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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>

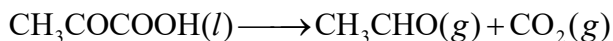
Who did you work with?

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

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum \Delta_f G(\text{products}) - \sum \Delta_f G(\text{reactants}) \\ \Delta G_{\text{rxn}}^\circ &= (\Delta_f G_{\text{CH}_3\text{CHO}} + \Delta_f G_{\text{CO}_2}) - (\Delta_f G_{\text{CH}_3\text{COCOOH}}) \\ \Delta G_{\text{rxn}}^\circ &= \left[ (-133 \frac{\text{kJ}}{\text{mol}}) + (-394 \frac{\text{kJ}}{\text{mol}}) \right] - (-463 \frac{\text{kJ}}{\text{mol}}) \\ \Delta G_{\text{rxn}}^\circ &= -64 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

The reaction is spontaneous under standard state conditions because  $\Delta G_{\text{rxn}}^\circ < 0$  (negative). A reaction is spontaneous when  $\Delta G < 0$

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

$$\begin{aligned} -64 \frac{\text{kJ}}{\text{mol}} \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) &= -64 \times 10^3 \frac{\text{J}}{\text{mol}} & \Delta G_{\text{rxn}}^\circ &= -RT \ln K_{\text{eq}} \\ \ln K_{\text{eq}} &= - \frac{\Delta G_{\text{rxn}}^\circ}{RT} \\ \ln K_{\text{eq}} &= - \frac{(-64 \times 10^3 \frac{\text{J}}{\text{mol}})}{(8.314 \frac{\text{J}}{\text{mol K}})(80.0 \text{ K})} = 96.2 \\ K_{\text{eq}} &= 6.15 \times 10^{41} \end{aligned}$$

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

The reaction favors the reactants.

2. For a pure substance

a. Derive the following expression

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

$$\text{Know that: } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \beta V$$

$$\partial S_m = \frac{\partial S}{n}$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\kappa V}$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$(\beta V) \left(-\frac{1}{\kappa V}\right) \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\beta V \left(-\frac{1}{\kappa V}\right) = -\left(\frac{\partial P}{\partial T}\right)_V$$

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

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

$$\beta > 0, \kappa > 0$$

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

$$\Delta S_m = \left(\frac{\beta}{n\kappa}\right) \Delta V \Rightarrow \therefore \text{molar entropy would increase with increasing volume}$$

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

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

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

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

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

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

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

d. Pure phosphine is allowed to decompose according to the following reaction.



Assuming ideal gas behavior, and using the Maxwell relationship above, derive an expression for  $\left( \frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}}$

**How does the chemical potential change with increasing pressure?**

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

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

If increase  $P$ , the position of the equilibrium will move to the left and  $\text{COCl}_2$  will form. Hence as you increase  $\text{COCl}_2$ , pressure increases and there is an increase in chemical potential.

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

$$\text{Pressure is constant} \Rightarrow \int_{\mu_{o_i}}^{\mu_i} d\mu_i = \int_{P^\circ}^P \left( \frac{\partial V}{\partial n_i} \right) dP \Rightarrow (\mu_i - \mu_{o_i}) = \frac{dV}{d\mu_i} (P - P^\circ)$$

$\mu_{o_i}$  is chemical potential at pressure  $P^\circ$ .

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

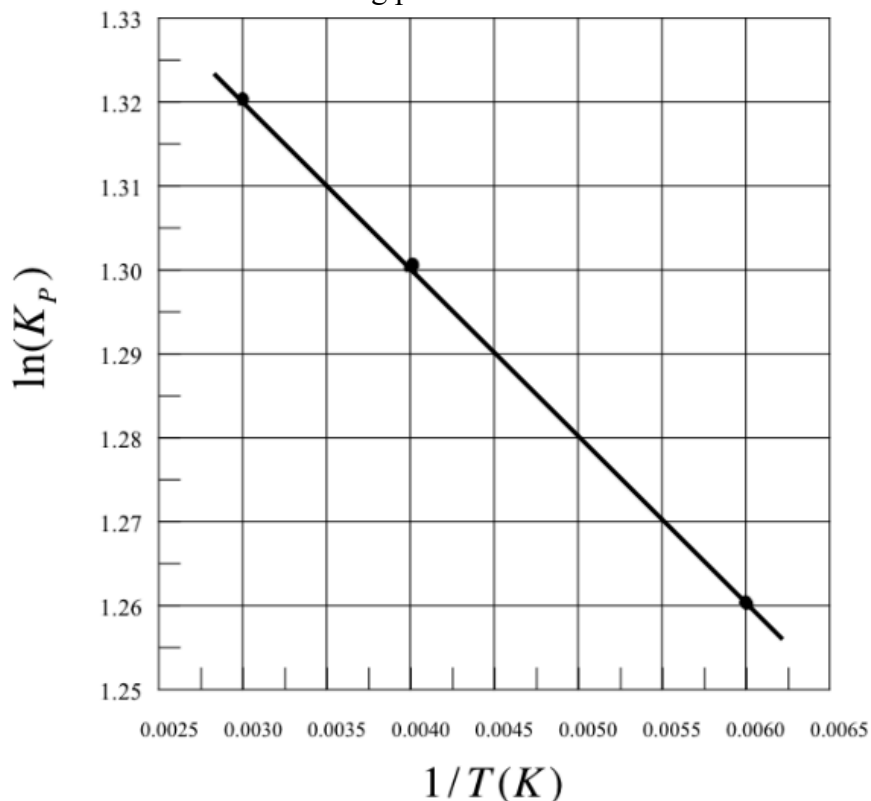
T (K)	K <sub>p</sub>
167	3.53
250	3.67
333	3.74

