Solutions
to

Chem 664 **Problem Set #8** **Due: November 18, 2002**

A. 4.2

B. 4.3

C. 4.4

D. 4.7

E. 4.8

F. 4.9

G. 4.12

H. 5.1

I. 5.2

J. 5.6

A. (4.2)(i) $\Delta \bar{S}_m (\text{per site}) = -k\left(\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B\right)$

$$= -k\left(\frac{1/2}{50}\ln\frac{1}{2} + \frac{1/2}{50}\ln\frac{1}{2}\right) = \frac{k}{50}\ln 2 \cong \frac{1.38\cdot 10^{-23}}{50}\ln 2$$

$$\cong 1.9\cdot 10^{-25}\ \text{J/K}$$

(ii) identical chains, no configurational difference before & after mixing, hence $\Delta\bar{S}_m = 0$

B. (4.3) χ between PS & PB at r.t.?

$$\chi \approx \frac{v_0}{kT}(\delta_{PS} - \delta_{PB})^2 \cong \frac{10^2\,Å^3 \cdot 10^{-30}\,m^3/Å^3}{1.38\cdot 10^{-23}\cdot 300}(0.25\cdot 10^4)^2$$

$$\cong \underline{\underline{0.15}}$$

$v_0 = 10^2\,Å^3$

$\delta_{PS} = 1.87\cdot 10^4\ (J/m^3)^{1/2}$

$\delta_{PB} = 1.62\cdot 10^4\ (J/m^3)^{1/2}$

C. (4.4) 1 mol of PS ($M = 2\cdot 10^5$ g/mol, $\rho = 1.06\ g/cm^3$) mixed with 10^4 L of toluene ($\rho = 0.87\ g/cm^3$) at 298K, with χ(PS/toluene) $= 0.37$.

Using the same notations as in the text,

$$\Delta F_{mix} = nkT\left[\frac{\phi}{N}\ln\phi + (1-\phi)\ln\phi + \chi\phi(1-\phi)\right]$$

total free energy

where n = total # of lattice sites

N = d.p. of PS

ϕ = vol fraction of PS

$\frac{n\phi}{N} = N_{PS}$ (total # of PS molecules in the mixture)

$n(1-\phi) = N_{tol}$ (total # of toluene in the mixture)

$$\phi = \frac{2\cdot 10^5/1.06}{10^7 + \frac{2\cdot 10^5}{1.06}} = 0.0185$$

$$\Delta F_{mix} = N_{AV}kT\Big[\underbrace{\frac{n\phi}{N_{AV}\cdot N}}_{\substack{\#\text{ of mol}\\ \text{of PS}}}\ln\phi + \underbrace{\frac{n(1-\phi)}{N_{AV}}}_{\substack{\#\text{ of mol}\\ \text{of toluene}}}\ln\phi + \underbrace{\frac{n(1-\phi)}{N_{AV}}}_{\substack{\#\text{ of mol}\\ \text{of toluene}}}\chi\phi\Big]$$

$$\frac{10^7\cdot 0.87}{92} = 9.5\cdot 10^4 \text{ mol}$$

$$= R(298)\big[1\cdot\ln(0.0185) + 9.5\cdot 10^4\ln(0.9815) + 9.5\cdot 10^4\cdot(0.37)(0.0185)\big]$$

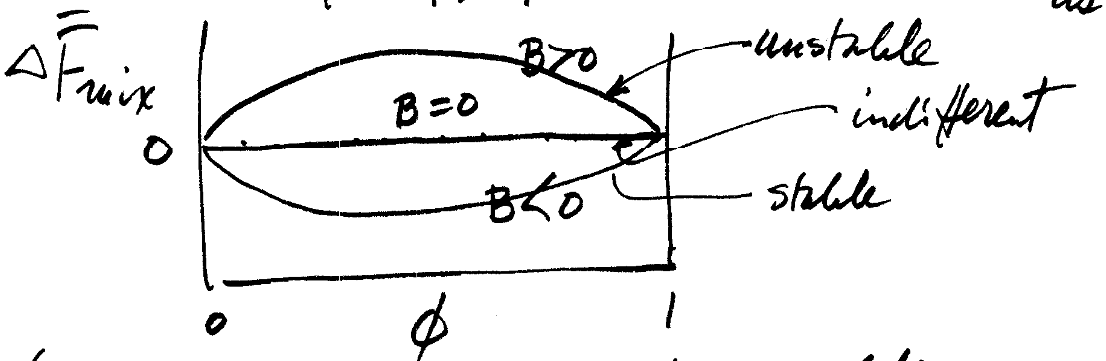
$$\cong -\underline{\underline{2.7\cdot 10^6\ \text{J}}}$$

