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

Name: Gabriela Inojosa Tenorio

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. Valeria Van Merkerk

b. George Paxos

c. Ashley Faro

d.

Who else did you ask for help?

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

Name: Gabriela Iniguez Tenorio

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

$\Delta_f H(25\ C)_{CH_3COCOOH} = -584\ kJ\ mol^{-1}$ $\Delta_f G(25\ C)_{CH_3COCOOH} = -463\ kJ\ mol^{-1}$

$\Delta_f H(25\ C)_{CH_3CHO} = -166\ kJ\ mol^{-1}$ $\Delta_f G(25\ C)_{CH_3CHO} = -133\ kJ\ mol^{-1}$

$\Delta_f H(25\ C)_{CO_2} = -394\ kJ\ mol^{-1}$ $\Delta_f G(25\ C)_{CO_2} = -394\ kJ\ mol^{-1}$

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

ΔG°_r = products − reactants

$\Delta G^{\circ}_r = [(-133kJ/mol) + (-394kJ/mol)] - (-463kJ/mol)$

$\Delta G^{\circ}_r = -64\ kJ/mol$

the reaction is spontaneous when $\Delta G < 0$; making it spontaneous under standard conditions in this case.

$\Delta H^{\circ}_r = 24\ kJ/mol$

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

$K_p = e^{\left(\frac{-64}{R(298)}\right)}$

$K_p = 1.65 \times 10^{11}$

$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^{\circ}_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\ln\left(\frac{K_2}{1.65 \times 10^{11}}\right) = -\left(\frac{24}{0.008314}\right)\left(\frac{1}{80} - \frac{1}{298}\right)$

-26.3968

$K_2 = 0.567$

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

it will favor the reactants.

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

2. For a pure substance

a. Derive the following expression

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

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

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

$\Delta G^\circ_m = H^\circ_m - TS^\circ_m$

$= TS^\circ_m$

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

$\Delta H = \Delta U + P\Delta V$

$\Delta G = \Delta U + P\Delta V - T\Delta S$

$dU = TdS - PdV$; $dG = dU + PdV - TdS - SdT + VdP$

$dG = TdS - PdV + PdV - TdS - SdT + VdP$

$dG = -SdT + VdP$

at constant T

$\left(\frac{\partial Gm}{\partial P}\right)_T = V$ or $\left(\frac{\partial Gm}{\partial V}\right)_T = P$

$\Rightarrow -\left(\frac{\partial Sm}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T n}\right)_V$

$\frac{1}{n}\left[\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{B}{\kappa}\right)\right]$

$\Rightarrow \left(\frac{\partial Sm}{V}\right)_T = \frac{B}{n\kappa}$

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

molar entropy increases as volume increases.

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

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

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

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

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

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

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

$dG = nV\,dP - nS\,dT$

$\left(\frac{\partial nG}{\partial P}\right)_{T,n} = nV \qquad \left(\frac{\partial nG}{\partial T}\right)_{P,n} = -nS$

$nG\,d = \left(\frac{\partial nG}{\partial P}\right)_{T,n} dP + \left(\frac{\partial nG}{\partial T}\right)_{P,n} dT + \sum_i \underbrace{\left(\frac{\partial nG}{\partial n_i}\right)_{P,T,n_{j\neq i}}}_{\mu_i} dn_i$

$nG\,d = nV\,dP - nS\,dT + \sum_i \mu_i\,dn_i$

$V = \left(\frac{\partial nG}{\partial P}\right)_{T,P,n_{j\neq 1}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq 1}}$

$\mu_i = \left(\frac{\partial nG}{\partial n_i}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq 1}}$

$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq 1}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq 1}}$

d. $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$ $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$

$dn_{COCl_2} = -dn_{CO}$; $dn_{COCl_2} = -dn_{Cl_2}$

$\rightarrow \left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{j\neq 1}} = \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{j\neq 1}}$

↳ n_{CO}, n_{Cl_2} ↳ n_{CO}, n_{Cl_2}

$\mu \uparrow$ as $P \uparrow$

e. $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq 1}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq 1}}$

$\int_{P_0}^{P} d\mu_{COCl_2} = \int_{P_0}^{P} \frac{\partial V}{\partial n_i}\,dP$

