1. You need to find the enthalpy of sublimation of solid A at 300 K. The following equilibrium vapor pressure measurements have been made on pure A: (1) at 250 K, the pressure is 0.258 bar and (2) at 350 K, the pressure is 2.00 bar. The following heat capacity data are known:

$$c_{p,m}^{sol} = 40 \ \ [\text{J/mol-K}]$$
$$c_{p,m}^{vap} = 40 + 0.1T \ \ [\text{J/mol-K}]$$

a) Assumptions:

(i) $V_m^v >> V_m^s$; This is a very good assumption

(ii) Vapor acts ideally; Pretty OK, low pressure → $V_m^v = \frac{RT}{P}$

(iii) Δh_m^{sub} is assumed constant; May be bad, discussed in (c)

$$\frac{dP}{dT} = \frac{h_m^v - h_m^s}{T(V_m^v - V_m^s)} \approx \frac{\Delta h_m^{sub}}{RT^2/P} \rightarrow \int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta h_m^{sub}}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}$$

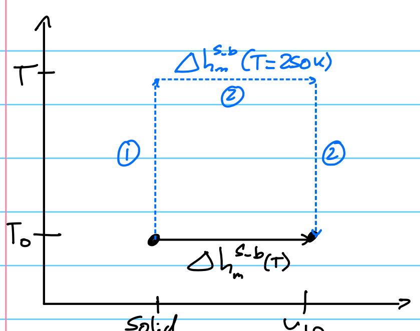
(use '1' as ref conditions)

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta h_m^{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta h_m^{sub} = 14.898 \ \frac{\text{kJ}}{\text{mol}}$$

$$\Rightarrow \Delta h_m^{sub} = -\frac{R\ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = -\frac{8.314\ln\left(\frac{2}{0.258}\right)}{\left(\frac{1}{350} - \frac{1}{250}\right)} = 14898.27 \ \frac{\text{J}}{\text{mol}}$$

b) Calculation Path



$$\Delta h_m^{sub}(T) = \Delta h_m^{sub}(T=250) + \Delta h_{m,1} + \Delta h_{m,2}$$
$$= \Delta h_m^{sub}(T=250) + \int_T^{250} C_{p,m}^s dT + \int_{250}^T C_{p,m}^v dT$$
$$= \Delta h_m^{sub}(T=250) + 40(250-T) + \int_{250}^T (40+0.1T)\, dT$$
$$= \Delta h_m^{sub}(T=250) + \cancel{40(250-T)} + \cancel{40(T-250)} + \frac{0.1}{2}(T^2 - 250^2)$$
$$\therefore \Delta h_m^{sub}(T) = \Delta h_m^{sub}(T=250) + 0.05T^2 - 3125$$

Plug into CC eq. with only assumptions (i) & (ii)

constants

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta h_m^{sub}(T)}{T^2} dT = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta h_m^{sub}(T=250) + 0.05T^2 - 3125}{T^2} dT$$

$$R\ln\left(\frac{P_2}{P_1}\right) = \left(3125 - \Delta h_m^{sub}(T=250)\right)\left(\frac{1}{T}\right)\Bigg|_{T_1}^{T_2} + 0.05\,T\Bigg|_{T_1}^{T_2}$$

$$R\ln\left(\frac{P_2}{P_1}\right) = \left(3125 - \Delta h_m^{sub}(T=250)\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + 0.05(T_2 - T_1)$$

But what is $\Delta h_m^{sub}(T=250)$?

$$\Delta h_m^{sub}(T=250) = -\left[R\ln\left(\frac{P_2}{P_1}\right) - 0.05(T_2 - T_1)\right]\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} + 3125$$

Conditions @ 1, 2

$$= -\left[8.314\ln\left(\frac{2}{.258}\right) - 0.05(350-250)\right]\left(\frac{1}{350} - \frac{1}{250}\right)^{-1} + 3125 = 13648.27 \ \frac{\text{J}}{\text{mol}}$$

Use result of $\Delta h_m^{sub}(T=250)$: $\Delta h_m^{sub}(T) = \Delta h_m^{sub}(T=250) + 0.05\,T^2 - 3125$

$$\Delta h_m^{sub}(T=300) = 13648.27\ \frac{J}{mol} + 0.05(300)^2 - 3125$$

$$= 15023.27\ \frac{J}{mol}$$

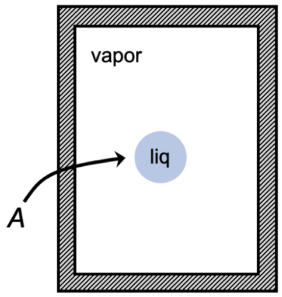
$$\Delta h_m^{sub}(T=300K) = 15.023\ \frac{J}{mol}$$

c) Assume b's result is actual Δh_m^{sub}

$$\text{Error}\,\% = \frac{|14.898 - 15.023|}{15.025} \times 100 = 0.832\%$$

0.832% error, so not a bad assumption!

