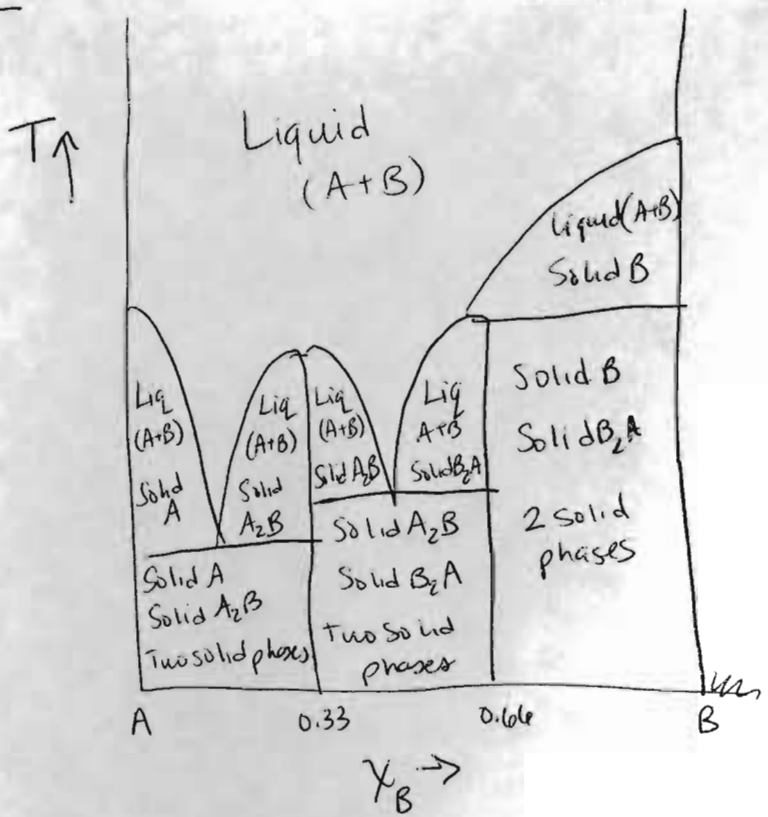


# HW4 KEY

## D6.6



## E6.2a

At 300K:  $P_A^* = 76.7 \text{ kPa}$       $P_B^* = 52.0 \text{ kPa}$

$P_A = y_A P = x_A P_A^* = 0.350 P = x_A (76.7 \text{ kPa})$

$P_B = y_B P = (1 - x_A) P = 0.650 P = x_B P_B^* = (1 - x_A) 52.0 \text{ kPa}$

$$\frac{y_A P}{y_B P} = \frac{x_A P_A^*}{x_B P_B^*} = \frac{0.350}{0.650} = \frac{x_A (76.7)}{(1 - x_A) 52.0}$$

$x_A = 0.268$      and      $x_B = 1 - 0.268 = 0.732$

$$P = \frac{x_A P_A^*}{0.350} = \frac{(0.268)(76.7)}{0.350} = 58.7 \text{ kPa}$$

EG.4a DE,  $P_{DE}^* = 22.9 \text{ kPa}$  at 358 K

DP,  $P_{DP}^* = 17.1 \text{ kPa}$

If  $z_{DE} = 0.60$ , find

a)  $P_{\text{total}}$  when system is all liquid

$$P_{\text{total}} = P_{DE} + P_{DP} \quad (\text{Dalton's Law})$$

$$P_{\text{tot}} = x_{DE} P_{DE}^* + x_{DP} P_{DP}^* \quad (\text{Raoult's Law})$$

If all liquid,  $x_{DE} = z_{DE}$  and  $x_{DP} = (1 - x_{DE})$

$$P_{\text{tot}} = (0.60)(22.9 \text{ kPa}) + (0.40)(17.1 \text{ kPa}) = 13.7 + 6.8$$

$$\boxed{\text{a) } P_{\text{tot}} = 20.5 \text{ kPa}}$$

b)  $y_{DE}$  and  $y_{DP}$  when almost all liquid

$$y_{DE} = \frac{P_{DE}}{P} = \frac{13.7 \text{ kPa}}{20.5 \text{ kPa}} =$$

b)

$$0.67 = y_{DE}$$

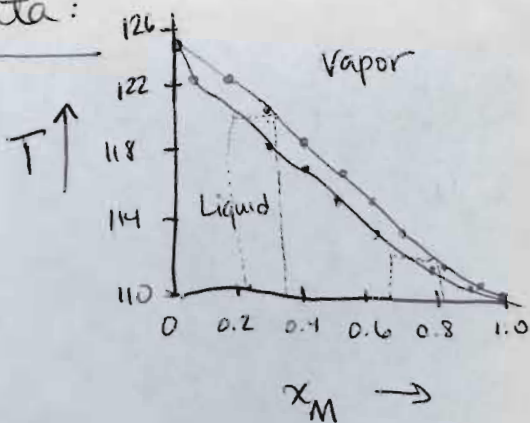
$$y_{DP} = 1 - 0.67 = 0.33$$

Ex. 5a Octane (O) Methylbenzene (M) at 1 atm

$T_B = 125.6$

$T_M = 110.6^\circ\text{C}$

Plot data:

