Name: _Andrew Kilade_

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. Jasleen Gill

b. Rebecca Epright

c.
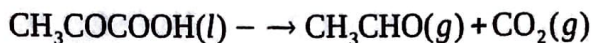
d.

Who else did you ask for help?

Name: Andrew Kilada

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

$$CH_3COCOOH(l) - \rightarrow CH_3CHO(g) + CO_2(g)$$

Given the following thermodynamic data

$$\Delta_f H(25\ C)_{CH_3COCOOH} = -584\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CH_3COCOOH} = -463\ kJ\ mol^{-1}$$
$$\Delta_f H(25\ C)_{CH_3CHO} = -166\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CH_3CHO} = -133\ kJ\ mol^{-1}$$
$$\Delta_f H(25\ C)_{CO_2} = -394\ kJ\ mol^{-1} \quad \Delta_f G(25\ C)_{CO_2} = -394\ kJ\ mol^{-1}$$

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

$$\Delta G_{rxn}^{\circ} = \Sigma \Delta_f G\ products - \Sigma \Delta_f G\ reactants$$
$$\Delta G_{rxn}^{\circ} = (-133\ KJ/m + -394\ KJ/m) - (-463\ KJ/m)$$
$$\Delta G_{rxn}^{\circ} = (-527\ kJ/m) - (-463\ KJ/m)$$
$$\boxed{\Delta G_{rxn}^{\circ} = -64\ KJ/m}$$

ΔG_{rxn}° is negative ∴ reaction is spontaneous

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

$$Kp = e^{-\Delta G^{\circ}/RT}$$
$$\ln Kp(T_f) = \frac{-\Delta G^{\circ}}{RT} - \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\ln Kp\ Tf = \frac{64,000}{8.314(298)} - \frac{24,000\ J/m}{3.3145\ J/mol\ k}\left(\frac{1}{80K} - \frac{1}{298K}\right)$$

$$\Delta_f H_{rxn} = \Sigma \Delta_f H\ products - \Sigma \Delta_f H\ react$$
$$\Delta_f H_{rxn} = (-166\ KJ/m + -394\ KJ/m) - (-589 KJ/m)$$
$$\Delta_f H_{rxn} = 24\ KJ/mol = 24,000\ J/m$$

$$\ln Kp\ Tf = 25.832 - 26.3968$$
$$e^{\ln Kp} = e^{-0.5648}$$
$$\boxed{Kp = 0.5685}$$

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

The reaction favors the reactants since for a lower temperature $Kp < 1$.

2. For a pure substance

    a. Derive the following expression

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

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

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

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

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

$$dS = \frac{C_V}{T}\partial T \quad \{\text{constant } V\}$$

Right column:

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

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

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

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

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

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

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

An increase of volume will increase the amount of ways molecules can distribute thus increasing entropy.

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

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

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

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

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j \neq i}$$

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

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

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

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V, S, n_j \neq i}$$

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

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

$$d\mu = VdP - SdT$$

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

Right side:

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

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

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

$$\int_{\mu^\circ}^{\mu} d\mu = \int_{P_0}^{P} V dP$$

$$\int_{\mu^\circ}^{\mu} d\mu = \frac{RT}{P}\int_{P_0}^{P} dP$$

    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 $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}}$ How does the chemical potential change with increasing pressure?

Left margin:

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

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

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

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

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°

#3 on next page! $\rightarrow$

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

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

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

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

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

$\frac{1}{250} = 0.004$
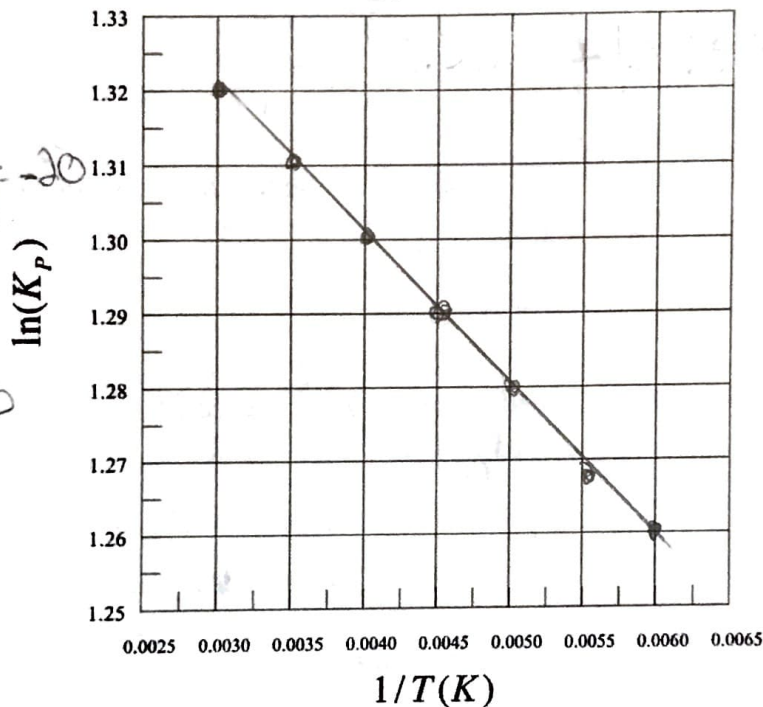
$\frac{1}{333} = 0.003$

