

Homework IV

$$6.2) \quad P_A = y_A p = 0.350p$$

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

$$P_B = y_B p = (1 - y_A) p = 0.650p$$

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

Two equations, two unknowns:
Divide by the two equations

$$\frac{P_A}{P_B} = \frac{y_A p}{y_B p} = \frac{x_A P_A^*}{x_B P_B^*}$$

$$\text{xx} \quad \frac{0.350}{0.650} = \frac{x_A \cdot 76.7 \text{ kPa}}{(1 - x_A) \cdot 52.0 \text{ kPa}}$$

$$\text{solve for } x_A = \boxed{0.27}, \quad x_B = 1 - x_A = \boxed{0.73}$$

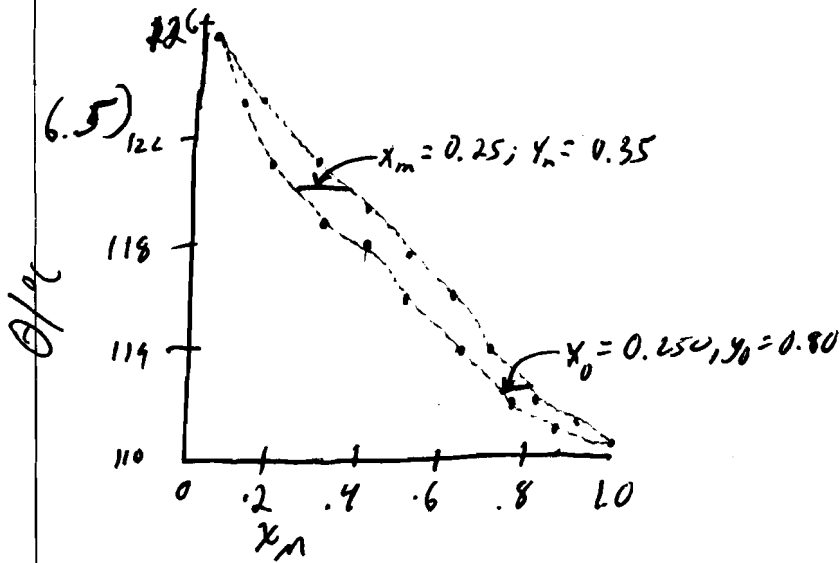
$$0.350p = x_A P_A^*$$

$$p = \frac{(0.27)(76.7 \text{ kPa})}{0.350} \approx \boxed{59 \text{ kPa}}$$

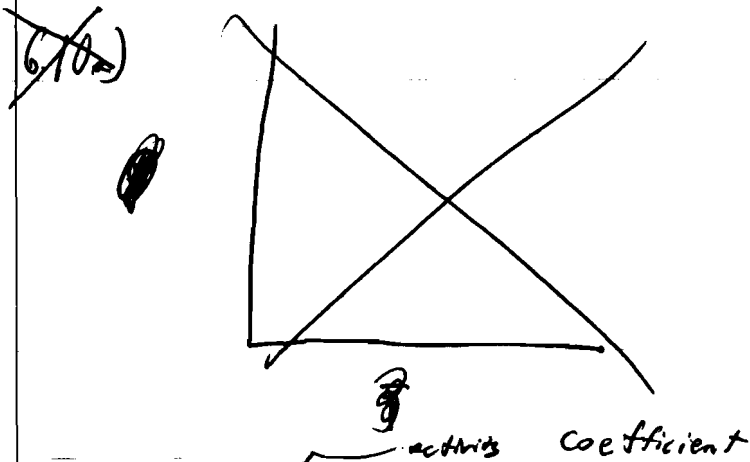
6.4) a) Dalton's Law: $P_{\text{total}} = P_{OE} + P_{OP} = x_{OE} P_{OE}^* + x_{OP} P_{OP}^*$ (Raoult's Law)
system of all liquid: $z_{OE} = x_{OE}$ & $x_{OP} = 1 - z_{OE}$

$$P_{\text{total}} = (0.60)(22.9 \text{ kPa}) + (0.40)(17.1 \text{ kPa}) = 13.7 + 6.8 = \boxed{20.5 \text{ kPa}}$$

$$b) \quad y_{OE} = \frac{P_{OE}}{p} = \frac{13.7 \text{ kPa}}{20.5 \text{ kPa}} = \boxed{0.67} \quad y_{OP} = 1 - y_{OE} = \boxed{0.33}$$



a) $x_m = 0.250; y_m = 0.35$
 b) $x_0 = 0.250; y_0 = 0.80$ } approximate



P6.3) $P_A = a_A P_A^* = \gamma_A x_A P_A^*$

$$\gamma_A = \frac{P_A}{x_A P_A^*} = \frac{y_A P}{x_A P_A^*}; \text{ @ } 80\text{K: } \gamma_{O_2} = \frac{(0.11)(100 \text{ kPa})}{(0.39)(225 \text{ Torr})} \left(\frac{760 \text{ Torr}}{101.325 \text{ kPa}} \right)$$

$$= 1.079$$

T(K)	77.3	78	80	82	84	86	88	90.2
γ_{O_2}	-	1.079 0.877	1.079	1.039	0.995	0.993	0.990	0.987

The solution is very close to ideal. AT 78,
 O_2 @ 78K may be due to nonideality or experimental error.

