

SOLUTIONS

PROBLEM SET 9

CHM 3400, Dr. Chatfield

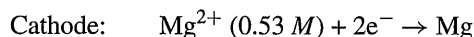
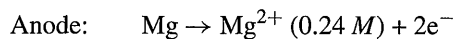
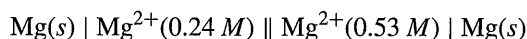
The ratio of  $[\text{Sn}^{2+}]$  to  $[\text{Pb}^{2+}]$  at equilibrium is directly related to the equilibrium constant, which can be calculated from  $E^\circ$ .

$$K = \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = \exp\left(\frac{\nu FE^\circ}{RT}\right) = \exp\left[\frac{2(96500 \text{ C mol}^{-1})(0.012 \text{ V})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}\right] = 2.55$$

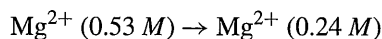
The standard Gibbs energy is

$$\Delta_r G^\circ = -\nu FE^\circ = -2(96500 \text{ C mol}^{-1})(0.012 \text{ V}) = -2.32 \times 10^3 \text{ J mol}^{-1}$$

**7.14** Calculate the emf of the following concentration cell at 298 K:



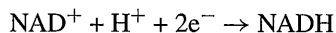
The overall reaction is



The emf of the cell depends on the concentrations of  $\text{Mg}^{2+}$  at both the anode and the cathode.

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{0.24}{0.53} = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.24}{0.53} = 0.010 \text{ V}$$

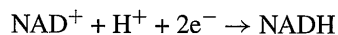
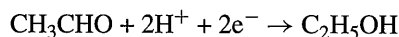
**7.16** For the reaction



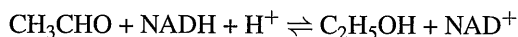
$E^\circ$  is  $-0.320 \text{ V}$  at  $25^\circ \text{ C}$ . Calculate the value of  $E'$  at  $\text{pH} = 1$ . Assume that both  $\text{NAD}^+$  and  $\text{NADH}$  are at unimolar concentration.

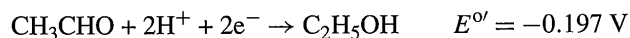
$$\begin{aligned} E' &= E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{[\text{NADH}]}{[\text{NAD}][\text{H}^+]/10^{-7}} \\ &= -0.320 - \frac{0.0257 \text{ V}}{2} \ln \frac{1}{(1)(0.1/10^{-7})} \\ &= -0.142 \text{ V} \end{aligned}$$

**7.18** Look up the  $E^\circ$  values in Table 7.2 for the reactions

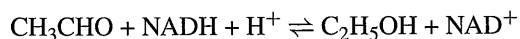


Calculate the equilibrium constant for the following reaction at 298 K.





The standard emf for the reaction



is

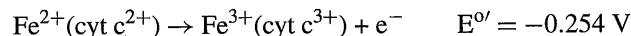
$$E^{\circ'} = -0.197 \text{ V} - (-0.320 \text{ V}) = 0.123 \text{ V}$$

The equilibrium constant for this reaction is

$$K' = \exp\left(\frac{\nu FE^{\circ'}}{RT}\right) = \exp\left[\frac{2(96500 \text{ C mol}^{-1})(0.123 \text{ V})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}\right] = 1.45 \times 10^4$$

**7.20** Calculate the number of moles of cytochrome  $c^{3+}$  formed from cytochrome  $c^{2+}$  with the Gibbs energy derived from the oxidation of 1 mole of glucose. ( $\Delta_r G^{\circ} = -2879 \text{ kJ}$  for the degradation of 1 mole of glucose to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .)

The standard emf for the oxidation of cyt  $c^{2+}$  to cyt  $c^{3+}$  is



$\Delta_r G^{\circ}$  for the oxidation reaction is the same as  $\Delta_r G^{\circ'}$ , since no  $\text{H}^+$  is involved.

$$\Delta_r G^{\circ} = \Delta_r G^{\circ'} = -\nu FE^{\circ'} = -(96500 \text{ C mol}^{-1})(-0.254 \text{ V}) = 2.451 \times 10^4 \text{ J mol}^{-1}$$

The number of moles of cyt  $c^{3+}$  formed from the oxidation of 1 mole of glucose is

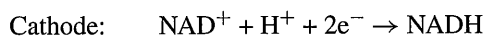
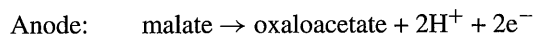
$$\frac{2879 \times 10^3 \text{ J}}{2.451 \times 10^4 \text{ J mol}^{-1}} = 117 \text{ mol}$$

**7.22** The oxidation of malate to oxaloacetate is a key reaction in the citric acid cycle:



Calculate the value of  $\Delta_r G^{\circ'}$  and the equilibrium constant for the reaction at pH 7 and 298 K.

