Chapter 9

Reaction Energetics

1. What are the signs of $\Delta H^0$ and $\Delta S^0$ for the evaporation of water?
   First write the process: $H_2O(l) \rightarrow H_2O(g)$. Evaporation is endothermic ($\Delta H^0 > 0$) because the potential energy of the vapor is greater than that of the liquid. The vapor is much more disordered than the liquid so $\Delta S^0 > 0$.

3. A system gives off 600 J of heat while 200 J of work is done on it. What are $\Delta E$, $\Delta E_{\text{sur}}$, and $\Delta E_{\text{univ}}$?
   $q = -600$ J and $w = 200$ J
   $\Delta E = q + w = -600 + 200 = -400$ J
   The system gives off 400 J of energy, which goes into the surroundings $\Delta E_{\text{sur}} = - \Delta E = +400$ J
   $\Delta E_{\text{univ}} = 0$ for any process

5. What is the difference between $\Delta H$ and $\Delta E$? Why is $\Delta H$ used more frequently?
   $\Delta E$ is the energy change of a system, while $\Delta H$ is the heat absorbed by a system at constant temperature and pressure. Most chemical processes are carried out at constant pressure, and the heat absorbed or given off is more important to chemists than the work term in Equation 9.2, so $\Delta H$ is used more frequently.

7. When is the entropy change of a reaction expected to be significant?
   Entropy changes are important when gases are produced or consumed.

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) $\Delta G < 0$ False. $\Delta G = 0$ at equilibrium.
   b) $\Delta H^0 < 0$ False. Reaction is endothermic, so $\Delta H^0 > 0$
   c) $\Delta G^0 < 0$ True. Reaction is extensive.
   d) $\Delta S_{\text{univ}} > 0$ False. $\Delta S_{\text{univ}} > 0$ for spontaneous processes, but this process is at equilibrium, so $\Delta S_{\text{univ}} = 0$
   e) $\Delta S^0 > 0$ True. If $\Delta G^0 < 0$ and $\Delta H^0 > 0$ then $\Delta S^0$ must be positive
   f) the extent of reaction increases with T: True. $\Delta S^0$ is positive, so increasing T makes $\Delta G^0$ less positive or more negative.

11. The combustion of 0.150 g of C$_2$H$_5$OH(l) (grain alcohol) releases 4.47 kJ of heat.
   a) What is the enthalpy of combustion of C$_2$H$_5$OH(l)?
      The heat of combustion is the heat absorbed when one mole of the substance reacts with oxygen, but we are given the amount of heat released when 0.150 g is combusted. The molar mass of C$_2$H$_5$OH is 46.1 g/mol, and so we may write $\frac{-4.47 \text{ kJ}}{0.150 \text{ g C$_2$H$_5$OH}} \times \frac{46.1 \text{ g C$_2$H$_5$OH}}{\text{mol C$_2$H$_5$OH}} = -1.37 \times 10^3$ kJ/mol
   b) Write the chemical equation for the combustion reaction: C$_2$H$_5$OH(l) + 3O$_2$(g) $\rightarrow$ 2CO$_2$(g) + 3H$_2$O(l)
   c) What is the enthalpy change for 4CO$_2$(g) + 6H$_2$O(l) $\rightarrow$ 2C$_2$H$_5$OH(l) + 6O$_2$(g)?
      The reaction is the reverse of twice the combustion reaction, $\Delta H^0 = -2 \times \Delta H_{\text{comb}}^0 = -2 \times (-1.37 \times 10^3) = +2.74 \times 10^3$ kJ

