Chapter 9

Reaction Energetics

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

First write the process: $H_2O(l) \rightarrow H_2O(g)$. Evaporation is endothermic ($\Delta H^O > 0$) because the potential energy of the vapor is greater than that of the liquid. The vapor is much more disordered than the liquid so $\Delta S^O > 0$.

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

$q = -600$ J and $w = 200$ J $\qquad \Delta E = q + w = -600 + 200 = -400$ J

The system gives off 400 J of energy, which goes into the surroundings $\Delta E_{sur} = -\Delta E = +400$ J

$\Delta E_{univ} = 0$ for any process

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

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

11. The 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 $C_2H_5OH(l)$?

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_2H_5OH is 46.1 g/mol, and so we may write

$$\frac{-4.47\text{ kJ}}{0.150\text{ g } C_2H_5OH} \times \frac{46.1\text{ g } C_2H_5OH}{\text{mol } C_2H_5OH} = -1.37 \times 10^3 \text{ kJ/mol}$$

b) Write the chemical equation for the combustion reaction: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

c) What is the enthalpy change for $4CO_2(g) + 6H_2O(l) \rightarrow 2C_2H_5OH(l) + 6O_2(g)$?

The reaction is the reverse of twice the combustion reaction,

$$\Delta H^O = -2 \times \Delta H^o_{comb} = -2 \times (-1.37 \times 10^3) = +2.74 \times 10^3 \text{ kJ}$$

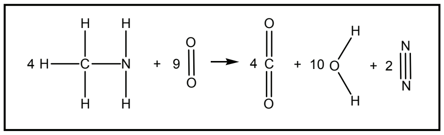
13. Use the data in Table 9.2 to estimate the following enthalpies of combustion:

a) $H_2C{=}CH_2(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

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

$\Delta H \sim 4 D_{C-H} + D_{C=C} + 3 D_{O=O} - 4 D_{C=O} - 4 D_{O-H} = 4(413) + 612 + 3(495) - 4(799) - 4(463) = -1299$ kJ

b) $4CH_3NH_2(g) + 9O_2(g) \rightarrow 4CO_2(g) + 10H_2O(g) + 2N_2(g)$



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.

$\Delta H \sim 12 D_{C-H} + 4 D_{C-N} + 8 D_{N-H} + 9 D_{O=O} - 8 D_{C=O} - 20 D_{O-H} - 2 D_{N\equiv N}$

$\Delta H \sim 12(413) + 4(305) + 8(391) + 9(495) - 8(799) - 20(463) - 2(941) = -3775$ kJ

c) $CCl_4(g) + O_2(g) \rightarrow CO_2(g) + 2Cl_2(g)$

$\Delta H \sim 4 D_{C-Cl} + D_{O=O} - 2 D_{C=O} - 2 D_{Cl-Cl} = 4(328) + 495 - 2(799) - 2(242) = -275$ kJ

d) $4H\text{-}C{\equiv}N(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g) + 2N_2(g)$

$\Delta H \sim 4\,D_{C\equiv N} + 4\,D_{C\text{-}H} + 5\,D_{O=O} - 8\,D_{C=O} - 4\,D_{O\text{-}H} - 2\,D_{N\equiv N}$

$= 4(891) + 4(413) + 5(495) - 8(799) - 4(463) - 2(941) = -2435$ kJ

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

a) $H_3CI(aq) + OH^{1-}(aq) \rightarrow H_3COH(aq) + I^{1-}(aq)$ No gases are involved, so $\square S^o \sim 0$.

b) $CCl_4(l) \rightarrow CCl_4(g)$ Gas is produced so, $\square S^o > 0$.

c) $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$ The number of moles of gas decreases, so $\square S^o < 0$.

d) $H_2(g) + CO_2(g) \rightarrow H_2O(g) + CO(g)$ There is no change in the number of moles of gas, so $\square S^o \sim 0$.

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

a) $H_2CBr_2(g) + F_2(g) \rightarrow H_2CF_2(g) + Br_2(g)$

$\Delta H^o < 0$ (Exercise 10) and $\Delta S^o \sim 0$ (no change in number of moles of gas).
Because $\Delta S^o \sim 0$, $\Delta G^o \sim \Delta H^o < 0$ at all temperatures.

b) $H_3CI(g) + H_2O(g) \rightarrow H_3COH(g) + HI(g)$

$\Delta H^o > 0$ (Exercise 10) and $\Delta S^o \sim 0$ (no change in number of moles of gas).
Because $\Delta S^o \sim 0$, $\Delta G^o \sim \Delta H^o > 0$ at all temperatures.

c) $HC{\equiv}CH(g) + 2H_2(g) \rightarrow H_3C\text{-}CH_3(g)$

$\Delta H^o < 0$ (Exercise 10) and $\Delta S^o < 0$ (gas is consumed).
At low temperature, $\Delta G^o \sim \Delta H^o < 0$. At high temperature, ΔG^o can have the sign of $-T\Delta S^o > 0$.

d) $CH_4(g) \rightarrow C(g) + 2H_2(g)$

$\Delta H^o > 0$ (Exercise 10) and $\Delta S^o > 0$ (moles of gas increases).
At low temperature, $\Delta G^o \sim \Delta H^o > 0$. At high temperature, ΔG^o can have the sign of $-T\Delta S^o < 0$.

