Equilibrium

CHEM 361A: Introduction to Physical Chemistry

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Lecture 11

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Learning Objective: Show that minimizing the Gibbs Free Energy of a mixture can determine equilibrium concentrations of the components of the mixture and derive how shifts in conditions affect this equilibrium

References:

- Atkins and de Paula Focus 5A - 5C
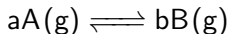- Chang Chapter 9

When the Mixtures React

At constant temperature and pressure, a reaction mixture tends to adjust its composition until its Gibbs Free Energy is a minimum.
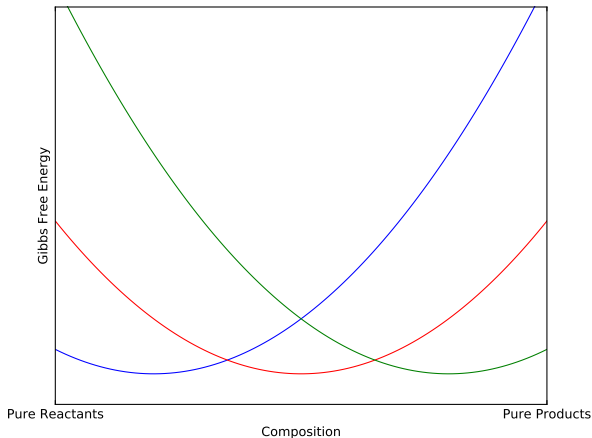
When the system is at a minimum, it is said to be in **equilibrium**

In the Context of a Chemical Reaction

A generic chemical reaction can be expressed as:

$$aA(g) \rightleftharpoons bB(g)$$

The change in Gibbs Free Energy for this process can be expressed as:

$$dG = \mu_A dn_A + \mu_B dn_B$$

Since dn_i can be different for each species, we will instead use a common term $d\xi$ to denote the infinitesimal extent of reaction:

$$dG = -a\mu_A d\xi + b\mu_B d\xi$$

where we explicitly give the reactants negative signs to denote that as they are consumed. Dividing both sides by $d\xi$ and assuming constant temperature and pressure:

$$\left(\frac{dG}{d\xi} \right)_{T,P} = b\mu_B - a\mu_A$$

Defining the Direction of the Reaction

$$\left(\frac{dG}{d\xi}\right)_{T,P} = \Delta_r G = b\mu_B - a\mu_A$$

This relationship leads to the following conclusions:

$\mu_{react} > \mu_{prod}$ $\Delta_r G < 0$ Forward reaction is spontaneous

$\mu_{react} = \mu_{prod}$ $\Delta_r G = 0$ System at Equilibrium

$\mu_{react} < \mu_{prod}$ $\Delta_r G > 0$ Reverse reaction is spontaneous

Review of Activities for Real Solutions

For substances, the chemical potential can be written as:

$$\mu_J = \mu_J^{\ominus} + RT \ln a_J$$

where a_J is the activity of the substance. Activities are dimensionless quantities, where the reference chemical potential is in the standard state and γ indicates the deviation from ideal conditions:

Substance	Standard State	Activity, a
Solid	Pure Solid, 1 bar	1
Liquid	Pure Liquid, 1 bar	1
Gas	Pure Gas, 1 bar	$\gamma p/p^{\ominus}$
Solute	Molal concentration of 1 mol kg^{-1}	$\gamma m/m^{\ominus}$
Solute	Molar concentration of 1 mol dm^{-3}	$\gamma[J]/c^{\ominus}$
Solvent	Pure Liquid, 1 bar	γx_A

Chemical Potential of Mixtures

Using activities we can write

$$\Delta_r G = b(\mu_B^\ominus + RT \ln a_B) - a(\mu_A^\ominus + RT \ln a_A)$$
$$= (b\mu_B^\ominus - a\mu_A^\ominus) + RT(b \ln a_B - a \ln a_A)$$

We know that $\Delta_r G^\ominus = b\mu_B^\ominus - a\mu_A^\ominus$ and rearrange the ln terms to get

$$\Delta_r G = \Delta_r G^\ominus + RT \ln \frac{a_B^b}{a_A^a}$$

We can define the **reaction quotient**, Q, as

$$Q = \frac{a_B^b}{a_A^a}$$

Giving the expression

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

The Equilibrium Constant

When the system is at equilibrium ($\Delta_r G = 0$) a special case for the reaction quotient is defined (such that $Q = K$):

$$0 = \Delta_r G^{\ominus} + RT \ln K$$
$$\Delta_r G^{\ominus} = -RT \ln K$$

K is the **equilibrium constant**. This expression is a very important relationship since:

- Thermodynamic properties of the constituent parts can predict the equilibrium concentration of the mixture.
- The measurement of K allows for a quantification of $\Delta_r G^{\ominus}$.

The Equilibrium Composition of the Haber-Bosch Process

The Haber-Bosch Process is one of the most important chemical reactions in the progress of the human species:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
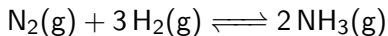
1. Find $\Delta_r G^\ominus$ for this reaction
2. Determine K for this process at 298 K.
3. For an industrial process, suppose that 1.00 bar of N_2 is mixed with 3.00 bar of H_2. Determine the equilibrium concentration of all the reactants and products.

