 q = 3 + e - 7.192 \times 10 \times 850 + 5e - 7.192 \times 10 \times 1100 = 3 + 0.543 + 5 \times 0.453 = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 - 4 \times (v j / cm - 1) - 4 q = 3 + e - 7.192 \times 10 \times 100 = 3 + 0.543 + 5 \times 0.453 = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 - 4 \times (v j / cm - 1) - 4 q = 3 + e - 7.192 \times 10 \times 100 = 3 + 0.543 + 5 \times 0.453 = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 - 4 \times (v j / cm - 1) - 4 q = 3 + e - 7.192 \times 10 \times 100 = 3 + 0.543 + 5 \times 0.453 = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 - 4 \times (v j / cm - 1) - 4 q = 3 + e - 7.192 \times 10 \times 100 = 3 + 0.543 + 5 \times 0.453 = 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 - 23 J K - 1 \times 2000 K - 4 = 7.192 \times 10 + 1.381 \times 10 + 1.3$ 5.809 The individual terms in the last expression are the relative populations of the levels, namely 5×0.453 to 0.543 to 3 (second excited level to first to ground) or 0.756:0.181:1. Solutions to problems 15B.2 According to the "integral" approximation (2π mkT)1/2 X [15B.10b], h A and hence, for an H atom in a one-dimensional 100-nm box, when qT = 10, X qT = = T (1) (q h) = T | |x| (2 \pi mk) (X / 2 () 10 × 6.626 × 10 - 34 J s 1 × | | -27 - 23 - 1 100 × 10 - 9 m (2 \pi × 1.008 × 1.6605 × 10 kg × 1.381 × 10 J K)) 2 = 0.030 K The exact partition function in one dimension is $\infty \infty$ qT = $\Sigma e^{-(n-1)h\beta/8mL}$ = e h $\beta/8mL$) n [15B.1a] 2 2 2 2 2 2 2 2 n=1 n=1 For our H atom, (6.626 × 10 - 34 J s 1 × | | -27 - 23 - 1 100 × 10 - 9 m (2 \pi × 1.008 × 1.6605 × 10 kg × 1.381 × 10 J K)) 2 = 0.030 K The exact partition function in one dimension is $\infty \infty qT = \Sigma e^{-(n-1)h\beta/8mL}$ 10-34 J s) 2 h2 $\beta = 8\text{mL2} 8 \times 1.008 \times 1.6605 \times 10-27 \text{ kg} \times 1.381 \times 10-23 \text{ J} \text{ K} - 1 \times 0.030 \text{ K} \times (100 \times 10-9 \text{ m})$ 2 = $7.9 \times 10-3 \text{ h}$ 2 $\beta/8\text{mL}$ = $e-7.9 \times 10 = 1.008 \times (0.992 + 0.969 + 0.932 + ...) = 9.57 \infty 2 \text{ n}$ = 1 Comment. Even under these conditions, the integral approximation is less than 5% from the explicit sum. 15B.4 (a) First, evaluate the partition function $-\beta\epsilon - hc\beta\nu j = q \sum = g j e j [15B.1b] \sum g j e j j At 3287^{\circ}C = 3560 \text{ K}, hc\beta = hc\beta = q = 5 + 7e - \{(4.041 \times 10 -
4 \text{ G}) + 26 \text{ G}) + 26 \text{ G} +$ $\{(4.041 \times 10 - 4 \text{ cm}) \times (387 \text{ cm} - 1)\} + 3e - \{(4.041 \times 10 - 4 \text{ cm}) \times (6557 \text{ cm} - 1)\} = 5 + 7 \times (0.934) + 9 \times (0.855) + 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je j g je = = q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je j g je = = q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je j g je = = q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je j g je = = q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je je = = q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 19.444 \text{ The fractions of molecules in the various energy levels are } [15A.6, with degeneracy gj included] - \beta \epsilon - hc \beta v j N j g je je = -q q N N (3 F3) 7 \times (0.934) = 0.336 = 19.444 \text{ N N} (4 F1) 3 \times (0.0707) = 0.012 \text{ Hz}$ 19.444 N (3 F2) 5 = 0.257 = N 19.444 N (3 F4) 9 × (0.855) = 0.396 = 19.444 N 10 Comment. Nj Σ N j 15B.6 = 1. Note that the most highly populated level is not the lowest level. The absorption lines are the values of differences in adjacent rotational terms. The wavenumbers of the lines are [42.8a] + 1) - F(J) = 2 B(J + 1) \nu(J + 1 \leftarrow J) = F(J) for J = 0, 1, ... Therefore, we can find the rotational constant and reconstruct the energy levels from the data. To make use of all of the data, one would plot the wavenumbers, which . represent $\nu(J + 1 \leftarrow J)$ vs. J; from the above equally spaced with a separation of 21.19 cm-1, so that is the slope: so B = 10.595 cm -1 slope = 21.19 cm -1 = 2 B The partition function is $q = \sum gJ e \infty = \sum (2J + 1)e - \beta E (J) [15B.1b]$ where $-\beta E (J) [15B.1b]$ where $-\beta E (J) [15B.1b] = 0 J$ and the factor of 2J+1 is the degeneracy of the energy levels. 6.626 × 10-34 J s × 2.998 × 1010 cm s -1 × 10.595 cm -1 β hcE At 25°C, hcB = = $0.05112 \text{ kT} 1.381 \times 10 - 23 \text{ J} \text{ K} - 1 \times 298.15 \text{ K} = q \infty \sum (2 \text{ J} + 1)e - 0.05112 \times 1 \times 2 + 5e - 0.05112 \times 1 \times 2 + 5e - 0.05112 \times 1 \times 2 + 5e - 0.05112 \times 3 \times 4 + = 1 + 2.708 + 3.679 + 3.791 + 3.238 + = 19.90 15B.8$ (a) The electronic partition function, qE, of a perfect, atomic hydrogen gas consists of the electronic energies En that can be written in the form: 1) ($n = 1, 2, 3, ..., \infty E = n | 1 - 2 | hcRH , n | Jwhich is given by eqn. 9A.14 with the zero of energy of a proton and electron at infinite separation). The degeneracy of each level is gn = 2n2 where the n2 factor is the orbital$ degeneracy of each shell and the factor of 2 accounts for spin degeneracy. ∞ q E = \sum gne - En /kT ∞ = $2\sum$ n 2 e n=1 () - | 1-1 | C (n2 / [15B.1b] n=1 where C = hcR H / kTphotosphere = 27.301. qE, when written as an infinite sum, is infinitely large because lim n2 e () - | 1-1 | C (n2 / = lim n2 e - C = e - C lim n2 = ∞ n $\rightarrow \infty$ The inclusion of partition function terms corresponding to large n values is clearly an error. (b) States corresponding to large n values have very large average radii and most certainly interact with other atoms, thereby blurring the distinct energy level of the state. Such interactions most likely occur during the collision between an atom in state n and an atom in the ground state n = 1. (Even at high temperatures, the ground state is the most probable state.) Collisional lifetime broadening is given by $\delta En = zn$ [Topic 12A.2(b)] τ where the last equality employs the collision frequency (derived in Topic 1B). The collision frequency of the nth state of an atomic perfect gas is given by $\sigma v p 21/2 \sigma n$ vmean ρ N A 21/2 σ n vmean p [1B.10a] = zn = n rel [1B.11b] = MH kT kT The mean speed is [1B.8] vmean = (8RT) π + a0)2 From Example 9A.2, the mean radius of a hydrogen atom with principal quantum number n might be surmised to be 3n2 a0 rm = 2 In fact, this is true of ns orbitals, which is good enough for this problem. So the collision cross-section is 2 σ n = π a02 (3n + 2) $\parallel 1 \leq 2$ Any quantum state within δE of the continuum. Only states having energies in the range $0 \leq E < E \infty$ $-\delta E$ will be a distinct atomic quantum state. The maximum term, nmax, that should be retained in the partition function of a hydrogen atom is given by E n = E $\infty - \delta E$ n max max 2 (3n 2 + 2) 2 π a | max |vmean ρ N A 2 (1) () hcRH = MH (nmax) -4 -3 -3 with ρ = 1.99×10 kg m and MH =1.01×10 kg mol-1. The root function of a calculator or mathematical software may be used to solve this equation for nmax: nmax = 28 for atomic hydrogen of the photosphere Furthermore, examination of the partition function terms n = 2, 3, ..., nmax indicates that they are negligibly small and may be discarded. they do not reflect reality. 1/2 2 0 (c) The equilibrium probability of finding a hydrogen atom in energy level n is [15A.6 with degeneracy] – $\beta \epsilon N g e v 2n2 e - En /kT pn = n = n = N q qE$ where T = 5780 K. (Note: the probability for each distinct state omits the factor of 2n2.) This function is plotted in Figure 15B.5. Figure 15B.5 Even at the high temperature of the Sun's photosphere only the ground electronic state is significantly populated. This leads us to expect that at more ordinary temperatures only the ground state of atoms and molecules are populated. It is significantly populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium populated at equilibrium. It would be a mistake to thoughtlessly apply equilibrium. bombarded with extremely high energy radiation from the direction of the Sun's core while 12 radiating at a much lower energy. The photosphere may show significant deviations from equilibrium. See S. J. Strickler, J. Chem. Educ. 43, 364 (1966). 15C Molecular energies Solutions to exercises 15C.1(b) The mean energy is $\Sigma \epsilon = \beta \epsilon \sum e \beta \epsilon - 1 \epsilon = \Sigma \epsilon$ ie $-\beta\epsilon i [15C.2] = q i i i - i i = \epsilon e - \beta\epsilon 1 + e - \beta\epsilon = \epsilon 1 + e \beta\epsilon, i where the last expression specializes to two non-degenerate levels. Substitute \\ \epsilon = hc\nu = 6.626 \times 10 - 34 J s \times 2.998 \times 1010 cm s - 1 \times 600 cm - 1 = 1.192 \times 10 - 20 J = 2.158 1.381 \times 10 - 23 J K - 1 \times 400 K 1.192 \times 10 - 20 J = 1.235 \times 10 - 21 J 1 + e$ 2.158 15C.2(b) The mean energy is 1 1 1 $\varepsilon = \sum \varepsilon$ ie - $\beta \varepsilon$ i [15C.2] = \sum gic ie - $\beta \varepsilon$ i [15C.2] = $\sum (2J + 1)\varepsilon J = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon =
-\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) $\varepsilon = -\varepsilon J/kT q J q$ levels q states - 34 (J + 1) (J + 1) (J + 1) (J 1) × 1.293 × 10-22 J × e - J (J+1)×9.366 K/T q J Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms of the sum and to sum the terms until they converge. For the partition function, see Exercise 15B.5(b). The equipartition value is simply kT (i.e., kT/2 for each rotational degree of freedom). The explicit and equipartition expressions are compared in Figure 15C.1. The explicit sum reaches 95% of the equipartition value at about 63 K. and = Figure 15C.1 15C.3(b) The mean energy is 1 1 1 $\epsilon = \sum \epsilon$ ie $-\beta \epsilon$ i [15C.2] = $\sum gi\epsilon$ ie $-\beta \epsilon$ ie $-\beta \epsilon$ i [15C.2] = $\sum gi\epsilon$ ie $-\beta \epsilon$ ie $-\beta \epsilon$ order to avoid multiple counting, we sum over all J without restriction and divide the result by the symmetry number σ . $(J + 1) = J (J + 1) \times 1.136 \times 10 - 24 J = J (J + 1) \times 1.136 \times 10 + 24 J = J (J + 1) \times 1.136 \times 10^{-1}$ 1.136 × 10-24 J × e- J (J +1)×0.0823 K/T σq J Use a spreadsheet or other mathematical software to evaluate the terms of the sum and to sum the terms of the symmetry number into account; in effect, the sum evaluated here and the sum evaluated in the earlier exercise contain factors of σ , which cancel. The equipartition value is simply 3kT/2 (i.e., kT/2 for each rotational degree of freedom). The explicit and equipartition value at about 0.27 K. and = Figure 15C.2 15C.4(b) The mean energy is $1 1 = \varepsilon = \Sigma \varepsilon i e - \beta \varepsilon i q$ states $1 \left(J \right) 2 \left(2J + 1 \right) e - hcBJ \left(J + 1 \right) / kT \right| \Sigma \varepsilon J$, K e - hc (A - B) K / kT |[12B.13] $\Sigma \sigma q J = 0 \left(K = -J \right) Note that the sum over levels is restricted by nuclear statistics; in order to avoid multiple counting, we sum over all J without$ restriction and divide the result by the symmetry number σ . (See Exercise 15C.3(b).) (J + 1) + A - B K 2 . = ϵ hc BJ = { J, K () } hcB = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × 9.444 cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J = 13.585 K k 1.381 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 - 34 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J = 13.585 K k 1.381 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 - 34 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J hcB 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J s = 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 22 J s = 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 23 J K - 1 hc A - B = 6.626 × 10 - 34 J s × 2.998 × 1010 cm s - 1 × (6.196 - 9.444) cm - 1 = 1.8760 × 10 - 23 J K - 1 hc A - 1 = 1.8760 × 10 - 23 J K - 1 hc A - 1 = 1.8760 × 10 - 23 J K - 1 hc A - 1 = 1.8760 × 10 - 23 J K - 1 -1 - 34 Use () = $-6.452 \times 10 - 23$ J, (hc A - B and k) = $-6.452 \times 10 - 23$ J = -4.672 K $1.381 \times 10 - 23$ J K -1 14 so $\epsilon = \times 1$ or Σ (2 J + 1) e -13.585 K × J (J + 1)/T J = 0 J Σ {J (J + 1) × $1.8760 \times 10 - 23$ J K -1 14 so $\epsilon = \times 1$ or Σ (2 J + 1) e -13.585 K × J (J + 1)/T J = 0 J Σ {J (J + 1)/T J = 0 J Σ {J (J + 1) × $1.8760 \times 10 - 23$ J K -1 14 so $\epsilon = \times 1$ or Σ (2 J + 1) e -13.585 K × J (J + 1)/T J = 0 J Σ {J (J + 1) × $1.8760 \times 10 - 23$ J K -1 14 so $\epsilon = \times 1$ or Σ (2 J + 1) e -13.585 K × J (J + 1)/T J = 0 J Σ {J (J + 1)/T J = the sum and to sum the terms until they converge. Nested sums are straightforward to program in languages such as BASIC or FORTRAN, whereas spreadsheets are more unwieldy. For σq , see Exercise 15B.7(b). The quantity evaluated explicitly in that exercise is σq , for there we computed the partition function without taking the symmetry number into account; in effect, the sum evaluated here and the sum evaluated in the equipartition value, namely 3kT/2. The explicit and equipartition value, namely 3kT/2. The explicit sum reaches 95% of the equipartition value at about 38 K. Figure 15C.3 15C.5(b) The mean vibrational energy is hcv [15C.8 with $\beta = 1/kT$]. $\epsilon V = hcv / kT e -1$ Use hcv = 6.626 × 10-21 J hcv 4.261 × mode. The explicit and equipartition values are compared in Figure 15C.4. The explicit expression reaches 95% of the equipartition value at 3000 K. so $\epsilon V = Figure 15C.4.15 \ 15C.6(b)$ The mean vibrational energy per mode is $hc\nu / kT = -1$ We draw up the following table: mode 1 2 $-1.3311 \ 712 \ \nu / cm \ hc\nu / (10-20 \ J)$ $(hc\nu/k)/K$ 3 712 4 2097 6.577 1.414 1.414 4.166 4763 1024 3016 1.414 × 10-20 J 4.166 × 10-20 95% of the equipartition value at 24000 K. So $\epsilon V =$ Figure 15C.5 15C.7(b) The mean vibrational energy per mode is $hc\nu / kT = -1$ We draw up the following table: mode
$\nu / cm - 1$ degeneracy $hc\nu / (10-21 \text{ J}) (hc\nu / k) / K 1 178 2 90 3 555 4 125 1 3.54 2 1.79 3 11.03 3 2.48 256 129 798 180 3.54 \times 10-21 \text{ J} 1.79 \times 10-21 \text{ J}$ 1.103 × 10-20 J 2.48 × 10-21 J + 2 × 129 K/T + 3 × 180 K/T 256 K/T 798 K/T -1 -1 -1 -1 -1 e e e The equipartition value is simply 9kT, that is, kT per vibrational mode. The explicit and equipartition values are compared in Figure 15C.6. The explicit expression reaches 95% of the equipartition value at 3700 K. So $\varepsilon V = 16$ Figure 15C.6 1 ∂q $1 \partial 1 [15C.3] = 3 + e -\beta \epsilon 1 + 5e - \beta \epsilon 2 = - -\epsilon 1e -\beta \epsilon 2 = - -\epsilon 1e -\beta \epsilon 2 = - -\epsilon 1e -\beta \epsilon 2 q \partial \beta q (-\epsilon = 15C.8(b)()) ((hc hc v1e - \beta hcv1 + 5v2 e - hcv2 + v1e - hcv1/kT + 5v2 e - hcv2/kT q q hcvj Use q = 5.809 = 7.192 \times 10 - 4 \times (v j/cm - 1) and kT 6.626 \times 10 - 34 J s \times 2.998 \times 1010 cm s - 1$ Thus $\epsilon = 5.809 = (\times 850 \text{ cm} - 1 \times e - 7.192 \times 10 = 1.010 \times 10^{-4} \text{ cm} + 5v2 e - \beta cv2 + 10 + 10 \text{ cm} + 5v2 e - \beta cv2 + 10 + 10 \text{ cm} + 5v2 e - \beta cv2 + 10 + 10 \text{ cm} + 5v2 e - \beta cv2 + 10 + 10 \text{ cm} + 10 \text{ cm} + 5v2 e - \beta cv2 + 10 + 10 \text{ cm} + 10$ We measure energies from the lower states and write $2 + 2e - hc\beta\nu = 2 + 2e - hc\beta\nu = 2 + 2e - hc\beta\nu = 2 + 2e - hc\beta\nu = 15C.7$ (a) At 300 K NO 2 1 = = 0.641 - 174.2/300 N q 1+ e N1 N = 1 - 0 = 0.359 N N (b) The electronic contribution to the mean molecular energy is $1 \frac{\partial q}{\partial r} 2hc\nu = -hc\beta\nu = 15C.7$. Here hc = $\beta v 17$ Figure 15C.7 (a) At 300 K NO 2 1 = = 0.641 - 174.2/300 N q 1+ e N1 N = 1 - 0 = 0.359 N N (b) The electronic contribution to the mean molecular energy is $1 \frac{\partial q}{\partial r} 2hc\nu = -hc\beta\nu = 15C.7$. $g \partial \beta q$ and $= 6.626 \times 10-34$ J s $\times 2.998 \times 1010$ cm s -1×121.1 cm $-1 \times e -174.2$ 300 1 + e -174.2 $2 \sin \frac{1}{2} = \frac{1}{2} \left[\frac{1}{2} 2q \right] = \frac{1}{2} \left[\frac{1}{2} 2q \right] = \frac{1}{2} \left[\frac{1}{2} - \frac{1}{2} + \frac{1}{$ - β hcν hcν 2sinh(β hcν / 2) 15D The canonical ensemble is a set of a large number of imaginary replications are identical in some respects but not in all respects. For example, in the canonical ensemble, all replications have the same number of particles, the same volume, and the same temperature, but they need not have the same energy. Ensembles are useful in statistical thermodynamics because it is mathematically more tractable to perform an ensemble average to determine these properties. Recall that macroscopic thermodynamic properties are averages over the time dependent properties of the particles that compose the macroscopic system. In fact, it is taken as a fundamental principle of statistical thermodynamics that the (sufficiently long) time average of every physical observable is equal to its ensemble average. This principle is connected to a famous assumption of Boltzmann's called the ergodic hypothesis. 15D.4 In the context of ensembles, the thermodynamic limit is the limit as the number of replications, N, approaches infinity. In that limit, the dominating configuration is overwhelmingly the most probable configuration, and its properties are essentially the same as those of the system. Note, however, that some authors use the phrase to refer to a limit of large numbers of particles. Solution to exercise 15D.1(b) Inclusion of a factor of 1/N! is necessary when considering indistinguishable particles. particles that are distinguishable by their positions. The factor must be included in calculations on (i) CO2 gas, but not (ii) graphite, (iii) diamond, or (iv) ice. 15E The internal energy and the entropy Answers to discussion questions 15E.2 The expressions for q, U, and S that were derived in this chapter are applicable to T < 0 as well as T > 0. g and U against T, for example, in a two-level system and other systems as well, we find sharp discontinuities on passing through zero, and T = +0 (corresponding to all populations in the lower state) is guite distinct from T = -0, where all populations in the lower state of the However, if we plot llation is in the upper state. The entropy S is continuous at T = 0, but all these functions are continuous if we use $\beta = 1/kT$ as the independent variable which indicates that $\beta \propto 1/T$ is a more natural variable than T. 15E.4 Given the statistical definition of entropy in terms of the number of configurations (microstates) consistent with a given energy [15E.7], the entropy for a collection of distinguishable particles must be greater than that of otherwise similar indistinguishable particles. If the particles are distinguishable, then exchanging, say, a pair of them would result in a different (albeit highly similar) microstate, but the same state. That is part of what it means for particles to be indistinguishable. As a result, the number of microstates available to distinguishable particles is greater by a factor of N! than the number of permutations of N 19 particles that would result in different microstates for distinguishable particles but the same microstate for indistinguishable particles. 15E.6 Residual entropy is due to the presence of some disorder in the system even at T = 0. It is observed in systems where there is very little energy difference—or none—between alternative arrangements of the molecules at very low temperatures. Consequently, the molecules cannot lock into a preferred orderly arrangement and some disorder persists. More precisely, more than one microstate is accessible even at the lowest temperature. Solutions to exercises 15E.1(b) CV, m = 12 (3 + v R* + 2v V*) R [15E.6] with a mode active if T > θ M. (i) O3: vR* = 3, vV* \approx 0; hence CV, m = 12 (3 + 3 + 2v V*) R [15E.6] with a mode active if T > θ M. 0 R = 3R [experimental = 3.7R] (ii) C2H6: $vR^* = 2$, $vV^* \approx 0$; hence CV m = 12 ($3 + 2 \times 1$) R = 4R [experimental = 6.3R] (iii) CO2: $vR^* \approx 0$; hence CV m = 12 ($3 + 2 \times 1$) R = 4R [experimental = 4.5R] Consultation of the book Herzberg (Molecular Structure II.) turns up only one vibrational mode among these molecules whose frequency is low enough to have a vibrational temperature near room temperature. That mode was in C2H6, corresponding to the "internal rotation" of CH3 groups. The discrepancies between the estimates and the experimental values suggest that there are vibrational modes in each molecule that contribute to the heat capacity albeit not to the full equipartition value—that our estimates have classified as inactive. 15E.2(b) The equipartition theorem would predict a contribution to molar heat capacity of 1 2 R for every translational and rotational degree of freedom and R for each vibrational mode. For an ideal gas, Cp.m = R + CV,m. So for CO2 6.5 With vibrations CV ,m / R= 3 (12) + 2 (12) + (3 × 3 - 6) = 5.5 and γ = = 1.18 5.5 3.5 Without vibrations can be neglected entirely. 15E.3(b) J mol - 1 K - 1 The experimental result is closer to that obtained by neglecting vibrations, but not so close that vibrations can be neglected entirely. 15E.3(b) $\int 1 \text{ for } \Sigma \text{ states}$, where $g = (2S + 1) \times \{ j \mid 2 \text{ for } \Pi, \Delta, \dots \text{ states} -1 \text{ hc} \times (7918.1 \text{ cm} \text{ is triply degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (orbitally) degenerate} (from spin), and the 1\Delta \text{ term is doubly (from spin), and the 1\Delta \text{ term is doubly (from spin), and the 1\Delta \text{ term is doubly (from spin)} (from spin), and the 1\Delta \text{ term is doubly (from spin)} (from spin), and the 1\Delta \text{ term is doubly (from spin)} (from s$ of oscillators is given by $V U - U m (0) R(\theta V / T) - R ln(1 - e - \theta / T) [15E.14b] + k lnQ [15E.8c] = \theta V / T Sm = m T e - 1 where \theta V = hc v / k is the vibrational temperature. A plot of Sm/R versus T/\thetaV is shown in
Figure 15E.1. 20 Figure 15E.1. 20 Figure 15E.1. 20 Figure 15E.1. The vibrational temperature.$ modes. The table below shows results from a spreadsheet programmed to compute Sm/R at a given temperature for the normal-mode wavenumbers of ethyne. T=298 K T=500 K v / cm - 1 θ V/K T/ θ V Sm/R T/ $0.00000217 \ 0.106 \ 0.000818 \ 3374 \ 4853 \ 0.0614 \ 0.00000146 \ 0.103 \ 0.000652 \ The total vibrational entropy is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes). (i) At 298 K, Sm = 0.708R = 5.88 J K-1 mol-1 (ii) At 500 K, Sm = 1.982R = 16.48 J K-1 mol-1 15.5(b) The translational$ contribution to the total entropy of a polyatomic molecule is determined in the same manner as the translational entropy of a monatomic molecule. $(e_{5/2} \text{ kT})$ S mo R = ln | O 3 | [15E.11b with p p O] = $(p \Lambda / (i) \Lambda = h 6.626 \times 10 - 27 \text{ kg})(1.381 \times 10 - 23 \text{ J K} - 1) T$ / (2 -10 = 4.113 × 10 m (T / K)1/2 $(e5/2) \times (1.381 \times 10 - 23 \text{ J K} - 17) (T) \times \text{SmO} = \text{R ln} = 5 - 10 3 (1.013 \times 10 \text{ Pa}) \times (4.113 \times 10 \text{ m}) \parallel (K \parallel 3/2) = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (298)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (298)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (298)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1 \text{ mol} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1) \ln \{5.302 \times (T/K)5/2\} = (8.3145 \text{ J K} - 1) \ln (10.314 \text{ mol} - 1) \ln (10.314 \text{ mol} - 1) \ln (10.314 \text{ mol} - 1) \ln$ $(e_5/2) \times (1.381 \times 10 - 23] K - 1T) T \times S = R \ln | 5 - 103 ((1.013 \times 10 Pa) \times (2.632 \times 10 m) ||| (K) || 3/2 Om = R \ln \{271.6 \times (T/K)5/2\} = (8.3145] K - 1 mol - 1 15E.6(b)$ From the solution to Exercise 15E.5(b) we have, for translational contributions, SmO = R ln {271.6 × (T/K)5/2} for CO2 SmO = R ln {271.6 × (T/K)5/2} = (8.3145] K - 1 mol - 1 15E.6(b) From the solution to Exercise 15E.5(b) we have, for translational contributions, SmO = R ln {271.6 × (T/K)5/2} for CO2 SmO = R ln {271.6 × (T/K)5/2} = (8.3145] K - 1 mol - 1 15E.6(b) $132 \text{ J K} - 1 \text{ mol} - 1 \text{ for H2O at } 298 \text{ K We solve for T: and (SO)} || (1 T = \times \exp | m || (271.6 2/5 (132 \text{ J K} - 1 \text{ mol} - 1)|) || (1 \times \exp | K = (-1 - 1) || (271.6 2/5 \text{ K} = 60.9 \text{ K} 15E.7(b))$ The high-temperature approximation to the rotational partition function of a non-linear molecule is (after substituting the numerical values of the constants in eqn 15B.14) 1.0270 (T / K)3/2 1.0270 × 2983/2 = = 5837 qR - / 312 / cm) σ (ABC (2) × (2.02736 × 0.34417 × 0.293535)1/2 The high-temperature approximation is valid if T > θ R)1/3 hc(ABC and θ R = k (6.626 × 10-34 J s)(2.998 × 1010 cm s - 1) {(2.02736)(0.34417)(0.293535) cm - 3} 1/3 = 1.381 × 10-23 J K -1 = 0.8479 K so it is valid in this case. All the rotational modes of water are fully active at 25°C; therefore 3 U mR - U mR (0) = E R = RT, the equipartition value 2 ER 3 SmR = + R lng R = R + R ln5837 = 84.57 J K - 1 mol - 1 2 T Comment. Division of qR by NA! is not required for the internal contributions; internal motions may be thought of as localized (distinguishable). It is the overall canonical partition function, which is a product of internal energy is proportional to a species with S = 5.2 is 6. The electronic contribution to molar entropy is $U m - U m (0) + R \ln q = R \ln q T$ (The term involving the internal energy is proportional to a temperature-derivative of the partition function, which in turn depends on excited state contributions to the partition function; those contributions are negligible.) Sm = Sm = (8.3145 J mol-1 K - 1 15E.9(b) The molar entropy of a collection of oscillators is given by VU - Um (0) $R(\theta V / T)$ Sm = m + k lnQ [15E.8c] = $\theta V / T$ $- R \ln(1 - e - \theta / T)$ [15E.14b] T e -1 where $\theta V = hc v / k$ is the vibrational temperature. The vibrational entropy of ethyne is the sum of contributions of this form from each of its seven normal modes. The table below shows results from a spreadsheet programmed to compute Sm/R at a given temperature for the normal-mode wavenumbers of ethyne. T=298 K 22 T=500 K v / cm -1 θ V/K T/ θ V Sm/R 612 880 0.336 0.216 0.568 0.554 729 1049 0.284 0.138 0.479 0.425 1974 2839 0.105 0.00000217 0.106 0.0000146 0.103 0.000652 The total vibrational entropy is obtained by summing the last column (twice for the first two entries, since they represent doubly degenerate modes). (i) At 298 K, Sm = 0.708R = 5.88 J K-1 mol-1 (ii) At 500 K, Sm = 1.982R = 16.48 J K-1 mol-1 (iii) At 500 K, Sm = 16.48 J K-1 mol-1 (iii) At 500 K, Sm = 16.48 J K-1 mol-1 (iii) At 500 K, Sm = 16.48 J K-1 mol-1 (knowledge of the rotational constants the total molar entropy cannot be calculated. Solutions to problems $\Delta \varepsilon = \varepsilon = ge \mu B0 [14A.12a] 15E.2 q = 1 + e - \beta \varepsilon$ or $[15E.2a] N (\partial q E) NA\varepsilon = -\beta \varepsilon - EA = Um - Um (0) = |q | \partial \beta | q E V Let x = \beta \varepsilon = 2 \mu B0 b [ge = 2], then d\beta = \varepsilon 1 dx$ Therefore, if 0 = 5.0 T, $x = (2) \times (9.274 \times 10 - 24$ J T -1) × (5.0 T) 6.72 = T K (1.381 × 10 - 23 J K -1) × T and (x 2 e - x) ∂ (e - x)(x) -k | |e| A - x | = -N A kx 2 × | = CV, m = R| -x | $-x 2 |\partial x (1 + e)$ ((1 + e)) (a) T = 50 K, x = 0.134, CV, m = 4.47×10-3R, implying that CV, m = 3.7×10-2 J K -1 nol-1. Since the equipartition value is about 3R [vR* = 3, vV* \approx 0], the field brings about a change of about 0.1 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b)