The half reactions are



The standard emf for the reaction is

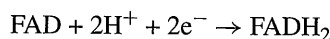
$$E^{\circ'} = -0.320 \text{ V} - (-0.166 \text{ V}) = -0.154 \text{ V}$$

The standard Gibbs energy and the equilibrium constant are

$$\Delta_r G^{\circ} = -\nu F E^{\circ} = -2 \left( 96500 \text{ C mol}^{-1} \right) (-0.154 \text{ V}) = 2.972 \times 10^4 \text{ J mol}^{-1} = 2.97 \times 10^4 \text{ J mol}^{-1}$$

$$K' = \exp \left( -\frac{\Delta_r G^{\circ}}{RT} \right) = \exp \left[ -\frac{2.972 \times 10^4 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K})} \right] = 6.17 \times 10^{-6}$$

**7.24** Flavin adenine dinucleotide (FAD) participates in several biological redox reactions according to the half-reaction



If the value of  $E^{\circ}$  of this couple is  $-0.219 \text{ V}$  at  $298 \text{ K}$  and  $\text{pH } 7$ , calculate its reduction potential at this temperature and  $\text{pH}$  when the solution contains (a) 85% of the oxidized form and (b) 15% of the oxidized form.

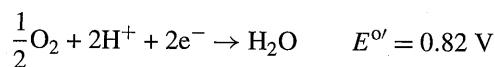
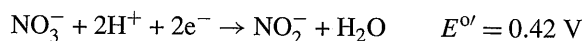
At  $\text{pH} = 7$  and  $298 \text{ K}$ , the emf for the reduction of FAD is

$$\begin{aligned} E' &= E^{\circ} - \frac{0.0257 \text{ V}}{\nu} \ln \frac{[\text{FADH}_2]}{[\text{FAD}] ([\text{H}^+]/10^{-7})^2} \\ &= -0.219 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{[\text{FADH}_2]}{[\text{FAD}] (10^{-7}/10^{-7})^2} \\ &= -0.219 \text{ V} - 0.01285 \text{ V} \ln \frac{[\text{FADH}_2]}{[\text{FAD}]} \end{aligned}$$

$$\text{(a)} \quad E' = -0.219 \text{ V} - 0.01285 \text{ V} \ln \frac{0.15}{0.85} = -0.197 \text{ V}$$

$$\text{(b)} \quad E' = -0.219 \text{ V} - 0.01285 \text{ V} \ln \frac{0.85}{0.15} = -0.241 \text{ V}$$

**7.26** The nitrite in soil is oxidized to nitrate by the bacteria *nitrobacter agilis* in the presence of oxygen. The half-reduction reactions are



Calculate the yield of ATP synthesis per mole of nitrite oxidized, assuming an efficiency of 55%. (The  $\Delta_r G^{\circ}$  value for ATP synthesis from ADP and  $\text{P}_i$  is  $31.4 \text{ kJ mol}^{-1}$ .)

The standard emf when 1 mole of nitrite is oxidized is

$$E^{\circ} = 0.82 \text{ V} - 0.42 \text{ V} = 0.40 \text{ V}$$

and the standard Gibbs energy is

$$\Delta_r G^{\circ} = -nFE^{\circ} = -2 \left( 96500 \text{ C mol}^{-1} \right) (0.40 \text{ V}) = -7.72 \times 10^4 \text{ J mol}^{-1}$$

Both  $\text{Mg}^{2+} | \text{Mg}$  ( $E^\circ = -2.372 \text{ V}$ ) and  $\text{Zn}^{2+} | \text{Zn}$  ( $E^\circ = -0.762 \text{ V}$ ) are more electropositive than  $\text{Fe}^{2+} | \text{Fe}$  ( $E^\circ = -0.447 \text{ V}$ ). The more electropositive metals will be preferentially oxidized, protecting the iron pipe. These protective electrodes are often called sacrificial anodes.

- 7.34 Given that the  $\Delta_r S^\circ$  value for the Daniell cell is  $-21.7 \text{ J K}^{-1} \text{ mol}^{-1}$ , calculate the temperature coefficient  $(\partial E^\circ / \partial T)_P$  of the cell and the emf of the cell at  $80^\circ \text{ C}$ .

The temperature coefficient is directly related to  $\Delta_r S^\circ$ .

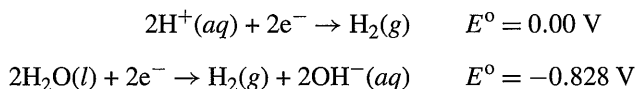
$$\begin{aligned}\Delta_r S^\circ &= \nu F \left( \frac{\partial E^\circ}{\partial T} \right)_P \\ \left( \frac{\partial E^\circ}{\partial T} \right)_P &= \frac{\Delta_r S^\circ}{\nu F} = \frac{-21.7 \text{ J K}^{-1} \text{ mol}^{-1}}{2 (96500 \text{ C mol}^{-1})} \\ &= -1.124 \times 10^{-4} \text{ V K}^{-1} = -1.12 \times 10^{-4} \text{ V K}^{-1}\end{aligned}$$

The standard emf of the cell at  $80^\circ \text{ C}$  can be calculated using the temperature coefficient and the standard emf ( $1.104 \text{ V}$ ) at  $25^\circ \text{ C}$ .

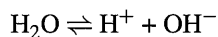
$$\begin{aligned}\left( \frac{\partial E^\circ}{\partial T} \right)_P &= \frac{E_{353.2 \text{ K}}^\circ - E_{298.2 \text{ K}}^\circ}{353.2 \text{ K} - 298.2 \text{ K}} = \frac{E_{353.2 \text{ K}}^\circ - 1.104 \text{ V}}{55.0 \text{ K}} = 1.124 \times 10^{-4} \text{ V K}^{-1} \\ E_{353.2 \text{ K}}^\circ &= 1.098 \text{ V}\end{aligned}$$

Note that because of the small temperature coefficient,  $E^\circ$  changes only slightly with temperature.

