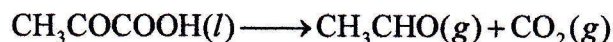Name: _Angela Tran_

Who did you work with?

a. Špela Kunstelj

b. Anas Saleh

c. Phuong Le

d. Angela Tran (Myself)

Who else did you ask for help?

No one else.

Name: Angela Tran

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

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

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.

$$\Delta G^\circ_{rxn} = \left[(-394\ KJ/mol) + (-133\ KJ/mol)\right] - \left[-463\ KJ/mol\right]$$

$$\Delta G^\circ_{rxn} = -527\ KJ/mol + 463\ KJ/mol$$

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

At standard state conditions, the reaction is spontaneous because ΔG°_{rxn} is negative.

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

$$K_p (298\ K) = e^{-\Delta G^\circ_R / RT} = e^{-(-64,000\ J/mol)/(8.314\ J/mol\ K)(298.15k)} = 1.63 \times 10^{11}$$

$$\Delta H^\circ_{rxn} = \left[(-394\ KJ/mol) + (-166\ KJ/mol)\right] - \left[-584\ KJ/mol\right]$$

$$\Delta H^\circ_{rxn} = 24\ KJ/mol = 24,000\ J/mol$$

$$K_p (80\ K) = e^{\left(\ln(1.63 \times 10^{11}) - \frac{24,000\ J/mol}{8.314\ J/mol\ K}\left(\frac{1}{80K} - \frac{1}{298\ K}\right)\right)}$$

$$\boxed{K_p (80\ K) = 0.56}$$

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

At lower temperature, the reaction favors the reactants.

2. For a pure substance

    a. Derive the following expression

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

⊛ Please see attached sheet for answers to these questions

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

        Molar entropy increases as volume increases.

For a mixture of substances, n_1, n_2, n_3 ...

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

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

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

$$COCl_2 \text{ (g)} \rightleftharpoons CO \text{ (g)} + Cl_2 \text{ (g)}$$

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?

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

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

Angela Tran

Thermo Exam II

Question 2

a) $dA = -SdT - PdV = \left(\dfrac{\partial A}{\partial T}\right)_V dT + \left(\dfrac{\partial A}{\partial V}\right)_T dV$

$\hookrightarrow \left(\dfrac{\partial A}{\partial T}\right)_V = -S \qquad \left(\dfrac{\partial A}{\partial V}\right)_T = -P$

$\dfrac{\partial}{\partial V}\left(\dfrac{\partial A}{\partial T}\right)_V = -\left(\dfrac{\partial S}{\partial V}\right)_T$

$\dfrac{\partial}{\partial T}\left(\dfrac{\partial A}{\partial V}\right)_T = -\left(\dfrac{\partial P}{\partial T}\right)_V$

$\left.\begin{array}{l} \\ \\ \\ \end{array}\right\}$ $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right) = \dfrac{\beta}{K}$

$\dfrac{\partial}{\partial V}\left(\dfrac{\partial A}{\partial T}\right)_V = \dfrac{\partial}{\partial T}\left(\dfrac{\partial A}{\partial V}\right)_T$

$\downarrow$

$\boxed{\left(\dfrac{\partial S_m}{\partial V}\right)_T = \dfrac{\beta}{nK}}$

b) Molar entropy increases as volume increases.

c) $dG = -SdT + VdP = \left(\dfrac{\partial G}{\partial T}\right)_P dT + \left(\dfrac{\partial G}{\partial P}\right)_T dP$

$\hookrightarrow \left(\dfrac{\partial G}{\partial P}\right)_T = V \qquad\qquad \left(\dfrac{\partial G}{\partial n_i}\right) = \mu_i$

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

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

$\left.\begin{array}{l} \\ \\ \end{array}\right\}$ $\boxed{\left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n_{j\neq i}}}$

Over $\rightarrow$

d) $\left(\dfrac{\partial \mu_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} = \left(\dfrac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}}$

$\quad = \left(\dfrac{\partial (nRT/P)}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}} = \dfrac{RT}{P} \dfrac{\partial (n_{COCl_2} + n_{CO} + n_{Cl_2})}{\partial n_{COCl_2}}$

$\quad = \dfrac{RT}{P}\left(\dfrac{\partial n_{COCl_2}}{\partial n_{COCl_2}} + \dfrac{\partial n_{CO}}{\partial n_{COCl_2}} + \dfrac{\partial n_{Cl_2}}{\partial n_{COCl_2}}\right)$

$\quad = \dfrac{RT}{P}\left(1 - 1 - 1\right) = \boxed{-\dfrac{RT}{P}}$

With increasing pressure, the chemical potential decreases

e) $\left(\dfrac{\partial \mu_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} = -\dfrac{RT}{P}$