T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.1 mJ K-1 mol-1, a change of about 4×10-3 per cent. (b) T = 298 K, x = 2.26 \times 10-2, CV,m = 1.3 ×10-4R, implying that CV,m = 1.3 $= E(J = 2) - E(J = 0) = 6hcB[E = hcB]U - U(0) 1 \partial q 5\varepsilon e - be = - = N q \partial b 1 + 5e - be [15E.5] (\partial U m)CV, m = -k\beta 2 | | \partial \beta N CV, m R = hcB k\beta) 2 (6.626 \times 10 - 34 J s)(2.998 \times 1010 cm s - 1) (60.864 cm - 1) = 87.571 K 1.381 \times 10 - 23 J K - 1 23 Hence, 1.380 \times 106 e$ -525.4KT (1+ 5e -525.4KT)2 × (T K)2 We draw up the following table CV, m R = T/K 50 100 150 200 250 300 350 400 450 500 CV, m/R 0.02 0.68 1.40 1.35 1.04 0.76 0.56 0.42 0.32 0.26 These points are plotted in Figure 15E.2. Figure 15E.2 15E.6 The contribution to the heat capacity from this system of states is [15E.5] (∂U) 2 (∂U 2 (∂U) 2 (u. Then Ev = $v\{1 - (v+1)xe\}$. The partition function becomes vmax $q = \sum e - \beta uv\{1 - (v+1)xe\}$ v=0 vmax = $\sum e - \beta uv\{1 - (v+1)xe\}$. The partition function to Problem 12D.7 for a derivation of this max 2 v formula. Since specific values of x, v, and D are required to solve this problem we will e e choose the case of HCl(g). Values of xe, v, and D e may be obtained from xe = v [12D.12]. The heat 4 D e capacity is calculated in the following MathCad worksheet and Figure 15E.3. 24 Figure 15E.3 Note the slight difference between the vibrational heat capacities of the harmonic oscillator approximation. Also note that for HCl(g) at room 25 temperature the vibrational heat capacity of 29.12 J K-1 mol-1. This is a result of the large spacing between the HCl energy levels 15E.8 The partition function of a system with energy levels $\epsilon(J)$ and degeneracies g(J) is $q = \sum g(J) = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V \rangle V = -(k\beta 2 | [15E.5] \langle \partial \beta | V$ terms of sums over energy levels $NN(U - U(0) = -|-\sum g(J)\epsilon(J)e - \beta\epsilon(J)| = \sum g(J)\epsilon(J)e - \beta\epsilon(J)| = \sum g(J)\epsilon(J)e - \beta\epsilon(J)| = -\sum g(J)e - \beta\epsilon(J)e - \beta\epsilon(J)| = -\sum g(J)e - \beta\epsilon(J)e - \beta\epsilon(J)e$ sum appears, one that has some resemblance to the terms in $\zeta(\beta)$. The fact that $\zeta(\beta)$ is a double sum encourages us to try to express the single sum in CV as a double sum. g (J') Σ , so We can do so by multiplying it by one in the form J' q and CV N = $-2 \Sigma g(J) \epsilon 2 (J) e - \beta \epsilon (J') \Sigma g(J') E - \beta \epsilon (J') E - \beta \epsilon (J')$ $(J')e - \beta \epsilon (J') + \epsilon (J') + \epsilon (J')e - \beta \{\epsilon (J) + \epsilon (J')\} - 2 \sum g(J)g(J')e - \beta \{\epsilon (J) + \epsilon (J')e - \beta \{\epsilon (J) + \epsilon$ all the other factors in that sum are related to J and J' in the same way. Thus, the first sum would not be changed by writing $\epsilon^2(J')$ to the sum with $\epsilon^2(J')$ to the sum $+ \epsilon 2 (J') - 2\epsilon (J)\epsilon (J') + Recognizing that \epsilon 2 (J) + \epsilon 2 (J') - \epsilon (J') = \{\epsilon (J) - \epsilon (J') + \epsilon 2 (J') - \epsilon (J') + \epsilon 2 (J$ are plotted in Figure 15E.4. One can evaluate CV,m/R using the following expression, derivable from eqn (1) above. It has the advantage of using single sums. CV, m R = $11(g(J)\beta 2\epsilon 2(J) - 2|\sum g(J)\beta\epsilon(J) - 2$ independently from 0 to infinity. Thus, identical terms appear twice. (For example, both (0,1) and (1,0) terms appear with identical value in ζ(β). In the plot, though, the (0,1) curve represents both terms.) One could redefine the double sum with an inner sum over J' running from 0 to J-1 and an outer sum over
J running from 0 to infinity. In that case, each term appears only once, and the overall factor of 1/2 in CV would have to be removed. 15E.10 The absorption lines are the values of differences in adjacent rotational terms. Using eqns. 12B.15, and 12B.10, we have E (J + 1) – E (J) F (J + 1) – E (J + 1reconstruct the energy levels from the data of Problem 15B.6. To make use of all of the data, one would plot the +1) - F(J), vs. J; the slope of that linear plot is 2 B. wavenumbers, which represent F(J However, in this case, plotting the data is not necessary because inspection of the data shows that the lines in the spectrum are equally spaced with a separation of 21.19 cm-1, so that is the slope: and hence B = 10.595 cm -1 slope = 21.19 cm -1 = 2 B The partition function is $\infty \propto q = \sum (2 J + 1)e - J (J + 1)\theta R/T [\theta R = hcB/k] = J 0 = J 0$ and the factor (2J + 1) is the degeneracy of the energy levels. For HCl, $\theta R = 15.244$ K. T Defining x = R, qR may be rewritten $\theta \neq R = \sum (2J + 1)e - J (J + 1)/x J$ At temperatures above about 30 K the high temperature approximation for qR would be adequate to calculate the molar entropy is calculated from U - U m (0) Sm = m + R lnq R [15E.8a] T and the molar energy from N ($\partial q R [15E.2a] Um - Um (0) = NA \langle \epsilon R \rangle = -RA | q | \partial \beta | V 27 Um = -Um (0) 1 NA hcB [(J + 1)] e - J ((J + 1)] e - J ((J$ with a spreadsheet program such as Excel® or a analytical mathematical software as Mathcad®. Here we have used Mathcad®. See the Mathcad® T worksheet below. Sm/R is plotted as a function of $x \equiv R$ in Figure 15E.5 15E.12 The translational contribution to the entropy is given by the Sackur-Tetrode equation [15E.11a]: (V 6.22 h where $\Lambda = [15B.7b]$ SmTO = R ln | m 3 | (2 π mkT)1/2 { NAA / After substituting values for the constants we obtain 6.626 × 10-27 kg)(1.381 × 10-23 \text{ J} \text{ K} - 1)(298 \text{ K})} 1/2 = 1.64 × 10-21 \text{ m} and () (2.479 × 10-2 m3) e5/2 S mTO = (8.3145 \text{ J} \text{ K} - 1 \text{ mol} - 1) ln | -1 - 11 23 3 | (6.022 10 \text{ mol}) 1/2 { 2 π (38.00 × 1.6605 × 10-27 kg)(1.381 × 10-23 \text{ J} \text{ K} - 1)(298 \text{ K})} 1/2 = 1.64 × 10-21 \text{ m} and () (2.479 × 10-2 m3) e5/2 S mTO = (8.3145 \text{ J} \text{ K} - 1 \text{ mol} - 1) ln | -1 - 11 23 3 | (6.022 10 \text{ mol}) 1/2 { 2 π (38.00 × 1.6605 × 10-27 kg)(1.381 × 10-23 \text{ J} \text{ K} - 1)(298 \text{ K})} 1/2 = 1.64 × 10-21 \text{ m} and () (2.479 × 10-2 m3) e5/2 S mTO = (8.3145 \text{ J} \text{ K} - 1 \text{ mol} - 1) ln | -1 - 11 23 3 | (6.022 10 \text{ mol}) 1/2 { 2} m \text{ mol} - 1 \text{ mol} - $(1.64 \ 10 \ m) \times \times (1 - 1 - 1 = 154 \ J \ K \ mol \ 28 \ The \ rotational \ contribution \ is \ [15E.13a] \ kT \ (12 \times 19.00 \times 10 - 3 \ kg \ mol \ -1) \times (12 \times 19.00 \times 10 - 3 \ kg \ mol \ -1) \times (12 \times 19.00 \times 10 - 12 \ m)^2 \ 10 = 0.4915 \ cm \ -1 \ It \ will \ be \ useful \ to \ note \ that$ $(1.381 \times 10 - 23 \text{ J K} - 1)(298 \text{ K}) \text{ kT} = 207.2 \text{ cm} - 1 \text{ k} (6.626 \times 10 - 34 \text{ J s})(2.998 \times 1010 \text{ cm} \text{ s} - 1) / 1 + \ln = 52.8 \text{ J K} - 1 \text{ mol} - 1 / 1 + \ln = 52.8 \text{ J K} - 1 \text{ mol} - 1) / 1 + \ln = 52.8 \text{ J K} - 1 \text{ mol} - 1 / 1 + \ln = 52.8 \text{ J K} - 1 \text{ mol} - 1 / 1 + \ln = 52.8 \text{ J K} - 1 \text{ mol} - 1 + \ln = 52.8 \text{ J K}$ $-1 \left[e \right] (1) (2.172) S mV (8.3145 J K - 1 mol - 1) = - ln (1 - e - 2.172) (3.33 J K - 1 mol - 1 2.172 - 1) e The Boltzmann factor for the lowest-lying excited electronic state is (-(1.609 eV) × (1.602 × 10 - 19 J eV - 1)) exp = 6 × 10 - 28 - 23 - 1 (1.381 × 10 J K) × (298K) || so we may take qE to equal the degeneracy of the ground state, namely 2$

and UE – UE(0) to be zero. So the electronic contribution is UE – UE(0) SE = + R lnq E = 0 + (8.3145 J K - 1 mol - 1 15E.14 The solution is provided in the MathCad® worksheet which is inserted below. 29 The plot of the Morse oscillator entropy against temperature, when compared to a similar plot for the harmonic oscillator has the greater number of available energy states at any temperature. However, the difference is remarkably small. 15E.16 A Sackur-Tetrode type of equation describes the translational entropy of the gas. Here $1/2 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ with $q xT = |X[15B.7a]|(\beta h 2 || where X is the length of the surface. Therefore, <math>30 (2 \pi m) q T = q xTq yT$ 1) = $|\operatorname{gm} n | T | \int (e 2 \operatorname{gm}) (e \operatorname{gm}) R + R \ln | R \ln | = | = (NA) (NA) Sm = = (2\pi e 2 \operatorname{m} \sigma m) | \sigma | R = \ln | 2 | | \sigma m n | (h NA \beta) (Call this molar entropy of the mobile two-dimensional) gas: \Delta Sm = Sm2 - Sm3$. The three-dimensional film Sm2. The molar entropy of the mobile two-dimensional film Sm2. value is given by the Sackur-Tetrode equation $[|(2\pi m/3/2 V)|]$ Sm = R ln $\{e5/2 | 2 | Nm \} [15E.11a] \ h\beta | A | | | So [|(\sigma)(h2\beta) 1/2]| e 2 (2\pi m/h2\beta) \times (\sigma m/NA) = R ln <math>\{|m| \times | \Delta Sm = R \ln 5/2 \} \ V | (2\pi m e)|| e (2\pi m/h2\beta) 3/2 \times (Vm/NA) \ | m | 12 \ Cp, m (\gamma RT), cs = | |, \gamma = CV, m (M) 15E.18$ (a) Cp, m = CV, m + R CV, m = 12 $R(3 + \nu R^* + 2\nu V^*) = 12 R(3 + 2) = 52 R C p, m = 52 R + R = 72 R 7 \gamma = = 1.40$; hence $5(1.40 RT) cs = | M | / (c) 12 CV, m = 12 R(3 + 2) = 52 R C p, m = 52 R + R = 72 R 7 \gamma = = 1.40$; hence 5(1.40 RT) cs = | M | / (c) 12 CV, m = 12 R(3 + 2) = 52 R C p, m = 52 R3) = 3R C p,m = 3R + R = 4R, (4RT) cs = | (3M || 4 3 y = , For air, 12 ((1.40) × (2.48 kJ mol - 1)) cs | = 350 m s - 1 = | -3 - 1 29 10 kg mol × () 15E.20 (a) The heat capacity is () CV = $-k\beta 2 | \partial U | [15E.5] (\partial \beta | V First express U as a function of \beta: N \varepsilon e - \beta \varepsilon U = U (0) + 1 + e - \beta \varepsilon 31 12$ Hence CV (∂U) N $\varepsilon 1 × (-\varepsilon e - \beta \varepsilon) × (-N \varepsilon 2e - \beta \varepsilon) - = -2 20 n s - 1 = | -3 - 1 29 10 kg mol × () 15E.20 (a) The heat capacity is () CV = <math>-k\beta 2 | \partial U | [15E.5] (\partial \beta | V First express U as a function of \beta: N \varepsilon e - \beta \varepsilon U = U (0) + 1 + e - \beta \varepsilon 31 12$ Hence CV ($\partial U | N \varepsilon 1 × (-\varepsilon e - \beta \varepsilon) × (-N \varepsilon 2e - \beta \varepsilon) - = -2 20 n s - 1 = | -3 - 1 29 10 kg mol × () 15E.20 (a) The heat capacity is () CV = <math>-k\beta 2 | \partial U | [15E.5] (\partial \beta | V First express U as a function of \beta: N \varepsilon e - \beta \varepsilon U = U (0) + 1 + e - \beta \varepsilon 31 12$ Hence CV ($\partial U | N \varepsilon 1 × (-\varepsilon e - \beta \varepsilon) × (-N \varepsilon 2e - \beta \varepsilon) - = -2 20 n s - 2 20 n s = -\beta \epsilon 2 | \partial \beta / V 1 + e (1 + e - \beta \epsilon) 2 - k \beta$ Collecting terms over a common denominator yields kN $\beta 2\epsilon 2e - 2 \epsilon kN (1/kT) 2 \epsilon 2e - 2 \epsilon m / RT R(\epsilon m / RT) 2 \epsilon 2e - 2 \epsilon kN (1/kT) 2 \epsilon 2 e - 2 \epsilon kN (1/kT) 2$) e so CV, $m = -\epsilon / RT (1 + e m) 2$ (b) It is convenient to plot CV, m (in units of R) as a function of x where $x = kT/\epsilon = RT/\epsilon m$. See Figure 15C.7 (c) F may be used to find a more accurate value for xmax of 0.775 and for c(xmax) of 0.0775. A formula for the maximum is determined by the criterion that dCV, m/R) d() 2e -2/x = | 2 dx | x (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dx x 4 (1 + e - 1/x) | dxxmax - xmax e -1/ xmax = 0 This is a transcendental equation so it is necessary to solve for xmax with a numerical method. xmax may be numerical method. xmax may be numerical method. represents the best value of xmax. Tmax = 32 ε m xmax R with xmax determined as above. 15F Derived functions Answer to discussion question 15F.2 The relationship between the equilibrium constant and the standard molar partition functions of the species involved is [15F.10b] [| (q O)v J || K = { [] | J,m |} e -\Delta r EO / RT | || U | N A || J he equilibrium constant, of course, is related to the Gibbs functions of reactants and products, as discussed
in Topic 6A. The Gibbs function itself is often interpreted as reflecting the entropy of the surroundings). We can clearly identify an energetic portion in the above expression, the exponential involving $\Delta r E0$, with which we are not concerned at the moment. The remaining portion, the continued product (quotient) is highly reminiscent of the equilibrium (J Thus, to the extent permitted by energetic considerations, the activities of reactants and products in a mixture at equilibrium are directly proportional to the number of accessible states they have. are directly proportional to the number of accessible states of that species. Finally, recall that each species involved with respect to the ground state of that species. If we computed the partition functions would absorb the energetic factor involving $\Delta r E0$. (Note that that energetic term has the same functional form as a Boltzmann factor.) So we conclude by saying that species activities in an equilibrium mixture are directly proportional to the number of accessible states they have—period. $-nRT \ln [15F.9 \text{ for non-tranlational modes}] \text{ Therefore, we first evaluate } qR \text{ and } qV. \text{ So } qR = 1 (kT) | |2 (hc) || + 3.35 \times 10 ((3.553) \times (0.4452) \times (0.3948) |GmR - GmR (0) = -(8.3145J \text{ mol} - 1K - 1) \times (298K) \ln 3.35 \times 103 = -20.1 \times 103 \text{ J mol} - 1 = -20.1 \text{ kJ} \text{ mol} - 1 \text{ mol} - 1 \text{ mol} + 1 \text{ mol} +$ function for each vibrational mode is given by [15B.15] 1 hcv θ V = 1.4388 K × (v / cm - 1) = qV where = $-\theta$ V / T k 1 - e The vibrational partition functions are so small that we are better off taking lnq V = $-\{1.4388(1110)/298\}$ = 4.70 × 10-3 and lnq 3V ≈ e $-\{1.4388(1042)/298\}$ = 6.53 × 10-3 33 lnq $2V \approx e - \{1.4388(705)/298\} = 3.32 \times 10 - 2 \text{ GmV} - \text{GmV}(0) = -(8.3145 \text{ J mol} - 1 \text{ K} - 1) \times (298 \text{ K}) \times (4.70 \times 10 - 3 + 3.32 \times 10 - 2 + 6.53 \times 10 - 3) = -110 \text{ J mol} - 1 = -0.110 \text{ kJ mol} - 1 \text{ SF}.2(b)$ See the solution to Exercise 15E.3(b). At 400 K hc × (7918.1 cm - 1) (1.4388 cm K) × (7918.1 cm - 1) At 400 K, $\beta \epsilon = = 22.78 \text{ kT} 500 \text{ K}$ Therefore, the contribution to Gm is $Gm - Gm (0) = -RT \ln [15F.9 \text{ for non-tranlational modes}] Gm - Gm (0) = -(8.3145] K - 1 \text{ mol} - 1) \times (400 \text{ K}) \times \ln(3 + 2 \times e - 28.48) = -3.65 \text{ kJ} \text{ mol} - 1 \text{ Comment. The contribution of the excited state is negligible at this temperature}$ NJ,m $|| \times e - \Delta r E0 / RT [15F.10b] = q mO (79 Br 81Br) 2 (A) Each of these partition functions is a product q mO = q mTq Rq Vq E with all qE = 1. The ratio of the translational partition functions. Although the$ moments of inertia cancel in the rotational partition functions, the two homonuclear species each have $\sigma = 2$, so q R (79 Br 2) q R (81 Br 2) = 0.25 q R (79 Br 2) q R (79 Br 2) q R (79 Br 81 Br) 2 The value of $\Delta rE0$ is also very small compared with RT, so K ≈ 0.25 Solutions to problems 15F.2 H 2O + DCl HDO + HCl (all in gas phase) The equilibrium constant is [15F.10, with $\Delta r E0$ here defined as the molecular, not molar, energy difference; NA factors cancel] q O (CHD3) q mO (HCl) - $\beta \Delta r E0 K = mO e q m (CD 4) q mO (HCl) Use partition functions is 3/2 q mT (HDO) q mT (HCl) (M (HDO) M (HCl)) (19.02 \times 36.46) = | = | = | = | = 1.041 T T q m (H 20.41 T T q m (H$ O)q m (DCl) $(M (H 2 O) M (DCl) / (18.02 \times 37.46)$ The ratio of rotational partition functions is, with $\sigma = 2$ for H2O and $\sigma = 1$ for the others. (H O)C (HDO)1/2 B (HCl) 1 q R (H2 O) q R (HDO) B 3/2 (27.88 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 1.707 (23.38 \times 14.51 \times 9.29)1/2 \times 5.449 = 2 \times 14.51 \times 14.5 $9.102 \times 6.417)1/2 \times 10.59$ The ratio of vibrational partition functions (call it fV) is q V (HDO)q V (HCl) q (2726.7)q (1402.2)q (3707.5)q (2991) = fV = V q (H 2O)q V (DCl) q (3656.7)q (1402.2) + 3707.5 + 2991) 2 hc - (3656.7 + 1594.8) - (3755.8)q (2145) where = q (x) 1 1 = - hcv / kT - 1.4388 x / (T / K) 1 - e 1 - e 34 \Delta r E0 1 = {(2726.7 + 1402.2 + 3707.5 + 2991) 2 hc - (3656.7 + 1594.8) - (3656.7 3755.8 + 2145) cm -1 = -162 cm -1 So the exponent in the energy term is ΔE hc $\Delta E = 1.4388 \times (-162) 233 - \beta \Delta r E0 = -r 0 = -x r 0 \times = - + kT k hc T T / K T / K Therefore$, $K = 1.041 \times 1.707 \times f V \times e 233/(T / K) = 1.777 f Ve 233/(T / K) = 1.777 f Ve 233/(T / K)$ We then draw up the following table T/K 100 200 300 400 500 600 700 800 900 1000 K 18.3 5.70 3.87 3.192 (T / K) = 1.777 f Ve 233/(T / K) = 1.777 f Ve 233/(T / K) $2.85\ 2.65\ 2.51\ 2.41\ 2.34\ 2.29$ and specifically (a) K = $3.89\ at\ 298\ K$ and (b) K = $2.41\ at\ 800\ K.\ 15F.4$ The standard molar Gibbs energy is given by qO q O q mTO R V E = GmO - GmO (0) RT ln m = where m q q q [15F.9] NA NA NA Translation: q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values
of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants, we obtain q mT O kT h = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants) = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants) = $= \Lambda O 3$ NA p Λ (2π mkT)1/2 After substituting the values of the constants) = = (\Lambda O 3 N A P \Lambda O A P \Lambda O A P \Lambda O A P \Lambda O $O = 2.561 \times 10 - 2 (T / K)5/2 \times (M / g mol - 1)3/2 NA = (2.561 \times 10 - 2) \times (2000)5 2 \times (38.90)3 2 = 1.111 \times 109 Rotation of a linear molecule: qR = kT \sigma hcB The rotational constant is = B 4 \pi cI 4 \pi c \mu R 2 where \mu = mB mSi 10 - 3 kg mol - 1 (10.81) \times (28.09) = 1.296 \times 10 - 26 kg \times = 23 - 1 10.81 + 28.09 mB + mSi 6.022 \times 10 mol so = B 1.0546 \times 10 - 20 kg \times 10 - 20 kg \times 10 - 26 kg \times 10 - 20 kg \times 10 - 20$ 10-34 J s = 0.5952 cm -1 4 π (2.998 × 10 cm s) × (1.296 × 10-26 kg) × (190.5 × 10-12 m)2 and qR = 10 - 1.2000 K k = 2335 × hc 2(0.5952 cm -1) T K) 1 - exp (1 = -1.4388(772) 2000) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) 2000) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) 2000) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388(772) - 2.467) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388) = 2.467 The Boltzmann factor for the lowest-lying electronic excited state is (-(1.4388) - 1.4388) × (8000) $-3 \exp |$ $\parallel = 3.2 \times 10\ 2000$ (The degeneracy = 2, orbital degeneracy = 4, orbital degeneracy = 2, orbital degeneracy = 4, orbital degeneracy = 2, orbital degeneracy = 4, orbital degeneracy = 2, orbital degenerac 109) × (2335) × (2.467) × (4.013)] = 5.135 × 105 J mol-1 = 513.5 kJ mo $(T K)52(M g mol-1)32NA q mTO = (2.561 \times 10 - 2) \times (10.00)52 \times (36.033)32 = 1752NA$ Rotation of a nonlinear molecule First, at 10.00 K: 1 (kT)(π)1.0270 (T K)32 = × || cm -3)12 σ || hc || || ABC σ (ABC The rotational constants are 32 12 = qR 3 1 B C = () = so A B || 4\pi c || I I], 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || A B C (1.0546 \times 10 - 34 J s) B C = A || 4\pi c || $(2.998 \times 1010 \text{ cm s} - 1)$ ||×3 (1010 m - 1)6 (39.340) × (39.032) × (0.3082) × (mu 2)3 × (1.66054 \times 10 - 27 \text{ kg mu} - 1)3 = 101.2 \text{ cm} - 3 \text{ qR} = \text{so } 1.0270 (10.00)3 2 = 1.614 \times 2 (101.2)1 2 \text{ Vibration: } \text{qV} = 1 = 1 - \text{e} - \text{hcv kT} 1 - \text{exp} (1 = -1.4388 (v \text{ cm} - 1) \text{ T K}) 1 - \text{exp} (1 = 1.0001 - 1.4388 (63.4) 10.00) Even the lowest-frequency mode has a vibrational partition function of 1; so the stiffer vibrations have qV even closer to 1. The degeneracy of the electronic ground state is 1, so qE = 1. Putting it all together yields $GmO = (10 \text{ K}) - GmO(0) (8.3145 \text{ J mol} - 1 \text{ K} - 1) \times (10.00 \text{ K}) \ln[(1752) \times (1.614) \times (1) \times (1)] = 660.8 \text{ J mol} - 1 \text{ Now at } 1000 \text{ K Translation}: q mTO = (2.561 \times 10 - 2) \times (1000) 5.2 \text{ Mol} + 2.561 \times 10 - 2 \text{ Mol}$ × $(36.033)32 = 1.752 \times 108$ NA Rotation: qR = q1V Vibration: $1.0270(1000)32 \times = 16142(101.2)121111.47 q2V = = 1.207 = (1.4388) \times (63.4)(1.4388) \times (63.4)(1$ = - GmO (0) (8.3145 J mol -1 K -1) × (1000 K) V × ln[(1.752 × 108) × (1614) × (14.62) × (1)] = 2.415 × 105 J mol -1 = 241.5 kJ mol -1 the whole molecule rotates into a new direction—and follows the field is high, a molecule cannot change in direction of the applied field and the dipole moment then makes no contribution to the polarization of the sample. Because a molecule takes about 1 ps to turn through about 1 radian in a fluid, the loss of this contribution to the polarization occurs when measurements are made at frequencies greater than about 1011 Hz (in the microwave region). We say that the orientation polarization, the polarization arising from the permanent dipole moments, is lost at such high frequencies The next contribution to the polarization to be lost as the frequency is raised is the distortion polarization, the polarization that arises from the distortion of the nuclei by the applied field. The molecule is bent and stretched by the applied field is approximately the inverse of the molecular vibrational frequency, so the distortion polarization disappears when the frequency of a particular mode of polarization occurs in stages: as shown in Justification 16A.3, each successive stage occurs as the incident frequency of a particular mode of vibration. At even higher frequencies, in the visible region, only the electrons are mobile enough to respond to the rapidly changing direction of the electron distribution, and the surviving contribution to the molecular polarizability is called the electronic polarizability. Solutions to exercises 16A.1(b) A molecule with a centre of symmetry may not be polar. 16A.2(b) μ res = (μ12 + μ12 $22 + 2 \mu 1 \mu 2 \cos \theta$)1/2 [16A.3a] = [(2.5) + (0.50) + (2) × (2.5) × (0.50) × (cos120)]1/2 = D 2.3 D 2 2 16A.3(b) $\mu = \sum Qi ri = 4e(0) - 2er2 - 2er3$ where r2 = ix2 and r3 = ix3 + jy3 i x2 = +162 pm x3 = r3 cos 30° = = y3 r3 sin = 30° (+143 pm) × (0 = The components of the vector sum are the sums of the vector sum are the sum of the vector sum are the components. { } μ x = -2ex2 - 2ex3 = -2e × (162) + (124) pm = -e × (572 nm) μ y = -2ey3 = -2e × (71.5 pm) = -e × (143 pm) 16:1 (μ = μ + μ y2) 1/2 2 x { [16A.4b] = × e (572 nm) μ y = -2ey3 = -2e × (71.5 pm) = -e × (143 pm) 16:1 (μ = μ + μ y2) 1/2 2 x { [16A.4b] = × e (572 nm) μ y = -2ey3 = -2e × (71.5 pm) = -e × (143 pm) 2 2 } 1 2 = (1.602 × 10 - 19 C) × (590 × 10 - 12 m) D 28 D = (9.45 × 10 - 29 C m) × (1 3.335641 × 10 = -30 Cm) The angle that μ makes with x-best of the the term of term axis is given by $(572) | \mu x | 572 \theta \theta \cos -1| = \cos so = = |14.2^{\circ} 590 \mu | 590 | 16A.4(b)$ Polarizability α , dipole moment μ , and molar polarization Pm are related by $(N) (\mu 2) Pm = |A| \times |\alpha + |[16A.12] 3kT || 3\epsilon 0 ||$ In order to
solve for α , it is first necessary to obtain μ from the temperature variation of Pm. $\mu 2 3\epsilon 0 Pm \alpha + = 3kT NA (3\mu k) \times (2\mu k)$ T1 - T1'=) 2 Therefore, and hence $\mu 2 = (3\epsilon 0) \times P - P' [Pat T, P'at T'] |N| (mm) mm (A) 9\epsilon 0 k \times (Pm - Pm') (11) NA \times |-||TT'| 9 \times (8.854 \times 10 - 12 J - 1 C 2 m - 1) \times (75.74 - 71.43) \times 10 - 6 m3 mol - 1 1 1 () (6.022 \times 1023 mol - 1) \times |-|| 320.0 K 421.7 K |= 1.045 \times 10 - 59 C2 m 2 1D () 3.23 10 - 30 C m$ × $0.968 \text{ D}\mu = x = -30 \sqrt{3.33564 \times 10 \text{ Cm}/3\epsilon} 0 \text{ Pm}\mu 2 - \text{NA } 3kT \alpha = 3 \times (8.854 \times 10 - 12 \text{ J} - 1 \text{ C} 2 \text{ m} - 1) \times (75.74 \times 10 - 6 \text{ m} 3 \text{ mol} - 1) 6.022 \times 1023 \text{ mol} - 1 = 2.56 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M}|\epsilon r = \text{M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 [16A.6] 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M} |\epsilon r = 1 \text{ M} \sqrt{\epsilon r} = 3 \times (8.854 \times 10 - 29 \text{ m} 3 (16A.6) 4\pi\epsilon 0 16A.5(b) \text{ M} = 85.0 \text{ g mol} - 1 \rho \text{ Pm} \times (\epsilon r + 2) [16A.11] \text{ M} 2 \rho \text{ Pm} (\rho \text{ Pm}) 1 + |1 - \text{M} |\epsilon r = 1 \text{ M} \sqrt{\epsilon r} + 1 \text{ M} \sqrt{\epsilon r} = 3 \times (\epsilon r + 1 \text{ M} 2 \rho \text{ Pm} + 1 \text{ M} 2 \rho \text{ Pm} \rho \text{ M} 2 \rho \text{ Pm} \rho \text{ Pm} \rho \text{ M} 2 \rho \text{ Pm} \rho \text$ $-=1 \ \text{er} = M + 2 \ \rho \ \text{Pm} \ M - \rho \ \text{Pm} \ 85.0 \ \text{g} \ \text{mol} - 1 + 2 \times (1.92 \ \text{g} \ \text{cm} - 3) \times (32.16 \ \text{cm} 3 \ \text{mol} - 1) = 8.97 \ 16.2 - 1.045 \times 10 - 23 \ \text{K} - 1) \times (320.0 \ \text{K}) \ \text{er} - 1 \ \rho \ \text{Naa} \ 1/2 \ (\text{e} = [16A.14] \ \text{and} \ [16A.13] \ \text{r}) \ \text{er} + 2 \ 3M \ \epsilon \ 0 \ 16A.6(b) \ \text{nr} \ \text{Therefore}, \ 3M \ \epsilon \ 0 \ \rho \ \text{Na} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ \text{mol} \ \alpha = (nr^2 - 1) \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \ | \ 2 \$ $nr + 2/3 \times (65.5 \text{ g mol} - 1) \times (8.854 \times 10 - 12 \text{ J} - 1 \text{ C2 m} - 1) (1.6222 - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.2 \times 10 - 30 \text{ m}^3) = 2.45 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 2 \text{ Mac} = 3M \epsilon 0 (865 \times 10 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (6.022 \times 1023 \text{ mol} - 1) | (1.6222 + 2) | = 3.40 \times 10 - 40 \text{ J} - 1 \text{ C2 m} - 1) \times (2.99 \times 106 \text{ g m} - 3) \times (2.99 \times 106$ $(6.022 \times 1023 \text{ mol}-1) \times (2.45 \times 10-40 \text{ J}-1 \text{ C2 m} 2) = 0.0665 3 \times (72.3 \text{ g mol}-1) \times (8.85419 \times 10-12 \text{ J}-1 \text{ C 2 m} -1) 3$ and solve the Clausius – Mossotti eqn [17A.13] for ε r with which we calculate the refractive index. ε r $-1 = C [16A.13, \text{ the Clausius} - \text{Mossotti eqn}] \varepsilon$ r $+ 2 1 + 2C \varepsilon$ r $= 1 - C 1 + 2 \times (0.0665) = 1 - 0.0665 = 1.2137 2 \text{ nr} \varepsilon$ r $= 1 - C 1 + 2 \times (0.0665) = 1 - 0.0665 = 1.2137 2 \text{ nr} \varepsilon$ r $= 1 - C + 2 \times (0.0665) = 1 - 0.0665 = 1.2137 2 \text{ nr} \varepsilon$ $[17.17] = 1 = (1.2137) 12 1.10 16A.8(b) = \mu 5.17 \times 10 - 30 C m$ for bromobenzene $(157.00 \text{ g mol} - 1) \alpha = 4\pi \epsilon 0\alpha' [16A.6] = (1.11265 \times 10 - 29 \text{ m}3) = 1.67 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2 \text{ N}3 \epsilon 0 = Pm (\mu 2)\alpha + ||16A.12| 3kT || ((1.67 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2) || |6.022 \times 10 \text{ mol} 2 - 30|| = 5.17 10 \text{ Cm} \times () ||3 \times (8.85419 \times 10 - 29 \text{ m}3) = 1.67 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2 \text{ N}3 \epsilon 0 = Pm (\mu 2)\alpha + ||16A.12| 3kT || (1.67 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2) || |6.022 \times 10 \text{ mol} 2 - 30|| = 5.17 10 \text{ Cm} \times () ||3 \times (8.85419 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2) || |6.022 \times 10 \text{ mol} 2 - 30|| = 5.17 10 \text{ Cm} \times () ||3 \times (8.85419 \times 10 - 39 \text{ J} - 1 \text{ C}2 \text{ m} 2) ||$ 10-12 J - 1 C 2 m - 1 | + 3 × (1.3807 ×