13. Use the data in Table 9.2 to estimate the following enthalpies of combustion:
   a) H$_2$C=CH$_2$(g) + 3O$_2$(g) $\rightarrow$ 2CO$_2$(g) + 2H$_2$O(g)
      The oxygen-oxygen bond in O$_2$ is a double bond as are the two carbon-oxygen bonds in CO$_2$. Therefore, four C-H bonds, a C=C bond, and three O=O bonds are broken. Four C=O bonds and four O-H bonds are formed $\Delta H \sim 4 \text{D}_{\text{C-H}} + \text{D}_{\text{C=C}} + 3 \text{D}_{\text{O=O}} - 4 \text{D}_{\text{C=O}} - 4 \text{D}_{\text{O-H}} = 4(413) + 612 + 3(495) - 4(799) - 4(463) = -1299$ kJ
   b) 4CH$_3$NH$_2$(g) + 9O$_2$(g) $\rightarrow$ 4CO$_2$(g) + 10H$_2$O(g) + 2N$_2$(g)
      Twelve C-H bonds, four C-N, eight N-H and nine O=O bonds must be broken. Eight C=O bonds, twenty O-H bonds and two N≡N must form.
      $\Delta H \sim 12 \text{D}_{\text{C-H}} + 4 \text{D}_{\text{C-N}} + 8 \text{D}_{\text{N-H}} + 9 \text{D}_{\text{O=O}} - 8 \text{D}_{\text{C=O}} - 20 \text{D}_{\text{O-H}} - 2 \text{D}_{\text{N≡N}}$
      $\Delta H \sim 12(413) + 4(305) + 8(391) + 9(495) - 8(799) - 20(463) - 2(941) = -3775$ kJ
   c) CCl$_4$(g) + O$_2$(g) $\rightarrow$ CO$_2$(g) + 2Cl$_2$(g)
      $\Delta H \sim 4 \text{D}_{\text{C-Cl}} + \text{D}_{\text{O=O}} - 2 \text{D}_{\text{C=O}} - 2 \text{D}_{\text{Cl-Cl}} = 4(328) + 495 - 2(799) - 2(242) = -275$ kJ
d) \[4\text{H-C≡N}(g) + 5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(g) + 2\text{N}_2(g)\]
\[\Delta H \approx 4 \text{D}_{\text{C-N}} + 4 \text{D}_{\text{C-H}} + 5 \text{D}_{\text{O=O}} - 8 \text{D}_{\text{C=O}} - 4 \text{D}_{\text{O-H}} - 2 \text{D}_{\text{N≡N}} = (4(891) + 4(413) + 5(495) - 8(799) - 4(463) - 2(941)) = -2435 \text{ kJ}\]

15. Indicate \(\Delta S^o > 0\), \(\Delta S^o \approx 0\), or \(\Delta S^o < 0\) for each of the following reactions:

a) \(\text{H}_3\text{Cl(aq)} + \text{OH}^-(aq) \rightarrow \text{H}_3\text{COH(aq)} + \text{I}^-(aq)\)
   No gases are involved, so \(\Delta S^o \approx 0\).

b) \(\text{CCl}_4(l) \rightarrow \text{CCl}_4(g)\)
   Gas is produced so, \(\Delta S^o > 0\).

c) \(\text{C}_2\text{H}_2(g) + 2\text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)\)
   The number of moles of gas decreases, so \(\Delta S^o < 0\).

d) \(\text{H}_2(g) + \text{CO}_2(g) \rightarrow \text{H}_2\text{O}(g) + \text{CO}(g)\)
   There is no change in the number of moles of gas, so \(\Delta S^o \approx 0\).

17. Indicate the sign of \(\Delta G^o\) at low and high temperatures for each of the reactions in Exercise 12.

a) \(\text{H}_2\text{CBr}_2(g) + \text{F}_2(g) \rightarrow \text{H}_2\text{CF}_2(g) + \text{Br}_2(g)\)
   \(\Delta H^o < 0\) (Exercise 10) and \(\Delta S^o \approx 0\) (no change in number of moles of gas).
   Because \(\Delta S^o \approx 0\), \(\Delta G^o \approx \Delta H^o < 0\) at all temperatures.

b) \(\text{H}_3\text{Cl}(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_3\text{COH}(g) + \text{HI}(g)\)
   \(\Delta H^o > 0\) (Exercise 10) and \(\Delta S^o \approx 0\) (no change in number of moles of gas).
   Because \(\Delta S^o \approx 0\), \(\Delta G^o \approx \Delta H^o > 0\) at all temperatures.

c) \(\text{HC≡CH}(g) + 2\text{H}_2(g) \rightarrow \text{H}_2\text{C}-\text{CH}_3(g)\)
   \(\Delta H^o < 0\) (Exercise 10) and \(\Delta S^o < 0\) (gas is consumed).
   At low temperature, \(\Delta G^o \approx \Delta H^o < 0\). At high temperature, \(\Delta G^o\) can have the sign of \(-T\Delta S^o > 0\).

d) \(\text{CH}_4(g) \rightarrow \text{C}(g) + 2\text{H}_2(g)\)
   \(\Delta H^o > 0\) (Exercise 10) and \(\Delta S^o > 0\) (moles of gas increases).
   At low temperature, \(\Delta G^o \approx \Delta H^o > 0\). At high temperature, \(\Delta G^o\) can have the sign of \(-T\Delta S^o < 0\).

