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Exam 2
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1a) $\Delta g°rxn = \left[\Delta_f G_{CH_3CHO} + \Delta_f G_{CO_2} \right] - \left[\Delta_f G_{CH_3COCOOH} \right]$

$= (-133 \text{ kJ/mol}^{-1}) - (394 \text{ kJ/mol}^{-1}) - (-463 \text{ kJ/mol}^{-1})$

$= \boxed{-64.0 \text{ kJ/mol}^{-}}$

$\rightarrow \Delta G rxn < 0 \rightarrow$ the reaction is spontaneous

b) $\Delta Grxn = -RT \ln Keq$

$-64 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/Kmol}) \times 80 K \times \ln Keq$

$\boxed{Keq = 6.15 \times 10^{41}}$

c.) At lower temperatures, the reaction favors the reactants.

2a.) $\left(\dfrac{\partial S}{\partial V} \right)_T = \left(\dfrac{\partial P}{\partial T} \right)_V$ $\partial Sm = \dfrac{\partial S}{n}$

$\beta = \dfrac{1}{V} \left(\dfrac{\partial V}{\partial T} \right)_P$ $K = -\dfrac{1}{V} \left(\dfrac{\partial V}{\partial P} \right)_T$

$\left(\dfrac{\partial V}{\partial T} \right)_P \left(\dfrac{\partial P}{\partial V} \right)_T \left(\dfrac{\partial T}{\partial P} \right)_V = -1$

$\rightarrow (\beta V) \left(\dfrac{1}{-KV} \right) = - \left(\dfrac{\partial P}{\partial T} \right)_V$

$\left(\dfrac{\partial P}{\partial T} \right)_V = \dfrac{\beta}{K}$ therefore $\boxed{\left(\dfrac{\partial Sm}{\partial V} \right)_T = \dfrac{\beta}{nk}}$

b) The molar ~~energy~~ entropy increases with increasing volume

$\left(\dfrac{\partial Sm}{\partial V} \right) = \dfrac{\beta}{nk}$

β, K, n are positive therefore $\int dsm = \left(\dfrac{\beta}{nk} \right) \int \partial V$ $\Delta sm = \left(\dfrac{\beta}{nk} \right)(\Delta v)$

c.)
$$\left(\frac{\partial U_i}{\partial P}\right)_{T,\, n_j \neq i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\, n_j \neq i}$$

The single phase fluid in the closed system and no chemical reactions. The total Gibbs energy is

$$d(nG) = (nV)\,dP - (nS)\,dT$$

#of moles ↙

$$\left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T}\right] = -nS$$

If the system is open, then the materials may go in/out of the system. nG becomes a function — the number of moles of the chemical species.

Total Gibbs Energy of T, P and n

$$nG = f(T, P, n_j, n_2, n_3 \dots n_i \dots)$$

Total differential of nG

$$d(nG) = \left[\frac{\partial nG}{\partial P}\right]_{T,n} dP + \left(\frac{\partial nG}{\partial T}\right)_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j \neq i} dn_i$$

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,\, n_j \neq i}$$

therefore $\boxed{d(nG) = (nV)\,dP + (-nS)\,dT + \sum_i \mu_i\, dn_i}$

$$V = \left.\frac{\partial(nG)}{\partial P}\right|_{T,n_i} \quad \text{and} \quad \mu_i = \left.\frac{\partial(nG)}{\partial n_i}\right|_{T,P}$$
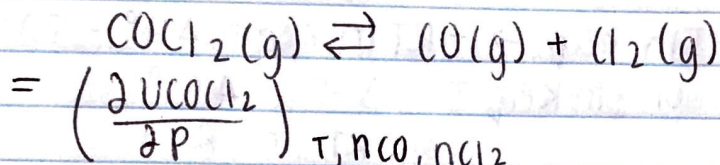
↓

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,P,\, n_j \neq i} = \frac{\partial^2(nG)}{\partial n\, \partial P} \quad \text{and} \quad \left.\frac{\partial U_i}{\partial P}\right|_{T,\, n_j \neq i} = \frac{\partial^2(nG)}{\partial n_i\, \partial P}$$

↓

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,P,\, n_j \neq i} = \left.\frac{\partial U_i}{\partial P}\right|_{T,\, n_j \neq i}$$

d) $\left(\dfrac{\partial V_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} = \left(\dfrac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}}$

If pressure increases, the equilibrium moves in the direction with less moles of gas. In the reaction, with increased pressure, equilibrium move to left and $COCl_2$ forms.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

