Lecture #12

Mixing Process

The formation of a mixture from the pure constituents occurs spontaneously. Our object is to calculate the free energy of mixing. Suppose we mix three pure substances keeping the temperature and pressure constant.

T, P	T, P	T, P
n_1	n_2	n_3

$\longrightarrow$

T, P
$N = n_1 + n_2 + n_3$

Free Energy of Mixing

The free energy of the initial state is the sum of the free energies of the pure substances.

$$G_{initial} = G_1 + G_2 + G_3$$
$$= n_1\mu_1^{\,o} + n_2\mu_2^{\,o} + n_3\mu_3^{\,o} = \sum n_i \mu_i^{\,o}$$

The free energy of the final state is;

$$G_{final} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3$$

Since G is a state function, the free energy of mixing is;

$$\Delta G_{mixing} = G_{final} - G_{initial}$$
$$= n_1\mu_1 + n_2\mu_2 + n_3\mu_3 - n_1\mu_1^{\,o} - n_2\mu_2^{\,o} - n_3\mu_3^{\,o}$$
$$= n_1(\mu_1 - \mu_1^{\,o}) + n_2(\mu_2 - \mu_2^{\,o}) + n_3(\mu_3 - \mu_3^{\,o})$$

The chemical potential of a substance in the mixture is;

$$\mu_i = \mu_i^{\,o} + RT \ln x_i$$

By using this equation, we may express free energy of mixing as;

$$\Delta G_{mixing} = RT(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3)$$

$$n_i = x_i N$$

$$\Delta G_{mixing} = NRT \sum x_i \ln x_i$$

All of the terms on the right-hand side of this equation are negative. So, the sum is always negative.

If there are only two substances in the mixture, a plot of ΔG_{mixing} has a minimum at x=1/2. The greatest decrease in free energy on mixing is obtained when equal numbers of moles of the two substances are mixed.

Entropy of Mixing

Differentiation of ΔG_{mixing} with respect to temperature yields ΔS_{mixing} ;

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

$$\Delta S_{mixing} = -NR \sum_i x_i \ln x_i$$

The minus sign means that the entropy of mixing is always positive. The positive entropy of mixing corresponds to the increase in randomness which occurs in mixing the molecules of several kinds. A plot of the entropy of mixing of a binary mixture gives a curve with a maximum at x=1/2.

Heat of Mixing

We may calculate the heat of mixing by using the equation;

$$\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$$

Substituting the values for ΔG_{mixing} and ΔS_{mixing},

$$NRT\sum_{i} x_i \ln x_i = \Delta H_{mixing} + TNR\sum_{i} x_i \ln x_i$$

and we obtain;

$$\Delta H_{mixing} = 0$$

There is no heat effect associated with the formation of an ideal mixture. Using this result, we may write;

$$\Delta G_{mixing} = -T\Delta S_{mixing}$$

This equation shows that the only effect that changes the free energy of mixing is the entropy effect. The mixed state is a more random state and therefore is a more probable state. The heat of mixing must be either;

$$\Delta H_{mixing} = 0 \qquad \text{or} \qquad \left|\Delta H_{mixing}\right| < \left|T\Delta S_{mixing}\right|$$

if the substances are to mix spontaneously. If not, then $\Delta G_{mixing} > 0$ and the substances do not mix spontaneously, they are not miscible, but remain in two distinct layers.

Volume of Mixing

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

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

The free energy of mixing is independent of pressure, so the derivative is zero.

$$\Delta V_{mixing} = 0$$

Thus, we may conclude that ideal mixtures are formed without any volume or energy change but with an increase in entropy and a decrease in free energy.