10-23 J K - 1) × (298.15 K) | = 8.69 × 10-5 m 3 mol - 1 23 - 1 Let - 1 (1.491 × 106 g m - 3) × (8.69 × 10-5 m 3 mol =) 0.825 = -1 M 157.00 g mol and solve the Debye eqn [16A.11] for εr . $\varepsilon r - 1 = C [16A.11]$, the Debye eqn [16A.11] for εr . $\varepsilon r - 1 = C [16A.11]$ for $\varepsilon r = 1 - 0.825 = -1 M 157.00 G m - 3 M C = -1 M 157.00 G m - 3 M$ Solutions to problems 16A.2 The point charge model can be used to estimate the magnitude of the electric dipole moment magnitude of the electric dipole moment magnitude as a function of φ (defined in Fig. 16A.1b as a view down the z axis of the O-O bond). Each hydrogen atom has a partial charge of δ; each oxygen atom has a partial charge of -δ. The dipole moment magnitude of the electric dipole moment of hydrogen atom has a partial charge of -δ. The dipole moment magnitude of the electric dipole moment magnitude of the electric dipole moment of hydrogen atom has a partial charge of -δ. The dipole moment magnitude of the electric dipole moment magnitude of the electric dipole moment of hydrogen atom has a partial charge of -δ. The dipole moment magnitude of the electric dipole moment magnitude o is $\mu = (\mu \cdot \mu) 1/2 \{ = (\mu x 2 + \mu y 2 + \mu z 2) \}$ where $\mu x = \sum QJ xJ = \delta \times xH1 - xO1 - xO2 + xH2 [16A.4a,b]$, etc. 1/2 J We will use the Cartesian coordinate system defined in Fig. 16A.1a. The bond lengths are IOH = 97 pm and IOO = 149 pm. We also use the ratio lratio = IOO / IOH = 1.54 and calculate μ in units of δ IOH so that it is unnecessary to estimate the magnitude of δ . The O-O-H bond angle, θ , may be estimated as 90° but we will use the experimental value of 100°. The computations of μx , μy , and μz require the coordinates of each atom; those of H1 and the oxygen atoms are shown in Fig. 16A.1a. (IOHcos($\theta - 900$), $0, -1OHsin(\theta - 900)$) x H1 H2 IOH 1800 - θ IOO z (0,0,0) H1 ϕ (0,0,100) y H2 (b) (a) Figure 16A.1 The coordinates of H2 can be determined by analogy to the relationships between Cartesian coordinates. They are: x lOH sin (180° - θ) = Substitution of variables into eqn. 16A.4b, yields (μ / δ lOH) 2 = = = ($\mu x / \delta$ $10H + (\mu y / \delta IOH) + (\mu z / \delta IOH) + (\alpha z /$ at each φ . Fig. 16A.2 is a plot of the variation. As expected, there the dipole is a maximum of almost twice the single O-H bond dipole when the hydrogen atoms are eclipsed and it is zero when they have a gauche conformation. φ / deg 0 15 30 45 60 φ / radians sq(μ / δ 1) 0 0.261799 0.523599 0.785398 1.047198 3.879385 3.813292 3.619516 $3.311262\ 2.909539\ 16:4\ \mu\/\delta l\ 0.45\ 0.65\ 0.65\ 0.65\ 1.902502\ 1.819687\ 1.705737\ Figure\ 16A.2\ deg\ 16A.4\ \pm\ Let\ the\ partial\ charge\ on\ the\ carbon\ atom\ equal\ \delta e\ and\ the\ N-to-C\ distance\ equal\ l.\ Then,\ \mu\ \delta =\ =\ el\ [16A.4a]\ or\ \delta\ \delta\ \mu\ el\ C\ m\ D\ -1\)\ =\ 0.123\ (1.602\ -1.90\$ ×10-19 C) × (299 ×10-12 m) (1.77 D) × (3.3356 ×10-30 16A.6 The induced dipole moment μ^* is given by $4\pi\epsilon \ 0\alpha' = 4\pi\epsilon \ 0r \ 2r^2$ Consequently, the dipole-proton distance needed to induce a particular dipole is = = $4\pi\epsilon \ 0\alpha' = 4\pi\epsilon \ 0r^2 \ r^2$ Consequently, the dipole-proton distance needed to induce a particular dipole is = = $4\pi\epsilon \ 0\alpha' = 4\pi\epsilon \$ × (3.336 × 10-30 C m D -1) || / 2 NA μ 2 M (ϵ -1) 4 π [16A.12, with α = 4 $\pi\epsilon$ 0 α '] 16A.8 Pm =× | r |[16A.11] and Pm =N A α ' + ρ (ϵ r + 2) 3 9 ϵ 0 kT Eqn 16A.12, with α = 4 $\pi\epsilon$ 0 α '] 16A.8 Pm =× | r |[16A.11] and Pm =N A α ' + ρ (ϵ r + 2) 3 9 ϵ 0 kT Eqn 16A.12, with α = 4 $\pi\epsilon$ 0 α '] 16A.8 Pm =× | r |[16A.12] indicates that, when the permanent dipole moment in the presence of the applied 4π field (i.e., free rotation), a plot of Pm against 1/T should be linear with an intercept at 1/T = 0 equal to N Aa 3 N μ 2 dPm equals A. Eqn 16A.13], in the case for which either the molecules are non-polar or because the 3 frequency of the applied field is so high that the molecules cannot orientate quickly enough to follow the change in direction of the field. expression, Pm = To examine the possibility that either solid or liquid methanol exhibits the change in direction of the field. against 1/T. The molar polarization Pm is calculated with eqn 16A.11 at all temperatures and, since the data have been corrected for the variation in methanol density, we use $\rho = 0.791$ g cm-3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These
problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 16:5 θ / $^{\circ}$ C T/K 1000 T /K ϵ r ϵ r -1ϵ r +2 Pm / (cm3 for all entries and M = 32.0 g mol-1. ‡ These problems were supplied by Charles Trapp and Carmen Giunta 10:5 θ / $^{\circ}$ C /K ϵ C +2 mol-1) -185 88 -170 103 -150 123 -140 133 -110 163 -80 193 -50 223 -20 253 0 273 20 293 11.3 9.69 8.12 7.51 6.13 5.18 4.48 3.95 3.66 3.41 3.2 3.6 4 5.1 67 57 49 43 38 34 0.42 0.46 0.50 0.58 0.957 0.949 0.941 0.933 0.925 0.917 17.1 18.8 20.2 23.4 38.7 38.4 38.1 37.7 37.4 37.1 Figure 16A.3 40 Pm / cm3 mol-1 35 liquid phase 30 solid phase 25 melting point 20 15 2 4 6 8 10 12 1000 K / T Inspection of Figure 16A.3 reveals that the molar polarization Pm is not a linear function of 1/T for either phase. Thus, we conclude that the conditions of eqns 16A.12 and 16A.13 are not applicable and it is not possible to extract reliable values for either the polarizability volume or the dipole moment from this data. The data does provide valuable conceptual information about molecular motion in the condensed phases. Figure 16A.3 indicates that, as the temperature of liquid methanol is reduced, Pm increases less rapidly than would be expected for the linear case of thermal equilibrium of the dipole with the applied field. The progression toward lower temperatures appears to have a negative second-order regression fit for $\theta \leq -110^{\circ}$ C reflects this significant non-linearity: Pm / cm3 mol-1 = 31.246 + 2.3788 × (103 K / T) - 0.1904 × (103 K / 0.9914 This indicates that hydrogen-bonding between methanol molecules is hindering molecular rotation and reducing the orientation. The effect extends below the melting point with the -110°C data point exhibiting liquid-like, hindered rotation. The large decline of Pm below -110°C is interpreted as corresponding to a stronger hindrance of the dipole moment rotation but the non-constancy of Pm seems to indicate that rotational excitation is never completely eliminated. 16A.10 Calculate the dipole moment of H2O and its polarizability volume. N μ 2 4 π Pm = N A α' + A [16A.12, with α = 4 π ϵ 0 α'] 3 9 ϵ 0 kT Eqn 16A.12 indicates that a plot of Pm against 1/T should be linear with a slope, N μ 2 dPm , equal to A and a 9 ϵ 0 k d (1/T) 4 π N A α . Therefore, we draw up the following table and prepare a plot f Pm 3 against 1/T. If it is linear, we perform a linear least squares regression fit of the plot so as to acquire the slope and intercept from which we calculate α and μ . A suitable plot is shown in Figure 16A.4. 1/T = 0 intercept that equals 16:6 T/K 1000 T /K Pm / (cm3 mol-1) 384.3 420.1 444.7 484.1 522.0 2.602 2.380 2.249 2.066 1.916 57.4 53.5 50.1 46.8 43.1 Figure 16A.4 The plot of Pm against 1/T is linear with a regression fit that gives an intercept of 3.44 cm3 mol-1 (not shown in the figure), and the slope is such that dPm/d(1/T) = 2.08×104 cm3 mol-1 K. It follows that $3 \times (3.44 \text{ cm} 3 \text{ mol} - 1)$ 3Pm (at intercept) $(1.36 \times 10 - 24 \text{ cm} 3 = = \alpha - 1.23 4 \pi \text{N} \text{ A} 4 \pi \times (6.022 \times 10 \text{ mol}) \mid 2 = 9\epsilon 0 \text{ k} dPm \text{ N} \text{ A} d(1/T) \mid 9 \times (8.85419 \times 10 - 23 \text{ J} \text{ K} - 1) \mid 3 - 2 - 1 \text{ k} \times (2.08 \times 10 \text{ mol} \text{ K}) 23 - 16.022 \times 10 \text{ mol} \mid 1/2 \text{ 1D} (3.80 \times 10 - 59 \text{ C2 m} 2 + 10 \text{ mol}) \mid 2 = 9\epsilon 0 \text{ k} dPm \text{ N} \text{ A} d(1/T) \mid 9 \times (8.85419 \times 10 - 23 \text{ J} \text{ K} - 1) \mid 3 - 2 - 1 \text{ k} \times (2.08 \times 10 \text{ mol} \text{ K}) 23 - 16.022 \times 10 \text{ mol} \mid 1/2 \text{ 1D} (3.80 \times 10 - 59 \text{ C2 m} 2 + 10 \text{ mol}) \mid 2 = 9\epsilon 0 \text{ k} dPm \text{ N} \text{ A} d(1/T) \mid 9 \times (8.85419 \times 10 - 23 \text{ J} \text{ K} - 1) \mid 3 - 2 - 1 \text{ k} \times (2.08 \times 10 \text{ mol} \text{ K}) 23 - 16.022 \times 10 \text{ mol} \mid 1/2 \text{ 1D} (3.80 \times 10 - 59 \text{ C2 m} 2 + 10 \text{ mol} \text{ K}) = 0$ $1.85 \text{ D} \times |\mu| = -30 \sqrt{3.33564 \times 10 \text{ Cm}}$ () 16A.12 Since the refractive index nr and, therefore, the relative permittivity ε r are close to 1, we infer that the dipole moment does not contribute to the molar polarization because either the gas phase molecules are nonpolar or the molecular rotational frequency is much lower than the frequency of the applied electric field, which $\varepsilon - 1$ is the case for infrared, visible, and ultraviolet radiation. Furthermore, the observation that the ratio $C \equiv r \varepsilon r + 2$ must be much less than 1 greatly simplifies mathematical manipulations. $\varepsilon r - 1 \rho N A \alpha \rho M p / RT$, perfect gas] $\equiv C = [16A.13, Clausius - Mossotti eqn] = [\rho = M \varepsilon r + 2 3 \varepsilon 0 3\varepsilon 0 kT Solving the$ Clausius-Mossotti eqn for εr gives 1 + 2C αp where C = $\varepsilon r = 1 - C 3\varepsilon 0 kT = (1 + 2C) \times (1 - C + C 2 - C 3 +)$ [Taylor series expansion of (1 - C) - 1 for C 1] = 1 + C [Second order and higher order terms] = 1 + αp $6\epsilon 0$ kT Thus, nr is linear in pressure p with an intercept equal to 1, which corresponds to a vacuum. The slope, $\alpha 6\epsilon 0$ kT, is so small (~10-4 bar-1) that we normally consider the refractive index of a gas to be 1.00. Very sensitive measurements of the refractive index as a function of pressure may be used to find the polarizability. Solving the above equation for α gives the computational equation using measured values of temperature, pressure, and refractive index: $\alpha = 6\epsilon 0 \text{ kT} \times (nr - 1) / p$ The polarizability volume is calculated with $\alpha' = \alpha / 4\pi\epsilon 0$ [16A.6] 16B Interactions between molecules Answers to discussion questions 16B.2 See Fig. 16A.2 of the text for typical charge arrays corresponding to electric multipoles. As a generality we may write $V \propto 1/r$ n + m -1 [16B.6] for the potential energy of interaction between a n-pole and an m-pole and an m-pole. More specifically, the interaction between a n-pole and an m-pole and an distance between O2 and the multipole. This is a steeper potential energy decrease with r than that observed for the Coulombic interaction between two point charges: V \approx 1/r. The steeper decline originates in the case for which r 1, where l is the separation of charge within the multipole, because, as r becomes relatively large, the array of charges lower order interaction terms to cancel. For example, the dipole terms within the monopole-quadrupole (m = 3) interaction potential cancel leaving only a 1/r3 term when r 1. We use the linear quadrupole charge order terms. Since we are interested in the case x = l/r 0 (see Brief illustration 18C.2 of the text for the significance of this distribution). f (x, z) = 18:15 $\infty \infty E = \infty 18C.4$ N e = $\int \rho(E) dE = \int \rho(E) d$ $exp\{(E - \mu)/kT\}$ must remain constant. It is apparent that, when $exp\{E/kT\}$ gets smaller as T grows larger for each value of E, it must be multiplied by a larger value of E, it must be multiplied by a larger value of E, it must be multiplied by a larger value of E, it must be multiplied by a larger value of E, it must be multiplied by a larger value of E, it must be multiplied by a larger value of E ($E - \mu$) / kT 0 18C.6 Tans and coworkers (S.J. Tans et al., Nature, 393, 49 (1998)) have draped a semiconducting carbon nanotube (CNT) over metal (gold in Fig. 18C.1) electrodes that are 400 nm apart atop a silicon surface coated with silicon dioxide. A bias voltage between the electrode and the thin silicon oxide layer (at least 100 nm thick) insulates the gate from the CNT circuit. By adjusting the magnitude of an electric field applied to the gate, current flow across the CNT may be turned on and off. Figure 18C.1 Wind et al., Applied Physics Letters, 80(20, May 20), 3817 (2002)) have designed (Fig. 18C.2) a CNTFET of improved current carrying capability. The gate electrode is above the conduction channel and separated from the channel by a thin oxide dielectric. In this manner the CNT-to-air contact is eliminated, an arrangement also reduces the gate oxide thickness to about 15 nm, allowing for much smaller gate voltages and a steeper subthreshold slope, which is a measure of how well a transistor turns on or off. Figure 18C.2 A single-electron transistor (SET) has been prepared by putting two bends in a CNT with the tip of an AFM (Fig. 18C.3). Bending 18:16 causes two buckles that, at a distance of 20 nm, serves as a conductance barrier. When an appropriate voltage is applied to the gate below the barrier, electrons tunnel one at a time across the barrier. Figure 18C.3 Weitz et al. (Phys. Stat. Sol. (b) 243, 13, 3394 (2006)) report on the construction of a single-wall CNT using a silane-based organic self-assembled monolayer
(SAM) as a gate dielectric on top of a highly doped silicon wafer. The organic SAM is made of 18-phenoxyoctadecyltrichlorosilane. This ultrathin layer (Fig. 18C.4) ensures strong gate coupling and therefore low operation voltages. Single-electron transistors (SETs) were obtained from individual metallic SWCNTs. Field-effect transistors made from individual semiconducting SWCNTs operate with gate-source voltages of -2 V, show good saturation, small hysteresis (200 mV) as well as a low subthreshold swing (290 mV/dec). Figure 18C.4 John Rodgers and researchers at the University of Illinois have reported a technique for producing near perfect alignment of CNT transistors (Fig. 18C.5). The array is prepared by patterning thin strips of an iron catalyst on quartz crystals and then growing nanometer-wide CNTs along those strips using conventional carbon vapor deposition. The quartz crystal aligns the nanotubes. Transistor development then includes depositing source, drain, and gate electrodes using conventional photolithography. Transistors made with about 2,000 nanotubes can carry currents of one ampere. The research group also developed a technique for transferring the nanotube arrays onto any substrate, including silicon, plastic, and glass. See Coskun Kocabas, Seong Jun Kang, Taner Ozel, Moonsub Shim, and John A. Rogers, J. Phys. Chem. C 2007, 111, 17879, Improved Synthesis of Aligned Arrays of Single-Walled Carbon Nanotubes and Their Implementation in Thin Film Type Transistors. Figure 18C.5 Further background discussion of carbon nanotube field-effect transistors (CNTFET) can be found at wikipedia.org. For a review of the CNT catalytic growth technique, methods to grow oriented long CNTs with controlled diameters, and process steps for the fabrication of both back and top-grated CNTFET see K.C. Narasimhamurthy and R. Paily, IETE Technical Review, 2011, V 28, Issue 1, 57, Fabrication of Carbon Nanotube Field Effect Transistor. 18C.8 Only two electronic levels are accessible to nitric oxide at low temperature. The ground state is a doubly degenerate $2\Pi 1/2$ state while the excited state is a doubly degenerate $2\Pi 3/2$ state that is 121.1 cm-1 above the ground state. These states originate from spin-orbital coupling of angular momentum. Let $\varepsilon = hcv$ be the energy separation between these levels, then the probabilities that a molecule is in one (p1/2) or the other level 18:17 (p3/2) are given by the following equations, which are derived from the Boltzmann distribution in the note below. $e-\epsilon / kT = -\epsilon / k$ 18C.10a for the molar paramagnetic susceptibility must be modified with the inclusion of a factor p3/2. = $p1/2 \chi m = 1$ and = p3/2 p3/2 NA ge2 $\mu 0 \mu B2$ S (S + 1) 3kT [18C.10a] Substitution of S (S + 1) = (m / ge μB) gives 2 [18C.9] where m is the magnetic moment into the above expression p3/2 NA $\mu 0 \mu B2$ (m / μB) 2 $\chi m = 3kT$ (m / μ) = B 3kT × + ec / kT NA μ 0 μ B2 2 () () ϵ /k = 174.2 K hcv / k = hc × 121.1 cm - 1 / k = where Thus, with m / μ B = 2 χ m = 6.286 × 10 - 6 m3 mol - 1 (T/K) × (1 + e174.2 / (T/K)) This relation gives the molar paramagnetic susceptibility of NO as a function of temperature. For example, χ m at 90 K is = χ m 6.286 × 10 - 6 m3 mol - 1 (T/K) × (1 + e174.2 / (T/K)) This relation gives the molar paramagnetic susceptibility of NO as a function of temperature. $(90)(90) \times 1 + e()$ The mass paramagnetic susceptibility is ()() 8.81 \times 10-9 m3 mol-1 / 0.03001 kg mol-1 = 2.94 \times 10-7 m3 kg-1 xmass = $\chi m / M$ = Wishing to compare this with the value found in the older literature, we must convert the SI unit of susceptibility to the cgs (or emu) unit by dividing the SI unit by 4π , converting the m3 to cm3, and converting kg to g. () $2.94 \times 10-4$ cm3 g $-1/4\pi = 23.4 \times 10-6$ cm3 cm3 cm3 cm3 cm3 cm3 (110 K) of nitric oxide. The curve is remarkably different than the χm (T) behavior of most paramagnetic substances. Paramagnetism is normally a property of the ground electronic state and, consequently, there is an inverse relation between χm and T [18C.10b] so that χm decreases with increasing T. Effective angular momentums of individual molecules align in a magnetic field at low temperature and become disoriented by thermal agitation as the temperature is increased. In the ground state at absolute zero, $\chi m = 0$. As T is increased from absolute zero, $\chi m = 0$. As T is increased from absolute zero, $\chi m = 0$. excited state and the observed paramagnetism increases as shown in Fig. 18C.6. Comment: The explanation of the magnetic properties of NO is more complicated by the solution here. In fact the full solution for this case was one of the important triumphs of the quantum theory of magnetism which was developed about 1930. See J. H. van Vleck, The theory of electric and magnetic susceptibilities. Oxford University Press (1932). Note: The Boltzmann distribution indicates that the probability that a molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the probability that the molecule is in energy level is given by p0 \approx g0 where g0 is the degeneracy of the ground state while the ground state while the ground state while the ground state where g0 is the degeneracy of the ground state where g0 is the degeneracy of the ground state where g0 is the degeneracy of the ground state where g0 is the degeneracy of the ground state where g0 is the degeneracy of the ground state where "1" that is ε above the ground state is given by p1 \propto g1e- ε/kT . For a two-level system the constant of proportionality is provided by the normalization condition that p0 + p1 = 1. Thus, the constant of proportionality is provided by the normalization condition that p0 + p1 = 1. Thus, the constant of proportionality is 1/(g0 + g1e- ε/kT) and the probabilities are p0 = g0/(g0 + g1e- ε/kT) and p1 = g1e- ε/kT . For a two-level system the constant of proportionality is 1/(g0 + g1e- ε/kT) and the probabilities are p0 = g0/(g0 + g1e- ε/kT). which g0 = g1 the probabilities simplify to those given at the top. 18:18 Figure 18C.6 18D The optical properties of solids Answers to discussion questions 18D.2 Figure 18D.1 is a simplified schematic of a light-emitting diode. The upper portion of the figure shows the electric circuit symbol of the LED. The lower portion represents the electron motion and energy flows of the LED when, as shown, it is forward-biased (see text Fig. 18C.9 and associated discussion). Electrons are represent with solid circles while electron holes are white circles Here's a list of important features that you should label within the figure: the location of both the p-type and n-type semiconductors, the junction between semiconductors, the line representing the energy of the conduction band, the line representing the energy of the valence band, electron flow in the circuit, flow of electrons and holes in the semiconductors, and light-emitting transitions. The intensity of radiative emissions depends upon the applied voltage but the wavelength depends upon the band gap energy. In addition to having the basic features of the LED, the laser diode must have a resonant cavity, which can be formed by using the high refractive index. 18:19 Figure 18D. Solutions to exercises 18D.1(b) Eg = hvmin h 6.626 × 10-34 J s (1 eV) vmin = = × 3.69 10-15 s -1 = 3.69 fHz | -19 | Eg 1.12 eV (1.602 × 10 J) Solutions to problems 18D.2 (a) = H^{+}\psi + or - v + or - \psi + or - and (H^{-} - v =)\psi + or - v + or - \psi + or - 0.2 \beta (vmon - v + or 0.5 nm. Figure 18D.2 The ratio of $\mu + 2/\mu - 2$ (and the relative intensitions) doesn't depend upon β or θ because $\mu + = 0$. To see this, we use the coefficients of the normalized wavefunctions for $\psi +$ and $\psi -$ and the overlap integral $S = \psi 1 | \psi 2 | 18:201 \rangle (c + or - 1) (x + or - 1) (x + or - 1) (x + or - 2) (1 +$ $+ c + or - 2 = 0 x + or - = \pm 1$ where c + or - 2 = -x + or - c + or - 10 (i) The coefficients must also satisfy the normalization condition. c + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 2y = 0 + or - 10 + or - 10distributed around the monomer transition. The lowest energy transition changes only slightly with N giving a value that goes to
25000 cm-1 + 2V = 25000 cm-1 + 2Vthe size of the chain. 18:21 Figure 18D.3 Integrated activities 18.2 The electron density distribution into eqn. 18A.3 for the scattering factor f yields a computational feasible expression for scattering from 1s (n = 1) and 2s (n = 2) atomic orbitals. ∞ sin ($4\pi\xi$ r) 2 sin θ f (ξ , Z, n) $4\pi\xi$ r r dr [18A.3] where ξ λ 2 2 ∞ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ λ 2 ∞ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ λ 2 ∞ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ λ 2 ∞ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ λ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] where ξ = 1 R(r, Z, n) $4\pi\xi$ r r dr [18A.3] orbital against $\xi = \sin(\theta)/\lambda$ for Z = 1 and 2. Scattering factor is a maximum in 18:22 the forward direction angle increases as the reflection angle increases. The scattering factor decreases as the reflection angle increases as the reflection angle increases as the reflection angle increases. The scattering factor of a 2s hydrogen-like orbital against $\xi = \sin(\theta)/\lambda$ for Z = 1 and 2. Scattering factor is a maximum in the forward direction angle increases as the reflection angle increases. The scattering factor decreases less rapidly for larger Z values. Also, the 2s scattering factor decreases far more rapidly with θ than that of the 1s scattering factor of part (a) so we say that an increase in the atomic number effectively moves the scattering factor away from the forward direction. 18:23 19 Molecular motion 19A Transport properties of a perfect gas Answers to discussion questions 19A.2 Simple molecular kinetic theory finds that the diffusion and viscosity coefficients are related to T, p, and the collision cross-section $\sigma = \pi d 2$ by the following expressions. It is important to recognize that these formulations are not applicable at either very low pressure where the mean free path becomes comparable to the container size or at very high densities where the mean free path becomes comparable to molecular size. Using L to represent container size, simple molecular size, simple molecular size, simple molecular size or at very high densities where the mean free path becomes comparable to the range σ 0 when t = 0 on account of the very (- b (x - x0) 2) \rightarrow 0 more strongly than 112 $\rightarrow \infty$. The term x0 + vv t in the concentration t expression is the movement of the centroid due to fluid flow, xcentroid. strong exponential factor e t To prepare a very general set of concentration profiles at a series of times without specifying either x0, vv, or D, define z and C as follows. x - xcentroid c C = and z = 1/2 1/2 c 0 / ($4\pi D h$) (4D h) The hour (h) has been chosen for the unit because of the slow pace of diffusion activity. With these definitions the concentration profiles as C against t at various times (1, 5, and 20 h) are displayed in Fig. 19C.2. 19:16 Figure 19C.2. 10:16 Figure 19C.2. 10:17 Figure 19C.2. 10:1 $y_j + zk$ 19C.13 Using the definitions N = NR + NL and n = NR - NL, solve for NR and NL to find NR = $\frac{1}{2}(N - n)$ P ($n\lambda$) = total number of paths (N L)! N R ! 2 N = N! { $\frac{1}{2}(N - n)$ } 2 N This is the "exact" random walk probability. After application of Stirling's approximation we have the "approximate" probability. PApprox may be written in terms of the variables (x,t) or (n,N) because $x = n\lambda$ and $t = N\tau$. 2 2 (2 τ) (2) - n2/2 N PApprox = ||e - x \tau/2t\lambda [19C.15] = ||e $\pi t \int \int (1 - N\tau) dt = 0$ for N = 6, 8,...180 using Mathcad Prime 2 and we plot PExact against N. We include a plot of the fractional deviation of PApprox against N from which we see that the deviation drops below 0.1% when N > 60. 1/ 2 1/ 2 19:17 19C.14 Eqn 19C.14, x 2 = 2 Dt, gives the mean square distance traveled in any one dimension in time t. We need the distance traveled from a point in any direction. The distinction here is the distinction between the one-dimensional and three-dimensional diffusion. The mean square three-dimensional diffusion. The mean square three-dimensional diffusion are independent. r 2 = x 2 + y 2 + z 2 [Pythagorean theorem] $r^2 = x 2 + y 2 + z 2$ [Pythagorean theorem] $r^2 = x 2 + y 2 + z$ $= 3 \times 2$ [independent motion] 3×2 Dt [81.14 for x 2] = 6 Dt = Therefore, $= t r^2 - 2 (1.0 \times 10 - 6 m) 2 = = 1.7 \times 10 s - 11 2 - 16 D 6(1.0 \times 10 m s)$ 19:18 Integrated activities 19B.2 The rate constant, kr, for a transport process in which a molecule and its hydration sphere move a single step is governed by the activation energy for the step, Ea, where the general definition of activation energy is $\int d \ln kr = RT 2 \int d\eta dT d\eta = -dT \eta dT = -RT 2 d\eta \eta dT d\eta = -RT 2 d\eta d\eta = -RT 2 d\eta d\eta dT d\eta = -RT 2 d\eta d\eta d$ RT where $A = \eta$ ref e - Ea / RT [19B.2]. This (d ln kr) demonstrates that the pre-exponential factor A is a constant, the pre-exponential factor A is a constant. We explore the possibility that the Problem 19B.2 empirical equation for the viscosity of water reflects an activation energy that has a dependence upon temperature is 20° C and from the CRC Handbook (71st ed., 1990-1991) $\eta 20 = 1002 \ \mu Pa \ s = 1.002 \times 10-3 \ kg \ m-1 \ s-1$ (the value is not actually necessary $||-a + 2b(20 - x)a(20 - x) - b(20 - x)2|| - = \eta(x) \times \ln(10) \times ||2x + c(x + c)||| R \times (x + 273.15) K d\eta(x) RT 2 d\eta Ea = - = -d(x) \eta dT \eta(x) 2 || - a + 2b(20 - x) - b(20 - x)2|| = -R \times (x + 273.15) K \times \ln(10) \times ||2x + c(x + c)||||2x + c(x + c)|||2x + c(x + c)||2x + c||2x + c||2x + c||2x + c||2x + c||2x + c|$ shown in Fig. 19.1. The activation energy drops from 17.5 kJ mol-1 at 20° C to 12.3 kJ mol-1