$= \left(\dfrac{\partial V_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}}$
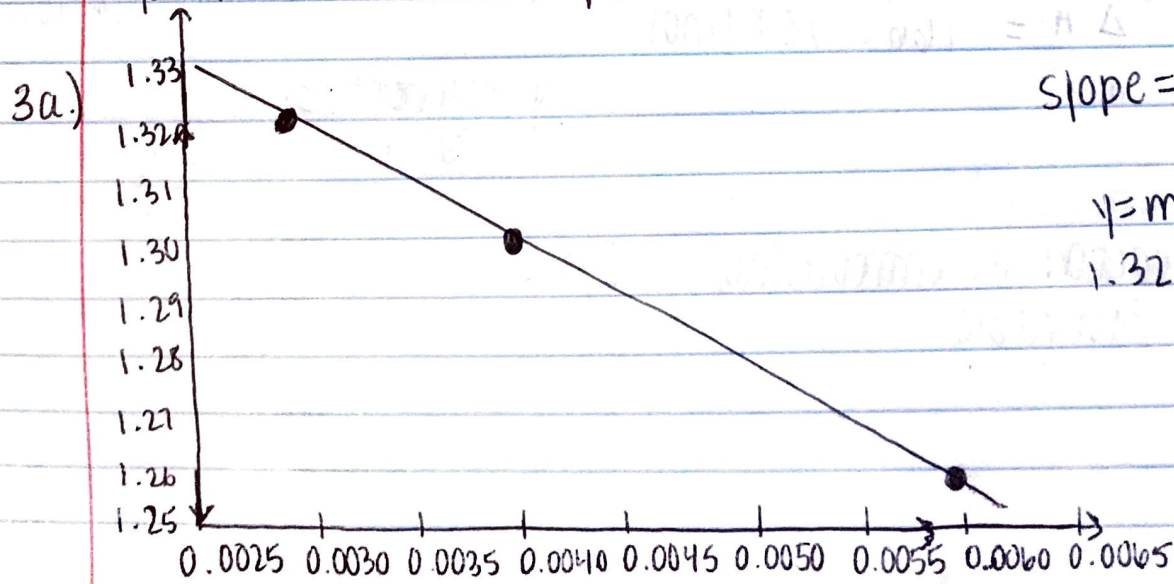
The chemical potential changes by increasing with the increase of pressure.

e) $\dfrac{\partial \mu_i}{\partial P}\Big|_{T, n_j \neq i} = \dfrac{\partial V}{\partial n_i}\Big|_{T, P, n_j \neq i}$

R.H.S is constant
therefore $\displaystyle\int_{\mu_{0i}}^{\mu_i} \partial \mu_i = \int_{P_b}^{P} \dfrac{\partial V}{\partial n_i} \, \partial P$

$$\boxed{(\mu_i - \mu_{0i}) = \dfrac{\partial V}{\partial n_i}\left(P - P_0\right)}$$

μ_{0i} is a chemical potential when it is at P_0 pressure

3a)

slope $= \dfrac{1.32 - 1.30}{0.003 - 0.004} = \boxed{-20}$ $\frac{b}{m}$

$y = mx + b$

$1.32 = (-20)\,0.003 + b$

$b = \boxed{1.38}$

$\text{I}/T(K)$

$T(K)$	$1/T(K)$	K_p	$\ln(K_p)$
167	$1/167 = 0.006$	3.53	$\ln(3.53) = 1.26$
250	$1/250 = 0.004$	3.67	$\ln(3.67) = 1.30$
333	$1/333 = 0.003$	3.74	$\ln(3.74) = 1.32$

b.) $\Delta G° = -RT \ln k_{eq} \rightarrow -RT \ln k_{eq} = \Delta H° - T\Delta S°$