- 7.36 Given the following standard reduction potentials, calculate the ion-product  $K_w$  value ( $[\text{H}^+][\text{OH}^-]$ ) at  $25^\circ \text{ C}$ :



The ion-product is the equilibrium constant for the following process.



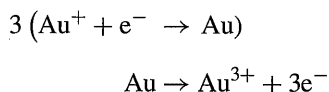
The standard emf for this reaction can be calculated using those for the half-cells described in the question.

$$E^\circ = -0.828 \text{ V} - 0 \text{ V} = -0.828 \text{ V}$$

The ion-product is calculated from  $E^\circ$ .

$$K_w = \exp \left( \frac{\nu F E^\circ}{RT} \right) = \exp \left[ \frac{(96500 \text{ C mol}^{-1}) (-0.828 \text{ V})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.2 \text{ K})} \right] = 1.01 \times 10^{-14}$$

(b) The disproportionation can be considered as the sum of the two half reactions,

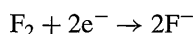


so that the standard emf for the reaction is

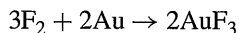
$$E^\circ = 1.692 \text{ V} - 1.498 \text{ V} = 0.194 \text{ V}.$$

Since  $E^\circ$  for the reaction is positive, the disproportionation will be spontaneous under standard state conditions.

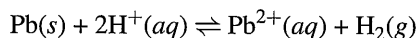
(c) With  $E^\circ = 2.87 \text{ V}$ , the half reaction



is able to oxidize gold completely to  $\text{Au}^{3+}$  via

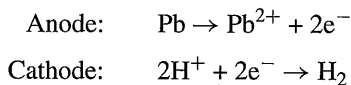


**7.42** Calculate the pressure of  $\text{H}_2$  (in bar) required to maintain equilibrium with respect to the following reaction at  $25^\circ \text{C}$

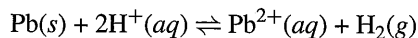


given that  $[\text{Pb}^{2+}] = 0.035 \text{ M}$  and the solution is buffered at pH 1.60.

The cell reaction is



The standard emf for the reaction



is

$$E^\circ = 0 \text{ V} - (-0.126 \text{ V}) = 0.126 \text{ V}$$

The emf of the cell is

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{[\text{Pb}^{2+}] P_{\text{H}_2}}{[\text{H}^+]^2}$$

From the pH,  $[\text{H}^+] = 10^{-1.60} = 2.51 \times 10^{-2} \text{ M}$ . At equilibrium,  $E = 0$ . Therefore, the above equation becomes

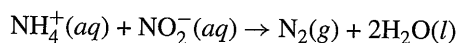
$$0 = 0.126 - \frac{0.0257 \text{ V}}{2} \ln \frac{(0.035) P_{\text{H}_2}}{(2.51 \times 10^{-2})^2}$$

$$P_{\text{H}_2} = 3.3 \times 10^2 \text{ bar}$$

## Chemical Kinetics

## PROBLEMS AND SOLUTIONS

9.2 The rate law for the reaction



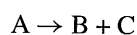
is given by rate =  $k [\text{NH}_4^+] [\text{NO}_2^-]$ . At 25°C, the rate constant is  $3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . Calculate the rate of the reaction at this temperature if  $[\text{NH}_4^+] = 0.26 \text{ M}$  and  $[\text{NO}_2^-] = 0.080 \text{ M}$ .

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$$\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-] = (3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}) (0.26 \text{ M}) (0.080 \text{ M}) = 6.2 \times 10^{-6} \text{ M s}^{-1}$$


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9.4 The following reaction is found to be first order in A:



If half of the starting quantity of A is used up after 56 s, calculate the fraction that will be used up after 6.0 min.

From the half-life (56 s),  $k$  can be determined:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{56 \text{ s}} = 1.24 \times 10^{-2} \text{ s}^{-1}$$

The fraction of A that will remain after 6.0 min ( $3.6 \times 10^2 \text{ s}$ ) is

$$\frac{[\text{A}]}{[\text{A}]_0} = e^{-kt} = e^{-(1.24 \times 10^{-2} \text{ s}^{-1})(3.6 \times 10^2 \text{ s})} = 0.0115$$

Thus, the fraction that will be used up after 6.0 min is  $1 - 0.0115 = 0.99$ .

