

6.7: DESCRIBING A REACTION - EQUILIBRIA, RATES, AND ENERGY CHANGES

OBJECTIVES

After completing this section, you should be able to

- write the equilibrium constant expression for a given reaction.
- assess, qualitatively, how far a reaction will proceed in a given direction, given the value of K_{eq} .
- explain the difference between rate and equilibrium.
- state the relationship between ΔG° and K_{eq} , and use this relationship to determine the value of either of the two variables, given the other.
- state the relationship between Gibbs free-energy, enthalpy and entropy, and use the relationship to calculate any one of ΔG° , ΔH° and ΔS° , given the other two.
- make a qualitative assessment of whether ΔS° for a given process is expected to be positive or negative.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

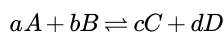
- exergonic
- endergonic
- exothermic
- endothermic
- enthalpy change (heat of reaction), ΔH°
- entropy change, ΔS°
- reaction mechanism
- standard Gibbs free-energy change, ΔG°

STUDY NOTES

Throughout this course you will be paying a great deal of attention to the mechanisms of the reactions that you study. Some students see this as a laborious task of little practical use. However, you will find that a knowledge of reaction mechanisms can help reduce the number of reactions to memorize, provide a connecting link between apparently unrelated reactions, and enable someone with a basic knowledge of organic chemistry to deduce how a previously unseen reaction might proceed. The investigation of reaction mechanisms is a popular research area for organic chemists.

EQUILIBRIUM CONSTANT

For the hypothetical chemical reaction:



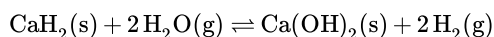
the equilibrium constant is defined as:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The notation $[A]$ signifies the molar concentration of species A. An alternative expression for the equilibrium constant involves partial pressures:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Note that the expression for the equilibrium constant includes only solutes and gases; pure solids and liquids do not appear in the expression. For example, the equilibrium expression for the reaction



is the following:

$$K_C = \frac{[H_2]^2}{[H_2O]^2}$$

Observe that the gas-phase species H_2O and H_2 appear in the expression but the solids CaH_2 and $Ca(OH)_2$ do not appear.

The equilibrium constant is most readily determined by allowing a reaction to reach equilibrium, measuring the concentrations of the various solution-phase or gas-phase reactants and products, and substituting these values into the Law of Mass Action.

FREE ENERGY

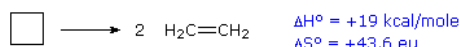
The interaction between enthalpy and entropy changes in chemical reactions is best observed by studying their influence on the equilibrium constants of reversible reactions. To this end a new thermodynamic function called Free Energy (or Gibbs Free Energy), symbol ΔG , is defined as shown in the first equation below. Two things should be apparent from this equation. First, in cases where the entropy change is small, $\Delta G \cong \Delta H$. Second, the importance of ΔS in determining ΔG increases with increasing temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where the temperature is measured in absolute temperature (K).

The free energy function provides improved insight into the thermodynamic driving forces that influence reactions. A negative ΔG° is characteristic of an **exergonic reaction**, one which is thermodynamically favorable and often spontaneous, as is the melting of ice at 1 °C. Likewise a positive ΔG° is characteristic of an **endergonic reaction**, one which requires an input of energy from the surroundings.

For an example of the relationship of free energy to enthalpy consider the decomposition of cyclobutane to ethene, shown in the following equation. The standard state for all the compounds is gaseous.



This reaction is endothermic, but the increase in number of molecules from one (reactants) to two (products) results in a large positive ΔS° .

At 25 °C (298 K):

$$\Delta G^\circ = 19 \text{ kcal/mol} - 298(43.6) \text{ cal/mole} = 19 - 13 \text{ kcal/mole} = +6 \text{ kcal/mole}.$$

Thus, the entropy change opposes the enthalpy change, but is not sufficient to change the sign of the resulting free energy change, which is endergonic. Indeed, cyclobutane is perfectly stable when kept at room temperature.

Because the entropy contribution increases with temperature, this energetically unfavorable transformation can be made favorable by raising the temperature. At 200 °C (473 K),

$$\Delta G^\circ = 19 \text{ kcal/mol} - 473(43.6) \text{ cal/mole} \quad (6.7.1)$$

$$= 19 - 20.6 \text{ kcal/mole} \quad (6.7.2)$$

$$= -1.6 \text{ kcal/mole}. \quad (6.7.3)$$

This is now an **exergonic reaction**, and the thermal cracking of cyclobutane to ethene is known to occur at higher temperatures.

$$\Delta G^\circ = -RT \ln K = -2.303RT \log_{10} K \quad (6.7.4)$$

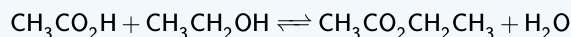
where $R = 1.987 \text{ cal/K mole}$ $T = \text{temperature in K}$ and $K = \text{equilibrium constant}$

NOTE

Equation 6.7.4 is important because it demonstrates the fundamental relationship of ΔG° to the equilibrium constant, K . Because of the negative logarithmic relationship between these variables, a negative ΔG° generates a $K > 1$, whereas a positive ΔG° generates a $K < 1$. When $\Delta G^\circ = 0$, $K = 1$. Furthermore, small changes in ΔG° produce large changes in K . A change of 1.4 kcal/mole in ΔG° changes K by approximately a factor of 10. This interrelationship may be explored with the calculator on the right. Entering free energies outside the range -8 to 8 kcal/mole or equilibrium constants outside the range 10^{-6} to 900,000 will trigger an alert, indicating the large imbalance such numbers imply.

? EXERCISE 6.7.1

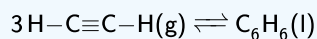
At 155°C, the equilibrium constant, K_{eq} , for the reaction



has a value of 4.0. Calculate ΔG° for this reaction at 155°C.

? EXERCISE 6.7.2

Acetylene (C_2H_2) can be converted into benzene (C_6H_6) according to the equation:



At 25°C , ΔG° for this reaction is -503 kJ and ΔH° is -631 kJ . Determine ΔS° and indicate whether the size of ΔS° agrees with what you would have predicted simply by looking at the chemical equation.

Answer

The entropy change is negative, as one would expect from looking at the chemical equation, since three moles of reactants yield one mole of product; that is, the system becomes much more “ordered” as it goes from reactants to products.

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