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

Name: Jasleen Gill

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. Andrew Kilada

b. Rebecca Epright

c.

d.

Who else did you ask for help?

Victoria Savino

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

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.

$\Delta G°rxn = \sum \Delta G°f_{products} - \sum \Delta G°f_{reactants}$

$\Delta G°rxn = (-133\ kJ/m + -394\ kJ/m) - (-463\ kJ/m)$

$\Delta G°rxn = (-527\ kJ/m) - (-463\ kJ/m)$

$\Delta G°rxn = -64\ kJ/m$

Since $\Delta G°rxn$ is negative, the reaction is spontaneous.

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

$\Delta f H°rxn = \sum \Delta f H°_{products} - \sum \Delta f H°_{reactants}$

$\Delta f H°rxn = (-166\ kJ/m + -394\ kJ/mol) - (-584\ kJ/m)$

$\Delta f H°rxn = 24\ kJ/mol \Rightarrow 24{,}000\ J/mol$

$K_P = e^{-\Delta G°/RT}$

$\ln K_P(T_f) = \frac{-\Delta G°}{RT} - \frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\ln K_P(T_f) = \frac{64{,}000}{8.314(298)} - \frac{24{,}000}{8.314\ J/mol\,K}\left(\frac{1}{80K} - \frac{1}{298K}\right)$

$\ln K_P(T_f) = 25.832 - 26.3968$

$e^{\ln K_P} = e^{-0.5648}$

$K_P = 0.568$

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

Because K_P is less than 1 ($K_P < 1$) at the lower temperature, the reaction favors the reactants.

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

2. For a pure substance

a. Derive the following expression

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

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

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

$dS = \frac{1}{T}\left[C_V dT + \left(\frac{dU}{dV}\right)_T dV\right] + \frac{P}{T}dV$

$dS = \frac{C_V}{T}dT + \frac{1}{T}\left[P + \left(\frac{dU}{dV}\right)_T\right]dV$

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

$dS = \frac{C_V}{T}dT \rightarrow$ constant V

$\left(\frac{d}{dT}\left(\frac{dS}{dV}\right)_T\right)_V = \left(\frac{d}{dV}\left(\frac{dS}{dT}\right)_V\right)_T$

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

$\left(\frac{d}{dT}\left(\frac{dS}{dV}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{dP}{dT}\right)_V + \left(\frac{d}{dT}\left(\frac{dU}{dV}\right)_T\right)_V\right]$

$P + \left(\frac{dU}{dV}\right)_T = T\left(\frac{dP}{dT}\right)_V - \frac{1}{T^2}\left[P + \left(\frac{dU}{dV}\right)_T\right]$

$\left(\frac{dS}{dV}\right)_T = \left(\frac{dP}{dT}\right)_V = \frac{-(dV/dT)_P}{(dV/dP)_T} = \frac{\beta}{\kappa}$

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

Increasing volume leads to an increase in entropy because it gives more space for interactions to occur.

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

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

$dU = TdS - PdV + \sum_i \mu_i dn_i$

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

$dH = TdS - VdT + \sum_i \mu_i dn_i$

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

$dA = -PdV - TdS + \sum_i \mu_i dn_i$

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

$dG = Vdp - SdT + \sum_i \mu_i dn_i$

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

$d\mu = Vdp - SdT$

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

$\int_{\mu^\circ}^{\mu} d\mu = V\int_{P^\circ}^{P} dP$

$\mu - \mu^\circ = V(P - P^\circ)$

$\mu = \mu^\circ + V(P - P^\circ)$

$V = \frac{RT}{P}$

$\int_{\mu^\circ}^{\mu} d\mu = RT\int_{P^\circ}^{P}\frac{dP}{P}$

d. Pure phosphine is allowed to decomposeaccording 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: $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$, $dn_{COCl_2} = -dn_{CO}$, $dn_{COCl_2} = -dn_{Cl_2}$

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

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

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

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

The chemical potential increases with increasing pressure.