$\partial \mu_{COCl_2} = \dfrac{-RT}{P} dP$

$\mu_{COCl_2} - \mu^{\circ}_{COCl_2} = -RT \ln \dfrac{P}{P^{\circ}}$
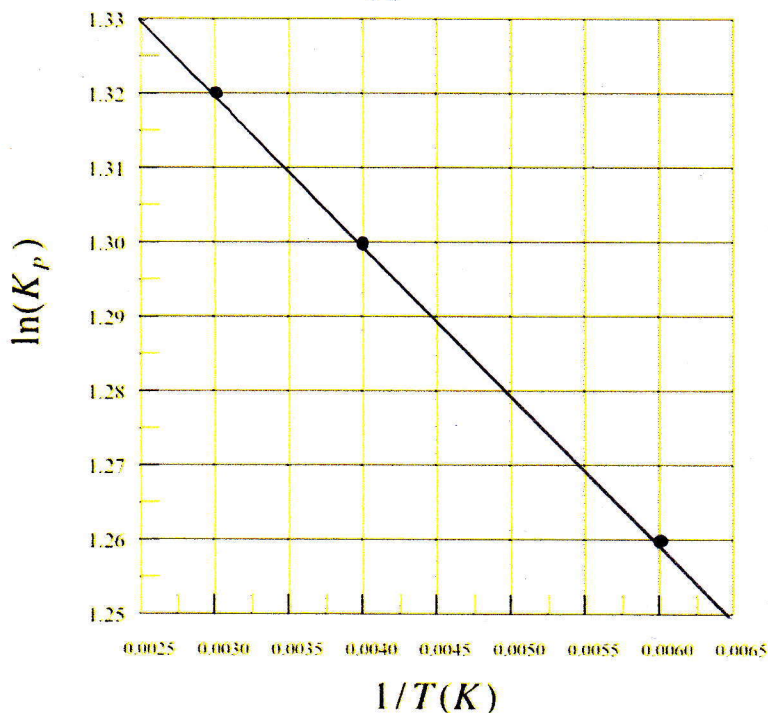
$\boxed{\mu_{COCl_2} = \mu^{\circ}_{COCl_2} - RT \ln \dfrac{P}{P^{\circ}}}$

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

T (K)	Kp
167	3.53
250	3.67
333	3.74

$\frac{1}{T}$ (K)	$\ln K_p$
0.005988	1.261298
0.004	1.300192
0.003003	1.319086

a. Plot the data on the following plot

Work for Part (b)

$$\text{slope} = \frac{-\Delta H}{R} = \frac{1.32 - 1.30}{0.0030 - 0.0040}$$

$$= -20 \text{ K}$$

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

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

$$1.32 = -20 \text{ K} \left(0.0030 \text{k}\right) + \frac{\Delta S_r^\circ}{R}$$

$$\frac{\Delta S_R^\circ}{R} = 1.38$$

$$\Delta S_R^\circ = 11.47 \text{ J/mol K}$$

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

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

$$\Delta G_r^\circ = 166.28 \text{ J/mol} - (298.15 \text{ K})(11.47 \text{ J/mol k})$$

$$\boxed{\Delta G_r^\circ = -3253.50 \text{ J/mol}}$$

⤷ The reaction is spontaneous because ΔG_r° is negative $(\Delta G_r^\circ < 0)$.

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

This reaction is entropically driven because for ΔG° to be negative, or spontaneous, the overall sum must be negative. Since ΔH_r° is positive, the reaction depends on ΔS_r° to be more positive to make ΔG_r° negative.

<u>Short Answers:</u>

4. What is the second law of thermodynamics?

The second law of thermodynamics is the total entropy of an isolated system can never decrease over time and is constant only if all processes are reversible.

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

The third law states that the entropy of a pure, perfectly crystalline substance is zero at 0 K. Entropy is different because it has an absolute value, while enthalpy and energy have relative values. Entropy also tells us why a reaction is spontaneous or why heat flows in a direction.

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

We can't build a perpetual motion machine because a cyclic process can't convert heat to work with 100% efficiency.

$$\varepsilon = \frac{-W_{cycle}}{q_{abs}} < 1 \quad (\text{not } 100\% \text{ efficiency})$$

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

Gibbs free energy is more useful to chemists than Helmholtz energy because ΔG depends on ΔH while ΔA depends on ΔU. It is easier to measure ΔH through heat than ΔU (the internal energy).

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

$$\frac{\partial G}{\partial n} = \mu$$

$\mu_I > \mu_{II}$

| I | II |

$dn_i \rightarrow$

It is called a potential because the change for "μ" goes from high to low direction wise, and potentials always go from high to low.

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

Yes, the mixing of different types of molecules in an ideal gas is spontaneous. As seen in the equation, $\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$, $\ln x_i$ is always negative and this makes the whole solution negative. Since $\Delta G_{mixing} < 0$, the reaction is spontaneous.

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.

If $\Delta G^\circ_{rxn} > 0$, the reaction is nonspontaneous, so there is more reactants. As seen in the equation $K_p = e^{-\Delta G/RT}$, when ΔG gets more positive, K_p gets smaller. This means very little product is formed and that the reaction has mostly reactants.

Extra Credit (5 pts)

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

My favorite equation from this semester was the van der Waals
equation, $P = \dfrac{nRT}{V-nb} - \dfrac{n^2a}{V^2}$. The van der Waals equation allows us to
see or estimate the equation of state for real gases at moderate or high
densities since they vary from ideal gases at these conditions. Real gases
have molecular volume and interaction (attraction or repulsion) between
molecules at moderate/high densities, and this equation allows us to predict
behavior of a real gas depending on pressure, volume, and temperature.