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

Name: Joel Atog

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. Anushan Alagaratnam

b. N/A

c. N/A

d. N/A

Who else did you ask for help?

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Name: Joel Atoa

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.

$\Delta G^\circ_{Rxn} = \sum[\Delta G_f^\circ(prods) \times (mols\ of\ prod)] - \sum[\Delta G_f^\circ(reactanst) \times (mol\ of\ reactants)]$

$= [(-133 KJmol^{-1}) + (-394 KJmol^{-1})] - [(-463 KJmol^{-1})]$

$\Delta G^\circ_{Rxn} = -64 KJmol^{-1}$, Spontaneous because ΔG°_{Rxn} is negative

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

$\ln Kp(T_f) = \ln Kp(298.15K) - \frac{\Delta H^\circ_R}{R}\left(\frac{1}{T_f} - \frac{1}{298.15K}\right)$

$\Delta H^\circ_R = [(-166 KJmol^{-1}) + (-394 KJmol^{-1})] - [(-584 KJmol^{-1})]$

$\Delta H^\circ_R = 24\ KJmol^{-1}$

$\ln Kp = -\frac{\Delta G^\circ_R}{RT}$

$\ln Kp = -\frac{(-64 KJmol^{-1})}{(8.3145\ J/mol\cdot K)(298.15K)}$ $Kp = 1.026$

$\ln Kp(80K) = \ln(1.026) - \frac{(24 KJmol^{-1})}{(8.3145\ J/mol\cdot K)}\left(\frac{1}{80K} - \frac{1}{298.15K}\right)$

$Kp(80K) = 0.999$

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

Reactants Favored

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2. For a pure substance

   a. Derive the following expression

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

$S_m = \frac{S}{n}$ ← moles

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

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

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

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

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$

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

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

molar entropy increases with increasing volume

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

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

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

$d(n,G) = (nV)dP - (n,S)dT$

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

$d(n,G) = \left[\frac{\partial (nG)}{\partial P}\right]_{Tn} + \left[\frac{\partial (nG)}{\partial T}\right]_{Pn} dT$

$d(nG) = (nV)dP + (-nS)dT + \varepsilon u_i + dn_i$

$V = \frac{\partial (nG)}{\partial P}\Big|_{T,n_j}$

$\frac{\partial V}{\partial n_i}\Big|_{T,P,n_j\neq i} = -\frac{\partial V_i}{\partial P}\Big|_{T,n_j\neq i}$

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

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

$\left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$

$\left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T,n_{CO_2},n_{Cl_2}} = \left(\frac{\partial U}{\partial n_{COCl_2}}\right)_{T,P,n_{CO},n_{Cl_2}}$

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

Chemical potential increases as pressure increasses

How does the chemical potential change with increasing pressure?

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

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

$\left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$

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

$\partial N_i\Big|_{T,n_j\neq i} = \frac{\partial U}{\partial U_i}\Big|_{T,P,n_j\neq i}$

$\int_{V_i} dU_i = \int_{P_0}^{P} \left(\frac{\partial V}{\partial N_i}\right) dP$

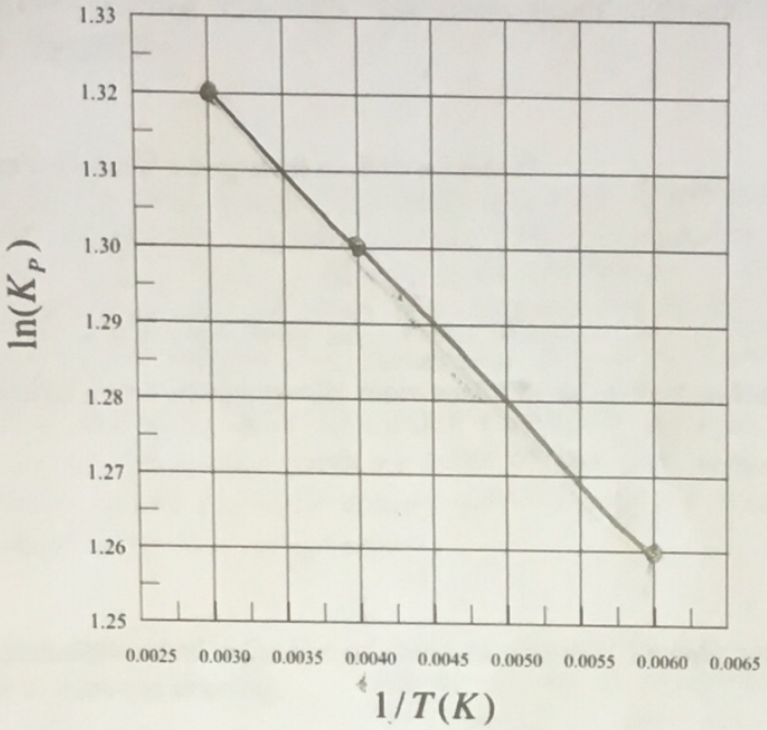
$(N_i - N_{oi}) = \frac{\partial U}{\partial N_i}(P - P_i)$

N_o is chemically potential at P_o

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**



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

$-\Delta G = -19.388\ K.$

$\Delta G = 19.388 \times R.$

$\Delta G = 19388 \times 8.314\ J/mol \cdot K$

$\Delta G = 161.19\ J/mol$

not spontaneous

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

This reaction is enthalpically driven

$$\frac{d\ln K_p}{dT} = \frac{\Delta H^\circ_{Rxn}}{RT^2}$$

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Short Answers:

4. **What is the second law of thermodynamics?**
The total entropy of an isolated system can never decrease over time, and is constant only if all processes are reversible

5. **What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.** The entropy of a system approaches a constant value as its temperature reaches zero in a closed system.

6. **Why can't we build a perpetual motion machine?**
It violates the First & Second Law of Thermodynamics. A perpetual machine producing work without energy violates the First Law stating that the total energy of an isolated system is constant, energy can't be created or destroyed. Also, it's suppose to convert thermal energy into mechanical work with only one heat reservoir being spontaneously cooled without transfer to a cooler reservoir. This conversion of heat to work with no side effects is impossible according to Second Law

7. **Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?**
Gibbs free energy is defined under constant pressure which is how we as chemists conduct most of our experiments. Helmholtz is defined under constant volume which is better suited for other areas such as engineering.

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

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

- It is called a potential because it measures the change in Gibbs Free Energy per mole of substance added at constant pressure

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 it is spontaneous. Mixing of different types of molecules in an ideal gas increases entropy. Adding a molecule to an ideal gas, the number of mols increases → increasing entropy. Chemical potential in inversly proportional to number of molecule, potential decreases as number of particles increase. Higher the entropy → more spontaneous

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

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.**
Negative ΔG°_{rxn} gives a spontaneous reaction in forward direction.

$\Delta G^\circ_{rxn} = -RT\ln K_{eq}$
$RT\ln K_{eq} > 0$
$\hookrightarrow K_{eq} < 1 \rightarrow \frac{[Prod]}{[React]} < 1 \rightarrow [Prod] < [React]$

Reactants favored over products if $\Delta G^\circ_{rxn} > 0$

Extra Credit (5 pts)

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

Favorite Equation: $\ln Kp(T_F) = \ln Kp(298.15K) - \frac{\Delta H^\circ_R}{R}\left(\frac{1}{T_F} - \frac{1}{298.15K}\right)$

This equation allows to determine the equilibrium constant for a reaction at a specific temperature.