

## 10.1: Reaction Quotient and Equilibrium Constant

Let's consider a prototypical reaction at constant  $T, P$ :



The Gibbs free energy of the reaction is defined as:

$$\Delta_{\text{rxn}} G = G_{\text{products}} - G_{\text{reactants}} = G^C + G^D - G^A - G^B, \quad (10.1.2)$$

and replacing the absolute Gibbs free energies with the chemical potentials  $\mu_i$ , we obtain:

$$\Delta_{\text{rxn}} G = c\mu_C + d\mu_D - a\mu_A - b\mu_B. \quad (10.1.3)$$

Assuming the reaction is happening in the gas phase, we can then use [Equation 9.4.6](#) to replace the chemical potentials with their value in the reaction mixture, as:

$$\begin{aligned} \Delta_{\text{rxn}} G &= c(\mu_C^\ominus + RT \ln P_C) + d(\mu_D^\ominus + RT \ln P_D) - a(\mu_A^\ominus + RT \ln P_A) - b(\mu_B^\ominus + RT \ln P_B) \\ &= \underbrace{c\mu_C^\ominus + d\mu_D^\ominus - a\mu_A^\ominus - b\mu_B^\ominus}_{\Delta_{\text{rxn}} G^\ominus} + RT \ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}. \end{aligned} \quad (10.1.4)$$

We can define a new quantity called the *reaction quotient* as a function of the partial pressures of each substance:<sup>1)</sup>

$$Q_P = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}, \quad (10.1.5)$$

and we can then simply rewrite [Equation 10.1.4](#) using [Equation 10.1.5](#) as:

$$\Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^\ominus + RT \ln Q_P. \quad (10.1.6)$$

This equation tells us that the sign of  $\Delta_{\text{rxn}} G$  is influenced by the reaction quotient  $Q_P$ . For a spontaneous reaction at the beginning, the partial pressures of the reactants are much higher than the partial pressures of the products, therefore  $Q_P \ll 1$  and  $\Delta_{\text{rxn}} G < 0$ , as we expect. As the reaction proceeds, the partial pressures of the products will increase, while the partial pressures of the reactants will decrease. Consequently, both  $Q_P$  and  $\Delta_{\text{rxn}} G$  will increase. The reaction will completely stop when  $\Delta_{\text{rxn}} G = 0$ , which is the chemical equilibrium point. At the reaction equilibrium:

$$\Delta_{\text{rxn}} G = 0 = \Delta_{\text{rxn}} G^\ominus + RT \ln K_P, \quad (10.1.7)$$

where we have defined a new quantity called **equilibrium constant**, as the value the reaction quotient assumes when the reaction reaches equilibrium, and we have denoted it with the symbol  $K_P$ .<sup>2</sup> From [Equation 10.1.7](#) we can derive the following fundamental equation on the standard Gibbs free energy of reaction:

$$\Delta_{\text{rxn}} G^\ominus = -RT \ln K_P. \quad (10.1.8)$$

To extend the concept of  $K_P$  beyond the four species in the prototypical reaction (10.1), we can use the product of a series symbol ( $\prod_i$ ), and write:

$$K_P = \prod_i P_{i,\text{eq}}^{\nu_i}, \quad (10.1.9)$$

where  $P_{i,\text{eq}}$  are the partial pressure of each species at equilibrium. Eq. (10.1.9) is in principle valid for ideal gases only. However, reaction involving ideal gases are pretty rare. As such, we can further extend the concept of equilibrium constant and write:

$$K_{\text{eq}} = \prod_i a_{i,\text{eq}}^{\nu_i}, \quad (10.1.10)$$

where we have replaced the partial pressure at equilibrium,  $P_{i,\text{eq}}$ , with a new concept introduced initially by Gilbert Newton Lewis (1875–1946),<sup>3</sup> that he termed **activity**, and represented by the letter  $a$ . For ideal gases, it is clear that  $a_i = P_i/P^\ominus$ . For non-ideal gases, the activity is equal to the fugacity  $a_i = f_i/P^\ominus$ , a concept that we will investigate in the next chapter. For pure liquids and solids, the activity is simply  $a_i = 1$ . For diluted solutions, the activity is equal to a measured concentration (such as, for example, the mole fraction  $x_i$  in the liquid phase, and  $y_i$  in the gas phase, or the molar concentration  $[i]/[i]^\ominus$  with  $[i]^\ominus = 1 \text{ [mol/L]}$ ). Finally

for concentrated solutions, the activity is related to the measured concentration via an activity coefficient. We will return to the concept of activity in chapter 14, when we will specifically deal with solutions. For now, it is interesting to use the activity to write the definition of the following two constants:

$$K_y = \prod_i (y_{i,\text{eq}})^{\nu_i} \qquad K_C = \left( \prod_i [i]_{\text{eq}} / [i]^\ominus \right)^{\nu_i}, \quad (10.1.11)$$

which can then be related with  $K_P$  for a mixture of ideal gases using:

$$P_i = y_i P \qquad P_i = \frac{n_i}{V} RT = [i] RT, \quad (10.1.12)$$

which then results in:

$$K_P = K_y \cdot \left( \frac{P}{P^\ominus} \right)^{\Delta\nu} \qquad K_P = K_C \left( \frac{[i]^\ominus RT}{P^\ominus} \right)^{\Delta\nu}, \quad (10.1.13)$$

with  $\Delta\nu = \sum_i \nu_i$ .

Using the general equilibrium constant,  $K_{\text{eq}}$ , we can also rewrite the fundamental equation on  $\Delta_{\text{rxn}} G^\ominus$  that we derived in Equation 10.1.8 to be applicable at most conditions, as:

$$\Delta_{\text{rxn}} G^\ominus = -RT \ln K_{\text{eq}}, \quad (10.1.14)$$

and since  $\Delta_{\text{rxn}} G^\ominus$  depends on  $T$ ,  $P$  and  $\{n_i\}$ , it is useful to explore how  $K_{\text{eq}}$  depends on those variables as well.

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1. Notice that since we used Equation 9.4.5 to derive the reaction quotient, the partial pressures inside it are always dimensionless since they are divided by  $P^\ominus$ .
  2. The subscript  $P$  refers to the fact that the equilibrium constant is measured in terms of partial pressures.
  3. Gilber Lewis is the same scientist that invented the concept of Lewis Structures.
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