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Course 565/665 Lecturer Prof. Cavagnero.
Day 4.5.04 Date 9:55 am
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ch. 15 Solutions & Mixtures

consider solutions, mixtures of more than one component;
a solution is a mixture that is homogeneous.

aim to derive $\mu = \mu^0 + kT \ln x$, which relates μ and the concentration x of one component in the solution.

approach: the lattice model

work with canonical ensemble (N, T, V)

entropy of mixing —

Imagine particles A and B, occupying a lattice of N sites completely (each occupies 1 site) — a 2-component solution model

A and B are the same size

$N = N_A + N_B$

so, $W = \dfrac{N!}{N_A! \, N_B!}$

The translational entropy of the mixed system:

$$\Delta S_{mix} = k(N\ln N - N_A \ln N_A - N_B \ln N_B)$$
$$= k(N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B)$$

note: before mixing: $W_A = 1$, $W_B = 1$,

define mole fraction $x_A = \dfrac{N_A}{N}$, $x_B = \dfrac{N_B}{N}$; if $x_A = x$, $x_B = 1 - x$

1 of 3

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So, $\Delta S_{mix} = -k(N_A \ln x_A + N_B \ln x_B)$

$$\frac{\Delta S_{mix}}{Nk} = -x\ln x - (1-x)\ln(1-x)$$

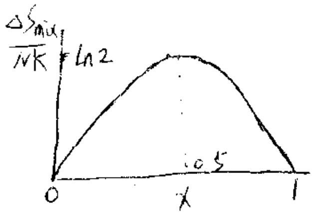

Fig. show $\Delta S_{mix}/Nk$ depends on x, has maximum at $x = \frac{1}{2}$

$\Delta S_{mix} > 0$ —— the driving force for mixing.

Ex. a solution containing 20% methanol. calculate ΔS_{mix}.

$$\frac{\Delta S_{mix}}{N} = k(-0.2\ln 0.2 - 0.8\ln 0.8) \approx 1.0 \frac{cal}{mol\cdot K}$$

its corresponding free energy (F): $\frac{\Delta F_{mix}}{N} = -\frac{T\Delta S_{mix}}{N} = -300$ cal/mol

Ideal solution —

$\Delta G_{mix} = -T\Delta S_{mix}$ (at const. T); $\Delta H_{mix} = 0$

$\Delta F_{mix} = -T\Delta S_{mix}$ (at const T) $\Delta U_{mix} = 0$

mixing ideal solution involves no change in energy, no other $\Delta S > 0$ due to changes in volume or structuring, or ordering in the solution.

$\Delta V_{mix} = 0$

energy of mixing —— non ideal solution

The total energy of mixing is (in this model) ~~as~~ the sum of the contact interactions of noncovalent bonds of all the pairs of nearest neighbors in the mixture

2 of 3

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3 types of contact (or interactions): AA bond, AB, BA

$$U = m_{AA} W_{AA} + m_{BB} W_{BB} + m_{AB} W_{AB}$$

m_{AA}: # of AA bonds ...

W_{AA}: the corresponding contact energy. ...

m_{AA}, m_{AB} m_{BB} are generally not known, but N_A, N_B are known.

convert m to N: each lattice site has z sides, every contact involves 2 sides

total # of sides of A particles

$$\left.\begin{aligned} zN_A &= 2m_{AA} + m_{AB} \\ zN_B &= 2m_{BB} + m_{AB} \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} m_{AA} &= \frac{zN_A - m_{AB}}{2} \\ m_{BB} &= \frac{zN_B - m_{AB}}{2} \end{aligned}\right.$$

$$\Rightarrow U = \left(\frac{zW_{AA}}{2}\right) N_A + \left(\frac{zW_{BB}}{2}\right) N_B + \left(W_{AB} - \frac{W_{AA} + W_{BB}}{2}\right) m_{AB}$$

now use the 'Bragg-Williams,' or mean-field approximation to evaluate m_{AB}.

more realistic situation: many possible configurations of different m_{AB}.

A simpler approach: use the mean-field approximation that for any given N_A, N_B, the particles are mixed as randomly and uniformly as possible.

Consider a specific site next to an A molecule, what is the probability that a B occupies that neighboring site?

Based on B-W approximation, for any site $P_B = \frac{N_B}{N} = x_B = 1-x$

the average # of AB contacts by one A: $z \cdot \frac{N_B}{N} = z(1-x)$

$$\therefore \quad m_{AB} \approx N_A \cdot z \frac{N_B}{N} = zNx(1-x)$$

exchange parameter

$$\Rightarrow U = \frac{zW_{AA}}{2} \cdot N_A + \frac{zW_{BB}}{2} \cdot N_B + kT\chi_{AB} \frac{N_A N_B}{N}; \quad \chi_{AB} = \frac{z}{kT}\left(W_{AB} - \frac{W_{AA} + W_{BB}}{2}\right)$$

3 of 3