at 100° C. This decrease may be caused by the density decrease that occurs across this temperature range because the increased average intermolecular distance may also be a decrease in the hydration sphere of a molecule, thereby, making movement easier. 19:19 Figure I19.1 18 Ea / kJ mol-1 17 16 15 14 13 12 20 30 40 50 60 θ / oC 19:20 70 80 90 100 20 Chemical Kinetics 20A The rates of chemical reactions Answers to discussion question D20A.2 Reaction orders need not be integers, except for elementary reactions. Indeed, reaction orders can change during the course of the reaction. Consider the zero-order reaction is independent of that concentration; what limits the rate is the availability of catalytical section 20A.2(c)), the decomposition of phosphine is present, the rate of reaction is independent of that concentration; what limits the rate is the availability of catalytical section 20A.2(c)). sites on the tungsten. Clearly the integrated rate law for a zero-order reaction cannot be correct at long times, where it would predict negative concentrations. Before that unphysical situation would occur, the concentration of the reactant drops to such an extent that it limits the rate of reaction, and the reaction order changes from zero to a non-zero value. The text's treatment of the Lindemann-Hinshelwood mechanism (Section 20F.1) also illustrates how a reaction order can change from first- to second-order over the course of a reaction. D20A.4 The determination of a rate law is simplified by the isolation method in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law has been forced into first-order form by [B]0 and write v = kr[A][B], we can approximate [B] by [B]0 and write v = kr[A][B], where kr' = kr[B]0 which has the form of a first-order form by a first-order form by a first-order rate law. Because the true rate law has been forced into first-order form by a firstassuming that the concentration of B is constant, it is called a pseudo first-order rate law. The dependence of the rate on the concentration of each of the rate and so constructing the overall rate law. In the method of initial rates, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is v = kr[A]a; then its initial rate, v0, is given by the initial values of the concentration of A, and we write v0 = kr[A]0a. Taking logarithms gives log v0 = log kr + a log [A]0 For a series of initial concentrations, a plot of the initial concentrations, a plot of the initial concentrations, a plot of the initial concentrations of A should be a straight lime with slope a. The method of initial rates might not reveal the full rate law, for the products may participate in the reaction and affect the rate. For example, products participate in the synthesis of HBr, where the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. comparing it with the data. Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions are easily obtained and prove to be very useful. These are summarized in Table 20B.3. In order to determine the rate law, one plots the right hand side of the integrated rate laws shown in the table against t in order to see which of them results in a straight line through the origin. The one that does is the correct rate law. amount be nam, and let α be the fraction of that final amount produced during any given time. Thus, α varies from 0 to 1 over the 20:1 course of the reaction. At any given time, the amount of hydrogen consumed is α nam/2. If we let ninitial be the total quantity of gas initially present (H2 and N2), then the total at any given time will be notal = ninitial - $\alpha nam/2 + \alpha nam = ninitial - \alpha nam = ninit$ volume and temperature do not change, we may also write ptotal = pinitial - α pam E20A.3(b) 1 d[J] d[J] [20A.3b] so = ν Jv ν J dt dt Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of A = v = 2.7 mol dm-3 s-1 Rate of consumption of A = v = 2.7 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of A = v = 2.7 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of A = v = 2.7 mol dm-3 s-1 Rate of consumption of B = 3v = 8.1 mol dm-3 s-1 Rate of consumption of B $d[B] 1 v = [20A.3b] = 0.9 \text{ mol dm} - 3 \text{ s} - 1 = x (2.7 \text{ mol dm} - 3 \text{ s} - 1) = 3.3 \text{ dt } v \text{ J} \text{ dt} \text{ Rate of formation of } C = v = 0.9 \text{ mol dm} - 3 \text{ s} - 1 \text{ Rate of consumption of } B = 3v = 2.7 \text{ mol dm} - 3 \text{ s} - 1 \text{ expressed in mol dm} - 3 \text{ s} - 1; therefore mol dm} + 3 \text{ s} - 1 \text{ Rate of consumption of } B = 3v = 2.7 \text{ mol dm} - 3 \text{ s} - 1 \text{ expressed in mol dm} - 3 \text{ s} - 1; therefore mol dm} + 3 \text{ s} - 1 \text{ mol dm} - 3 \text{ s} - 1 \text{ expressed in mol dm} - 3 \text{ s} - 1 \text{ expressed in mol dm} - 3 \text{ s} - 1; therefore mol dm} + 3 \text{ mol dm} - 3 \text{ s} - 1 \text{ mol dm} - 3 \text{ s} - 1 \text{ mol dm} - 3 \text{ s} - 1 \text{ mol dm} - 3 \text{ s} - 1 \text{ mol dm} - 3 \text{$ $1 = [kr] \times (mol \ dm-3) \times (mol \ d$ $(mol dm-3) \times (mol dm-3) - 1$ Therefore [kr] = s-1 E 20A.6(b) (i) For a second-order reaction, denoting the units of kr by [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or $m3 s-1 = [kr] \times (molecule m-3)^2$; therefore [kr] = m3 molecule -1 s-1 or m3 s-1 o or m6 s-1 Comment. Technically, "molecules is simply a number of molecules is simply a number of individual objects, that is, a pure number. In the chemical kinetics literature, it is common to see rate constants reported in molecules units of m3 s-1, etc. with the number of molecules left unstated. (ii) For a second-order reaction Pa s-1 = $[kr] \times Pa2$; therefore [kr] = Pa-1 s-1 For a third-order reaction 20:2 Pa s-1 = $[kr] \times Pa3$; therefore [kr] = Pa-2 s-1 Solutions to problems P20A.2 We suppose
that the rate law for the reaction of isolated glucose (glu) with the enzyme hexokinase at 1.34 mmol dm-3 is v = kr, eff[glu]a. Evaluating this rate law at initial conditions and taking the logarithms gives = log v0 log kr,eff + a log [glu]0 Thus, if the supposition is correct, a plot of log v0 against log [glu]0 with be linear with a slope equal to the reaction order a and an intercept equal to log kr,eff . We draw the following table with the requisite logarithm transformations, prepare the plot (see Figure 20A.1), and check whether the plot is linear. [glu]0 / mmol dm-3 1.00 1.54 3.12 4.02 v0 / mol dm s 5.0 7.6 15.5 20.0 log ([glu]0/mmol dm-3) 0.00 0.188 0.494 0.604 0.699 0.881 1.19 1.30 -3 -1 log(v0/mol dm -3) 1.4 y = 0.9986x + 0.6968 R² = 0.9999 1.2 1 0.8 0.6 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 log([glu]0/mmol dm-3) Inspection of the plot reveals that it is linear so we conclude that the supposed form of the rate law is valid and we perform the computation of the linear least squares regression fit of the data, which is shown in Figure 20A.1. (a) The plot slope is extremely close to 1.00 so we conclude that the reaction order w/r/t glucose is 1. (b) The regression intercept tells us that log (kr,eff / mol dm - 3 s - 1) = 0.6968. Thus, kr,eff = 100.6968 mol dm - 3 s - 1 = 5.0 mol dm - 3 s - 1 =values but the 2nd has twice the [ICl]0 value and an initial rate that is three times as large. The rate must be first-order in [ICl]0 value and an initial rate that is three times as large. Once again, the rate is proportional to the concentration so it must be first-order in [ICl]0 value and an initial rate that is three times as large. order in [H2]. (b) kr = v / ([IC]] [H2]) = $3.7 \times 10-7$ mol dm-3 s-1 / ($1.5 \times 10-3$ mol dm-3) = 0.16 dm3 mol-1 s-1 (c) v0 = (0.16 dm3 mol-3 s-1 20B Integrated rate laws Answers to discussion guestions D20B.2 (a) dA d[A] d[A] = -kr. (b) = -kr (A dt Solutions to exercises E20B.1(b) Table 20B.3 gives a general expression for the half-life of a reaction of the type A \rightarrow P for orders other than 1: 2n -1 - 1 = α [A]10 - n α p10 - n t1/2 n -1 (n - 1)kr [A]0 Form a ratio of the half-lives at different initial pressures: t1/2 (p0, 2) 1 - n (p0, 2) || p0, 2 || $(p0,1)(p) = (n-1)\ln|0,2|$ Hence $\ln||t(p)|||p|(1/20,2)(0,1/340 \text{ s ln 178 s or } (n-1) = -0.992 \approx -1.28.9 \text{ kPa ln 55.5 kPa Therefore}, n = 0 (()) E20B.2 (b) The rate law is 1 d[A] = -kr[A] dt That is, it would be accurate to take the half-life$ from the table and say $\ln 2 t 1/2 = kr'$ where kr' = 2kr. Thus $\ln 2 t 1/2 = 9.74 \times 105 s - 7 - 1 2(3.56 \times 10 s) \times (50 s) = 32.999 kPa 20:4$ (ii) After $20 \text{ min}, -7 - 1 = p (33.0 \text{ kPa}) e - 2 \times (3.56 \times 10 \text{ s}) \times (20 \times 60 \text{ s}) 32.97 \text{ kPa} E20B.3(b)$ The integrated rate law is [A]0 ([B]0 - 2[C]) 1 [Table 20B.3] kr t = ln [B]0 - 2[A]0 (-2[A]0 - 2[A]0 - 2[A]0 - 2[A]0 - 2[A]0 - 2[A]0 (-2[A]0 - 2[A]0 - 2[$2 \times 0.027 \times t/s - 1) = so mol dm - 3 (0.130) \times e0.34 \times (0.130 - 2 \times 0.027) \times t/s - 2 \times (0.027) \times t/s - 2 \times (0.027) \times t/s - 0.42 0.027 \times (e0.026 \times 15 \times 60 - 1) = [C] = mol dm - 3 0.027 mol dm - 3 (0.130) \times e0.34 \times (0.130 - 2 \times 0.027) \times t/s - 2 \times (0.027) \times t/s - 2 \times$ the reaction is essentially complete after 15 min. In fact, it is essentially complete considerably before this time. When is the reaction 99% complete? = [C] (i) E20B.4(b) The rate law is 1 d[A] v = - kr [A] 3 2 dt which integrates to 1(11)1(11) - 2krt = sot = || |2 2 |2 | [A] [A] 0 / 4kr [A] [A] 0 / (11) 1 = x - t || -4 - 2 - 1 || -3 2 - 3 2 $6 (4(6.50 \times 10 \text{ dm mol s}) \parallel (0.015 \text{ mol dm}) (0.067 \text{ mol dm}) = 1.6 \times 106 \text{ s} = 19 \text{ days}$. Solutions to problems P20B.2 The concentration of A varies with time as [A]0 [A] = [20B.4] 1 + kr t[A]0 and [B]/[A]0 are plotted against the dimensionless time krt[A]0 in Fig. 20B.1(a). The same variables are plotted against a logarithmic horizontal axis in Fig. 20B.1(b). The second-order plots have longer "tails" than the first-order plots of Problem 20B.1 Figures 20B.1(a) and (b) 20:5 P20B.4 A simple but practical approach is to make an initial guess at the order by observing whether the halflife of the reaction appears to depend on concentration. If it does not, the reaction is first-order; otherwise refer to Table 20B.3. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn. 20B.1: (A) = -kr t [A] = -k= (CH3)3CBr): t/h 0 3.15 6.20 10.00 18.30 30.80 10.39 8.96 7.76 6.39 3.53 2.07 [A] [A]0 1 0.862 0.747 0.615 0.340 0.199 ([A]) ln | [A]0 / 0 -0.148 -0.292 -0.486 -1.080 -1.613 9.62 11.16 12.89 15.65 28.3 48.3 [A] (10-2 mol dm -3) (1)3 -1 | / (dm mol) [A] / Figure 20B.2 20:6 The data are plotted in Fig. 20B.2. The fit to a straight line is only fair, but the deviations look more like experimental scatter than systematic curvature. The correlation coefficient is 0.996. If we try to fit the data to the expression for a second-order reaction in Table 21.3, the fit is not as good; that correlation coefficient is 0.985. Thus we conclude that the reaction is most likely first-order. A noninteger order, neither first nor second, is also possible. The rate constant kr is the negative of the slope of the first-order plot: kr = $0.0542 \text{ h} - 1 = 1.51 \times 10 - 5 \text{ s} - 1 \text{ At } 43.8 \text{ h} ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1 \ln | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 ([A]) - 1$ integrated second-order rate law is [A] ([B]0 - 2[P])] 1 kr t = ln | 0 | [B]0 - 2[A]0 [([A]0 - [P])(B]0] By the time [B] falls to 0.040 mol dm-3, it has dropped by 0.020 mo $(0.030 - 2 \times 0.010)$ $1 \times \ln | kr = | -33 (3.6 \times 10 s) \times (0.030 - 2 \times
0.050) mol dm | (0.050 - 0.010) \times 0.030 | = 3.5 \times 10 - 3 dm 3 mol - 1 s - 1 (b)$ The half-life in terms of A is the time when [A] = [A]0/2 = 0.025 mol dm-3. The stoichiometry requires [B] to drop by 0.050 mol dm-3; however, since [B]0 was only 0.030 mol dm-3, this concentration cannot be reached from the given initial conditions. The half-life of A, then, is infinite, since there is not enough B to react with it. The half-life in terms of B is the time when [B] = [B]0/4 = 0.0425 mol dm - 3 [A] = [B]0/4 = 0.0075 mol dm - 3 [A] = [B]0/ $[Bl0 | 1 = -3.3 - 1 - 1.(3.5 \times 10 \text{ dm mol s}) \times (0.030 - 2 \times 0.050) \text{ mol dm} - 3.)(0.050 \times 0.015) \times \ln | 0.0425 \times 0.030| = 2.2 \times 103 \text{ s} = 0.61 \text{ h}, 20.7 \text{ P20B.8 A simple but practical approach is to make an initial guess at the order by observing whether the halflife of the reaction appears to depend on concentration. If it does not, the reaction is first$ order, if it does, it may be second-order. Examination of the data shows that the half-life is roughly 90 minute data, in both intervals the concentration drops by less than half.) If the reaction is first-order, it will obey (c) ln |= -krt [20B.1] (c) /If it is second-order, it will obey 1 1 [20B.4] = krt + c c0 See whether a first-order plot of 1/c vs. time or a second-order plot of 1/c vs. time has a substantially better fit. We draw up the following table: t / min c / (ng cm-3) / c ln {c/(ng cm-3)} 30 699 0.00143 6.550 60 622 0.00161 6.433 120 413 0.00242 6.023 Figure 20B.3(a) Figure 20B.3(b) 20:8 150 292 0.00342 5.677 240 152 0.00658 5.024 360 60 0.0167 4.094 480 24 0.0412 3.178 The data are plotted in Figs. 20B.3(a) and (b). The first-order plot fits closely to a straight line with just a hint of curvature near the outset. The second-order plot, conversely, is strongly curved throughout. Hence, the reaction is first-order. The rate constant is the negative of the slope of the first-order plot: kr = 0.00765 min-1 = 0.459 h-1. The half-life is (eqn. 20B.2) ln 2 ln 2 t1/2 = h 91 min = = 1.51 = kr 0.459 \text{ h}-1. The half-life is (eqn. 20B.2) ln 2 ln 2 t1/2 = h 91 min = = 1.51 = kr 0.459 \text{ h}-1. drug, two processes with distinct rates. Elimination is characteristically slower, so the later data points reflect elimination only, because absorption and elimination. It is, therefore, not surprising that the early points do not adhere so closely to the line so well defined by the later data. P20B.10 Since both reactions are first-order, d[A] - = k1[A] + k2 [A] = (k1 + k2) t [20B.1 with kr = k1 + k2] We are interested in the yield of ketene, CH2CO; call it K: <math>d[K] k2 [A] 0 e - (k1 + k2) t = k = 2 [A] dt Integrating yields $\int [K] 0 d[K] = k2 [A] 0 e - (k1 + k2) t dt 0 k2 [A] 0 e - (k1 + k2)$ e - (k1 + k2)t) = ([A]0 - [A])k1 + k2k1 + k2 The percent yield is the amount of K produced compared to complete conversion; since the stoichiometry of reaction (2) is one-to-one, we can write: k[K] % yield = $\times 100\% = 2(1 - e - (k1 + k2)t) \times 100\% [A]0k1 + k2$ which has its maximum value when the reaction reaches completion k2 4.65 s -1 max % yield = $\times 100\% = \times 100\% = \times 100\% = 55.4\%$ k1 + k2 (3.74 + 4.65) s -1 Comment. If we are interested in yield of the desired product (ketene) compared to the products of reaction 1), it makes sense to define the conversion ratio, the ratio of desired product formed to starting material reacted, namely [K] [A]0 - [A] [K] = 100\% 20:9 which works out in this case to be independent of time k2 [K] = [A]0 - [A] k1 + k2 If a substance reacts by parallel processes of the same order, then the ratio of the amounts of products will be constant and independent of the extent of the reaction, no matter what the order. Question. Can you demonstrate the truth of the statement made in the above comment? P20B.12 The stoichiometry of the reaction concentrations as follows: [A] = [A]0 - 2[B] When the reaction goes to completion, [B] = [A]0/2; hence [A]0 = 0.624 mol dm-3. We can therefore tabulate [A], and examine its half-life of A from its initial concentration is approximately 20 min, and that its half-life from the concentration at 20 min is also 20 min. This indicates a first-order reaction. We confirm this conclusion by plotting the data accordingly (in Fig. 20B.4), using [A] = -kA [A] dt t / min 0 10 20 30 40 ∞ [B] (mol dm -3) 0 0.089 0.153 0.200 0.230 0.312 [A] (mol dm -3) $0.624\ 0.446\ 0.318\ 0.224\ 0.164\ 0\ 0\ -0.34\ -0.67\ -1.02\ -1.34\ \ln[A]\ [A]\ 0\ -0.67\ -1.02\ -1.34\ \ln[A]\ [A]\ 0\ -0.67\ -1.02\ -1.34\ \ln[A]\ (A)\ =\ 12\ kA\ [A]\ 2\ dt$ and hence = kr 1 2 k = $1.7 \times 10-2$ min -1 A P20B.14 If the reaction is first-order the concentrations obey 20:10 ([A]) ln | = -kr t [20B.1] ([A]) and, since pressures and concentrations of gases are proportional, the pressures should obey p ln 0 = kr t p and 1 p0 should be a constant. We test this by drawing up the following table: ln t p p0 / Torr 200 200 400 400 600 600 t/s 100 200 100 200 100 200 p / Torr 186 173 373 347 559 520 (1) p0 104 | $\ln t/s p$ 7.3 7.0 7.1 7.1 7.2 The values in the last row of the table are virtually constant, and so (in the pressure range spanned by the data) the reaction has first-order kinetics with kr = 7.2 × 10-4 s-1 P20B.16 The rate of change of [A] is d[A] = -kr [A]n dt [A] d[A] t = -kr dt = -= kr (A0 - 2x) 2 × (B0 - x) = kr (A0 - 2x) 2 × (B0 - x) = kr (A0 - 2x) × (A0 - x) dt x dx kr t = 20 (A - 2x) × (A - x) 0 0 We proceed by the method of partial fractions (which is employed in the general case too), and look for the values of α , β , and γ such that $\alpha \beta \gamma 1 = +22 (A0 - 2x) \times (A0 - x) dt x dx kr t = 20 (A - 2x) × (A0 - x) + \beta (A0 - 2x) + \beta (A0$ x) × (A0 - x) + y (A0 - 2x) 2 = 1 Expand and gather terms by powers of x: (A0 α + A02 β + A02 γ) - (α + 3 β A0 + 4 γ A0) x + (2 β + 4 γ) x 2 = 1 This must be true for all x; therefore A0 α + A02 β + A02 γ = 0 and \int Solving this system yields α = -2 2 1, β = 2, and γ = 2 A0 A0 A0 Therefore, = kr t $\int x 0 (2/A0)$ (2 / A02)(1 / A02) - + | dx 2 A0 - 2x A0 - x | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) - 2 ln(A0 - x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) | A0 | (A0 - 2x) / (A0 - 2x) / (A0 - 2x) / (A0 - 2x)
 (A0 - 2x) / (Ajumps, usually by ultrasonic methods, can be used to alter the rate of the reaction must be non-zero. Solutions to exercises E20C.1(b) The equilibrium constant of the reaction is the ratio of rate constants of the reaction must be non-zero. -1) = 1.7 × 10-7 s -1 and Solutions to problems P20C.2 We proceed as in Section 20C.1. The individual reactions are (analogous to eqn. 84.1) A \rightarrow 2B v = kr[A] and 2B \rightarrow A v = kr[A] and 2B \rightarrowA v = kr[A] and 2B \rightarrow A v = kr[A] and 2B \rightarrowA v = kr[A] and 2B \rightarrow A v = kr[A] and 2B \rightarrowA v = kr[A] and 2B \rightarrow A v = kr[A] and 2B \rightarrowA v = k stoichiometry requires that [B] = 2([A]0 - [A]) Substituting this into the differential equation for [A] yields $d[A] = -kr [A] + 2 kr' {[A]0 - [A]} +$ approaches its equilibrium value. At equilibrium d[A] = 0 = -kr[A] + kr'[B]2 dt so kr[A]eq = kr'[B]eq 2 and 2 kr [B]eq = K = kr' [A]eq The approach of concentrations to their equilibrium values is plotted in Fig. 84.1 for initial concentration [A]0 = 1.0 mol dm-3 (and no B initially) and rate constants kr = 1.0 min-1 and kr' = 1.0 dm3 mol min-1. Figure $200.1 \ 20.13 \ P200.4 \ Consider$ a two-step equilibrium involving an intermediate I: AI with rate constants k1 and k1' IB with rate constants k2 and k2' The rate of change of [A] is d[A] = -k1[A] + k1'[I] dt and at equilibrium [I]eq k d[A] = -k1[A] + k1'[I] dt and at equilibrium [I]eq k d[A] = 1 so = 0 = -k1[A]eq + k1'[I]eq [A]eq k1' dt But we wish to express our equilibrium constant in terms of reactantand product concentrations, eliminating intermediates. So consider the rate of change of [B]: d[B] = k2 [I] - k2' [B] dt and at equilibrium [B] and at equilibrium [B] and at equilibrium [B] and [I] and intermediate and there is another step to arrive at a final product C: BC with rate constants k3 and k3' Now consider the rate of change of [C]: d[C] = k3 [B] - k3'[C] eq [B]eq k3' dt Multiplying this expressions with the previous one yields: [B]eq [C]eq [C]eq k3 k2 k1 = = [A]eq [B]eq [A]eg k3' k2' k1' It should be clear that this process can be carried on for any number of steps, if the procedure to this point is correct. One possible objection is worth addressing here, and that is that once B becomes an 20:14 intermediate rather than a final product, the expression for its rate of change becomes more complicated, namely d[B] = k2 [I] - k2' [B] - k3 [B] + k3' [C] dt This is true in general. However, at equilibrium, forward and reverse rates of reaction are equal for each step. Therefore it is still true that each of the following is true separately and 0 = k2 [I]eq - k2' [B] = k3' [C] dt This is true in general. However, at equilibrium, forward and reverse rates of reaction are equal for each step. Therefore it is still true that each of the following is true separately and 0 = k2 [I]eq - k2' [B]eq 0 = k3 [B]eq - k3' [C]eq and the same would be true for any additional steps. P20C.6 d[A] = -2kr [A]2 + 2kr [A]2 + 2] dt Define the deviation from equilibrium, x, by the following equations, which satisfy the law of mass conservation. [A] = [A]eq + 2 x and [A 2] = [A 2]eq - x Then, d([A]eq + 2 x) = -kr ([A]eq + 2 x) 2 + kr' ([A 2]eq - x) = -kr ([A]eq + 4 x 2) + kr' ([A 2]eq - x) dt r 2 A A2 k' kr { \approx $- \{(x' + 4k [A]) x + k [A] = - 4kr x 2 + (kr' + 4kr [A]eq - kr'[A 2]eq r r eq r 2 eq - kr'[A 2]eq \} \} 2$ In the last equation the term containing x has been dropped because x will be small near equilibrium and the x2 term will be negligibly small. The equation may now be rearranged and integrated using the following integration. which is found in standard mathematical handbooks. dw 1 = ln (aw + b) aw + b a dx = -dt (kr' + 4kr [A]eq) x + kr [A]eq - kr'[A 2]eq $\int \int \int 1 (kr' + 4kr [A]eq) x + kr [A]eq - kr'[A 2]eq = -t + constant.$ where y = (kr' + 4kr [A]eq) x + kr [A]eq - kr'[A 2]eq $\int \int \int 1 (kr' + 4kr [A]eq) x + kr [A]eq + kr'[A]eq - kr'[A 2]eq$ -kr' + 4kr [A]eq t Comparison of the above exponential to the decay equation $y = y0 e - t/\tau$ reveals that $\tau = 1 / kr + 4kr$ [A]eq Comment. Note that this equation can be used as the basis of an alternate derivation of the equation discussed in Problem 20C.5. The manipulations use the facts that K = [A]eq / [A]eq 2 = kr / kr' and [A]tot = [A]eq + 2[A2]eq by conservation of mass, which can be used to show that 2k 2k r 2 2 [A] [A]eq + r [A]eq [A]eq 0 or = + $[A]eq - [A]tot = tot kr' kr' This quadratic equation into = kr' + 4kr [A]eq] and some algebraic manipulation yields the (<math>2 \tau 1 2$

result of Problem 20C.5: = kr' + 8kr kr'[A] tot $\tau 2$ 20:15 20D The Arrhenius equation Answers to discussion question D20D.2 The temperature dependence of some reactions is not Arrhenius-like, in the sense that a straight line is not obtained when ln k is plotted against 1/T. However, it is still possible to define an activation energy as (d ln k) Ea = RT 2 [20D.3] (dT]) This definition reduces to the earlier one (as the slope of a straight line) for a temperature of interest) of a plot of ln k against 1/T even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling (Section 8A) is playing a significant role in the reaction. In biological reactions it might signal that an enzyme has undergone a structural change and has become less efficient. A reaction with a very small or zero activation energy, so that kr = A, such as for some radical recombination reactions in the gas phase, has a rate that is largely temperature independent. Solutions to exercises E20D.1(b) The Arrhenius equation for two different temperatures can be rearranged to yield the activation energy: $k 4.01 \times 10-2$ R ln r, 2 (8.3145 J K -1 mol-1) ln kr, 1 2.25 $\times 10-3 = Ea = (11)(11)(273 + 29)$ K - (273 + 37) K $|T - T|(12) = 5.62 \times 104$ J mol-1 = 56.2 kJ mol-1 With the activation energy in hand, the pre-exponential factor can be found from either rate constant by rearranging eqn. 20D.4. A = kr e Ea / RT = (2.25 \times 10-2 \text{ dm 3 mol}-1 \text{ s}-1)e5.62 \times 104 J mol-1 (8.3145 J K -1 mol-1)(273+29) K A = 1.19 \times 108 dm3 mol-1 s -1 Computing A from both provides a useful check on the calculation. A = kr e Ea / RT = $(4.01 \times 10-2 \text{ dm 3 mol}-1 \text{ s} -1)e5.62 \times 104 \text{ J mol}-1$ (8.3145 J K - 1 mol-1) (273+37) K A = $1.19 \times 108 \text{ dm 3 mol}-1$ s - 1 (273+37) Solutions to problems P20D.2 A simple but practical approach is to make an initial guess at the order by observing whether the half-life is roughly independent of 0.199 ([A])ln | | [A]0 /0 -0.148 -0.292 -0.486 -1.080 -1.613 9.62 11.16 12.89 15.65 28.3 48.3 [A] (10-2 mol dm -3) (1)3 -1 | // (dm mol) [A] / Figure 20D.1 The data are plotted in Fig. 20D.1. The fit to a straight line is only fair, but the deviations look more like experimental scatter than systematic curvature. The correlation coefficient is 0.996. If we try to fit the data to the expression for a second-order reaction in Table 21.3, the fit is not as good; that correlation coefficient is 0.985. Thus we conclude that the reaction is most likely first-order plot: kr = $0.0542 \text{ h} - 1 = 1.51 \times 10 - 5 \text{ s} - 1 \text{ At } 43.8 \text{ h} ([A] \ln | ([A] 0] - 1 | = -(0.0542 \text{ h}) \times (43.8 \text{ h}) = -2.374 / [A] = (10.39 \times 10 - 2 \text{ mol dm} - 3) \times e - 2.359 = 9.67 \times 10 - 3 \text{ mol dm} - 3 \text{ P20D.4}$ The Arrhenius expression for the rate constant is (eqn. 20D.1) 20:17 ln kr = ln A - Ea/RT A plot of ln kr versus 1/T will have slope -Ea/R and y-intercept ln A. The transformed data and plot (Fig. 85.2) follow: T/K - 6 3 - 1 - 1 10 kr/(dm mol s) 3 - 1 - 1 ln kr/(dm mol s) - 3 10 K / T 295 223 218 213 206 200 195 3.55 0.494 0.452 0.379 0.295 0.241 0.217 15.08 13.11 13.02 12.85 12.59 12.39 12.29 3.39 4.48 4.59 4.69 4.85 5.00 5.13 Figure 20D.2 So and Ea = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) = 1.37 × 104 J mol-1 = -(8.3145 J K-1 mol-1) × (-1642 K) 13.7 kJ mol-1 A = e20.585 dm3 mol-1 s-1 = 8.7×108 dm3 mol-1 s-1 20E Reaction mechanisms Answers to discussion questions D20E.2 The rate-determining step is not just the slowest step: it must be slow and be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped. The rate-determining step is like a slow ferry crossing between two fast highways: the overall rate at which it can cross on the ferry. If the first step in a mechanism is the slowest step with the highest activation energy, then it is ratedetermining, and the overall reaction rate is equal to the rate of the first step because all subsequent steps are so fast that once the first intermediates cascade into products. However, a ratedetermining step may also stem from the low concentration of a crucial reactant or catalyst and need not correspond to the step with highest activation barrier. A rate-determining step arising from the low activity of a crucial enzyme can sometimes be identified by determining step arising from the low activity of a crucial enzyme can sometime activation barrier. suggests that the step may be slow enough to be rate-determining D20E.4 Refer to Table 20B.3. We will consider only reaction, the rate of reaction, the rate of reaction, the rate of reaction, the rate of reaction is directly proportional to the concentration of a single reactant. 20:18 In a first-order reaction, the rate of reactant. of the logarithm of reactant concentration against time is a straight line. In a zero-order reaction, the rate of reactant concentration itself against time is a straight line. In a second-order reaction, the rate of reaction is proportional to the square of the reactant concentration: 1 1 and = + kr t v = kr[A] 2 [A] [A]0 A plot of the reciprocal of reactant concentration against time is a straight line. Reaction orders need not be integers, except for elementary reactions. Indeed, reactant concentration against time is a straight line. mentioned in the text (Section 20A.2(c)), the decomposition of phosphine on hot tungsten. As long as enough phosphine is present, the rate of reaction is independent of that concentration; what limits the rate is the availability of catalytic sites on the tungsten. Clearly the integrated rate law for a zero-order reaction cannot be correct at long times where it would predict negative concentrations. Before that unphysical situation would occur, the concentration of the reaction order changes from zero to a non-zero value. The text's treatment of the Lindemann-Hinshelwood mechanism (Section 20F.1) also illustrates how a reaction order can change from first- to second-order over the course of a reaction. D20E.6 Yes, a negative activation energy is guite possible for composite reaction, as a product or ratio of rate constants and equilibrium constants of elementary reactions. The rate constant of a composite reaction, as a product or ratio of rate constant of a composite reaction. illustrated in Section 20E.5. In general, elementary reactions that have a positive activation energy whose rate constant tend to reduce the activation energy of the overall reaction, as illustrated in eqn 20E.13. There is no reason why that reduction cannot be to a negative value. The most common molecular interpretation of the activation energy is as the "height" of an energy barrier that must be overcome by reactants in order to form products, as discussed in connection with collision theory in
