

#### ④ Free Energy of Mixing

For a solution to form, the free energy change when two substances are mixed must be negative. The sign of ~~as soon~~ as spontaneous process. This free energy change is known as the free energy of mixing  $\Delta G^M$ .

Considering the formation of a solution between two substances, A and B, where  $X_A$  moles of A and  $X_B$  moles of B, so that  $X_A + X_B = 1$  and  $a_A, a_B$  the ~~activity~~ activities of A and B in the solution. The free energy changes per mole of solution when the pure substances are dissolved in the solution are:-

$$\Delta G_A^M = X_A RT \ln \frac{a_A}{1} \quad \left| \begin{array}{l} \text{because the activity of A and B} \\ \text{change from 1 to } a_A \text{ and to } a_B \\ \text{respectively.} \end{array} \right.$$
$$\Delta G_B^M = X_B RT \ln \frac{a_B}{1}$$

The total free energy change  $\Rightarrow \Delta G^M = \Delta G_A^M + \Delta G_B^M$

For an ideal solution  $a_A = X_A$  and  $a_B = X_B$  and the free energy of mixing is:

$$\Delta G^M = X_A RT \ln X_A + X_B RT \ln X_B$$

#### Regular Solution

\* when two substances form an ideal solution, there will be no change in enthalpy:  $\Delta G^M = \Delta H^M - T \Delta S^M$

and as ①  $\Delta H^M = 0$

②  $\Delta G^M = -T \Delta S^M \Rightarrow \Delta S^M = -\frac{\Delta G^M}{T}$

$\therefore \Delta S^M = -X_A R \ln X_A - X_B R \ln X_B$

③  $X_i = a_i$

\* For non-ideal solution

①  $X_i \neq a_i$

②  $\Delta H^M \neq 0$  (because there will be heat changes due to changes in bonding energy.)

③ it is still possible to assume random mixing in certain cases.

## (\*) Regular solution

$$\textcircled{1} \Delta H^M \neq 0, \Delta S^M = \Delta S^M \text{ id}$$

+ for regular solutions the entropy of mixing is the same as for ideal solution, so that

$$\Delta S^M = -R(x_A \ln x_A + x_B \ln x_B) \quad \textcircled{1}$$

$$\Delta G^M = RT(x_A \ln a_A + x_B \ln a_B) \quad \textcircled{2}$$

$$\Delta H^M = \Delta G^M + T\Delta S^M$$

$$= RT(x_A \ln a_A + x_B \ln a_B) - RT(x_A \ln x_A + x_B \ln x_B)$$

$$= RT(x_A \ln \frac{a_A}{x_A} + x_B \ln \frac{a_B}{x_B}) \quad \textcircled{3}$$

$$= RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

where  $\gamma_A$  and  $\gamma_B$  are the activity coefficients of A and B.

## CHAPTER 4

(\*) Reaction kinetics: includes the study of the influence of variables such as temperature and concentration on reaction rates.

There are two types of reaction:-

① Homogeneous reaction:- take place entirely within one phase such as reactions between gas molecules to produce gaseous products, or reactions in an aqueous solution where the reactants and products all remain dissolved in water.

② Heterogeneous reaction:- involve more than one phase, such as the transfer of a substance from liquid slag to a liquid metal in a smelting process or the reaction between gaseous oxygen and solid metal to form an oxide film on the metal surface.

(\*) order of the reaction:- the sum of the power to which the concentrations of the reacting atoms or molecules must be raised to determine the rate of reaction.

(\*) Molecularity of the reaction:- The number of atoms or molecules taking part in a reaction.