$\frac{1}{T} (K)$	$\ln(K_p)$
0.006	1.26
0.004	1.30
0.003	1.32

$$y = -20.0x + 1.38$$

$$m = \text{slope} = -20$$

a. Plot the data on the following plot



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

$$K_p = e^{-\Delta G/RT} \Rightarrow \ln K_p = -\frac{\Delta G}{R} \times \frac{1}{T} \Rightarrow -\frac{\Delta G}{R} = -20.0 K$$

$$\Delta G = (20.0 K)R = (20.0 K)(8.314 \frac{J}{mol \cdot K}) = 166 \frac{J}{mol}$$

Since  $\Delta G > 0$ , reaction is not spontaneous.

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

The reaction is enthalpically driven because  $\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$

Short Answers:

4. What is the second law of thermodynamics?

The second law of thermodynamics states that it is impossible for a system to undergo a cyclic process whose sole effects are the flow of heat into the system from a heat reservoir and the performance of an equal amount of work by the system on the surroundings. The total entropy of an isolated system can't decrease over time and always increases and is constant for a reversible process.

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

It states that the entropy of a pure, crystalline substance (element or compound) is 0 at 0 Kelvin. It would be possible to grow a perfect crystal where all the spaces are occupied by atoms with identical size. It's not possible to reach a temperature of absolute 0. If the perfect crystalline solid doesn't possess any kinetic energy, there would be no motion between compounds of that system, so  $entropy = 0$ , but there isn't any change in the energy or enthalpy.

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

We can't because the perpetual motion machine violates both the first and second law of thermodynamics.

- The first law states that energy can't be created or destroyed, only transformed from one form to the other. But with the machine it has to produce work without energy input.
- Based on the second law, an isolated system will move towards a state of disorder. The more energy is transformed, the more of it is wasted. A perpetual motion machine has to have energy that was never wasted and never moved toward a disordered state.

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

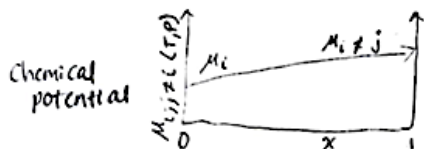
Gibbs' free energy and Helmholtz energy are both thermodynamic potentials. Yet, Gibbs' free energy is most useful when you have controlled temperature and pressure, while Helmholtz energy is more useful when you have controlled temperature and volume. Since most reactions are carried out under constant pressure and temperature, compared to controlled volume, Gibbs' free energy is more useful to chemists.

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

Chemical potential is defined as the potential molar free energy:

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

It is called potential because energy is stored in matter, which is composed of molecules that are a combination of atoms that are held together by bonds. Its originated from energy stored in molecules (in form of interactions) that can do work.



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

It is spontaneous.  $\Delta G < 0$ : spontaneous  
 $\Delta G > 0$ : nonspontaneous

$$\mu = \mu^\circ + RT \ln P \rightarrow P = \frac{P}{P^\circ}$$

1  
standard chemical potential

$$G_i = n_A \mu_A + n_B \mu_B = n_A (\mu_A^\circ + RT \ln P_A) + n_B (\mu_B^\circ + RT \ln P_B)$$

$$G_f = n_A (\mu_A^\circ + RT \ln P_A) + n_B (\mu_B^\circ + RT \ln P_B)$$

$$G_{\text{mix}} = G_i - G_f = n_A RT (\ln P_A - \ln P) + n_B RT (\ln P_B - \ln P) = n_A RT \ln \frac{P_A}{P}$$

Since  $x_j = \frac{P_j}{P}$ ;  $x_A = \frac{n_A}{n_A + n_B}$ ;  $x_B = \frac{n_B}{n_A + n_B}$

$$n_A = n_{\text{total}} \cdot x_A ; n_B = n_{\text{total}} \cdot x_B$$

$$G_{\text{mix}} = n_{\text{total}} RT (x_A \ln x_A + x_B \ln x_B + \dots + x_n \ln x_n) \text{ since mole fraction } \leq 1$$

then  $\ln x \leq 0$

$$\therefore \Delta G_{\text{mix}} < 0 \Rightarrow \text{spontaneous}$$

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

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

$$\text{since } \Delta G_{rxn}^{\circ} > 0 \Rightarrow -RT \ln K_{eq} > 0$$

$$\ln K_{eq} < 0 \text{ if } K_{eq} < 1$$

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} < 1$$

$$\therefore [\text{Product}] < [\text{Reactant}]$$

$$\therefore \text{reactants are favored if } \Delta G_{rxn}^{\circ} > 0$$

Extra Credit (5 pts)

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

My favorite equation this semester is the equation used for enthalpy, which is  $H = U + PV$ . This is a useful equation because it involves the use of state functions. From this equation we can know how much heat (energy) is in a system and from this are able to know the work in system. To add, it can also inform us how much heat was lost or gained in the system.