Secret Code 20:

Problem Set 4

4.1A)

1) $\Delta \bar{S}_m = \frac{\Delta \bar{H}_m}{T_m} = \frac{9.9\ kJ/mol}{278.6\ K} = 0.0355\ kJ \cdot mol^{-1} \cdot K^{-1}$

2) $\Delta \bar{S}_v = \frac{\Delta \bar{H}_v}{T_v} = \frac{33.9\ kJ/mol}{353.9\ K} = 0.0960\ kJ \cdot mol^{-1} \cdot K^{-1}$

4.1AC) $d\bar{H}^{solid} = C_p^{solid}\, dT$

From Fit:

$$C_p^{solid}(T) = 0.441\ T$$

$$\int_{\bar{H}_1}^{0} d\bar{H} = \int_{T}^{T_m=278.6} 0.441T\, dT$$

$$\bar{H}\Big|_{\bar{H}}^{0} = 0.441T^2\Big|_{T}^{278.6}$$

$$0 - \bar{H} = 0.441(278.6)^2 - 0.441T^2$$

$$\boxed{\bar{H}^{solid}(T) = 0.441T^2 - 34229.52}$$

4.1A.D) $d\bar{S} = \frac{C_p}{T} dT$

$$\int_0^{\bar{S}} d\bar{S} = \int_0^T \frac{0.441\cancel{T}}{\cancel{T}} dT$$

$$\boxed{\bar{S}^{solid} = 0.441T}$$

4.1A.E) $\mu^{solid} = \bar{H}^{solid} - T\bar{S}^{solid}$

$$\mu^{solid} = \cancel{0.441T^2} - 34229.52 - \cancel{0.441}$$

$$\boxed{\mu^{solid} = -34229.52\ J}$$

4.1A.F1) $\int_{\bar{H}_m}^{H} d\bar{H}^{liq} = \int_{T_m}^{T} C_p^{liq}\, dT$

$$C_p^{liq} = \underset{aT^2}{-1.0407\times10^{-3}T^2} + \underset{bT}{8.702\times10^{-1}T} \underset{+C}{- 3.187\times10^{1}}$$

$$\bar{H}^{liq} - \bar{H}^{liq}_{melting} = \int_{T_m}^{T} aT^2 + bT + C\, dT$$

From Pt. A.1 $= 9.9\frac{kJ}{mol}$

$$= \frac{aT^3}{3} + \frac{bT^2}{2} + CT \Big|_{T_m}^{T}$$

$\Delta\bar{H}_m = \bar{H}_\ell - \overset{0}{\bar{H}_m}$

$= 9.9$ kJ/mol

$$\bar{H}^{liq} - \bar{H}^{liq}_{melt} = \frac{aT^3}{3} + \frac{bT^2}{2} + CT - \underbrace{\left(\frac{aT_m^3}{3} + \frac{bT_m^2}{2} + CT_m\right)}_{17391.2}$$

$$\bar{H}^{liq} - 9{,}900 = \frac{a}{3}T^3 + \frac{b}{2}T^2 + CT - 17391.2$$

$$\boxed{\bar{H}^{liq}(T) = \frac{a}{3}T^3 + \frac{b}{2}T^2 + CT - 7491.2}$$

$$\int d\bar{S}^{liq} = \int \frac{C_p}{T}\, dT = \int \frac{aT^2 + bT + C}{T}\, dT = \int aT + b + \frac{C}{T}$$

$$\bar{S}\Big|_{\bar{S}^{liq}_m}^{\bar{S}^{liq}} = \frac{aT^2}{2} + bT + C\ln(T)\Big|_{T_m}^{T}$$

J/mol

$$\bar{S}^{liq} - \bar{S}^{liq}_m = \frac{aT^2}{2} + bT + C\ln(T) - \underbrace{\left[\frac{a}{2}T_m^2 + bT_m + C\ln(T_m)\right]}_{-22.6}$$

