Chapter 9 Exercises

1. What are the signs of ΔH^o and ΔS^o for the evaporation of water?

2. What are the signs of ΔH^o and ΔS^o for cooling liquid water?

3. A system gives off 600 J of heat while 200 J of work are done on it. What are ΔE, ΔE_{sur}, and ΔE_{univ}?

4. A system does 400 J of work and absorbs 150 J of heat. What are ΔE, ΔE_{sur} and ΔE_{univ}?

5. What is the difference between ΔH and ΔE? Why is ΔH used more frequently by chemists than ΔE?

6. What are the standard states of a gas and a solute?

7. When is the entropy change of a reaction expected to be significant?

8. Indicate whether each of the following is true, false, or cannot be determined for a non-extensive reaction at constant pressure and temperature that is proceeding spontaneously to consume gas molecules.
   a) $\Delta G < 0$ b) $\Delta S^o \sim 0$ c) $\Delta G^o < 0$ d) $\Delta E_{univ} = 0$
   e) $\Delta H^o < 0$ f) the extent of reaction increases with T

9. Indicate whether each of the following is true, false, or cannot be determined for an extensive endothermic reaction that is at equilibrium at constant pressure and temperature.
   a) $\Delta G < 0$ b) $\Delta H^o < 0$ c) $\Delta G^o < 0$ d) $\Delta S_{univ} > 0$
   e) $\Delta S^o > 0$ f) the extent of reaction increases with T

10. The enthalpy of combustion of propane gas, $C_3H_8(g)$, is -2,220 kJ/mol.
   a) Write the balanced equation for the combustion reaction.
   b) Propane is often used for gas grills, which usually have a propane tank with 20 pounds of propane. How much heat can be obtained by burning all of the propane in a 20 lb tank? (1 lb = 454 g)
   c) What is the enthalpy change for $6CO_2(g) + 8H_2O(l) \rightarrow 2C_3H_8(g) + 10O_2(g)$?

11. Combustion of 0.150 g of $C_2H_5OH(l)$ (grain alcohol) releases 4.47 kJ of heat.
   a) What is the enthalpy of combustion of $C_2H_5OH(l)$?
   b) Write the chemical equation for the combustion reaction.
   c) What is ΔH^o for $4CO_2(g) + 6H_2O(l) \rightarrow 2C_2H_5OH(l) + 6O_2(g)$?

12. Use the data in Table 9.2 to estimate the enthalpies of the following reactions:
   a) $H_2CBr_2(g) + F_2(g) \rightarrow H_2CF_2(g) + Br_2(g)$
   b) $H_3CI(g) + H_2O(g) \rightarrow H_3COH(g) + HI(g)$
   c) $HC\equiv CH(g) + 2H_2(g) \rightarrow H_3C\text{-}CH_3(g)$
   d) $CH_4(g) \rightarrow C(g) + 2H_2(g)$

13. Use Table 9.2 to estimate the enthalpies of the following reactions:
   a) $H_2C=CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
   b) $4CH_3NH_2(g) + 9O_2(g) \rightarrow 4CO_2(g) + 10H_2O(g) + 2N_2(g)$
   c) $CCl_4(g) + O_2(g) \rightarrow CO_2(g) + 2Cl_2(g)$
   d) $4HC\equiv N(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g) + 2N_2(g)$

14. Indicate $\Delta S^o > 0$, $\Delta S^o \sim 0$, or $\Delta S^o < 0$ for each of the following reactions:
   a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
   b) $HF(aq) + NO_2^{1-}(aq) \rightarrow F^{1-}(aq) + HNO_2(aq)$
   c) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
   d) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

15. Indicate $\Delta S^o > 0$, $\Delta S^o \sim 0$, or $\Delta S^o < 0$ for each of the following reactions:
   a) $H_3CI(aq) + OH^{1-}(aq) \rightarrow H_3COH(aq) + I^{1-}(aq)$
   b) $CCl_4(l) \rightarrow CCl_4(g)$
   c) $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$
   d) $H_2(g) + CO_2(g) \rightarrow H_2O(g) + CO(g)$

