Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

Name: Kevin Zhang

Important: This exam must be turned in handwritten. It can be on lined paper.

It must be turned in as a single PDF. Image files for each page will not be accepted.

You can download Adobe Scan on your phone to make the PDF.
https://acrobat.adobe.com/us/en/mobile/scanner-app.html

Who did you work with?

a. Harleen Gill

b.

c.

d.

Who else did you ask for help?

Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

Name: ______________________________

1. The decarboxylation of pyruvic acid occurs via the following reaction:

$$CH_3COCOOH(l) \longrightarrow CH_3CHO(g) + CO_2(g)$$

Given the following thermodynamic data

$$\Delta_f H(25\ C)_{CH_3COCOOH} = -584\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CH_3COCOOH} = -463\ kJ\ mol^{-1}$$
$$\Delta_f H(25\ C)_{CH_3CHO} = -166\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CH_3CHO} = -133\ kJ\ mol^{-1}$$
$$\Delta_f H(25\ C)_{CO_2} = -394\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CO_2} = -394\ kJ\ mol^{-1}$$

a. Calculate ΔG°_{rxn}. Is this reaction spontaneous under standard state conditions? Justify your answer.

$\Delta G_{rxn} = \sum \Delta G_f \text{ products} - \sum \Delta G_f \text{ reactants}$

$= [(-133\ kJ/mol \cdot 1\ mol) + (-394\ kJ/mol \cdot 1\ mol)] - [-463\ kJ/mol \cdot 1\ mol]$

$= \boxed{-64\ kJ/mol}$

The rxn is spontaneous since entropy is increasing

b. Calculate the equilibrium constant, K_P, for this reaction at 80.0 K.

$K_p = e^{-\Delta G/RT}$

$\ln K_p(T_f) = \frac{-\Delta G^\circ}{RT} - \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$= \frac{64000}{(8.314)(298)} - \frac{24000}{8.314}\left(\frac{1}{80K} - \frac{1}{298K}\right)$

$= -0.5848$

$e^{\ln K_p} = e^{-0.5848} \Rightarrow K_p = .568$

$\Delta_f H_{rxn} = \sum \Delta_f H_{prod} - \sum \Delta_f H_{reac}$

$\Delta_f H_{rxn} = [(-166\ kJ/mol) + (-394\ kJ/mol)] - [-584\ kJ/mol]$

$= \boxed{24\ kJ/mol}$

c. At the lower temperature, does the reaction favor the reactants or the products?

The reaction favors the reactants at lower temperatures.

$\mu_{mixture}\ COCl_2(T,P) = \mu^\circ_{COCl_2} + RT\ln(P/P_0) + RT\ln \chi_{COCl_2}$

Exam #2: 4-2-2020: **Please show all work for credit,** Don't Panic

2. For a pure substance

$dS = \frac{C_v}{T} dT$ @ constant V

$\left(\partial/\partial T\left(\frac{\partial S}{\partial V}\right)_T\right)_V - \left(\partial/\partial V\left(\frac{\partial S}{\partial T}\right)_V\right)_T$

a. Derive the following expression

$\left(\partial/\partial T\left(\partial S/\partial T\right)_V\right)_T = \frac{1}{T}\left(\partial/\partial V\left(\frac{\partial U}{\partial T}\right)_V\right)_T$

$dS = 1/T\, dU + P/T\, dV$

$= (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV$

$= 1/T[C_v dT + (\partial U/\partial V)_T dV] + P/T\, dV$

$= \frac{C_v dT}{T} + 1/T[P + (\partial U/\partial V)_T)]dV$

$\left(\frac{\partial S}{\partial T}\right)_V = C_v/T \quad \left(\frac{\partial S}{\partial V}\right)_T = 1/T[P + (\partial U/\partial V)_T]$

$$\left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{n\kappa}$$

$\left(\partial/\partial T\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\partial/\partial T\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right]$

$P + (\partial U/\partial V)_T = T\left(\frac{\partial P}{\partial T}\right)_V - \left[-1/T^2[P + (\frac{\partial U}{\partial V})_T)\right]$

$\left(\frac{\partial S}{\partial V}\right)_T = (\partial P/\partial T)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \beta/\kappa$

b. How does the molar entropy change with increasing volume?

Increasing volume will increase entropy b/c molecules will have more space.