P. 6.13) i) No, the protein will be either unfolded or in its native form.

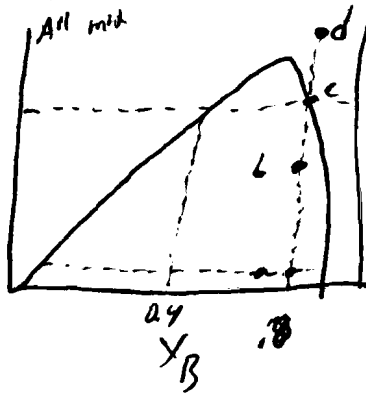
ii) At first only the native form will be stable. At a temperature of about 0.7, there is an equilibrium between the native and globule forms.

Next only the globule will be stable.

Finally there is an equilibrium between the globule and the unfolded protein polymer at about 0.9. After this, the unfolded protein is stable.

E. G. 10a)

Temp

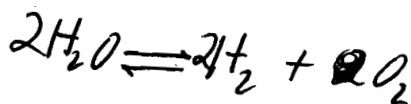
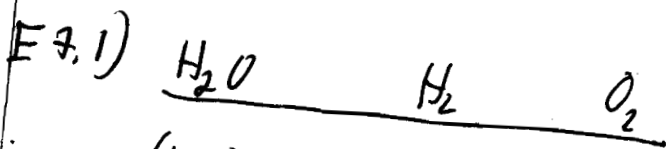


As the temperature is heated from T_c , the composition of B is greater than 0.8.

At b , the composition of B is becoming less.

At c , the liquid is $X_B = 0.8$ and one drop at a composition of ≈ 0.4

Above c , the liquid is all mixed



a) $K = \left(\prod a_i^{\nu_i} \right)_{eq}$

$a_i = \frac{P_i}{P^0}$

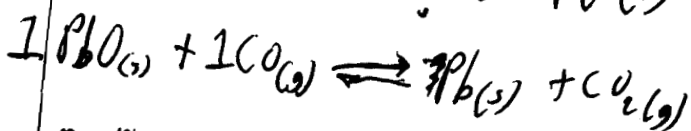
$$K = \frac{\left(\frac{P_{H_2}}{P^0} \right)^2 \left(\frac{P_{O_2}}{P^0} \right)}{\left(\frac{P_{H_2O}}{P^0} \right)^2} = \frac{\left(\frac{\alpha p}{1+\frac{1}{2}\alpha} \right)^2 \left(\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha} \right)}{\left(\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha} \right)^2}$$

simplify: $\frac{\alpha^3 p}{2(1-\alpha)^2(1+\frac{1}{2}\alpha)p^0} = \frac{(0.01773)^3}{2(1-0.0177)^2(1+\frac{1}{2}0.0177)} = \boxed{2.85 \times 10^{-6}}$

b) $\Delta G^0 = -RT \ln K = -(8.314 \text{ J/Kmol})(2257 \text{ K}) \ln(2.85 \times 10^{-6})$
 $= \boxed{2.40 \times 10^5 \text{ J/mol}} = 240 \text{ kJ/mol}$

c) $\Delta_r G = 0$ because reaction in equilibrium

7.3 a) a) $\Delta_r G^0 = \sum \nu_i \Delta_f G^0(i) = 0$



$$0 = Pb(s) + CO_2(g) - PbO(s) - CO(g)$$

$$\Delta_r G = \Delta_f G^0(Pb(s)) + \Delta_f G^0(CO_2(g)) - \Delta_f G^0(PbO(s)) - \Delta_f G^0(CO(g))$$

$$= -394.36 \text{ kJ/mol} - (-137.17 \text{ kJ/mol}) - (-188.93 \text{ kJ/mol})$$

$$= \boxed{-68.26 \text{ kJ/mol}}$$

$$\ln K = \frac{-\Delta_r G^\circ}{RT} = \frac{68.26 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/Kmol})(298 \text{ K})} = 27.55$$

$$e^{27.55} = \boxed{K = 9.2 \times 10^{11}}$$

b) ~~At 400 K~~ $\ln K_{400} = \ln K_{298} - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}} \right)$

~~$\ln K = 27.55 + \dots$~~

$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ(\text{Pb, s}) + \Delta_f H^\circ(\text{CO}_2) - \Delta_f H^\circ(\text{PbO}) - \Delta_f H^\circ(\text{CO}) \\ &= -393.51 \text{ kJ/mol} - (-218.99 \text{ kJ/mol}) - (-110.53 \text{ kJ/mol}) \\ &= \del{103.99} \quad 63.99 \text{ kJ/mol} \end{aligned}$$

$$\ln K = 27.55 - \left(\frac{-63.99 \text{ kJ/mol}}{8.314 \text{ J/Kmol}} \right) \left(-8.56 \times 10^{-7} \text{ K}^{-1} \right) = \boxed{20.96}$$

$$K = e^{20.96} = \boxed{1.3 \times 10^9}$$

$$\begin{aligned} \Delta_r G^\circ(400 \text{ K}) &= -RT \ln K = -(8.314 \text{ J/Kmol})(400 \text{ K})(20.96) \\ &= \boxed{-69.7 \text{ kJ/mol}} \end{aligned}$$

