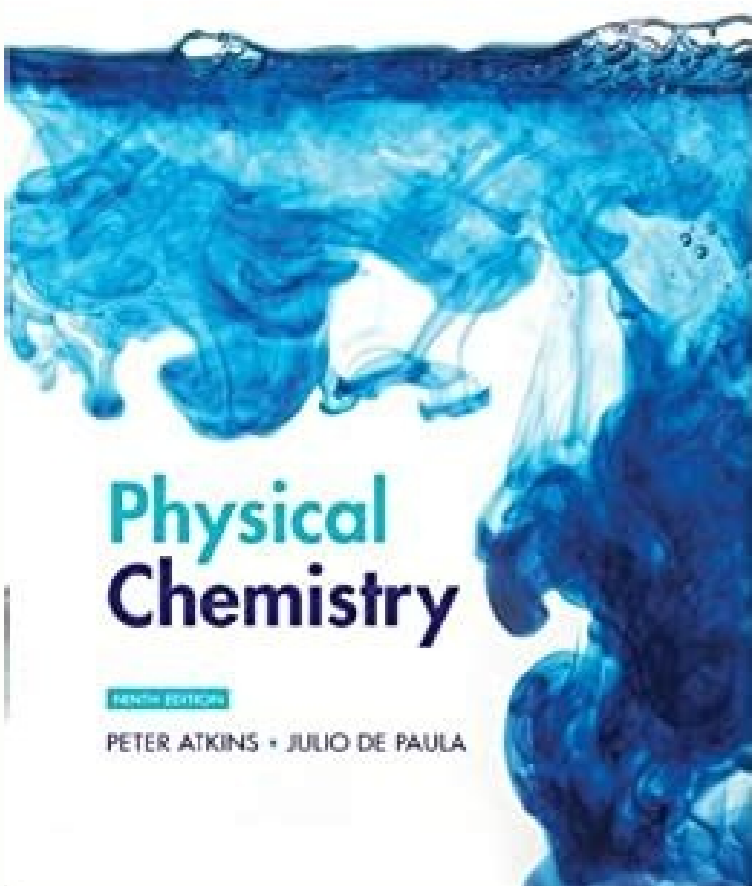
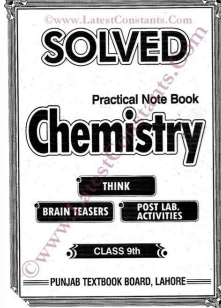
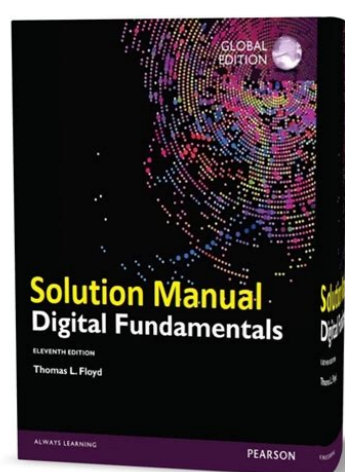
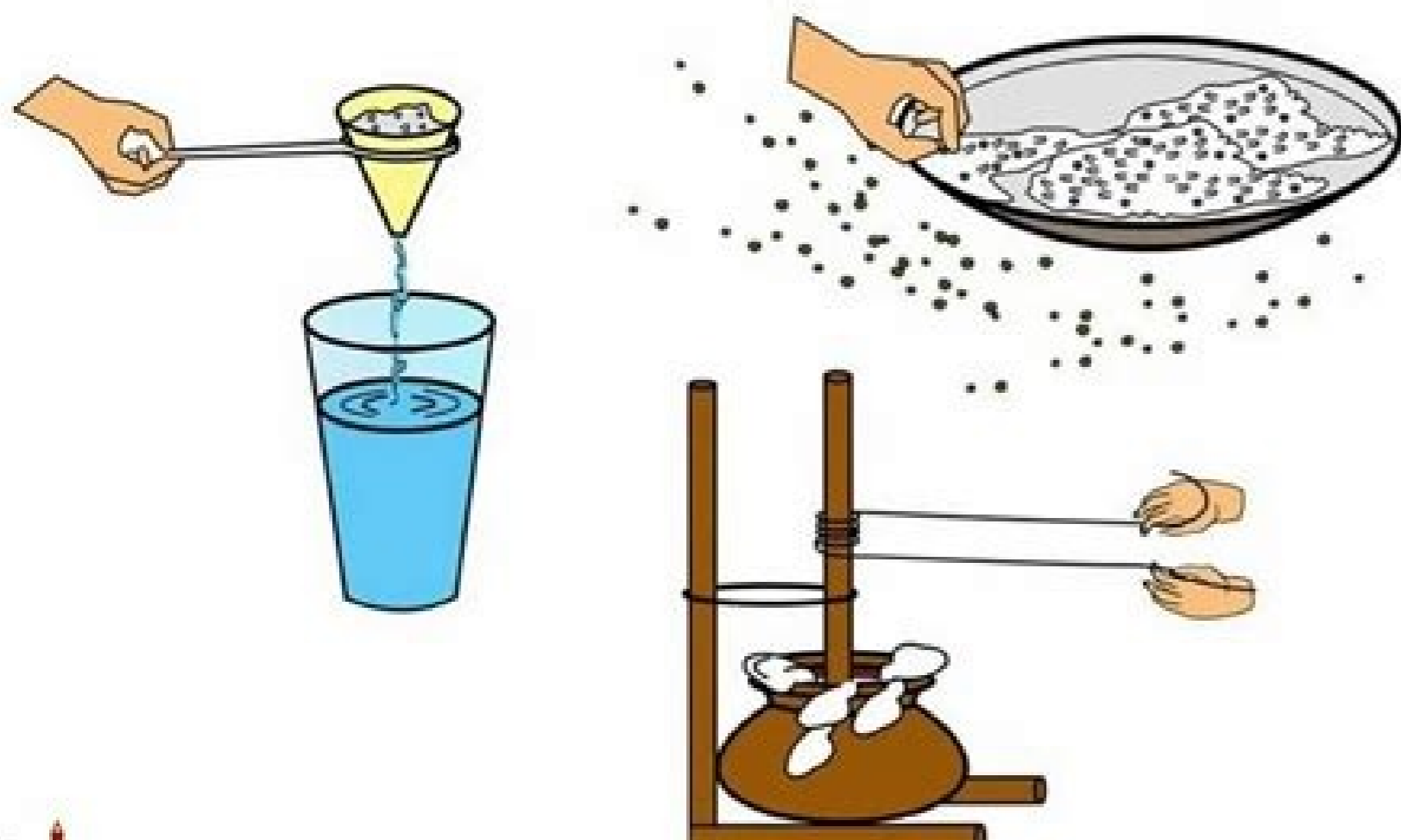


