

Name: Harleen 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. Kevin Zhang

b.

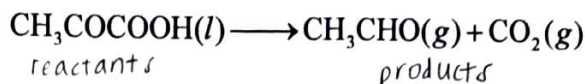
c.

d.

Who else did you ask for help?

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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  $\Delta G^\circ_{\text{rxn}}$ . Is this reaction spontaneous under standard state conditions? Justify your answer.

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ_f \text{ products} - \sum \Delta G^\circ_f \text{ reactants}$$

$$\Delta G^\circ_{\text{rxn}} = (-133\text{ kJ/mol} + -394\text{ kJ/mol}) - (-463\text{ kJ/mol})$$

$$\Delta G^\circ_{\text{rxn}} = (-527\text{ kJ/mol}) - (-463\text{ kJ/mol})$$

$$\Delta G^\circ_{\text{rxn}} = \boxed{-64\text{ kJ/mol}}$$

since  $\Delta G^\circ_{\text{rxn}}$  is negative the reaction is spontaneous

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

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

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

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

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

$$= e^{-0.5648}$$

$$\boxed{K_p = 0.568}$$

$$\Delta_f H_{\text{rxn}} = \sum \Delta_f H^\circ_{\text{prod}} - \sum \Delta_f H^\circ_{\text{reactants}}$$

$$= (-166\text{ kJ/mol} + -394\text{ kJ/mol}) - (-584\text{ kJ/mol})$$

$$= 24\text{ kJ/mol}$$

$$= 24,000\text{ J/mol}$$

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

Because  $K_p < 1$  for the lower temperature, the reaction favors the reactants

## 2. For a pure substance

## a. Derive the following expression

1)  $ds = \frac{1}{T} du + \frac{p}{T} dv$

2)  $ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$

3)  $ds = \frac{1}{T} [C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv] + \frac{p}{T} dv = \frac{C_v}{T} dT + \frac{1}{T} [p + \left(\frac{\partial u}{\partial v}\right)_T] dv$

4)  $\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$  and  $\left(\frac{\partial s}{\partial v}\right)_T = \frac{1}{T} [p + \left(\frac{\partial u}{\partial v}\right)_T]$

5)  $ds = \frac{C_v}{T} dT, \text{ constant } v$

$$\left(\frac{\partial s_m}{\partial v}\right)_T = \frac{\beta}{n\kappa}$$

6)  $\left(\frac{\partial}{\partial T} \left(\frac{\partial s}{\partial v}\right)_T\right)_v = \left(\frac{\partial}{\partial v} \left(\frac{\partial s}{\partial T}\right)_v\right)_T$

7)  $\left(\frac{\partial}{\partial v} \left(\frac{\partial s}{\partial T}\right)_v\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial v} \left(\frac{\partial u}{\partial T}\right)_v\right)_T$

8)  $\left(\frac{\partial}{\partial T} \left(\frac{\partial s}{\partial v}\right)_T\right)_v = \frac{1}{T} \left[\left(\frac{\partial p}{\partial T}\right)_v + \left(\frac{\partial}{\partial T} \left(\frac{\partial u}{\partial v}\right)_T\right)_v\right]$

9)  $p + \left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - \frac{1}{T} [p + \left(\frac{\partial u}{\partial v}\right)_T]$

10)  $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v = \frac{-(\partial v / \partial T)_p}{(\partial v / \partial p)_T} = \frac{\beta}{n\kappa}$

## 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

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

$$d\mu = T ds - p dv + \sum_i \mu_i dn_i$$

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

$$dH = T ds - v dT + \sum_i \mu_i dn_i$$

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

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T, n_j \neq i} = - \left(\frac{\partial v}{\partial n_i}\right)_{T, p, n_j \neq i}$$

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

$$dA = v dp - s dT + \sum_i \mu_i dn_i$$

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

$$d\mu = v dp - s ds$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v$$

$$\int_{\mu^0}^{\mu} d\mu = v \int_{p^0}^p dp$$

$$\mu - \mu^0 = v(p - p^0)$$

$$\mu = \mu^0 + v(p - p^0)$$

$$v = \frac{RT}{p}$$

$$\int_{\mu^0}^{\mu} d\mu = RT \ln \frac{p}{p^0}$$

## 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  $\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial p}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} \left(\frac{\partial \mu_i}{\partial p}\right)_{T, n_j \neq i} \Rightarrow \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial p}\right)_{T, n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}} \Rightarrow - \left(\frac{\partial v}{\partial n_{\text{COCl}_2}}\right)_{T, p, n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}}$

How does the chemical potential change with increasing pressure?