1) A B

$$P_A = 3P_B$$

$$P_A = \chi_A P_A^*$$

③ = 60 C $P_A^* = 550 \text{ TORR}$

$$P_B^* = 150 \text{ TORR}$$

$$P_A = 3P_B$$

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

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

$$Y_A = \frac{P_A}{P}$$

$$Y_B = \frac{P_B}{P}$$

$$3Y_B = Y_A$$

$$Y_A = 0.75$$

$$Y_B = 0.25$$

$$P = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) Y_A}$$

$$\frac{(550 \text{ TORR})(150 \text{ TORR})}{(550 \text{ TORR}) + (150 - 550) \text{ TORR} \cdot 0.75}$$

$$P_{\text{total}} @ 60C = \underline{330 \text{ TORR}}$$

$$(550 \text{ TORR}) + (150 - 550) \text{ TORR} \cdot 0.75$$

$$\chi_A = \frac{330 \text{ TORR} - 150 \text{ TORR}}{(550 \text{ TORR} - 150 \text{ TORR})}$$

$$\chi_A = 0.45$$

$$\chi_B = 0.55$$

④ 40C

$$P_A = 2.5 P_B$$

find P_A^* @ 40C

$$Y_A = 0.7125$$

$$Y_B = 0.2875$$

$$\chi_A$$

amount of vapor produced is small so one can assume that x_A & x_B are the same as at 60°C

$$P_B = x_B P_B^* = 0.45 (100 \text{ TORR}) = 45 \text{ TORR}$$

$$x_B = 0.45$$

$$P_A = 2.5 P_B = 2.5 \cdot 45 \text{ TORR} = 112.5 \text{ TORR}$$

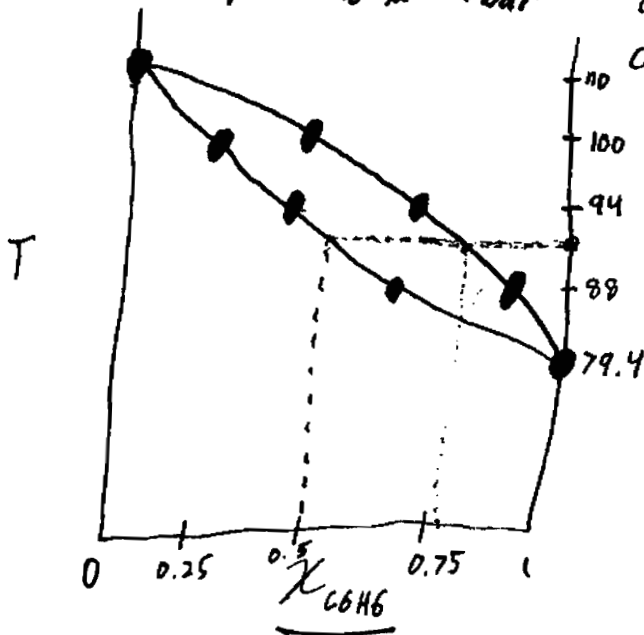
$$P = P_A + P_B = 45 \text{ TORR} + 112.5 \text{ TORR} = 157.5 \text{ TORR}$$

$$P_A = x_A P_A^*$$

$$P_A^* = \frac{P_A}{x_A} = \frac{112.5 \text{ TORR}}{0.55} = 204.5 \text{ TORR}$$

$P_A^* = 204.5 \text{ TORR}$
$P = 157.5 \text{ TORR}$

2) total pressure is 1 bar



$C_6H_6 = A$
 $C_7H_8 = B$

$P = 1 \text{ bar}$

$$Y_A = \frac{P_A}{P} = \frac{\chi_A P_A^*}{P} = \frac{0.633(1.285 \text{ bar})}{1 \text{ bar}}$$

@ 88°C

$$\chi_A = \frac{P - P_B^*}{(P_A^* - P_B^*)} = \frac{(1 \text{ bar} - 0.508 \text{ bar})}{(1.285 \text{ bar} - 0.508 \text{ bar})} = 0.1$$

$$\chi_B = 1 - 0.633$$

$$\chi_B = 0.367$$

@ 94

$$\chi_A = \frac{(1 \text{ bar} - 0.616)}{(1.526 - 0.616)} = 0.422$$

$$Y_A = \frac{0.422(1.526 \text{ bar})}{1 \text{ bar}} = 0.644$$

@ 100

$$\frac{1 - 0.742}{1.801 - 0.742} = \chi_A = 0.244$$

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

$$\chi_A = \chi_B = 0.5$$

at ~91°C the first drop of vapor would form
w/ a composition ~ 0.76 = $Y_{C_6H_6}$ and 0.24 = $Y_{C_7H_8}$