

Exam 2

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*Worked with
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1a.

$$\Delta G^\circ_{rxn} = [\Delta_f G_{\text{CH}_3\text{CHO}} + \Delta_f G_{\text{CO}_2}] - [\Delta_f G_{\text{CH}_3\text{COCOOH}}]$$

$$= \left(-\frac{133}{\text{kJ/mol}} - \frac{394}{\text{kJ/mol}}\right) - \left(-\frac{463}{\text{kJ/mol}}\right) = \boxed{-64.0 \text{ kJ/mol}}$$

→ $\Delta G^\circ_{rxn} < 0 \rightarrow$ The reaction is spontaneous.

b.

$$\Delta G^\circ_{rxn} = -RT \ln K_{eq}$$

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

$$\boxed{K_{eq} = 6.15 \times 10^{41}}$$

c.

At lower temperature, the reaction favors the reactants.

2a.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$2S_m = \frac{\partial S}{\partial n}$$

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

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

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K} \quad \text{therefore} \quad \boxed{\left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{nK}}$$

b. The molar entropy increases with increasing volume.

$$\left(\frac{\partial S_m}{\partial V}\right) = \frac{\beta}{nK}$$

$$\beta, K, n \text{ are positive therefore } \int dS_m = \left(\frac{\beta}{nK}\right) \int dV$$

$$\Delta S_m = \left(\frac{\beta}{nK}\right) (\Delta V)$$

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

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

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

$$nG = f(T, P, n_1, n_2, n_3, \dots, n_i, \dots)$$

Total differential of nG

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

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

Therefore
$$d(nG) = (nv)dP + (-ns)dT + \sum_i \mu_i d n_i$$

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

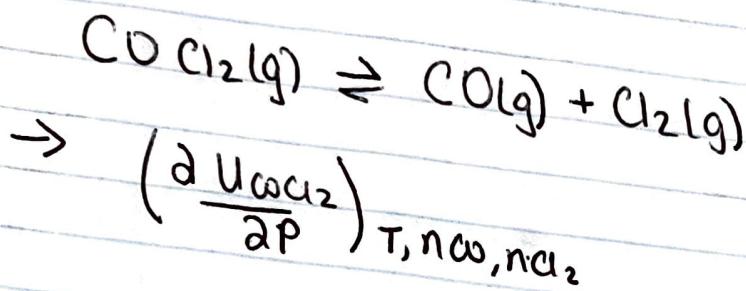
$$\left. \frac{\partial V}{\partial n_i} \right|_{T,P,n_j \neq i} = \left. \frac{\partial^2(nG)}{\partial n \partial P} \right|_{T,P,n_j \neq i} \quad \text{and} \quad \left. \frac{\partial(\mu_i)}{\partial P} \right|_{T,n_j \neq i} = \left. \frac{\partial^2(nG)}{\partial n_i \partial P} \right|_{T,n_j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

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

d.

$$\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = \left(\frac{\partial V}{\partial n_{\text{COCl}_2}} \right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}}$$

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.



The chemical potential changes by increasing with the increase of pressure.

e.

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

R.H.S is constant

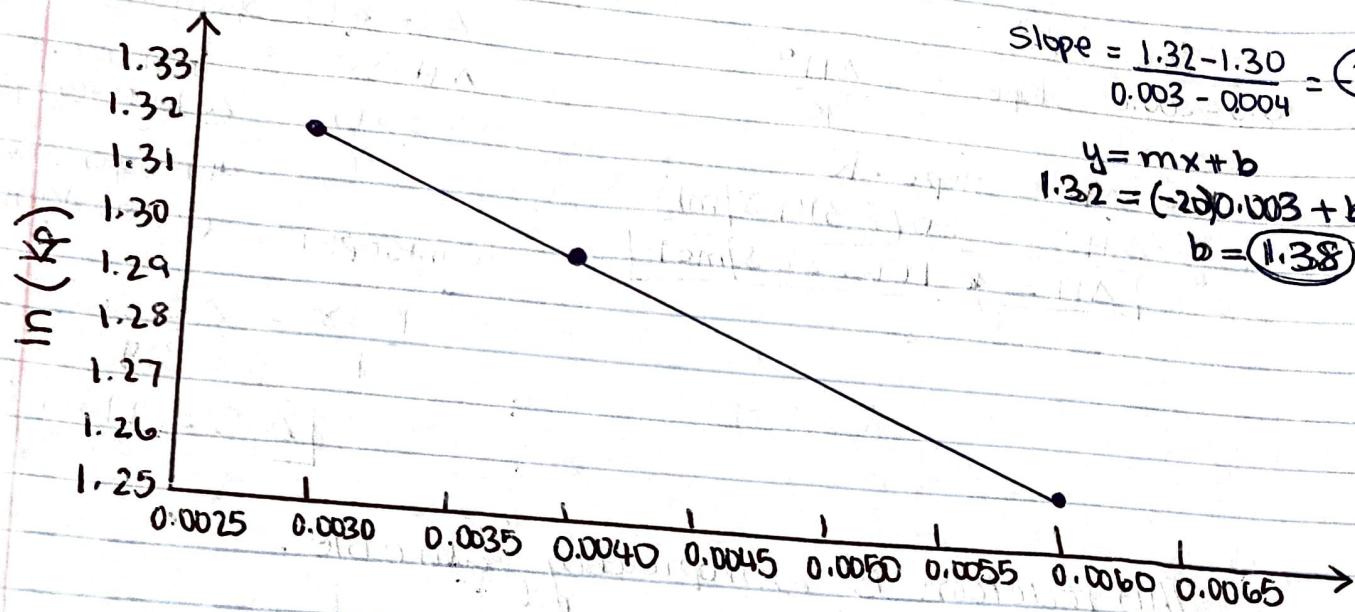
therefore

$$\int_{\mu_{0i}}^{\mu_i} \frac{\partial \mu_i}{\partial P} dP = \int_{P_0}^P \frac{\partial V}{\partial n_i} dP$$

$$(\mu_i - \mu_{0i}) = \frac{\partial V}{\partial n_i} (P - P_0)$$

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

3a.