2. Consider a two-phase, vapor–liquid equilibrium. In this case, we will assume the liquid is a spherical droplet with volume V, surface area A, and radius, r. We have an isolated system (there is no gravity).



$$dU^L = T^L dS^L - P^L dV^L + \mu^L dn^L + \gamma dA^L \quad \text{(FE)}$$

where A is the surface area of the droplet

Spherical droplet

$V = \frac{4}{3}\pi r^3$; $A = 4\pi r^2$

a) $\frac{dV^L}{dr^L} = \frac{d}{dr^L}\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 \Rightarrow dr^L = \frac{dV^L}{4\pi r^2}$

$\frac{dA^L}{dr^L} = \frac{d}{dr^L}\left(4\pi r^2\right) = 8\pi r \Rightarrow dA^L = 8\pi r \, dr^L$

$dA^L = 8\cancel{\pi r}\left(\frac{dV^L}{4\cancel{\pi r^2}}\right) = \frac{2}{r}dV^L$ $\qquad dA^L = \frac{2}{r}dV^L$

b) $\cancel{dU^L}^{0} = T^L dS^L - P^L dV^L + \mu^L dn^L + \gamma dA^L$ liquid phase

closed $\cancel{dU^{vap}}^{0} = T^{vap} dS^{vap} - P^{vap} dV^{vap} + \mu^{vap} dn^{vap}$ vapor phase

(i) Equate as $dU^L = dU^{vap} = 0$ as it is a closed system

$T^L dS^L - P^L dV^L + \mu^L dn^L + \gamma dA^L = T^{vap} dS^{vap} - P^{vap} dV^{vap} + \mu^{vap} dn^{vap}$

Isolated System (Loss from one system = gain of another) $\begin{cases} dS^L = dS^{vap} \\ dn^L = dn^{vap} \\ dV^L = dV^{vap} \end{cases}$ This has to be true @ equilibrium for an isolated/closed system

$T^L dS^L - T^{vap} dS^{vap} - P^L dV^L + P^{vap} dV^{vap} + \mu^L dn^L - \mu^{vap} dn^{vap} + \gamma dA^L = 0$

$(T^L - T^{vap}) dS^L + (P^{vap} - P^L) dV^L + (\mu^L - \mu^{vap}) dn^L + \gamma dA^L = 0$

(ii) dS^L, dV^L, and dn^L are independent of each other, and dV^L depends on dA^L

$\rightarrow (T^L - T^{vap}) dS^L = 0 \Rightarrow T^L = T^{vap}$; $(\mu^L - \mu^{vap}) dn^L = 0 \Rightarrow \mu^L = \mu^{vap}$

$(P^{vap} - P^L) dV^L + \gamma dA^L = 0$ (substitute the result from a)

$(P^{vap} - P^L) \cancel{dV^L} + \gamma \frac{2}{r} \cancel{dV^L} = 0 \Rightarrow P^L - P^{vap} = \frac{2}{r}\gamma$

This result shows P^L is always greater than P^{vap} when surface tension is included, compared to the $P^L = P^{vap}$ result expected in 'normal' problems. The surface tension creates a force that influences pressure (on the liquid phase only).

3. The molar enthalpy of a ternary mixture of species *a, b*, and *c* can be described by the following expression:

$$h_m = -5000x_a - 3000x_b - 2200x_c - 500x_a x_b x_c \quad \text{[J/mol]}$$

a) $\bar{H}_a \underset{\text{def'n}}{\equiv} \left(\frac{\partial H}{\partial n_a}\right)_{T,P,n_b,n_c} = \left(\frac{\partial (n_{tot} h_m)}{\partial n_a}\right)_{T,P,n_b,n_c} = \left(\frac{\partial ((n_a+n_b+n_c) h_m)}{\partial n_a}\right)_{T,P,n_b,n_c}$

$h_m = -5000x_a - 3000x_b - 2200x_c - 500 x_a x_b x_c$

$x_a = \frac{n_a}{n_a+n_b+n_c}$; $x_a = \frac{n_b}{n_a+n_b+n_c}$; $x_a = \frac{n_c}{n_a+n_b+n_c}$; $n_{tot} = n_a+n_b+n_c$