19. Consider the reaction, \(2\text{HI(g)} \rightarrow \text{H}_2(g) + \text{I}_2(g)\)

a) Use bond energies to estimate the value of \(\Delta H^o\) at 298 K.
   \(\Delta H^o \approx 2 \text{D}_{\text{H-I}} - \text{D}_{\text{H-H}} - \text{D}_{\text{I-I}} = 2(299) - 436 - 151 = 11\) kJ

b) Is \(\Delta S^o > 0\), \(\Delta S^o \approx 0\), or \(\Delta S^o < 0\)?
   Two moles of gas react and two moles are produced, so the number of moles of gas is unchanged and \(\Delta S^o \approx 0\).

c) Indicate the sign of \(\Delta G^o\) at high and at low temperatures.
   \(\Delta H^o > 0\) and \(\Delta S^o \approx 0\) from parts a and b. Because \(\Delta S^o \approx 0\) we approximate the free energy change as \(\Delta G^o \approx \Delta H^o\). Therefore, \(\Delta G^o > 0\) at all temperatures.

d) Write the equilibrium expression for the reaction.
   \[2\text{HI(g)} \rightleftharpoons \text{H}_2(g) + \text{I}_2(g); \quad K = \frac{P_{\text{H}_2}P_{\text{I}_2}}{P_{2\text{HI}}^{2}}\]

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?
   Exothermic reactions have relatively large equilibrium constants unless the entropy change is large and negative.

b) Will the value of the equilibrium constant increase, decrease, or remain unchanged when \(T\) is increased?
   The reaction is exothermic, which means that the reactants are at higher energy than the products. A increase in temperature favors the more energetic materials, which are the reactants in this case. The equilibrium constant decreases as the reactant concentrations increase and the product concentrations decrease. Therefore, the equilibrium constant of an exothermic reaction decreases with an increase of temperature.

c) Will the value of the equilibrium constant increase, decrease, or remain unchanged when more reactant is added?
   The value of the equilibrium constant changes only when the temperature changes. Adding or removing any material has no effect on the value of the equilibrium constant.
d) Will the value of the equilibrium constant increase, decrease or remain unchanged when a catalyst is added?

A catalyst affects the speed with which equilibrium is reached. It has no effect on the value of the constant or on the concentrations of the reactants and products when equilibrium is established.

e) Is the rate constant of the forward reaction larger or smaller than the rate constant for the reverse reaction?

The rate constant consists of two terms: steric and energy. We have no information about differences in the steric terms, so we will assume they are comparable for the two reactions. This means that the relative rate constants depend on the activation energies. Since this is an exothermic reaction, the activation energy for the forward reaction is less than the activation energy of the reverse reaction. Therefore, the rate constant for the forward reaction is greater than for the reverse reaction. However, the rate constant for both reactions is small because the activation energy for the reaction is large.

23. Indicate the effect of each of the following on the equilibrium concentration of CO:

\[ H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad \Delta H^\circ = 41 \text{ kJ/mol} \]

a) increasing the concentration of H\(_2\)

Some CO\(_2\) reacts with some of the additional H\(_2\) to produce H\(_2\)O and CO. Consequently, the equilibrium concentration of CO increases.

b) decreasing the concentration of CO\(_2\)

H\(_2\)O and CO must react to replace some of the lost CO\(_2\). Therefore, the equilibrium concentration of CO decreases.

c) increasing the concentration of H\(_2\)O

Some of the added water reacts with CO causing a decrease in the CO concentration.

d) increasing the temperature

The reaction is endothermic so heat is a reactant. Increasing the temperature is equivalent to adding a reactant, which has the effect of making more product. Consequently, the equilibrium concentration of CO increases.

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

As the thermal energy (temperature) increases, the fraction of the collisions that have sufficient energy to reach the transition state also increases.

27. Express the rate law for each of the following one-step processes:

a) \( \text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I} \)

\[ R = k[\text{CH}_3][\text{I}] \]

b) \( 2\text{H}_2 \rightarrow 4\text{H} \)

\[ R = k[\text{H}_2]^2 \]

c) \( \text{HO} + \text{H} \rightarrow \text{H}_2\text{O} \)

\[ R = k[\text{HO}][\text{H}] \]

29. Write the equilibrium constant expression in terms of the concentrations of the reactants and products for each of the following reactions:

a) \( H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \)

\[ K = \frac{[HCl]^2}{[H_2][Cl_2]} \]

b) \( H_2SO_3(aq) + 2CN^{1-}(aq) \rightleftharpoons 2HCN(aq) + SO_3^{2-}(aq) \)

\[ K = \frac{[HCN]^2[SO_3^{2-}]}{[H_2SO_3][CN^{1-}]^2} \]

c) \( \text{NH}_3(aq) + HF(aq) \rightleftharpoons \text{NH}_4^{1+}(aq) + F^{1-}(aq) \)

\[ K = \frac{[\text{NH}_4^{1+}][F^{1-}]}{[\text{NH}_3][HF]} \]

31. Consider the following equilibrium: \( 2\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2\text{NOBr} \quad K = 2.0 \). What is the equilibrium pressure of NOBr if the equilibrium pressures of NO and Br\(_2\) are 1.6 and 3.6 atm, respectively?

