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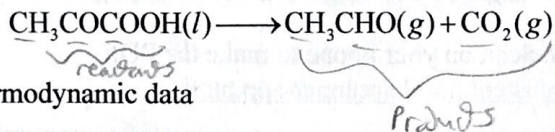
Name: _David DeLuca_

Who did you work with?

a. David DeLuca (me)

b. Gabrielle Singh

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Who else did you ask for help?

- Brooke Butler

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

$$CH_3COCOOH(l) \longrightarrow CH_3CHO(g) + CO_2(g)$$

reactants   Products

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.

$$\Delta G^{\circ}_{rxn} = \sum \Delta G^{\circ}_f\ products - \sum \Delta G^{\circ}_f\ reactants$$

$$\Delta G^{\circ}rxn = \left(-133\ kJ/m + -394\ kJ/m\right) - \left(-463\ kJ/m\right)$$

$$\Delta G^{\circ}rxn = \left(-527\ kJ/m\right) - \left(-463\ kJ/m\right)$$

$$\Delta G^{\circ}rxn = -64\ kJ/m$$

Since $\Delta G^{\circ}rxn$ is negative the reaction is spontaneous

24.000

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

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

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

$$\ln kp(0F) = \frac{64,000 - 24,000\ J/m}{8.314(298)}\ \frac{1}{8.314\ J/molk}\left(\frac{1}{80k} - \frac{1}{298k}\right)$$

$$\ln kPOP = 25.832 - 26.3968$$

$$e^{\ln kP} = e^{-0.5648} \quad KP = 0.568$$

$$\Delta H_{rxn} = \sum \Delta H^{\circ}_{products} - \sum \Delta H^{\circ}_{reactants}$$

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

$$\Delta H rxn = 24\ kJ/mol$$

$$\llcorner\rightarrow 24,000\ J/mol$$

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

Because $Kp < 1$ for the lower temperature the reaction favors the reactants

2. For a pure substance

    a. Derive the following expression

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

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

5) $ds = \frac{C_V}{T}dT$, constant V

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

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

3) $ds = \frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv\right] + \frac{P}{T}dv \cdot \frac{C_V}{T}dT + \frac{1}{T}\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]dv$

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

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

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

9) $P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T^2}\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]$

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, $n_1, n_2, n_3 \ldots$

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

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

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

3) $dH = TdS - VdS + \sum_i \mu_i dn_i$

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

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

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

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

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

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

9) $d\mu = VdP - SdT$

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

11) $\int d\mu = \int V_{Sp} dP$

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

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

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

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

    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 $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$ Start $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq i}} = \left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{Cl_2}+n_{CO}+n_{Cl_2}} \Rightarrow +\left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P_i}$

Answers

    How does the chemical potential change with increasing pressure?

    Hint: $n = n_{COCl_2} + n_{CO} + n_{Cl_2}$, $dn_{COCl_2} = -dn_{CO}$, $dn_{COCl_2} = -dn_{Cl_2}$