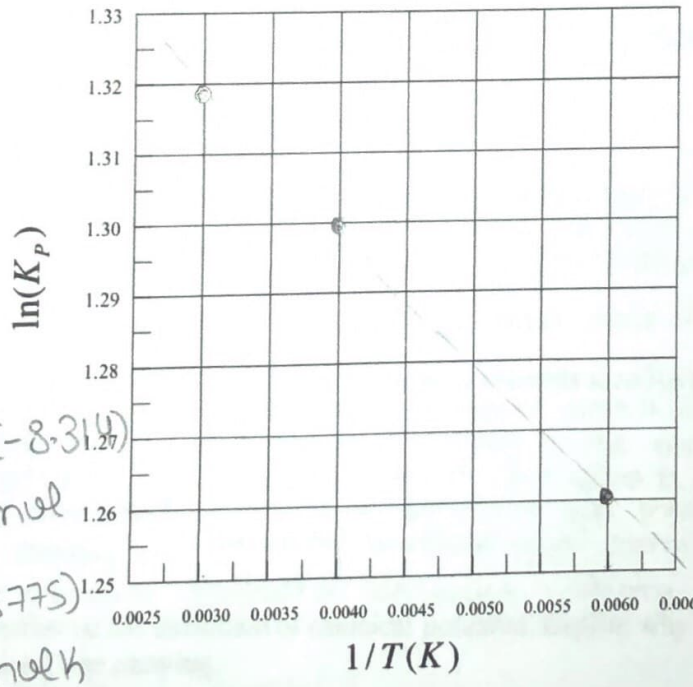
$\mu_{COCl_2}(P) = RT \int_{P_0}^{P} \frac{1}{P}\,dP = RT \ln \frac{P}{P_0}$

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:

T (K)	K_P
167	3.53
250	3.67
333	3.74

a. Plot the data on the following plot



endothermic reaction

$y = -19.388x + 1.3775$

$\Delta H = (-19.388)(-8.314)$

$\Delta H = 161.19$ J/mol

$\Delta S = (8.314)(1.3775)$

$\Delta S = 11.45$ J/molK

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

$\Delta G^\circ_r = (161.19\ \text{J/mol}) - \left(\frac{167+250+333}{3}\right)(11.45\ \text{J/mol K})$

$\Delta G^\circ_r = -2701.33$ J/mol $\Rightarrow -2.701$ kJ/mol

it is spontaneous, both ΔH and ΔS are positive.

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

entropically driven at high temperature whenever ΔH and ΔS are positive; since it is an endothermic reaction, with products favoring disorder and it is spontaneous.

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

Short Answers:

4. What is the second law of thermodynamics?

it is impossible for a system to undergo a CYCLIC process where the conversion of heat to work has 100% efficiency

5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.

Entropy is always increasing in the universe and there is a reference point where entropy is zero. Non of these properties are seen in enthalpy or energy

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

we can't build a perpetual motion machine because it violates the 1st or 2nd law of thermodynamics. It will violate the 2nd law because for an engine to produce work, the area of the cycle in a P-V diagram must be greater than 0, and in a simple cycle using a single heat reservoir, it's impossible

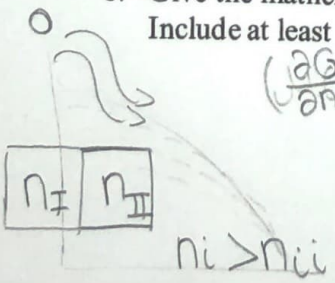
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?

Helmholtz energy is the maximum amount of work a system can do at constant volume and temperature; while Gibbs free energy is the maximum work a system can do at constant pressure and temperature; it is also a minimum for a closed system at equilibrium with a fixed temperature and pressure.
Gibbs free energy is more useful because most chemical reactions occur at constant pressure instead of constant volume

8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing.

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

it's called potential because of the energy that can be absorbed or released in the change of particle numbers.



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

$\mu = \left(\frac{\partial G}{\partial n}\right)$

$d\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P,n}$

$\Delta\mu = \Delta\mu_0 + RT\ln k_e$

$\Delta G_m = \Delta H_m - T\Delta S_m$

as ΔS_m increases, so does ΔG_m

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.

more reactants

$\Delta G = -RT\ln K$

$\Delta G^{\circ} > 0$ makes $K < 0$

$\therefore K = \frac{\text{products}}{\text{reactants}}$

Extra Credit (5 pts)

Write your favorite equation from this semester and briefly explain the insight into chemistry that it provides.

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

This has become my favorite equation because once I was able to understand how entropy and enthalpy separately, once I was able to link that to ΔG I felt like I was truly able to understand a system.