

Name: Brandon Guthrie

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.

b.

c.

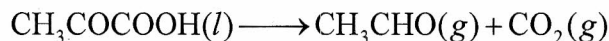
d.

Who else did you ask for help?

Gabrielle Singh

Name: Brandon Guthrie

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

Products - reactants

$$(-133\text{ kJ/mol}) + (-394\text{ kJ/mol}) - (-463\text{ kJ/mol}) - (-463\text{ kJ/mol}) = 64\text{ kJ/mol}$$

$$\Delta G_{\text{rxn}} = 64\text{ kJ/mol}$$

$$0) \Delta G_{\text{rxn}} = \text{spontaneous}$$

- b. Calculate the equilibrium constant,
- K_p
- , for this reaction at 80.0 K.
- $\ln K_p = \frac{-\Delta H}{L} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\ln K_p = \left(\frac{(-166 + (-394)) - (-584)}{81314\text{ J/mol} \cdot \text{K}} \right) \left(\frac{1}{298\text{ K}} - \frac{1}{80\text{ K}} \right) = \left(\frac{24000}{81314\text{ J/mol} \cdot \text{K}} \right) (-0.009142953)$$

$$\ln K_p = 26.3968$$

$$\ln K_p = - \left(\frac{64000\text{ J}}{(81314\text{ J/mol} \cdot \text{K})(298\text{ K})} \right) - 26.366$$

$$K_p = 569$$

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

The reaction favors reactant because $K_p < 1$

2. For a pure substance

a. Derive the following expression

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

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

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

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

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

the entropy increase with the volume because it helps with the interaction between molecules

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

$$d\mu = V dp - S dT \quad \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_{j \neq i}} = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V \quad \int_{P_0}^P d\mu = \int_{P_0}^P V dP$$

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 $\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}}$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_{j \neq i}} = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}} \Rightarrow \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = \left(\frac{\partial V}{\partial n_{\text{COCl}_2}}\right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}}$$

How does the chemical potential change with increasing pressure?

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

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

$$\mu_i(T, P) = G_i^\circ(T) + n_i RT \ln(P/P^\circ)$$

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

$$K_P = K_A P$$

$$\mu_{\text{mixture}}(T, P) = \mu^\circ_{\text{COCl}_2}(T) + RT \ln \frac{P}{P^\circ} + RT \ln K_{\text{COCl}_2}$$

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

T (K)	K _P
167	3.53
250	3.67
333	3.74

$$\ln(3.53) = 1.26$$

$$\ln(3.67) = 1.30$$

$$\ln(3.74) = 1.32$$

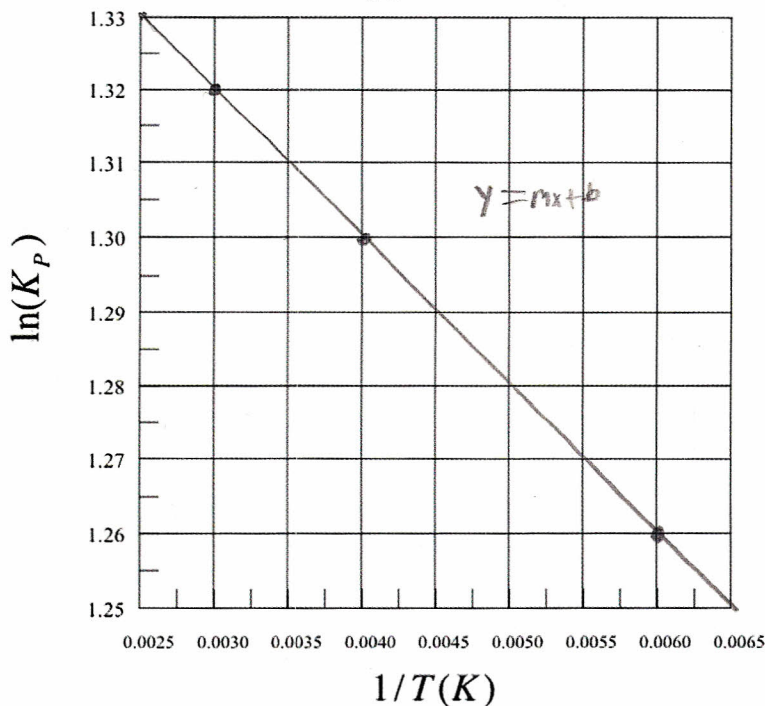
$$\rightarrow \text{average} = 1.293$$

$$\frac{1}{167} = .005988$$

$$\frac{1}{250} = .004 \quad \text{average} = .0043$$

$$\frac{1}{333} = .003$$

a. Plot the data on the following plot



$$\text{slope} = \frac{1.32 - 1.30}{.003 - .004} = -20 = \frac{\Delta H^\circ}{R}$$

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

$$b / y\text{-int} = 1.38 = \frac{\Delta S}{R}$$

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

$$\Delta G_r^\circ = \Delta H - T\Delta S, \Delta H = 166.28 \text{ J/mol}, \Delta S = 11.479$$

$$\Delta G_r^\circ = (166.28 \text{ J/mol}) - (298.15 \text{ K})(11.479)$$

$$\Delta G_r^\circ = -3254.395 \text{ J/mol}$$

$$0 > \Delta G_r^\circ = \text{spontaneous}$$

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

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

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

$$= (-20)(8.314)$$

$$-\Delta H = 166.28$$

$$-1$$

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

enthalpy \rightarrow measures energy * entropy \rightarrow measures activity

$\Delta G < 0 = \text{spontaneous}$, $\Delta H > 0$, $\Delta S > 0 \Rightarrow$ entropically favorable

spontaneous @ $\uparrow T$

$$\frac{1.32}{1} = \frac{\Delta S}{8.314}$$

$$\Delta S = 11.479 \text{ J/mol} \cdot \text{K} \therefore \text{entropically favorable}$$

Short Answers:

4. What is the second law of thermodynamics?

that the process of conversion to heat energy is irreversible and no process can convert heat back to work

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

when an object gets to absolute zero kelvin the atoms of the object will stop moving

entropy measures activity compared to enthalpy measuring energy

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

because it's impossible for a machine to work without an energy source it violates the 1st & 2nd rules of thermodynamics

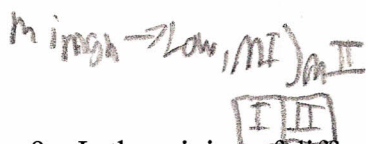
7. Why is Gibbs free energy usually more useful to chemists than Helmholtz energy?

Gibbs free energy is used to figure out how likely a reaction will happen which is important for chemists when making an experiment. Helmholtz measures useful work obtainable from closed system

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

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

the chemical potential shows energy absorbed and released due to particle numbers increase or decrease



a change in Gibbs energy per mol of substance
↳ natural direction of change dictated by chemical potential

9. Is the mixing of different types of molecules in an ideal gas spontaneous? Justify your answer using mathematical expressions for the chemical potential.

an increase in molecule increases chemical potential as n increases

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.

Gibbs free energy is positive, $\Delta G > 0$ = nonspontaneous $\Delta G = \Delta H - T\Delta S$

none to little product is formed, so more reactant is present or produced

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta H - T\Delta S = \text{positive } \Delta H > T\Delta S; \therefore \Delta S \text{ is smaller} \Rightarrow \text{no rxn or more reactant present}$$

Extra Credit (5 pts)

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

$\Delta S_{univ} \geq 0$ it's easy to remember and it's related to
the Second Law and is just a easy reminder
System + surrounding-universe for the complicated nature of the
spontaneity of a reaction