$\Delta\bar{S}_m = \bar{S}_\ell - \bar{S}_s$

$35.5\frac{J}{mol} = \bar{S}_\ell - (0.441 \times T_m)$

$158.36 = \bar{S}_{liq}$ @ T_m

$$\bar{S} - 158.36 = \frac{aT^2}{2} + bT + C\ln(T)$$

$$\boxed{\bar{S}^{liq}(T) = \frac{aT^2}{2} + bT + C\ln(T) + 135.76}$$

$$\mu^{liq} = \bar{H}^{liq} - T\bar{S}^{liq}$$

$$= \frac{a}{3}T^3 + \frac{b}{2}T^2 + CT - 7491.2 - T\left[\frac{aT^2}{2} + bT + C\ln(T) + 135.76\right]$$

$$= \quad '' \quad - \left[\frac{aT^3}{2} + bT^2 + CT\ln(T) + 135.76T\right]$$

$$= \frac{a}{3}T^3 + \frac{b}{2}T^2 + CT - 7491.2 - \frac{aT^3}{2} - bT^2 - CT\ln(T) - 135.76T$$

$$= \frac{2aT^3}{6} - \frac{3aT^3}{6} + \frac{b}{2}T^2 - \frac{2bT^2}{2} + CT - 135.76T - CT\ln(T) - 7491.2$$

$$\mu^{liq}(T) = \boxed{-\frac{aT^3}{6} - \frac{bT^2}{2} + (C - 135.76)T - CT\ln(T) - 7491.2}$$

4.1AF2)

$$\int_{\bar{H}_v^{gas}}^{\bar{H}^{gas}} d\bar{H}^{gas} = \int_{T_v}^{T} C_p\, dT \qquad C_p = \frac{aT}{b+T} = a\left[\frac{T}{b+T}\right] = \quad b+T\,\overline{\big)(T+b)-b}\ \ 1-\frac{b}{b+T}$$

(polynomial Division)

$$a\left[\int 1\,dT - \int \frac{b}{b+T}\,dT\right] = a\left[T - b\ln(b+T)\right] = aT - ab\ln(b+T)$$

$\Delta\bar{H}_v = \bar{H}_v^{gas} - \bar{H}_v^{liq}$

$\Delta\bar{H}_v + \bar{H}_v^{liq} = \bar{H}_v^{gas}$

$33{,}900 + \bar{H}_v^{liq}$

w/eq above: $20{,}231$

$\bar{H}_v^{gas} = 54{,}131$

$$\bar{H}^{gas} - \bar{H}_v^{gas} = \int_{T_v}^{T} \frac{aT}{b+T}\,dT = a\int_{T_v}^{T} \frac{T}{b+T}\,dT = a\left[T - b\log(b+T)\right]_{T_v}^{T}$$

$$= a\left(T - b\log(b+T) - \left[T_v - b\log(b+T_v)\right]\right)$$

$$= aT - ab\log(b+T) - a\left[T_v - b\log(b+T_v)\right]$$

$$\text{''} \qquad +\underbrace{\left[aT_v - ab\log(b+T_v)\right]}$$

$$\bar{H}^{gas} - \bar{H}_v^{gas} = aT - ab\log(b+T) + 1{,}941{,}385.3$$

$$\bar{H}^{gas} - 54131 = \text{''}$$

$$\bar{H}^{gas}(T) = aT - ab\log(b+T) + 1941{,}385.3 + 54131$$

$$\boxed{\bar{H}^{gas}(T) = aT - ab\log(b+T) + 1{,}995{,}516.7}$$

$$\int_{\bar{S}_v^{gas}}^{\bar{S}^{gas}} d\bar{S}^{gas} = \int_{T_v}^{T} \frac{C_p}{T}\,dT = \int_{T_v}^{T} \frac{a}{b+T}\,dT = a\log(b+T)\Big|_{T_v}^{T}$$

$\Delta\bar{S}_v = \bar{S}_v^{gas} - \bar{S}_v^{liq}$

0.0960

$96.0 + \bar{S}_v^{liq} = \bar{S}_v^{gas}$

$\bar{S}_v^{gas} = 287.18\ \frac{J}{mol\,K}$

$\bar{S}^{liq}(T_v)$ as solved above

$$\bar{S}^{gas} - \cancel{\bar{S}_v^{gas}} = a\log(b+T) - a\log(b+T_v) + \bar{S}_v^{gas}$$

$$\bar{S}^{gas}_{(T)} = a\log(b+T) + \left(-a\log(b+T_v)\right) + 287.18$$

$$\boxed{\bar{S}^{gas}(T) = a\log(b+T) - 2271.8}$$

$$\mu^{gas} = \bar{H}^{gas} - T\bar{S}^{gas}$$

$$= aT - ab\log(b+T) + 1{,}995{,}516.7 - T\left[a\log(b+T) - 2271.8\right]$$

$$\boxed{\mu^{gas}(T) = aT - ab\log(b+T) + 1{,}995{,}516.7 - aT\log(b+T) + 2271.8T}$$

