

1. **【Exercise 2.7 (b)】**

A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 L to 31.7 L

(a) reversibly;

(b) against a constant external pressure equal to the final pressure of the gas;

(c) freely (against zero external pressure).

For the three processes calculate  $Q$ ,  $W$ ,  $\Delta U$ , and  $\Delta H$ .

2. **【2.8 (b)】**

A sample consisting of 2.00 mol of perfect gas molecules, for which  $C_{v,m} = 2.5R$ , initially at = 111 kPa and  $T_1 = 277$  K, is heated reversibly to 356 K at constant volume. Calculate the final pressure,  $\Delta U$ ,  $Q$ , and  $W$ .

3. **【2.9 (b)】**

A sample of argon of mass 6.56 g occupies 18.5 L at 305 K.

(a) Calculate the work done when the gas expands isothermally against a constant external pressure of 7.7 kPa until its volume has increased by 2.5 L.

(b) Calculate the work that would be done if the same expansion occurred reversibly.

4. **【2.10(b)】**

In the isothermal reversible compression of 1.77 mmol of a perfect gas at 273 K, the volume of the gas is reduced to 0.224 of its initial value. Calculate  $W$  for this process.

5. **【2.11 (b)】**

A sample of 2.00 mol  $\text{CH}_3\text{OH}(\text{g})$  is condensed isothermally and reversibly to liquid at  $64^\circ\text{C}$ . The standard enthalpy of vaporization of methanol at  $64^\circ\text{C}$  is  $35.3 \text{ kJ mol}^{-1}$ . Find  $W$ ,  $Q$ ,  $\Delta U$ , and  $\Delta H$  for this process.

6. **【2.12(b)】**

A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature  $23^\circ\text{C}$ .

7. 【2.14 (b)】

The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression  $C_p/(\text{J K}^{-1}) = 20.17 + 0.4001(T/\text{K})$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  when the temperature is raised from  $0^\circ\text{C}$  to  $100^\circ\text{C}$  (a) at constant pressure, (b) at constant volume.

8. 【2.17 (b)】

Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 mL to a final volume of 3.0 L. Take  $\gamma = 1.3$ .

9. 【2.23 (b)】

A sample of 5.0 mol  $\text{CO}_2$  is originally confined in 15 L at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate  $Q$ ,  $W$ ,  $\Delta T$ ,  $\Delta U$ , and  $\Delta H$ . (The final pressure of the gas is not necessarily 78.5 kPa.)

10. **【2.25 (b)】**

A sample consisting of 1.5 mol of perfect gas molecules with  $C_{p,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$  is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

11. **【2.27 (b)】**

Consider a system consisting of 3.0 mol  $\text{O}_2$  (assumed to be a perfect gas) at 25°C confined to a cylinder of cross-section  $22 \text{ cm}^2$  at 820 kPa. The gas is allowed to expand adiabatically and irreversibly against a constant pressure of 110 kPa. Calculate  $W$ ,  $Q$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta T$  when the piston has moved 15 cm.

12. **【2.28 (b)】**

A sample consisting of 15.0 g of nitrogen is confined in a container at 220 kPa and 200 K and then allowed to expand adiabatically (a) reversibly to 110 kPa, (b) against a constant pressure of 110 kPa. Calculate the final temperature in each case.

13. 【3.8(b)】

Express  $\left(\frac{\partial C_p}{\partial p}\right)_T$  as a second-derivative of  $H$  and find its relation to  $\left(\frac{\partial H}{\partial p}\right)_T$ . From this relation show that  $\left(\frac{\partial C_p}{\partial p}\right)_T = 0$  for a perfect gas.

14. 【3.9(b)】

Confirm that  $\left(\frac{\partial H}{\partial U}\right)_p = 1 + p\left(\frac{\partial V}{\partial U}\right)_p$  by expressing  $\left(\frac{\partial H}{\partial U}\right)_p$  as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

15. 【3.10(b)】

Write an expression for  $dp$  given that  $p$  is a function of  $V$  and  $T$ . Deduce an expression for  $d \ln p$  in terms of the expansion coefficient and the isothermal compressibility.

16. 【4.5(b)】

Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is  $154.84 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at 298 K.