Solve the equilibrium constant expression for the unknown pressure

\[ K = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}}^2P_{\text{Br}_2}} \]

\[ P_{\text{NOBr}} = \sqrt{KP_{\text{NO}}^2P_{\text{Br}_2}} = \sqrt{(2.0)(1.6)^2(3.6)} = 4.3 \text{ atm} \]
33. What is the concentration of $\text{Ba}^{2+}$ ions in an equilibrium mixture that contains 0.12 mol $\text{Ba(OH)}_2$ and is 0.086 M in hydroxide ion? $\text{Ba(OH)}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \quad K = 5.0 \times 10^{-3}$

Solids enter the equilibrium expression as 1, so the number of moles of solid is irrelevant. The equilibrium constant expression is $K = [\text{Ba}^{2+}][\text{OH}^-]^2$. Solving for the $\text{Ba}^{2+}$ ion concentration, we obtain

$$[\text{Ba}^{2+}] = \frac{K}{[\text{OH}^-]^2} = \frac{5.0 \times 10^{-3}}{0.086^2} = 0.68 \text{ M}$$

35. Compound $\text{X}$ rearranges to $\text{Y}$ in the gas phase. Refer to the reaction energy diagram for $\text{X(g)} \rightarrow \text{Y(g)}$ in your text.

a) What is $\Delta E$ of the reaction $\text{X} \rightarrow \text{Y}$? Is it an endothermic or an exothermic reaction?

The energy of the reactants is -22 kJ, and the energy of the products is -10 kJ. The energy change is the final energy (energy of the products) minus the initial energy (energy of the reactants), so $\Delta E = E_f - E_i = -10 - (-22) = +12 \text{ kJ}$. The reaction is endothermic because the energy of the products is greater than the energy of the reactants.

b) What is the $E_a$ for the forward reaction ($\text{X} \rightarrow \text{Y}$)?

The activation energy for the forward reaction is the energy of the transition state (+6 kJ) less the energy of the reactants (-22kJ), so $E_a(f) = 6 - (-22) = 28 \text{ kJ}$

c) What is the $E_a$ for the reverse reaction ($\text{Y} \rightarrow \text{X}$)?

The activation energy for the reverse reaction is the energy of the transition state (+6kJ) less the energy of the products (-10 kJ), so $E_a(r) = 6 - (-10) = 16 \text{ kJ}$

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

$\text{Y} \rightarrow \text{X}$ if the steric factors of the reverse and forward reactions are comparable, because it has the lower activation energy.

e) Does the pressure of $\text{X}$ in the equilibrium mixture increase or decrease as the temperature rises?

An increase in temperature favors the side at higher energy, the products in this reaction. Consequently, a rise in temperature increases the equilibrium concentration of $\text{Y}$ and decreases the equilibrium concentration of $\text{X}$.

f) Which point(s) would change in the presence of a catalyst.

A catalyst reduces the activation energy, so the energy of the transition state would be less than 6 kJ.

37. Consider the gas phase reaction $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$.

a) Which of the following statements is true for this reaction? Explain your choice.

$$\Delta S^0 > 0 \quad \Delta S^0 \sim 0 \quad \Delta S^0 < 0$$

Two moles of gas goes to one mole of gas, so $\Delta S^0 < 0$.

b) Which of the following statements is true for this reaction: $\Delta H^0 > 0$, $\Delta H^0 \sim 0$, or $\Delta H^0$ ? Why.

No bonds are broken, but an N-N bond is formed in the reaction. Thus, $\Delta H^0 = -\Delta_{\text{N-N}}$. Since all bond energies are positive, $\Delta H^0 < 0$.

c) Which of the following statements is true for this reaction at high temperatures: $\Delta G^0 > 0$, $\Delta G^0 \sim 0$, or $\Delta G^0 < 0$?