Section 21A. Among the limitations of collision theory is that it is only applicable to elementary reactions, those which can possibly occur in one collision or reactive molecular encounter. Thus, it is no surprise that this interpretation fails to apply to composite reactions. The more general interpretation of the temperaturedependence of the reactions. The more general interpretation fails to apply to composite reactions. activation energy for the rate of formation of P if Ea(2) > Ea(3). A \rightarrow I k1 (slow) I \rightarrow B k2 I \rightarrow P k3 Solutions to exercises E20E.1(b) Call the stable double helix S and the unstable one U. The rate of the overall rate law. (i) Assume a pre-equilibrium with [U] K = , which implies [U] = K[A][B] = v 20:19 and v = k2[U] = k2K[A][B] = keff[A][B] with keff = k2K (ii) Apply the steady-state approximation: $d[U] = \approx 0 k1[A][B] = keff[A][B] =$ equilibrium rate law if k1' >> k2, which is likely to be the case if the first step is characterized as fast and the second slow. The steady-state approximation also encompasses the opposite possibility, that $k1' 1 \alpha > 1$ and $\alpha' > 1$ kcat = $\nu \max / [E]0 [20H.4] = 1.40 \times 104$ s $-1 (0.0224 \text{ mmol dm} - 3 \text{ s} - 1) / (1.60 \times 10 - 6 \text{ mmol dm} - 3) = (b) \eta = \text{kcat} / \text{K M}$ $[20H.5] 0.015 \text{ dm3 mol}-1 \text{ s} -1 = (1.40 \times 104 \text{ s}-1) / (9.0 \times 105 \text{ mol} \text{ dm}-3) = \text{Diffusion limits the catalytic efficiency}, \eta, to a maximum of about 108-109 dm3 mol-1 \text{ s}-1.$ mechanism the inhibition by the substrate SES ES + S KI = [ES][S]/[SES] where the inhibited enzyme, SES, forms when S binds to ES and, thereby, prevents the formation of product. This inhibition might possibly occur when S is at a very high concentration. Enzyme mass balance is written in terms of [ES], KI, KM (= [E][S]/[ES]), and [S]. (For practical purposes the free substrate concentration is replaced by [S]0 because the substrate is typically in large excess relative to the enzyme.) [E] + [ES] + [formation becomes ν max where = ν max kb [E]0. K M [S]0 + 1 + [S]0 K I The denominator term [S]0/KI reflects a reduced reaction rate caused by inhibition as the concentration of S becomes very large. = ν k= b [ES] (b) To examine the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal, Lineweaver-Burk plot of $1/\nu$ against 1/[S]0 take there the effect that substrate inhibition has on the double reciprocal. inverse of the above rate expression and compare it to the uninhibited expression [20H.3b]: $(K | 1 | 1 | . = + | M | \nu \nu \max | \nu \max | V \max |$ shapes are sketched in Figure 20H.1. 20:30 Figure 20H.1 Comparing the two expressions, we see that the two curves match at high values of 1/[S]0 increases (1/[S]0 decreases) the 1/v curve with inhibition curves upward because the reaction rate is decreasing. Integrated activities 20.2 The description of the progress of infectious diseases can be represented by the mechanism $S \rightarrow I \rightarrow R$. Only the first step is autocatalytic as indicated in the first step is autocatalytic as indicated of $S \, dt \, dt \, dt$ and, hence there is no change with time of the total population, that is S(t) + I(t) + R(t) = N. Whether the infection spreads or diseases can be represented by the mechanism $S \rightarrow I \rightarrow R$. out is determined by dI = rSI - aI. dt At= t 0,= I I(0) = I0. Since the process is auto catalytic, I(0) \neq 0. (dI) \mid = 0 (dt t = 0 (dr t = 0 (dr t = 0 (an epidemic). Thus, a a >S0 [infection dies out]. < S0 [infection spreads] and r r 20.4 The number-average molar mass of the polymer is the average chain length times the molar mass of the monomer 20:31 M1 [20F.12(a)] 1 - p The probability that it has N - 1 reacted end groups and one unreacted end groups and ond groups and ond groups and the total probability of finding an N-mer is PN = pN-1(1-p) We need this probability to get at M 2, again using number averaging: = M = N M 12 (1 - p) $\Sigma N 2 p N - 1 N = M 12 (1 - p) D N 2 p N - 1 D N 2 p N$ $M = M - = 1 N | (1 - p) 2 (1 - p) 2 (1 - p) 2 (1 - p) 2 | (J - p) 2 | (J - p) 2 | (J - p) 2 p / 2 M 1 = 1 - p The time dependence is obtained from k t[A]0 (1 + kr t[A]0 1 - p N = [20F.12] Hence p 1 2 1 / 2 = p 1 2 (1 + kr t[A]0 (1 + kr t[A]0)] 1 - p and (M 2 N - M) = 2 1 / 2 N M 1 { kt[A]0 (1 + kr t[A]0) } 12 The rates$ of the individual steps are d[B] $A \rightarrow B =$ Ia dt d[B] $B \rightarrow A = -kr$ [B]2 dt In the photostationary state, Ia - kr[B]2 = 0. Hence, 1/2 (I) [B] = |a| (kr) This concentration can differ significantly from an equilibrium distribution because changing the illumination may change the rate of the forward reaction. Contrast this concentration can differ significantly from an equilibrium distribution because changing the illumination may change the rate of the forward reaction. situation to the corresponding equilibrium expression, in which [B]eq depends on a ratio of rate constants for the forward and reverse reactions. In the equilibrium case, the rates of forward and reverse reactions 21A.2 To the extent that real gases deviate from perfect gas behavior, they do so because of intermolecular interactions. Interactions tend to be more important at high pressures, when the size of the molecules themselves is not negligible compared to the average intermolecular distance (mean free path). Attractive interactions, might enhance a reaction rate compared to the predictions of collision theory, particularly if the parts of the molecules that are attracted to each other are the reactive sites. (In that case, the both the collisions compared to what would be predicted for perfect gases. In supercritical fluids, densities can be comparable to those of liquids, so the considerations explored in the next topic (Diffusion-controlled reactions, Topic 21B) for reactions in solution might be more relevant than those of a perfect gas. 21A.4 The RRK theory proposes a P-factor that is more related to statistical energetic considerations than to geometric ("steric") ones. The P-factor in RRK theory is [21A.10a]: s-1 (E *) P = | 1 - E || where E* is the energy can be dissipated. Like more geometric interpretations of the P-factor, the RRK theory assigns smaller P factors to complex molecules than to simple ones, but for different reasons. A more geometric theory would say that an active site is only a small fraction of the "surface area" of a complex molecule, whereas RRK theory says that complex molecules are much more effective than simple ones at dispersing energy away from the reactive site. Solutions to exercises 21A.1(b) The collision frequency is [1B.11a] $z = \sigma vrelN(16kT)$ where $vrel = | \ \pi m | 1/2 \ (1B.10a \& 1B.9], \sigma = \pi d2 = 4\pi R^2$, and N = (16kT) Therefore, $z = \sigma N | \ \pi m | 1/2 \ (\pi = 16 \times (120 \times 103 \text{ Pa}) \times (180 \times 10 - 12 \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text{
m}) 2 \ (\pi = 16 \times 10^{-12} \text{ m}) 2 \ (\pi = 16 \times 10^{-12} \text$ $1/2 = 7.90 \times 109$ s -1 The collision density is [Justification 21A.1] zN A z (p) 7.90 \times 109 s $-1(120 \times 103$ Pa Z = $| = | | -23 - 12 | kT / 22 | 1.381 \times 1035$ s -1 m -3 For the percentage increase at constant volume, note that N is constant volume, so the only constant-volume temperature dependence on z (and on Z) is in the speed factor. $z \propto T1/2$ so $1 \left(\frac{\partial Z}{\partial T} \right) = z \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = \delta Z \approx \delta T = 1 \left(\frac{\partial T}{\partial Z} \right) = 0.017 \text{ 2T} \delta z = 0.017 \text{ 2$ constant (eqn. 21A.9) those factors that can be identified as belonging to the steric factor or collision rate: f = e (i) (ii) $-E/RT = (1) - 1() - 15 \times 103$ J mol -3f = exp $| = 2.4 \times 10 - 1 - 1) \times (300 \text{ K})$ mol $(8.3145 \text{ J K} / (2) - 1() - 15 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ J mol -27f = exp $| = 7.7 \times 103$ \times 10 -1 -1 mol) × (300 K) (8.3145 J K / (2) -1 () -150 × 103 J mol -10 f = exp / |= 1.6 × 10 - 1 - 1 mol) × (800 K) (8.3145 J K / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / |= 1.6 × 10 - 1 - 1 mol) × (800 K) (8.3145 J K / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / |= 1.6 × 10 - 1 - 1 mol) × (800 K) (8.3145 J K / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / |= 1.6 × 10 - 1 - 1 mol) × (800 K) (8.3145 J K / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / |= 1.6 × 10 - 1 - 1 mol) × (800 K) (8.3145 J K / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / - E /RT 21A.3(b) A straightforward approach would be to note that f (- Exp / exp | changes from f0 = e a |, where x is the fractional increase in the RT (1 + x) temperature. If x is small, the exponent changes from f0 = e - Ea / RT e - Eaexpressed as a percentage is $f - x - f0 f - f0 \times 100\% = (f0 - x - 1) \times 100\% \times 100\% = 1.2$ and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. (2) f0 - x = (0.105) - 10/300 = 1.2 and the percentage change is 20%. $(1.61 \times 10 - 10) - 10/800 = 1.33$ and the percentage change is 33%. $(8kT) \parallel (\pi \mu \parallel 1/2 kr = P\sigma \mid NAe - Ea/RT [21A.9]$ We take P = 1, so $(8(1.381 \times 10 - 23 \text{ J K} - 1) \times (450 \text{ K}) kr = [0.30 \times (10 \text{ m})] \times | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 23 \text{ J K} - 1) \times (450 \text{ K}) kr = [0.30 \times (10 \text{ m})] \times | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 23 \text{ J K} - 1) \times (450 \text{ K}) kr = [0.30 \times (10 \text{ m})] \times | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 23 \text{ J K} - 1) \times (450 \text{ K}) kr = [0.30 \times (10 \text{ m})] \times | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg
m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} - 1) | (\pi (3.930 \text{ m}) \times (1.661 \times 10 - 27 \text{ kg m} -$ $(450 \text{ K}) = 1.7 \times 10 - 15 \text{ m} 3 \text{ mol} - 1 \text{ s} - 1 = 1.7 \times 10 - 12 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 \text{ s}$ $(\sigma 1/2 A + \sigma B1/2) 2 4 \{(0.88 \text{ nm}) 2 1/2 = + (0.40 \text{ nm} 2) 1/2 \} 2 4 = 0.62 \text{ nm} 2$. Therefore, P = 8.7 × 10-22 m 2 = 1.41 × 10-3 0.62 × (10-9 m) 2 21A.6(b) According to RRK theory, the steric P-factor is given by eqn. 21A.10a s-1 (E *) P = |1 - E || where s is the number of vibrational modes in the reacting molecule. For a non-linear molecule composed of N atoms, the number of modes is [Topic 12E.1] $s = 3N - 6 = 3 \times 4 - 6 = 6$. Rearranging eqn. 21A.10a yields 1 1 E* = 1 - P s - 1 = 1 - (0.025) 5 = 0.52 E 21A.7(b) According to RRK theory, the steric P-factor is given by eqn. 21A.10a (E*)P = |1 - E||(s - 1 (300 kJ mol - 1) = |1 - ||(500 kJ mol - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 - 1) ||(1 problems 21A.2 Draw up the following table as the basis of an Arrhenius plot: T/K 600 700 800 1000 10 K / T 1.67 1.43 1.25 1.00 kr / (cm3 mol-1 s-1) 4.6×102 9.7×103 1.3×105 3.1×106 ln (kr / cm3 mol-1 s-1) 4.6×102 9.1×105 1.3×105 1 $mol-1 s-1) = e28.3 = 2.0 \times 1012$ 3 But comparison of eqn. 21A.9 to the Arrhenius equation tells us that P = so A (μ) N A σ | (8kT |) (8kT |) ($2 = 3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg so, evaluating P in the center of the range of temperatures spanned by the data, () 2.0 × 1012 ($12 \times 10-27$ kg mu-1) / 2 = $3.8 \times 10-26$ kg × $(10-2 \text{ m})3 \text{ mol}-1 \text{ s} - 1 \text{ m} \times 3.8 \times 10-26 \text{ kg} \times P = |-1-23 2 -9 23 -1 (6.022 \times 10 \text{ mol}) \times 0.60 \times (10 \text{ m}) (8 \times 1.381 \times 10 \text{ J K} \times 800 \text{ K} || 1/2 = 6.5 \times 10-3) \times (0.60 \text{ nm}2) = 3.9 \times 10-3 \text{ nm}2 = 3.9 \times 10-3 \text{$ Taking $\sigma = \pi d2$ gives (e2) 2 6.5 nm 2 $\sigma^* \approx \pi$ | = {(I - Eea) / eV} 2 \ 4 \pi \epsilon 0 [I(M) - Eea (X 2)] / Thus, σ^* is predicted to increase as I - Eea decreases. We construct the following table from the data: σ^* / nm2 Na K Rb Cs Cl2 0.45 0.72 0.77 0.97 Br2 0.42 0.68 0.72 0.90 I2 0.56 0.97 1.05 1.34 All values of σ^* in the
table are smaller than the experimental ones, but they do show the correct trends down the columns. The variation with Eea across the table is not so good. 21A.6 Collision theory gives for a rate constant with no energy barrier $1/2 \text{ k} (\pi \mu) (8kT) \text{ N A} [21A.9]$ so $P = r | kr = P\sigma | \sigma \text{ N A} (8kT || (\pi \mu) P = 1/2 \text{ kr} / (dm 3 \text{ mol} - 1 \text{ s} - 1) \times (10 - 3 \text{ m} 3 \text{ dm} - 3) (\sigma / \text{ mm} 2) \times (10 - 9 \text{ m}) 2 \times (10 - 9 \text{ m$ $(6.022 \times 1023 \text{ mol}-1) (\pi \times (\mu/u) \times (1.66 \times 10-27 \text{ kg}) \times | -1-23 (8 \times (1.381 \times 10 \text{ J K}) \times (298 \text{ K}) | = 1/2 (6.61 \times 10-13) \text{ kr} / (\text{dm 3 mol}-1 \text{ s} - 1) (\sigma/\text{ nm 2}) \times (\mu/\text{ mu}) 1/2$ The collision cross-section for O2 is listed in the Data Section. We would not be far wrong if we took that of the ethyl radical to equal that of ethene; similarly, we will take that of cyclohexyl to equal that of benzene. For O2 with ethyl 2 σ AB = π dAB where dAB = (dA + d B) = σ = (0.401/2 + 0.641/2) 2 nm 2 = 0.51nm 2 4 4 μ = mO met (32.0 mu) × (29.1mu) = 15.2 mu mO + met (32.0 + 29.1) mu (6.61 × 10-13) × (4.7 × 109) $= 1.6 \times 10-3 (0.51) \times (15.2)1/2$ For O2 with cyclohexyl so P= (0.401/2 + 0.881/2)2 nm 2 = 0.62 nm 2 4 m m (32.0 mu) × (77.1 mu) μ = O C = = 22.6 mu mO + mC (32.0 + 77.1) mu σ = so P= $(6.61 \times 10-13) \times (8.4 \times 109) = 1.8 \times 10-3 (0.62) \times (22.6)1/2$ 21B Diffusion-controlled reactions Answer to discussion question D21B.2 In the cage effect, a pair of molecules may be held in close proximity for an extended on the microscopic scale, mind you) by the presence of other neighboring molecules. Such a pair is called an encounter may include a series of collisions. Furthermore, an encounter pair may pick up enough energy to react from collisions with neighboring molecules, even though the pair may not have had enough energy at the time of its initial collision. Solutions to exercises 21B.1(b) The rate constant for a diffusion-controlled bimolecular reaction is kd = 4nR*DNA [21B.3] where D $= DA + DB = 2 \times (5.2 \times 10-9 \text{ m2 s}-1) = 1.04 \times 10-8 \text{ m2 s}-1 \text{ kd} = 4\pi \times (0.4 \times 10-9 \text{ m}) \times (1.04 \times 10-8 \text{ m2 s}-1) \times (6.022 \times 1023 \text{ mol}-1) \text{ kd} = 3.1 \times 1010 \text{ dm} 3 \text{ mol}-1 \text{ s} -1$ $= \eta 3\eta$ (i) For decylbenzene, $\eta = 3.36$ cP = $3.36 \times 10-3$ kg m-1 s-1 kd = 6.61×103 J mol-1 s $-1 = 2.4 \times 105$ m 3 mol-1 s --1 s -1 21B.3(b) The rate constant for a diffusion-controlled bimolecular reaction is [21B.4] kd = 8RT = 3\eta 8 × (8.3145 J K -1 mol-1 s -1 = 1.18 × 1010 dm 3 mol-1 s -1 = 1.18 × 107 m 3 mol} = 1 s -1 = 1.18 × 107 m 3 mol} = 1 s -1 = 1.18 × 107 m 3 mol} = 1 s -1 = 1.18 × 107 m 3 mol} = 1 s -1 = 1.18 × 107 m 3 mol} = 1 s -1 = 1.18 × 107 m 3 mol} = 1 s 2kd because 2 atoms are consumed] 2kd [A]0 t1/2 = 1 = $2.1 \times 10-8$ s $-3-3-12 \times (1.18 \times 10$ dm mol s) $\times (2.0 \times 10$ mol dm) 10 3 -121B.4(b) Since the reaction is diffusion-controlled, the rate-limiting step is bimolecular and therefore second-order; hence d[P] = kd [A](B) dt where kd = 4π R* DN A [88.3] = 4π N A R* (DA + DB) = 4π N A X (RA + DB) = 4π N A R* (DA + DB) = 4π N + RB) × kd = $(1 2 \text{RT kT} (11)1) + |[19B.19b] = (\text{RA + RB}) \times | + ||
3\eta 6\pi\eta (\text{RA RB}) (11)2 \times (8.3145 \text{ J K} - 1 \text{ mol} - 1) \times (293 \text{ K}) + \times (421 + 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 1 - 3 (421 945) \times | -1 - 3 ($ dm -3) × (0.195mol dm -3) dt = 1.71 × 108 mol dm -3 s -1 Comment. If the approximation of eqn. 21B.4 is used, kd = 4.81×109 dm3 mol-1 s-1. In this case the approximation results in a difference of about 15% compared to the expression used above. Solutions to problems 21B.2 See Brief illustration 21B.3 for a sample scenario. In the graphs shown here, the same parameters are used, except for the value of the rate constant. That is, n0 = 3.9 mmol of I2, A = 5.0 cm2, and D = 4.1×10-9 m2 s-1. Using these parameters, we will plot the spatial variation in concentration at 102 s, 103 s, and 104 s. In Figure 21B.1(a), the concentration is plotted against position in the absence of reaction. That is, kr = 0. The concentration profile spreads with time. That is, the maximum concentration, has a barely noticeable effect on the concentration profiles (plotted in Figure 21B.1(b)); the longer-time profiles are very slightly depresses the 104-s profile: by that time the material has practically all reacted away (Figure 21B.1(c)). Speeding up the reaction by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21B.1(d)) suppresses the 103-section by a further factor of 10 (Figure 21 s profile practically completely as well, and even the 102-s is visibly lower. 6 Figure 21B.1(a) Figure 21B.1(b) Figure 21B.1(c) Figure 21B.1(diffusion-limited reaction is kd = 8RT 8 × (8.3145 [K - 1 mol - 1) × (298 K) [21B.4] = $3\eta 3 \times (1.06 \times 10 - 3 \text{ kg m} - 1 \text{ s} - 1) = 6.23 \times 106 \text{ m} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1) = 6.23 \times 106 \text{ m} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1) = 6.23 \times 106 \text{ m} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} - 1 \text{ s} - 1 = 6.23 \times 109 \text{ dm} 3 \text{ mol} - 1 \text{ s} -$ $R^* = 4\pi$ DN A $4\pi \times (1 \times 10-9 \text{ m } 2 \text{ s} - 1) \times (6.022 \times 1023 \text{ mol} - 1) = 4 \times 10-10 \text{ m} = 0.4 \text{ nm} 21\text{ C}$ Transition-state theory Answers to discussion questions 21C.2 See Topic 21C.1(e) for detailed examples of how femtosecond spectroscopy has been used to detect activated complexes and transition states of reactions. Because the activated complexes are not even local minima on potential energy surfaces, they are extremely transitory, and laser pulses of duration less than 1 ps are needed in order to detect them. Typically one very short pulse will detect a reaction product. Not only must the pulses themselves be very short, but the delay between the creation of the complex and the detection of its effects must also be short. By such techniques, investigators have been able to determine just how stretched the bond in ICN must get before it breaks (yielding free CN). Also, decay of the ion pair Na+I- has been studies in detail, revealing the existence of two potential energy surfaces, one largely ionic and one corresponding to a covalent NaI. 21C.4 The primary isotope effect is the change in rate constant of a reaction in which the breaking of a bond involving the isotope occurs. The reaction coordinate in a C-H bond-breaking process corre bond. The vibrational energy of the stretching depends upon the effective mass of the C and H atoms (µCH). Upon deuteration, the zero point energy barrier is not much changed because the relevant vibration in the activated complex has a very low force constant (bonding in the complex is very weak), so there is little zero point energy associated with the complex and little change in its zero point energy of the reaction. We then expect that the rate constant for the reaction will be lowered in the deuterated molecule and that is what is observed. See the derivation leading to eqns 21C.19 and 21C.20 for a quantitative description of the reaction mechanism to an extent even greater than can be accounted for by these equations. In such cases, quantum-mechanical tunneling (Topic 8A) may be part of the reaction mechanism The probability of tunneling is highly sensitive to mass, so it is much less likely (and therefore much slower) for deuterium than for 1H. If the rate of a reaction is altered by isotopic substituted site plays an important role in the mechanism of the reaction. For example, an observed effect on the rate can identify bond breaking events in the rate determining step of the mechanism. On the other hand, if no isotope effect is observed, the site of the isotopic substitution may play no critical role in the mechanism of the reaction. Solutions to exercises 21C.1(b) The enthalpy of activation for a bimolecular solution reaction is [Topic 21C.2(a) footnote] Δ‡H = Ea - RT = 8.3145 J K-1 mol-1 × (5925 K - 298 K) = 46.9 kJ mol-1 8 ‡ (kT kr = B e Δ S / R e $-\Delta$ H / RT, B = | h | RT | A | F | B = a / RT + (A) ‡ Therefore, A = e B e Δ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e <math>\Delta$ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e \Delta$ S / R e -A H / RT, B = | h | R | A
| S + (A) ‡ Therefore, A = e B e Δ S / R e $-Ea / RT + (A) ‡ Therefore, A = e B e \Delta$ S / R e -A H / RT (8.3145] K -1 mol-1) × (8.3145] K -1 mol-1 $1.54 \times 1011 \text{ m 3 mol} - 1 \text{ s} - 1 = 1.54 \times 1014 \text{ dm 3 mol} - 1 \text{ s} - 1 \text{ (} 6.92 \times 1012 \text{ dm 3 mol} - 1 \text{ s} - 1 \text{ (} 1.54 \times 10 \text{ dm mol s} \text{)} = 8.3145 \text{ J K} - 1 \text{ mol} - 1 \times (-4.10) = -34.1 \text{ J K} - 1 \text{ mol} - 1 \times ($ $mol-1 K-1 \times (4972 K-298 K) = 38.9 kJ mol-1 The entropy of activation is [Exercise 21C.1(b)] (A) + \Delta = S R | ln - 1 | B | with B = kRT 2 = 1.59 \times 1014 dm 3 mol-1 s - 1 hp O[(4.98 \times 1013)] Therefore, \Delta = 8.3145 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.7 J K - 1 mol-1 × | ln | -1 | = -17.$ kJ mol-1 = +44.1 kJ mol-1 21C.3(b) Use eqn. 21C.15(a) to relate a bimolecular gas-phase rate constant to activation energy and entropy: kr = e 2 B e Δ S / R e - Ea / RT ‡ (kT) (RT) where B = | |×| O | [21C.14] (h | p) = (1.381 \times 10 - 23 \text{ J K} - 1) × (338 \text{ K})2 × (8.3145 \text{ J mol} - 1 \text{ K} - 1) (6.626 \times 10 - 34 \text{ J s}) × (105 \text{ Pa}) = 1.98 \times 1011 \text{ m 3 mol} - 1 \text{ s} - 1 Solve for the entropy of activation: $(k)E = \Delta \ddagger SR | \ln r - 2 | + a B (JT () 39.7 \times 103 J mol - 1 0.35 m 3 mol - 1 s - 1 Hence \Delta \ddagger SR | \ln r - 2 | + a B (JT () 39.7 \times 103 J mol - 1 0.35 m 3 mol - 1 s - 1 Hence \Delta \ddagger SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | \ln r - 2 | + = R | \ln - 1 21C.4(b)$ For a bimolecular gas-phase reaction [Exercise 21C.3(b)], $(A E)Ea(A) \ddagger \Delta = SR | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + = R | + =$ $a - 2 + = R | \ln - 2 | B | B | T | B RT | T kRT 2 hp O For two structureless particles, the rate constant is the same as that of collision theory where B = (8kT)kr = NA\sigma * | (\pi \mu | 1/2 e - \Delta E0 / RT [Example 21C.1] 9 The activation energy is [20D.3] d ln kr d Ea = RT 2 = RT 2 dT dT (\Delta E0) 1 8 k 1 * | ln N A\sigma + 2 ln m + 2 ln T - RT | () (1 \Delta E0) RT$ $+ = RT 2 | = \Delta E0 + 2 , (2T RT 2) so the prefactor is 1/2 1/2 (8kT) - \Delta E0 / RT 1/2 (8kT) 1/2 A k = N A\sigma | N A\sigma * | e = e = |e| |e| re (\pi \mu) (\pi \mu) 1/2 1/2 * O (8kT) kRT 2 1 3 |) |(1) | (\sigma p h (8) Hence \Delta \ddagger S R { ln N A\sigma * | ln R 2 ln = - - = + } { |e| - } . O 3/2 | 2 2 || p h (\pi \mu) |(1) | (kT) (\pi \mu) For identical particles, \mu = m/2 = (92 u)$ $(1.661 \times 10-27 \text{ kg u}-1)/2 = 7.6 \times 10-26 \text{ kg}$, and hence $\Delta \ddagger S = 8.3145 \text{ J} \text{ K} - 1 \text{ mol} - 1 \text{ Ea} / \text{RT}$ (*) $1/2 [0.45 \times (10-9 \text{ m}) 2 \times 105 \text{ Pa} \times 6.626 \times 10-34 \text{ J} \text{ s})] \times \{\ln \mid - -23 - 1 - 26 \text{ s}/2 2 \mid \}$ (1.381×10 J K × 450 K) $(\pi \times 7.6 \times 10 \text{ kg}) | 1 = -79 \text{ J} \text{ K} - 1 \text{ mol} - 1 \text{ . 21C.5(b)}$ At low pressure, the reaction can be assumed to be bimolecular. (The rate constant is certainly second-order.) (A) $\ddagger (a) \Delta = SR | ln - 2 | [Exercise 21C.4(b)] \setminus B | where B = 1.381 \times 10 - 23 | K - 1 \times 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1 + 1.54 \times 1014 dm 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54
\times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1011 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1014 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 - 34 | s \times 105 Pa hp = 1.54 \times 1014 m 3 mol - 1 s - 1. (2.3 \times 1013 dm 3 mol - 1 s - 1) Hence \Delta \ddagger S 8.3145 | K - 1 mol - 1 \times (298 K) 2 kRT 2 [Exercise 21C.4(b)] = 0.6.26 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K - 1 mol - 1 \times 10 + 3.3145 | K$ $\ln = -2 \left[-1 - 1 \ 14 \ 3 \left(1.54 \times 10 \ \text{dm mol s} \right) = -32 \ \text{J K} - 1 \ \text{mol} - 1 \ \text{(b)}$ The enthalpy of activation for a bimolecular gas-phase reaction is [Topic 21C.2(a) footnote] $\Delta \pm H = \text{Ea} - 2RT = 30.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{K} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{c} + 298 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{mol} - 1 \ \text{kJ} \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{mol} - 1 \ \text{k} = 25.0 \ \text{kJ} \ \text{mol} - 1 \ \text{mol} - 1 \ \text{mol} - 1 \ \text{kJ} \ \text{kJ} \ \text{mol} - 1 \ \text{kJ} \ \text{mol} - 1 \ \text{kJ} \ \text{kJ} \ \text{mol} - 1 \ \text{mol$ K-1 mol-1 $\Delta \ddagger G = +34.7 \text{ kJ} \text{ mol}-1$ 21C.6(b) Use eqn. 21C.18 to examine the effect of ionic strength on a rate constant: log kr = log kr^{\circ} + 2A|zAzB|11/2 = 0.032, and kr^{\circ} = 1.08 dm6 mol-2 min-1. Solutions to problems 21C.2 log kr = log kr + 2 AzA zB I 1/2 [21C.18] This expression suggests that we should plot log kr against 11/2 and determine zB from the slope, since we know that |zA| = 1. We draw up the following table: $I / (mol kg-1) \{I / (mol kg-1)\} 1/2 \log \{kr / (dm3 mol-1 s-1)\} 0.0025 0.050 0.021 0.0037 0.061 0.049 10 0.0045 0.067 0.064 0.0065 0.081 0.072 0.0085 0.092 0.100 These points are plotted in$ Figure 21C.1. Figure 21C.1. Figure 21C.1 The slope of the limiting line in Figure 21C.1 is approximately 2.5. Since this slope is equal to 2 AzA zB × (mol dm -3)1/2 = 1.018 zA zB × (mol dm -3)1 that log kr is proportional to the ionic strength even when one of the reactants is a neutral molecule. Figure 21C.2 From the graph, the intercept at I = 0 is -0.182, so the limiting value of kr is kr° = 10-0.182 = 0.658 dm3 mol-1 min-1 Compare the equation of the best-fit line to eqn 21C.16b: log = kr log kr ° - log yC yI yH O yI yH O $\gamma C = \log kr^\circ + \log \ddagger - which implies that \log \gamma I \gamma H O - 2 \gamma C 2 2 2 - 2 2 \ddagger = 0.145I \ddagger If the Debye-Hückel limiting law holds (an approximation at best), the activity coefficients of I- and the activity coeffi$ strength. 11 Ka = 21C.6 2 - + [H +][A -] 2 [H][A] $\gamma \pm \gamma \pm \approx$ [HA] [HA] γ HA Therefore, [H +] = log K a + log [HA] [HA] - 2 log $\gamma \pm = \log K a + \log [HA] [HA] - 2 \log (\pi + 1) [HA] + 2 (\pi + 1) [HA]$ That is, the logarithm of the rate should depend linearly on the square root of the ionic strength. 1/2 v v = v° × 102 AI log = 2 AI 1/2 so v° That is, the rate depends exponentially on the square root of the ionic strength. 1/2 v v = v° × 102 AI log = 2 AI 1/2 so v° That is, the rate depends exponentially on the square root of the ionic strength. $O 2 O kT (RT) N Aq C (-\Delta E0) (RT) q C (-\Delta E0) = \approx kr \kappa exp exp | O O O h p q H q D2 (RT) hp q H q D2 (RT)$ kTmH)3/2 RT O = q = and AH | |so q H O 3 p AH p O h3 (2π kTmH)We have neglected the spin degeneracy of H, which will cancel the spin degeneracy of H, which will cancel the spin degeneracy of the activated complex. The partition function of D2 has a rotational term as well. RkT 2 (2π kTmD2)3/2 RT kT O q D2 = O 3 × = p AD2 σ hcBD2 2 p O h 4 cBD2 We have neglected the vibrational partition function of D2, which is very close to unity at the temperature in question. The symmetry number σ is 2 for a homonuclear diatomic, and the rotational constant is 30.44 cm-1. Now, the partition function of the activated complex will have a translational piece that is the same regardless of the model: \times q CR[‡] \times q CV[‡] q CO[‡] = q CTO \ddagger O H where RT (2 π kTmHD) 3/2 q C \ddagger = TO 2 p O h3 Let us aggregate the model-independent factors into a single term, F where 2h3 cBD2 mHD2 3/2 (RT) 2 q CTO \ddagger ($-\Delta E0$) = exp exp | F = | | O O O 3/2 hp q H q D2 (RT) kT (2π mH mD2 kT) (RT) 1/2 () 53 ($-\Delta E0$) = h cBD2 = exp | 2.71 × 104 dm3 mol-1 s -1 | 3 3 3 3 5 | (RT) 2 q CTO \ddagger (RT) 4π mH mD2 kT) (RT mH mD2 kT) (RT) 4π mH mD2 kT) (RT mH mD2 kT) (RT mH mD2 kT) (RT mH mD2 /(2mH (4) p T k /where we have taken mHD = 5mH and mD = 4mH . 3 2 Now 2 kr = F × q C‡ R V 12 The number of vibrational modes in the activated complex; however, in either case, one mode is the reaction coordinate, and is removed from the partition function. Therefore, assuming all real vibrations to have the same wavenumber v 2 3 q CV[‡] = q mode (non-linear) or q mode (linear) $-1 \left[\left(-hcv \right) \right]$ where q mode = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp |
kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | | = (||| = 1.028 | 1 - exp | kT | 1 - exp | kT | | 1 - e where the rotational constants are related to moments of inertia by 2 = B = where I Σ mr 4π cI and r is the distance from an atom to a rotational axis. (a) The first model for the activated complex is triangular, with two equal sides of s =1.30 × 74 pm = 96 pm and a base of b =1.20 × 74 pm = 89 pm R The moment of inertia about the axis of the altitude of the triangle (z axis) is II = 2mD (b/2) 2 = mH b 2 so $A = 21.2 cm - 1.4 \pi cmH b 2$ To find the other moments of inertia, we need to find the center of mass is the position z at which Σ mi (zi - z) = 0 = 2(2mH)(0 - z) + mH (H - z) i where H is the height of the triangle, H = [s 2 - (b / 2)2]1/2 = 85 pm so the center of mass is z = H / 5. The moment of inertia about the axis in the plane of the triangle perpendicular to the altitude is $I 2 = 2(2mH)(H / 5)2 + (mH / 5)H 2 = 28.3 \text{ cm} - 14\pi c(4mH$ pm and the moment of inertia about the axis perpendicular to the plane of the triangle is I 3 = 2(2mH)rD 2 + mH (4H / 5)2 = 2(2mH)[(H / 5)2 + (b / 2)2] + mH (4H / 5)2 so = B = (4mH / 5)(s 2 + b 2). so 13 = 12.2 cm - 14\pi c(4mH / 5)(s 2 + b 2). The rotational partition function is = C 1 (kT) (\pi) 47.7 = ||\sigma|| σ is 2 for this model.) The vibrational partition function is 2 q CV[‡] = q mode = 1.057 3/2 1/2 = q CR[‡] so the rate constant is: kr = F × q CR[‡] × q CV[‡] = 1.37 × 106 dm 3 mol-1 s -1 (b) To compute the moment of inertia, we need the center of mass. Let the terminal D atom be at x = b, and the H atom at x = b + s. The center of mass is the position X at which \sum mi (xi - X) = 0 = 2mH (b - X) + mH (s + b - X) i 5X = 3b + s so x = (3b + s) / 5 The moment of inertia is I = \sum mi (xi - X) 2 = 2mH X 2 + 2mH (b - X) + mH (s + b - X) 2 i = 3.97 × 10-47 m kg 2 and = B = 7.06 cm - 1 4 \pi cI The rotational partition function is kT = q R[‡] = 39.4 C \sigma hcB (The symmetry number σ is 1 for this model.) The vibrational partition function is 3 q CV[‡] = q mode = 1.09 So the rate constant is kr = F × q CR[‡] × q CV[‡] = 1.16 × 106 dm 3 mol-1 s -1 (c) Both models are already pretty good, coming within a factor of 3 to 4 of the experimental result, and neither model has much room for improvement. Consider how to try to change either model to reduce the rate constant toward the experimental value. The factor F is modelindependent. The factor F is modelindependent. The factor q CV[‡] is nearly at its minimum possible value, 1, so stiffening the vibrational modes will have almost no effect. the rotational constants were increased, which means decreasing the moments of inertia and the bond lengths. Reducing the lengths s and b in the model a) or 6.9×105 (model a) or 6.9×105 (model a) or 6.9×105 (model a) or 6.9×105 (model b) dm3 mol-1 s-1, even with a stiffening of vibrations. Reducing the HD distance in model (a) to 80% of the H2 bond length does produce a rate constant of 4.2×105 dm3 mol-1 s-1 (assuming stiff vibrations of 2000 cm-1); such a model is not intermediate in structure between reactants and products, though. It appears that the rate constant is rather insensitive to the geometry of the complex. 21C.10 Eqn. 21C.18 may be written in the form: o 1 $\log(kr/kr) 2zA = 2AI1/2$ where we have used zA = zB for the cationic protein. This equation suggests that zA can be log (kr/kr) 2 k = 01 log (kr/kr) 2 k = for the computation: I kr/kro log(kr/kro) / I1/2 0.0100 8.10 9.08 0.0150 13.30 9.18 log (kr / kro) I 1/2 zA = 0.0200 20.50 9.28 0.0250 27.80 9.13 0.0300 38.10 9.13 0.0300 38 to discussion questions 21D.2 The saddle point on the potential energy surface corresponds to the transition state of a reaction. The saddle-point energy is the minimum energy for a path on the surface between reactants and products do not pass through points of greater energy, so the activation energy is a lower limit to the activation energy is a lower limit to the activation energy is a lower limit to the activation energy. An attractive surface is one whose saddle point is closer to reactants than to products, so that the transition at end in products whereas trajectories in which the reactant is vibrationally excited tend not to cross the saddle point and end in products. Conversely, on a repulsive surface, the oscillatory motion of a trajectory that has excess vibrational energy in the reactant enhances the likelihood that the trajectory will end in products rather than simply reflect back to reactants. Solutions to exercises 21D.1(b) Refer to Figure 21D.20 of the main text, which shows a repulsive potential energy surface as well as trajectories of both a successful reaction and an unsuccessful reactory is fairly straight from the lower right, representing reactants. The successful trajectory is fairly straight from the lower right through the transition state, indicating little or no vibrational excitation in the reactant. Therefore most of its energy is in translation. That trajectory runs up a steep portion of the surface and rolls back down the valley representing the reactant. conversely, is able to turn that corner only because it has a substantial amount of energy in vibration (which is represented by
side to side motion in the valley represented by side to side motion. valley representing products, so the product is high in translational energy and low in vibrational energy. 15 21D.2(b) The numerator of eqn. 21D.6 is V 1 - E / RT e - = P (E) e - E / RT dE = () (1 - e - V / RT) $\int 0 e dE = E 0 RT RT$ Thus, if the cumulative reaction probability were a step function that vanishes at high temperature then the numerator would decrease with increasing temperature. (The exponential term increasing temperature, but it diminishes the expression because of the negative sign in front of it. The 1/T factor also decreases with increasing temperature.) rate constant would decrease with increasing temperature even faster, because the denominator of eqn. 21D.6 would increase with increasing temperature.) Comment: The solution to Exercise 21D.2(a) can be obtained from this solution by taking the limit $V \rightarrow \infty$. $\int \infty 0$ Solutions to problems 21D.2 The number density of scatterers (Ns) and the path length L are the same in the two experiments. Because I so I = I 0 e - σ N L [Problem 21D.1] ln = $-\sigma$ N L [Problem 21D.1] ln = $-\sigma$ N L [Problem 21D.2] In 0.6 = $= 5 \ln 0.9 \sigma$ (Ar) CH2F2 is a polar molecule; Ar is not CsCl is a polar ion pair and is scattered more strongly by the polar CH2F2. 21D.4 Refer to Figure 21D.1. Figure 2 R1 + R2 (v) || 0 b > R1 + R2 (v) $|| where R2(v) = R2e-v/v^*$, R1 = R2/2 = b. () 1 θ (v) = $\pi - 2 \arctan | (a) - v/v^* || 1 + 2e / (Note: The restriction is plotted as curve (a) in Figure 21D.2. 16 Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*$, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. 16 Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*, which is valid for all v.) This function is plotted as curve (a) in Figure 21D.2. (b) The kinetic energy of approach is E = mv2/2, so () = R2e-v/v^*. 1 θ (E) = π - 2 arcsin where -(E/E*)1/2 || 1 + 2e] This function is plotted as curve (b) in Figure 21.6. E* = m(v*)2/2. 21E Electron transfer in homogeneous systems Answer to discussion question 21E.2 Electron transfer. From considerations in Topic 8A, we would expect that tunneling would be more that tunneling would be more to discussion question 21E.2 Electron transfer. important for electrons than any other participate in chemical reactions because they are so much lighter than even the lightest atoms or ions. Tunneling is responsible for the exponential distance dependence of the factor Het(d)2 (eqn. 21E.4), which is directly proportional to the electrontransfer rate constant (eqn. 21E.5). A more thorough discussion can be found in Topic 21E.2(a). Solutions to exercises 21E.1(b) For a donor-acceptor pair separated by a constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molar units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units rather than molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecular units, (Δ G O)2 Δ r G O + constant – In ket = – r 2RT 4RT ΔER or, using molecu $-r - + \text{constant} 4kT \Delta \text{ER} 2kT$ Two sets of rate constants and reaction Gibbs energies can be used to generate two equations (eqn. 21E.9 applied to the two sets) in two unknowns, ΔGr and the constant. ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G
O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) 2 $\Delta \text{ G O}$ ($\Delta \text{ G O}$) $GO - \Delta r GIO = \ln et_2 + r 2 4kT \Delta ER ket_1 2kT (\Delta r GIO) 2 - (\Delta r G2O) 2 \Delta ER = k 4kT ln et_2 + 2 (\Delta r G2O - \Delta r G1O) k et_1 17 (-0.665 eV) 2 - (-0.975 - 0.665) eV ln 2.02 × 105 1.602 × 10 - 19 J eV - 1 If we knew the activation Gibbs energy, we could use eqn. 21E.5 to$ compute Het (d) from either rate constant, and we can compute the activation Gibbs energy from eqn. 21E.6: (Δ G O + Δ Er) 2 {(-0.665 + 1.53) eV} Δ ER = Now ket = 2{H et (d)} + 1/2 ($-\Delta$ ‡G) exp | || 4kT Δ ER) H et (d) = | et || exp | | 3 || 2 || π (2kT) 1/2 $(6.626 \times 10-34 \text{ J s})(2.02 \times 105 \text{ s} - 1) = |2 / 1/4 (4(1.53 \text{ eV})(1.602 \times 10-19 \text{ J eV} - 1)(2.881 \times 10-23 \text{ J K} - 1)(298 \text{ K}) |s_0 = 9.6 \times 10-24 \text{ J } 21\text{ E.2(b)}$ Equation 21E.8 applies: ln ket = $-\beta d$ + constant The slope of a plot of ket versus d is $-\beta$. The slope of a line defined by two points is: slope = so $\Delta y \ln ket$, 2 - ln ket, 1 ln 4.51 × 104 - ln 2.02 × 105 = - β = $-\beta$ = $\Delta x d^2 - d1$ (1.23 - 1.11) nm β = 12.5 nm -1 lnserting data from either rate constant = ln 2.02 × 105 + (12.5 nm -1)(1.11 nm) = 26.1 Taking the exponential of eqn. 21E.8 yields: ket = e - βd + constant $s - 1 = e - (12.5/nm)(1.59 \text{ nm}) + 26.1 \text{ s} - 1 = 5.0 \times 102 \text{ s} - 1$ Solutions to problems 21E.2 Estimate the bimolecular rate constant kr for the reaction Ru(bpy)32 + +Fe(H 2 O)63 + by using the approximate Marcus cross-relation: kr \approx (kDDkAAK)1/2 The standard cell potential for the reaction is O O (Fe(H 2 O)63 +) = $(1.26 - 0.77)V = 0.49 V (Ru(bpy)33 +) - Ered E O = Ered so the equilibrium constant is (1)(96485 C mol-1 s - 1)(0.49 V) (vFEO) 8 = exp K = exp | | (8.3145 J K - 1 mol-1)(298 K) | = 1.9 \times 10 (RT || The rate constant is approximately kr ~ {(4.0×108 dm3 mol-1 s-1)(4.2 dm3 mol-1 s$ eqn. 21E.8 ln ket = $-\beta d$ + constant apply to these data? Draw the following table and plot ln ket vs. d (Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 17.5 4.14 Figure 21E.1): 18 d / nm 0.48 0.95 0.96 1.23 1.35 2.24 ket / s-1 1.58×1012 3.98×107 6.31×101 ln ket / s-1 28.1 22.1 20.7 18.9 ln ket / s-1 28.1 28.1 28.1 apply. The least-squares linear fit equation is: ln ket / s = 34.7 - 13.4d / nm R 2 (correlation coefficient) = 0.991 so we identify β = 13.4 nm -1 21F Processes at electrode, several steps are necessary. A species in a bulk solution phase must lose its solvating species and make its way through the electrodesolution interface to the electrode. Once there, its hydration sphere must be adjusted by the electron transfer itself, and then the species must detach and reverse its steps as it were, passing back through the interface into the bulk solution phase. Because there are energy requirements associated with these steps, they are said to be activated. How the activation Gibbs function depends on applied potentials and on the resemblance of transition state to oxidized and reduced species is treated in Topic 21F.2(a). Solutions to exercises 21F.1(b) The conditions are in the limit of large, positive overpotentials, so eqn 21F.5b applies: ln j = ln j0 + (1 - α)fn 9684556 (1 - α)fn 968456 (1 - α)fn 96866 ($C \mod -1$ F = 38.9 V -1 RT (8.3145 J K -1 mol -1) × (298 K) Subtracting this equation from the same relationship between another set of currents and overpotentials, we have where f = 19 j' = (1 - α) f (η ' - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) η ' = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) \eta = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) \eta = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) j which rearranges to ln (j'/j) ln(72/17.0) \eta = η + = (105 × 10-3 V) + = 0.169 V (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) f (η - η) = (1 - α) = (1 - α) f (η - η) = (1 - α) = (1 - \alpha) = (1 - α) = (1 - \alpha) = (1 - α) = (1 - \alpha) 21F.5a; then $j0 = j e^{-(1-\alpha)\eta f} = (17.0 \text{ mA cm}^{-2}) \times e^{-(1-0.42)} \times 0.105 \text{ V} \times 38.9/\text{V} = 1.59 \text{ mA cm}^{-2}$. 21F.3(b) In the high overpotential limit $[21F.5a](1-\alpha) f(\eta 1-\eta 2) j = j0e$ so 1 = e and j2 So the current density at $0.60 \text{ V} j2 = (1.22 \text{ mA cm}^{-2}) \times e^{j2} = j1e(1-0.50) \times (0.60 \text{ V} - 0.50 \text{ V}) \times (38.9/\text{V}) (1-\alpha) f(\eta 2-\eta 1)$. $= 8.5 \text{ mA cm}^{-2}$ about a 7-fold increase compared to the current at 0.50 V. 21F.4(b) (i) The Butler-Volmer equation is [21F.1]j = j0 (e(1- α) f η - e - α f η) = (2.5 × 10-3 A cm -2) × (e(1-0.58)×(0.30 V)×(38.9/V) - e -0.58×(0.30 V)×(38.9/V)) = 0.34 A cm -2 (ii) Eqn 21F.5a (also known as the Tafel equation) corresponds to the neglect of the second exponential above, which is very small for an overpotential of 0.3 V. (Even when it was kept, in part (a), it was negligible.) Hence j = 0.34 A cm-2. The validity of the Tafel equation increases at lower overpotentials, but decreases at lower overpotentials. A plot of j against $\eta \rightarrow 0$. The validity of the Tafel equation improves as the overpotential increases. 21F.5(b) The Butler-Volmer equation (21F.1]), with transfer coefficients from Table 21F.1, is $1-\alpha f \eta j = j$ (e() $-e -\alpha f \eta) = j$ (e() $-a -\alpha f \eta) = j$ (2+) RT 1 a(Fe 2+) ln = 0.77 V - ln Q = E O - ln f a(Fe 3+) vF f a(Fe 3+) vF f a(Fe 3+) = E' - 0.77 V + ln r, ln f f a(Fe 3+) where r is the ratio of activities. Specializing to the condition that the ions have equal activities. Specializing to the condition that the ions have equal activities. Specializing to the condition that the ions have equal activities. constant parts of the exponentials (with f = 38.9 V-1). and incorporating them as numerical factors yields Thus $\eta = E' - 0.77 \text{ V} + j = (8.6 \times 10 - 6 \text{ mA cm} - 2) \times e0.42 \text{ fE}' - (8.8 \times 10 - 7 \text{ mA cm} - 2) = -0.58 \text{ fE}' 21\text{ F}.6(b)$ The current density of electrons is j0/e because each one carries a charge of magnitude e. Look up j0 values in Table 21F.1, and recall that 1 A = 1 C s-1. j0 = $1.0 \times 10-6$ A
cm-2 For Cu | H2 | H+ -6 j0 1.0×10 A cm -2 = 6.2×1012 cm -2 s -1 e $1.602 \times 10-19$ C For Pt | Ce4+, Ce3+ j0 = $4.0 \times 10-5$ M cm -2 s -1 = e $1.602 \times 10-19$ C 20 There are approximately ($1.0 \times 10-2$ m)2 = 1.5×1015 atoms in each square centimeter of $(260 \times 10-12 \text{ m})2$ surface. The numbers of electrons per atom are therefore $4.2 \times 10-3 \text{ s}-1$ and 0.17 s-1, respectively. 21F.7(b) When the overpotential is small, its relation to the current density is [21F.4] RT i j n = Fi0 fi0 which implies that the current through surface area S is I = Si = Si0 fn. An ohmic resistance r obeys n = Ir, and so we can identify the resistance as $r = \eta I = 112.57 \times 10-2 \Omega = 112.57 \times 10-2 \Omega = 112.57 \times 10-2 \Omega = 10. \Omega r = 2.5 \times 10-3 r = 21F.8(b)$ Zn can be deposited if the H+ discharge if the H+ discharg current is less than about 1 mA cm-2. The exchange current, according to the high negative overpotential limit, is $j = j0e-\alpha\eta$ [21F.6a] = (0.79 mA cm-2) × e-0.5×(38.9/V)×(-0.76 V) = 2.1×106 mA cm-2 This current density is much too large to allow deposition of zinc; that is, H2 would begin being evolved, and fast, long before zinc began to deposit. Solutions to problems 21F.2 Deposition may occur when the potential falls to below E. (Recall that $\eta < 0$ for cathodic processes.) E is given by the Nernst equation (6C.4): RT E = EO + ln a(M +) zF Simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by EO (Sn, Sn 2+) + RT ln a(Sn 2+) = EO $(Pb, Pb2+) + RT \ln a(Pb2+) 2F 2F 2+ a (Sn) 2F \{E O (Pb, Pb 2+) - E O (Sn, Sn 2+)\}$ or = ln RT $a(Pb 2+) () = 2 \times (38.9 V - 1) \times (-0.126 + 0.136) V = 0.78$ That is, we require $a(Sn2+) = 2.2a(Pb2+) \cdot 21F \cdot 4$ This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of $Ox + e^- \rightarrow Red$ we have here $\ln 3 + + 3 = - \rightarrow \ln \alpha$ and $\ln j = \ln j0 + z(1 - \alpha)\eta$ cathode $\ln (-j) = \ln j0 + z(1 - \alpha)\eta$ cathode $\ln (-j) = \ln j0 - z\alpha\eta$ We draw up the following table $(A m-2) - E/V \ln (j/A m-2) \eta/V 0 0.388 \ 0.590 \ 0.365 \ 0.023 - 0.5276 \ 1.438 \ 0.350 \ 0.038 \ 0.3633 \ 3.507 \ 0.335 \ 0.053 \ 1.255 \ 21 We carry out a linear regression of ln j against \eta with the following results (see Figure 20F.1). Figure 20F.1 standard deviation = 0.0154 slope = z(1 - \alpha)f = 59.42 V-1$, standard deviation = 0.0006 y-intercept = ln j = -1.894. K = 1 almost exactly The fit of the three data points to the Tafel equation is almost exact. Solving for α from the slope, we obtain (59.42 V - 1) 59.42 V - 1 (59.42 V - 1) 59.42 V - 1 (59.42 V - 1) 59.42 V - 1) which matches the usual value of α exactly. J0 = e-1.894 A m-2 = 0.150 A m-2 = 0.150 A m-2 = 0.150 A m-2. The cathodic current density at E = -0.365 V is obtained from ln(- jc) = $\ln j0 - z\alpha f\eta = -1.894 - (3 \times 0.50 \times 0.023 V) \times (38.9 V - 1) = -3.26$ so jc = e - 3.26 = 0.038A m - 2 Start from the Butler-Volmer equation (21F.1), and expand it in powers of η : = j j0 ($e(1-\alpha) f\eta - e - \alpha f\eta$) = $j0 \{1 + (1 - \alpha) \eta f + 12 (\eta f) 2 (1 - 2\alpha) + \} 21F.6$ Average over one cycle (of period $2\pi/\omega$): { } = j j0 η f + 12 (1 - 2 α) f 2 η 2 + where η = 0, because ω 2 π η 2 = 12 η 02, because Therefore, and j = 1 4 $\int 2\pi/\omega 0 \, \omega \, 2\pi \int \cos \omega t \, dt = 0.2 \pi/\omega 0 \, \omega \, dt = 0.2 \pi/\omega 0 \, \omega \, 2\pi \int \cos \omega t \, dt = 0.2 \pi/\omega 0 \, \omega \, dt = 0.2 \pi/\omega$ (10 mV)2 4 = 7.2 µA 21F.8 (a) The roughly symmetrically distributed positive maximum and negative minimum suggest a reversible one-electron transfer. Compare to Figures 21F.12 and 21F.13 (b) of the main part of the chapter as discussed in Topic 21F.3 and Example 21F.2. negative minima, suggesting a reversible two-electron transfer brought about by sequential reversible oneelectron transfers. (c) The shape is typical of an irreversible reduction: the positive maximum has no corresponding negative minimum. Compare to Figure 21F.13(a) of the main part of the chapter as discussed in Example 21F.2. (d) Two reductions are apparent in this voltammogram, the second of which is reversible and the first positive maximum has no corresponding minimum; the second does.) Compare to Figure 21F.14 of the main part of the text. Integrated activity 21.2 Both the Marcus theory of photo-induced electron transfer (Topic 21E) and the Förster theory of resonance energy transfer (Topic 20G) examine interactions between a molecule excited by absorption of electromagnetic energy (the chromophore S) and another molecule Q. They explain different mechanisms of quenching, that is, different ways that the chromophore gets rid of extra energy after absorbing a photon through intermolecular interactions. Another common feature of the two is that they depend on physical proximity of S and O: they must be close for action to be efficient. In the Marcus theory, the rate of electron transfer depends on the reaction Gibbs energy of electron transfer depends on the reaction for the two is that they depend on physical proximity of S and O: they must be close for action to be efficient. rearrangement. The rate is enhanced when the driving force (ΔrG) and the reorganization energy transfer in the Förster mechanism is most efficient when Q can directly absorb electromagnetic radiation from S. The oscillating dipole moment of S is induced by the electromagnetic radiation it absorbed. It transfers the excitation energy of the radiation to Q via a mechanism in which its oscillating dipole moment induces an oscillating dipole moment in Q. This energy transfer can be efficient when the absorption spectrum of the acceptor (Q) overlaps with the emission spectrum of the donor (S). 23 22 Processes on surfaces 22A An introduction to solid surfaces Answers to discussion questions 22A.2 AFM, atomic force microscopy, drags a sharp stylus attached to a cantilever. Tiny changes in deflection indicate attraction to or repulsion from atoms on a sample surface. Since no current is involved, both conductive and nonconductive surfaces may be viewed. Surface damage is avoided by using a cantilever that has a very small spring constant. The method does not require a vacuum, and it has been applied in a liquid environment. Biological polymers may be viewed and nanometre resolutions have been achieved. image artifacts and distortions. Thermal drift of adsorbates may result in image distortions during relatively slow surface scans. FIM, field-ionization microscopy, points a tip, with a point radius of about 50 nm, toward a fluorescent screen in a chamber containing about 1 mTorr to 1 nTorr of either hydrogen or helium. A positive 2-20 kV potential applied to the tip causes the hydrogen or helium gas adsorbate molecules to ionize and accelerate to the fluorescent screen. The image portrays the
electrical characteristics of the adsorbate are deduced. See the very interesting historical review of the technique in the issue of C&EN 83, no. 48 (November 28, 2005): 13-16. LEED, low-energy electron diffraction, uses electrons with energies in the range 10-200 eV, which ensures diffraction from atoms only on or near the sample surface. Diffraction intensities depend on the vertical location of the atoms. The diffraction pattern is sharp if the surface is well-ordered for long distances compared with the wavelength of the incident electrons. Diffuse patterns indicate a poorly ordered surface or the presence of impurities. If the LEED pattern does not correspond to the pattern expected by extrapolation of the surface, then either a reconstruction of the surface has occurred or there is order in the arrangement of an adsorbed layer. The interpretation of LEED data can be very complicated. SAM, scanning Auger electron microscopy, uses a focused 1-5 keV electron beam to probe and map surface composition to a resolution of about 50 nm. The high energy impact causes the ejection of an electron from a low-lying orbital, and an upper electron falls into it. The energy this releases may result either in the generation of X-ray fluorescence or in the ejection of a second electron, the Auger effect. The emissions are used to identify chemical constituents at interfaces and surfaces of conducting materials to a depth of 1-5 nm. SEM, scanning electron microscopy, uses magnetic fields to focus and scan a beam of electrons across a sample surface. Scattered electrons from a small irradiated area are detected and the electrical signal is sent to a video screen. Resolution is typically between 1.5 and 3.0 nm. Nonconductive materials require a thin conductive materials requi microscopy, reveals atomic details of surface and adsorbate structure. Surface chemical reactions can be viewed as they happen. The tip of the STM, which may end in a single atom, can also be used to manipulate adsorbed atoms on a surface, making possible the fabrication of complex and yet very tiny structures. devices. The method is based upon the quantum mechanical tunneling effect in the presence of a bias voltage between the STM tip and sample surface, and the electrical current of tunneling generates an image of the surface topography with a resolution in the nanometre range. Images of surface electronic states may be generated. A host of very interesting STM images can be viewed at . TEM, transmission electron beam through the sample and collects the image on a screen. Electron wavelengths can be as short as 10 pm and typical resolutions are about 2 nm so the method cannot resolve individual atoms. Samples must be very thin cross-sections of a dry (therefore, nonliving) sample. Electron microscopy is very useful in the study of internal structures of cells. 22:1 Solutions to exercises 22A.1(b) The collision frequency, ZW, of gas molecules with an ideally smooth surface area is given by eqn 22A.1. p $= ZW = [22A.1; m M / N A] 1/2 (2\pi MkT / N A) = \{ \} p \times (kg m - 1 s - 2) / Pa \times (10 - 4 m 2 / cm 2) \{ 2\pi \times (1.381 \times 10 - 23 JK - 1) \times (298.15 K) \times (kg mol) / (6.022 \times 10 - 1 23) \} \{ M / (kg mol) \} mol - 1) 1/2 - 1 1/2 () p / Pa | | cm - 2 s - 1 at 25^{\circ} C 4.825 \times 10 | = 1/2 | -1 | M / (kg mol) | (j) Nitrogen (M = 0.02802 kg mol - 1) p = 10.0 Pa, ZW = 10.0 Pa, ZW = 10.0 Pa = 10.0 Pa = 10.0 Pa = 10.0 Pa = 10.0 Pa$ $3.88 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ p} = 0.150 \mu \text{Torr} = 2.00 \times 10 - 5 \text{ Pa}$, $ZW = 5.76 \times 1013 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, $ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)}$ Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ s} - 1 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 1019 \text{ cm} - 2 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10.0 Pa, ZW = 3.81 \times 10004 \text{ cm} - 2 \text{ (i)} Methane (M = 0.01604 kg mol-1) p = 10. with surface area A is ZWA = $5.00 \times 1019 \text{ s} - 1.$ ZW A = p p A [95.1; m M / N A] = $1/2(2\pi \text{MkT} / \text{N A})(7 \text{ W A}) \times (2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s}) \times \{2\pi (28.02 \times 10 \text{ = } 19 / \text{A} - 1 - 3) / (3.14 \times 10 \text{ kg mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s}) \times \{2\pi (28.02 \times 10 \text{ = } 19 / \text{A} - 1 - 3) / (3.14 \times 10 \text{ kg mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s}) \times \{2\pi (28.02 \times 10 \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10 \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) 1/2 - 6 \text{ m2}) = 733 \text{ Pa Solutions to problems} = 22A.2 \text{ ZW} = p = [22A.1; m M / \text{N A}] = 1/2(2\pi \text{MkT} / \text{N A}) 1/2(5.0 \times 10^{10} \text{ s} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{ K}) / (6.022 \times 1023 \text{ mol} - 1) \times (525 \text{$ NA] 1/2 ($2\pi MkT/NA$) { } p × (kg m -1 s -2) / Pa × (10-4 m 2 / cm 2) { $2\pi × (1.381 \times 10 - 23$ JK -1) × (300 K) × (0.03200 kg mol) / ($6.022 \times 10 = 2.69 \times 1018$ × (p / Pa) cm -2 s -1 (a) At 100 kPa, ZW = 2.69×1018 cm -2 s -1 (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = $2.69
