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

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**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. Kylee McDonald

d.

Who else did you ask for help?

Brooke Butler, Brandon Guthrie

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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 $\Delta G^\circ_{rxn}$. Is this reaction spontaneous under standard state conditions? Justify your answer.

[products - reactants]

$((-133\ kJ/mol) + (-394\ kJ/mol)) - (-463\ kJ/mol) = -64\ kJ/mol$

$\Delta G_{rxn} = -64\ kJ/mol$

$0 > \Delta G_{rxn}$ = spontaneous

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

$\ln K_P = \frac{-\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)$

$\ln K_P = \left(\frac{((-166) + (-394)) - (-584))\ kJ}{8.314\ J/mol\cdot K}\right)\left(\frac{1}{298K} - \frac{1}{80K}\right)$

$= \left(\frac{24000\ J}{8.314\ J/mol\cdot K}\right)(-0.009144295)$

$\ln K_P = -26.396$

$\ln K_P = -\left(\frac{64000\ J}{(8.314\ J/mol)(298K)}\right) - (26.366)$

$K_P = e^{\ln K_P} = e^{-26.396}$

$K_P = 0.569$

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

- favors the reactant because $K_P < 1$

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2. For a pure substance

   a. Derive the following expression

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

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

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

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

• increasing the volume increases the entropy because it leaves more space for interaction between molecules

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

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

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

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

$$\int_{\mu_0}^{\mu} d\mu = \int_{p_0}^{p} V dp$$

   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 $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$ $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_{j\neq i}} \Rightarrow \left(\frac{\partial \mu_{COCl_2}}{\partial p}\right)_{T,n_{CO},n_{Cl_2}} \Rightarrow \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{CO},n_{Cl_2}}$

**How does the chemical potential change with increasing pressure?**

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

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

   e. Use your result in part **d** to derive an expression for $\mu_{COCl_2}(P)$ with respect to some reference pressure, $P^\circ$ $G(T,P) = G^\circ(T) = nRT \ln(P/P^\circ)$

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

$$* P_A = \chi_A P$$

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

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

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

$\frac{1}{250} = 0.004$ → Avg = 0.0048

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

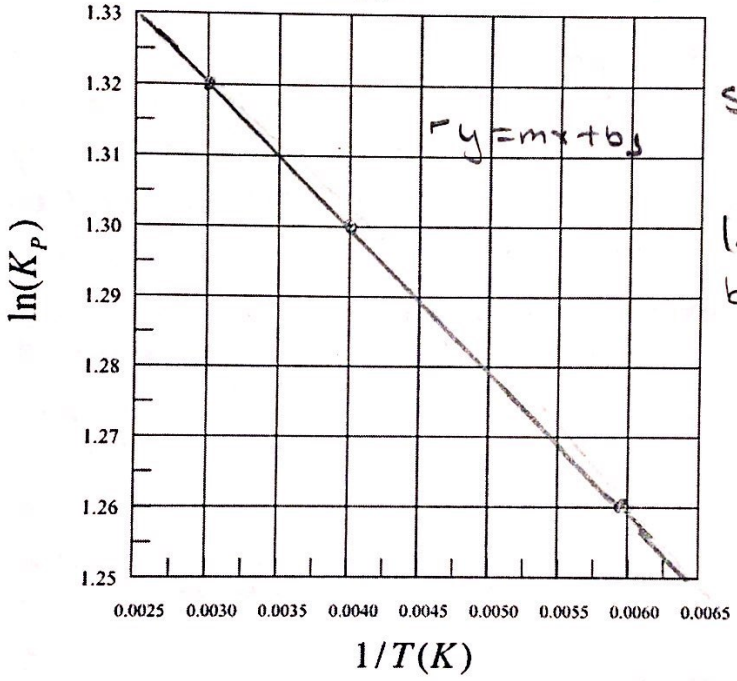
| | T (K) | $K_P$ |
|---|---|---|
| ① | 167 | 3.53 |
| ② | 250 | 3.67 |
| ③ | 333 | 3.74 |