9.6 (a) The half-life of the first-order decay of radioactive  $^{14}\text{C}$  is about 5720 years. Calculate the rate constant for the reaction. (b) The natural abundance of  $^{14}\text{C}$  isotope is  $1.1 \times 10^{-13} \text{ mol } \%$  in living matter. Radiochemical analysis of an object obtained in an archaeological excavation shows that the  $^{14}\text{C}$  isotope content is  $0.89 \times 10^{-14} \text{ mol } \%$ . Calculate the age of the object. State any assumptions.

$$(a) \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5720 \text{ yr}} = 1.212 \times 10^{-4} \text{ yr}^{-1} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

$$(b) \quad \frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} = e^{-kt}$$

$$t = -\frac{1}{k} \ln \frac{[^{14}\text{C}]}{[^{14}\text{C}]_0}$$

Due to constant exchange of material with the surroundings, the mol % of  $^{14}\text{C}$  of all living matter is assumed to be the same. However, when the object ceases to live, it no longer exchanges material with the environment and the mol % of  $^{14}\text{C}$  will decrease according to first-order decay kinetics. Therefore, the ratio between  $[^{14}\text{C}]$  and  $[^{14}\text{C}]_0$  depends on the time elapsed since the object's "death." Thus,  $t$  in the equation above gives the age of the object.

$$t = -\frac{1}{1.212 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{0.89 \times 10^{-14}}{1.1 \times 10^{-13}} = 2.1 \times 10^4 \text{ yr}$$

A key assumption in radiocarbon dating is that the natural abundance of  $^{14}\text{C}$  has remained constant throughout the ages. Since the production of terrestrial  $^{14}\text{C}$  is due to bombardment of  $^{14}\text{N}$  by cosmic rays, variations in cosmic ray flux have in fact led to variations in the natural abundance of  $^{14}\text{C}$ .

- 9.8 When the concentration of A in the reaction  $\text{A} \rightarrow \text{B}$  was changed from 1.20 M to 0.60 M, the half-life increased from 2.0 min to 4.0 min at 25°C. Calculate the order of the reaction and the rate constant.

The half life is related to the initial concentration of A by

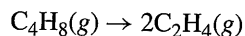
$$t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$$

According to the data, the half-life doubled when  $[\text{A}]_0$  was halved. This is only possible if the half-life is inversely proportional to  $[\text{A}]_0$ , or the reaction order,  $n = 2$ , indicating a second-order reaction.

The rate constant can be calculated using either  $[\text{A}]_0 = 1.20 \text{ M}$  or  $0.60 \text{ M}$  and the corresponding half-life.

$$k = \frac{1}{[\text{A}]_0 t_{1/2}} = \frac{1}{(1.20 \text{ M})(2.0 \text{ min})} = 0.42 \text{ M}^{-1} \text{ min}^{-1}$$

- 9.10 Cyclobutane decomposes to ethylene according to the equation

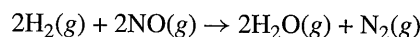


Determine the order of the reaction and the rate constant based on the following pressures, which were recorded when the reaction was carried out at 430°C in a constant-volume vessel:



$$\frac{d[\text{HBr}]}{dt} = \frac{\alpha[\text{H}_2][\text{Br}_2]^{1/2}}{1 + \beta[\text{HBr}]/[\text{Br}_2]}$$

**9.22** The following data were collected for the reaction between hydrogen and nitric oxide at 700° C:



| Experiment | [H <sub>2</sub> ]/M | [NO]/M | Initial rate/M · s <sup>-1</sup> |
|------------|---------------------|--------|----------------------------------|
| 1          | 0.010               | 0.025  | 2.4 × 10 <sup>-6</sup>           |
| 2          | 0.0050              | 0.025  | 1.2 × 10 <sup>-6</sup>           |
| 3          | 0.010               | 0.0125 | 0.60 × 10 <sup>-6</sup>          |

(a) What is the rate law for the reaction? (b) Calculate the rate constant for the reaction. (c) Suggest a plausible reaction mechanism that is consistent with the rate law. (*Hint*: Assume that the oxygen atom is the intermediate.) (d) More careful studies of the reaction show that the rate law over a wide range of concentrations of reactants should be

$$\text{rate} = \frac{k_1[\text{NO}]^2[\text{H}_2]}{1 + k_2[\text{H}_2]}$$

What happens to the rate law at very high and very low hydrogen concentrations?

(a) Comparing Experiment 1 and Experiment 2, the concentration of NO is constant and the concentration of H<sub>2</sub> has decreased by one-half. The initial rate has also decreased by one-half. Therefore, the initial rate is directly proportional to the concentration of H<sub>2</sub>. That is, the reaction is first order in H<sub>2</sub>.

Comparing Experiment 1 and Experiment 3, the concentration of H<sub>2</sub> is constant and the concentration of NO has decreased by one-half. The initial rate has decreased by one-fourth. Therefore, the initial rate is proportional to the squared concentration of NO. That is, the reaction is second order in NO.

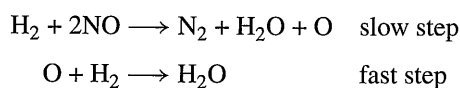
Therefore, the rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

(b) Using Experiment 1 to calculate the rate constant,

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{2.4 \times 10^{-6} \text{ M s}^{-1}}{(0.025 \text{ M})^2 (0.010 \text{ M})} = 0.38 \text{ M}^{-2} \text{ s}^{-1}$$

(c) The rate law suggests that the slow step in the reaction mechanism will probably involve one H<sub>2</sub> molecule and two NO molecules. Additionally, the hint suggests that the O atom is an intermediate. A plausible mechanism is



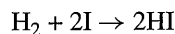
(d) At very high hydrogen concentrations,  $k_2 [\text{H}_2] \gg 1$ . Therefore, the rate law becomes

$$\text{rate} = \frac{k_1[\text{NO}]^2[\text{H}_2]}{k_2[\text{H}_2]} = \frac{k_1}{k_2}[\text{NO}]^2$$

At very low hydrogen concentrations,  $k_2 [\text{H}_2] \ll 1$ . Therefore, the rate law becomes

$$\text{rate} = k_1[\text{NO}]^2[\text{H}_2]$$

9.24 The gas-phase reaction between  $\text{H}_2$  and  $\text{I}_2$  to form HI involves a two-step mechanism:



The rate of formation of HI increases with the intensity of visible light. (a) Explain why this fact supports the two-step mechanism given. (*Hint*: The color of  $\text{I}_2$  vapor is purple.) (b) Explain why the visible light has no effect on the formation of H atoms.

