

Name: Nhi Vo

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. *Barbara Perez*

b. *Catherine Marrero*

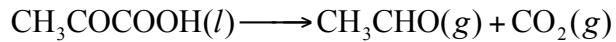
c.

d.

Who else did you ask for help?

Name: _____

1. The decarboxylation of pyruvic acid occurs via the following reaction:



Given the following thermodynamic data

$$\Delta_f H(25\text{ C})_{\text{CH}_3\text{COCOOH}} = -584 \text{ kJ mol}^{-1} \quad \Delta_f G(25\text{ C})_{\text{CH}_3\text{COCOOH}} = -463 \text{ kJ mol}^{-1}$$

$$\Delta_f H(25\text{ C})_{\text{CH}_3\text{CHO}} = -166 \text{ kJ mol}^{-1} \quad \Delta_f G(25\text{ C})_{\text{CH}_3\text{CHO}} = -133 \text{ kJ mol}^{-1}$$

$$\Delta_f H(25\text{ C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1} \quad \Delta_f G(25\text{ C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1}$$

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

$$\begin{aligned}\Delta G_{rxn}^\circ &= [\Delta_f G_{\text{CH}_3\text{CHO}} + \Delta_f G_{\text{CO}_2}] - [\Delta_f G_{\text{CH}_3\text{COCOOH}}] \\ &= (-133 - 394) - (-463) = -64.0 \text{ kJ/mol}\end{aligned}$$

$\Rightarrow \Delta G_{rxn}^\circ < 0 \Rightarrow \text{the reaction is spontaneous}$

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

$$\Delta G_{rxn}^\circ = -RT \ln K_p$$

$$\Leftrightarrow -64 \times 10^3 \text{ J/mol} = -(8.314 \text{ J/K mol}) \times 80 \text{ K} \times \ln K_p$$

$$\Rightarrow K_p = 6.15 \times 10^{41}$$

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

The reaction favors reactants

2. For a pure substance

- a. Derive the following expression

$$\left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{nK} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \Delta S_m = \frac{\Delta S}{n}$$

Since $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$; $K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

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

$$\Rightarrow (\beta V) \left(\frac{-1}{KV}\right) = \left(\frac{-\partial P}{\partial T}\right)_V \Rightarrow \frac{\beta}{K} = \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{nK}$$

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

$$\rho > K > 0 \Rightarrow \int \Delta S_m = \left(\frac{\beta}{nK}\right) \int \Delta V$$

$$\Rightarrow \Delta S_m = \left(\frac{\beta}{nK}\right) \Delta V$$

\Rightarrow molar entropy would increase with increasing volume

For a mixture of substances, $n_1, n_2, n_3 \dots$

- c. Show that the pressure dependence of the chemical potential is related to the volume as follows

$$\frac{dG}{dT} = V \frac{dP}{dT} - S \frac{dT}{dT} + \sum \mu_i dn_i$$

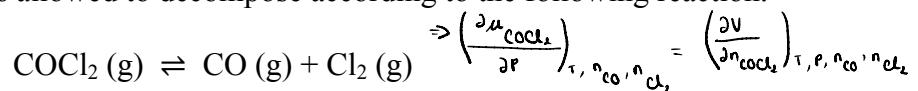
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}$$

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

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

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

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



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: $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$, $dn_{COCl_2} = -dn_{CO}$, $dn_{COCl_2} = -dn_{Cl_2}$
 If $\uparrow P$, the position of the equilibrium will move to the left and $COCl_2$ will form
 $\Rightarrow n \uparrow COCl_2 \rightarrow \uparrow P \rightarrow \uparrow$ chemical potential

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

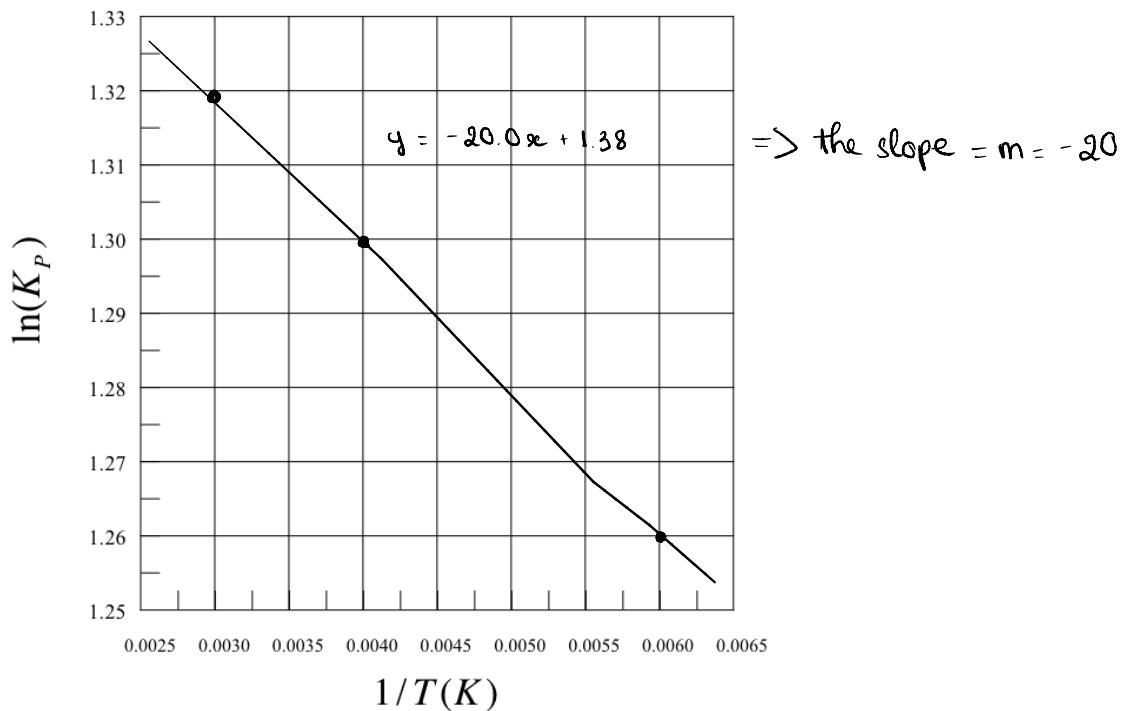
$$\text{Pressure is constant} \Rightarrow \int_{n_{COCl_2}}^{n_i} d\mu_i = \int_{P_0}^P \left(\frac{\partial V}{\partial \mu_i}\right) dP \Rightarrow (\mu_i - \mu_{COCl_2}) = \frac{dV}{d\mu_i} (P - P_0)$$