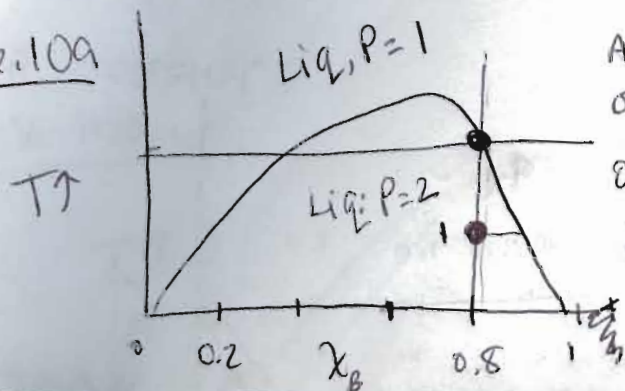


a)  $x_M = 0.250$   
 use tie line to determine  $y_M \approx 0.35$

b)  $x_O = 0.25, x_M = 0.75$   
 use tie line to determine  $y_M \approx 0.83$

Please know your values might not exactly match due to different graphs

Ex. 10a



At 1 there are 2 phases with compositions of  $x_B = 0.8$  and  $x_B = 0.15$  (lever rule approx).  
 On heating the phases merge and the single phase region is encountered.

Pl.3  $P_A = a_A P_A^* = \gamma_A \chi_A P_A^*$

$$\gamma_A = \frac{P_A}{\chi_A P_A^*} = \frac{y_A P}{\chi_A P_A^*}$$

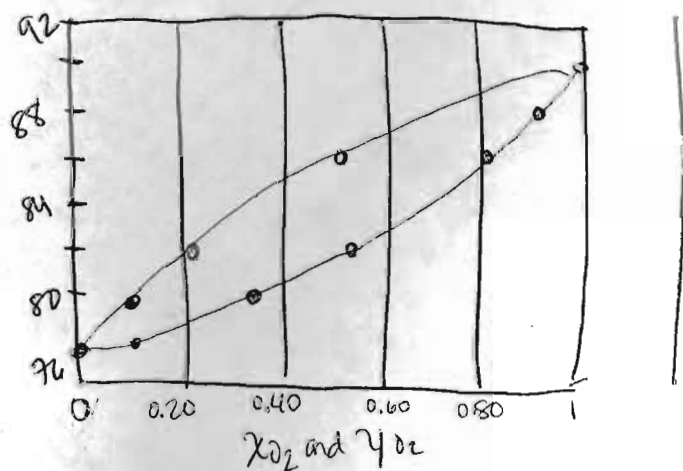
At 78 K

$$\gamma_{O_2}(78) = \frac{(0.02)(100 \text{ kPa})}{(0.10)(171 \text{ Torr})} \left( \frac{760 \text{ Torr}}{101.32 \text{ kPa}} \right) = 0.877$$

This is done the same way for each composition.

Temperature (K)	77.3	78	80	82	84	86	88	90.2
$\gamma_{O_2}$	—	0.877	1.079	1.039	0.995	0.993	0.990	<del>0.987</del> 0.987

The solution appears ideal ( $\gamma_{O_2} \approx 1$ ). The low value of  $\gamma_{O_2}$  (~~at 78 K~~<sup>78</sup>) may be caused by non-ideality, but could also be contributed to the high relative uncertainty of  $\gamma_{O_2}$  at this temperature.



Pl.13 (i) Below denaturant concentration of 0.15, only native and unfolded forms are stable

(ii) At denaturant concentration 0.15, only the native form is stable below 70°. At 0.70 Temperature, the molten globule and native forms are in equilibrium. Heating above 0.70 turns all native into molten globule. At T=0.90, equilibrium between molten globule and unfolded protein is observed. Above T=0.90, unfolded is the only stable form.

# DR VDB's Questions:

① At 60°C  
 $P_A = 3P_B$       $P_{\text{vap}}^*(A) = 550 \text{ Torr}$       $P_{\text{vap}}^*(B) = 150 \text{ Torr}$

At 40°C  
 $P_A = 2.5P_B$      Find  $P_A^*$  at 40°C      $P_B^* = 100 \text{ Torr (40°C)}$