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Different separation methods



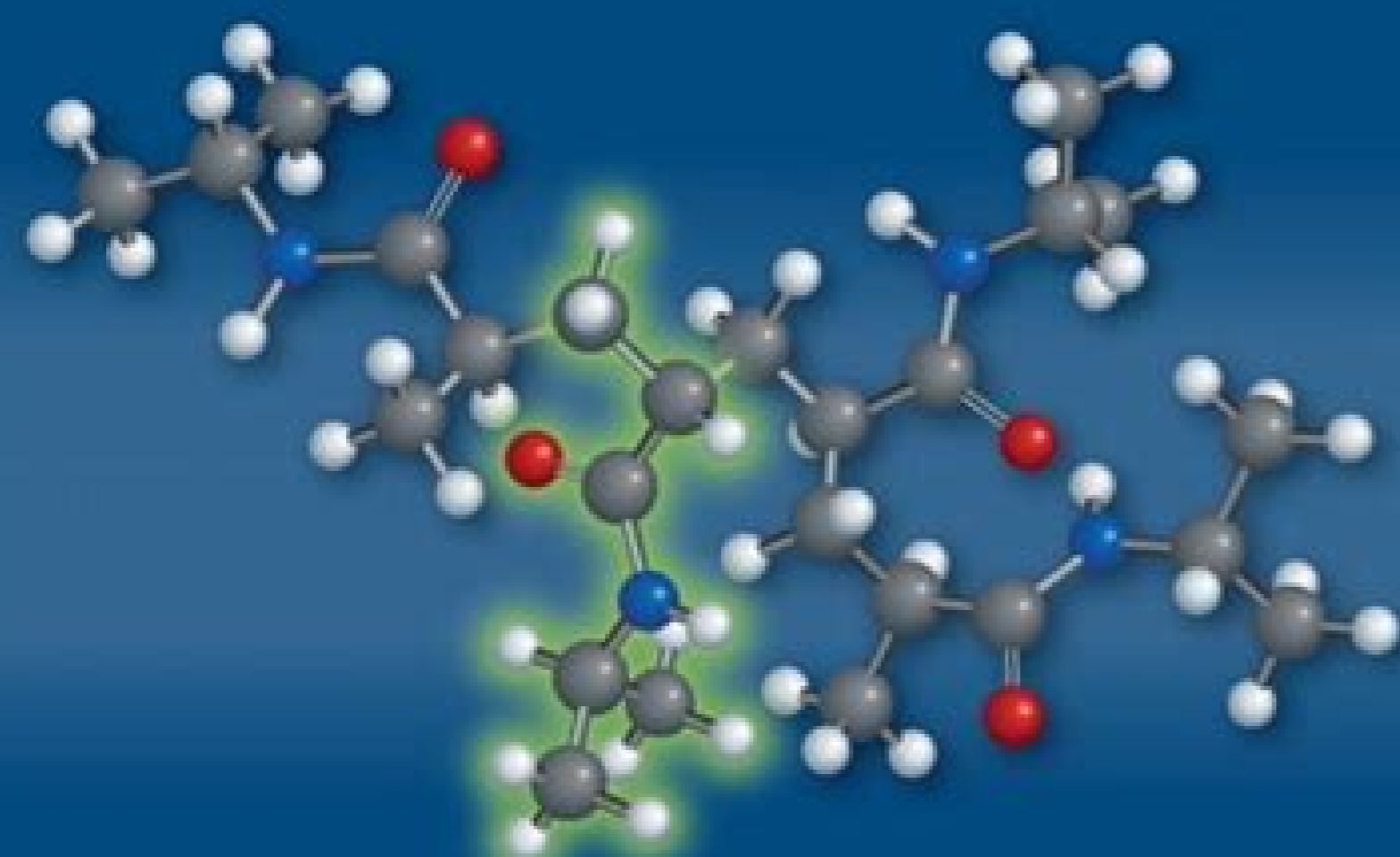
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COMPLETE SOLUTIONS MANUAL