16. Indicate the sign of ΔG^o at low and high temperatures for each of the following processes:
   a) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ $\Delta H^o < 0$
   b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta H^o > 0$
   c) $CH_3OH(l) \rightarrow CH_3OH(g)$ $\Delta H^o > 0$
   d) $2Cl_2(g) + 7O_2(g) \rightarrow 2Cl_2O_7(l)$ $\Delta H^o > 0$

17. Indicate the sign of ΔG^o at low and high temperatures for each of the reactions in Exercise 12.

18. Consider the reaction, $2NH_3(g) \rightarrow 3H_2(g) + N_2(g)$.
  a) Use bond energies to estimate the value of ΔH^o at 298 K.
  b) Is $\Delta S^o > 0$, $\Delta S^o \sim 0$, or $\Delta S^o < 0$?
  c) Indicate the sign of ΔG^o at high and at low temperatures.
  d) Write the equilibrium expression for the reaction.

19. Consider the reaction, $2\,HI(g) \rightarrow H_2(g) + I_2(g)$
  a) Use bond energies to estimate the value of ΔH^o at 298 K.
  b) Is $\Delta S^o > 0$, $\Delta S^o \sim 0$, or $\Delta S^o < 0$?
  c) Indicate the sign of ΔG^o at high and at low temperatures.
  d) Write the equilibrium expression for the reaction.

20. Consider the reaction, $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$
  a) Use bond energies to estimate the value of ΔH^o at 298 K.
  b) Is $\Delta S^o > 0$, $\Delta S^o \sim 0$, or $\Delta S^o < 0$?
  c) Indicate the sign of ΔG^o at high and at low temperatures.
  d) Write the equilibrium expression for the reaction.

21. A reaction has a very high activation energy, is very exothermic, and involves almost no entropy change.
  a) Is the equilibrium constant expected to be large or small?
  b) Will the value of the equilibrium constant increase, decrease, or remain unchanged when the temperature is increased?
  c) Will the value of the equilibrium constant increase, decrease, or remain unchanged when more reactant is added?
  d) Will the value of the equilibrium constant increase, decrease or remain unchanged when a catalyst is added?
  e) Is the rate constant of the forward reaction larger or smaller than the rate constant for the reverse reaction?

22. Indicate the effect of each of the following on the equilibrium concentration of iodine: $I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$ $\Delta H^o < 0$

  a) add H_2 **b)** add HI   **c)** remove H_2 **d)** increase the temperature

23. Indicate the effect of each of the following on the equilibrium amount of CO: $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H^o = 41$ kJ/mol
  a) increasing the concentration of H_2
  b) decreasing the concentration of CO_2
  c) increasing the concentration of H_2O
  d) increasing the temperature

24. Explain why the rate of a reaction increases as the concentrations of the reactants increase. What happens to the rate of the reaction when the concentrations of the products increase? Why?

25. Explain why the rate of a reaction increases as the temperature increases.

26. Express the rate law for each of the following *one-step processes*:
  a) $2NO_2 \rightarrow NO_3 + NO$
  b) $O_3 + NO \rightarrow O_2 + NO_2$
  c) $NO_2Cl \rightarrow NO_2 + Cl$

27. Express the rate law for each of the following *one-step processes*:
  a) $CH_3 + I \rightarrow CH_3I$
  b) $2H_2 \rightarrow 4H$
  c) $HO + H \rightarrow H_2O$

28. Write the equilibrium constant expression in terms of the concentrations of the reactants and products for each of the following reactions:
  a) $2HNO_2(aq) + PO_4^{3-}(aq) \rightleftharpoons 2NO_2^{1-}(aq) + H_2PO_4^{1-}(aq)$
  b) $2H_2S(g) + 3O_2(g) \rightleftharpoons 2SO_2(g) + 2H_2O(g)$
  c) $NO(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons NOCl(g)$

29. Write the equilibrium constant expression in terms of the concentrations of the reactants and products for each of the following reactions:
  a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
  b) $H_2SO_3(aq) + 2CN^{1-}(aq) \rightleftharpoons 2HCN(aq) + SO_3^{2-}(aq)$
 **c)** $NH_3(aq) + HF(aq) \rightleftharpoons NH_4^{1+}(aq) + F^{1-}(aq)$

30. A solution is made 0.1 M each in A and B. A and B then react by the following equation: $A + B \rightleftharpoons C + D$. Indicate the *approximate* concentrations of A and C at equilibrium (use ~ 0 M to indicate a very small concentration) when K has the following values:

a) $K = 1 \times 10^8$ **b)** $K = 1$ **c)** $K = 1 \times 10^{-8}$

31. Consider the following equilibrium: $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr$ $K = 2.0$. What is the equilibrium pressure of NOBr if the equilibrium pressures of NO and Br_2 are 1.6 and 3.6 atm, respectively?