$h_m = -5000\frac{n_a}{n_a+n_b+n_c} - 3000\frac{n_b}{n_a+n_b+n_c} - 2200\frac{n_c}{n_a+n_b+n_c} - 500\frac{n_a n_b n_c}{(n_a+n_b+n_c)^3}$

$(n_a+n_b+n_c)h_m = -5000n_a - 3000n_b - 2200n_c - 500 n_a n_b n_c = H$

$\left(\frac{\partial H}{\partial n_a}\right)_{T,P,n_b,n_c} = \frac{\partial}{\partial n_a}\left[-5000n_a - \cancelto{0}{3000n_b} - \cancelto{0}{2200n_c} - 500\frac{n_a n_b n_c}{(n_a+n_b+n_c)^2}\right]$

$= -5000 - 500\left[\frac{n_b n_c}{(n_a+n_b+n_c)^2} - \frac{2n_a n_b n_c}{(n_a+n_b+n_c)^3}\right]$

$= -5000 - 500(x_b x_c - 2x_a x_b x_c)$

$\Rightarrow \bar{H}_a = -5000 - 500x_b x_c(1-2x_a) \ \frac{J}{mol}$

b) $n_a = n_b = n_c = 1$ $\qquad \bar{H}_a = -5000 - 500(\frac{1}{3})(\frac{1}{3})(1-2(\frac{1}{3}))$

$x_a = \frac{1}{3} = x_b = x_c$ $\qquad \bar{H}_a = -5018.5 \frac{J}{mol}$

c) $n_a = 1$, $n_b = n_c = 0$

$x_a = 1$ $\qquad \bar{H}_a = -5000 - 500(0)(0)(1-2(0))$ $\qquad \bar{H}_a = -5000 \frac{J}{mol}$

d) $n_a = n_c = 0$, $n_b = 1$

$x_b = 1$ $\qquad \bar{H}_b = \frac{\partial}{\partial n_b}\left[-\cancelto{0}{5000n_a} - 3000n_b - \cancelto{0}{2200n_c} - 500\frac{n_a n_b n_c}{(n_a+n_b+n_c)^2}\right]$

$= -3000n_b - 500\left(\frac{n_a n_c}{(n_a+n_b+n_c)^2} - \frac{2n_a n_b n_c}{(n_a+n_b+n_c)^3}\right)$

$n_b = 1 \Rightarrow \bar{H}_b = -3000(1)$

$\bar{H}_b = -3000 \frac{J}{mol}$

4. The molar enthalpy of a binary liquid mixture of species 1 and 2 is given by:

$$h_m = x_1(275 + 75T) + x_2(125 + 50T) + 750x_1x_2 \left[\frac{\text{J}}{\text{mol}}\right]$$

where T is the temperature in [K].

a) $\Delta H_{mix} = (n_1 + n_2)[h_m - x_1 h_1 - x_2 h_2)$

$$\begin{cases} n_1 + n_2 = 2 + 3 = 5 \quad \rightarrow \quad x_1 = \frac{2}{2+3} = 0.4 \,, \quad x_2 = 0.6 \\ T = 20°C + 273 = 293\,K \end{cases}$$

$\Delta h_{mix} = h_m - (x_1 h_{m,1} + x_2 h_{m,2})$

$h_m = x_1(275 + 75T) + x_2(125 + 50T) + 750x_1x_2$

$h_{m,1}(x_2 = 0) = 275 + 75T$

$h_{m,2}(x_1 = 0) = 125 + 50T$

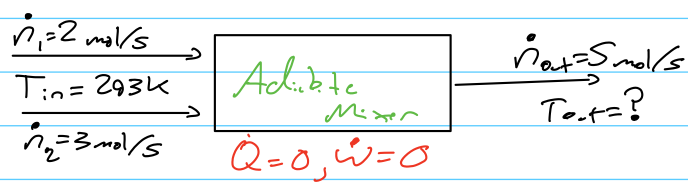
$$\Delta h_{mix} = \cancel{x_1(275 + 75T)} + \cancel{x_2(125 + 50T)} + 750x_1x_2$$
$$- \cancel{x_1(275 + 75T)} - \cancel{x_2(125 + 50T)}$$
$$= 750x_1x_2$$

$\Rightarrow \Delta h_{mix} = 750(0.4)(0.6) = 180 \ \frac{\text{J}}{\text{mol}}$

$\Delta H_{mix} = (n_1 + n_2)\Delta h_{mix} = (2+3)\,180 = 900$

$\Delta H_{mix} = 900\text{ J}$

b)



