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

Name: Barbara Perez

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.

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Who did you work with?

a. Catherine Marrero

b. Nhi Vo

c.

d.

Who else did you ask for help?

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Name: _____

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.

$\Delta G^\circ_{Rxn} = [\Delta_f G_{CH_3CHO(g)} + \Delta_f G_{CO_2(g)}] - [\Delta_f G_{CH_3COCOOH(l)}]$

$= [-133 + (-394)] - [-463]$

$= -64.0\ kJ/mol$

Since $\Delta G^\circ_{Rxn} < 0$, the reaction is spontaneous

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

$\Delta G^\circ_{rxn} = -RT \ln K_{eq}$

$-64 \times 10^3\ J/mol = -(8.314\ J/K\cdot mol) \times 80K \times \ln eq$

$\frac{-64 \times 10^3\ J/mol}{-665.12\ J/mol} = \frac{-665.12\ J/mol}{-665.12\ J/mol}$

$\ln eq = 96.22$ → $e^{96.22} = 6.13 \times 10^{41}$

$K_{eq} = 6.13 \times 10^{41}$

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

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

since $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

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

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

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

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

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

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

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

$\beta \& \kappa > 0 \Rightarrow \int \partial S_m = \left(\frac{\beta}{n\kappa}\right)\int \partial V$

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

molar entropy would increase 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

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

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

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

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

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

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

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

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

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

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

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 P↑, the position of the equilibrium will move to the left and $COCl_2$ will form

$\Rightarrow$ As $COCl_2$↑ → P↑ → 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^o

Pressure is constant $\Rightarrow \int_{\mu_{oi}}^{\mu_i} d\mu_i = \int_{P_o}^{P}\left(\frac{\partial V}{\partial n_i}\right)dP \Rightarrow (\mu_i - \mu_{oi}) = \frac{\partial V}{\partial n_i}(P - P_o)$

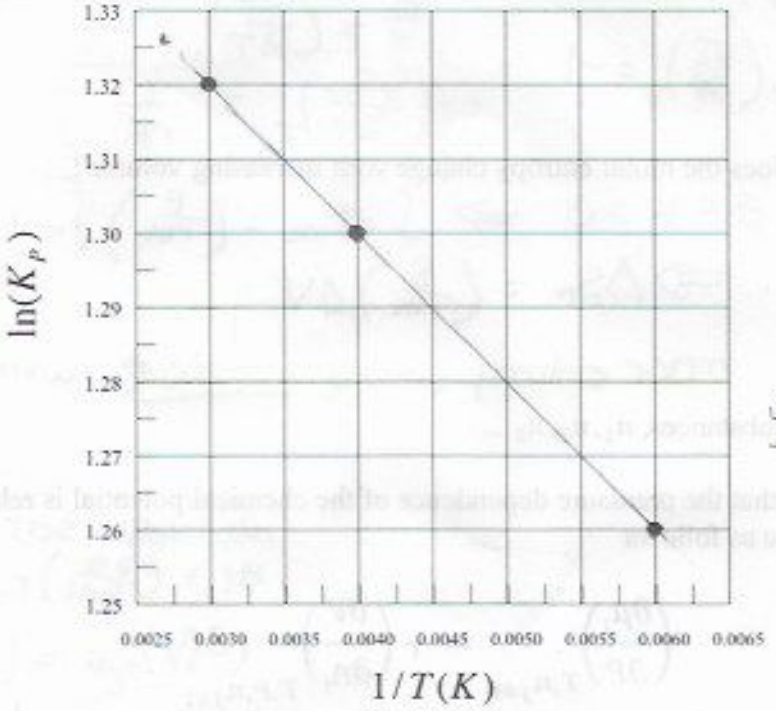
$\Rightarrow \mu_{oi}$ is chemically potential at pressure, P^o.

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

1/T(K)	ln(Kp)
0.0060	1.26
0.004	1.30
0.003	1.32



y = -20.0x + 1.38

slope = m = -20

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

$K_p = e^{-\Delta G/RT}$

$\Rightarrow \ln K_p = -\frac{\Delta G}{R} \times \frac{1}{T} \Rightarrow \frac{-\Delta G}{R} = -20.0\,K$

$\Rightarrow \Delta G = (20.0\,K)R$

$= (20.0\,K)(8.314\ J/mol\,K)$

$= 166\ J/mol$

Since $\Delta G > 0$ (+) the reaction is NOT spontaneous

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

The reaction is Enthalpically driven because

$\frac{d \ln K_P}{dt} = \frac{\Delta H}{RT^2}$

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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 effects are the flow of the 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 sizes. It is not possible to reach temperature of absolute 0.
If that perfectly crystalline solid that does not possess kinetic energy, there will be no motion between compounds of that system making entropy = 0 while there would be no change on energy or enthalpy

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

Because this machine violates both the 1st and 2nd law of thermodynamics
- According to 1st law, energy can be created/destroyed, only transformed from one form to another, this machine has to produce work without energy input
- According to 2nd law an isolated system will move toward a state of disorder, more energy is transformed the more wasted this machine has to have energy that was never wasted and never moved toward a disorder state

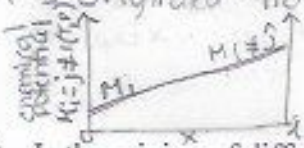
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?

Because most reactions carried out by chemists are under controlled pressure and temperature, which are the conditions for Gibbs free energy.
Helmoltz energy conditions are controlled temperature and volume

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

Chemical potential defined as partial molar free energy $\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq n_i} = \overline{M_i} = \overline{G}$

Because energy stored in matter, which is made of compounds held together by bonds, It is originated from energy stored in molecules 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.

yes $\begin{cases} \Delta G < 0 : \text{spon} \\ \Delta G > 0 : \text{nonspon} \end{cases} \Rightarrow \Delta G_{mix} < 0$

$M = M^\circ + RT \ln P$ → $P = \frac{n}{V}$
M° = standard chemical potential

$G_i = n_A M_A + n_B M_B = n_A(M_A^\circ + RT \ln P_A) + n_B(M_B^\circ + RT \ln P_B)$

$G_f = n_A(M_A^\circ + RT \ln P_A) + n_B(M_B^\circ + RT \ln P_B)$

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

$= n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}$

Since $x_j = \frac{P_j}{P}$, $x_A = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$, $n_A = n_{total} \times x_A$, $n_B = n_{total} \times x_B$

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

$\Delta G_{mix} < 0$ 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.

$\Delta G^\circ_{Rxn} = -RT \ln K_{eq}$

Since $\Delta G^\circ_{Rxn} > 0 \Rightarrow -RT \ln K_{eq} > 0 \Rightarrow \ln K_{eq} < 0$ if $K_{eq} < 1 \Rightarrow K_{eq} = \frac{[prod]}{[react]} < 1$

$[product] < [reactant]$

So, Reactants are favored 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.

$\Delta G^\circ = -RT \ln K$

Because this equation has a controlled temperature and pressure, making it an easier factor in lab to control

It can also be used to calculate the spontaneity of the reaction