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

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It must be turned in as a single PDF. Image files for each page will not be accepted.

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https://acrobat.adobe.com/us/en/mobile/scanner-app.html

Who did you work with?

a. myself

b.

c.

d.

Who else did you ask for help?

myself

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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.

ΔG°_{rxn} = products − reactants

$= (\Delta_f G(298.15K)_{CO_2} + \Delta_f G(298.15K)_{CH_3CHO}) - (\Delta_f G(298.15K)_{CH_3COCOOH})$

$= \left(-394\ \frac{kJ}{mol} + -133\ \frac{kJ}{mol}\right) - \left(-463\ \frac{kJ}{mol}\right)$

ΔG_{rxn}° $= -64\ \frac{kJ}{mol}$ Since $\Delta G^\circ_{rxn} < 0$ the reaction is spontaneous

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

$\Delta G^\circ_R = -RT \ln K_P$

$-64\ \frac{kJ}{mol} = -\left(8.314\ \frac{J}{mol \cdot K}\right)(80K) \ln K_P$

$K_P = 6.15 \times 10^{41}$

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

At the lower temperature the reaction favors the products

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2. For a pure substance

   a. Derive the following expression

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

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

Molar entropy increases 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

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

   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?

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

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

SEE following Pages

2a

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

1st Law: $dU = dq + dw = dq - P_{ex} + dV = dq_{rev} - PdV = TdS - PdV$

only expansion

reversible pathway

↳ solve for dS

$$dS = \frac{dU}{T} + \frac{1}{T} P dV$$

$$= \frac{1}{T}\left(\frac{dU}{dT}\right)_V dT + \left(\frac{dU}{dV}\right)_T dV + \frac{1}{T} P dV$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T}\left(P + \frac{\partial U}{\partial V_T}\right) dV$$

Everything that's multiplied by dV is equal to $\left(\frac{\partial S}{\partial V}\right)_T$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(P + \frac{\partial U}{\partial V}\right)_T$$

Take mixed 2nd derivatives and plug in

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T \rightarrow P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

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

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

so for S_m we can just divide by n = # of moles

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

(2c) $d(nG) = (nV)\,dP - (nS)\,dT$

$$\therefore \left[\frac{\partial (nG)}{\partial P}\right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial (nG)}{\partial T}\right] = -nS$$

Total differential of nG

$$d(nG) = \left[\frac{\partial (nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial (nG)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial nG}{\partial n_i}\right]_{P,T,n_{l \neq i}} dn_i$$

$$\mu_i = \left[\frac{\partial nG}{\partial n_i}\right]_{P,T,n_{i \neq i}} dn_i \quad \text{so plugging that in we get....}$$

$$\boxed{d(nG) = (nV)\,dP + (-nS)\,dT + \sum_i \mu_i\, dn_i}$$

From above...

$$V = \left.\frac{\partial (nG)}{\partial P}\right|_{T,n_i} \qquad \mu_i = \left.\frac{\partial (nG)}{\partial n_i}\right|_{T,P}$$

$$\left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_{l \neq i}} = \frac{\partial^2 (nG)}{\partial n_i \partial P} \qquad \left.\frac{\partial \mu_i}{\partial P}\right|_{T,n_{i \neq i}} = \frac{\partial^2 (nG)}{\partial n_i \partial P}$$

Thus we can set them equal to each other and....

$$\boxed{\left.\frac{\partial V}{\partial n_i}\right|_{T,P,n_{l \neq i}} = \left.\frac{\partial \mu_i}{\partial P}\right|_{T,n_{i \neq i}}}$$

(2d) $$\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} = \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO_2}, n_{Cl_2}}$$

Chemical potential will increase with increasing pressure.

(2e) $$\left.\frac{\partial \mu_i}{\partial P}\right|_{T, n_{i \neq j}} = \left.\frac{\partial V}{\partial n_i}\right|_{T, P, n_{i \neq j}}$$

↑ At constant pressure

$$\int_{\mu_{0i}}^{\mu_i} \partial \mu_i = \int_{P_0}^{P} \left(\frac{dV}{\partial n_i}\right) dP$$

