

20.2: 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

$$\mu_A = \mu_B \quad (20.2.2)$$

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

$$\mu_A^o + RT \ln \left(\frac{P_A}{P_{tot}} \right) = \mu_B^o + RT \ln \left(\frac{P_B}{P_{tot}} \right) \quad (20.2.3)$$

where [Dalton's Law](#) has been used to express the mole fractions.

$$\chi_i = \frac{P_i}{P_{tot}} \quad (20.2.4)$$

Equation 20.2.3 can be simplified by collecting all chemical potentials terms on the left

$$\mu_A^o - \mu_B^o = RT \ln \left(\frac{P_B}{P_{tot}} \right) - RT \ln \left(\frac{P_A}{P_{tot}} \right) \quad (20.2.5)$$

Combining the logarithms terms and recognizing that

$$\mu_A^o - \mu_B^o = -\Delta G^o \quad (20.2.6)$$

for the reaction, one obtains

$$-\Delta G^o = RT \ln \left(\frac{P_B}{P_A} \right) \quad (20.2.7)$$

And since the equilibrium constant is $P_A/P_B = K_P$ for this reaction (assuming perfectly ideal behavior), one can write

$$\Delta G^o = RT \ln K_P \quad (20.2.8)$$

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

$$Q_P = \frac{\prod_i P_i^{\nu_i}}{\prod_j P_j^{\nu_j}} \quad (20.2.9)$$

where ν_i are the stoichiometric coefficients for the products, and ν_j are those for the reactants. Or if the stoichiometric coefficients are defined by expressing the reaction as a sum

$$0 = \sum_i \nu_i X_i \quad (20.2.10)$$

where X_i refers to one of the species in the reaction, and ν_i is then the stoichiometric coefficient for that species, it is clear that ν_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

$$Q_P = \prod_i P_i^{\nu_i} \quad (20.2.11)$$

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

$$\Delta G = \Delta G^o + RT \ln Q_P \quad (20.2.12)$$

And since at equilibrium

$$\Delta G = 0 \quad (20.2.13)$$

and

$$Q_P = K_P \quad (20.2.14)$$

It is evident that

$$\Delta G_{rxn}^o = -RT \ln K_P \quad (20.2.15)$$

It is in this simple way that K_P and ΔG^o 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 ΔG_{rxn}^o , as is stated in many texts! Recall that ΔG_{rxn}^o 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 20.2.1:

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^o (kJ / mol)	51.53

Solution:

First calculate the value of ΔG_{rxn}^o from the ΔG_f^o data.

$$\Delta G_{rxn}^o = 2 \times (51.53 \text{ kJ/mol}) - 2 \times (86.55 \text{ kJ/mol}) = -70.04 \text{ kJ/mol} \quad (20.2.17)$$

And now use the value to calculate K_p using Equation [20.2.15](#)

$$-70040 \text{ J/mol} = -(8.314 \text{ J/(mol K)})(298 \text{ K}) \ln K_p \quad (20.2.18)$$

$$K_p = 1.89 \times 10^{12} \quad (20.2.19)$$

Note: as expected for a reaction with a very large negative ΔG_{rxn}^o , the equilibrium constant is **very** large, favoring the formation of the products.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)

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