Chemical Equilibrium

Chapter 9 of Atkins: Sections 9.1 - 9.2

Spontaneous Chemical Reactions

The Gibbs Energy Minimum
The reaction Gibbs energy
Exergonic and endergonic reactions

The Description of Equilibrium
Perfect gas equilibria
The general case of a reaction
The relation between equilibrium constants
molality and mole fractions

The Boltzmann Distribution

Introduction

The concept of the chemical potential is used to account for the equilibrium composition of chemical reactions.

Some forms in which we have seen the chemical potential:

\[ \mu_i = \mu_i^\circ + RT \ln \left( \frac{f_i}{P_i} \right) \]
\[ \mu_i = \mu_i^\circ + RT \ln (a_i) \]

The composition at equilibrium corresponds to a minimum in the Gibbs energy plotted against the extent of reaction. This provides a powerful and direct relationship between the equilibrium constant and the standard Gibbs energy of reaction.

Dynamic Equilibrium

Reactants \( \rightleftharpoons \) Products

Static equilibrium - forward and reverse processes have both ceased.
Dynamic equilibrium - both forward and reverse processes occur at the same rate.

rate of reaction

forward
reverse

time
Spontaneous Chemical Reactions

We have learned the general principle that at constant \( T \) and \( p \), the direction of spontaneous change is to lower values of Gibbs energy (\( G \)). This idea can be generalized to apply to discussions of chemical reactions as well.

Idea: Calculate the Gibbs energy of a reaction mixture and then identify the composition that corresponds to minimum \( G \).

The Extent of Reaction

Consider: \( A \rightarrow B \)

Suppose an infinitesimal amount \( d\xi \) of \( A \) turns into \( B \). Then:

\[
\begin{align*}
 dn_A &= -d\xi \\
 dn_B &= +d\xi
\end{align*}
\]

The quantity \( \xi \) is called the extent of reaction. The units are the same as \( n \), and therefore \( \xi \) is usually reported in moles. For a finite amount, write \( \Delta \xi \), and can then calculate:

\[
\begin{align*}
 n_A &= n_{iA} - \Delta \xi \\
 n_B &= n_{iB} + \Delta \xi
\end{align*}
\]

The Reaction Gibbs Energy, I

Remember that for this two component system:

\[
dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi
\]

So:

\[
\left( \frac{\partial G}{\partial \xi} \right)_p,T = \mu_B - \mu_A
\]

This is the difference between the chemical potentials of the reactants and products at the composition of the reaction mixture. Therefore it is natural to define the reaction Gibbs energy as the slope of the graph of the Gibbs energy vs. the extent of reaction:

\[
\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_p,T
\]

The Reaction Gibbs Energy, II

The chemical potential varies with composition, and therefore \( \Delta_r G \) changes as the reaction proceeds.

\( A \rightarrow B \) spontaneous when \( \mu_A > \mu_B \)

\( B \rightarrow A \) spontaneous when \( \mu_A < \mu_B \)

\( \Delta_r G = 0 \) when \( \mu_A = \mu_B \)

If we can find the composition of the reaction mixture where \( \mu_A = \mu_B \), then we can identify the composition at equilibrium.
Types of Reactions: Ability to Do Work

If we know $\Delta_r G$ at constant $T$ and $p$, then we know whether forward or reverse reaction is spontaneous.

$\Delta_r G > 0$, the reverse reaction is spontaneous

**Endergonic** - work consuming

$\Delta_r G < 0$, the forward reaction is spontaneous

**Exergonic** - work producing

$\Delta_r G = 0$, the reaction is at equilibrium

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Perfect Gas Equilibria, I

We will first examine the case of two perfect gases:

$$
\Delta_r G = \mu_b - \mu_a = (\mu_b^\circ + R T \ln p_b) - (\mu_a^\circ + R T \ln p_a)
$$

$$
= \Delta_r G^\circ + RT \ln \frac{p_b}{p_a}
$$

where:

$$
\Delta_r G^\circ = \mu_b^\circ - \mu_a^\circ
$$

The ratio of the partial pressures is denoted by $Q$:

$$
\Delta_r G = \Delta_r G^\circ + RT \ln Q
$$

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Perfect Gas Equilibria, II

We have seen the standard molar Gibbs energy of reaction before, and in practice it can be calculated from:

$$
\Delta_r G^\circ = \Delta_f G^\circ (B) - \Delta_f G^\circ (A)
$$

So these are tabulated (huge array of thermodynamic tables like Table 2.6 in Atkins, 7th Ed.)

At equilibrium, $\Delta_r G = 0$:

$$
0 = \Delta_r G^\circ + R T \ln K
$$

$$
R T \ln K = -\Delta_r G^\circ
$$

equilibrium constant

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The Importance of Mixing

The position of the equilibrium composition depends upon the mixing of the products and reactants.