17. 【4.9(b)】

Calculate the increase in entropy when 3.50 mol of a monatomic perfect gas with  $C_{p,m} = \frac{5}{2}R$  is heated from 250 K to 700 K and simultaneously expanded from 20.0 L to 60.0 L.

18. 【4.10(b)】

A system undergoes a process in which the entropy change is  $+5.51 \text{ J}\cdot\text{K}^{-1}$ . During the process, 1.50 kJ of heat is added to the system at 350 K. Is the process thermodynamically reversible? Explain your reasoning.

19. **【4.11(b)】**

A sample of copper of mass 2.75 kg is cooled at constant pressure from 330 K to 275 K. Calculate (a) the energy that must be removed as heat and (b) the change in entropy of the sample.

20. **【4.12(b)】**

A sample of nitrogen gas of mass 35g at 230 K and 21.1 atm expands isothermally until its pressure is 4.3 atm. Calculate the change in entropy of the gas.

21. **【4.13(b)】**

A sample of perfect gas that initially occupies 11.0 L at 270 K and 1.20 atm is compressed isothermally. To what volume must the gas be compressed to reduce its entropy by  $3.0 \text{ J}\cdot\text{K}^{-1}$  ?

22. 【4.14(b)】

Calculate the change in entropy when 25 g of ethanol at 50°C is poured into 70 g of ethanol at 10°C in an insulated vessel, given that  $C_{p,m} = 111.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

23. 【4.15(b)】

Calculate  $\Delta H$  and  $\Delta S_{\text{total}}$  when two iron blocks, each of mass 1.00 kg, one at 200°C and the other at 25°C, are placed in contact in an isolated container. The specific heat capacity of iron is  $0.449 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$  and may be assumed constant over the temperature range involved.

24. 【4.16(b)】

Consider a system consisting of 1.5 mol  $\text{CO}_2(\text{g})$ , initially at 15°C and 9.0 atm and confined to a cylinder of cross-section  $100.0 \text{ cm}^2$ . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with  $C_{v,m} = 28.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , and calculate

(a)  $Q$  ; (b)  $W$  ; (c)  $\Delta U$  ; (d)  $\Delta T$  ; (e)  $\Delta S$ .



25. 【4.23(b)】

Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 L to 4.60 L in

- (a) an isothermal reversible expansion
- (b) an isothermal irreversible expansion against  $p_{\text{ex}} = 0$
- (c) an adiabatic reversible expansion.

26. 【4.24(b)】

Calculate the change in entropy when a diatomic perfect gas is compressed to one-third its volume and simultaneously heated to three times its initial temperature.

27. 【4.25(b)】

Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

28. 【5.5(b)】

Suppose that 2.5 mmol Ar(g) occupies 72 L at 298 K and expands to 100 L. Calculate  $\Delta G$  for the process.

29. 【5.6(b)】

The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression  $\Delta G/\text{J} = -73.1 + 42.8(\text{T/K})$ . Calculate the value of  $\Delta S$  for the process.

30. 【5.7(b)】

Calculate the change in Gibbs energy of 25 g of methanol (mass density  $0.791 \text{ g cm}^{-3}$ ) when the pressure is increased isothermally from 100 kPa to 100 MPa.

31. **【5.8(b)】**

When 3.00 mol of a gas at 230 K and 150 kPa is subjected to isothermal compression, its entropy decreases by 15.0 J/K. Calculate

- (a) the final pressure of the gas
- (b)  $\Delta G$  for the compression.

32. **【5.9(b)】**

Calculate the change in molar Gibbs energy of a perfect gas when its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50°C.

33. **【5.13(b)】**

Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

34. 【7.5(b)】

At 20°C, the density of a 20 per cent by mass ethanol–water solution is 968.7 kg/m<sup>3</sup>. Given that the partial molar volume of ethanol in the solution is 52.2 cm<sup>3</sup>/mol, calculate the partial molar volume of the water.

35. 【7.8(b)】

Calculate the cryoscopic and ebullioscopic constants of naphthalene.

36. 【7.9(b)】

The vapour pressure of 2–propanol is 50.00 kPa at 338.8°C, but it fell to 49.62 kPa when 8.69 g of an involatile organic compound was dissolved in 250g of 2–propanol. Calculate the molar mass of the compound.

