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

Name: Valeria van Merkerk

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. George Paxos

b. Ashley Faro

c. Gabriela Inojosa Tenaru

d.

Who else did you ask for help?

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Name: Valena van Merkerk

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.

$\Delta G^\circ_{rxn} = [(-394)+(-133)] - [-463] = -64\ kJ/mol$

It is spontaneous because $\Delta G < 0$.

$\Delta H^\circ_{rxn} = [(-394$

$k = e^{-\left(\frac{64}{(0.008314)(298)}\right)}$

$k = 1.65 \times 10^{+11}$

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

$\ln \frac{K_2}{K_1} = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

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

$K_2 = 0.567$

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

At the lower temperature the reaction will become less spontaneous. Less spontaneous would favor the reactants.

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2. For a pure substance

   a. Derive the following expression

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

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

$dA = -SdT - PdV$

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

$\frac{\partial^2 A}{\partial V \partial T} = \left(-\frac{\partial S}{\partial V}\right)_T \quad \left(\frac{\partial^2 A}{\partial T \partial V}\right)_V = \left(\frac{\partial P}{\partial T}\right)$

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

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

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

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

   - as V increases the S_m 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

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

$dG = -SdT + VdP + \mu_i dn_i$

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

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

$\frac{\partial^2 G}{\partial n_i \partial P} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P} \quad \frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq i}}$

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

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

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?

$dG = -SdT + VdP + \mu_{Cl_2} dn_{Cl_2} + \mu_{CO} dn_{CO} + \mu_{COCl_2} dn_{COCl_2}$

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

$\left(\frac{\partial V}{\partial n_i}\right) = \left(\frac{\partial \mu_i}{\partial P}\right)$

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

as $\mu_A \propto P^P$

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

$\int_{P^o}^{P} d\mu_{(COCl_2)} = \int_{P^o}^{P} \left(\frac{\partial V}{\partial n_{(COCl_2)}}\right) dP$

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

for an ideal gas:

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

$V = \frac{nRT}{P} \rightarrow dV = \frac{dn\,RdT}{dP}$

$dV = \frac{nRT}{dP} \quad \left(\frac{\partial V}{\partial P}\right)_{n,T} = \frac{nRT}{P^2}$

$dV = \frac{dn\,RT}{P} \quad \left(\frac{\partial V}{\partial n}\right)_{P,T} = \frac{RT}{P}$

$dV = \frac{n\,RdT}{P} \quad \left(\frac{\partial V}{\partial T}\right)_{n,P} = \frac{nR}{P}$

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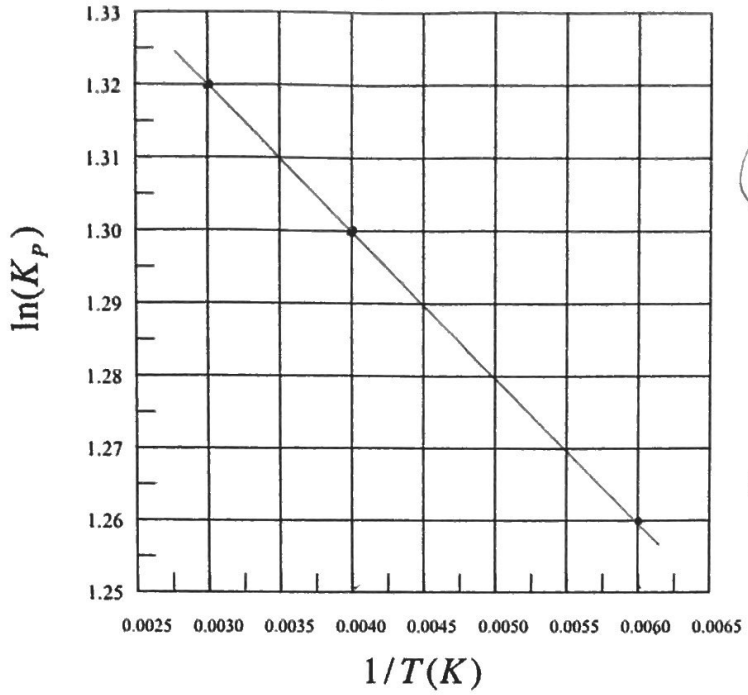
3. The following thermodynamic data was measured for a chemical reaction:

T (K)	1/T	Kp	Ln Kp
167	0.005988	3.53	1.26
250	0.004	3.67	1.30
333	0.003	3.74	1.32

a. Plot the data on the following plot



Slope = $-\frac{\Delta H}{R}$

Intercept = $\frac{\Delta S}{R}$

$y = -19\,399x + 1.3775$

$\Delta H = 161.20$ J/mol

$\Delta S = 11.45$ J/mol

$\ln K_{eq} = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R}$

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

- endothermic RXN
- $\Delta G = \Delta H - T\Delta S$ ⟶ $\Delta G = 161.20 - (167)\,11.45 = -1750.95$ J/mol
- $\Delta G = RT\ln K_{eq}$ $\Delta G = 161.20 - (250)\,11.45 = -2701.3$ J/mol
  $\Delta G = 161.20 - (333)\,11.45 = -3651.65$ J/mol

↑T & ↓G

avg G = −2701.3 J/mol

spontaneous RXN

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

entropically driven ΔH & ΔS positive, + entropy is able to overcome the unfavorable enthalpy

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Short Answers:

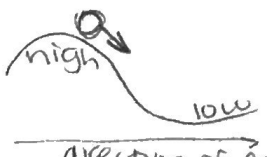
4. What is the second law of thermodynamics?
It states that processes go from lower to higher entropy (in the universe overall).

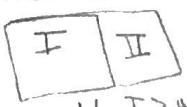
5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.
The entropy of a system approaches a constant value as its temperature approaches absolute zero. Entropy has a reference point (absolute zero) while enthalpy & energy don't.

6. Why can't we build a perpetual motion machine?
To keep a machine moving there can be no energy loss, and one can't create energy (1st Law). The system should move from lower to higher entropy. No heat engine can be more efficient heat engine due to irreversibility from the perfect process (violates 1st & 2nd Law).

7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?
Because chemists usually work at constant pressure rather than constant volume.

8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing.
$\mu_i \left[\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_{j\neq i}} \right]$ is called potential because of the natural direction of change dictated by gravitational potential





$\mu_I > \mu_{II}$

9. Is the mixing of different types of molecules in an ideal gas spontaneous? Justify your answer using mathematical expressions for the chemical potential.
$\mu^{mix} = \underbrace{\mu_{pure}(T,P)}_{\text{reference}} + \underbrace{RT \ln x_A}_{\text{mixture-perturbation}}$
perturbation lowers potential of pure substance
* $\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$ → always spontaneous

? 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.
$K_p = e^{-G_R/RT}$ $G_{rxn} = -RT \ln K$ $\Delta G_r = \Delta G_r^\circ + RT \ln Q_p$

$\Delta G > 0 \rightarrow K < 0$
reactants are favored.

Extra Credit (5 pts)

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

$\Delta G_r^\circ = -RT \ln K_p$ because it relates Gibbs energy with the equilibrium constant. It's also an equation that seems familiar to me as it relates concepts from General Chemistry. Another useful insight is that it can be used for the van't Hoff plot and later get ΔS & ΔH.