D(A.7) $\chi \cong A + \frac{B}{T} \doteq \frac{B}{T}$ as $T\to 0$

$$\underset{\text{per site}}{\Delta\bar{F}_{mix}} = kT\Big[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + A\phi(1-\phi)\Big] + Bk\phi(1-\phi)$$

$\downarrow$ 0 as $T\to 0$

$$\approx \chi\phi(1-\phi)kT$$



The same conclusions apply to any solutions, be they polymer solutions, polymer blends & regular solutions

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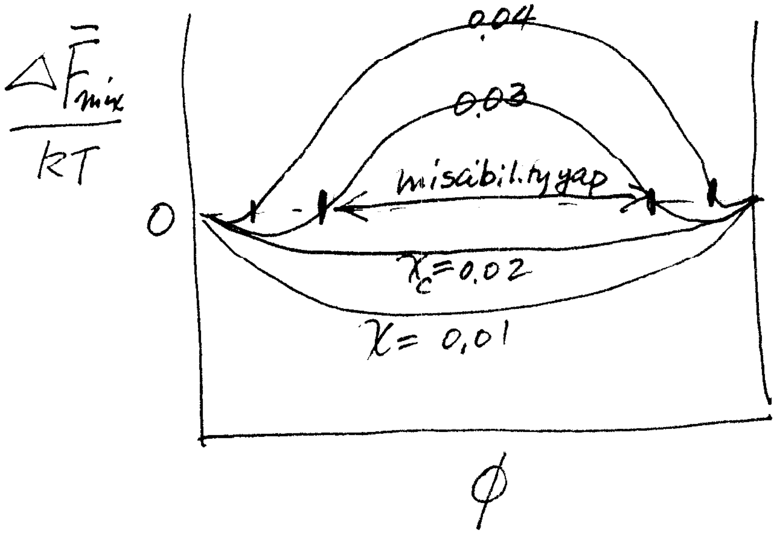
E. (4.8) $\frac{\Delta \bar{F}_{mix}}{RT} = \frac{\phi}{N_A}\ln\phi + \frac{(1-\phi)}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)$

$N_A = 100, \quad N_B = 100$

$\chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}}\right)^2 = \frac{1}{2}(0.1+0.1)^2 = 0.02$



$\chi \leq \chi_c = 0.02$
It should be miscible in all proportions.

F. (4.9)

$\frac{\Delta F_m}{\text{per mol}} = RT\left[\phi\ln\phi + (1-\phi)\ln(1-\phi) + \frac{B}{T}\phi(1-\phi)\right]$

where $\chi = \frac{B}{T}$, $B = 600K$

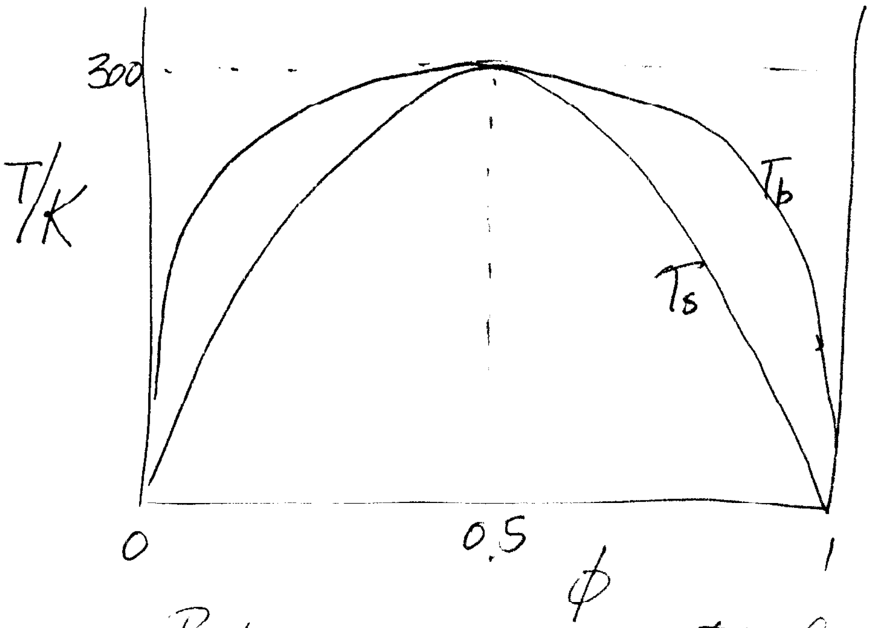
$\left(\frac{\partial \Delta F_m}{\partial \phi}\right) = 0 = RT\left[\ln\phi - \ln(1-\phi) + \frac{B}{T}(1-2\phi)\right]$