37. **【7.15 (b)】**

The mole fractions of  $\text{N}_2$  and  $\text{O}_2$  in air at sea level are approximately 0.78 and 0.21. Calculate the molalities of the solution formed in an open flask of water at  $25^\circ\text{C}$ .

38. **【7.17 (b)】**

Calculate the freezing point of a glass of water of volume  $200\text{ cm}^3$  in which 10 g of glucose has been dissolved.

39. **【7.18 (b)】**

Predict the ideal solubility of lead in bismuth at  $280^\circ\text{C}$  given that its melting point is  $327^\circ\text{C}$  and its enthalpy of fusion is  $5.2\text{ kJ}\cdot\text{mol}^{-1}$ .

40. 【6.4 (b)】

The vapour pressure of a substance at  $20.0^{\circ}\text{C}$  is  $58.0\text{ kPa}$  and its enthalpy of vaporization is  $32.7\text{ kJ mol}^{-1}$ . Estimate the temperature at which its vapour pressure is  $66.0\text{ kPa}$ .

41. 【6.8 (b)】

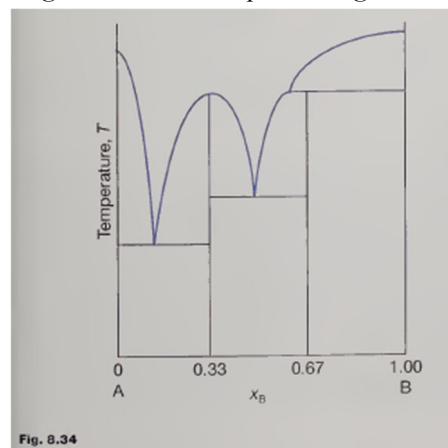
When a certain liquid freezes at  $-3.65^{\circ}\text{C}$  its density changes from  $0.789\text{ g}\cdot\text{cm}^{-3}$  to  $0.801\text{ g}\cdot\text{cm}^{-3}$ . Its enthalpy of fusion is  $8.68\text{ kJ mol}^{-1}$ . Estimate the freezing point of the liquid at  $100\text{ MPa}$ .

42. 【6.12(b)】

Calculate the melting point of ice under a pressure of  $10\text{ MPa}$ . Assume that the density of ice under these conditions is approximately  $0.915\text{ g cm}^{-3}$  and that of liquid water is  $0.998\text{ g cm}^{-3}$ .

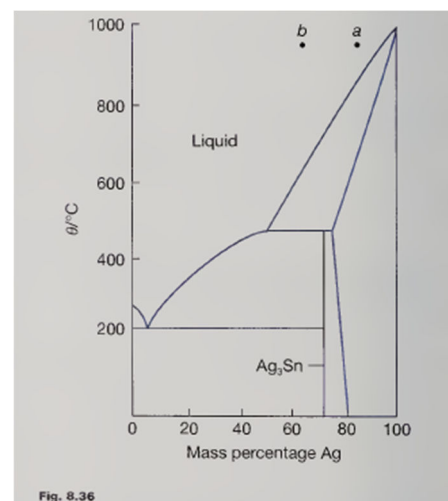
43. 【8.3 (b)】

Label the regions of the phase diagram in Fig. 8.34. State what substances (if compounds, give their formulas) exist in each region. Label each substance in each region as solid, liquid, or gas.



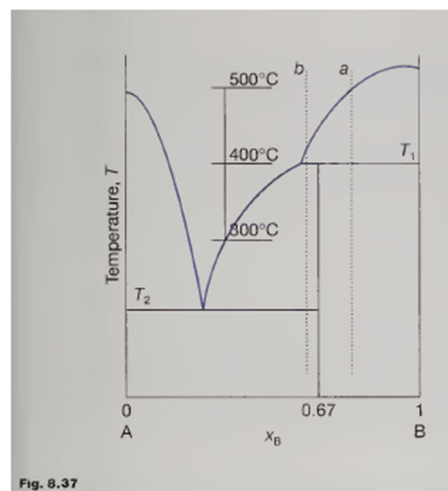
44. 【8.13 (b)】

Figure 8.36 is the phase diagram for silver and tin. Label the regions, and describe what will be observed when liquids of compositions a and b are cooled to 200 K.