(a) In this two-step mechanism, the rate determining step is the second one where a hydrogen molecule collides with two iodine atoms. The absorption of visible light by the colored molecular iodine vapor weakens the  $\text{I}_2$  bond and increases the number of I atoms present, which in turn increases the reaction rate.

(b) Hydrogen gas is colorless and does not absorb visible light. Ultraviolet light is required to photodissociate  $\text{H}_2$  molecules.

9.26 Use Equation 9.23 to calculate the rate constant at 300 K for  $E_a = 0, 2,$  and  $50 \text{ kJ mol}^{-1}$ . Assume that  $A = 10^{11} \text{ s}^{-1}$  in each case.

For  $E_a = 0 \text{ kJ mol}^{-1}$ ,

$$k = (10^{11} \text{ s}^{-1}) e^{-(0 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 10^{11} \text{ s}^{-1}$$

For  $E_a = 2 \text{ kJ mol}^{-1}$ ,

$$k = (10^{11} \text{ s}^{-1}) e^{-(2 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 4.5 \times 10^{10} \text{ s}^{-1}$$

For  $E_a = 50 \text{ kJ mol}^{-1}$ ,

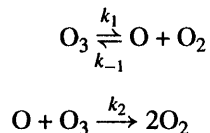
$$k = (10^{11} \text{ s}^{-1}) e^{-(50 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 2.0 \times 10^2 \text{ s}^{-1}$$

9.28 Over a range of about  $\pm 3^\circ \text{ C}$  from normal body temperature the metabolic rate,  $M_T$ , is given by  $M_T = M_{37} (1.1)^{\Delta T}$ , where  $M_{37}$  is the normal rate and  $\Delta T$  is the change in  $T$ . Discuss this

9.23 The rate law for the decomposition of ozone to molecular oxygen ( $2\text{O}_3 \rightarrow 3\text{O}_2$ ) is

$$\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

The mechanism proposed for this process is



Derive the rate law from these elementary steps. Clearly state the assumptions you use in the derivation. Explain why the rate decreases with increasing  $\text{O}_2$  concentration.

The first step involves forward and reverse reactions that are much faster than the second step. The rates of the reaction in the first step are given by

$$\text{Forward rate} = k_1[\text{O}_3]$$

$$\text{Reverse rate} = k_{-1}[\text{O}][\text{O}_2]$$

Assume that these two processes rapidly reach a state of dynamic equilibrium in which the rates of the forward and reverse reactions are equal:

$$k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2]$$

Solving for  $[\text{O}]$ ,

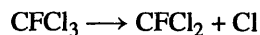
$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

The rate for the second step gives the rate of reaction,

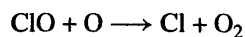
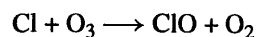
$$\text{Rate} = k_2[\text{O}][\text{O}_3] = k_2 \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} [\text{O}_3] = \frac{k_1 k_2}{k_{-1}} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

The rate law shows that higher concentrations of  $\text{O}_2$  will decrease the reaction rate. This is due to the reverse reaction in the first step of the mechanism. If more  $\text{O}_2$  molecules are present, they will serve to scavenge free O atoms and thus slow the disappearance of  $\text{O}_3$ .

9.25 In recent years, ozone in the stratosphere has been depleted at an alarmingly fast rate by chlorofluorocarbons (CFCs). A CFC molecule such as  $\text{CFCl}_3$  is first decomposed by UV radiation:



The chlorine radical then reacts with ozone as follows:



(a) Write the overall reaction for the last two steps. (b) What are the roles of Cl and ClO? (c) Why is the fluorine radical not important in this mechanism? (d) One suggestion for reducing the concentration of chlorine radicals is to add hydrocarbons such as ethane ( $\text{C}_2\text{H}_6$ ) to the

equation in terms of a possible molecular interpretation. [Source: "Eco-Chem," J. A. Campbell, *J. Chem. Educ.* **52**, 327 (1975).]