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

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

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

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

$* P_A = X_A P$

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

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

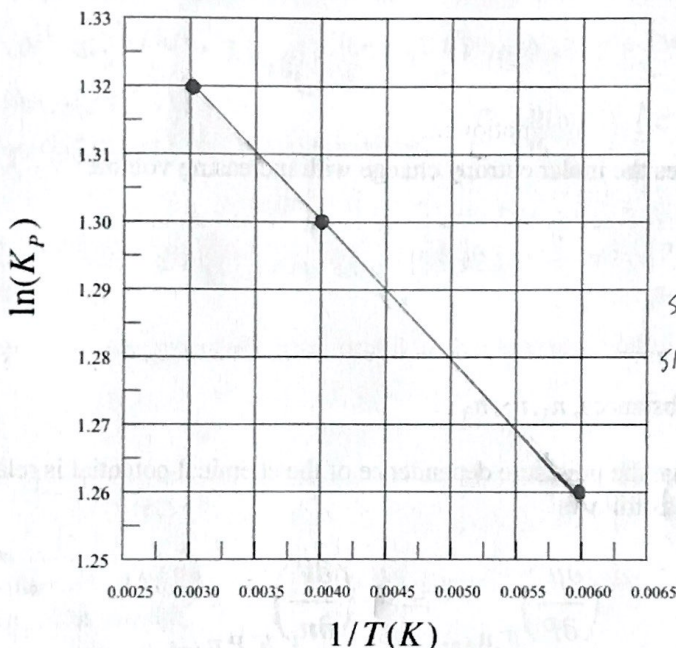| T (K)	K_P
167	3.53
250	3.67
333	3.74

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

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

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

$\ln(3.53) = 1.26$

$\ln(3.67) = 1.30$

$\ln(3.74) = 1.32$

a. Plot the data on the following plot

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

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

$\frac{1}{T}$

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

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

$y = mx + b$

$1.32 = (-20)0.003 + b$

$b = 1.38$ intercept

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

$\Delta G_r^\circ = \Delta H - T\Delta S$

$\Delta G_r^\circ = 166.28 \text{ J/m} - (298.15 K)(11.473 \text{ J/m K})$

$\Delta G_r^\circ = 166.28 \text{ J/m} - 3,420.67495 \text{ J/m}$

$\boxed{\Delta G_r^\circ = -3,254.395 \text{ J/m} \\ \rightarrow \text{reaction is spontaneous because } \Delta G_r^\circ < 0}$

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

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

$-\Delta H^\circ = slope \cdot R$

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

$-\Delta H = -166.28$

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

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

$\Delta G < 0, \text{ Spontaneous}$

$\Delta H > 0$

$\Delta S > 0$

* Spontaneous @ high T

* Nonspontaneous @ low T

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

$\Delta S = 11.473 \text{ J/mk}$

Entropically favorable
$\rightarrow$ because $\Delta H > 0$ and $\Delta S > 0$

Short Answers:

4. What is the second law of thermodynamics?

Total entropy of isolated system can never decrease over time and only constant if process is reversible.

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

Entropy of pure, perfect crystalline substance (element or compound) is zero at zero kelvin. It is different because entropy measures activity while enthalpy measures energy.

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

It is impossible to make because saying that the machine could do work indefinitely without an energy source violates the first and second laws of thermodynamics.

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

Gibbs free energy is important because you can use it to determine how likely a reaction is to occur, which is essential for chemists when constructing an experiment. While Helmholtz measures useful work obtainable from a closed thermodynamic system which is more of a general application. For example, potential for Gibbs free energy, while helmholtz deals with work applied to a system.

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

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

μ_i^I high → low $\mu_i^I > \mu^{\neq}$
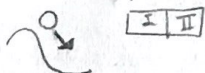
- chemical potential is the change in Gibbs energy per mole of substance i added at constant concentration
- chemical potential shows absorbed or released energy due to change of particle number of other species.
- Natural direction of change dictated by chemical potential → natural direction of change dictated by given point

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

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

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

$\Delta G < 0$ spontaneous
$\Delta G > 0$ nonspontaneous
$\Delta G = 0$ equilibrium

$\Delta H < 0$ and $\Delta S < 0$
$\quad \Delta H < T\Delta S, \Delta G +$
$\quad \Delta H > T\Delta S, \Delta G -$
enthalpically favorable

$\Delta H > 0$ and $\Delta S > 0$
$\quad \Delta H < T\Delta S, \Delta G -$
$\quad \Delta H > T\Delta S, \Delta G +$
entropically favorable

$\mu_i \frac{\partial G}{\partial n_i}$
$\quad{}_{T,P,n_j}$

as n increases overall μ_i will decrease

When a molecule is added in ideal gas, it will not react with it, and hence number of molecules increase and entropy increases, due to increase in particles. Increase in particles causes decrease in chemical potential. Entropy increase, more spontaneous reaction.

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.

When ΔG_{rxn} is greater than 0 the process is endergonic and not spontaneous in forward reaction, will proceed spontaneously in reverse direction to make more starting materials.

$\Delta H > 0$ and $\Delta S > 0$ and $\Delta H > T\Delta S$ then $\Delta G +$

Extra Credit (5 pts)

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

Chemical Potential, $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{P, T, n_j}$, is my favorite equation

because it represents the energy that can be absorbed or released
due to a change in particle number of given species, it helps
determines the stability of substances, such as chemical species,
compounds, and solution and their tendency to chemically react to
form new substances, to transform to new physical states, or to
migrate from one spatial location to another.