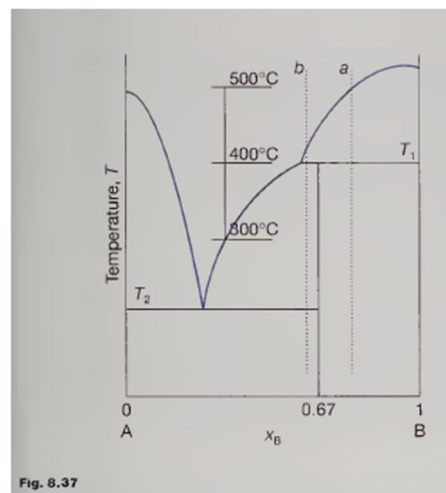
45. 【8.14 (a)】

Indicate on the phase diagram in Fig. 8.37 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?



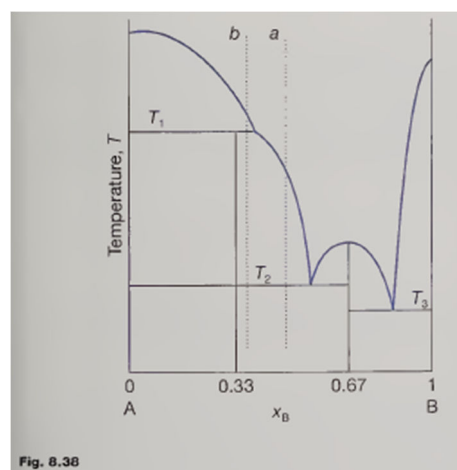
46. 【8.14 (b)】

Indicate on the phase diagram in Fig. 8.38 the feature that denotes incongruent melting. What is the composition of the eutectic mixture and at what temperature does it melt?



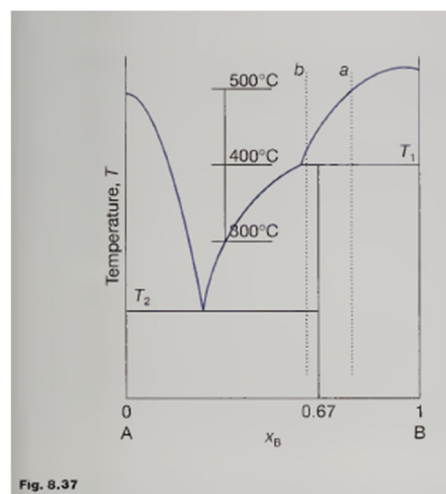
47. 【8.15 (b)】

Sketch the cooling curves for the isopleths a and b in Fig. 8.38.



48. 【8.16 (b)】

Use the phase diagram in Fig. 8.37 to state (a) the solubility of B in A at 500°C, (b) the solubility of AB<sub>2</sub> in A at 390°C, (c) the solubility of AB<sub>2</sub> in B at 300°C.





49. 【10.7(b)】

Relate the ionic strengths of (a)  $\text{MgCl}_2$ , (b)  $\text{Al}_2(\text{SO}_4)_3$ , and (c)  $\text{Fe}_2(\text{SO}_4)_3$  solutions to their molalities, b.

50. 【10.9(b)】

Calculate the masses of (a)  $\text{KNO}_3$  and, separately, (b)  $\text{Ba}(\text{NO}_3)_2$  to add to a  $0.110 \text{ mol kg}^{-1}$  solution of  $\text{KNO}_3(\text{aq})$  containing 500 g of solvent to raise its ionic strength to 1.00.

51. 【10.10(b)】

What molality of  $\text{Al}_2(\text{SO}_4)_3$  has the same ionic strength as  $0.500 \text{ mol kg}^{-1} \text{ Ca}(\text{NO}_3)_2(\text{aq})$ ?

52. 【10.12 (b)】

Estimate the mean ionic activity coefficient and activity of a solution that is  $0.020 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaCl(aq)}$  and  $0.035 \text{ mol} \cdot \text{kg}^{-1}$   $\text{Ca(NO}_3)_2\text{(aq)}$ .