GENERAL CHEMISTRY

PRINCIPLES AND MODERN APPLICATIONS

ELEVENTH EDITION



PETRUCCI HERRING MADURA BISSONNETTE

solutions to b) exercises and even-numbered problems (instructor) answers to a) exercises and odd-numbered problems (student) PHYSICAL CHEMISTRY Thermodynamics, Structure, and Change Tenth Edition Peter Atkins | Julio de Paula Foundations A Matter Answers to discussion questions A.2 Metals conduct electricity, have luster, and they are malleable and ductile. Nonmetals do not conduct electricity and are neither malleable nor ductile. Metalloids typically have the appearance of metals but behave chemically like a nonmetal. 1 IA 1 H 1.008 3 Li 6.941 11 Na 22.99 19 K 39.10 37 Rb 85.47 55 Cs 132.9 87 Fr (223) 2 IIA 3 IIIB 4 IVB 5 VB 6 VIB 7 VIIB 8 9 10 VIIIB VIIIIB VIIIIB 11 IB 12 IIB 13 IIIA 14 IVA 15 VA 16 VIA 17 VIIA 5 B 10.81 13 Al 26.98 31 Ga 69.72 49 In 114.8 81 Tl 204.4 6 C 12.01 14 Si 28.09 32 Ge 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 83 Bi 209.0 8 O 16.00 16 S 32.07 34 Se 78.96 52 Te 127.6 84 Po (209) 9 F 19.00 17 Cl 35.45 35 Br 79.90 53 I 126.9 85 At (210) 13 IIIA 14 IVA 15 VA 16 VIA 17 VIIA 5 B 10.81 13 Al 26.98 31 Ga 69.72 49 In 114.8 81 Tl 204.4 6 C 12.01 14 Si 28.09 32 Ge 72.59 50 Sn 118.7 82 7 N 14.01 15 P 30.97 33 As 74.92 51 Sb 121.8 83 8 O 16.00 16 S 32.07 34 Se 78.96 52 Te 127.6 84 9 F 19.00 17 Cl 35.45 35 Br 79.90 53 I 126.9 85 Periodic Table of the Elements 4 Be 9.012 12 Mg 24.31 20 Ca 40.08 38 Sr 87.62 56 Ba 137.3 88 Ra 226 21 Sc 44.96 39 Y 88.91 57 La 138.9 89 Ac (227) 22 Ti 47.88 40 Zr 91.22 72 Hf 178.5 23 V 50.94 41 Nb 92.91 73 Ta 180.9 24 Cr 52.00 42 Mo 95.94 74 W 183.9 25 Mn 54.94 43 Tc (98) 75 Re 186.2 26 Fe 55.85 44 Ru 101.1 76 Os 190.2 27 Co 58.93 45 Rh 102.9 77 Ir 192.2 58 Ce 140.1 90 Th 232.0 59 Pr 140.9 91 Pa (231) 60 Nd 144.2 92 U 238.0 61 Pm 145.9 3 Np 237 62 Sm 150.4 94 Pu (244) 28 Ni 58.69 46 Pd 106.4 78 Pt 195.1 63 Eu 152.0 95 Am (243) 29 Cu 63.55 47 Ag 107.9 79 Au 197.0 64 Gd 157.3 96 Cm (247) 30 Zn 65.38 48 Cd 112.4 80 Hg 200.6 65 Tb 158.9 97 Bk (247) 18 VIIIA 2 He 4.003 10 Ne 20.18 18 Ar 39.95 36 Kr 83.80 54 Xe 131.3 86 Rn (222) 66 Dy 162.5 98 Cf (251) Transition metals Lanthanoids Actinoids 1 IA 1 H 1.008 3 Li 6.941 11 Na 22.99 19 K 39.10 37 Rb 85.47 55 2 IIA 3 IIIB 4 IVB 5 VB 6 VIB 7 VIIB 8 9 10 VIIIB VIIIIB VIIIIB 11 IB 12 IIB Periodic Table of the Elements 4 Be 9.012 12 Mg 24.31 20 Ca 40.08 38 Sr 87.62 56 21 Sc 44.96 39 Y 88.91 57 22 Ti 47.88 40 Zr 91.22 72 23 V 50.94 41 Nb 92.91 73 24 Cr 52.00 42 Mo 95.94 74 25 Mn 54.94 43 Tc (98) 75 26 Fe 55.85 44 Ru 101.1 76 27 Co 58.93 45 Rh 102.9 77 28 Ni 58.69 46 Pd 