1st law:

$$\cancel{\frac{dU}{dt}}^{0} = \dot{n}_{in} h_{m,in} - \dot{n}_{out} h_{m,out} + \cancel{\dot{Q}}^{0} + \cancel{\dot{W}_s}^{0}$$

adiabatic, no shaft work, steady

$\Rightarrow 0 = \dot{n}_1 h_{m,1} + \dot{n}_2 h_{m,2} - \dot{n}_{out} h_{m,out}$

$\dot{n}_1 h_{m,1} = 2\big(275 + 75(293)\big) = 44500 \ \frac{\text{J}}{\text{s}}$

$\dot{n}_2 h_{m,2} = 3\big(125 + 50(293)\big) = 44325 \ \frac{\text{J}}{\text{s}}$

$\dot{n}_{out} h_{m,out} = 5\Big(0.4(275 + 75T_{out}) + 0.6(125 + 50T_{out}) + 750(0.4)(0.6)\Big)$

$= 5(110 + 30T_{out} + 75 + 30\,T_{out} + 180)$

$= 1825 + 300\,T_{out}$

$\Rightarrow 0 = 44500 + 44325 - 1825 - 300T_{out}$

$-87000 = -300\,T_{out}$

$T_{out} = 290\text{ K}$

5. The partial molar volume of benzene (1) in cyclohexane (2) at 30℃ is given by the following equation:

$$\bar{V}_1 = 92.6 - 5.28x_1 + 2.64x_1^2 \quad [\text{cm}^3/\text{mol}]$$

Find an expression for the partial molar volume of cyclohexane. The density of cyclohexane at 30℃ is 0.769 g/cm³.

MW

(1) Benzene $= 78.114 \frac{g}{mol}$

(2) Cyclohexane $= 84.162 \frac{g}{mol}$

Use: G-D @ const T,P: $0 = n_1 d\bar{V}_1 + n_2 d\bar{V}_2$

↳ divide by n_1+n_2: $0 = x_1 d\bar{V}_1 + x_2 d\bar{V}_2$

(i) To use given Eq, we need $\frac{d\bar{V}_1}{dx_1}$, so 'divide' by dx_1

$$0 = x_1 \frac{d\bar{V}_1}{dx_1} + x_2 \frac{d\bar{V}_2}{dx_1}$$

$$\frac{d\bar{V}_1}{dx_1} = \frac{d}{dx_1}\left(92.6 - 5.28x_1 + 2.64x_1^2\right) = -5.28 + 5.28x_1$$

$$\Rightarrow 0 = x_1\left(-5.28 + 5.28x_1\right) + (1-x_1)\frac{d\bar{V}_2}{dx_1}$$

$$\frac{5.28x_1 - 5.28x_1^2}{(1-x_1)} = \frac{d\bar{V}_2}{dx_1}$$

$$\frac{5.28x_1\cancel{(1-x_1)}}{\cancel{(1-x_1)}} = \frac{d\bar{V}_2}{dx_1} \longrightarrow \frac{d\bar{V}_2}{dx_1} = 5.28x_1$$

(ii) Integrate and use density to get $\bar{V}_2$ expression

$$\int d\bar{V}_2 = \int 5.28x_1\,dx_1 \Rightarrow \bar{V}_2 = 2.64x_1^2 + C$$

$$V_{m,2} = \bar{V}_2(x_2=1) = \bar{V}_2(x_1=(1-1)) = 2.64(0)^2 + C = C$$

$$V_{m,2} = C = \frac{1}{\frac{\rho_2}{MW_2}} = \frac{MW_2}{\rho_2} = \frac{84.162 \frac{g}{mol}}{0.769 \frac{g}{cm^3}} = 109.44 \frac{cm^3}{mol}$$

$$\bar{V}_2 = 2.64x_1^2 + 109.44 \ \frac{cm^3}{mol}$$

6. Answer the following reflection questions (5 points):

   a. What about the way this class is taught is helping your learning?

   b. What about the way this class is taught is inhibiting your learning?

A) With the second midterm coming up, I have found it is useful to have the practice midterms up on canvas but not the solutions available immediately. This effectively makes me study better and properly asses what I know and what I need to review, as I don't have an answer key to fall back on and reference. Another thing that helps my learning is the way new topics are presented in class. With us just starting the Fugacity chapter, it was great to see the derivation and physical meaning of Fugacity before being given a definition. This greatly helped my immediate understanding, and will be useful when we get further into the chapter.

B) There is nothing currently inhibiting my learning. The way this class is structured promotes a productive and engaging learning environment, and there is nothing I can comment on regarding potential changes.