53. 【10.13 (a)】

The mean activity coefficient in a  $0.500 \text{ mol} \cdot \text{kg}^{-1}$   $\text{LaCl}_3\text{(aq)}$  solution is 0.303 at  $25^\circ\text{C}$ . What is the percentage error in the value predicted by the Debye–Huckel limiting law?

54. 【10.15 (b)】

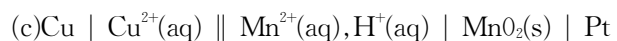
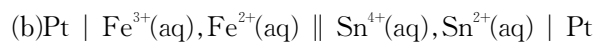
For  $\text{PbI}_2$ ,  $K_s = 1.4 \times 10^{-8}$  at  $25^\circ\text{C}$  and the standard Gibbs energy of formation of  $\text{PbI}_2\text{(s)}$  is  $-173.64 \text{ kJ mol}^{-1}$ . Calculate the standard Gibbs energy of formation of  $\text{PbI}_2\text{(aq)}$ .

55. 【10.17 (b)】

Devise a cell in which the cell reaction is  $\text{Cd(s)} + \text{Ni(OH)}_3\text{(s)} \rightarrow \text{Cd(OH)}_2\text{(s)} + \text{Ni(OH)}_2\text{(s)}$ . Give the half-reactions for the electrodes.

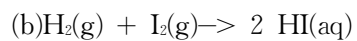
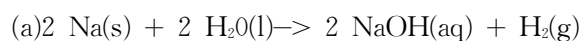
56. 【10.18 (b)】

Write the cell reactions and electrode half-reactions for the following cells:



57. 【10.19 (b)】

Devise cells in which the following are the reactions:

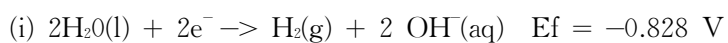


58. 【10.21 (b)】

Use standard potentials to calculate the standard emfs of the cells in Exercise 10.19b.

59. 【10.23 (b)】

Two half-cell reactions may be combined in such a way as to form (a) a new half-cell reaction or (b) a complete cell reaction. Illustrate both (a) and (b) by using the half-cell reactions listed below and calculate  $E^\ominus$  for both the new half-cell and complete cell reaction.



60. 【10.25 (b)】

Use the information in Tables 10.7 to calculate the standard emf of the cell  $\text{Ag} \mid \text{AgNO}_3(\text{aq}) \parallel \text{Fe}(\text{NO}_3)_2(\text{aq}) \mid \text{Fe}$  and the standard Gibbs energy and enthalpy of the cell reaction at  $25^\circ\text{C}$ . Estimate the value of  $\Delta_r G_m^\ominus$  at  $35^\circ\text{C}$ .

61. 【10.27 (b)】

Determine the standard emf of a cell in which the reaction is  $\text{Co}^{3+}(\text{aq}) + 3 \text{Cl}^{-}(\text{aq}) + 3 \text{Ag}(\text{s}) \rightarrow 3 \text{AgCl}(\text{s}) + \text{Co}(\text{s})$  from the standard potentials of the couples  $\text{Ag}/\text{AgCl}, \text{Cl}^{-}$  (+0.22 V),  $\text{Co}^{3+}/\text{Co}^{2+}$  (+1.81 V), and  $\text{Co}^{2+}/\text{Co}$  (−0.28 V).

62. 【10.29 (b)】

Derive an expression for the potential of an electrode for which the half-reaction is the reduction of  $\text{MnO}_4^{-}$  ions to  $\text{Mn}^{2+}$  ions in acidic solution.

63. 【10.32 (b)】

The emf of the cell  $\text{Bi} \mid \text{Bi}_2\text{S}_3(\text{s}) \mid \text{Bi}_2\text{S}_3(\text{aq}) \mid \text{Bi}$  is +0.96 V at 25°C. Calculate (a) the solubility of  $\text{Bi}_2\text{S}_3$  and (b) its solubility constant.

64. 【25.6 (b)】

The rate of consumption of B in the reaction  $A + 3 B \rightarrow C + 2 D$  is  $1.0 \text{ mol L}^{-1} \text{ s}^{-1}$ . State the reaction rate, and the rates of formation or consumption of A, C, and D.