If no mixing, then a linear change in Gibbs energy from that of pure A to pure B (slope depends on overall difference, position then depends on amount of B). The exact slope is:

$$
\Delta_r G = nRT(x_A \ln x_A + x_B \ln x_B)
$$

But we have seen that if the mixing is complete for ideal gases, then:

$$
\Delta_r G = nRT(x_A \ln x_A + x_B \ln x_B)
$$

Now a minimum occurs and its position marks the equilibrium composition.
General Reactions

To generalize the idea of extent of reaction:
Consider the reaction:

\[ 2A + B \rightarrow 3C + D \]

Which we can rewrite as

\[ 0 = -2A - B + 3C + D \]

In a more general form,

\[ 0 = \sum v_J f \]

And in the above reaction

\[ v_A = -2 \quad v_B = -1 \quad v_C = +3 \quad v_D = +1 \]

Stoichiometric numbers are positive for products and negative or reactants. Then we modify the definition of \( \xi \) so that if it changes by \( \Delta \xi \) then the change in the amount of any species \( J \) is \( \nu_J \Delta \xi \).

The General Reaction Gibbs Energy, I

For a reaction with known stoichiometric numbers, \( \nu_J \), the reaction can advance by \( d\xi \) and the amounts of reactants/products changes by:

\[ dn_J = \nu_J d\xi \]

Then:

\[ dG = \mu_J d\xi \]

Since:

\[ \Delta rG = \left( \frac{\partial G}{\partial \xi} \right)_p,T = \nu_J \mu_J \]

and in general we write:

\[ \mu_J = \mu_J^0 + RT \ln a_J \]

then we can obtain a general expression for \( \Delta rG \).

The General Reaction Gibbs Energy, II

Remember that:

\[ \ln x = \ln x^a \quad \ln x + \ln y + c = \ln xy + c \]

A general expression for \( \Delta rG \):

\[ \Delta rG = \sum \nu_J \mu_J = \sum \nu_J \left( \mu_J^0 + RT \ln a_J \right) \]

\[ = \sum \nu_J a_J^0 + \sum \nu_J RT \ln a_J \]

\[ = \Delta rG^0 + RT \sum \ln a_J^0 \]

\[ = \Delta rG^0 + RT \ln \prod a_J^0 \]

\[ = \Delta rG^0 + RT \ln Q \]

At equilibrium:

\[ K = \left( \prod a_J^0 \right)_{equilibrium} \]

And now drop the “equilibrium” subscript.

This is a thermodynamic equilibrium constant, defined in terms of activities or fugacities (for gas phase species). Since \( a_J \) and \( f_J \) are dimensionless, then \( K \) (and \( Q \)) are also dimensionless.

Approximations made in earlier classes may have included substituting molar concentration for activities, and partial pressures for fugacities.
A Most Useful and Important Result

At equilibrium (\(\Delta_r G = 0\))

\[ RT \ln K = -\Delta_r G^\circ \]

Some useful things to do:
- Given standard Gibbs energies of formation for reactants and products, calculate \(K\).
- Given \(K\), calculate extent of reaction (such as degree of dissociation)

Relation to Molalities/Mole Fractions

We use the definitions of activities in terms of mole fractions or molalities:

\[ a_j = \gamma_j x_j \quad a_j = \gamma_j \frac{b_j}{b_j^\circ} \]

For the reaction:

\[ A + B \rightarrow C + D \]

we write:

\[
K = \frac{a_C a_D}{a_A a_B} = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{x_C x_D}{x_A x_B} \\
= \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \frac{b_C b_D}{b_A b_B} = K \gamma \]

This can be a complicated set of calculations, since activity coefficients can vary with composition, and must be evaluated at the equilibrium composition. Often, we start with the assumption:

\[ K = 1 \]
Molecules of either reactants or products exist in particular energy states. Placement of atoms, electrons, etc. lead to a distribution of possible energy states for the reactants and products, and the distribution of populations within these states (in a particularly useful picture) are given at equilibrium by the Boltzmann distribution. In the field of statistical mechanics (or here, statistical thermodynamics) it is found that the population in the state with energy \( E \) follows a well-defined form:

\[
P_n \propto \exp\left(-\frac{E}{kT}\right)
\]

The Boltzmann Distribution

\[
\frac{P_n}{P_m} = \exp\left(-\frac{E_n - E_m}{kT}\right)
\]

- \( P_n \propto \exp\left(-\frac{E_n}{kT}\right) \)
- \( \frac{P_n}{P_m} = \exp\left(-\frac{E_n - E_m}{kT}\right) < 1 \) if \( E_n > E_m \) and \( T > 0 \)
- \( \frac{P_n}{P_m} = 1 - \frac{\Delta E}{kT} \) if \( kT >> \Delta E \) (high T approx.)

Here, \( \Delta E \) is the energy difference between states \( n \) and \( m \), and \( k \) is the Boltzmann constant. The Boltzmann distribution describes how the population is distributed across energy states, with higher populations in states of lower energy.