32. What is the concentration of IO_3^{1-} ion in an equilibrium solution that is 0.10 M in HIO_3 and 0.00026 M in H^{1+}?

$$HIO_3(aq) \rightleftharpoons H^{1+}(aq) + IO_3^{1-}(aq) \qquad K = 0.77$$
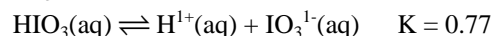
33. What is the concentration of Ba^{2+} ions in an equilibrium mixture that contains 0.12 mol $Ba(OH)_2$ and is 0.086 M in hydroxide ion?

$$Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^{1-}(aq) \quad K = 5.0 \times 10^{-3}$$
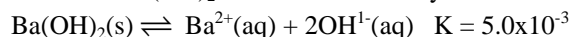
34. What is the concentration of H^{1+} ions in an equilibrium solution of HClO in which the $HClO/ClO^{1-}$ mole ratio is 0.66?

$$HClO(aq) \rightleftharpoons H^{1+}(aq) + ClO^{1-}(aq) \ K = 3.5 \times 10^{-8}$$
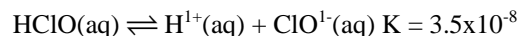
35. Consider the following energy diagram for the process $X(g) \rightleftharpoons Y(g)$.

a) What is ΔE of the reaction $X \rightarrow Y$? Is it an endothermic or an exothermic reaction?
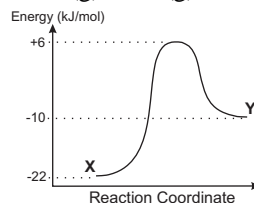
b) What is the activation energy for the forward reaction $(X \rightarrow Y)$?

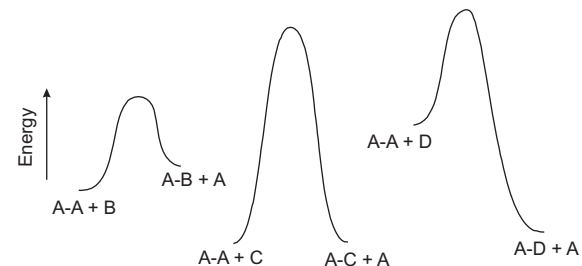**c)** What is the activation energy for the reverse reaction $(Y \rightarrow X)$?

d) Which reaction has the greater rate constant, $X \rightarrow Y$ or $Y \rightarrow X$?

e) Does the pressure of X in the equilibrium mixture increase or decrease as the temperature rises?
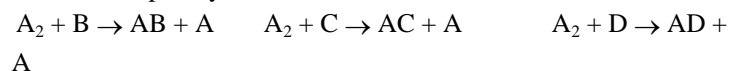
**f)** Which point(s) would change in the presence of a catalyst.

**36.** Compare the reaction energy diagrams for the three gas phase reactions shown below.

a) Assume that the steric factors are all comparable and predict which of the following reactions would most likely have the largest rate constant? Explain your choice.

$A_2 + B \rightarrow AB + A$ $A_2 + C \rightarrow AC + A$ $A_2 + D \rightarrow AD + A$

b) Which of the following reactions would have the largest equilibrium constant? Why?

$A_2 + B \rightleftharpoons AB + A$ $A_2 + C \rightleftharpoons A\text{-}C + A$ $A_2 + D \rightleftharpoons AD + A$
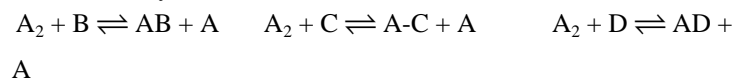
c) The equilibrium constant of which of the following would increase the most with an increase in temperature? Explain your choice.