or $\ln k_{eq} = -\dfrac{\Delta H°}{RT} + \dfrac{\Delta S°}{R}$

$\ln K_p = -20 + 1.38$

$e^{\ln K_p} = -18.62$

$\Delta G = -RT \ln K_p$

$\Delta G_1 = -8.314 \text{ J/mk}(167 k) \ln(3.53)$

$[\Delta G_1 = -1,751.234 \text{ J/m}]$

$\Delta G_2 = -8.314 \text{ J/mk}(250 k) \ln(3.67)$

$[\Delta G_2 = -2,702.448 \text{ J/m}]$

$\Delta G_3 = -8.314 \text{ J/mk}(333 k) \ln(3.74)$

$[\Delta G_3 = -3,651.970 \text{ J/m}]$

$K_p = 8.193 \times 10^{-9}$

$\Delta g° = -RT \ln K_p$

$\Delta g° = -8.314 (250) \ln (8.193 \times 10^{-9})$

$\Delta g° = 38,701.640 \text{ J/m}$

Average $\Delta g =$
$-2,701.884 \text{ J/m}$

3c.) slope $= -\dfrac{\Delta H°}{R}$

$-\Delta H° = \text{slope} \cdot R$

$-\Delta H° = -20 (8.314 \text{ J/mk})$

$\Delta H = 166.28 \text{ J/mol}$

$\Delta G < 0$ spontaneous
$\Delta H > 0$ ✗spontaneous @ high temp
$\Delta S > 0$ ✗ spontaneous @ low temp

y-intercept b
↓ $\dfrac{1.38}{1} = \dfrac{\Delta S}{8.314}$

$[\Delta S = 11.473]$

this reaction is entropically favorable

4.) The second law of thermodynamics states that the total entropy of an isolated system can't decrease overtime. It always increases and is constant if all processes are reversible. The second law of thermodynamics is expressed as

$$\left[ds = \frac{dQ}{T} \right]$$

5.) The third law of thermodynamics states the determination of absolute value of entropy. The entropy of a pure substance in perfect crystalline form at absolute zero is (0 J/K).

$$\left[S = k \ln W = k \ln 1 = 0 \right]$$

6.) We can't build a perpetual motion machine because according to the first law of thermodynamics — law of conservation of energy in order to keep the machine moving, it is important for the applied energy to stay with the machine without any loss. There shouldn't have any rubbing parts due to friction. The machine must be operated inside a vacuum with no air and the machine should not produce any sound.

7.) Gibbs free energy is usually more useful to chemists than Helmholtz energy because Gibbs free energy is more straightforward when having to manipulate variables — pressure and temperature. Helmholtz energy is useful when dealing with mechanical systems.

8.) $\left(\frac{\partial G}{\partial n_i} \right)_{T,P} \ldots n_j = G = \mu_i \rightarrow N \frac{u_c}{N}$

This is called potential because it is under the constant pressure, temperature and number of moles for all species except "i". The equatio is potential because it increases in Gibbs free energy when compared to the increase of # of moles
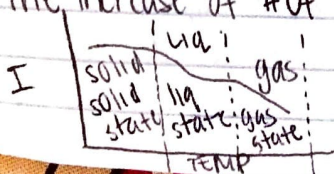
9. The chemical potential is defined as the Δ in Gibbs free energy in respect to # of moles. For instance, adding a molecules to an ideal doesn't cause a reaction and in result it cause an increases for the # of moles and entropy due to increase in particles. When examined the relationship of the chemical potential ~~decreases~~ to # of molecules added it is inverse. The chemical potential decreases as # of particles increases. Entropy increase which is spontaneous. It can be said that mixing non ideal gas is spontaneous and defined by

$$dU = \left(\frac{\partial G}{\partial n}\right)_{T,P,n} \rightarrow \begin{array}{l} \mu_A{}^\alpha = \mu_A{}^\beta \\ \mu_B{}^\alpha = \mu_B{}^\beta \\ \Delta U = \Delta \mu_0{}^* + RT \ln [keq] \end{array}$$

$$\Delta B = \Delta H - T\Delta S$$
$$\Delta S = k \ln w$$
$$\Delta S mix = -nR[x_A \ln x_A + x_B \ln x_B]$$
$$\Delta S = \uparrow \Delta G \uparrow$$
$$\mu = \left(\frac{\partial G}{\partial n}\right) = \text{chemical potential}$$

10.) If $\Delta grxn° > 0$ there will be more reactants than products. The free energy of the reaction is positives, therefore if is not spontaneous and no product will form, but more reactant will form.

$$\Delta grxn = -RT \ln keq$$
$$\Delta grxn > 0 \ keq \quad keq < 0$$

$$\nearrow keq = \frac{product}{reactant} \rightarrow keq < 0$$

$$\downarrow$$

$$\uparrow reactants\ formed > products$$

Extra Credits

My favorite equation from this semester was the second law of thermodynamics. As the electrical energy flows through transmission lines to our house, the wires are heated by the flowing electrons and more energy is lost as it heats up the air around the wires. When the electrical energy reaches our houses where it is converted to heat or mechanical energy.