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

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

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

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

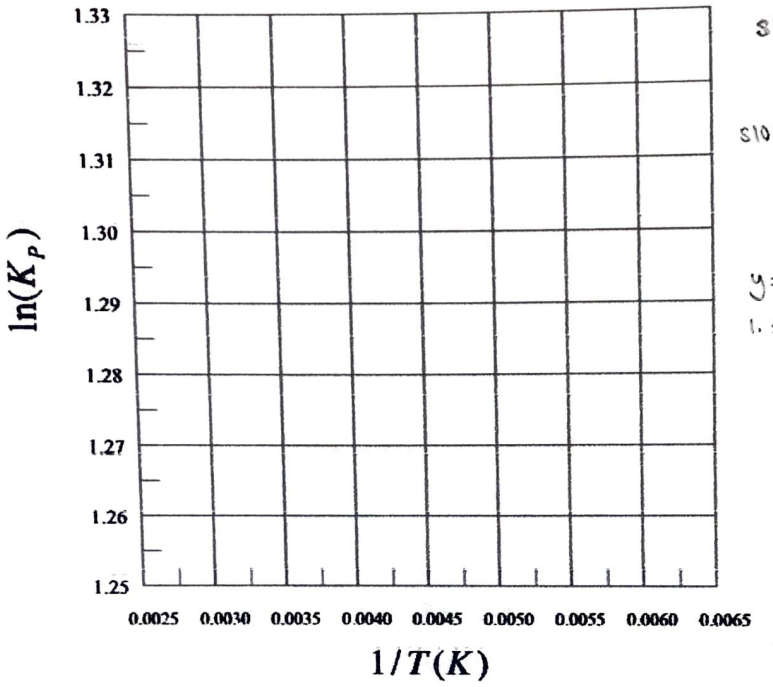
Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

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

all points on graph: $\frac{1}{167} = 0.005988 \approx 0.006$; $\frac{1}{250} = 0.004$; $\frac{1}{333} = 0.003$

T(K)	K_P
167 point 1	3.53 ln (3.53) = 1.26
250 point 2	3.67 ln (3.67) = 1.30
333 point 3	3.74 ln (3.74) = 1.32

a. Plot the data on the following plot



slope $= \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x}$

slope $= \frac{1.32 - 1.30}{0.003 - 0.004} = -20.0$

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

$y = mx + b$

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

$b = 1.36$

↳ intercept $= \frac{\Delta S^\circ}{R}$

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

$\Delta G_1 = (-8.314\ J/mol\cdot K)(167\ K)\ln(3.53)$

$\Delta G_1 = -1,751.234\ J/mol$

$\Delta G_2 = (-8.314\ J/mol\cdot K)(250\ K)\ln(3.67)$

$\Delta G_2 = -2,702.448\ J/mol$

$\Delta G_3 = (-8.314\ J/mol\cdot K)(333K)\ln(3.74)$

$\Delta G_3 = -3,651.970\ J/mol$

$\Delta G = -RT\ln K_P$

average $\Delta G = \frac{\Delta G_1 + \Delta G_2 + \Delta G_3}{3}$

average $\Delta G = -2,701.884\ J/mol$

$\Delta G < 0$, $\Delta S > 0$, $\Delta H > 0$

Since ΔG is negative @ High temperature it is therefore spontaneous, but since ΔG is positive @ lower temperature, it is also nonspontaneous.

$\Delta G^\circ = RT\ln K_{eq} \rightarrow -RT\ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$

$\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ ← substitute from part a

$\ln K_{eq} = -20.0 + 1.38$

$\ln K_{eq} = e^{-18.62}$

$K_{eq} = 8.193 \times 10^{-9}$

$\Delta G^\circ = (8.314\ J/mol\cdot K)(250\ K) - \ln(8.193 \times 10^{-9})$

$\Delta G^\circ = 38,701640\ J/mol$

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

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

$-\Delta H^\circ =$ slope (R)

$-\Delta H^\circ = (-20\ K)(8.314\ J/mol\cdot K)$

$\frac{-\Delta H^\circ}{-1} = \frac{-166.28\ J/mol}{-1}$

$\Delta H^\circ = 166.28\ J/mol$

intercept $= \frac{\Delta S^\circ}{R}$

$\Delta S^\circ =$ intercept (R)

$\Delta S^\circ = (1.38)(8.314\ J/mol\cdot K)$

$\Delta S^\circ = 11.473\ J/mol\cdot K$

The reaction is entropically favorable.