Converting to kelvin, and using the Arrhenius equation,

$$\ln \frac{M_T}{M_{37}} = -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{310 \text{ K}} \right)$$

Since the temperature range is so small,  $f(T) = \frac{1}{T} - \frac{1}{310 \text{ K}}$  may be expanded in a Taylor series about  $T_0 = 310 \text{ K}$ . Keeping only the first non-zero term results in  $f(T) \approx -\frac{\Delta T}{T_0^2}$ , where  $\Delta T = 310 \text{ K} - T$ . Thus,

$$\ln \frac{M_T}{M_{37}} = \frac{E_a \Delta T}{R T_0^2}$$

or

$$M_T = M_{37} e^{\frac{E_a \Delta T}{R T_0^2}} = M_{37} \left( e^{\frac{E_a}{R T_0^2}} \right)^{\Delta T} = M_{37} (\text{constant})^{\Delta T}$$

which is of the observed form, providing an implicit factor of  $1 \text{ K}^{-1}$  is incorporated into the argument of the exponential function and the  $\Delta T$  is interpreted as a unitless number. Specifically, it must be true that

$$e^{\frac{E_a}{R T_0^2}} = 1.1$$

$$\frac{E_a}{R T_0^2} = \ln 1.1 = 0.0953$$

$$E_a = (1 \text{ K}^{-1}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K})^2 (0.0953) = 7.6 \times 10^4 \text{ J mol}^{-1}$$

This activation energy is consistent with a single rate determining step controlling the metabolic rate within this temperature range.

**9.30** The rate constants for the first-order decomposition of an organic compound in solution are measured at several temperatures:

|                    |                       |        |        |       |      |
|--------------------|-----------------------|--------|--------|-------|------|
| $k/\text{s}^{-1}$  | $4.92 \times 10^{-3}$ | 0.0216 | 0.0950 | 0.326 | 1.15 |
| $t/^\circ\text{C}$ | 5.0                   | 15     | 25     | 35    | 45   |

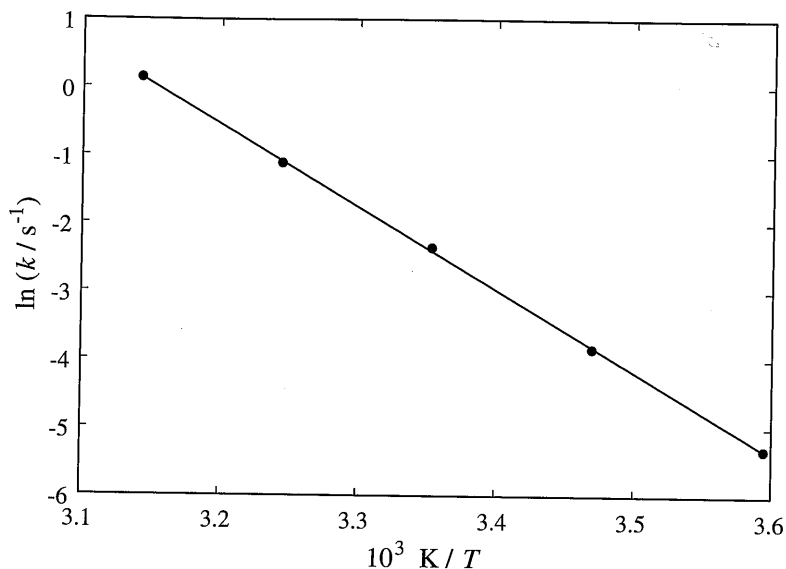
Determine graphically the pre-exponential factor and the energy of activation for the reaction.

Since

$$\ln k = \ln A - \frac{E_a}{RT}$$

A plot of  $\ln k$  vs  $1/T$  gives a slope of  $-E_a/R$  and an intercept of  $\ln A$ . The following data are used for the plot:

|                        |        |        |        |        |       |
|------------------------|--------|--------|--------|--------|-------|
| $10^3 \text{ K}/T$     | 3.595  | 3.470  | 3.353  | 3.245  | 3.143 |
| $\ln(k/\text{s}^{-1})$ | -5.314 | -3.835 | -2.354 | -1.121 | 0.140 |



The equation for the line that best fits these points is  $y = -1.207 \times 10^4 x + 38.06$ . Therefore,

$$E_a = - \left( -1.207 \times 10^4 \text{ K}^{-1} \right) \left( 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) = 1.00 \times 10^5 \text{ J mol}^{-1}$$

$$A = e^{38.06} = 3.38 \times 10^{16} \text{ s}^{-1}$$

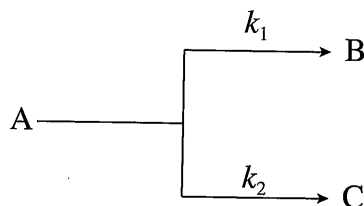
- 9.32 The rate constant of a first-order reaction is  $4.60 \times 10^{-4} \text{ s}^{-1}$  at  $350^\circ \text{C}$ . If the activation energy is  $104 \text{ kJ mol}^{-1}$ , calculate the temperature at which its rate constant is  $8.80 \times 10^{-4} \text{ s}^{-1}$ .

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{8.80 \times 10^{-4}}{4.60 \times 10^{-4}} = -\frac{104 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{T_2} - \frac{1}{623.2 \text{ K}} \right)$$

$$T_2 = 644.0 \text{ K} = 371^\circ \text{C}$$

- 9.34 Consider the following parallel reactions



The activation energies are  $45.3 \text{ kJ mol}^{-1}$  for  $k_1$  and  $69.8 \text{ kJ mol}^{-1}$  for  $k_2$ . If the rate constants are equal at  $320 \text{ K}$ , at what temperature will  $k_1/k_2 = 2.00$ ?