At high temperature, the sign of $\Delta G^0$ is that of $-T\Delta S^0$. Therefore, $\Delta G^0 > 0$.

d) Which of the following statements is true for this reaction at low temperatures: $\Delta G^0 > 0$, $\Delta G^0 \sim 0$, or $\Delta G^0 < 0$?

At low temperature, the sign of $\Delta G^0$ is that of $\Delta H^0$. Therefore, $\Delta G^0 < 0$.

e) What is the equilibrium constant expression for this reaction?

$$K = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

f) What would be the effect on the equilibrium concentration of $\text{NO}_2$ of each of the following?

i. $\text{N}_2\text{O}_4$ is removed. Equilibrium shifts to replace $\text{N}_2\text{O}_4$, so $[\text{NO}_2]$ decreases.

ii. The temperature is increased. Exothermic reaction, so temperature increase favors the reactant right side of the reaction. $[\text{NO}_2]$ increases.

iii. A catalyst is added. Catalysts have no effect on equilibrium concentrations.
39. Write the equilibrium constant expression for each of the following reactions:

a) \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \)

\[ K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}P_{\text{I}_2}} \]

b) \( \text{HF(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^{+}(aq) + \text{F}^{-}(aq) \)

\[ K = \frac{[\text{H}_3\text{O}^{+}][\text{F}^{-}]}{[\text{HF}]} \]

Recall that the solvent water is treated as a pure liquid and enters the expression as 1.

c) \( \text{CaCO}_3(s) \rightleftharpoons \text{CaO(s)} + \text{CO}_2(g) \)

\[ K = P_{\text{CO}_2} ; \text{the solids enter the expression as ones.} \]

d) \( 2\text{NO}_3^{-}(aq) + 8\text{H}^+(aq) + 6\text{Br}^{-}(aq) \rightleftharpoons 2\text{NO(g)} + 4\text{H}_2\text{O(l)} + 3\text{Br}_2(aq) \)

\[ K = \frac{P_{\text{NO}}^2}{[\text{Br}_2]^3[\text{NO}_3^{-}]^2[\text{H}^+]^8[\text{Br}^{-}]^6} ; \text{Gases enter as P (atm), solutes as concentration (M), and liquids as 1.} \]

41. The following pressures were measured in an equilibrium mixture at some temperature: \( P_{\text{NH}_3} = 0.20 \text{ atm}; P_{\text{H}_2} = 0.080 \text{ atm} \) and \( P_{\text{N}_2} = 0.16 \text{ atm} \). What is the value of the equilibrium constant for the following reaction at this temperature: \( 2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g) \)?

\[ K = \frac{P_{\text{N}_2}P_{\text{H}_2}^3}{P_{\text{NH}_3}^2} = \frac{(0.16)(0.080)^3}{(0.20)^2} = 2.0 \times 10^{-3} \]

43. What is the pressure of \( \text{I}_2 \) in equilibrium with \( 0.065 \text{ atm of H}_2 \) and \( 0.021 \text{ atm of HI} \) at a temperature where \( K = 6.7 \) for the reaction \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \)?

\[ K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}P_{\text{I}_2}} = 6.7, \text{ so } P_{\text{I}_2} = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}K} = \frac{(0.021)^2}{(0.065)(6.7)} = 0.0010 \text{ atm} \]

45. Consider the following thermochemical reaction,

\( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)

\[ \Delta H^o = -91.8 \text{ kJ/mol} \]

a) How much heat is released when 1.0 g of \( \text{NH}_3 \) is formed?

\[ 1.0 \text{ g NH}_3 \times \frac{1 \text{ mol} \text{ NH}_3}{17 \text{ g NH}_3} \times \frac{91.8 \text{ kJ}}{2 \text{ mol} \text{ NH}_3} = 2.7 \text{ kJ} \]

b) How much heat is released when 1.0 mol of \( \text{H}_2 \) reacts?

\[ 1 \text{ mol H}_2 \times \frac{91.8 \text{ kJ}}{3 \text{ mol} \text{ H}_2} = 30.6 \text{ kJ} \]

c) How much heat must be absorbed to form 2.0 g of \( \text{N}_2 \)?

\[ 2.0 \text{ g N}_2 \times \frac{1 \text{ mol} \text{ N}_2}{28 \text{ g N}_2} \times \frac{91.8 \text{ kJ}}{1 \text{ mol} \text{ N}_2} = 6.6 \text{ kJ} \]

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

\[ 200 \text{ kJ} \times \frac{2 \text{ mol} \text{ NH}_3}{91.8 \text{ kJ}} \times \frac{17 \text{ g NH}_3}{\text{mol NH}_3} = 74 \text{ g NH}_3 \]
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