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

Name: Kylee McDonald

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. Victoria Savino

b. David DeLuca

c. Gabrielle Singh

d.

Who else did you ask for help?

Brooke Butler

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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°_{rxn} = prod − reactants = $(-394\ kJ/mol - 133\ kJ/mol) - -463\ kJ/mol$

$= -64\ kJ/mol$

The reaction is spontaneous because ΔG°_{rxn} is negative.

b. Calculate the equilibrium constant, K_P, for this reaction at 80.0 K. (T_2)

$$\ln K_P = -\frac{\Delta G^\circ_R}{RT} - \frac{\Delta H^\circ_R}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{64000\ \frac{J}{mol}}{2477\ \frac{J}{mol}} - \left(\frac{-24000\ \frac{J}{mol}}{8.314\ \frac{J}{mol\,K}}\right)\left(\frac{1}{80\ K} - \frac{1}{298\ K}\right)$$

$\Delta H = (-394\ \frac{kJ}{mol} - 166\ \frac{kJ}{mol}) - (-584\ \frac{kJ}{mol})$

$= 24\ \frac{kJ}{mol}\ \frac{1000\ J}{1\ kJ} = 24000\ \frac{J}{mol}$

$\ln K_P = -0.565$

$K_P = 0.568$

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

At the lower temperature, the reaction favors the reactants because $K_P < 1$.

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2. For a pure substance

   a. Derive the following expression

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

① $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \Rightarrow$ ② $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$

③ $\left(\frac{\partial S_m}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\beta}{n\kappa}$

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

increasing volume will increase the molar entropy because it gives more space for molecular interaction.

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

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

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

$\left(\frac{\partial \mu}{\partial p}\right)_T = V$

$\int_{\mu^\circ}^{\mu} d\mu = \int_{p^\circ}^{p} V\,dp$

   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 $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$. $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq i}} \rightarrow \left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO}+n_{Cl_2}} \rightarrow \left(\frac{\partial}{\partial n_{COCl_2}}\right)_{T,P,n_{CO}+n_{Cl_2}}$

How does the chemical potential change with increasing pressure?

$\Rightarrow \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{COCl_2}+n_{CO}+n_{Cl_2}}$ **Hint**: $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$, $\quad dn_{COCl_2} = -dn_{CO}$, $\; dn_{COCl_2} = -dn_{Cl_2}$

$\Rightarrow \left(\frac{\partial V}{\partial n_{CO}}\right)_{T,P,n_{COCl_2}+n_{CO}+n_{Cl_2}}$ + chemical potential increases w/ increasing P

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

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

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

$\mu_{pure}(T,P_{COCl_2}) = \mu^{mixture}_{CO\,Cl_2}(T,P_{COCl_2}) = \mu^{V}_{COCl_2}(-1) + RT\ln\frac{P_{partial}}{P^\circ}$

$\mu^{mixture}_{COCl_2}(T,P) = \mu^{\circ}_{COCl_2}(T) + RT\ln\frac{P}{P^\circ} + RT\ln X_{COCl_2}$

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

T (K)	K_P
167	3.53
250	3.67
333	3.74

$\frac{1}{167} = 0.005988$

$\frac{1}{250} = 0.004$

$\frac{1}{333} = 0.003$

Avg: 250 K

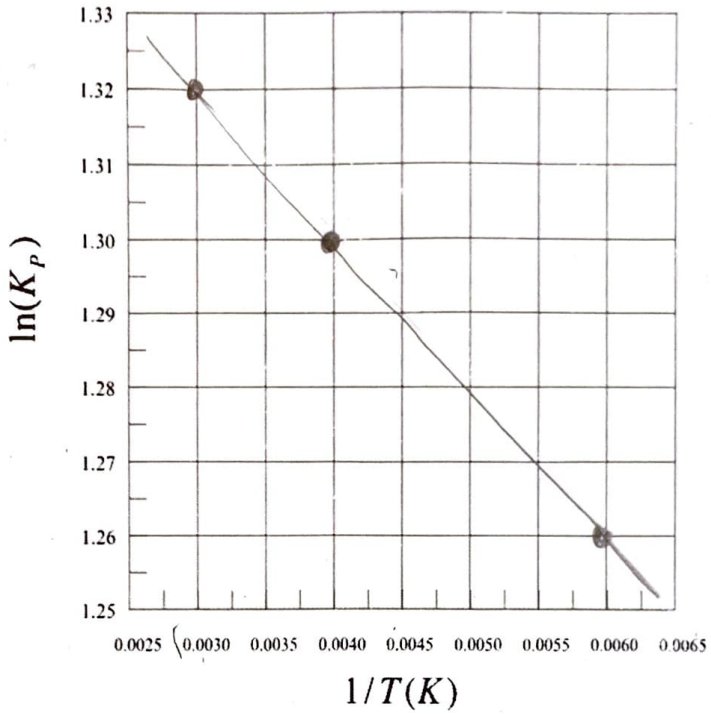
$\ln(3.53) = 1.26$

$\ln(3.67) = 1.30$

$\ln(3.74) = 1.32$

Avg = 1.293

a. Plot the data on the following plot



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

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

$\Delta G^\circ_r = 166.28\ J/mol - (295.15\ K)(11.473\ J/mol\,K)$

$\Delta G_r = 166.28\ J/mol - 3420.67495\ J/mol$

$\Delta G^\circ r = -3254.395\ J/mol$

The reaction is spontaneous because $\Delta G^\circ_r < 0$!

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

$-1751.2 \frac{J}{mol} = 166.28 - (167)\Delta S$

$\Delta S = 11.5$

$\text{slope} = \frac{\Delta H}{R}$

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

$= (20)(8.314)$

$\Delta H = 166.28$

$\Delta H > 0$

$\Delta S > 0$

] Both > 0 so the reaction is entropically driven!

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Short Answers:

4. What is the second law of thermodynamics?

It is impossible for a system to undergo a cyclic process whose sole effect are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by system on surroundings

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

The entropy of a pure, perfectly crystalline substance is 0 @ 0K. Entropy is different than energy or enthalpy because it measures activity, not energy

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

We can't build one because they violate the second and third laws of thermodynamics

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

Gibbs is more useful to chemists because it can determine how likely a reaction is to occur. Helmholtz is more general because it measures work attainable only from a closed system.

chemical potential

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 is the change in gibbs energy per mol of substance i added @ constant concentration

μ_i high → low

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

The reaction is not spontaneous because mixing molecules increases entropy (ΔS) and that makes $\Delta G > 0$.
The relationship between ΔG and ΔS: $\Delta G = \Delta H - T\Delta S$

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.

More reactant is formed! $\Delta G = \Delta H - T\Delta S$

(+) value $= \Delta H - T\Delta S$

$\Delta H > T\Delta S$

ΔS is smaller, so no reaction occurs.

Extra Credit (5 pts)

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

so far, my favorite equation is Gibbs free energy change: $\Delta G = \Delta H - T\Delta S$. This equation is important in chemistry because it can tell us alot about a reaction, especially a reaction's spontaneity. If ΔG is negative, a reaction is spontaneous. The reaction is also exergonic. Gibbs free energy change equation (shown above) is only true at constant temperature and pressure.