Name: <u>Victoria Savino</u>

Who did you work with?

    a. Kylee McDonald

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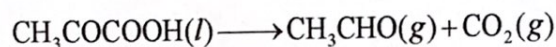
    c. Gabrielle Singh

    d. Brooke

Who else did you ask for help?

Brooke Butler
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Name: Victoria Savino

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.

$\Delta G_{rxn}^{\circ} = \Sigma \Delta G_f$ products $- \Sigma \Delta G_f$ reactants

$\Delta G_{rxn}^{\circ} = [-133\ kJ/mol\ +\ -394\ kJ/mol] - [-463\ kJ/mol]$

$\boxed{\Delta G_{rxn}^{\circ} = -64\ kJ/mol = -64,000\ J/mol}$

Since ΔG_{rxn}° is negative, the reaction is spontaneous.

$\Delta G_{rxn}^{\circ} < 0$, spontaneous reaction

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

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

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

$\ln K_p = -0.5651$

$e^{\ln K_p} = e^{-0.5651}$

$\boxed{K_p = 0.5683}$

$\Delta_f H = \Sigma \Delta_f H$ products $- \Sigma \Delta_f H$ reactants

$\Delta_f H = [(-166 + -394)kJ/mol]$

$\quad\quad - [-584\ kJ/mol]$

$\Delta_f H = 24\ kJ/mol$

$\Delta_f H = 24,000\ J/mol$

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

At the lower temperature, the reaction favors the reactants because $K_p < 1$.

2. For a pure substance

    a. Derive the following expression

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \boxed{\left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{n\kappa}}$$

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

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

    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

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

$dU = TdS - PdV + \Sigma_i \mu_i dn_i$

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

$dH = TdS - VdT + \Sigma_i \mu_i dn_i$

$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i}} \longrightarrow dA = -PdV - TdS + \Sigma_i \mu_i dn_i$

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

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

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

$d\mu = VdP - SdT$

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

$\int_{\mu^0}^{\mu} d\mu = V\int_{P^0}^{P} dP$

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

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

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

$\int_{\mu^0}^{\mu} d\mu = \frac{RT}{P}\int_{P^0}^{P} dP$

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

$$COCl_2 \text{ (g)} \rightleftharpoons CO \text{ (g)} + Cl_2 \text{ (g)}$$
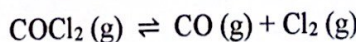
Assuming ideal gas behavior, and using the Maxwell relationship above, derive an expression for $\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}}$

The chemical potential increases with increasing pressure

How does the chemical potential change with increasing pressure?

$\left(\frac{\partial \mu_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2},n_{COCl_2}}$

$\left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{COCl_2}}$

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

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

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

$$G(T,P) = G^\circ(T) + nRT \ln\left(\frac{P}{P^\circ}\right)$$

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

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

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

$\frac{1}{167} = 0.005988$
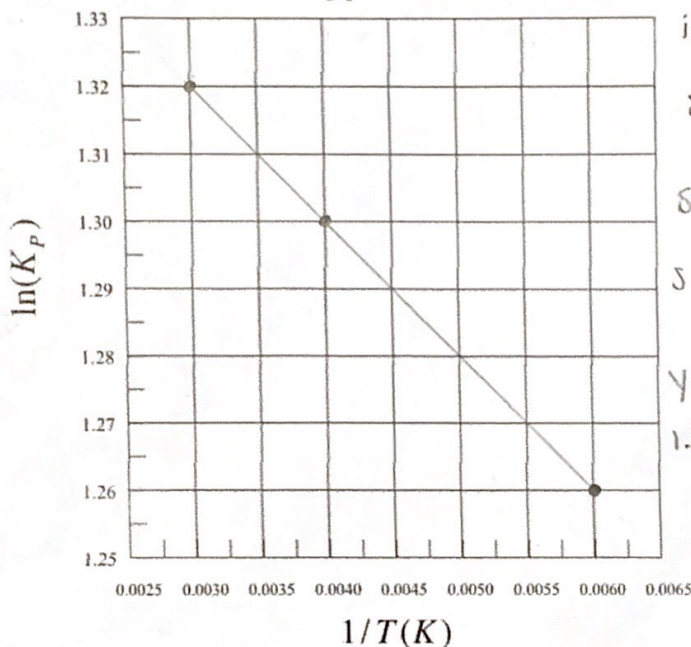
$\frac{1}{250} = 0.004$

