

6.5: Equilibrium Constants

Let's derive a general expression for the thermochemistry of chemical reactions with arbitrary numbers of reactants and products; example problems 6.3 and 6.4 are also helpful for your understanding in this regard. For any reaction:

$$\Delta_r G = \sum_{\text{products}} \{ \nu_i \cdot \mu_i \} - \sum_{\text{reactants}} \{ \nu_i \cdot \mu_i \} = \left(\sum_{\text{products}} \{ \nu_i \cdot \mu_i \} - \sum_{\text{reactants}} \{ \nu_i \cdot \mu_i \} \right)$$

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$$\prod_{\text{reactants}} \left(\frac{1}{\nu_i} \right)^{\nu_i}$$

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$$\left(\frac{1}{\nu_i} \right)^{\nu_i}$$

The argument of the natural log (highlighted in red) has a name. At the beginning of a reaction it is called the reaction quotient and is symbolized with the letter “Q”. If this ratio is determined at equilibrium, it is called the equilibrium constant “K”. Consequently, at equilibrium:

$$K = \exp \left(\frac{- \left\{ \sum_{\text{products}} \nu_i \cdot \mu_i - \sum_{\text{reactants}} \nu_i \cdot \mu_i \right\}}{RT} \right) = \exp \left(\frac{-\Delta_r G^\circ}{RT} \right) \quad (6.5.1)$$

Equation 6.5.1 reveals that a simple Hess's Law calculation can be used to determine $\Delta_r G^\circ$, which, in turn defines the equilibrium concentrations and reaction yield. It is important to note that this relationship was defined for a gas phase reaction and may not be rigorously true for a chemical process occurring in solution. These topics are discussed in Chapter 7

6.5.1 Temperature dependent equilibrium constants

There is a subtlety to Equation 6.18, which is that the equilibrium constant K is a function of $\Delta_r G^\circ$ and T, although $\Delta_r G^\circ$ is strictly defined from the data in Table 6.1 for T=298.15 K. Consequently, it isn't straightforward to determine how the equilibrium constant changes with temperature. To do so, we first note:

$$\Delta_r G^\circ = -RT \cdot \ln(K) \quad (6.5.2)$$

where T must be the standard state temperature. Our approach to determine the how K changes with temperature, and then add that change onto the standard state K, as determined where T = 25 °C. First, we rearrange Equation 6.19: $\ln(K) = \frac{-\Delta_r G^\circ}{RT}$ and take the temperature derivative:

$$\frac{\partial \ln(K)}{\partial T} = \frac{1}{R} \frac{\partial \frac{-\Delta_r G^\circ}{T}}{\partial T} = \frac{\Delta_r H^\circ}{RT^2}$$

using the Gibbs-Helmholtz equation. Next the partials are rearranged as: $\partial \ln(K) = \frac{\Delta_r H^\circ}{RT^2} \partial T$. This allows us to determine how K changes over a finite temperature range:

$$\int_{\ln[K(T_1)]}^{\ln[K(T_2)]} \partial \ln(K) = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} \partial T$$

Assuming $T_1 = T^\circ$ (the standard temperature), and following the established rules of integration:

$$\ln[K(T_2)] = \ln[K(T^\circ)] + \frac{\Delta_r H^\circ}{R} \left(\frac{T_2 - T^\circ}{T_2 \cdot T^\circ} \right) \quad (6.5.3)$$

Note that in the derivation of Equation 6.20 that the integration of the enthalpy did not include temperature dependence (the value of $\Delta_r H^\circ$ from a data table is valid only at T = 25 °C). We previously demonstrated how to account for enthalpy's temperature

dependence in Chapter 3 using the heat capacity; regardless, inclusion of this factor makes the final result very complex so we will stick with this approximation here.

Conclusion

In this chapter we revealed that the absolute value of energy, whether internal, enthalpic or Gibbs' energy, of a real chemical substance is unfortunately unknowable. This forces us to tabulate thermodynamic data relative to a standard state defined by the intensive variables pressure and temperature. We can use these data to predict reaction yields with good accuracy at the standard state. It is possible to obtain such information outside the standard state, say at a higher temperature, at the expense of performing somewhat more complex calculations. From here on we will now move away from gases and study chemical processes in condensed phases (liquid and solid). However, you will find our knowledge of thermodynamic processes becomes increasingly more abstract and inexact as a result.

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