The ratio of the rate constants is

$$\begin{aligned}\frac{k_1}{k_2} &= \frac{A_1 e^{-E_{a1}/RT}}{A_2 e^{-E_{a2}/RT}} \\ &= \frac{A_1}{A_2} e^{(E_{a2}-E_{a1})/RT} = \frac{A_1}{A_2} e^{(69.8 \times 10^3 \text{ J mol}^{-1} - 45.3 \times 10^3 \text{ J mol}^{-1}) / [(8.314 \text{ J K}^{-1} \text{ mol}^{-1})T]} \\ &= \frac{A_1}{A_2} e^{2.947 \times 10^3 \text{ K}/T}\end{aligned}$$

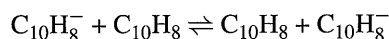
First use data at 320 K to calculate  $A_1/A_2$ :

$$\begin{aligned}\frac{k_1}{k_2} = 1.00 &= \frac{A_1}{A_2} e^{2.947 \times 10^3 \text{ K}/320 \text{ K}} \\ \frac{A_1}{A_2} &= 1.001 \times 10^{-4}\end{aligned}$$

When  $k_1/k_2 = 2.00$ ,

$$\begin{aligned}2.00 &= \frac{A_1}{A_2} e^{2.947 \times 10^3 \text{ K}/T} = (1.001 \times 10^{-4}) e^{2.947 \times 10^3 \text{ K}/T} \\ \frac{1}{T} &= \frac{1}{2.947 \times 10^3 \text{ K}} \ln \frac{2.00}{1.001 \times 10^{-4}} = 3.360 \times 10^{-3} \text{ K}^{-1} \\ T &= 298 \text{ K}\end{aligned}$$

**9.36** The rate of the electron-exchange reaction between naphthalene ( $\text{C}_{10}\text{H}_8$ ) and its anion radical ( $\text{C}_{10}\text{H}_8^-$ ) is diffusion-controlled:



The reaction is bimolecular and second order. The rate constants are

|  |      |      |      |      |
|--|------|------|------|------|
| $T/\text{K}$                                     | 307  | 299  | 289  | 273  |
| $k/10^9 \cdot \text{M}^{-1} \cdot \text{s}^{-1}$ | 2.71 | 2.40 | 1.96 | 1.43 |

Calculate the values of  $E_a$ ,  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$  and  $\Delta G^{\ddagger}$  at 307 K for the reaction. [Hint: Rearrange Equation 9.41 and plot  $\ln(k/T)$  versus  $1/T$ .]

Equation 9.41 gives

$$k = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

or

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

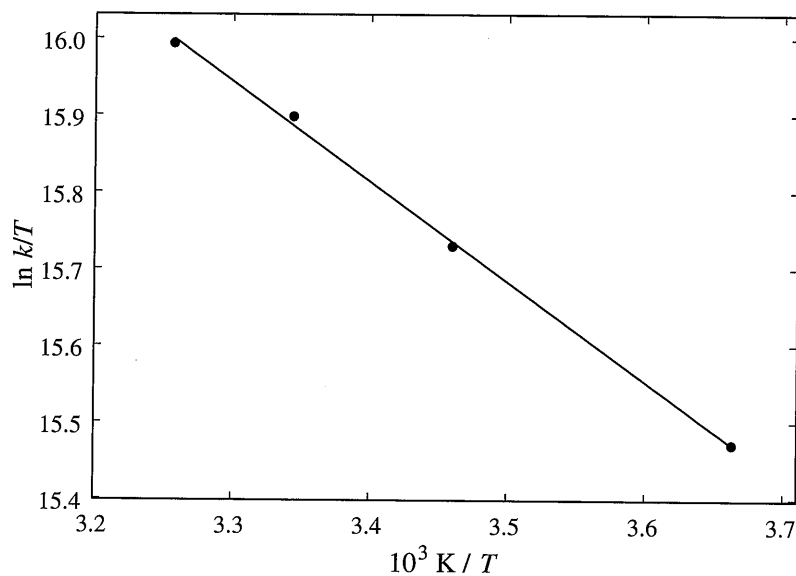
A plot of  $\ln k/T$  vs  $1/T$  gives a slope of  $-\Delta H^{\ddagger}/R$  and an intercept of  $\ln k_B/h + \Delta S^{\ddagger}/R$ . The data used for the plot are

|                    |         |         |         |         |
|--------------------|---------|---------|---------|---------|
| $10^3 \text{ K}/T$ | 3.257   | 3.344   | 3.460   | 3.663   |
| $\ln \frac{k}{T}$  | 15.9934 | 15.8983 | 15.7298 | 15.4715 |

The best fit line has a formula of  $y = -1302.0x + 20.24$ . Therefore,

$$\begin{aligned}\Delta H^{\ddagger} &= -(-1302.0 \text{ K}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 1.082 \times 10^4 \text{ J mol}^{-1} \\ &= 1.08 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

and



$$\begin{aligned}\Delta S^{\ddagger} &= R \left( 20.24 - \ln \frac{k_{\text{B}}}{h} \right) \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left( 20.24 - \ln \frac{1.381 \times 10^{-23}}{6.626 \times 10^{-34}} \right) \\ &= -29.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

From Equation 9.43 and the discussion following it, the activation energy for this reaction, which occurs in solution (condensed phase), is

$$\begin{aligned}E_{\text{a}} &= \Delta H^{\ddagger} + RT \\ &= 1.082 \times 10^4 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (307 \text{ K}) \\ &= 1.34 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

From  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ ,  $\Delta G^{\ddagger}$  at 307 K is calculated.

$$\begin{aligned}\Delta G^{\ddagger} &= \Delta H^{\ddagger} - T \Delta S^{\ddagger} \\ &= 1.082 \times 10^4 \text{ J mol}^{-1} - (307 \text{ K}) (-29.3 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 1.98 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

- 9.38** A person may die after drinking  $D_2O$  instead of  $H_2O$  for a prolonged period (on the order of days). Explain. Because  $D_2O$  has practically the same properties as  $H_2O$ , how would you test the presence of large quantities of the former in a victim's body?