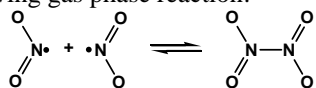$A_2 + B \rightleftharpoons AB + A$ $A_2 + C \rightleftharpoons A\text{-}C + A$ $A_2 + D \rightleftharpoons AD + A$
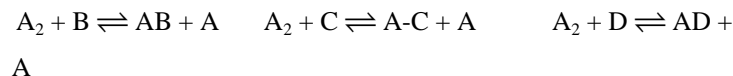
d) Rank the following bonds in order of increasing bond strength?

    A-A   A-B   A-C   A-D

37. Consider the following gas phase reaction:

Indicate which statement is true in each set of a - d.

a) $\Delta S^o > 0$ $\Delta S^o \sim 0$; $\Delta S^o < 0$

b) $\Delta H^o > 0$ $\Delta H^o \sim 0$ $\Delta H^o < 0$

c) at high temperatures

     $\Delta G^o > 0$ $\Delta G^o \sim 0$ $\Delta G^o < 0$

d) at low temperatures

     $\Delta G^o > 0$ $\Delta G^o \sim 0$ $\Delta G^o < 0$

e) Write the equilibrium constant expression for this reaction.

f) What would be the effect on the equilibrium concentration of NO_2 of

     i) removing N_2O_4 **ii)** increasing the temperature   **iii)** adding a catalyst

38. Draw a reaction diagram for a reaction in which the activation energies of the forward and reverse reactions are 20 and 40 kJ/mol, respectively. What is ΔH for the reaction? Draw the reaction diagram for the same reaction in the presence of a catalyst.

39. Write the equilibrium constant expression for each of the following reactions:

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + F^{1-}(aq)$

c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

d) $2NO_3^{1-}(aq) + 8H^{1+}(aq) + 6Br^{1-}(aq) \rightleftharpoons 2NO(g) + 4H_2O(l) + 3Br_2(aq)$

40. Write the equilibrium constant expression for each of the following reactions:

a) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

b) $H_2SO_3(aq) + 2NH_3(aq) \rightleftharpoons SO_3^{2-}(aq) + 2NH_4^{1+}(aq)$

c) $2Ag^{1+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons Ag_2CrO_4(s)$

d) $3Fe(s) + 2Au^{3+}(aq) \rightleftharpoons 2Au(s) + 3Fe^{2+}(aq)$

41. The following pressures were measured in an equilibrium mixture at some temperature: $P_{NH_3} = 0.20$ atm; $P_{H_2} = 0.080$ atm and $P_{N_2} = 0.16$ atm. What is the value of the equilibrium constant for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ at this temperature?

42. An equilibrium mixture at 25 ^{o}C consists of an aqueous solution that is 0.010 M in Pb^{2+} ions and 0.041 M in Cl^{1-} ions above 0.010 mol of solid $PbCl_2$. What is the value of the equilibrium constant for the following reaction: $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{1-}(aq)$?

43. What is the pressure of I_2 in equilibrium with 0.065 atm of H_2 and 0.021 atm of HI at a temperature where $K = 6.7$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$?

44. Given that $K = 7.2 \times 10^{-4}$ for $HF(aq) + H_2O(l) \rightleftharpoons F^{1-}(aq) + H_3O^{1+}(aq)$, determine the molar concentration of F^{1-} ion in equilibrium with [HF] = 0.10 M and $[H_3O^{1+}] = 5.0 \times 10^{-4}$ M.

45. Consider the following thermochemical reaction,

     $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H^o = -91.8$ kJ/mol

a) How much heat is released when 1.0 g of NH_3 is formed?

b) How much heat is released when 1.0 mol of H_2 reacts?

c) How much heat must be absorbed to form 2.0 g of N_2?

d) How many moles of ammonia are formed in a reaction that produces 200 kJ of heat?

46. Consider the combustion of methane,

     $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$ $\Delta H^o = -882$ kJ/mol

a) How many grams of methane must burn to produce 1,000 kJ of heat?

b) How much heat is released when 4.0 g of O_2 react?

c) How much heat is released when 1.5 mol of CO_2 is formed?