Hint:  $n = n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}, dn_{\text{COCl}_2} = -dn_{\text{CO}}, dn_{\text{COCl}_2} = -dn_{\text{Cl}_2}$

$$\Rightarrow - \left(\frac{\partial v}{\partial n_{\text{COCl}_2}}\right)_{T, p, n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}} \Rightarrow - \left(\frac{\partial v}{\partial n_{\text{CO}}}\right)_{T, p, n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}} + - \left(\frac{\partial v}{\partial n_{\text{Cl}_2}}\right)_{T, p, n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}}$$

e. Use your result in part d to derive an expression for  $\mu_{\text{COCl}_2}(P)$  with respect to some reference pressure,  $P^0$ 

$$G(T, P) = G^0(T) + nRT \ln(P/P^0)$$

$$\mu^{\text{pure}}(T, P_{\text{COCl}_2}) = \mu_{\text{COCl}_2}^{\text{mixture}}(T, P_{\text{COCl}_2}) = \mu_{\text{COCl}_2}^0(T) + RT \ln \frac{P_{\text{COCl}_2}}{P^0}$$

$$\mu_{\text{COCl}_2}^{\text{mixture}}(T, P) = \mu_{\text{COCl}_2}^0(T) + RT \ln \frac{P}{P^0} + RT \ln x_{\text{COCl}_2}$$

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:

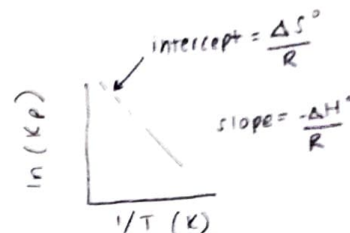
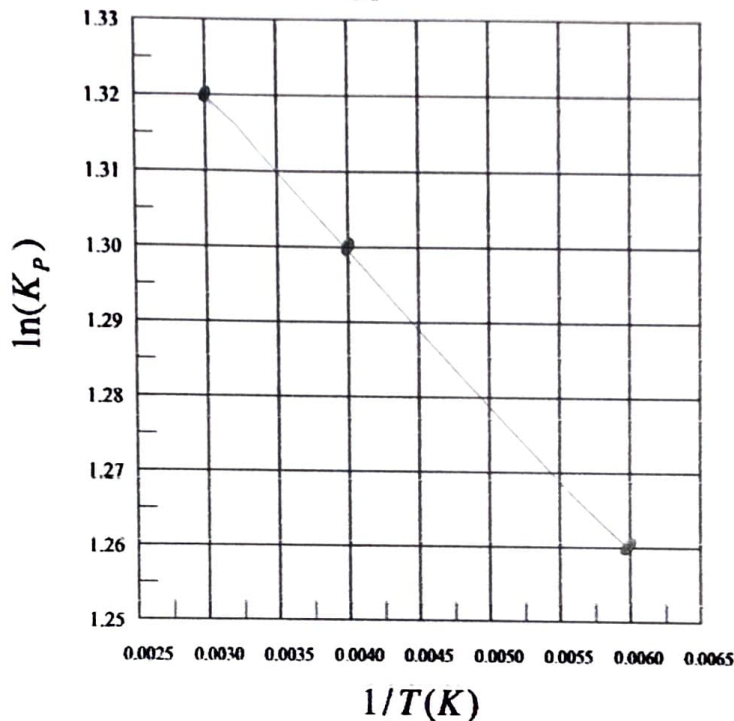
$$\frac{1}{167} = 0.005998$$