   Hint: Use an ICE table

Le Chatelier's Principle

Le Chatelier's Principle is defined as:

Le Chatelier's Principle

When a system at equilibrium is subjected to a disturbance, the composition of the system adjusts so as to tend to minimize the effect of the disturbance.

- Le Chatelier's Principle is a qualitative rule of thumb
- Temperature is the only disturbance that changes the equilibrium constant K (by modifying $\Delta_r G^{\ominus}$)
- All disturbances shift the reaction in order to return to K

The Effect of a Catalyst on Equilibria

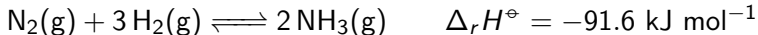To determine the effect of a catalyst on the composition of the equilibrium mixture recall that:

$$0 = \Delta_r G^{\ominus} + RT \ln K$$

- Since $\Delta_r G^{\ominus}$ is a state function, the pathway that the reaction takes is irrelevant to K
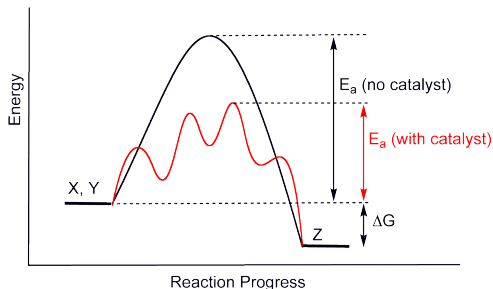
The Effect of Temperature Changes on Equilibria

Consider the Haber-Bosch process

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta_r H^{\ominus} = -91.6 \text{ kJ mol}^{-1}$$

How would an increase in temperature change the composition of the equilibrium?

- Le Chatelier's Principle tells us that by increasing temperature (and as a consequence heat), the equilibrium will shift left to consume the added heat and favour more reactants.

Quantifying the Modification to K with changes in Temperature

Recall the Gibbs-Helmholtz Equation

$$\left(\frac{\partial}{\partial T} \left[\frac{\Delta_r G^{\ominus}}{T} \right] \right)_p = -\frac{\Delta_r H^{\ominus}}{T^2}$$

If we substitue in the equilibrium expression

$$\left(\frac{\partial}{\partial T} \left[\frac{-RT \ln K}{T} \right] \right)_p = -\frac{\Delta_r H^{\ominus}}{T^2}$$

$$\left(\frac{\partial}{\partial T} \left[\ln K \right] \right)_p = \frac{\Delta_r H^{\ominus}}{RT^2}; \quad \text{van't Hoff equation}$$

Quantifying the Modification to K with changes in Temperature (cont.)

If we can assume that $\Delta_r H^{\ominus}$ do not change significantly over the change in temperature then we can integrate both sides so that the change in K can be quantified as:

$$\int_{K_1}^{K_2} d \ln K = \int_{T_1}^{T_2} \frac{\Delta_r H^{\ominus}}{RT^2} dT$$

$$\ln K \Big|_{K_1}^{K_2} = \frac{\Delta_r H^{\ominus}}{R} \left(\frac{-1}{T} \right) \Big|_{T_1}^{T_2}$$

$$\ln K_2 - \ln K_1 = \frac{\Delta_r H^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Effect of Temperature Changes on Haber-Bosch Process

Recall the Haber-Bosch process

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
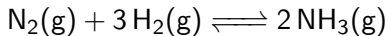
- $\Delta_r H^\ominus = -91.6$ kJ mol^{-1} at 298 K
- $\Delta_r G^\ominus = -32.9$ kJ mol^{-1} at 298 K

1. Calculate the equilibrium constant K for this process when T = 463 K.

2. For an industrial process, suppose that 1.00 bar of N_2 is mixed with 3.00 bar of H_2. Determine the equilibrium concentration of all the reactants and products.

   Hint: Use an ICE table

The Effect of Pressure Changes

Continuing with the Haber-Bosch process

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
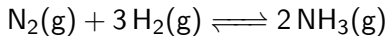
How would an increase in pressure due to compression affect the composition of the gas-phase equilibrium?

- Le Chatelier's Principle tells us that by increasing the pressure through a compression of all species, the equilibrium will favour the side of the reaction with the fewer number of moles of gas. Therefore, the equilibrium shifts right.

Quantifying the Change in Equilibrium Composition due to Pressure Changes

Note that

$$\ln K \propto \Delta_r G^{\ominus}$$

Since $\Delta_r G^{\ominus}$ is defined to be at 1 bar, **changes in pressure do not affect K.**

- However, equilibrium compositions are affected by changes in pressure.

Compressing the Haber-Bosch Process

1. An increase in temperature is applied to increase the rate of the reaction, however, it also shifted the equilibrium composition left (relative to room temperature) to favour the reactants. If this process were performed at 4 times the pressure and at 463 K, predict the equilibrium composition of the mixture.

   Hint: Use an ICE table

Summary

- Chemical reactions, like mixtures, minimize their chemical potential until equilibrium is established

$$\Delta_r G^{\ominus} = -RT \ln K$$

- Le Chatelier's Principle states that when a system at equilibrium is subjected to a disturbance, the composition of the system adjusts so as to tend to minimize the effect of the disturbance.
    - Only temperature modifies the equilibrium constant

$$\ln K_2 - \ln K_1 = \frac{\Delta_r H^{\ominus}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$