106.4 78 29 Cu 63.55 47 Ag 107.9 79 30 Zn 65.38 48 Cd 112.4 80 18 VIIIA 2 He 4.003 10 Ne 20.18 18 Ar 39.95 36 Kr 83.80 54 Xe 131.3 86 Cs 132.9 87 Fr (223) Ba 137.3 88 Ra 226 La 138.9 89 Ac (227) Hf 178.5 Ta 180.9 W 183.9 Re 186.2 Os 190.2 Ir 192.2 58 Ce 140.1 90 Th 232.0 59 Pr 140.9 91 Pa (231) 60 Nd 144.2 92 U 238.0 61 Pm 145.9 3 Np 237 62 Sm 150.4 94 Pu (244) Pt 195.1 63 Eu 152.0 95 Am (243) Au 197.0 64 Gd 157.3 96 Cm (247) Hg 200.6 65 Tb 158.9 97 Bk (247) Tl 204.4 Pb 207.2 Bi 209.0 Po (209) At (210) Rn (222) 66 Dy 162.5 98 Cf (251) A.4 Valence-shell electron pair repulsion theory (VSEPR theory) predicts molecular shape with the concept that regions of high electron density (as represented by single bonds, multiple bonds, and lone pair) take up orientations around the central atom that maximize their separation. The resulting positions of attached atoms (not lone pairs) are used to classify the shape of the molecule. When the central atom has two or more lone pair, the molecular geometry must minimize repulsion between the relatively diffuse orbitals of the lone pair. Furthermore, it is assumed that the repulsion between a lone pair and a bonding pair is stronger than the repulsion between two bonding pair, thereby, making bond angles smaller than the idealized bond angles that appear in the absence of a lone pair. Solutions to exercises A.1(b) Example (i) Group 3 (ii) Group 5 (iii) Group 13 Element Sc, scandium V, vanadium Ga, gallium Ground-state Electronic Configuration [Ar]3d14s2 [Ar]3d34s2 [Ar]3d104s24p1 A.2(b) (i) chemical formula and name: CaH2, calcium hydride ions: Ca²⁺ and H⁻ oxidation numbers of the elements: calcium, +2; hydrogen, -1 (ii) chemical formula and name: CaC2, calcium carbide ions: Ca²⁺ and C²⁻ (a polyatomic ion) oxidation numbers of the elements: calcium, +2; carbon, -1 (iii) chemical formula and name: LiN3, lithium azide ions: Li⁺ and N³⁻ (a polyatomic ion) oxidation numbers of the elements: lithium, +1; nitrogen, -1/3 (iv) Ammonia, NH3, illustrates a molecule with one lone pair on the central atom. H N H (ii) Water, H2O, illustrates a molecule with two lone pairs on the central atom. H O H (iii) The hydrogen fluoride molecule, HF, illustrates a molecule with three lone pairs on the central atom. Xenon difluoride has three lone pairs on both the central atom and the two peripheral atoms. H F F Xe F A.4(b) (i) Ozone, O3. Formal charges (shown in circles) may be indicated. O O O (ii) O O F ClF3+ Cl O F F (iii) azide anion, N3- N N N A.5(b) The central atoms in XeF4, PCl5, SF4, and SF6 are hypervalent. A.6(b) Molecular and polyatomic ion shapes are