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

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

T(K)	K <sub>p</sub>
167	ln 3.53 = 1.26
250	ln 3.67 = 1.30
333	ln 3.74 = 1.32

a. Plot the data on the following plot



$$\text{slope} = \frac{\Delta y}{\Delta x}$$

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

$$y = mx + b$$

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

$$b = 1.38$$

↳ intercept

b. Calculate  $\Delta G_r^\circ$  for this reaction. Is this reaction spontaneous? Justify your answer.

$$\Delta G = -RT \ln K_p$$

$$\Delta G_1 = -8.314 \text{ J/mK} (167 \text{ K}) \ln(3.53)$$

$$\Delta G_1 = -1,751.234$$

$$\Delta G_2 = -8.314 \text{ J/mK} (250) \ln(3.67)$$

$$\Delta G_2 = -2,702.448 \text{ J/m}$$

$$\Delta G_3 = -8.314 \text{ J/mK} (333) \ln(3.74)$$

$$\Delta G_3 = -3,651.970 \text{ J/m}$$

$$\text{Average } \Delta G = -2,701.884 \text{ J/m}$$

$$K_p = 8.193 \times 10^{-9}$$

we see  $\Delta G^\circ = -RT \ln K_{eq}$   
 thus we can write  $-RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$   
 or  $\ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$   
 $\ln K_p = -20 + 1.38$   
 $e^{\ln K_p} = e^{-18.62}$

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

$$= 8.314 (250) \ln(8.193 \times 10^{-9})$$

$$\Delta G^\circ = 88,701.640 \text{ J}$$

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

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

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

$$-\Delta H^\circ = -20 \cdot 8.314 \text{ J/mK}$$

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

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

$$\Delta G < 0 \text{ spontaneous}$$

$$\Delta H > 0$$

$$\Delta S > 0$$

\* spontaneous at high Temp.

\* nonspontaneous at low temp.

$$\frac{1.38}{1} = \frac{\Delta S}{8.314}$$

$$\Delta S = 11.473$$

entropically favorable



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 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 1<sup>st</sup> and 2<sup>nd</sup> laws of thermodynamics.  
1<sup>st</sup> law) It produces mechanical work without any energy being input - which violates conservation of energy.  
2<sup>nd</sup> 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.

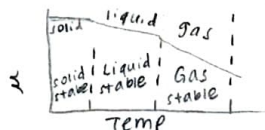
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?

Gibb's free energy is straight forward when manipulating variables such as pressure and 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.  $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\dots,n_j} = \bar{G}_i = \mu_i \rightarrow \mu = \frac{\partial G}{\partial n}$

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



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 increases and entropy increases because of an increase in particles. Chem potential is inversely proportional to the # of molecules added  $\rightarrow$  chem potential decreases as the # of particles increase. Also  $\uparrow$  change = entropy  $\rightarrow$  more spontaneous. Meaning mixing non ideal gas is spontaneous  $\rightarrow dU = \left(\frac{\partial G}{\partial n}\right)_{T,P,n} \rightarrow \mu_A^A = \mu_A^B$   
 $\mu_B^A = \mu_B^B$   
 $\Delta \mu = \Delta \mu^\circ + RT \ln[K_{eq}] \rightarrow \Delta \mu^\circ = \Delta H^\circ - T \Delta S^\circ$   
 $\Delta S^\circ = -nR \ln \left[ \frac{x_A^A x_B^B}{x_A^B x_B^A} \right]$

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.

Free energy of the reaction is positive  $\rightarrow$  not spontaneous  $\rightarrow$  no product formed.

$$\mu = \left(\frac{\partial G}{\partial n}\right) = \text{chem potential}$$

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

$$\Delta G_{rxn} > 0 \quad K_{eq} < 1$$

$$K_{eq} = \frac{\text{product}}{\text{reactant}} \rightarrow K_{eq} < 1$$

forms more reactants than products

more reactants produced.

Extra Credit (5 pts)

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

favorite equation: Hess's equation  $(\Delta H_{\text{reaction}} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}))$

Insight: This equation is a relationship in physical chemistry named after Germain Hess, a Switzerland-born Russian chemist and physician who published it in 1840. The law states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps. Hess's law is now understood as an expression of the principle of conservation of energy, also expressed in the first law of thermodynamics, and the fact that the enthalpy of a chemical process is independent of the path taken from the initial to the final state.