$T_b = -\frac{B(1-2\phi)}{\ln\phi - \ln(1-\phi)} = -\frac{600(1-2\phi)}{\ln\phi - \ln(1-\phi)}$

when $\phi' = \phi''$ $= \frac{600(2\phi-1)}{\ln(\phi/(1-\phi))}$

$\left(\frac{\partial^2 \Delta F_m}{\partial \phi^2}\right) = 0 = RT\left[\frac{1}{\phi} + \frac{1}{1-\phi} - \frac{2B}{T}\right] = 0$

$T_S = \frac{2B}{\frac{1}{\phi} + \frac{1}{1-\phi}} = \frac{2B(1-\phi)\phi}{1-\phi+\phi} = 2B\phi(1-\phi)$



Both T_b & T_s are symmetric function of ϕ

G.(4.12) 1 g of PS, $M=10^5$ g/mol + 1 mol of $\boxed{S}$ at 34°C

$$\chi=\frac{1}{2},\ \bar{V}_{PS}=9.5\cdot10^4\ \text{cm}^3/\text{mol},\quad \bar{V}_{CH}=108\ \text{cm}^3/\text{mol}$$

$$\Delta F_{mix}=RT\left[\frac{n_{PS}}{N_{AV}}\ln\phi+\frac{n_{CH}}{N_{AV}}\ln(1-\phi)+\frac{n_{CH}}{N_{AV}}\chi\phi\right]$$

$$=RT\left[10^{-5}\ln\phi+\ln(1-\phi)+\chi\phi\right]$$

$$V_{PS}=\bar{V}_{PS}/M_{PS}=0.95\ \text{cm}^3/\text{g}$$

$$V_{CH}=\bar{V}_{CH}=108\ \text{cm}^3$$

$$\phi=0.0087\ ,\ T=34^\circ C$$

$$\Delta F_{mix}=R(307)\left[10^{-5}\ln(8.7\cdot10^{-3})+\ln(0.9913)+0.5\cdot8.7\cdot10^{-3}\right]$$

$$=-11.3\ \text{J}$$

(ii) In general nothing
The sign does not give rise to the stability criterion

(iii) $\left(\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2}\right) < 0$ Concave part of ΔF_{mix} curve

(iv) metastability refers to the interval of ΔF_{mix} inflection points with the common tangent.

See Fig. 4.8

H. (5.1) Dilute solution with excluded volume $v = -12.5 \mathring{A}^3$ for a chain with $b = 5\mathring{A}$

(i) $N = 50$, (ii) $N = 10^2$, (iii) $N = 10^3$

$g_T \approx b^6/v^2 \cong \frac{(25)^3}{\left(\frac{25}{2}\right)^2} = 10^2$

Hence, (i) $N = 50 < g_T$, $R = bN^{1/2} \cong 35\mathring{A}$

(ii) $N = 10^2 = g_T$, $R = bN^{1/2} \cong 50\mathring{A}$

(iii) $N = 10^3 > g_T$, $R_{gl} \approx b^2 \frac{N^{1/3}}{|v|^{1/3}} = 25 \frac{10}{(12.5)^{1/3}} \cong 108\mathring{A}$

I (5.2) $N = 10^4$, $\chi = 0.55 > \frac{1}{2}$ at $\phi = 0.01$, $b = 4\mathring{A}$ Uniphasic or Biphasic?