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. $\Delta H^o \sim 2\,D_{H\text{-}I} - D_{H\text{-}H} - D_{I\text{-}I} = 2(299) - 436 - 151 = 11$ kJ

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

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

d) Write the equilibrium expression for the reaction.

$$2\,HI(g) \rightleftharpoons H_2(g) + I_2(g); \qquad K = \frac{P_{H_2}P_{I_2}}{P_{HI}^2}$$

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:**

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H^o = 41$ kJ/mol

a) **increasing the concentration of H_2**

Some CO_2 reacts with some of the additional H_2 to produce H_2O and CO. Consequently, the equilibrium concentration of CO increases.

b) **decreasing the concentration of CO_2**

H_2O 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_2O**

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) **$CH_3 + I \rightarrow CH_3I$** $R = k[CH_3][I]$

b) **$2H_2 \rightarrow 4H$** $R = k[H_2]^2$

c) **$HO + H \rightarrow H_2O$** $R = k[HO][H]$

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

a) **$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$** $K = \dfrac{{P_{HCl}}^2}{P_{H_2}P_{Cl_2}}$

b) **$H_2SO_3(aq) + 2CN^{1-}(aq) \rightleftharpoons 2HCN(aq) + SO_3^{2-}(aq)$** $K = \dfrac{[HCN]^2[SO_3^{2-}]}{[H_2SO_3][CN^{1-}]^2}$

c) **$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^{1+}(aq) + F^{1-}(aq)$** $K = \dfrac{[NH_4^{1+}][F^{1-}]}{[NH_3][HF]}$

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?**

Solve the equilibrium constant expression for the unknown pressure

$$K = \frac{P^2_{NOBr}}{P^2_{NO}P_{Br_2}}, \text{ so } P_{NOBr} = \sqrt{KP^2_{NO}P_{Br_2}} = \sqrt{(2.0)(1.6)^2(3.6)} = 4.3 \text{ atm}$$

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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? $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^{1-}(aq)$ $K = 5.0\mathrm{x}10^{-3}$

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

$$[Ba^{2+}] = \frac{K}{[OH^{1-}]^2} = \frac{5.0\times10^{-3}}{0.086^2} = 0.68\ M$$

35. Compound X rearranges to Y in the gas phase. Refer to the reaction energy diagram for X(g) Í Y(g) in your text.

a) What is ΔE of the reaction X → 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 $\Delta E = E_f - E_I = -10 - (-22) = +12$ kJ. The reaction is endothermic because the energy of the products is greater than the energy of the products.

b) What is the E_a for the forward reaction (X → 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 $E_a(f) = 6 - (-22) = 28$ kJ

c) What is the E_a for the reverse reaction (Y → 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 $E_a(r) = 6 - (-10) = 16$ kJ

d) Which reaction has the greater rate constant, X → Y or Y → X?

Y → 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 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 Y and decreases the equilibrium concentration of 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 $2NO_2(g) \rightarrow N_2O_4(g)$.

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

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

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

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

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

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

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

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

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

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

$$K = \frac{P_{N_2O_4}}{P^2_{NO_2}}$$

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

i. N_2O_4 is removed. Equilibrium shifts to replace N_2O_4, so $[NO_2]$ decreases.

ii. The temperature is increased.

Exothermic reaction, so temperature increase favors the reactant right side of the reaction. $[NO_2]$ 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) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$$

b) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + F^{1-}(aq)$ $K = \frac{[H_3O^{1+}][F^{1-}]}{[HF]}$

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

c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K = P_{CO_2}$ `; the solids enter the expression as ones.`

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

$K = \frac{P_{NO}^2[Br_2]^3}{[NO_3^{1-}]^2[H^{1+}]^8[Br^{1-}]^6}$; 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_{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 following reaction at this temperature: $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$?

$$K = \frac{P_{N_2}P_{H_2}^3}{P_{NH_3}^2} = \frac{(0.16)(0.080)^3}{(0.20)^2} = 2.0\times10^{-3}$$

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

$$K = \frac{P_{HI}^2}{P_{H_2}P_{I_2}} = 6.7\text{, so } P_{I_2} = \frac{P_{HI}^2}{P_{H_2}K} = \frac{(0.021)^2}{(0.065)(6.7)} = 0.0010 \text{ atm}$$

45. Consider the following thermochemical reaction,

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ΔH^o = -91.8 kJ/mol

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

$$1.0\text{ g }NH_3 \times \frac{1\text{ mol }NH_3}{17\text{ g }NH_3} \times \frac{91.8\text{ kJ}}{2\text{ mol }NH_3} = 2.7\text{ kJ}$$

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

$$1\text{ mol }H_2 \times \frac{91.8\text{ kJ}}{3\text{ mol }H_2} = 30.6\text{ kJ}$$

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

$$2.0\text{ g }N_2 \times \frac{1\text{ mol }N_2}{28\text{ g }N_2} \times \frac{91.8\text{ kJ}}{1\text{ mol }N_2} = 6.6\text{ kJ}$$

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

$$200\text{ kJ} \times \frac{2\text{ mol }NH_3}{91.8\text{ kJ}} \times \frac{17\text{ g }NH_3}{\text{mol }NH_3} = 74\text{ g }NH_3$$