... by drawing the Lewis structure and applying the concepts of VSEPR theory. (ii) H2O2 Lewis structure: H O H Orientations caused by repulsions between two lone pair and two bonding pair around each oxygen atom: Bent (or angular) with bond angles somewhat smaller than 109.5° ...

The complex nature of the solvent-solvent interaction. Polar solvent-polar solute interactions are an electric field effect that usually causes deshielding of the solute protons. Solvent magnetic anisotropy can cause shielding or deshielding, for example, for solutes in benzene solution. In addition, there are a variety of specific chemical interactions...

Problem 20C.5: $k = k_1 + 8k_2 \rightarrow \ln A(T) = 2.015 \ln \frac{A(T)}{A(T_0)}$. 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 $(d \ln k / d(1/T))^{-1}$. This does not mean that the activation energy is constant, but it is constant over a small range of $1/T$. The plot of straight line $\ln k$ vs $1/T$ is a straight line in some cases, but not in others. In biological reactions it might be that an enzyme has undergone a structural change and has become less efficient at reacting with a small zero activation energy, but that $A(T)$ is not constant, so the 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 be that an enzyme has undergone a structural change and has become less efficient at reacting with a small zero activation energy, but that $A(T)$ is not constant, so the 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 be that an enzyme has undergone a structural change and has become less efficient at reacting with a small zero activation energy, but that $A(T)$ is not constant, so the 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 be that an enzyme has undergone a structural change and has become less efficient at reacting with a small zero activation energy, but that $A(T)$ is not constant, so the Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling (Section 8A) is playing a significant role in the reaction.

Solutions to exercises E20D.1(b) The Arrhenius equation for two different temperatures can be rearranged to yield the activation energy: $k_1(0.1 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}) = A \exp(-E_a/RT_1)$ and $k_2(0.1 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}) = A \exp(-E_a/RT_2)$. Taking the ratio of these two equations gives $k_1/k_2 = \exp(-E_a/R(1/T_1 - 1/T_2))$. Solving for E_a gives $E_a = R \ln(k_1/k_2) / (1/T_1 - 1/T_2) = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(2.25/0.4) / (1/310 \text{ K} - 1/330 \text{ K}) = 52.6 \text{ kJ mol}^{-1}$.

