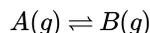


## 9.2: Chemical Potential

Equilibrium can be understood as accruing at the composition of a reaction mixture at which the aggregate chemical potential of the products is equal to that of the reactants. Consider the simple reaction



The criterion for equilibrium will be

$$\mu_A = \mu_B$$

If the gases behave ideally, the chemical potentials can be described in terms of the mole fractions of  $A$  and  $B$

$$\mu_A^o + RT \ln\left(\frac{p_A}{p_{tot}}\right) = \mu_B^o + RT \ln\left(\frac{p_B}{p_{tot}}\right) \quad (9.2.1)$$

where Dalton's Law has been used to express the mole fractions.

$$\chi_i = \frac{p_i}{p_{tot}}$$

Equation 9.2.1 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT \ln\left(\frac{p_B}{p_{tot}}\right) - RT \ln\left(\frac{p_A}{p_{tot}}\right) \quad (9.2.2)$$

Combining the logarithms terms and recognizing that

$$\mu_A^o - \mu_B^o - \Delta G^o$$

for the reaction, one obtains

$$-\Delta G^o = RT \ln\left(\frac{p_B}{p_A}\right)$$

And since  $p_A/p_B = K_p$  for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = RT \ln K_p$$

Another way to achieve this result is to consider the Gibbs function change for a reaction mixture in terms of the **reaction quotient**. The reaction quotient can be expressed as

$$Q_p = \frac{\prod_i p_i^{\nu_i}}{\prod_j p_j^{\nu_j}}$$

where  $\nu_i$  are the stoichiometric coefficients for the products, and  $\nu_j$  are those for the reactants. Or if the stoichiometric coefficients are defined by expressing the reaction as a sum

$$0 = \sum_i \nu_i X_i$$

where  $X_i$  refers to one of the species in the reaction, and  $\nu_i$  is then the stoichiometric coefficient for that species, it is clear that  $\nu_i$  will be negative for a reactant (since its concentration or partial pressure will reduce as the reaction moves forward) and positive for a product (since the concentration or partial pressure will be increasing.) If the stoichiometric coefficients are expressed in this way, the expression for the reaction quotient becomes

$$Q_p = \prod_i p_i^{\nu_i}$$

Using this expression, the Gibbs function change for the system can be calculated from

$$\Delta G = \Delta G^o + RT \ln Q_p$$

And since at equilibrium

$$\Delta G = 0$$

and

$$Q_p = K_p$$

It is evident that

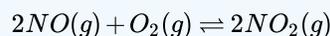
$$\Delta G_{rxn}^{\circ} = -RT \ln K_p \quad (9.2.3)$$

It is in this simple way that  $K_p$  and  $\Delta G^{\circ}$  are related.

It is also of value to note that the criterion for a spontaneous chemical process is that  $\Delta G_{rxn} < 0$ , rather than  $\Delta G_{rxn}^{\circ}$ , as is stated in many texts! Recall that  $\Delta G_{rxn}^{\circ}$  is a function of all of the reactants and products being in their standard states of unit fugacity or activity. However, the direction of spontaneous change for a chemical reaction is dependent on the composition of the reaction mixture. Similarly, the magnitude of the equilibrium constant is insufficient to determine whether a reaction will spontaneously form reactants or products, as the direction the reaction will shift is also a function of not just the equilibrium constant, but also the composition of the reaction mixture!

#### ✓ Example 9.2.1:

Based on the data below at 298 K, calculate the value of the equilibrium constant ( $K_p$ ) for the reaction



	$NO(g)$	$NO_2(g)$
$G_f^{\circ}$ (kJ/mol)	86.55	51.53

#### Solution

First calculate the value of  $\Delta G_{rxn}^{\circ}$  from the  $\Delta G_f^{\circ}$  data.

$$\Delta G_{rxn}^{\circ} = 2 \times (51.53 \text{ kJ/mol}) - 2 \times (86.55 \text{ kJ/mol}) = -70.04 \text{ kJ/mol}$$

And now use the value to calculate  $K_p$  using Equation 9.2.3.

$$-70040 \text{ J/mol} = -(8.314 \text{ J/(mol K)})(298 \text{ K}) \ln K_p$$

$$K_p = 1.89 \times 10^{12}$$

*Note:* as expected for a reaction with a very large negative  $\Delta G_{rxn}^{\circ}$ , the equilibrium constant is **very** large, favoring the formation of the products.

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