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

T (K)	K_P
167	3.53
250	3.67
333	3.74

$\ln(3.53) = 1.26$

$\ln(3.67) = 1.30$

$\ln(3.74) = 1.32$

a. Plot the data on the following plot

$1/T(K)$

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

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

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

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

$y = mx + b$

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

$b = 1.38$
↑
y-intercept

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

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

$\Delta G_r^\circ = 166.28 \text{ J/mol} - (298 K)(11.473 \text{ J/mol} \cdot k)$

$\boxed{\Delta G_r^\circ = -3252.674 \text{ J/mol}}$

The reaction is spontaneous since $\Delta G_r^\circ < 0$.

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

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

$-\Delta H^\circ = \text{Slope}(R)$

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

$-\Delta H = -166.28$

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

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

$\Delta H > 0$

$\Delta S > 0$

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

$\Delta S = 11.473 \text{ J/mol} \cdot k$

This reaction is entropically driven.

Short Answers:

4. What is the second law of thermodynamics?

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.

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 (element or compound) is zero at zero kelvin. Entropy is different because it measures random activity while enthalpy or energy measures the overall amount of energy.

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

We can't build a perpetual motion machine because saying that the machine can 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?

Gibb's free energy is more useful because it determines the condition for spontaneity, equilibrium and how likely a reaction is to occur which is essential for chemists. Helmholtz energy is a general condition of spontaneity and measures useful work obtainable from a closed thermodynamic system which is more general. For example, potential for Gibb's 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.

Chemical potential is the change in Gibb's energy per mole of substance added at constant concentration. Chemical potential shows absorbed or released energy due to change of particle number of given species. The natural direction of change is dictated by chemical potential.

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

μ_i
high → low $\mu_i^{I} > \mu^{II}$

$\boxed{I \mid II}$

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 mixing of different types of molecules in an ideal gas is spontaneous because mixing molecules increases entropy (ΔS) which results in $\Delta G > 0$ since there is an increase in number of molecules. An increase in particles causes a decrease in chemical potential. An increase in entropy
$$\Delta G = \Delta H - T\Delta S$$
equals a more spontaneous reaction.

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

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

When ΔG°_{rxn} is greater than zero, the process endergonic and not spontaneous in the forward reaction. The reaction will proceed in reverse and more reactants will be formed.

$\Delta G = \Delta H - T\Delta S$
$\oplus$ value $= \Delta H - T\Delta S$ } $\Delta H > T\Delta S$

$\left.\begin{array}{l} \Delta H > 0 \\ \Delta S > 0 \end{array}\right\}$ $\Delta H > T\Delta S$ so ΔG is positive

Extra Credit (5 pts)

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

My favorite equation is work.

$$w = \int_{x_i}^{x_f} F \cdot dx = -\int_{x_i}^{x_f} P_{external} \, A \, dx = -\int_{v_i}^{v_f} P_{external} \, dV$$

In thermodynamics, work is defined as any quantity of energy that flows across the boundary between the system and surroundings as a result of a force acting through a distance. Work is important because it is associated with the initial and final states of the systems. The net effect of work is to change U of the system and surroundings in accordance with the first law of thermodynamics. The sign of work (negative or positive) tells us if work is done by or on the system. If work is negative, work is done by the system on the surroundings. If work is positive, work is done on the system by the surroundings. There are many types of work which are all very important in chemistry as it allows us to see how the internal energy, U, of a system can be changed.