\times 1018$ cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.000 Pa, ZW = 2.69×1018 cm -2 s -1 (cm 2) for O 2 at 300 K (b) at 1.00 titanium is 291 pm, so the number of atoms per cm2 is approximately 1.4×1015 (the precise value depends on the details of the surface). The number of collisions per exposed atom is therefore Z W / (1.4×1015 cm -2). (a) When p = 1.000 Pa, Zatom = 2.0 \times 108 s -1 (b) When p = 1.000 Pa, Zatom = 2.0 × 108 s -1 (b) When p = 1.000 Pa, Zatom = 2.0 × 108 s -1 (c) When p = 1.000 Pa, Zato 2.0 × 103 s -1 22A.4 The farther apart the atoms responsible for the pattern (a), yields a reconstructed face, which has LEED pattern (a), yields a reconstructed face, which has LEED pattern (b). (b) (a) 22B Adsorption and desorption Answers to discussion questions 22B.2 The characteristic conditions of the Langmuir isotherm are: 1. Adsorption cannot proceed beyond monolayer coverage. 2. All sites are equivalent and the surface is uniform. 3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites. For the BET isotherm condition number 1 above is removed and the isotherm applies to multi-layer coverage. In Example 22B.1 it is shown that a gas exhibits the characteristics of a Langmuir adsorption isotherm when p p 1 = + V V $\propto \alpha V \propto$ where V is the volume of the adsorbate and V $\propto \alpha V \propto$ where V is the volume of the adsorbate and V $\propto \alpha V \propto \alpha V \propto$ slope $1/V \propto$ and intercept $1/\alpha V \propto$. In contrast the BET adsorption isotherm is followed when, as shown in Example 22B.3, (c - 1) z z 1 = + (1 - z)V cVmon cVmon where z = p/p^* and p^* is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, Vmon is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid, Vmon is the vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles a pure bulk liquid. monolayer coverage, and c is a constant. Thus, the BET adsorption mechanism is indicated when a plot of $z/{(1 - z)V}$ against z is linear. Solutions to exercises V V αp [22B.2] = = V ∞ Vmon 1 + αp This rearranges to [Example 22B.1] p p 1 = + V Vmon α Vmon θ 22B.1(b) = Hence, p2 p1 p2 p - = -1 V2 V1 Vmon Vmon Solving for Vmon : = Vmon p2 -p1 = (p2/V2 - p1/V1)(108-56.4) kPa = (108/2.77 - 56.4/1.52) kPa cm-3 27 cm3 22B.2(b) The enthalpy of adsorption is typical of chemisorption (Table 22A.2) for which $\tau 0 \approx 10-14$ s because 22:3 the adsorbate-substrate bond is stiff (see Brief illustration 22B.2). The half-life for remaining on the surface is = t1/2 $\tau 0$ e Ea,des RT 3/ (8.3145×500) [22B.13] $\approx (10-14 \text{ s}) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p}] \text{m} 2 \theta 2 \text{ p} 2 1 + \alpha \text{ p} 1 \text{ which solves to } (\text{m} 1 \text{ p} 2 / \text{m} 2 \text{ p} 1) - 1 (\text{m} 1 / \text{m} 2) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p}] \text{m} 2 \theta 2 \text{ p} 2 1 + \alpha \text{ p} 1 \text{ which solves to } (\text{m} 1 \text{ p} 2 / \text{m} 2 \text{ p} 1) - 1 (\text{m} 1 / \text{m} 2) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p}] \text{m} 2 \theta 2 \text{ p} 2 1 + \alpha \text{ p} 1 \text{ which solves to } (\text{m} 1 \text{ p} 2 / \text{m} 2 \text{ p} 1) - 1 (\text{m} 1 / \text{m} 2) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p}] \text{m} 2 \theta 2 \text{ p} 2 1 + \alpha \text{ p} 1 \text{ which solves to } (\text{m} 1 \text{ p} 2 / \text{m} 2 \text{ p} 1) - 1 (\text{m} 1 / \text{m} 2) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p} 1] \text{m} 2 \theta 2 \text{ p} 2 1 + \alpha \text{ p} 1 \text{ which solves to } (\text{m} 1 \text{ p} 2 / \text{m} 2 \text{ p} 1) - 1 (\text{m} 1 / \text{m} 2) \times (e155 \times 10)$ [Ed $\approx -\Delta \text{ ad } \text{H}$] $\approx 200 \text{ sm} 1 \theta 1 \text{ p} 1 1 + \alpha \text{ p} 2 = \times [22B.2 \text{ and } \text{V} \propto \text{m}/\text{p} 1] + \alpha \text{ p} 2 \text{ m} 2 \theta 2 \text{ p} 1 + \alpha \text{ p} 1 \text{ m} 1 + \alpha \text{ p} 2 \text{ m} 2 \theta 2 \text{ m} 1 + \alpha \text{ p} 1 \text{ m} 1 + \alpha \text{ p} 2 \text{ m} 1 + \alpha \text{ p} 1 \text{ m} 1 + \alpha \text{ p} 2 \text{ m} 1 + \alpha \text{ m} 1 \text{ m} 1 + \alpha \text{ m} 1 + \alpha$ Therefore, = $\theta 1 (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (2b.2] = and \theta 2 0.75 (0.083) \times (4.0) = (1) + (0.083) \times (4.0) = (1) + (0.083) \times (4.0) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} -
1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa} - 1) \times (36.0 \text{ kPa}) = (1) + (0.083 \text{ kPa}) = (1) + (0.083 \text{ kPa}) = (1) + ($ /p) Δ ad H Δ H [Example 22B.2, Δ ad H = $-\Delta$ des H = -12.2 J / 1.00 mmol] = - des || || = R R $\langle \partial (1/T) \rangle \partial$ Assuming that Δ des H is independent of temperature, integration and evaluation gives ln (12.2 kJ mol--1 - 1 || p1 R $\langle T2 T1 \rangle \langle 8.3145 J K mol \rangle \langle 318 K 298 K \rangle$ which implies that p2 = kPa // 240 K 180 K /-1 = -6.40 kJ mol-1 22B.7(b) The desorption times at two different temperatures is given by: = t (2) / t (1) t1 = e / 2 (2) / t (1) t1 = e / 2 (2) / t1 / 2 (1) Ea, des RT1 Solving for the activation energy for desorption, Ea,des, gives: 22:4 Ea,des $(1/T2 - 1/T1)/R = Ea,des R \ln \{t(2)/t(1)\}(1/T2 - 1/T1) - 18.44 s (1/T - 1/T1)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: <math>(11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = 285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = -1 = -285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = -285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = -285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = -285 k mol - 1 The desorption time, t, for the same volume at temperature T is given by: (11)/R = -1 = -285 k mol - 1 The desorption time, t, for the same volume at temperature$ $285 \times 103 \text{ J} \text{ mol}-1$) × |(-|/(8.3145 J K mol)| 873 K T |||| = [11]| - ||| (T/1000 K 0.873 |||) (1856 s) exp $||| (34.3) \times ||| (1000 \text{ K} 0.873 |||)$ (1856 s) exp ||| (1000 K 0.873 |||) (1856 s) exp ||| (1times at two different temperatures is given by: t (2)/t(1) t1 = e = /2(2)/t1/2(1) Ea,des RT2 /e [22B.13] e = Ea,des RT1 Ea,des, gives: Ea,des = R ln {t (2)/t(1)} (1/T2 - 1/T1) = R ln {0.65 × t (1)/t(1)} (1/T2 - 1/T1) = R ln {0.65}(1/T2 K -- 1 -- 1 1 (1 - mol-- 1) × ln (0.65) × | (1000 K 600 K) - 1 -- 1 = 5.34 kJ mol -- 1 22B.9(b) At 298 = K: t1/2 τ 0 e Ea,des / RT [22B.13] = (0.12 ps) × e (i) 0.404 Ea,des / kJ mol -- 1 0.150 Ea,des / kJ mol -- 1 22B.9(b) At 298 = K: t1/2 τ 0 e Ea,des / RT [22B.13] = (0.12 ps) × e (i) 0.404 Ea,des / kJ mol -- 1 0.150 Ea,des / kJ mol -- 1 1 (2.6.13) = (0.12 ps) × e (i) 0.404 Ea,des / kJ mol -- 1 22B.9(b) At 298 = K: t1/2 τ 0 e Ea,des / RT [22B.13] = (0.12 ps) × e (i) 0.404 Ea,des / kJ mol -- 1 0.150 Ea,des = 20 kJ mol -- 1 t1/2 (298 K) = (0.12 ps) × e (i) 0.404 × 20 = 388 ps , t1/2 (800 K) = (0.12 ps) $(0.12 \text{ ps}) \times e0.150 \times 20 = (ii) 2.4 \text{ ps}$. Ea,des = 200 kJ mol-- 1 t1/2 (298 K) = (0.12 \text{ ps}) \times e0.404 \times 200 = 1.5 \times 1022 \text{ s}, t1/2 (800 K) = (0.12 ps) × e0.150 × 200 = 1.3 s 22B.10(b) The Langmuir isotherm would be (i) $\theta = \alpha p 1 + \alpha p (ii) \theta = (\alpha p) 1/2 1 + (\alpha$ denominator is approximately 1) would show progressively weaker dependence on p for dissociation into two or three fragments. Solutions to Problems 22B.1 of the text, where it is shown that for a Langmuir isotherm: $p p 1 [\alpha = K] = + V V \infty KV \infty$ Since this expression predicts that a plot of p/V against p is linear with intercept 1/KV and slope equal to 1/V are draw up the following table. 22:5 p / Pa p / V / Pa cm -3 25 129 253 540 1000 1593 595 791 1145 1682 2433 3382 p/V is plotted against p in Fig. 22B.1. The plot is observed to be linear so we conclude that the data fits the Langmuir isotherm for these low pressures and, therefore, low coverage. The regression slope equals $1/V\infty$; the regression intercept equals $1/KV\infty$. Thus, $V\infty = 1/(1.77 \text{ cm}-3) = 0.565 \text{ cm} 3 \text{ and } K = 1/(V\infty \times \text{intercept}) = 1/(0.565 \text{ cm} 3 \times 629 \text{ Pa cm}-3) = 2.81 \times 10-3 \text{ Pa}-1$ Comment. It is unlikely that low-pressure data can be used to obtain an accurate value of the volume corresponding to complete coverage. See Problem 22B.4 for adsorption data at higher pressures Figure 22B.1 4000 y = 1.7667x + 629.13 R² = 0.9947 p/V / Pa cm-3 3000 2000 1000 0 400 800 1200 1600 p / Pa cm-3 3000 2000 1000 0 400 800 1200 1600 p / Pa cm-3 3000 2000 1000 p / Pa cm-3 3000 2000 p / Pa cm-3 minute matche m shown in Fig. 22B.2: p / atm V / cm3 p / V /(10-2 atm cm -3) 0.050 1.22 4.10 0.100 1.33 7.52 0.150 1.31 11.5 22:6 0.200 1.36 1.47 0.250 1.40 17.9 Figure 22B.2 The plot fits closely to a straight line with slope 0.720 dm-3. Hence, $V \propto = 1$ / slope = 1.39 cm - 3 = × 1.39 10 - 3 dm - 3 × Umon The number of H 2 molecules corresponding to this volume is pVN A (1.00 atm) × (1.39 × 10-3 dm3) × (6.02 × 1023 mol-1) = $3.73 \times 1019 2 \text{ RT}$ (0.0821dm3 atm K -1 mol-1) × (273K) The area per molecule can be estimated from the density of the liquid. N = H 23 () (3V) || = M || 3M = A \pi = |V volume of molecule| | ρN A $|| 4\pi || 4\pi ||$

and illustrates the point that these kinds of calculations provide only rough value surface areas. 22B.6 For the Langmuir and BET isotherm (using eqns 22B.2 and 22B.6 with the methods of Examples 22B.1 and 22B.3. p/kPa p /V 3 10 z -3 (kPa cm) 13.3 26.7 40.0 53.3 66.7 80.0 0.743 0.809 $0.851\ 0.877\ 0.886\ 0.876\ 67\ 134\ 200\ 267\ 334\ 400\ 22:7\ 103\ z\ (1-z)$ (V/cm3) $3.98\ 4.67\ 5.32\ 5.98\ 6.65\ 7.30\ p/V$ is plotted against z in Fig. 22B.3. z/(1-z) k = 165430 p/V / (kPa cm-3) $0.85\ 0.80\ 0.75\ 0.7\ 0\ 20\ 40\ 60\ 80\ 100\ p$ / kPa Figure 22B.4 z/{((1-z)V} × 103\ cm3\ 8\ 7\ y = 9.9387x + 3.3294\ R^2 = 165430 0.1 0.2 z 0.3 0.4 We see that the plot of p/V against p is non-linear so we reject the proposition that it is described by a Langmuir isotherm. The plot of z /(1 - z)V against z appears to be linear so we accept the proposition that it is described by the BET isotherm has an intercept of $3.33 \times 10-3$ cm-3 and a slope of $9.94 \times 10-3$ cm-3. Since 1/cVmon equals the intercept of a BET isotherm and (c - 1)/cVmon equals the slope, we find that c = 1 + 9.94/3.33 = 3.96 and Vmon = $1/(c \times intercept) = 1/(3.96 \times 3.33 \times 10-3 \text{ cm}-3) = 75.8 \text{ cm} + 32.82 \times 10-3 \text{ cm} + 32.82 \times 10-32 \times 1$ according to the van't Hoff equation [22B.5, K = αp_{2}] which can be written in the form $-\lceil \Delta$ ad H O (T1 - T1) / R \rceil K2 2 1 $\rceil = -\exp[||0.0247 - 1 - 1|| K1 \lfloor 8.3145]$ K mol (773K 673K)] As measured by the equilibrium constant of absorption, NO is less strongly absorbed by a factor of 0.0247 at 500°C than at 400°C. 22B.10 θ = c1 p1/ c2 [Freundlich isotherm, 22B.10] We adapt the Freundlich gas isotherm to a liquid by noting that wa $\propto \theta$ and replacing p by [A]/ c O, the concentration of the acid divided by the standard concentration c O = 1 mol dm3. Then wa = c1 ([A]/ c O) 1/ c2/g) ln (c1/g) + (with c1, c2 modified constants), and hence ln ($wa = 1 \times ln$ ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln ($wa = 1 \times ln$ ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln ($wa = 1 \times ln$ ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). A plot of ln (wa/g) c2 against ln ([A] / cO). $0.10\ 0.50\ 1.0\ 1.5\ 0.04\ -3.00\ 0.06\ -2.30\ 0.12\ -0.693\ 0.16\ -0.00\ 0.19\ 0.405\ ln(wa/g)\ -3.22\ -2.81\ -2.12\ -1.83\ -1.66\ Figure\ 22B.5\ Since\ the\ plot\ is\ linear,\ the\ linear\ regression\ fit\ shown\ in\ Figure\ 22B.5\ Since\ the\ plot\ shown\ show\ shown\ shown\ shown\ shown\ shown\ shown\ shown\$ so $V V \propto KV \propto$ that it describes adsorption from solution. This can be done with the transforms: $p \rightarrow$ concentration, c and $V \rightarrow$ amount adsorbed per gram adsorbent, s. This gives 22B.12[‡] We must adapt the Langmuir isotherm, 22:9 Langmuir iso that a plot of c/s against c should be linear and we find that the linear regression fit of the data gives 1 slope = 0.163 g mmol-1, standard deviation = 0.073 K = slope 0.163 g mmol-1 = 0.0046 dm³ k = 0.0046 mmol-1 intercept 35.6 (mmol dm -3) × (g mmol-1) Similarly, the Freundlich solution isotherm [22B.10] and regression analysis of the data is: = s c1 (c / mmol g -1) + 1 c2 ln (c / that the linear regression fit of the data gives intercept = c1 = mmol dm - 3, standard deviation = 0.003 R (Freundlich) = 0.999 94 The Temkin solution isotherm [22B.9] and regression analysis gives: $s = c1 \ln(c2 c / mmol dm - 3)$, c1 = 1.08 mmol dm - 3, c2 = 0.074, c2 = 0.standard deviation = 0.14 mmol dm -3 standard deviations indicate that the Freundlich isotherm provides the best fit of the data. 22B.14[‡] We write the isotherms in the following forms where q is milligrams of solvent sorbed per gram of ground rubber (gR) and K, KF, KL, and M are empirical constants. Linear isotherm: $q = K \times (ceq / mg dm - 3)$ Freundlich isotherm: q = K L M ceq / mg dm - 3) or ln (q / mg g R - 1) = ln (K F / mg g RK F unit: mg g R -1 K L unit: mg g R -1 K L unit: mg g R -1 M unit: mg -1 dm3 (b) Determination of best description is a large percentage of data. Data analysis with the linear sorption is a large percentage of data. Data analysis with the linear sorption is a large percentage of data. K, which may indicate some combination of random and/or systematic variation. A test of a relationship is often facilitated by checking the appearance of a plot. To further test the linear hypothesis between q and c, we prepare the plot, shown in Figure 22B.6, with the constraint that the intercept equal zero. The plot appears to have a systematic nonlinear component and only 88% of the 22:10 variation is explained by the linear regression. However, with the small number of data points random error could give this appearance so we tentatively reject the linear hypothesis. Figure 22B.6 Data analysis with the Freundlich isotherm. To test the Freundlich hypothesis between q and c, we prepare the plot of lnq against lnceq, shown in Figure 22B.7. The appearance of the plot appears to be linear with considerable random scatter but there is no definitive visual indicator of systematic non-linearity. 94% of the variation is explained by the linear regression fit. Figure 22B.7 Data analysis with the Langmuir isotherm. To test the Langmuir hypothesis between q and c, we prepare the plot of 1/q against 1/ceq, shown in Figure 22B.8. The appearance of the plot appearance of the variation is explained by the linear regression fit. However, the negative, but very small, intercept of the regression fit implies either that KL < 0 or that KL is so small that it has been swamped by the random scatter. 22:11 We further recognize that a Langmuir isotherm must have a positive KL because it is an equilibrium constant. The data, such as it is, does not firmly support the Langmuir isotherm must have a positive KL because it is an equilibrium constant. The data, such as it is, does not firmly support the Langmuir isotherm must have a positive KL because it is an equilibrium constant. Freundlich isotherm gives an
adequate description of the data. The empirical constants for this isotherm are calculated with the linear regression fit shown as an insert in the Freundlich constants: -1.81 = KF eintercept = mg g R -1 = n 1/= slope 1/= 0.878 1.14 0.164 ceq0.878 g (c) The ratio of rubber-to-charcoal Freundlich sorption isotherms = is rubber = qcharcoal c1.6 eq 0.164 ceq-0.72 The sorption efficiency of ground rubber is much less than that of activated charcoal, which might convert to a lower cost per gram of contaminant adsorbed. 22C Heterogeneous catalysis Answers to discussion questions 22C.2 Heterogeneous catalysis on a solid surface requires the reacting molecules or fragments to encounter each other by adsorption on the surface. Therefore, the rate of the catalyzed reaction is determined by the sticking probabilities of the species on the surface as described by Fig. 22C.2 of the text. Solutions to exercises 22C.1(b) Let us assume that the carbon monoxide molecules are close-packed, as shown in Fig. 22C.1 as spheres, in the monolayer. Then, one molecules are close-packed, as shown in Fig. 22C.1 as spheres, in the monolayer. is expected to be comparable to the radius of an adsorbed nitrogen molecule. Furthermore, let us assume that the collision cross-section of Table 1B.1 ($\sigma \sim \sigma dinitrogen = 0.43 \text{ nm2} = 4\pi r^2$) gives a reasonable estimate of r: r = ($\sigma/4\pi$) 1/2. With these assumptions the surface area occupied by one molecule is: 22:12 = Amolecule 2= 3 ($\sigma/4\pi$) = 3 $\sigma/2\pi$ = 3 (0.43 nm 2) / 2π 0.12 nm 2 In this model the surface area per gram of the catalyst equals Amolecules. N can be calculated with the 0° C data, a temperature that is so high compared to the boiling point of nitrogen that all molecules. N can be calculated with the 0° C data, a temperature that is so high compared to the boiling point of nitrogen that all molecules. N can be calculated with the 0° C data, a temperature that is so high compared to the boiling point of nitrogen that all molecules. N can be calculated with the 0° C data, a temperature that is so high compared to the boiling point of nitrogen that all molecules. $(1.00 \times 10 \text{ Pa}) \times (3.75 \times 10 \text{ m}) = = 9.94 \times 1019 \text{ N} = kT (1.381 \times 10 - 23 \text{ J K} - 1) \times (273.15 \text{ K})$ Amolecule N = $(0.12 \times 10 - 18 \text{ m} 2) \times (9.94 \times 1019) = 12 \text{ m} 2$ Figure 22C.1 r 600 Integrated activities 22.2 Electron microscopes can obtain images with much higher resolution than optical microscopes because of the short wavelength obtainable from a beam of electrons. For electrons moving at speeds close to c, the speed of light, the expression for the de Broglie wavelength (eqn 7A.14, $\lambda = h/p$) needs to be corrected for relativistic effects: = h $@2me\ c\ 2$ where c is the speed of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of light in vacuum and $\Delta \phi$ is the potential difference through which the electrons area of ligh accelerated through 50 kV. (b) Is the relativistic correction is calculated as follows: h h h λ non-relativistic = = p (2m E)1/2 (2m eV)1/2 e = k {2 (9.109 × 10 e) 1/2 $6.626 \times 10-34$ Js -31) () (kg × $1.602 \times 10-19$ C × 50.0×103 V = 5.48 pm The relativistic de Broglie wavelength is 22:13) 1/2 Å relativistic 5.48 pm = 1/2 1/2 () eV $1.602 \times 10-19$ C)(50.0×103 V) (| + 1 | 2 | {1 + } 2 mec | -31 - 1 2 8 | 2 (9.109×10 kg)(3.00×103 V = 5.48 pm The relativistic de Broglie wavelength is 22:13) 1/2 Å relativistic 5.48 pm = 1/2 1/2 () eV $1.602 \times 10-19$ C)(50.0×103 V) (| + 1 | 2 | {1 + } 2 mec | -31 - 1 2 8 | 2 (9.109×10 kg)(3.00×103 V) (| + 1 | 2 | {1 + } 2 mec | -31 - 1 2 8 | 2 (9.109×10 kg)(3.00×103 V = 5.48 pm The relativistic de Broglie wavelength is 22:13) + 1/2 Å relativistic de Broglie wavelength is 22:13) + 1/2 10 m s) |] = = 5.35 pm (b) For an electron accelerated through 50 kV the non-relativistic de Broglie wavelength is calculated to be high by 2.4%. This error may be insignificant for many applications. However, should an accuracy of 1% or better be required, use the relativistic de Broglie wavelength is calculated to be high by 2.4%. for which the non-relativistic equation yields a value that has less than 1% error: $(2m c 2) (\lambda (2m c 2) - \lambda relativistic) V 2 | e | × | non-relativistic 2 | e | (0.01) = 20.4 kV = 2.4 V - E = 2.00 eV = 3.20 × 10-19 J = \kappa {2m (V - E)} 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109
\times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055 \times 10 = 2 \times (9.109 \times 10-31 kg) \times (3.20 \times 10-19 J) 1/2 e / [8A.20] {} / (1.055$ -34 J s) = 7.24 × 109 m -1 Since $\kappa L \gg 1$ for the distances of this problem, we use eqn 8A.23B for the transmission probability. T $\approx 16\epsilon$ (1 - ϵ) e -2 κ L where $\epsilon = E$ /V We regard the tunnelling current to be proportional to the transmission probability. probabilities. current at L2 T (L2) e -2κ L2 -2κ L $- L = = e(21) - 2\kappa$ L1 current at L1 T (L1) e = e()($-2\times 7.24\times 109$ m $- 1 \times 1.00\times 10 - 10$ m) = 0.235 We conclude that, at the distance of 0.60 nm between the surface and the needle, the current is about 24% of the value measured when the distance of 0.60 nm. 22:14 Atkins & de Paula: Atkins & de Physical Chemistry 10e Solutions to a) exercises Foundations Topic A EA.1(a) Example (i) Group 2 (ii) Group 15 EA.2(a) Element Ca, calcium Mn, manganese As, arsenic Ground-state Electronic Configuration [Ar]4s2 [Ar]3d104s24p3 (i) Chemical formula and name: MgCl2, magnesium chloride ions: Mg2+ and Cl- oxidation numbers of the elements: magnesium, +2; chlorine, -1 (ii) Chemical formula and name: FeO, iron(II) oxide ions: Fe2+ and O2- oxidation numbers of the elements: iron, +2; oxygen, -2 (iii) Chemical formula and name: Hg2Cl2, mercury(I) chloride ions: Cl- and Hg22+ (a polyatomic ion) oxidation numbers of the elements: mercury, +1; chlorine, -1 EA.8(a) (i) CO2 is a linear, nonpolar molecule. (ii) SO2 is a bent, polar molecule. (iii) N2O is linear, polar molecule. (iii) N2O is linear, polar molecule. (iii) Temperature is a polar molecule. (iii) N2O is linear, polar molecule. (iii) SO2 is a bent, polar molecule. (iii) SO2 is a bent, polar molecule. (iii) Temperature is an intensive property. (iv) Number density is an intensive property. EA.11(a) (i) 0.543 mol (ii) 3.27 × 1023 molecules EA.12(a) 0.43 bar EA.13(a) 0.43 bar EA.14(a) 0.43 bar) EA.18(a) 105 kPa EA.19(a) S8 EA.20(a) 1.8 MPa EA.21(a) 4.6 × 105 Pa , 6.9×105 Pa , 6.9×105 Pa or θ F / °F = 95 × θ / °C + 32 , = θ F 173 °F Topic B EB.1(a) (i) 2.25 × 10-20 J EB.5(a) (i) 1.88 × 108 m s -1 , 100 keV EB.6(a) 1.15 × 10-18 J , 1.48 × 10-20 J EB.7(a) -2.40 V EB.8(a) 24.1 kJ, $28.8 ^{\circ}\text{C}$ EB.9(a) 27.2 K or $27.2 ^{\circ}\text{C}$ EB.10(a) 128 J EB.11(a) 2.4194 J K -1 g -1 EB.12(a) 75.3 J K -1 mol -1 EB.12(a) -1 EB.12(a)J (ii) 0.021 Atkins & de Paula: Atkins' Physical Chemistry 10e EB.23(a) 0.47 kJ EB.24(a) (i) 1.38 kJ EB.25(a) 12.47 J mol-1 K -1 Topic C EC.1(a) 2.26×108 m s -1 EC.2(a) 4.00 µm , 7.50×1013 Hz Chapter 1 Topic 1A E1A.1(a) 24 atm, no E1A.2(a) (i) 3.42 bar E1A.3(a) 30 lb in-2 E1A.4(a) 4.20 × 10-2 E1A.5(a) 0.50 m3 E1A.6(a) 102 kPa E1A.7(a) 8.3147 J K-1 mol-1 E1A.8(a) 58 E1A.9(a) 6.2 kg E1A.10(a) (i) 0.762, 0.238, 0.752 bar, 0.235 bar 0.205 bar 0.205 bar 0.205 bar 0.205 bar 0.205 bar 0.205 bar, 0.238, 0.752 bar, 0.235 bar 0.205 b (ii) 2.0 atm, 1.0 atm (iii) 3.0 atm Atkins & de Paula: Atkins' Physical Chemistry 10e E1B.2(a) 1.90×103 m s-1 = 1.90 km s-1, 458 m s-1 E1B.5(a) (i) 475 m s-1 E1B.6(a) ***** Pa 0.195 E1B.7(a) (ii) $8.3 \times 10-8$ m (iii) $8.1 \times 10-9$ s-1 $1.4 \times 10-6$ m Topic 1C (ii) 1.8×103 atm E1C.1(a) (i) 1.0 atm E1C.2(a) 7.61×10-2 kg m5 s -2 mol-2, 2.26 × 10-5 m3 mol-1 E1C.3(a) (i) 0.88 E1C.4(a) 140 atm E1C.5(a) (i) 50.7 atm E1C.6(a) 1.78 dm6 atm mol-2, 0.0362 dm3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) (i) 3.64 × 103 K, 8.7 atm 0.18 atm E1C.9(a) 0.46 × 10-4 m3 mol-1, 0.122nm E1C.7(a) 0.46 × 10-4 0.139 m (ii) 2.62×103 K, 4.5 atm (iii) 4.5 atm (iiii) 4.5 atm (iii) 4.5 atm (ii (ii) $-167 J \odot Oxford University Press, 2014.$ (iii) 7R, $17.35 kJ mol - 1 \Delta H = 0$, -1.62 kJ, +10.1 kJ, w = 0, $+10.1 kJ (ii) \Delta U = (iii) \Delta t kins$ de Paula: Atkins' Physical Chemistry 10e Topic 2B E2B.1(a) -1 - 1 30 J K - 1 0.1 kJ (ii) + 10.7 kJ, +10.1 kJ (ii) + 10.7 kJ, +10.1 kJ (ii) + 10.7 kJ, +10.1 kJ (ii) + 10.7 kJ, $+10.1 kJ (ii) \Delta U = (iii) \Delta U = (iii)$ +2.2 kJ, +1.6 kJ Topic 2C E2C.1(a) 22.5 kJ, -1.6 kJ, 20.9 kJ E2C.2(a) -4564.7 kJ mol-1 E2C.3(a) +53kJ mol-1 E2C.3(a) +53kJ mol-1 E2C.3(a) +53kJ mol-1 E2C.3(a) +53kJ mol-1 E2C.3(a) -167 kJ/mol-1 E2C.3(a) +111.92 kJ mol-1 E2C.3 mol-1 E2C.10(a) -1892 kJ mol-1 , -241.82 kJ mol-1 , -7.39 × 103 J mol-1 , -7.39 × 103 J mol-1 , +7.52 × 103 J mol-1 , +7.52 × 103 J mol-1 , -7.39 × 103 J mol-1 , +7.52 × 103 J & de Paula: Atkins' Physical Chemistry 10e Topic 2E E2E.1(a) Closer, closer E2E.2(a) 13 1 K E2E.3(a) 0.00846 m3, 257 K, -0.89×103 J E2E.4(a) -194 J E2E.5(a) 9.7 kPa Chapter 3 Topic 3A E3A.1(a) Not spontaneous. E3A.2(a) Tc = 191.2 K E3A.3(a) (i) 366 J K -1 E3A.4(a) I2(g) E3A.5(a) 3.1 J K -1 E3A.6(a) 30.0 kJ/mol-1 E3A.7(a) 152.67 J K -1 $mol-1 E3A.9(a) \Delta H = 0$, +2.7 J K - 1, $\Delta H tot = 0 E3A.10(a) (i) +2.9 J K - 1$, 0 E3A.11(a) (i) +87.8 J K - 1 mol-1 E3B.2(a) (i) -87.8 J K - 1 mol-1 E3B.2(a) (i) -87.8 J K - 1 mol-1 (ii) 309 J K - 1, (ii) 309 J K - 1, (ii) 309 J K - 1, (ii) -386.1J K - 1 mol-1 E3B.2(a) (i) -87.8 J K - $-178.6 \text{ kJ mol}-1 \text{ (b) two phases (c) three phases Topic 3D E3D.1(a) -17 J E3D.2(a) -36.5 J K -1 E3D.3(a) +10 \text{ kJ mol}-1 E4B.4(a) 2.71 \text{ kPa}$ E4B.5(a) +45.23J K - 1 mol - 1 + 16 kJ mol - 1 E4B.8(a) (i) +34.08 kJ mol - 1 E4B.9(a) 281.8 K or 8.7°C E4B.10(a) 25 g s - 1 E4B.11(a) (i) 1.7 × 103 g E4B.12(a) (i) +4.9 × 104 J mol - 1 = +49 kJ mol - 1 E4B.13(a)272.80 K E4B.14(a) 0.0763 (ii) 350.5 K (ii) 31× 103 g (iii) 1.4 g (ii) 215°C , +101 J K -1 mol-1 E5A.6(a) 6.7 kPa E5A.7(a) 886.8 cm3 mol-1 E5A.3(a) -1.2 J mol-1 E5A.4(a) -0.35 kJ , +1.2 J K -1 E5A.5(a) +4.70 J K -1 mol-1 E5A.6(a) 6.7 kPa E5A.7(a) 886.8 cm3 E5A.8(a) 56 cm3 mol-1 E5A.9(a) 6.4×103 kPa E5A.10(a) 3.67 × 10-3 mol dm -3 E5A.11(a) (i) 3.4 × 10-3 mol dm -3 E5A.12(a) 0.17 mol dm-3 E5A.12(a) 0.17 mol dm -3 E5A.12(a) 0.17 mol dm-3 E0.09°C E5B.5(a) -3.10 kJ , +10.4 J K -1 , 0 E5B.6(a) (i) 1 E5B.7(a) 0.135 mol kg-1, 24.0 g anthracene E5B.8(a) 87 kg mol-1 E5B.9(a) 32.2 Torr, 6.1 Torr, 38.3 Torr, 0.840 , 0.160 E5B.11(a) 0.267, 0.733, 58.6 kPa E5B.12(a) (i) 20.6 kPa (ii) 0.8600 Topic 5CC. E5C.1(a) (i) yM = 0.36 E5C.4(a) 0.25, 1930C E5C.6(a) (i) 76% (ii) 52% (iii) 1.11, 1.46 E5C.7(a) (ii) 490 Torr (iv) 0.50, 0.30 (ii) yM = 0.80 (i.e., yO = 0.20) Chapter 6 Topic 6A E6A.1(a) 0.9 mol, $1.2 \text{ mol} E6A.2(a) -0.64 \text{ kJ} E6A.3(a) <math>5.80 \times 105 E6A.4(a) 2.85 \times 10-6 E6A.5(a)$ (i) 0.141 E6A.6(a) (i) -68.26 kJ mol - 1, 9.13×1011 (ii) 13.5 © Oxford University Press, 2014. (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (i) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical
Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -69.8 kJ mol-1 Atkins' Physical Chemistry 10e E6A.7(a) K = K c × (c O RT / p O) E6A.8(a) (ii) 1.32 × 109, -+0.90 +0.90 0.90 0.196 D 1.00 Total 4.00 +0.60 1.60 0.348 4.60 1.001 (iv) +2.8 k mol-1 E6A.9(a) +12.3 k mol-1 E6A.9(a) -14.4 k mol-1 E6A.9(a) +2.77 k mol-1, -16.5 J K -1 mol-1 E6B.3(a) 50% E6B.4(a) 0.9039, 0.0961 E6B.5(a) (i) 52.89 k mol-1E6B.6(a) 1110 K E6B.7(a) 70.2 kJ mol-1, 110 kJ mol-1 K -1, -6.3 kJ mol-1, 3.0 (ii) -52.89 kJ mol-1 Topic 6C (ii) +0.22 V (iii) +1.23 V E6C.2(a) (i) +1.23 V -3 © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e Chapter 7 Topic 7A E7A.1(a) (i) 6.6 × 10-19 J, 4.0 × 10-13 kJ mol-1 (ii) 6.6 × 10-20 J, 40 kJ mol-1 E7A.2(a) λ / nm E / aJ Em / (kJ mol-1) (i) 600 331 199 (ii) 550 361 218 (iii) 400 497 299 E7A.3(a) λ / nm Ephoton / aJ v / (km epho s-1) (i) 600 331 19.9 (ii) 550 361 20.8 (iii) 400 497 24.4 E7A.4(a) 21 m s -1 E7A.5(a) (i) 2.77 × 1018 E7A.6(a) (i) no electron ejection E7A.7(a) 6.96 keV E7A.9(a) 0.024 m s -1 E7A.10(a) 332 pm E7A.11(a) (i) 6.6 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford University Press, 2014. (ii) 3.19 × 10-19 J, (ii) 6.0 × 10-29 m (ii) 2.77 × 1020 Topic 7B © Oxford Univers 837 km s - 1 (ii) $6.6 \times 10 - 36 \text{ m}$ (iii) 99.7 pm (iii) Atkins & de Paula: Atkins' Physical Chemistry 10e 1/2 E7B.3(a) (1 / 2π) d ϕ E7B.4(a) (1 / 2π) d ϕ E7B.4(b) (1 / 2π) d ϕ E7B.4(b) (1 / 2π) d ϕ E7B.4(c) (1 / 2π) d ϕ Aeikx E8A.3(a) (i) $1.81 \times 10 - 19$ J, 1.13 eV, 9100 cm - 1, 109 kJ mol-14.1 eV, $33\ 000 \text{ cm} - 1$, 400 kJ mol-1E8A.4(a) (i) $0.04\ E8A.5(a)$ h = C $81/2\ E8A.6(a)$ h = C E8A.9(a) - 17.4% $E8A.10(a) 2kTmL2 1 - 2 h2 E8A.11(a) n1=1, n2=4 E8A.12(a) 3 E8B.4(a) 8.3673 \times 10-21 J E8B.3(a) 2.64 \mu m E8B.4(a) 8.3673 \times 10-27 kg$, $93.3 THz E8B.5(a) (i) 3.3 \times 10-21 J E8B.7(a) ± 0.525 \alpha or ± 1.65 \alpha E8B.8(a) ± \alpha E8B.9(a) 0.056, 0.112 kg$ Topic 8C E8C.1(a) 0, ± E8C.2(a) (1) || 2 π / E8C.3(a) 3.32 × 10-22 J E8C.4(a) 2.11× 10-22 J E8C.6(a) 21/2, 1.49×10-34 J s E8C.8(a) 7 1/2 © Oxford University Press, 2014. (ii) 3.3 × 10-33 J Atkins & de Paula: Atkins' Physical Chemistry 10e Chapter 9 Topic 9A E9A.1(a) (i) g = 1 (ii) g = 9 (iii) g = 25 E9A.2(a) N = E9A.3(a) N = 4a0, r = 0. E9A.4(a) r = 0.35a0 E9A.5(a) 101 pm and 376pm E9A.6(a) 2 E1s, -E1s E9A.7(a) 5.24 E9A.8(a) r = 2a0 / Z E9A.10(a) 6a0 / Z, xy plane, $\theta = \pi/2$, yz, $\theta = 0$, xz, $\theta = 0$ 2 a03 2 a0 Z Topic 9B E9B.2(a) (i) [Ar]3d8 (ii) S = 1, 0, MS = -1, 0, +1, MS = 0 Topic 9C E9C.1(a) 9.118 × 10-6 cm , 1.216 × 10-5 cm E9C.2(a) 3.292 × 105 cm-1 , 3.0388 \times 10-6 cm , 9.869 \times 1015 s-1 E9C.3(a) 14.0 eV E9C.4(a) (i) Forbidden (ii) 32 , 32 (ii) 72 , 52 E9C.6(a) l = 1 E9C.7(a) L = 2, S = 0, J = 2 E9C.8(a) (i) 1, 0 , 3,1 (iii) allowed (ii) 32 , 12 , and 12 , 4, 2, 2 © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e E9C.9(a) E9C.10(a) 3 D3 , 3 D 2 , 3 D1 , 1D 2 , 3 D set of terms are the lower in energy (ii) J = 32, 12, 4, 2 states respectively (i) J = 0, 1state (iii) J = 2,1,0,5,3,1 states respectively E9C.12(a) (i) Allowed (ii) forbidden (iii) allowed Chapter 10 Topic 10A E10A.1(a) {s(1)pz(2)+s(2)pz(1)} × {a(1)\beta(2)-a(2)\beta(1)} E10A.2(a) $\psi = a\psi VB + b\psi HF + c\psi HF$ E10A.6(a) N=3 - + -1/2, ψ =3 + - -1/2 (s + 21/2p) Topic 10B 1/2 E10B.1(a) 1 ()N = 2 || 1 + 2\lambda S + \lambda | E10B.2(a) N = 1.12, ψ 1 = 0.163A + 0.947B, b = 0.412, a = -1.02, ψ 2 = -1.02A + 0.412B E10B.3(a) 1.9 eV, 130 pm E10B.4(a) u, g Topic 10C E10C.1(a) (i) 1 σ g2, b=1 (ii) 1 σ g21 σ u2, b=0 E10C.2(a) C2 E10C.3(a) F2+ E10C.4(a) b=1, b=0, b=1 b=2, b=3, b=2, b=1 E10C.5(a) 1 σg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 1 σu , 1 πu , 2 σg , 1 πg , 2 σu E10C.6(a) 4 × 105 m s -1 E10C.7(a) (i) 1 $\sigma 22\sigma 21\pi 43\sigma 2$ E10D.3(a) NO+ E10D.5(a) 7.2, 8.3 E10D.6(a) -6.6 or -8.9 E10D.7(a) -5.0 or -10.7 eV (ii) $1\sigma 22\sigma 23\sigma 21\pi 42\pi 1$ (iii) $1\sigma 22\sigma 23\sigma 21\pi 43\sigma 2$ Topic 10E E10E.3(a) (i) 7 β , 0 E10E.3(a) (i) 7 β , 0 E10E.3(a) (i) 7β planes ov E11A.2(a) D2h, 3C2 axes, a centre of inversion, 3oh mirror planes E11A.3(a) (i) C2v (ii) C2v (ii) C2v (ii) C2v (ii) C2v (ii) C2v (ii) D3h (iv) D∞h (iii) C2v (ii) C2 2014. Cs 1,5 1,6 1,7 1,8 C2v C2h Cs Cs 2,3 2,6 2,7 C2v C2v C2h C2v C2h C2v C2h C2v C2h C2v C2h C2v Atkins & de Paula: Atkins' Physical Chemistry 10e E11A.8(a) i, σ h Topic 11B E11B.1(a) (-1 0 0 0) | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 |
0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 0 | 0 -1 B1 + E E11C.7(a) (i) Either E1u or A2u E11C.8(a) zero (ii) B3u (x - polarized), B1u (z - pol Atkins & de Paula: Atkins' Physical Chemistry 10e E12A.5(a) 450 dm3 mol-1 cm -2 E12A.6(a) 159 dm3 mol-1 cm -2 E12A.6(a) 1.3 × 108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 E12A.6(a) 1.3 × 108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 E12A.6(a) 1.3 × 108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 E12A.6(a) 1.3 × 108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 E12A.6(a) 1.3×108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 E12A.6(a) 1.3×108 dm3 mol-1 cm -2 (ii) 5×107 dm3 mol-1 cm -2 (ii) $5 \times$ 0.53 cm - 1 (ii) 2.9 m (ii) 2.7 ps Topic 12B E12B.1(a) $6.33 \times 10 - 46 \text{ kg m } 2$, 0.4421 cm - 1 E12B.3(a) (i) Asymmetric E12B.4(a) 106.5 pm, $115.6 \text{ pm} \text{ E12B.5(a)} 2.073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) Asymmetric E12B.4(a) 106.5 pm, $115.6 \text{ pm} \text{ E12B.5(a)} 2.073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) Asymmetric E12B.4(a) 106.5 pm, $115.6 \text{ pm} \text{ E12B.5(a)} 2.073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m } 2$, 10421 cm - 1 E12B.3(a) (i) $2073 \times 10 - 46 \text{ kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ Kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ Kg m} - 1 \text{ E12B.3(a)}$ (i) $2073 \times 10 - 46 \text{ Kg m} - 1 \text{ E12B.3(a)}$ (E12C.6(a) (iii) CH4 is inactive, (i), (ii), and (iv) are active. E12C.7(a) 20 475cm -1 E12C.8(a) 198.9 pm E12C.9(a) 5 3 (ii) 23 Topic 12D © Oxford University Press, 2014. (iv) prolate symmetric Atkins & de Paula: Atkins' Physical Chemistry 10e E12D.1(a) 1.6 × 102 N m -1 E12D.2(a) 1.077 % E12D.3(a) 328.7 N m -1 E12D.4(a) 967.0, 515.6, 411.8 314.2 E12D.5(a) (i) 0.067 E12D.6(a) 1580.38 cm -1, 7.644 × 10-3 E12D.7(a) 5.13 eV (ii) 0.20 Topic 12E E12E.3(a) 127 (v1 + v2 + v3) E12E.4(a) 1 E12E.6(a) Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a) 4A1 + A 2 + 2B1 + 2B2 E12E.8(a) A1, B1 and B2 are infrared active, all modes are Raman active E12E.7(a E13A.3(a) 2 2 -2 ax02 /3 e 3 E13A.4(a) 1 (4) 3 + 32 (π E13A.5(a) 1 E13A.5(a) 1 E13A.6(a) 1 E13A.7(a) 30.4 cm -1 < B' < 40.5 cm -1 , greater E13A.8(a) Δ O = P - v , 14 × 10 cm (ii) forbidden (v) Chemistry 10e 1/ 2 E13A.9(a) 3 (a3) | $|8 \ b - 12 \ a$ /E13A.10(a) 1 4 e -1/16 a Topic 13B 13B.1(a) (i) Lower, v \approx 1800 cm -1 (ii) no information Topic 14A E14A.1(a) s-1 T -1 E14A.2(a) ±54.74 9.133 × 10-35 J s , ±0.9553 rad = E14A.3(a) 574 MHz E14A.4(a) -1.473 × 10-26 J × mI E14A.5(a) 165 MHz E14A.6(a) (i) 3.98 × 10-25 J E14A.7(a) (i) 1× 10-6 E14A.8(a) 13 E14A.9(a) 2 × 102 T , (ii) 6.11× 10-6 10 mT Topic 14B E14B.1(a) (i) Independent © Oxford University Press, 2014. (ii) 13 (iii) 3.4 × 10-5 Atkins & de Paula: Atkins' Physical Chemistry 10e (ii) 110µ T E14B.2(a) (i) 11µ T E14B.5(a) 753 MHz E14B.9(a) 0.39 ms, 2.6 × 103 s -1 Topic 14C E14C.1(a) 9.40 × 10-4 T, 6.25 µs E14C.2(a) 0.21 s E14C.2(a) 15A E15A.1(a) 21621600 E15A.2(a) (i) 40320 E15A.3(a) 1 E15A.4(a) 524 K E15A.5(a) 7.43 E15A.6(a) 354 K (ii) 5.63×103 Topic 15B © Oxford University Press, 2014. (iii) 3.99×104 Atkins & de Paula: Atkins' Physical Chemistry 10e E15B.1(a) (i) 8.23 × 10-12 m , 8.23 pm , 2.60 × 10-12 m , 2.60 pm E15B.2(a) 0.3574 E15B.3(a) 72.2 E15B.4(a) (i) 7.97 × 103 E15B.5(a) 18 K E15B.6(a) 37 K E15B.7(a) 4.5 K E15B.8(a) (i) 1 E15B.9(a) 660.6 E15B.10(a) 4500 K E15B.11(a) 2.571 E15B.12(a) 42.3 E15B.13(a) 4.292, 0.0353 to 0.0377 to 1 (ii) 2 (ii) 1.12 × 104 (iii) 2 (iv) 12 (v) 3 Topic 15C E15C.1(a) 8.16 × 10-22 J E15C.2(a) 18.5 K E15C.3(a) 25 K E15C.4(a) 4.5 K E15C.5(a) 4600 K E15C.6(a) 10500 K E15C.7(a) 6500 K E15C.8(a) 4.033 × 10-21 J Topic 15D E15D.1(a) He gas, CO gas, H2O vapour © Oxford University Press, 2014. (ii) 1.79 × 1027, 5.67 × 1028 Atkins & de Paula: Atkins' Physical Chemistry 10e Topic 15E E15E.1(a) (i) 7.8 (ii) 7.8 (iii) 1 E15E.5(a) (i) 126 J K - 1 mol - 1 (ii) 169 J K - 1 mol - 1 E15E.6(a) 2.35 × 103 K E15E.7(a) 43.1, 22.36 K, 43.76 J K - 1 mol - 1 E15E.8(a) 11.5 J K - 1 mol - 1 E15E.9(a) (i) 4.489 (ii) 119.06 J K - 1 mol - 1 Topic 15F E15F.1(a) - 13.8 kJ mol - 1 E15F.2(a) (i) -6.42 kJ mol - 1 E15F.3(a) 3.70 × 10 - 3 (ii) -14.0 kJ mol - 1 Chapter 16 Topic 16A E16A.1(a) CIF3, O3, H2O2 E16A.2(a) 1.4 D E16A.3(a) 37 D, 11.7° E16A.4(a) 1.66 D, 1.01×10-39 J -1 C2 m 2, 9.06×10-39 J -1 C2 m 2, 103 kJ mol-1 E16B.2(a) 6l 4 Q12 πε 0 r 5 E16B.3(a) 0.071 J mol-1 E16B.4(a) 289 kJ mol-1 Topic 16C E16C.1(a) 2.6 kPa E16C.2(a) 72.8 mN m -1 E16C.3(a) 72.8 mN m when N = 1000, +9.84 × 104 % when N = E17A.8(a) 1.6 × 102 pm Topic 17B E17B.1(a) -19 mJ mol-1 K -1 E17B.2(a) $3.7 \times 10-14$ N © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e Topic 17C E17C.1(a) 3.43 Topic 17D E17D.1(a) 70 kg mol-1 E17D.2(a) (i) 18 kg mol-1 E17D.3(a) 100 E17D.4(a) 64 kg mol-1 E17D.5(a) 0.73 mm s -1 E17D.6(a) 31 kg mol-1 E17D.7(a) 3.4×103 kg mol-1 (ii) 20 kg mol-1 (iii) 20 kg mol-1 Chapter 18 Topic 18A.4(a) 229 pm , 397 pm , 115 pm E18A.4(a) 220 pm E18A.4(a) 220 pm E18A.5(a) 70.7 pm E18A.6(a) 10.1 , 14.4 , 17.7 E18A.7(a) 8.16° , 4.82° , 11.75° E18A.8(a) f Br - = 36 E18A.9(a) f Br - = 36 E18A.10(a) f E18A.11(a) 3 f for h + k even and - f for h + k odd E18A.15(a) 6.1 km s - 1 © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e E18A.16(a) 233 pm Topic 18B E18B.1(a) 0.9069 E18B.2(a) (i) 0.5236 (ii) 0.6802 E18B.3(a) (i) 74.9 pm (ii) 132 pm E18B.4(a) Expansion E18B.5(a) 3500. kJ mol-1 (iii) 0.7405 Topic 18C E18C.1(a) 9.3 × 10-4 cm 3 E18C.2(a) Group 14. n-type; the dopant, arsenic, belongs to Group 15 whereas germanium belongs to E18C.3(a) Three unpaired spins E18C.4(a) -6.4 × 10-5 cm 3 mol -1 = -6.4 × 10-11 m3 mol-1 E18C.5(a) 4.326, 5 E18C.6(a) +1.6 × 10-8 m3 mol-1 Topic 18D E18D.1(a) 3.54 eV Chapter 19 Topic 19A E19A.1(a) 7.6 × 10-3 J K -1 m -1 s -1 E19A.2(a) (i) D = 1.5 m2 s-1, Jz/NA = -6.1 × 10-5 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (ii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2
s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-6 mol m-2 s-1 (iii) D = 1.5 × 10-7 m2 s-1, Jz/NA = -6.1 × 10-7 10e E19A.4(a) 0.0795 nm 2 E19A.5(a) 103 W E19A.6(a) 0.201 nm 2 E19A.7(a) (i) η = 178 μP (ii) η = 186 μP (iii) η = 342 μP E19A.8(a) 1.9 × 1020 E19A.9(a) 1.04 mg E19A.10(a) 2.15 × 103 Pa E19A.11(a) 42.4 g mol-1 E19B.1(a) 16.8 J mol-1 E19B.2(a) 7.63 × 10-3 S m 2 mol-1 E19B.3(a) 283 μm s - 1 E19B.4(a) 13.87 mS m 2 mol-1 E19B.5(a) $4.01 \times 10-8$ m 2 V -1 s -1 , $5.19 \times 10-8$ m 2 V -1 s -1 , $7.62 \times 10-8$ m 2 V -1 s -1 E19B.6(a) 420 pm E19B.7(a) $1.90 \times 10-9$ m 2 s -1 Topic 19C E19C.1(a) 6.2×103 s E19C.2(a) (i) 0.00 mol dm -3 E19C.3(a) 25 kN mol-1 , ∞ E19C.4(a) 67.5 kN mol-1 E19C.5(a) 1.3×103 s E19C.6(a) 0.42 nm © Oxford University Press 2014. (ii) 0.0121 mol dm -3 Atkins & de Paula: Atkins' Physical Chemistry 10e E19C.7(a) 27.3 ps E19C.8(a) 113 µm , 56 µm Chapter 20 Topic 20A E20A.1(a) No change in pressure E20A.2(a) 8.1 mol dm-3 s-1, 2.7 mol -3 s -1 E20A.4(a) dm3 mol-1 s-1, E20A.5(a) 1 kr [A][B][C], dm 6 mol-2 s -1 2 E20A.6(a) (i) [kr] = dm3 mol-1 s-1, [kr] = dm6 mol-2 s-1 (i) kr[A][B] (ii) 3kr[A][B] (ii) 3kr[(ii) 461Torr Topic 20C E20C.1(a) 7.1×105 s-1, 1.28 × 104 dm3 mol-1 s -1 Topic 20D E20D.1(a) E20D.2(a) 1.08 × 105 J mol-1 = 108 kJ mol-1 s-1, 6.50×1015 dm3 mol-1 s-1, 6.50× E20E.2(a) -3 kJ mol-1 (ii) k2 2 [B] 2 4k1′ (16k1′k1[A 2]) - 1 |, k2 K 1/2 [A 2] 1/2 [B], 2k1[A 2] || 1 + 2 2 |k [B] 2 ()Topic 20F E20F.1(a) 1.9 × 10-6 Pa -1 s -1 , 1.9 MPa-1 s-1 E20F.2(a) 251 , 0.996 E20F.3(a) 0.125 Topic 20G E20G.1(a) 3.3 × 1018 E20G.2(a) 0.56 mol dm -3 Topic 20H E20H.1(a) kb K [AH]2 [B] [BH +] E20H.2(a) 1.50 mmol dm -3 s -1 E20H.3(a) 2.0 × 10-5 mol dm -3 Chapter 21 Topic 21A E21A.1(a) 1.13 × 1010 s -1, 1.62 × 1035 s -1 m -3, 1.7% E21A.2(a) (i) 1.04×10-3, 0.069 (ii) 1.19×10-15, 1.57×10-6 E21A.3(a) (i) 22%, 3% (ii) 170%, 16% E21A.4(a) 1.03 × 10-5 m3 mol-1 s -1 (i) 0.05 × 10-2 dm3 mol-1 s -1 (i) 0.05 × 10-2 dm3 mol-1 s -1 (i) 0.05 × 10-5 m3 mol-1 s Atkins' Physical Chemistry 10e E21A.5(a) 0.79 nm 2, $1.16 \times 10-3 \text{ E21A.6(a)} 0.73 \text{ E21A.7(a)} 5.1 \times 10-7 \text{ Topic } 218 \text{ E21B.1(a)} 4.5 \times 107 \text{ m3 mol} - 1 \text{ s} - 1$, $6.61 \times 109 \text{ dm3 mol} - 1 \text{ s} - 1$, $6.61 \times 109 \text{ dm3 mol} - 1 \text{ s} - 1$, $6.61 \times 109 \text{ dm3 mol} - 1 \text{ s} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, $6.61 \times 107 \text{ m3 mol} - 1$, 6.61×107 $8.0 \times 109 \text{ dm3} \text{ mol} - 1 \text{ s} - 1$, $4.2 \times 10 - 8 \text{ s} \text{ E21B.4(a)} 1.81 \times 108 \text{ mol} \text{ dm} - 3 \text{ s} - 1 \text{ Topic} 21\text{ C} \text{ E21C.3(a)} + 73.4 \text{ k} \text{ mol} - 1$, $4.2 \times 10 - 8 \text{ s} \text{ E21B.4(a)} 1.81 \times 108 \text{ mol} \text{ dm} - 3 \text{ s} - 1 \text{ Topic} 21\text{ C} \text{ E21C.3(a)} + 73.4 \text{ k} \text{ mol} - 1$, $4.2 \times 10 - 8 \text{ s} \text{ E21B.4(a)} 1.81 \times 108 \text{ mol} \text{ dm} - 3 \text{ s} - 1 \text{ Topic} 21\text{ C} \text{ E21C.3(a)} + 73.4 \text{ k} \text{ mol} - 1$, $4.2 \times 10 - 8 \text{ s} \text{ E21B.4(a)} 1.81 \times 108 \text{ mol} \text{ dm} - 3 \text{ s} - 1 \text{ Topic} 21\text{ C} \text{ E21C.3(a)} + 73.4 \text{ k} \text{ mol} - 1 \text{ E21C.3(a)} + 73.4 \text{ mol} - 1 \text{$ E21D.1(a) Reactant is high in translational energy and low in vibrational energy, product is high in vibrational energy and relatively lower in translational energy Topic 21E E21E.1(a) 4×10-21 J, 2 kJ mol-1 E21E.2(a) 12.5 nm -1 Topic 21F © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e E21F.1(a) 0.138 V E21F.2(a) 2.82 mA cm - 2 E21F.3(a) Increases, factor of 50 E21F.4(a) (i) $1.7 \times 10-4 \text{ A cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107
\text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$, $3.1 \times 107 \text{ cm} - 2 \text{ s} - 1$ 1010 Ω Chapter 22 Topic 22A 22A.1(a) (i) 1.4 × 1014 cm-2 s-1 22B.3(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.3(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.3(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.83 , 0.36 E22B.2(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.3(a) 0.83 , 0.36 E22B.2(a) 0.13 bar (ii) 3.1 × 1013 cm-2 s-1 Topic 22B E22B.1(a) 33.6 cm3 E22B.2(a) 0.83 , 0.36 E22B.3(a) 0.83 Zeroth-order, (ii) 25 kPa (i) 1.6 × 1097 min (ii) 4.1× 106 s, 6.6 µs first-order © Oxford University Press, 2014. (ii) 2.8 × 10-6 min Atkins & de Paula: Atkins' Physical Chemistry 10e Topic 22C E22C.1(a) 12 m 2 © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e Solutions to odd-numbered problems Chapter 1 Topic 1A P1A.1 -233°N P1A.3 -272.950C P1A.5 (a) 0.0245 kPa (b) 9.14 kPa P1A.7 2.8 x 108 dm3 = 2.8 x 105 m3, 4.1 x 108 dm3 = 4.1 x 105 m3 P1A.9 (a) 1.7 x 10-5 P1A.13 51 km, 0.0029 atm (c) 0.0245 kPa (b) 0.72 Topic 1B 12 P1B.3 (2RT) | || M /P1B.5 0.47 vx P1B.7 n 2 e3(1 - n P1B.9 (a) 11.2 km s-1 (b) 5.04 km s-1 P1C.1 (a) 12.5 dm3 mol-1 (b) 12.3 dm3 mol-1 P1C.3 (a) 0.941dm3 mol-1 (b) 2.69 dm3 mol-1 , 2.67 dm3 mol-1 2 initial)/ 2 , 5.53 x 10-5, 2.71 x 10-9 Topic 1C inversion temperature P1C.5 (a) 0.1353dm3 mol-1 , 5.649 dm 6 atm mol-2 , 21 atm P1C.9 B= b - P1C.11 2 B3 3C 1 , B , 2 3 RC B 3 27C (b) 0.6957 (c) 0.7158 a , C = b 2 , 34.6 cm3 mol-1 , 1.26 dm 6 atm 6 atm mol-2 RT © Oxford University Press, 2014. (c) 5.11dm3 mol-1, Atkins & de Paula: Atkins' Physical Chemistry 10e P1C.13 0.0866 atm -1, 2.12 dm3 mol-1 P1C.17 0.011 P1C.21 b {1 ± (bRT / a)1/2} 1 - bRT / a Chapter 2 Topic 2A P2A.1 P2A.3 P2A.5 (V - nb)2(11) - nRT ln 2 - n al - 1 V1 - nb 1 V2 V1 / (a) -1.7 kJ (b) -1.8 kJ (a) -1.5 kJ (a) -1.5 kJ (a) -1.5 kJ (b) -1.8 kJ (a) -1.5 kJ (b) -1.8 kJ (c) -1.8 kJ (c (b) -1.6kJ 1 2 (c) -1.5 kJ kF xf 2 Topic 2B P2B.1 62.2 kJ mol-1 P2B.3 w = 0, ΔU = +2.35 kJ , +3.03 kJ Topic 2C P2C.1 -1270 kJ mol-1 P2C.5 -994.30 kJ mol-1 P2C.5 -994.30 kJ mol-1 P2C.5 +37 K , 4.09 kg Topic 2D P2D.1 1.6 m , 0.80 m , 2.8 m P2D.3 nR © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e P2D.5 (p) (na T=| × (V - nb) + 2 nR / RV P2D.7 γp cs = ρ P2D.11 (a) 23.5 K MPa - 1 () 1/2 (∂T) V - nb) | = × (V - nb) , nR / ∂p / V, 322 m s-1 (b) 14.0 K MPa - 1 Topic 2E P2E.1 41.40 J K - 1 mol-1 Chapter 3 Topic 3A P3A.5 1.00 kJ, 8.4 kJ P3A.7 10.7 J K - 1 mol-1 P3A.9 Path (a) -2.74 kJ, 0, +2.74 kJ, +9.13 J K -1, 0, -9.13 J K -1 Path (b) -1.66 kJ, 0, +1.66 kJ, 0, +1.66 kJ, (-1, +3.60 J K -1, +3.60 J K -+41.08 J K -1 mol-1 P3B.5 34.4 kJ mol-1, 243 J K -1 mol-1 Topic 3C P3C.1 (a) 50.7 J K -1, -11.5 J K -1 indeterminate (b) +3.46 kJ, indeterminate (c) +3.46 kJ, indeterminate (c) +3.46 kJ (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) 3.46 × 103 J, Atkins & de Paula: Atkins' Physical Chemistry 10e P3C.3 (b) 12 W m -3 (a) +35 J K -1 mol-1 (c) +30 J K -1 mo $0.46 \text{ mol ATP mol glutamine Topic 3D P3D.1 - 501 kJ mol - 1 P3D.3 - 21kJ mol - 1 P3D.5 (\partial \partial VS) P3D.7 () () = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial V T (\partial p) = |\partial T |, \partial S \partial p p () S \partial P () = |\partial T |, \partial S \partial P |, \partial S \partial P | S \partial P | S | S | S \partial$ P4B.9 (a) 227.5°C P4B.13 9.8Torr P4B.15 363 K P4B.17 α - α1 dp dp C p, m2 - C p, m1 = 2, = dT κ T, 2 - κ T, 1 dT TVm (α 2 - α1) Chapter 5 Topic 5A P5A.1 18.079 - 0.11482x 3/2 P5A.3 15.58 kPa, 47.03kPa P5A.5 4.6 cm3 © Oxford University Press, 2014. (b) +53 kJ mol-1 (c) + 6 × 102 J mol-1 Atkins & de Paula: Atkins' Physical Chemistry 10e Topic 5B P5B.3 109.0 cm3 mol-1, 279.3 cm3 mol-1, 279 = 0.18 - 1 Topic 5C (c) 0.532 P5C.1 (b) 391.0 K P5C.7 (b) Ca2Si and a Ca-rich liquid (xSi = 0.13), 0.5 P5C.9 xA pA* / pB* 1 + (pA* / pB* - 1) xA Topic 5E P5E.3 $\Pi = \phi[B]$ RT Chapter 6 Topic 6A P6A.1 (a) +4.48 kJ mol-1 P6A.3 0.007 mol H 2, 0.786 mol HI P6A.5 $\xi = 1 - |()10| + / 1$ ap p()(b) 0.101 atm 1/2 Topic 6B © Oxford University Press, 2014. (c) 0.53, 0.67 Atkins & de Paula: Atkins' Physical Chemistry 10e P6B.1 (a) $1.24 \times 10-9$ P6B.3 300. kJ mol-1 P6B.7 (a) 1.2×108 P6B.9 (T) K c (Tref) × | ref | e = (T)(c) $1.8 \times 10-4$ (b) $1.29 \times 10-8$ (b) 2.7×103 $\Delta v \Delta r$ H O R (11)×| - ||(Tref T) Topic 6C P6C.1 (a) +1.23V (b) +1.09 V P6C.3 +14.7 kJ mol-1, +18.8 kJ mol-1 Topic 6D P6D.1 +0.26843 V Chapter 7 Topic 7A (b) 2.5 × 10-4 J m -3 P7A.1 (a) 1.6 × 10-33 J m -3 P7A.7 (a) 8 nhc, hc P7A.9 (a) 223 1 K, $\theta E = 0.0315 1 5 hc/k cE 4 (4) (b) | \sigma WienT 4 (c/b) 343 K, \theta E = 0.897 Topic 7B 1/2 (2) P7B.1 (a) N = | |(L + 1) (L + 1$ P7B.3 0.0183 (b) N = © Oxford University Press, 2014. 1 c(2 L)1/2 (c) N = 1 (πa 3)1/2 (d) N = 1 ($32\pi a$ 5)1/2 Atkins & de Paula: Atkins' Physical Chemistry 10e P7B.5 (a) 9.0 × 10-6
P7B.7 xmax = a (b) 1.2 × 10-6 Topic 7C ((2 d 2 2 d 2 e 2) E \psi (b)) - - \psi = 2 2 4\pi c 0 x / 2m d x (2m e dx) (2 d 2) E ψ (c) - E ψ - cx | ψ = $|\psi$ = 2 2 m d x / P7C.1 (a) |-P7C.3 (a) Yes (b) Yes (c) No (d) No P7C.5 (a) Yes, -k 2 (b) Yes (c) Yes (d) No (i) (a) and (b) (ii) (c) P7C.7 (a) + k (b) 0 P7C.9 1 a P7C.11 (a) (i) N = ($32\pi a05$) - 12 (c) (i) 1.5a0, 4.5a02 30a02 P7C.15 [x^2 , p^2x] = i Chapter 8 Topic 8A P8A.1 $1.24 \times 10-39$ J, 2.2×109 , $1.8 \times 10-30$ J P8A.3 (a) P8A.5 1.2×106 P8A.7 $4k_{12}k_{22}T = |A3|_2 = A3 \times A3^* = 22(a + b) sinh 2(k_2L) + b2(a)L, L 2 31/2(2)1(b)L, |L - 2|_3 4(n\pi/L) 2||_1/2 where a 2 + b 2 = (k_{12} + k_{22})(k_{22} + k_{32}) and b 2 = k_{22}(k_1 + k_3) 2 Topic 8B © Oxford University Press, 2014. (ii) 5a0, Atkins & de Paula: Atkins' Physical Chemistry 10e P8B.1 HI < HBr < HCl < NO < CO P8B.5 1(1)|v + |A| + (k_{12} + k_{12})(k_{12} +$ -3, ρ node 0 = = and ρ node 4, ρ node = 0.27 a (r) 3s = 0.2 Z a0 Z 4a0 Z 4a0 P9A.7 (a) P9A.11 60957.4 cm -1, 329170 cm 137175cm -1, 185187 cm -1, 122.5 eV P9C.5 2 P1/2 and 2 P3/2, 2 D3/2 and 2 D5/2, 2 D3/2 P9C.7 3.3429 × 10-27 kg, 1.000272 P9C.9 (a) 0.9 cm -1 (b) small P9C.11 (a) 2kT (b) 23.8 Tm -1 Chapter 10 Topic 10A P10A.1 Z 3/2 e - ρ/2 (2 - ρρ sin θ) + 1/2 × (- cos φ + 31/2 sin φ)], 120° 1/2 3/2 | (24π) a (28) Topic 10B P10B.1 $1.87 \times 106 \text{ J} \text{ mol}-1 = 1.87 \text{ MJ} \text{ mol}-1 \text{ P10B.3 EH1s} - \text{P10B.5 (b)} 2.5a0 = 1.3 \times 10-10 \text{ m}, -0.555 \text{ j} 0/a0 = -15.1 \text{ eV}, -0.565 \text{ j} 0/a0 = -15.4 \text{ eV}, 0.055 \text{ j} 0/a0 = 1.5 \text{ eV}, 0.055 \text{ j} 0/a0 = 1.5 \text{ eV}, 0.055 \text{ j} 0/a0 = 1.5 \text{ eV}, 0.065 \text{ j} 0/a0 = 1.8 \text{ eV} \text{ j} + \text{k} \text{ j} 0 \text{ j} - \text{k} \text{ j} 0 + \text{k} 0$ $\alpha B (| 1 + 2(1 - S 2) (1/2 4 (\beta + \alpha A S) (\beta + \alpha B S)) | (\alpha A - \alpha B) 2], \alpha A - \beta S 1 - S 2 + (\beta + \alpha A S) (\beta + \alpha B S) , (\alpha A - \alpha B) (1 - S 2) (i) E/eV = -10.7, -8.7, and -6.6 © Oxford University Press, 2014. (ii) E/eV = -10.8, -8.9, and -6.9 Atkins & de Paula: Atkins' Physical Chemistry 10e Topic 10E P10E.1 E = \alpha O, 1 (12 \beta 2 | \alpha O + \alpha C) 1 + 2 | (\alpha O - \alpha C) 1 + 2 | (\alpha O - \alpha C) | 1 + -1 + 2 | (\alpha O - \alpha C) 2 (12 \beta 2 4 \beta 2 (\alpha O - \alpha C) 2 (12 \beta 2 4 \beta 2 (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (12 \beta 2 4 \beta 2 (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1 + -1 + 2 | (\alpha O - \alpha C) 2 (1$ A1 + T1 + T2 (e) D4d Topic 11B P11B.1 trans -CHCl=CHCl P11B.3 Γ = 3A1 + B1 + 2B2 P11B.7 +1 or - 1, +1, -1 P11B.9 (a) 2A1 + A 2 + 2B1 + 2B2 A 2u + T1u + T2u Topic 12A P12A.1 4.4 × 103 © Oxford University Press, 2014. (d) Atkins & de Paula: Atkins' Physical Chemistry $10e P12A.3 = A \epsilon \left[J \right] 0 \left(1 - e - L/\lambda \right), A = \epsilon \left[J \right] 0 P12A.7 1 (\pi) 4 3 - 1 - 2 | \epsilon max \Delta v1/2, 5.7 \times 10 \text{ dm mol cm } 2 | n 2 / P12A.9 (a) receding, 1.128 \times 10 - 3 c = 3.381 \times 105 \text{ m s} - 1 P12A.11 2 (kT/mc 2) 1/2 1/2 Topic 12B P12B.1 meff R 2 Topic 12C P12C.1 596 GHz, 19.9 cm - 1, 0.503 mm, 9.941 cm - 1 P12C.3 128.393 pm , 128.13 pm , slightly a start of the start o$ different P12C.5 116.28 pm , 155.97 pm P12C.7 14.35 m -1 , 26 , 15 P12C.9 (kT) | ||| 2hcB 12 12 - 1 (kT), 30 , ||2| hcB |-1 , 6 2 Topic 12D P12D.1 kf = 2 Da 2 . P12D.3 142.81 cm -1 , 3.36 eV , 93.8 N m -1 P12D.7 e / ν - 1 2D 2 P12D.9 112.83 pm , 123.52 pm P12D.11 0 = 10.433 cm-1 B P12D.13 x2 = 1 = 10.126 cm-1 , B 1 (v + $\frac{1}{2}$) ω , rotational constant B decreases, B decreases with increased kf anharmonicity © Oxford University Press, 2014. Atkins & de Paúla: Atkins' Physical Chemistry 10e P12D.15 (a) 2143.26 cm-1 (b) 12.8195 kJ mol-1 (c) 1.85563 × 103 N m -1 (d) (e) 113 pm Topic 12E P12E.1 (a) Cannot undergo simple harmonic motion P12E.3 (a) C3v (b) nine (c) 3A1 + 3E all modes are Raman active Chapter 13 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13C P13C.1 4 × 10-10 s or 0.4 ns Chapter 14 Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1 2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allowed P13A.1
2 P13A.3 6808.2 cm -1 or 0.84411 eV , 5.08 eV Topic 13A Σ g + $\leftarrow 2 \Sigma$ u + is allow 14C P14C.1 400 × 106 Hz ± 8 Hz, 0.29s © Oxford University Press, 2014. (d) all modes are infrared active (e) Atkins & de Paula: Atkins' Physical Chemistry 10e P14C.5 at (1) | 2 2 2 1 + (ω0 - ω) τ P14C.7 158 pm P14C.9 0.58 mT Topic 14D P14D.1 2.8 × 1013 Hz P14D.3 6.9 mT, 2.1mT Chapter 15 Topic 15A P15A.1 {2, 2, 0, 1, 0, 0}, {2, 1, 2, 0} 0, 0] P15A.7 e - Mgh / RT , 0.363 , 0.57 Topic 15B (ii) 6.26 (b) 1.00 , 0.80, 6.58 × 10-11 , 0.122 P15B.3 (a) (i) 5.00 P15B.5 1.209 , 3.004 P15B.7 (a) 1.049 (b) 1.548 , 0.953 , 0.645 , 0.044 , 0.230 , 0.002 , 0.083 P15B.9 (a) 660.6 (b) 4.26 × 104 (a) 104 K (b) 1 + a Topic 15C P15C.3 Topic 15E P15E.1 0.351, 0.079, 0.029 P15E.3 4.2 J K -1 mol-1 P15E.5 28, 258 J mol - 1 K - 1 © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e P15E.7 2 [eq](q] (q relative permittivity. (b) 0.7 D (c) 0.4 D Topic 16B P16B.1 1.9 nm P16B.3 - 1.8 × 10-27 J = -1.1 × 10-3 J mol-1 P16B.5 - 6C r7 P16B.7 (b) re = 1.3598 r0, A = 1.8531 © Oxford University Press, 2014. (kTi Λ H2i) 3 e - (D RTi) p O qiV qiR (Λ Hi) 6, Atkins & de Paula: Atkins' Physical Chemistry 10e Chapter 17 Topic 17A P17A.1 (a) 2 (b) 1 P17A.3 Nl 2 P17A.5 (a) 1 5 { } a, 0.046460 × (us / cm3 g - 1) × (M / g mol-1) 2 a, 2 a, a/2 1 12 (b) 1 2 a, 1 1 (RT) 2 |], 6.3 GHz 2 \pi l (M / Topic 17D P17D.1 (2 γ) M + | $(\pi / P17D.3 (a) 1/2 \theta / ^{\circ}, 1.96 nm l, 0.35 nm, 46 nm Topic 17B P17B.1 1/3 20 45 90 Irod / Icc 0.976 0.876 0.514 (b) 90^{\circ} P17D.5 3500 r.p.m. P17D.7 69 kg mol-1, 3.4 nm P17D.9 0.0716$ dm3 g -1 P17D.11 1.6 × 105 g mol-1 Chapter 18 Topic 18Å © Oxford University Press, 2014. 1 12 l (c) 2 5 a Atkins & de Paula: Atkins' Physical Chemistry 10e -1 P18A.1 3.61 × 105 g mol P18A.3 V = 3 3 / 2 a2c P18A.5 834 pm , 606 pm , 870 pm P18A.7 4 P18A.9 1 (h) (k) (l) = | +| +| | +| | d2 (a / b / c / P18A.11 Simple (primitive) cubic lattice, a = 344 pm P18A.13 629 pm , gave support P18A.15 0 P18A.17 (a) 14.00 , 24.20 , 0.720 , 1.230 () 2 2 2 (b) RCCl = 176 pm and RClCl = 289 pm Topic 18B P18B.1 0.340 P18B.3 7.654 g cm - 3 P18B.7 (a) 0.41421 (b) 0.73205 Topic 18C P18C.1 P18C.3 μ , $3\lambda + 2\mu 3 = P(E)$ 1 when $E < \mu$, lim lim f (E) 0 when $E > \mu$, (3N / 8π) = T $\rightarrow 0$ T $\rightarrow 0$ 2/3 (h 2 / 2me), 3.1 eV P18C.5 0.736 eV P18C.7 0.127 × 10-6 m3 mol-1, 0.254 × 10-6 m3 mol-1, 0.254 × 10-6 m3 mol-1, 0.254 cm mol P18C.9 0.41 3 Chapter 19 Topic 19A © Oxford University Press, 2014. -1 Atkins & de Paula: Atkins' Physical Chemistry 10e P19A.1 (a) $\sigma = 0.602 \text{ nm}2$, $d = (\sigma/\pi)1/2 = 438 \text{ pm pm P19A.3 } 2.37 \times 1017 \text{ m } 2 \text{ s} - 1$, 2.85 J K -1 $m - 1 s - 1 P19A.5 (a) 1.7 \times 1014 s - 1 (b) \sigma = 0.421 nm2, d = (\sigma/\pi)1/2 = 366 (b) 1.1 \times 1016 s - 1 Topic 19B P19B.1 10.2 kJ mol - 1 (b) (c) 172 \Omega Topic 19B P19B.5 12.6 mS m 2 mol - 1 (b) (c) 172 \Omega Topic 19B P19B.5 12.6 mS m 2 mol - 1 (c) (c) 172 \Omega Topic 19B P19B.5 (c) 18B P19B.5 (c) 18B P19B.5 mS m 2 mol - 1 (c) (c) 18B P19B.5 mS m 2 mol - 1 (c) (c) 18B P19B.$ s-1 Topic 20B P20B.3 Second-order, kr = 0.0594 dm3 mol-1 min -1, 2.94 g © Oxford University Press, 2014. Atkins & de Paula: Atkins' Physical Chemistry 10e P20B.5 7.0×10-5 s-1, 7.3×10-5 dm3 mol-1 s-1 P20B.7 14 yr 6 × 10-14 mol dm -3 s -1, 4.4 × 108 s = P20B.9 First-order, 5.84×10-3 s-1, kr = 2.92×10-3 s-1, first-order, 1.98 min P20B.11 3.65×10-3 min-1, 190 min , 274 min P20B.13 2.37 × 107 dm3 mol-1 s -1 , kr = 1.18×10 dm mol s , 4.98 × 10-3 s P20B.15 First-order, third-order P20B.17 () (2x - A0) B0) 1 | |ln| || 3A0 - 2B0 || A0 (3x - B0) /| P20B.1973 - 1 - 1 2n - 1 - 1 (34) n - 1 - 1 Topic 20C P20C.3 kr' ([A]0 + [B]0) + (kr [A]0 - kr'[B]0) e - (kr + kr')t (kr' || kr') + (kr' || kr' || kr') + (kr' || kr' || $| x ([A]0 + [B]0), kr + kr' (kr + kr' [B] \propto kr (kr + kr' [B] \propto kr (kr + kr' [B] \propto kr (kr + kr' P20C.5 (a) (i) 8ka ka' [A]tot + (ka') 2 (c) 1.7 × 107 s - 1, 2.7 × 109 dm3 mol - 1 s - 1, 2.7 × 109 dm3 mol - 1 s - 1, 2.7 × 107 s - 1, 2.7 × 109 dm3 mol - 1 s - 1, 1.6 × 102 Topic 20D P20D.3 (a) (a) 8ka ka' [A]tot + (ka') 2 (c) 1.7 × 107 s - 1, 2.7 × 107 s - 1, 2.7 × 109 dm3 mol - 1 s - 1, 2.7 × 107 s - 1, 2.7 × 10$ Steady-state intermediate P20E.5 kr K1 K 2 [HC]]3 [CH 3 CH=CH 2] Topic 20F © Oxford University Press, 2014. (b) 4.3 × 1011 kg or 430 Tg Atkins & de Paula: Atkins'
Physical Chemistry 10e P20F.3 (1 + 2k t[A]) 2 12 0 r Topic 20G P20G.1 1.11 P20G.3 (a) 6.7 ns P20G.5 1.98 × 109 dm3 mol-1 s -1 P20G.7 3.5 nm (b) 0.105 ns -1 Topic 20H P20H.1 ν = ν max 1 + P20H.5 1 K [S]0 Rate law based on rapid pre-equilibrium approximation 2.31 μmol dm-3 s-1, 115 s-175 kJ mol-1 (b) 0.15 Topic 21C P21C.1 Ea = 86.0 kJ mol-1, +83.9 kJ mol-1, +19.6 J K -1 mol-1, +79.0 kJ mol-1, +79.0 kJ mol-1, +29.9 kJ mol-1, +29.0 kJ mol-1, +29.0 kJ mol-1, +114.7 (a) 0.06 (b) 0.89, 0.83 Topic 21D P21D.1 I = I 0 e - σ N L Topic 21E P21E.1 kr ≈ (kAAkDDK)1/2 P21E.3 1.15 eV Topic 21F P21F.1 0.78, 0.38 P21F.3 (a) -0.618 V P21F.5 2.00×10-5 mA m-2, 0.498, no Chapter 22 Topic 22A P22A.1 -76.9 kJ mol-1, -348.1 -2 P22B.3 (a) 165, 13.1 cm3 (b) 263, 12.5 cm3 P22B.5 5.78 mol kg -1, 7.02 Pa -1 P22B.7 -20.0 kJ mol -1, -43.5 kJ mol -1, -43.5 kJ mol -1, -63.5 kJ mol -1, -1 (b) 3.68 × 10 -3, -8.67 kJ mol -1, -1 (c) -1, -1 (b) -1, -1 (c) -1, -1, -1 (c) -1, -1Physical Chemistry 10e P22B.11 0.138 mg g -1, 0.58 P22B.13 (a) k = 0.2289, n = 0.6180, k = 0.2289, n = 0.6180 Topic 22C P22C.1 - kr pNH 3 p - p0 p0 p = - ln, kc, kc = 2.5 × 10 - 3 kPa s - 1 K pH 2 t t p0 © Oxford University Press, 2014. (c) k = 0.5227, n = 0.7273

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