5. Simple mixtures

The thermodynamic description of mixtures

- **5.1** Partial molar quantities
- **5.2** The thermodynamics of mixing
- **5.3** The chemical potentials of liquids

Thermodynamic description of mixtures

5.1 Partial molar quantities

(a) Partial molar volume

The change in volume per mole of a substance added to a large volume of the mixture

- *it varies with composition* (see Fig. 5.1)
- definition: $V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$ for a substance J

where p, T and amount of other components (n') are constant

- for a binary mixture,
$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

= $V_A dn_A + V_B dn_B$

Provided the composition is held constant by the addition of A and B, the total volume, $V = n_A V_A + n_B V_B$



Fig. 5.1 The partial molar volumes of water and ethanol at 25°C. Note the different scales (water on the left, ethanol on the right).

5.1 Partial molar quantities

$$V_{J} = \left(\frac{\partial V}{\partial n_{J}}\right)_{p,T,n}$$

1

 Molar volumes are always positive but partial molar volumes can be negative! (see Fig. 5.2 & 5.5)



32

0

Fig. 5.2 The partial molar volume of a substance is the slope of the variation of the total volume of the sample plotted against the composition. In general, partial molar quantities vary with the composition, as shown by the different slopes at the compositions *a* and *b*. Note that the partial molar volume at *b* is negative: the overall volume of the sample decreases as A is added.

Fig. 5.5 The partial molar volumes of the components of an aqueous solution of potassium sulfate.

0.05

 $b/(\text{mol kg}^{-1})$

18.075

0.1

5.1 Partial molar quantities

(b) Partial molar Gibbs energies

For a pure substance, the chemical potential $\mu = G_m$

For a substance in a mixture,
$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$
 (see Fig. 5.4)

For a binary mixture (with constant *p*, *T* and *n*')

 $G = n_A \mu_A + n_B \mu_B$ For a multi-component system,

 $dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$ Fundamental equation of chemical thermodynamics

At constant p and T,

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

Since $dG = dw_{add,max}$, additional (non-expansion) maximum work can arise from the changing composition of a system.



Fig. 5.4 The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition, as shown for the two values at *a* and *b*. In this case, both chemical potentials are positive.

5.1 Partial molar quantities

(c) The wider significance of the chemical potential
: Since
$$G = H - TS = U + PV - TS$$
,
 $dU = -pdV - Vdp + SdT + TdS + dG = -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots)$
 $= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \cdots$
At constant V and S, $dU = \mu_A dn_A + \mu_B dn_B + \cdots$
Hence, $\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$ In the same way, $\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}$, $\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}$

(d) The Gibbs-Duhem equation:

At constant p and T, for a binary system, $n_A d\mu_A + n_B d\mu_B = 0$ since $dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$, while $dG = \mu_A dn_A + \mu_B dn_B$ $\sum_J n_J d\mu_J = 0$: Gibbs-Duhem equation In a binary mixture, $d\mu_B = -\frac{n_A}{n_B} d\mu_A$

5.2 The thermodynamics of mixing

(a) The Gibbs energy of mixing of perfect gases

For a mixture of two perfect gases,

 $\mu = \mu^{o} + RT \ln \frac{p}{p^{o}}$ where μ^{o} is the standard chemical potential

The Gibbs energy of total system is,

$$G_{i} = n_{A}\mu_{A} + n_{B}\mu_{B} = n_{A}\left(\mu_{A}^{o} + RT\ln\frac{p}{p^{o}}\right) + n_{B}\left(\mu_{B}^{o} + RT\ln\frac{p}{p^{o}}\right)$$

Let $p/p^{o} = p$, $G_{i} = n_{A}\left\{\mu_{A}^{o} + RT\ln p\right\} + n_{B}\left\{\mu_{B}^{o} + RT\ln p\right\}$

After mixing,
$$p_A + p_B = p$$

 $G_f = n_A \left\{ \mu_A^o + RT \ln p_A \right\} + n_B \left\{ \mu_B^o + RT \ln p_B \right\}$

The difference $G_f - G_i = \Delta_{mix}G$, $\Delta_{mix}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$ Using Dalton's law (see Section 1.2), $p_J/p = x_J$,

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B) \qquad \text{(see Fig. 5.7)}$$



Fig. 5.7 The Gibbs energy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The Gibbs energy of mixing is negative for all compositions and temperatures, so perfect gases mix spontaneously in all proportions.

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(b) Other thermodynamic mixing functions

Entropy of mixing for two perfect gases (see Fig. 5.9)

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR\left(x_A \ln x_A + x_B \ln x_B\right)$$

Enthalpy of mixing

$$\Delta_{mix} H = 0 \qquad \text{since } \Delta G = \Delta H - T \Delta S$$



Fig. 5.9 The entropy of mixing of two perfect gases and (as discussed later) of two liquids that form an ideal solution. The entropy increases for all compositions and temperatures, so perfect gases mix spontaneously in all proportions. Because there is no transfer of heat to the surroundings when perfect gases mix, the entropy of the surroundings is unchanged. Hence, the graph also shows the total entropy of the system plus the surroundings when perfect gases mix.

(a) Ideal solutions

Chemical potentials are equal at equilibrium (see Fig. 5.10) $\mu_A^* = \mu_A^o + RT \ln p_A^*$ If a solute is also present in the liquid,

 $\mu_A = \mu_A^{o} + RT \ln p_A$ By combining two equations,

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

Raoult's law for ideal solution

 $p_A = x_A p_A^*$

For an ideal solution, $\mu_A = \mu_A^* + RT \ln x_A$

Some solutions seriously deviating from Raoult's law However, a good approximation for a solvent with a dilute solute!



Fig. 5.10 At equilibrium, the chemical potential of the gaseous form of a substance A is equal to the chemical potential of its condensed phase. The equality is preserved if a solute is also present. Because the chemical potential of A in the vapour depends on its partial vapour pressure, it follows that the chemical potential of liquid A can be related to its partial vapour pressure.

5.3 The chemical potentials of liquids



Fig. 5.11 The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

Fig. 5.12 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.



Fig. 5.14 Strong deviations from ideality are shown by dissimilar liquids (in this case carbon disulfide and acetone, propanone).

(b) Ideal-dilute solutions

For real solutions at low concentrations, **proportionality constant** ≠ **vapor pressure of the pure liquid**

Henry's law for ideal dilute solution (see Fig. 5.15)

 $p_B = x_B K_B$

- X_B : the mole fraction of the solute - K_B : empirical constant (with the dimension of pressure) & the slope at $x_B = 0$

Ideal–dilute solutions :

Mixtures of the solute obeying Henry's law with the solvent obeying Raoult's law