4.2A) want:

$\mu_A(\chi_{H_2O})$

given: $\mu_A^* = 5$ kJ/mol when $\chi_A^* = 1$

$\mu_A = \mu_A^* + RT\ln(\chi_A)$

$\mu_A(\chi_{H_2O}) = \mu_A^* + RT\ln(1-\chi_{H_2O})$

B) y-Intercept is μ_A^* because it is defined when $\chi_A = 1$ ($\chi_{H_2O} = 0$ (y-intercept))

C) When $\chi_{H_2O} = 1$, $\mu_A = -\infty$

$$\Delta G_{mixing} = RT(\chi_A \ln(\chi_A) + (1-\chi_A)\ln(1-\chi_A))$$

$$G = \sum_i^2 n_i\mu_i = n_A \underbrace{\mu_A}_{\mu_A^* + RT\ln(\chi_A)} + n_B\mu_B \leftarrow \mu_B^* + RT\ln(\mu_B)$$

$$= n_A(\mu_A^* + RT\ln(\chi_A)) + n_B(\mu_B^* + RT\ln(\mu_B))$$

$$= \underbrace{\cancel{n_A\mu_A^*}}_{0 \cdot \text{const}} + \underbrace{n_ART\ln(\chi_A)}_{} + n_B\mu_{H_2O}^* + n_BRT\ln(\mu_{H_2O})$$

when $\chi_{H_2O} = 1$

$\frac{n_T + n_A}{n_T} = 1$

$n_A = 0$

A contribution to G is zero when $n_{H_2O} = n_T$ ($\chi_{H_2O} = 1$) in a binary solution

$$\lim_{n_A \to 0}\left(n_ART\ln\left(\frac{n_A}{n_T}\right)\right)$$

$$\lim_{n_A \to 0}\left(\frac{RT\ln\left(\frac{n_A}{n_T}\right)}{\frac{1}{n_A}}\right) =$$

$$\lim_{n_A \to 0}\frac{RT\frac{N_T}{\cancel{n_A}}}{\frac{-1}{\cancel{n_A}}} = \lim_{n_A \to 0}(-RTn_A)$$

$$= \boxed{0}$$

NO contribution

4.3) $G_{mixed} - G_{unmixed}$

$$\Delta G_{mixing} = n_A\mu_A + n_B\mu_B + n\mu_C - [n_A\mu_A^* + n_B\mu_B^* + n_C\mu_C^*]$$

$$= n_A(\mu_A^* + RT\ln(\chi_A)) + n_B(\mu_B^* + RT\ln(\chi_B)) + n_C(\mu_C^* + RT\ln(\chi_C)) - n_A\mu_A^* - n_B\mu_B^* - n_C\mu_C^*$$

$$= \cancel{n_A\mu_A^*} + n_ART\ln(\chi_A) + \cancel{n_B\mu_B^*} + n_BRT\ln(\chi_B) + \cancel{n_C\mu_C^*} + n_CRT\ln(\chi_C) - \cancel{n_A\mu_A^*} - \cancel{n_B\mu_B^*} - \cancel{n_C\mu_C^*}$$

$$\boxed{\begin{aligned} &\Delta G_{mixing} = RT[n_A\ln(\chi_A) + n_B\ln(\chi_B) + n_C\ln(\chi_C)] \\ &(\Delta \bar{G}_{mixing} = RT[\chi_A\ln(\chi_A) + \chi_B\ln(\chi_B) + \chi_C\ln(\chi_C)]) \\ &\Delta S_{mixing} = -\frac{\partial \Delta G}{\partial T} = -R[n_A\ln(\chi_A) + n_B\ln(\chi_B) + n_C\ln(\chi_C)] \\ &(\Delta \bar{S}_{mixing} = -R[\chi_A\ln(\chi_A) + \chi_B\ln(\chi_B) + \chi_C\ln(\chi_C)]) \end{aligned}}$$