T (K)	K_P
167	3.53
250	3.67
333	3.74

$\ln(3.53) = 1.26$ | $\ln(3.67) = 1.30$

$\ln(3.74) = 1.32$

a. Plot the data on the following plot

Slope $= \frac{\Delta y}{\Delta x}$

Slope $= \frac{1.32 - 1.30}{0.003 - 0.004} = -20$

$y = mx + b$

$1.32 = (-20).003 + b$

$\Rightarrow b = 1.38$
intercept

Y-axis: $\ln(K_P)$ — 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25

X-axis: $1/T(K)$ — 0.0025, 0.0030, 0.0035, 0.0040, 0.0045, 0.0050, 0.0055, 0.0060, 0.0065

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

$\Delta G_1 = (-8.314 \text{ J/mol k})(167) \ln(3.53)$
$\Delta G_1 = -1,751.234 \text{ J/mol}$

$\Delta G_2 = (-8.314 \text{ J/mol·k})(250K)(3.67)$
$\Delta G_2 = -2,702.448 \text{ J/mol}$

$\Delta G_3 = (-8.314 \text{ J/mol K})(333K)\ln 3.74$
$\Delta G_3 = -3,651.970 \text{ J/mol}$

$\Delta G = -RT \ln K_P$

Avg $\Delta G = -2,701.884 \text{ J/mol}$

↑ temp $= -\Delta G \Rightarrow$ spontaneous
↓ temp: $+\Delta G =$ nonspontaneous

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

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

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

$\ln K_{eq} = -18.62$ $\Delta G^\circ = 8.314 \text{ J/mol k} (250k)$

$e^{\ln K_{eq}} = e^{-18.62}$ $\ln(8.193 \times 10^{-9})$

$K_{eq} = 8.193 \times 10^{-9}$ $\Delta G = 38,701.640 \text{ J/mol}$

$\Delta G < 0 \Rightarrow$ spontaneous $\Delta H > 0$ $\Delta S > 0$

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

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

$-\Delta H^\circ = $ Slope · R

$-\Delta H = -20 \cdot 8.314 \text{ J/mol}$

$\frac{-\Delta H}{-1} = \frac{-166.28}{-1}$

$\Delta H = 166.28 \text{ J/mol}$

$\Delta G < 0 \Rightarrow$ spontaneous
$\Delta H > 0$
$\Delta S > 0$

high temp = spontaneous
low temp = nonspontaneous

$1.38 = \frac{\Delta S}{11.473} \Rightarrow \Delta S = 11.473$

| Entropically driven |

Short Answers:

4. What is the second law of thermodynamics? 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 entropy of a pure, perfectly 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 the overall amount of energy.

6. Why can't we build a perpetual motion machine? A perpetual motion machine violates the 1st & 2nd Laws of Thermodynamics. 1st Law) It produces mechanical work without any energy being input - which violates conservation of energy. 2nd Law) It converts thermal energy into mech work - with no heat being rejected. This violates the rule 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 straightforward when manipulating variables such as pressure & temperature (not entropy or volume) Most importantly, volume change is negligible. Helmholtz 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. $\left(\frac{\partial G}{\partial n_i}\right)_{T,P...n_j} = G = \overline{\mu_i} \rightarrow \mu \frac{U_c}{N}$

It is called potential as it is under constant temperature, pressure, & constant # of moles for all species except 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.
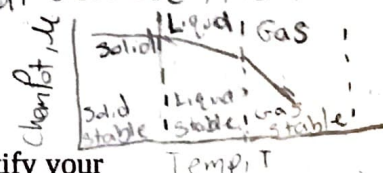
9. Is the mixing of different types of molecules in an ideal gas spontaneous? Justify your answer using mathematical expressions for the chemical potential. The chem potential is the change of free energy with respect to the # of molecules added. When a molecule is added in an ideal gas it will not react with it, therefore the # of molecules increase & entropy increases because of an increase in particles. Chem potential is inversely proportional to the # of molecules added → chem potential decreases as # of particles increase. Also ↑ change = entropy → more spontaneous. Meaning mixing in an ideal gas is spontaneous.

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

Free energy of the reaction is positive → not spontaneous → more reactants produced. $\Delta G_{rxn} = -RT \ln K_{eq}$, $\Delta G_{rxn} > 0$ $K_{eq} < 0$

$K_{eq} = \frac{Prod}{React} \rightarrow K_{eq} < 0$

forms more reactants than product

$\mu_A^\alpha = \mu_A^\beta$
$\mu_B^\alpha = \mu_B^\beta$
$\Delta\mu = \Delta\mu^o + RT \ln[K_{eq}]$

$\Delta G = \Delta H - T\Delta S$
$\Delta S = k \ln w$
$\Delta S_{mix} = -nR[x_A \ln x_A + x_B \ln x_B]$
$\Delta S = \uparrow \Delta G = \uparrow$
$\mu = \left(\frac{\partial G}{\partial n}\right) = $ chem potential

Extra Credit (5 pts)

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

Favorite Equation: Microscopic Entropy

$$S = k \ln W$$

Insight: Created in 1877 by Botzmann is an explanation for entropy. Every spontaneous change in nature often occurs in the direction of higher disorder → which is measured by entropy. That equation determines entropy from the size of disorder. $W =$ # of microstates at the same energy level & k is the Bolzman constant. It can be applied when a system is in thermal equilibrium. It also can be derived for non extensive systems:

$$S_{Tsallis} = k \frac{W^{1-q} - 1}{1-q}$$