$v_c \approx -\frac{b^3}{\sqrt{N}} \cong \frac{64}{10^2} \cong -0.64\mathring{A}^3$

$\phi_c \approx \frac{1}{\sqrt{N}} = 0.01$, hence $\phi = \phi_c$, right at the phase boundary

(i) $v = (1-2\chi)b^3 = (1-1.1)64\mathring{A}^3 = -6.4\mathring{A}^3$

$\phi'' \approx -\frac{v}{b^3} = -\frac{-6.4\mathring{A}^3}{64\mathring{A}^3} = 0.1$

(ii) In the sediment phase, $R \approx b\sqrt{N} = 400\mathring{A}$

(iii) In the dilute upper phase $\phi' \approx \phi''(e^{-|\frac{v}{b}|^{4/3} \cdot N^{2/3}}) \cong 4.6 \cdot 10^{-11} \approx 0$

(iv) $R_{gl} \approx b^2 \left(\frac{N}{|v|}\right)^{1/3} = 16\mathring{A}^2 \left(\frac{10^4}{64\mathring{A}^3}\right)^{1/3} \cong 186\mathring{A}$

(v) Volume Fraction of polymer within a globule: $Nb^3/R_{gl}^3 \approx \frac{|v|}{b^3} = \frac{6.4}{64} = 0.1$

90% solvent!

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J. (5.6) Overlap coverage (surface concentration)

With $R \approx a^{1/4} b^{2/4} N^{3/4}$ analogous to $R_F \approx v^{1/5} b^{2/5} N^{3/5}$

(i) $\sigma^* \approx \frac{Nb^2}{R^2} \approx \frac{Nb^2}{a^{1/2} b N^{3/2}} \approx \frac{b}{a^{1/2} N^{1/2}}$ (analogous to $\phi^* \approx \frac{Nb^3}{R^3} \approx \frac{b^{9/5}}{v^{3/5} N^{4/5}}$

(ii) Thermal blob is determined by

$a \frac{g_T^2}{\xi_T^2} \approx 1$ (analogous to $v \frac{N^2}{R^3} \approx 1$)

Ideal chain within a blob, $\xi_T^2 = b^2 g_T$, $g_T = \left(\frac{\xi_T}{b}\right)^2$,

so $a \frac{\xi_T^4 / b^4}{\xi_T^2} \approx 1$, $\frac{a}{b^2} \left(\frac{\xi_T}{b}\right)^2 \approx 1$, $\xi_T \approx \frac{b^2}{a^{1/2}}$, $g_T \approx b^2/a$

(iii) Correlation blob size on 2D?

$\sigma \approx \frac{g b^2}{\xi^2}$ analogous to $\phi \approx \frac{g b^3}{\xi^3} \approx b/\xi$

If $\xi > \xi_T$, $\xi \approx a^{1/4} b^{2/4} g^{3/4}$, $\sigma \approx \frac{g b^2}{a^{1/2} b g^{3/2}} \approx \frac{b}{a^{1/2} g^{1/2}}$

$g \approx \frac{b^2}{a \sigma^2}$

$\xi \approx \frac{b^2}{a^{1/2} \sigma^{3/2}}$, $\xi_T \approx \frac{b^2}{a^{1/2}} \Rightarrow \xi > \xi_T$ if $\sigma < 1$

(iv) $R \approx \xi \left(\frac{N}{g}\right)^{1/2} \approx \frac{b^2}{a^{1/2} \sigma^{3/2}} \left(\frac{N a \sigma^2}{b^2}\right)^{1/2} \approx \frac{b N^{1/2}}{\sigma^{1/2}} \approx R_{0,2D} \cdot \underbrace{\sigma^{-\frac{1}{2}}}_{\text{expansion factor}}$

$P \equiv \frac{\sigma}{\sigma^*} \approx \frac{\sigma R^2}{N b^2} \cong 1$, Chains do not overlap much and $R \approx b N^{1/2} / \sigma^{1/2}$

(v) $\Pi \approx \frac{kT}{\xi^2} \approx \frac{kT a \sigma^3}{b^4}$

Thermal energy density / blob

Analogous to 3D case of

$$\Pi \approx \frac{kT}{\xi^3} \approx \frac{kT}{b^3} \left(\frac{v}{b^3}\right)^{3/4} \phi^{9/4}$$