↳ Avg = 250

$\ln(3.53) = 1.26$
$\ln(3.67) = 1.30$
$\ln(3.74) = 1.32$

↳ Avg = 1.293

a. Plot the data on the following plot




$\text{slope} = \frac{1.32 - 1.30}{0.003 - 0.004} = -20 = \frac{\Delta H^\circ}{R}$

(0.003, 1.32)

$1.32 = (-20)(0.003) + b$

b/y-int $= 1.38 = \frac{\Delta S^\circ}{R}$

b. Calculate $\Delta G_r^\circ$ for this reaction. Is this reaction spontaneous? Justify your answer.

$\Delta G^\circ_r = \Delta H - T\Delta S$ ; $\Delta H = 166.28$ J/mol ; $\Delta S = 11.479$

$\Delta G^\circ_r = (166.28 \text{ J/mol}) - (298.15 \text{ K})(11.479)$

$\Delta G^\circ_r = -3,254.395$ J/mol

$0 > \Delta G^\circ_r$ = spontaneous

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

*enthalpy → measures energy * entropy → measures activity

$\Delta G < 0$ = spontaneous, $\Delta H > 0$, $\Delta S > 0$ ⇒ entropically favorable

*spontaneous @ ↑T*

$\frac{1.38}{1} = \frac{\Delta S}{8.314}$

$\Delta S = 11.479$ ∴ entropically favorable

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

$-\Delta H^\circ = \text{slope} \cdot R$
$= (-20)(8.314)$
$-\Delta H = -166.28$

$\Delta H = 166.28$ J/mol

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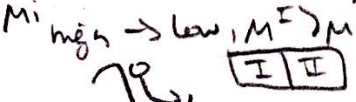
Short Answers:

4. What is the second law of thermodynamics?
   - the processes that involve the transfer of conversion of heat are irreversible & a cyclic process cannot convert heat (work)
5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.
   - if an object reaches absolute zero (0K), the atoms of said object will stop moving.
   - its different because entropy measures activity while enthalpy measures energy.
6. Why can't we build a perpetual motion machine?
   - it is impossible to make because saying that the machine could do work indefinitely without an energy source violates the 1st or 2nd Laws of thermodynamics.
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?
   - Gibbs free energy is important because you can use it to determine how likely a reaction is to occur, which is essential for chemists when constructing an experiment. While Helmholtz measures useful work obtainable from a closed thermodynamic system (which is a more general application) (potential vs work)
8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing.
   the chemical potential 'M' of a pure substance

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




   - chemical potential shows energy absorbed/released due to particle number ↑ or ↓
   - change in Gibbs energy per mol of substance
   ↳ natural direction of change dictated by chemical potential ⇒ natural direction of change dictates by given point
9. Is the mixing of different types of molecules in an ideal gas spontaneous? Justify your answer using mathematical expressions for the chemical potential.
   - When you increase number of particles, you increase the amount of entropy. This increase in particles decreases chemical potential, but leads to a more spontaneous reaction due to increase in entropy $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n}$ > as n ↑, overall $\mu_i$ ↓
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. $\Delta G = \Delta H - T\Delta S$
    - since free energy is positive, $\Delta G > 0$ = nonspontaneous
      - no/little product is formed, so more reactant is present/produced

$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta H - T\Delta S = (+)$

↳ (+) $\Delta H > T\Delta S$ ∴ $\Delta S$ is smaller = no rxn or more reactant present

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Extra Credit (5 pts)

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

- Gibbs Free Energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (① ② ③ ④)

① Gibbs Free Energy
② enthalpy
③ Temperature
④ entropy

I really like this equation because it is used to Calculate the maximum reversible work that may be performed by a system. The insight into Chemistry this has is it relates/produces the energy associated with a reaction that can be used to do work. The use of $\Delta G$ to determine the spontaneity of a reaction