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

b.

$$\Delta G^\circ = -RT \ln K_{eq} \rightarrow -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$$

$$\text{or } \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

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

$$\ln K_p = -20 + 1.38$$

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

$$\Delta G = -RT \ln K_p$$

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

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

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

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

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

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

$$\Delta G^\circ = -RT \ln K_p$$

$$\Delta G^\circ = -8.314 (250) \ln \left(\frac{8.193 \times 10^{-9}}{8.193 \times 10^{-9}} \right)$$

$$\boxed{\Delta G^\circ = 38,701.640 \text{ J/m}}$$

Average ΔG

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

3c.

$$\text{Slope} = -\frac{\Delta H^\circ}{R}$$

$$-\Delta H^\circ = \text{slope} \cdot R$$

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

$$\boxed{\Delta H = -166,28 \text{ J/mol}}$$

$\Delta G < 0$ Spontaneous

$\Delta H > 0$

$\Delta S > 0$

* Spontaneous *
@ high temp.

* Nonspontaneous *
@ low temp.

y-intercept b

$$\frac{1.38}{1} = \frac{\Delta S}{8.314}$$

$$\boxed{\Delta S = 11.473}$$

This reaction is entropically favorable.

(g)	(l)	(s)	(s)
$0.5 \times 10^3 \text{ J/mol}$	-23.8 J/mol	-20.6 J/mol	-19.7 J/mol
$0.8 \times 10^3 \text{ J/mol}$	-71.8 J/mol	-40.0 J/mol	-32.5 J/mol
$1.3 \times 10^3 \text{ J/mol}$	-115.8 J/mol	-80.2 J/mol	-68.8 J/mol

$$\Delta_f^\circ \text{ H}_2O = \Delta_f^\circ \text{ H}_2 + \Delta_f^\circ \text{ O}_2 - \Delta_f^\circ \text{ KCl}$$

$$\frac{\Delta_f^\circ \text{ H}_2}{K} + \frac{\Delta_f^\circ \text{ O}_2}{K} = \Delta_f^\circ \text{ KCl}$$

$$\Delta_f^\circ \text{ H}_2 = \Delta_f^\circ \text{ P}_\text{H}_2$$

$$\Delta_f^\circ \text{ O}_2 = \Delta_f^\circ \text{ P}_\text{O}_2$$

$$38.1 + 0.5 = \Delta_f^\circ \text{ KCl}$$

$$22.81 = \Delta_f^\circ \text{ KCl}$$

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

$$[dS = \frac{dQ}{T}]$$

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.

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

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.

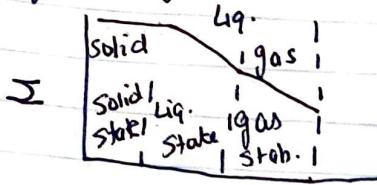
The machine must be operated inside a vacuum with no air and the machine should not produce any sound.

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

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

This is called potential because it is under constant pressure,

temperature and number of moles for all species except "i".
 The equation is potential because it increases in
 Gibb's free energy when compared to the increase of # of moles.



Temp

9. The chemical potential is defined as the Δ in Gibb's free energy in respect to # of moles. For instance, adding a molecule to an ideal gas doesn't cause a reaction and in result it causes an increase for the # of moles and entropy due to increase in particles. When examined the relationship of the chemical potential to # of molecules added it is inverse. The chemical potential decreases basis # of particles increase. Entropy increases which is spontaneous. It can be said that mixing non ideal gases is spontaneous and defined by

$$\text{and } \Delta U = \left(\frac{\partial G}{\partial n} \right)_{T, p, n} \rightarrow \mu_A^\infty = \mu_{AB}^\infty \text{ basis } \mu_B^\infty = \mu_B^\infty$$

$$\text{above will follow for binary system with } \Delta \mu = \Delta \mu^\infty + RT \ln [k_{eq}]$$

$$\Delta B = \Delta H - T\Delta S$$

$$\Delta S_f = k \ln W \text{ allows a pure and define } \Delta$$

$$\Delta S_{mix} = -nR \left[x_A \ln x_A + x_B \ln x_B \right] \text{ basis } \Delta$$

$$\Delta S = \uparrow \Delta G \uparrow \text{ basis } \Delta S = \uparrow \Delta G \uparrow$$

$$\mu = \left(\frac{\partial G}{\partial n} \right) = \text{Chemical potential.}$$

$$\frac{\partial}{\partial n} (H - TS) = \mu, \text{ at } T, P$$

trust me draw a h standard writing below is not

10. If $\Delta G_{rxn}^{\circ} > 0$ there will be more reactants than products. The free energy of the reaction is positive, therefore it is not spontaneous and no product will form, but more reactants will form.

$$\Delta G_{rxn} = -RT \ln K_{eq} \rightarrow K_{eq} = \frac{\text{product}}{\text{reactant}} \rightarrow K_{eq} < 0$$

$\Delta G_{rxn} > 0 \quad K_{eq} < 0$

↑ reactants formed ↑ products.

Extra Credit:

My favorite equation from this semester was the third law of thermodynamics. The law states the entropy of a perfect crystal at a temperature of zero is equal to zero. The state function 'S' for entropy is known to measure the disorder in a closed system.