$\Rightarrow \mu_{COCl_2}$ is chemically potential at pressure, P°

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

T (K)	K _P
167 0.0040	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



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

$$K_p = e^{-\Delta G / RT} \Rightarrow \ln K_p = \frac{-\Delta G}{R} \times \frac{1}{T} \Rightarrow \frac{-\Delta G}{R} = -20.0 \text{ K} \Rightarrow \Delta G = (20.0 \text{ K})R$$

$$= (20.0 \text{ K}) \times 8.314 \text{ J/mol K}$$

$$= 166 \text{ J/mol}$$

$\Rightarrow \Delta G > 0 \Rightarrow$ the reaction is not spontaneous.

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

this reaction is enthalpically driven because $\frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2}$

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 whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by the system on the 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 (element or compound) is zero at zero kelvin. It would be possible to grow a perfect crystal where all the spaces are occupied by atoms with identical size. If that perfectly crystalline solid that does not possess no kinetic energy, there will be no motion between compounds of that systems, making entropy = 0 while there would not be any change on the energy or enthalpy.

6. Why can't we build a perpetual motion machine? (PMM = perpetual motion machine)

Because the perpetual motion machine violates both first and second law of thermodynamics

- According to the 1st law, energy can't be created or destroyed, only transformed from 1 form to another \rightarrow PMM has to produce work without energy input.

- According to the 2nd law, an isolated system will move toward a state of disorder, more energy is transformed, the more of it is wasted \rightarrow PMM has to have energy that was never wasted and never moved toward a disordered state

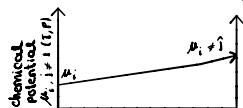
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?

Gibb's free energy and Helmholtz energy are both thermodynamic potentials. However, the Gibb's energy is more useful when you have controlled temperature and pressure while Helmholtz Free energy is most useful when you have controlled temperature and volume. Since most reactions are carried out under controlled pressure and temperature and not controlled volume. Gibb's Free energy is more useful to chemist than Helmholtz Free energy.

8. Give the mathematical definition of chemical potential. Explain why it is called a potential.

Include at least one drawing. Chemical potential is defined as the partial molar $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i}$ = $\bar{\mu}_i = \bar{G}$

Because the energy stored in a matter, which comprises of molecules, which are combination of atom that are held by bonds. It is originated from energy stored in molecules (in form of interaction) and can do work in the future.



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

$$\mu = \mu^\circ + RT \ln P \quad \xrightarrow{P = \frac{P^\circ}{x^\circ}}$$

$$G_i = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\circ + RT \ln P_A) + n_B (\mu_B^\circ + RT \ln P_B)$$

$$\text{standard chemical potential} \quad G_f = n_A (\mu_A^\circ + RT \ln P_A) + n_B (\mu_B^\circ + RT \ln P_B)$$

$$\Rightarrow G_{mix} = G_f - G_i = n_A RT (\ln P_A - \ln P) + n_B RT (\ln P_B - \ln P) = n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$$

$$\Rightarrow \Delta G_{mix} = n_{\text{total}} RT (x_A \ln x_A + x_B \ln x_B + \dots + x_n \ln x_n) \quad \text{since mole fraction} < 1 \Rightarrow \ln x_i \leq 0$$

$$\Rightarrow \Delta G_{mix} < 0 \Rightarrow \text{spontaneous}$$

10. For a given chemical reaction involving only gasses at equilibrium, if $\Delta G_{rxn}^\circ > 0$, will there be more product formed or more reactant. Justify your answer using one or more equations.

$$\Delta G_{rxn}^\circ = -RT \ln K_{eq}$$

$$\text{since } \Delta G_{rxn}^\circ > 0 \Rightarrow -RT \ln K_{eq} > 0 \Rightarrow \ln K_{eq} < 0 \text{ if } K_{eq} < 1 \Rightarrow K_{eq} = \frac{[\text{Product}]}{[\text{Reactant}]} < 1 \Rightarrow [\text{Product}] < [\text{Reactant}]$$

$$\Rightarrow \text{Reactants are favored if } \Delta G_{rxn}^\circ > 0$$

Extra Credit (5 pts)

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

$\Delta G^\circ = -RT \ln K$ since this equation have a controlled on only temperature and pressure, it makes lab is easier to control

It also can be calculated the spontaneity of the reaction