---

Because of the lower zero-point energy for bonds in which D is substituted for H, there is a higher activation energy required for reactions in which this bond breaks. Thus, the rate of  $H^+$  ion exchange is faster than that for the  $D^+$  ion. Additionally, the dissociation constants of deuterated acids are smaller than the corresponding acid with the normal  $H^+$  ion. These differences will affect the delicate acid-base balance in the body as well as the kinetics of biological processes, and could lead to death. A mass spectrum of a body fluid sample should reveal the presence of a larger than natural abundance of the heavier isotope of hydrogen.

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- 9.40** Lubricating oils for watches or other mechanical objects are made of long-chain hydrocarbons. Over long-periods of time they undergo auto-oxidation to form solid polymers. The initial step in this process involves hydrogen abstraction. Suggest a chemical means for prolonging the life of these oils.

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Deuterating the oils, that is, replacing the H atoms with D atoms, will slow down the rate of hydrogen abstraction.

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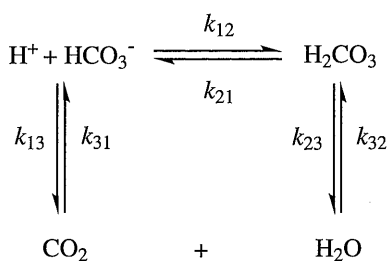
- 9.42** The term *reversible* is used in both thermodynamics (see Chapter 3) and in this chapter. Does it convey the same meaning in these two instances?

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The term has a different meaning in kinetics than it does in thermodynamics. In kinetics, a reversible reaction is one in which both the forward and the backward reaction occur. In thermodynamics, a reversible process is one that is in equilibrium at every point along the path connecting the initial and final states.

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- 9.44** The equilibrium between dissolved  $CO_2$  and carbonic acid can be represented by



Show that

$$-\frac{d[CO_2]}{dt} = (k_{31} + k_{32}) [CO_2] - \left( k_{13} + \frac{k_{23}}{K} \right) [H^+] [HCO_3^-]$$

where  $K = [H^+] [HCO_3^-] / [H_2CO_3]$ .

---



From the equilibrium,

$$\frac{d[\text{CO}_2]}{dt} = k_{13}[\text{H}^+][\text{HCO}_3^-] - k_{31}[\text{CO}_2] + k_{23}[\text{H}_2\text{CO}_3] - k_{32}[\text{CO}_2]$$

Since  $\text{H}_2\text{O}$  is present in a great quantity, the effectively constant concentration,  $[\text{H}_2\text{O}]$ , is incorporated into the constants  $k_{31}$  and  $k_{32}$ . Rearranging the expression gives

$$\frac{d[\text{CO}_2]}{dt} = -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23}[\text{H}_2\text{CO}_3] \quad (9.44.1)$$

Since  $\text{H}^+$  and  $\text{HCO}_3^-$  are in equilibrium with  $\text{H}_2\text{CO}_3$ , let

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K} \quad (9.44.2)$$

Substitute Eq. 9.44.2 into Eq. 9.44.1,

$$\begin{aligned} \frac{d[\text{CO}_2]}{dt} &= -(k_{31} + k_{32})[\text{CO}_2] + k_{13}[\text{H}^+][\text{HCO}_3^-] + k_{23} \frac{[\text{H}^+][\text{HCO}_3^-]}{K} \\ &= -(k_{31} + k_{32})[\text{CO}_2] + \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-] \\ -\frac{d[\text{CO}_2]}{dt} &= (k_{31} + k_{32})[\text{CO}_2] - \left(k_{13} + \frac{k_{23}}{K}\right)[\text{H}^+][\text{HCO}_3^-] \end{aligned}$$

- 9.46** In a certain industrial process involving a heterogeneous catalyst, the volume of the catalyst (in the shape of a sphere) is  $10.0 \text{ cm}^3$ . (a) Calculate the surface area of the catalyst. (b) If the sphere is broken down into eight spheres, each of which has a volume of  $1.25 \text{ cm}^3$ , what is the total surface area of the spheres? (c) Which of the two geometric configurations is the more effective catalyst? (*Hint*: The surface area of a sphere is  $4\pi r^2$ , where  $r$  is the radius of the sphere.)

**(a) One  $10.0 \text{ cm}^3$  sphere**

First calculate the radius of the sphere.

$$V = 10.0 \text{ cm}^3 = \frac{4}{3}\pi r^3$$

$$r = 1.337 \text{ cm}$$

The surface area is

$$A = 4\pi r^2 = 4\pi (1.337 \text{ cm})^2 = 22.5 \text{ cm}^2$$

**(b) Eight  $1.25 \text{ cm}^3$  spheres**

First calculate the radius of one sphere.