5.4: DESCRIBING A REACTION - EQUILIBRIUM AND FREE ENERGY CHANGES

Learning Objective

- perform calculations using the equation

$$\Delta G^{o} = -RT\ln K = -2.303RT\log_{10} K \tag{5.4.1}$$

and explain the relationship between equilibrium and free energy

EQUILIBRIUM CONSTANT

For the hypothetical chemical reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{5.4.2}$$

the equilibrium constant is defined as:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{5.4.3}$$

where the notation [A] signifies the molar concentration of species A. 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

$$\mathrm{CaH_2(s) + 2\,H_2O(g) \rightleftharpoons Ca(OH)_2(s) + 2\,H_2(g)} \tag{5.4.4}$$

is the following:

$$K_C = \frac{[H_2]^2}{[H_2O]^2} \tag{5.4.5}$$

Observe that the gas-phase species $\mathrm{H_2O}$ and $\mathrm{H_2}$ appear in the expression but the solids $\mathrm{CaH_2}$ and $\mathrm{Ca(OH)_2}$ 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

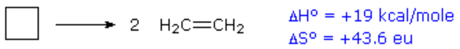
The interaction between enthalpy and entropy changes in chemical reactions is best observed by studying their influence on the equilibrium constants of reversible reactions. To this end a new thermodynamic function called Free Energy (or Gibbs Free Energy), symbol ΔG, is defined as shown in the first 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.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{5.4.6}$$

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^{o} is characteristic of an **exergonic reaction**, one which is thermodynamically favorable and often spontaneous, as is the melting of ice at 1 ºC. Likewise a positive ΔG^{o} 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 ΔSº.

At 25 ºC (298 K):

ΔGº = 19 kcal/mol – 298(43.6) cal/mole = 19 – 13 kcal/mole = +6 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 ºC (473 K),

$$\Delta G^{\circ} = 19\, kcal/mol – 473(43.6)\, cal/mole \tag{5.4.7}$$

$$= 19 – 20.6\, kcal/mole \tag{5.4.8}$$

$$= – 1.6 kcal/mole. \tag{5.4.9}$$

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

ΔGº = –RT \ln K = –2.303 RT \log_{10} K \label{eq2}

where R = 1.987 cal/ K mole T = temperature in K and K = equilibrium constant

Note

Equation 5.4.1 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 ΔGº generates a K>1, whereas a positive ΔGº generates a K<1. When ΔGº = 0, K = 1. Furthermore, small changes in ΔGº produce large changes in K. A change of 1.4 kcal/mole in ΔGº 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.

APPLICATIONS TO ORGANIC REACTIONS

The equation below can also be useful without performing any calculations.

ΔGº = –RT \ln K = –2.303 RT \log_{10} K \label{eq2}

Conceptually, this equation helps us compare the energetics of reaction mechanisms to predict the major products. For example, if ΔG° < 0, then K > 1, and products are favored over reactants. If ΔG° > 0, then K < 1, and reactants are favored over products. If ΔG° = 0, then K = 1, and the system is at equilibrium. Recognizing the underlying energetics of equilibrium, the stability of charged reactants and products can be used to predict reaction equilibrium. Reaction conditions can also be adjusted or controlled to shift the equilibrium in the desired direction by a range of experimental methods. A theoretical understanding of the reaction free energy and equilibrium helps us predict and design the optimum reaction conditions for a desired product.

Exercises

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

$$\mathrm{CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O} \tag{5.4.10}$$

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

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

$$\mathrm{3\,H{-}C{\equiv}C{-}H(g) \rightleftharpoons C_6H_6(l)} \tag{5.4.11}$$

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

Δ G ° = − R T ln K eq = − (8.314   J · K − 1 · mol − 1) (428   K) ln (4.0) = − (8.314   J · K − 1 · mol − 1) (428   K) (1.386) = − 4.9 × 10 3 J · mol − 1 = − 4.9   KJ · mol − 1 Δ G ° = Δ H ° − T Δ S ° Δ S ° = (Δ H ° − Δ G °) T = − 631   kJ − (− 503   kJ) 298   K = − 128   kJ 298   K = − 0.430   KJ · mol − 1 = − 430   J · mol − 1

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.

CONTRIBUTORS AND ATTRIBUTIONS

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