$$\boxed{(\mu_i - \mu_{0i}) = \frac{\partial V}{\partial n_i}(P - P_0)}$$

↑ Chemical potential at P_0

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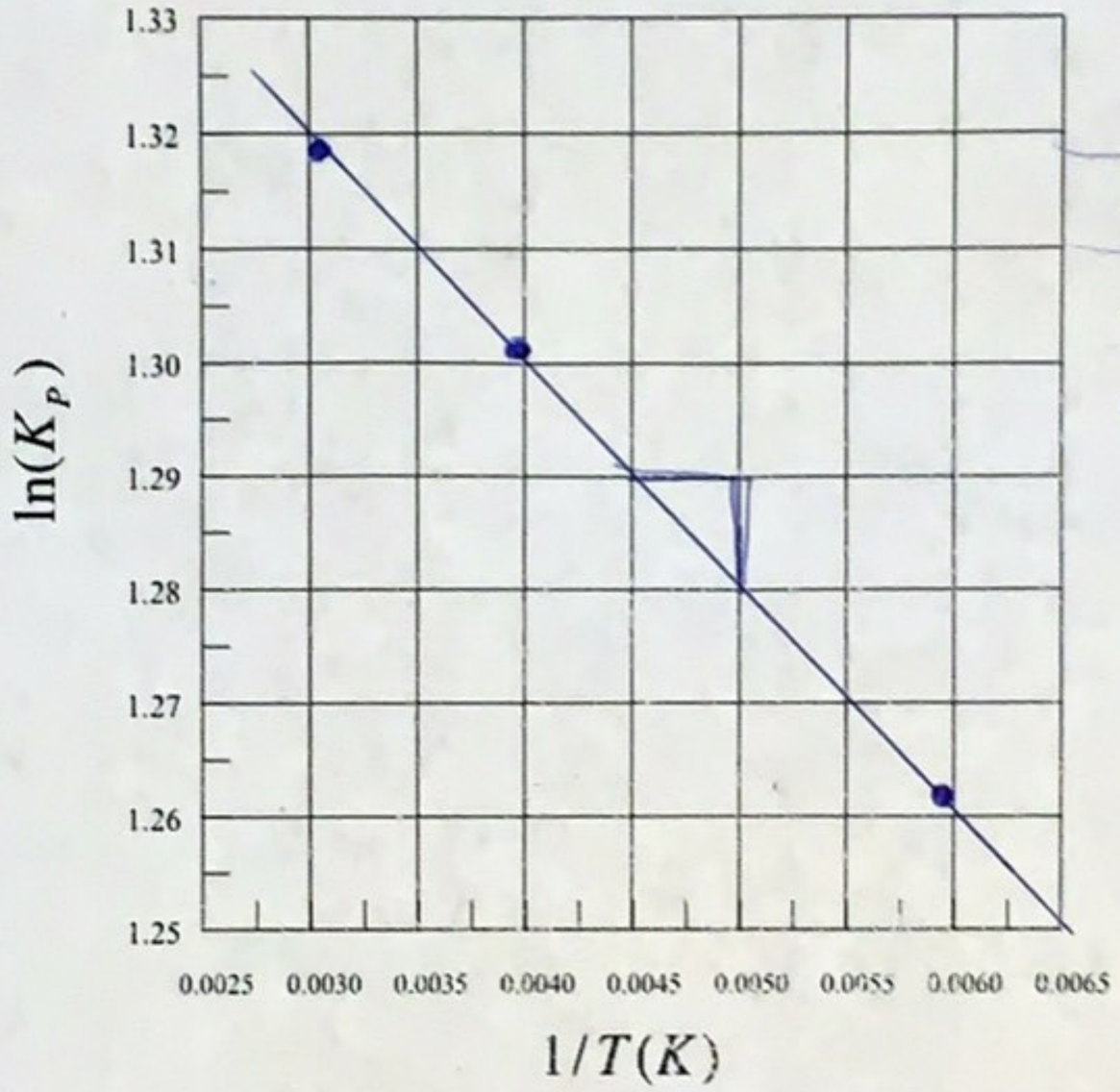
3. The following thermodynamic data was measured for a chemical reaction:

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)
.005988	1.2613
.004	1.30019
.003003	1.31909

slope = rise / run

= 0.01 / -.0005

slope = -20

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

$\Delta G_r^\circ = -RT \ln(k_p)$

slope = $\frac{\Delta G_r^\circ}{-R}$

Since $\Delta G = +$ the reaction is non-spontaneous.

$\ln(k_p) = \frac{\Delta G_r^\circ}{-RT}$

ΔG_r° = slope · -R

$\Delta G_r^\circ = 166.28 \frac{J}{mol}$

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

This is enthalpically driven because ΔG°_R is + so the reaction is non-spontaneous at all T, thus enthalpically driven..

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Short Answers:

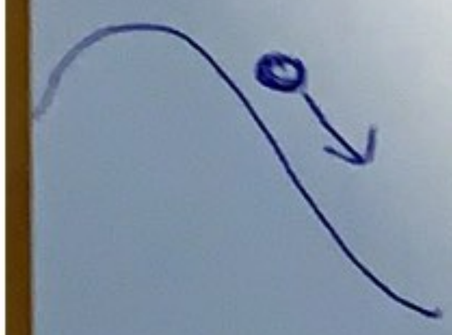
4. What is the second law of thermodynamics? 2nd law states that an isolated system will always become more disordered $\Delta S > 0$. It also states that its impossible for heat to flow into a system and preform an equal amount of work on the surroundings

5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy. 3rd law states entropy of pure crystalline substance is 0 at 0kelvin. The enthalpy or energy of a perfect crystal is not 0 at 0kelvin,

6. Why can't we build a perpetual motion machine?
we cannot build a perpetual motion machine as it would violate the 2nd law. It is impossible for a machine to convert heat into work with 100% efficiency.

7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?
Gibbs energy is at constant T and P, while helmholtz is at constant T and V. As chemists work with constant pressure so Gibbs is more useful.

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



Natural direction of change dictated by chemical potential goes from high → Low chemical potential just like water down a hill.

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 it is spontaneous. $\mu^{Pure}_{H_2}(T, P_{H_2}) = \mu^{mix}_{H_2}(T, P_{H_2}) = \mu^{\circ}_{H_2}(T) + RT \ln \frac{P_{H_2}}{P^{\circ}}$

$P_A = x_A P$ $\quad \mu^{mix}_{H} = \mu^{pure}_{A}(T,P) + RT \ln x_A$

$\Delta G_{mixing} = RT \sum n_i \ln x_i = \boxed{nRT \sum x_i \ln x_i}$ ← $\ln x_i < 0$ so $\Delta G < 0$ thus its 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.

$\Delta G^{\circ}_{rxn} = -RT \ln K_{eq}$ If $\Delta G^{\circ}_{rxn} > 0$

$K_{eq} = \frac{[products]}{[reactants]}$

$-RT \ln K_{eq} > 0$ ↝ $\ln K_{eq} < 0$ ↝ $K_{eq} < 1$

so there must be more Reactants

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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.

My favorite equation from this semester is

$$\Delta u = C_v \Delta T$$

This equation shows us that the internal energy depends only on temperature