EXAM NOV 2 A–J in 3-270

K–Z in 1-190

Lecture #21

10/31

Review

Regular Solution (molecules at random sites on lattice)

NOTATION

$A \equiv F \equiv$ Helmholtz Free Energy

$\mathcal{A}$ = surface area

Eqn 15.14 $\Delta A_{mix} = NkT\left[x\ln x + (1-x)\ln(1-x) + \chi_{AB}\, x(1-x)\right]$

Eqn 15.11 $\chi_{AB} = \frac{z}{kT}\left(w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right)$

How to get w_{AA}? w_{AB}?

$\underline{w_{AA}}$ ① Vapor pressure or Δh_{vap}

Vapor Pressure

$$P = P_0\, e^{z w_{AA}/2kT} \quad (\text{Eq}^{\underline{n}}\ 14.9)$$

$$P_2/P_1 = \frac{e^{z w_{AA}/2kT_2}}{e^{z w_{AA}/2kT_1}} \Longrightarrow \ln P_2/P_1 = \frac{z w_{AA}}{2k}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Clausius - Clapeyron (for Δh_{vap} independent of P, T)

$$\ln P_2/P_1 = \frac{-\Delta h_{vap}}{k}\left(1/T_2 - 1/T_1\right) \quad \boxed{\text{Eq}^{\underline{n}}\ 14.23}$$

Thus $z w_{AA} = -2\,\Delta h_{vap}$

② Surface Tension (pure substance)

NOTATION: a = interfacial area per molecule on lattice; $a = A/n$

O O O O } n surface
O O O O }
O O O O } $N-n$ bulk

$$U = \underbrace{\frac{z w_{AA}}{2}(N-n)}_{\text{Bulk}} + \underbrace{\frac{(z-1) z w_{AA}}{2}\, n}_{\text{surface}} = \underbrace{\frac{w_{AA}}{2}(Nz - n)}_{\text{TOTAL}}$$

DEFINE SURFACE TENSION

NOTATION

$\mathcal{A}$ = interfacial area

$$\gamma = \left.\partial F/\partial \mathcal{A}\right)_{T,V,N}$$

$$\gamma = \partial F/\partial \mathcal{A} = \frac{\partial F}{\partial n}\frac{dn}{d\mathcal{A}} = \frac{\partial u}{\partial n}\frac{dn}{d\mathcal{A}}$$

$$\partial u/\partial n = -w_{AA}/2$$

$$\frac{dn}{d\mathcal{A}} = 1/a$$

$$\mathcal{A} = na$$

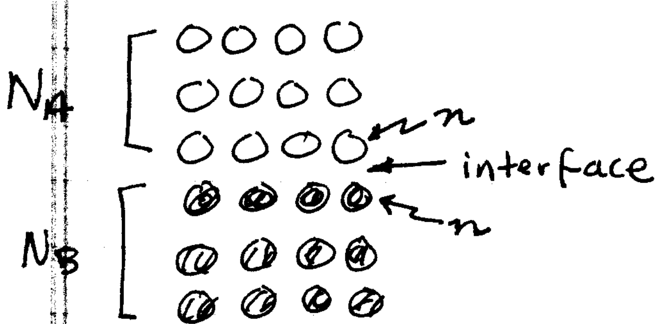
$$d\mathcal{A} = a\,dn$$

$$\boxed{\gamma = \frac{-w_{AA}}{2a}}$$

	γ dyne/cm
H_2O	72.8
ethanol	22.8

So can get w_{AA} by measuring surface tension if you have an estimate of a

w_{AB}? ⇒ interfacial tension provides this



$$U = (N_A - n)\frac{z w_{AA}}{2} + n\left(\frac{(z-1) w_{AA}}{2}\right) + n w_{AB} + (N_B - n)\frac{z w_{BB}}{2} + n\left(\frac{(z-1) w_{BB}}{2}\right)$$

bulk A — interface A — interface A-B — bulk B — interface B

interfacial tension

$$\gamma_{AB} = \left.\frac{\partial F}{\partial A}\right)_{N_A, N_B, T} = \frac{\partial U}{\partial A} = \frac{\partial U}{\partial n}\frac{dn}{dA}$$

$$\frac{dn}{dA} = \frac{1}{a}$$

$$\gamma_{AB} = \frac{1}{a}\left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right) = \left(\frac{kT}{2a}\right)\chi_{AB}$$

see example 15.3 to estimate χ_{AB} from γ_{AB} for water - benzene