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 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 shows that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn. 20B.1: $\ln[A]_t = \ln[A]_0 - kt$. We plot $\ln[A]_t$ against time to see if a straight line is obtained. We draw up $\ln[A]_t$ / the following table (A = CH33CB):

t / s	$\ln[A]_t$
0	1.25
10	1.00
20	0.75
30	0.50
40	0.25
50	0.00
60	-0.25
70	-0.50
80	-0.75
90	-1.00
100	-1.25

The plot is a straight line. The rate constant k is the negative of the slope of the first-order plot: $k = -(\ln[A]_t - \ln[A]_0) / (t - 0) = 0.025 \text{ s}^{-1}$. The Arrhenius expression for the rate constant is (eqn. 20D.1): $k = A \exp(-E_a/RT)$. We plot $\ln k$ versus $1/T$ to get a straight line. The slope of this line is $-E_a/R$ and the intercept is $\ln A$. We draw up the following table:

$1/T$ / K^{-1}	$\ln k$
3100	1.25
3200	1.00
3300	0.75
3400	0.50
3500	0.25
3600	0.00
3700	-0.25
3800	-0.50
3900	-0.75
4000	-1.00
4100	-1.25

The plot is a straight line. The slope of this line is $-E_a/R$, so $E_a = -R \times \text{slope} = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times (-0.8) = 6.65 \text{ kJ mol}^{-1}$. The intercept is $\ln A$, so $A = \exp(\text{intercept}) = \exp(2.0) = 7.4 \text{ mol}^{-1} \text{ s}^{-1}$.

Answers to discussion questions D20E.2 The rate-determining step is not just the slowest step; it must also 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 a slow ferry crossing between two fast highways: the overall rate at which traffic can reach its destination is determined by the 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 rate-determining, 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 intermediate is formed it reaches immediately in the formation of products. Once over the initial barrier, the intermediates cascade into products. However, a rate-determining step may also stem from the low energy of the transition state. A reaction with a low energy of activation can be rate-determining because the rate constant for the transition state is low. A reaction with a high energy of activation can be rate-determining because the rate constant for the transition state is high.

Solutions to problems 21A.2 to 21A.5. The reaction is first-order because the concentration of the reactant is constant. The rate constant k is the slope of the straight line in the $\ln[A]_t$ vs t plot. The half-life $t_{1/2}$ is $\ln 2 / k$. The activation energy E_a is $-R \ln(k_1/k_2) / (1/T_1 - 1/T_2)$. The pre-exponential factor A is $k \exp(E_a/RT)$.

Answers to problems 21A.6 to 21A.10. The reaction is first-order because the concentration of the reactant is constant. The rate constant k is the slope of the straight line in the $\ln[A]_t$ vs t plot. The half-life $t_{1/2}$ is $\ln 2 / k$. The activation energy E_a is $-R \ln(k_1/k_2) / (1/T_1 - 1/T_2)$. The pre-exponential factor A is $k \exp(E_a/RT)$.

Answers to problems 21A.11 to 21A.15. The reaction is first-order because the concentration of the reactant is constant. The rate constant k is the slope of the straight line in the $\ln[A]_t$ vs t plot. The half-life $t_{1/2}$ is $\ln 2 / k$. The activation energy E_a is $-R \ln(k_1/k_2) / (1/T_1 - 1/T_2)$. The pre-exponential factor A is $k \exp(E_a/RT)$.

Answers to problems 21A.16 to 21A.20. The reaction is first-order because the concentration of the reactant is constant. The rate constant k is the slope of the straight line in the $\ln[A]_t$ vs t plot. The half-life $t_{1/2}$ is $\ln 2 / k$. The activation energy E_a is $-R \ln(k_1/k_2) / (1/T_1 - 1/T_2)$. The pre-exponential factor A is $k \exp(E_a/RT)$.

Answers to problems 21A.21 to 21A.25. The reaction is first-order because the concentration of the reactant is constant. The rate constant k is the slope of the straight line in the $\ln[A]_t$ vs t plot. The half-life $t_{1/2}$ is $\ln 2 / k$. The activation energy E_a is $-R \ln(k_1/k_2) / (1/T_1 - 1/T_2)$. The pre-exponential factor A is $k \exp(E_a/RT)$.

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