65. 【25.8 (b)】

The rate law for the reaction in Exercise 25.6(b) was reported as  $d[C]/dt = k[A][B][C]^{-1}$ . Express the rate law in terms of the reaction rate; what are the units for k in each case?

66. 【25.9 (b)】

At 400 K, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa, was  $9.71 \text{ Pa} \cdot \text{s}^{-1}$  when 10.0 percent had reacted and  $7.67 \text{ Pa} \cdot \text{s}^{-1}$  when 20.0 percent had reacted. Determine the order of the reaction.

67. 【25.10 (b)】

At 400 K, the half-life for the decomposition of a sample of a gaseous compound initially at 55.5 kPa was 340 s. When the pressure was 28.9 kPa, the half-life was 178 s. Determine the order of the reaction.

68. 【25.11 (b)】

The rate constant for the first-order decomposition of a compound A in the reaction  $2 A \rightarrow P$  is  $k = 2.78 \times 10^{-7} \text{ s}^{-1}$  at 25°C. What is the half-life of A? What will be the pressure, initially 32.1 kPa, (a) 10 s, (b) 10 min after initiation of the reaction?

69. 【25.12 (b)】

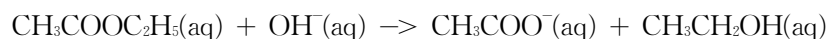
A second-order reaction of the type  $A + 2 B \rightarrow P$  was carried out in a solution that was initially  $0.075 \text{ mol L}^{-1}$  in A and  $0.030 \text{ mol L}^{-1}$  in B. After 1.0 h the concentration of A had fallen to  $0.045 \text{ mol L}^{-1}$ . (a) Calculate the rate constant, (b) What is the half-life of the reactants ?

70. 【25.13 (b)】

If the rate laws are expressed with (a) concentrations in molecules per metre cubed, (b) pressures in newtons per metre squared, what are the units of the second-order and third-order rate constants?

71. 【25.14 (a)】

The second-order rate constant for the reaction



is  $0.11 \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the concentration of ester after (a) 10 s, (b) 10 min when ethyl acetate is added to sodium hydroxide so that the initial concentrations are  $[\text{NaOH}] = 0.050 \text{ mol L}^{-1}$  and  $[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.100 \text{ mol L}^{-1}$ ?

72. 【25.14 (b)】

The second-order rate constant for the reaction  $\text{A} + 2\text{B} \rightarrow \text{C} + \text{D}$  is  $0.21 \text{ L mol}^{-1} \text{ s}^{-1}$ . What is the concentration of C after (a) 10 s, (b) 10 min when the reactants are mixed with initial concentrations of  $[\text{A}] = 0.025 \text{ mol L}^{-1}$  and  $[\text{B}] = 0.150 \text{ mol L}^{-1}$ ?



73. 【25.15 (b)】

A reaction  $2\text{A} \rightarrow \text{P}$  has a third-order rate law with  $k = 3.50 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ . Calculate the time required for the concentration of A to change from  $0.077 \text{ mol L}^{-1}$  to  $0.021 \text{ mol L}^{-1}$ .

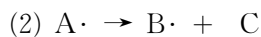
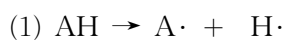
74. 【25.16 (a)】 The rate constant for the decomposition of a certain substance is  $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $30^\circ\text{C}$  and  $1.38 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $50^\circ\text{C}$ . Evaluate the Arrhenius parameters of the reaction.

75. 【25.16 (b)】 The rate constant for the decomposition of a certain substance is  $1.70 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $24^\circ\text{C}$  and  $2.01 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$  at  $37^\circ\text{C}$ . Evaluate the Arrhenius parameters of the reaction.

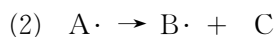
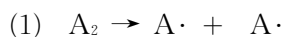
## 76. 【26.1 (a)】

Identify any initiation, propagation, retardation, inhibition, and termination steps in the following chain mechanisms:

(a)

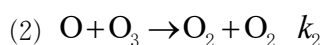
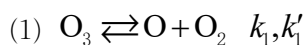


(b)



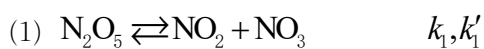
## 77. 【26.5 (a)】

Derive the rate law for the decomposition of ozone in the reaction  $2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g})$  on the basis of the following proposed mechanism:



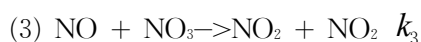
## 78. 【26.5 (b)】

On the basis of the following proposed mechanism, account for the experimental fact that the rate law for the decomposition  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  is  $v = k[\text{N}_2\text{O}_5]$ .