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

Short Answers:

4. **What is the second law of thermodynamics?**

Second law of thermodynamics states that there is a quantity (entropy) that can never decrease over time in an isolated system. Entropy always increases or stays constant (equilibrium) for an isolated system. $\Delta S \geq 0$ for any process in an isolated system.

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

The third law of thermodynamics states that the entropy of a pure, crystalline substance (element or compound) is zero at Kelvin [$S = k \ln(W)$]. This proves that when entropy (measure of random activity) is zero, then it is in equilibrium/order - where enthalpy is a measure of overall amount of energy

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

We cannot build a perpetual motion machine because it violates the 1st & 2nd law of thermodynamics

↳ 1st law by it produces mechanical work w/o any energy being in put, which violates the conservation of energy.

↳ 2nd law by it converts thermal energy into mechanical work - with no heat being rejected. This violates the rate of production of entropy, that entropy in a system must always increase.

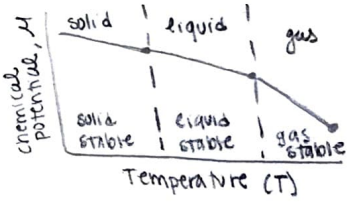
7. **Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?**

Gibb's free energy is usually more useful because it is straightforward when manipulating variables such as pressure & temperature (not entropy or volume). Most importantly, volume change is negligible. Helmholtz energy is more useful when dealing with mechanical systems.

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

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\ldots,n_j} = G = \mu_i \rightarrow \mu \frac{\mu_c}{N}$$

It is called potential as it is under constant temperature, pressure, and constant # of moles for all species "i". So it is potential because it is the rate of increase in Gibbs free energy of a system in respects to the increase in the # of moles of species i.



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 chemical potential is the change of free energy with respect to the # of molecules added. When a molecule is added in an ideal gas, it will not react with it. Therefore, the # of molecules ↑ and entropy increases because of an increase in particles. Chemical potential is inversely porportional to the # of molecules added, therefor, chemical potential decreases as # of particles increase. Also an increase in change = entropy, thus, it will more spontaneous. This means mixing an ideal gas is spontaneous. → $\Delta S = \uparrow, \Delta G \uparrow$ $\mu = \left(\frac{\partial G}{\partial n}\right)$ = chemical potential

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

$\mu_A^\circ = \mu_B^\circ$

$\mu_B^\circ = \mu_B^\circ$

$\Delta \mu = \Delta \mu_0^\circ + RT \ln [eq]$

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

$\Delta S = k \ln W$

$\Delta S = -nR[x_A \ln x_A + x_B \ln x_B]$

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.**

Free energy of the reaction is possible → not spontaneous → no product formed → more reactants produced

$\Delta G_{rxn} = -RT \ln K_{eq}$ $K_{eq} = \frac{\text{products}}{\text{reactants}} \rightarrow K_{eq} < 0$

$\Delta G_{rxn} > 0$ $K_{eq} < 0$

↳ forms more reactants than product

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

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 the Van der Waals Equation of state, which is $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$.

The reason as to why this equation has become my favorite is because this helps describe a real gas. Not only that but it also correctly defines the behavior of an ideal gas along with showing the P-V-T behavior of an ideal gas at low density. Furthermore, it includes the 2 parameters that is needed to determine a given gas.

↳ Parameter a = measure of strength of the attractive part of intermolecular potential

↳ Parameter b = measure of minimum volume that a mole of molecules can occupy.

This real gas equation of state is an empirical equation where it provides the best way to fit experimentally determined P-V-T data.