

Lecture No:1

CHEMICAL EQUILIBRIUM

In P.Chem I, you have studied systems composed of a pure substance or a mixture with fixed composition. If there is a chemical reaction, then the composition and the thermodynamic properties of the system change.

1. Chemical Potential

For a pure substance or for a mixture of fixed composition;

$$dG = -SdT + VdP$$

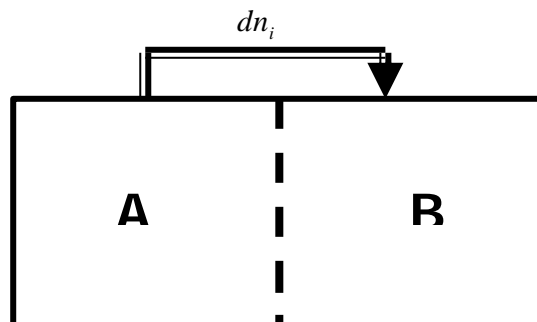
If the mole numbers of the substances in the system vary;

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 + \dots$$

The chemical potential of i , μ_i is the increase in free energy per mole of the substance added;

$$\mu_i = \left(\frac{dG}{dn_i}\right)_{T,P,n_j}$$

1.1 Spontaneity



The total free energy change for the system is;

$$dG = dG^A + dG^B = -m_i^A dn_i + m_i^B dn_i = (m_i^B - m_i^A) dn_i$$

If $m_i^A > m_i^B$, the transfer occurs spontaneously. Substance i flows spontaneously from a region of high m_i to a region of low m_i

1.2 Properties of Chemical Potential

Chemical potential is an intensive property. It has the same value at every point within a system at equilibrium.

The addition rule is a very important property of chemical potentials.

$$G = \sum n_i m_i$$

If the system contains only one substance;

$$G = nm \quad \text{or} \quad m = \frac{G}{n}$$

The chemical potential of a pure substance is simply its molar free energy.

1.3 Chemical Potential of Gases

The chemical potential of a pure ideal gas is equal to its molar free energy;

$$m = m^\circ(T) + RT \ln P$$

At a given temperature, the pressure is a measure of the chemical potential of an ideal gas.

The chemical potential for a real gas is;

$$m = m^\circ(T) + RT \ln f$$

The function f is the fugacity of the gas. It is a function of temperature and pressure. Fugacity is a measure of the chemical potential of a real gas.

1.4 Chemical Potential in an Ideal Gas Mixture

Consider the system below. One side contains pure H₂, the other side contains an ideal mixture of N₂+H₂. When equilibrium is attained, the pressure of the pure H₂ is equal to the partial pressure of H₂ in the mixture. The equilibrium condition is;

$$m_{H_2}(pure) = m_{H_2}(mixture)$$

$$m_{H_2}(mixture) = m^o_{H_2}(T) + RT \ln p_{H_2}$$

By using Dalton's Law;

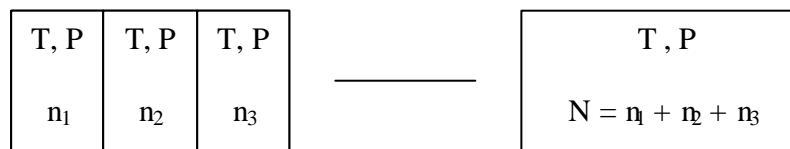
$$m_{H_2}(mixture) = m^o_{H_2}(T) + RT \ln x_i P$$

$$m_{H_2}(mixture) = m^o_{H_2}(T, P) + RT \ln x_i$$

The chemical potential of any gas in a mixture is always less than the chemical potential of the pure gas under the same total pressure.

2. Free Energy and Entropy of Mixing

The formation of a mixture from the pure constituents occurs spontaneously.



The free energy of the initial state is;

$$G_{initial} = n_1 m_1^o + n_2 m_2^o + n_3 m_3^o$$

The free energy of the final state is;

$$G_{final} = n_1 m_1 + n_2 m_2 + n_3 m_3$$

The free energy of mixing is;

$$\Delta G_{mix} = G_{initial} - G_{final} = n_1 (m_1 - m_1^o) + n_2 (m_2 - m_2^o) + n_3 (m_3 - m_3^o)$$

For any substance i in the mixture;

$$m_i - m_i^o = RT \ln x_i$$

$$\Delta G_{mix} = RT(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3) = NRT \sum x_i \ln x_i$$

Since all of the terms on the right-hand side are negative, the sum is always negative. If there are only two substances, a plot of ΔG_{mix} has a minimum at $x=1/2$.

Differentiation of ΔG_{mix} with respect to temperature yields the entropy of mixing;

$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{P, n_i} = -NR \sum_i x_i \ln x_i$$

The minus sign means that the entropy of mixing is always positive. A plot of the entropy of mixing of a binary mixture gives a curve with a maximum at $x=1/2$.

The heat of mixing may be calculated by using the equation;

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$

There is no heat effect associated with the formation of an ideal mixture. The only effect that changes the free energy of mixing is the entropy effect. If the substances are to mix spontaneously' the heat of mixing must be either;

$$\Delta H_{mix} < 0 \quad \text{or} \quad |\Delta H_{mix}| < |T\Delta S_{mix}|$$

The volume of mixing may be obtained by differentiating ΔG_{mix} with respect pressure;

$$\Delta V_{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial P}\right)_{T, n_i} = 0$$

Ideal mixtures are formed without any volume change.