## 79. 【26.6 (a)】

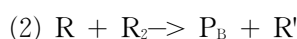
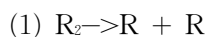
A slightly different mechanism for the decomposition of  $\text{N}_2\text{O}_5$  from that in Exercise 26.5(b) has also been proposed. It differs only in the last step, which is replaced by



Show that this mechanism leads to the same overall rate law.

## 80. 【26.6 (b)】

Consider the following mechanism for the thermal decomposition of  $\text{R}_2$  :

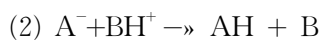
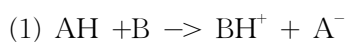


where  $\text{R}_2$ ,  $\text{P}_\text{A}$ ,  $\text{P}_\text{B}$  are stable hydrocarbons and  $\text{R}$  and  $\text{R}'$  are radicals. Find the dependence of the rate of decomposition of  $\text{R}_2$  on the concentration of  $\text{R}_2$ .

## 81. 【26.8 (a)】

The condensation reaction of propanone,  $(\text{CH}_3)_2\text{CO}$ , in aqueous solution is catalysed by bases,  $\text{B}$ , which react reversibly with propanone to form the carbanion  $\text{C}_3\text{H}_5\text{O}^-$ . The carbanion then reacts with a molecule of propanone to give the product.

A simplified version of the mechanism is



where  $\text{AH}$  stands for propanone and  $\text{A}^-$  denotes its carbanion. Use the steady-state approximation to find the concentration of the carbanion and derive the rate equation for the formation of the product.

82. 【26.8 (b)】

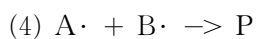
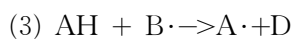
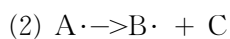
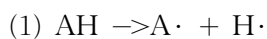
Consider the acid-catalysed reaction



Deduce the rate law and show that it can be made independent of the specific term  $[\text{H}^+]$ ,

83. 【26.9 (a)】

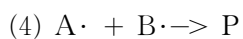
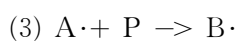
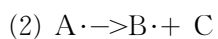
Consider the following chain mechanism:



Use the steady-state approximation to deduce that the decomposition of AH is first-order in AH.

84. 【26.9 (b)】

Consider the following chain mechanism:



Use the steady-state approximation to deduce that the rate law for the consumption of  $\text{A}_2$ .

85. **【6.14 (b)】**

Calculate the vapour pressure of a spherical droplet of water of radius 20.0 nm at 35.0°C. The vapour pressure of bulk water at that temperature is 5.623 kPa and its density is 994.0 kg m<sup>-3</sup>.

86. **【6.15 (b)】**

The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30°C given that at that temperature water climbs to a height of 9.11 cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30°C is 0.9956 g cm<sup>-3</sup>.

87. **【6.16 (b)】**

Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20°C. The surface tension of ethanol at that temperature is 22.39 mN m<sup>-1</sup>.

88. 【28.9 (b)】

The volume of gas at 20°C and 1.00 bar adsorbed on the surface of 1.50 g of a sample of silica at 0°C was 1.60 cm<sup>3</sup> at 52.4 kPa and 2.73 cm<sup>3</sup> at 104 kPa. What is the value of  $V_{\text{mon}}$ ?

89. 【28.12 (b)】

The adsorption of a gas is described by the Langmuir isotherm with  $K = 0.777 \text{ kPa}^{-1}$  at 25°C. Calculate the pressure at which the fractional surface coverage is (a) 0.20, (b) 0.75.

90. 【28.13 (b)】

A certain solid sample adsorbs 0.63 mg of CO when the pressure of the gas is 36.0 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 4.0 kPa and the temperature is 300 K is 0.21 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.