For a mixture of substances, n_1, n_2, n_3 ...

c. Show that the presssure dependence of the chemical potential is related to the volume as follows

$dU = T\,dS - P\,dV + \sum_i \mu_i dn_i$

$\mu_i = (\partial U/\partial n_i)_{S,V,n_j \neq i}$

$dH = T\,dS - V\,dT + \sum_i \mu_i dn_i$

$\mu_i = (\partial H/\partial n_i)_{S,P,n_j \neq i}$

$dA = -P\,dV - T\,dS + \sum_i \mu_i dn_i$

$\mu_i = (\partial A/\partial n_i)_{V,T,n_j \neq i}$

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

$dG = V\,dP - S\,dT + \sum_i \mu_i dn_i$

$\mu_i = (\partial G/\partial n_i)_{P,T,n_j \neq i}$

$d\mu = V\,dP - S\,dT$

$(\partial \mu/\partial P)_T = V$

$\int_{m_o}^{m} dm = V \int_{P^o}^{P} dP$

$\mu - \mu^o = V(P - P^o)$

$\mu = \mu^o + V(P - P^o)$

$V = RT/P$

$\int_{\mu_o}^{\mu} d\mu = RT \ln P|_{P^o}^{P}$

$\frac{dP}{P}$

d. Pure phosphine is allowed to decompose according to the following reaction.

$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j,x_i} = \left(\frac{\partial n COCl_2}{\partial P}\right)_{T,n COCl_2 + n CO + n Cl_2}$

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

$= -\left(\frac{\partial V}{\partial n COCl_2}\right)_{T,P,n COCl_2 + n CO + n Cl_2}$

Assuming ideal gas behavior, and using the Maxwell relationship above, derive an expression for $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$

How does the chemical potential change with increasing pressure?

Hint: $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$, $\quad dn_{COCl_2} = -dn_{CO}$, $\; dn_{COCl_2} = -dn_{Cl_2}$

$\left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{COCl_2}+n_{CO}+n_{Cl_2}} = -\left(\frac{\partial V}{\partial n_{CO}}\right)_{T,P,n_{COCl_2}+n_{CO}+n_{Cl_2}} + \left(\frac{\partial V}{\partial n_{Cl_2}}\right)_{T,P,n_{COCl_2}+n_{CO}+n_{Cl_2}}$

e. Use your result in part **d** to derive an expression for $\mu_{COCl_2}(P)$ with respect to some reference pressure, P^o

$G(T,P) = G^\circ(T) + nRT\ln(P/P^o)$

$\mu_{pure}(T, P_{COCl_2}) = \mu_{mixture\ COCl_2}(T, P_{COCl_2}) = \mu^{\circ}_{COCl_2}(T) + RT\ln\left(\frac{P_{COCl_2}}{P_o}\right)$

$\mu_{mixture\ COCl_2}(T,P) = \mu^\circ_{COCl_2} + RT\ln(P/P_o) + RT\ln x_{COCl_2}$

Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

3. The following thermodynamic data was measured for a chemical reaction:

$1/167 = 0.005988$ $\ln(3.53) = 1.26$

$1/250 = 0.004$ $\ln(3.67) = 1.30$

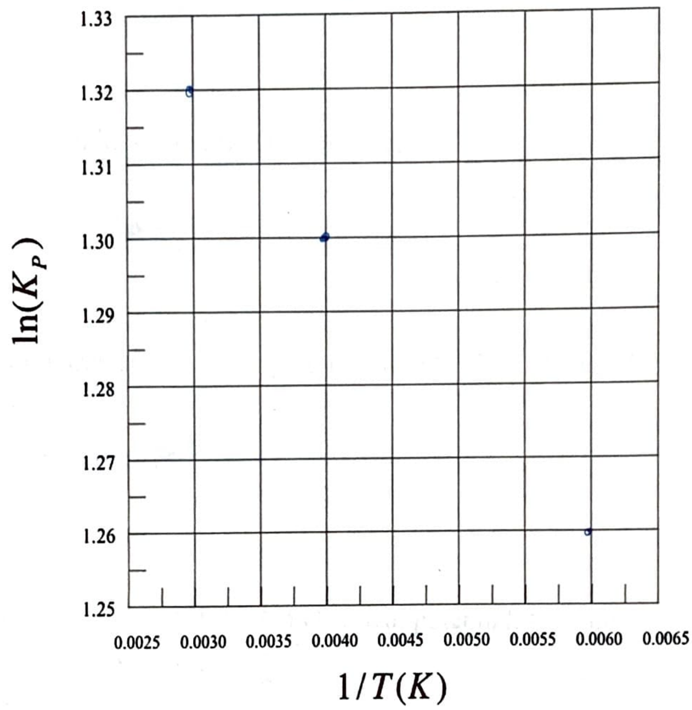
$1/333 = 0.003$ $\ln(3.74) = 1.32$

$m = \Delta y/\Delta x = \frac{0.02}{-0.001} = -20$

$y = mx + b \rightarrow b = y - mx$
$= 1.38$

T (K)	K_P
167	3.53
250	3.67
333	3.74

a. Plot the data on the following plot



b. Calculate ΔG_r° for this reaction. Is this reaction spontaneous? Justify your answer.

$\Delta G = -RT\ln K_p$

$\Delta G_1 = -(8.314)(167)(\ln 3.53)$

$= -1751.234$

$\Delta G_2 = -(8.314)(250)(\ln 3.67) = \underline{2702.448}$

$\rightarrow 2702.448$

$\Delta G_3 = -(8.314)(333)(\ln(3.74)) = 3651.970\ J/m$

$\boxed{\Delta G_{av} = -2701.884\ J/m}$

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

$\ln K_p = -20 + 1.38$

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

$K_p = \cancel{8.13}\ 8.193 \times 10^{-9}$

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

$= 38701.640\ J/mol$

c. Is this reaction enthalpically or entropically driven. Justify your answer.

$\frac{\text{Slope}}{1} = \frac{-\Delta H^\circ}{R}$

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

$= -20(8.314\ J/K \cdot m)$

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

$\Delta G < 0 \rightarrow$ spontaneous

$\Delta H > 0$

$\Delta S > 0$

Spontaneous @ high T
nonspontaneous @ low T

$1.38 \cdot 8.314 = \Delta S$

$\Delta S = 11.473$

entropically favorable

Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

Short Answers:

4. What is the second law of thermodynamics?

Entropy must remain constant or increase in an isolate system.
$\Delta S \geq 0$ for an ~~isol~~ process in an isolated system.

5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy. Entropy of a pure, crystalline substance is zero @ Kelvin. Proving that when entropy is zero, it is at equilibrium.

6. Why can't we build a perpetual motion machine?

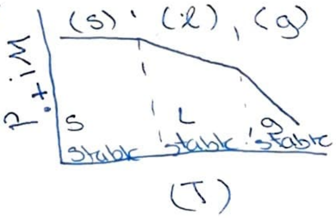
The perpetual motion machine would violate the first and second laws of thermodynamics. It would create energy w/o input and converts thermal energy w/ perfect/100% efficiency

7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?

Gibb's Free Energy is more applicable when factoring in T and P. while a change volume is neglible. Helmhotz energy is more useful w/ dealing w/ mechanical systems.

8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing. $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = G = \mu_i \to \mu$ $^{G}/_{N}$

It's called potential b/c it is under constant T, P, # of mols for all species except species "i", & The rate of increase in Gibb's free energy is consistent w/ increase in number of moles



9. Is the mixing of different types of molecules in an ideal gas spontaneous? Justify your answer using mathematical expressions for the chemical potential.

Chemical potential is the change in free energy in respect w/ # of molecules, when molecule is added to ideal gas, it will not react w/ it, b/c Therefore, the # of molecule- increase when entropy increases. Chem potential is inversely related to # of molecules

$$dU = (\partial G/\partial n)_{T,P,n}$$

10. For a given chemical reaction involving only gasses at equilibrium, if $\Delta G^{\circ}_{rxn}>0$, will there be more product formed or more reactant. Justify your answer using one or more equations.

Free energy of ~~pr~~ the rxn is positive and therefore nonspontaneous. No products form and # of reactants increases.

$\Delta G_{rxn} = -RT \ln K_{eq}$

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

$K_{eq} = {}^{Prod}/_{reac} \Rightarrow K_{eq} < 0$

$\mu_A^{\alpha} = \mu_A^{\beta}$

$\mu_B^{\alpha} = \mu_B^{\beta}$

$\boxed{\mu = \left(\frac{\partial G}{\partial n}\right) = \text{chem pot}}$

$\Delta\mu = \Delta\mu^{\alpha}_{0} RT \ln K_{eq}$

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

$\Delta S = k \ln W$

$\Delta S_m = -nR[x_A \ln x_A + x_B \ln x_B]$

$\Delta S \uparrow \quad \Delta G \uparrow$