

## ***PROPERTIES OF SOLUTIONS***

### Thermodynamics of Mixing of Liquids

#### **Liquid Mixtures**

##### **Ideal solutions**

We know the Gibbs energy of mixing two liquids, A and B is:

$$\Delta_{mix} G^{ideal} = nRT (x_A \ln x_A + x_B \ln x_B);$$

and that the entropy change is

$$\Delta_{mix} S^{ideal} = -nR (x_A \ln x_A + x_B \ln x_B),$$

which implies the enthalpy of mixing is zero.

Ideal Solution theory assumes A-A, A-B, and B-B interactions are all equal.

In general (*i.e.*, in real solutions) this is obviously not true. In general A-A, A-B, and B-B are all different, and hence the enthalpy of mixing is may be zero.

Also the arrangement of the molecules of A and B might increase or decrease entropy.

If the enthalpy change is large and positive (strongly endothermic) and/or entropy change is large and positive (*e.g.*, through clustering), the Gibbs energy of mixing may be positive.

That is, mixing is not spontaneous: the liquids separate or remain separate (*e.g.*, oil/water mixtures).

##### **The Excess Function**

Defined as the thermodynamic difference between ideal and real behaviour.

$$\text{Excess entropy, } S^E = \Delta_{mix} S - \Delta_{mix} S^{ideal}$$

Excess enthalpy and excess volume changes = observed  $\Delta_{mix} H$  and  $\Delta_{mix} V$  (since ideally these are both zero).

The magnitude of the excess indicates the degree of non-idealness.

### Regular Solution

A useful model: the molecules A and B are mixed randomly, but the interaction energies of A-A, A-B, and B-B are all different. That is, for a regular solution:

$$\Delta_{\text{mix}}H \neq 0, \text{ but } \Delta_{\text{mix}}S = 0.$$

### Colligative Properties

*E.g.*, elevation/suppression in boiling and freezing points, osmotic pressure, *etc.*

On mixing A and B, for example, the entropy of A increases. Therefore, the chemical potential of liquids reduces in the presence of a solute from  $\mu_A^*$  to  $\mu_A + RT \ln x_A$  (reduced since  $\ln x_A$  in a mixture is  $< 1$ ).

The change reflects a new equilibrium temperature for the phase transition.

### Boiling Point Elevation (at const $p$ )

Solvent A mixes with solute B.

Equilibrium is established at a temperature where:

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

The presence of the mole-fraction  $x_B$  causes  $T$  to change from  $T^*$  to  $T^* + \Delta T$ , where

$$\text{Since } K = \frac{RT^{*2}}{\Delta_{\text{vap}}H}, \quad \Delta T = Kx_B$$

### Depression of Freezing Point

Here we have equilibrium between pure solid solvent A and its solution with solute B with mole-fraction  $x_B$ . Equilibrium implies that at the freezing point both chemical potentials are equal.

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

The presence of the mole-fraction  $x_B$  causes  $T$  to change from  $T^*$  to  $T^* + \Delta T$ , where

$$\text{Since } K = \frac{RT^{*2}}{\Delta_{\text{vap}}H}, \quad \Delta T = Kx_B$$