At 60°C

$$P_A = \chi_A P_A^*$$

$$P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^* = \chi_A P_A^* + (1 - \chi_A) P_B^*$$

$$\chi_A = \frac{P - P_B^*}{P_A^* - P_B^*} = \frac{P_A + P_B - P_B^*}{P_A^* - P_B^*} = \frac{4P_B - P_B^*}{P_A^* - P_B^*}$$

$$y_A = \frac{P_A}{P} \quad y_B = \frac{P_B}{P} \quad 3y_B = y_A \quad y_A = 0.75$$

$$P_{\text{vap}} = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) y_A} = \frac{(550 \text{ Torr})(150 \text{ Torr})}{(550 \text{ Torr}) + (150 - 550) \text{ Torr} (0.75)} \quad y_B = 0.25$$

$$P_{\text{vap}}(60^\circ\text{C}) = 330 \text{ Torr}$$

$$\chi_A = \frac{330 \text{ Torr} - 150 \text{ Torr}}{(550 - 150) \text{ Torr}} = 0.45 \quad \chi_B = 0.55$$

At 40°C

$$P_A = 2.5P_B \quad y_A = 0.7125 \quad y_B = 0.2875$$

Since producing small amount of vapor at 40°C, assume mol fractions do not change from 60°C.

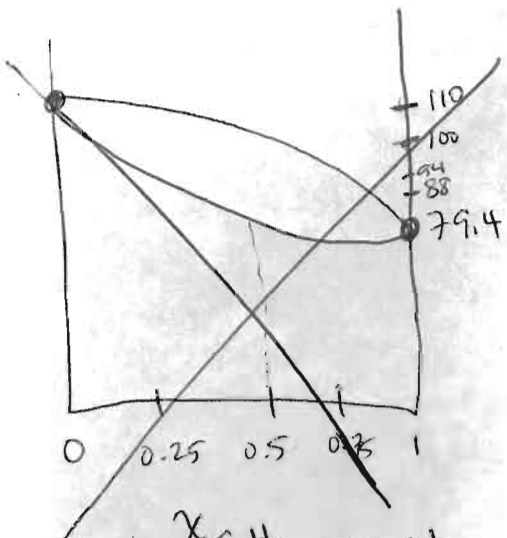
$$P_B = \chi_B P_B^* = (0.55)(100 \text{ Torr}) = 55 \text{ Torr}$$

$$P_A = 2.5P_B = 2.5(55 \text{ Torr}) = 137.5 \text{ Torr} \quad \text{and } P = P_A + P_B = 192.5 \text{ Torr}$$

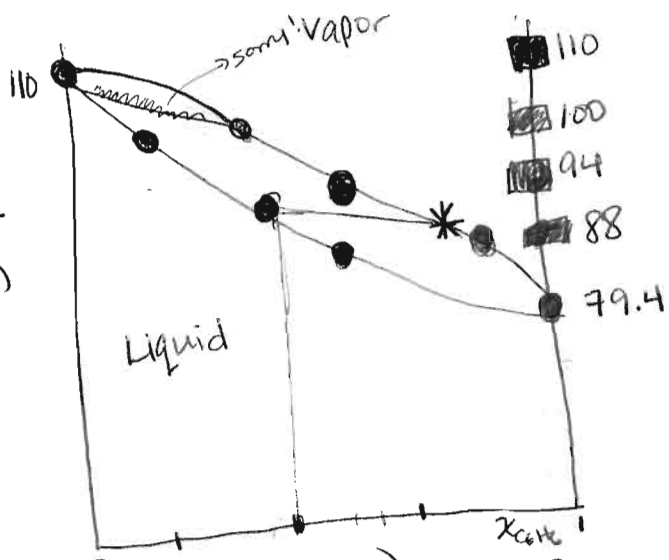
$$P_A^* = \frac{P_A}{\chi_A} = \frac{137.5 \text{ Torr}}{0.45} = \boxed{305 \text{ Torr} = P_A^*}$$

2

T



T (°C)



$x_{C_6H_6}$   
I'm a terrible artist!

$$y_A = \frac{P_A}{P} = \frac{x_A P_A^*}{P} = \frac{(0.633)(1.285 \text{ bar})}{1 \text{ bar}} = 0.813$$

at 88°C

$$x_A = \frac{P - P_B^*}{(P_A^* - P_B^*)} = \frac{(1 \text{ bar} - 0.508 \text{ bar})}{(1.285 \text{ bar} - 0.508 \text{ bar})} = \boxed{0.633 = x_A \mid x_B = 0.367}$$

at 94°C

Same way as above:  $x_A = 0.422$       $y_A = \frac{(0.422)(1.526 \text{ bar})}{1 \text{ bar}} = 0.644$

at 100°C

$$\frac{(1 - 0.742)}{(1.801 - 0.742)} = x_A = 0.244$$

$$y_A = \frac{(0.244)(1.801)}{1} = 0.439$$

If  $x_A = x_B = 0.5$

At around 90°C - from my crappy phase diagram - the first drop of vapor would form.

③ At given temperature T:  
unfolded  $\rightarrow$  folded  $\Delta G < 0$ ,  $\Delta S < 0$  (becoming more ordered)

$$\therefore \Delta H < 0 \text{ and } |\Delta H| > |T\Delta S|$$

As T  $\uparrow$ , expect  $|\Delta H| < |T\Delta S|$  and  $\Delta G > 0$  - the protein will unfold and go to its higher entropy and higher energy state