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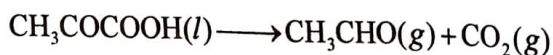
Who did you work with?

- a. Andrew Kalida
- b. Jasleen Gill
- c.
- d.

Who else did you ask for help?

Name: Rebecca Spright

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



Given the following thermodynamic data

$$\begin{array}{ll} \text{rea } \Delta_f H(25^\circ\text{C})_{\text{CH}_3\text{COCOOH}} = -584 \text{ kJ mol}^{-1} & \Delta_f G(25^\circ\text{C})_{\text{CH}_3\text{COCOOH}} = -463 \text{ kJ mol}^{-1} \text{ rea} \\ \text{pro } \Delta_f H(25^\circ\text{C})_{\text{CH}_3\text{CHO}} = -166 \text{ kJ mol}^{-1} & \Delta_f G(25^\circ\text{C})_{\text{CH}_3\text{CHO}} = -133 \text{ kJ mol}^{-1} \text{ pro} \\ \text{pro } \Delta_f H(25^\circ\text{C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1} & \Delta_f G(25^\circ\text{C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1} \text{ pro} \end{array}$$

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

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

$$\Delta G_{\text{rxn}}^\circ = (-133 \text{ kJ/mol} + -394 \text{ kJ/mol}) - (-463 \text{ kJ/mol})$$

$$\Delta G_{\text{rxn}}^\circ = -527 \text{ kJ/mol} + 463 \text{ kJ/mol}$$

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

The reaction is spontaneous under standard state conditions because $\Delta G_{\text{rxn}}^\circ$ is negative.

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

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

$$\Delta H_{\text{rxn}} = (-394 \text{ kJ/mol} + -166 \text{ kJ/mol}) - (-584 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}} = -560 \text{ kJ/mol} + 584 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}} = 24 \text{ kJ/mol} \rightarrow 24,000 \text{ J/mol}$$

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

$$\ln K_p(T_f) = 25.832 - 36.084 + 9.687$$

$$\ln K_p(T_f) = 25.832 - 26.397$$

$$\ln K_p(T_f) = -0.565$$

$$K_p = 0.568$$

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

The reaction favors the reactants because K_p is less than 1.

2. For a pure substance

a. Derive the following expression

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

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

$$dS = \left(\frac{dS}{dT}\right)_V dT + \left(\frac{dS}{dV}\right)_T dV$$

$$dS = \frac{1}{T} [C_V dT + \left(\frac{dU}{dV}\right)_T dV] + \frac{P}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{dU}{dV}\right)_T\right] dV$$

$$\left(\frac{dS}{dV}\right)_T = \frac{C_V}{T} = \frac{1}{T} \left[P + \left(\frac{dU}{dV}\right)_T\right]$$

$$dS = \frac{C_V}{T} dT \rightarrow \text{constant } V$$

$$\left(\frac{d}{dT} \left(\frac{dS}{dV}\right)_T\right)_V = \left(\frac{d}{dV} \left(\frac{dS}{dT}\right)_T\right)_T$$

$$\left(\frac{d}{dV} \left(\frac{dS}{dT}\right)_T\right)_T = \frac{1}{T} \left(\frac{d}{dV} \left(\frac{dU}{dT}\right)_T\right)_T$$

$$\left(\frac{d}{dT} \left(\frac{dS}{dV}\right)_T\right)_T = \frac{1}{T} \left[\left(\frac{dP}{dT}\right)_V + \left(\frac{d}{dT} \left(\frac{dU}{dV}\right)_T\right)_T\right]$$

$$P + \left(\frac{dU}{dV}\right)_T = T \left(\frac{dP}{dT}\right)_V - \frac{1}{T} \left[P + \left(\frac{dU}{dV}\right)_T\right]$$

$$\left(\frac{dS}{dV}\right)_T = \left(\frac{dP}{dT}\right)_V = \frac{-(dV/dT)_P}{(dV/dP)_T} = \frac{\beta}{nk}$$

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, $n_1, n_2, n_3 \dots$

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

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

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

$$dH = TdS + \sum_i \mu_i dn_i$$

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

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

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

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

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

$$d\mu = VdP - SdT$$

$$\left(\frac{d\mu}{dP}\right)_T = V$$

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

$$\mu - \mu^0 = V(P - P^0)$$

$$\mu = \mu^0 + V(P - P^0)$$

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

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

$$\mu = \mu^0 + RT \ln \frac{P}{P^0}$$

$$\mu = \mu^0 + RT \ln \left(\frac{P}{P^0}\right)$$

$$\mu = \mu^0 + RT \ln \left(\frac{P}{P^0}\right)$$

$$\mu = \mu^0 + RT \ln \left(\frac{P}{P^0}\right)$$

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

$$\left(\frac{d\mu_i}{dP}\right)_{T, n_j, n_i}$$

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

$$-\left(\frac{dV}{dn_{\text{COCl}_2}}\right)_{T, P, n_{\text{COCl}_2}, n_{\text{CO}}, n_{\text{Cl}_2}}$$

$$-\left(\frac{dV}{dn_{\text{CO}}}\right)_{T, P, n_{\text{COCl}_2}, n_{\text{CO}}, n_{\text{Cl}_2}}$$

$$-\left(\frac{dV}{dn_{\text{Cl}_2}}\right)_{T, P, n_{\text{COCl}_2}, n_{\text{CO}}, n_{\text{Cl}_2}} + \left(\frac{dV}{dn_{\text{Cl}_2}}\right)_{T, P, n_{\text{COCl}_2}, n_{\text{CO}}, n_{\text{Cl}_2}}$$

How does the chemical potential change with increasing pressure?

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

The chemical potential increases with increasing pressure.

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

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

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

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

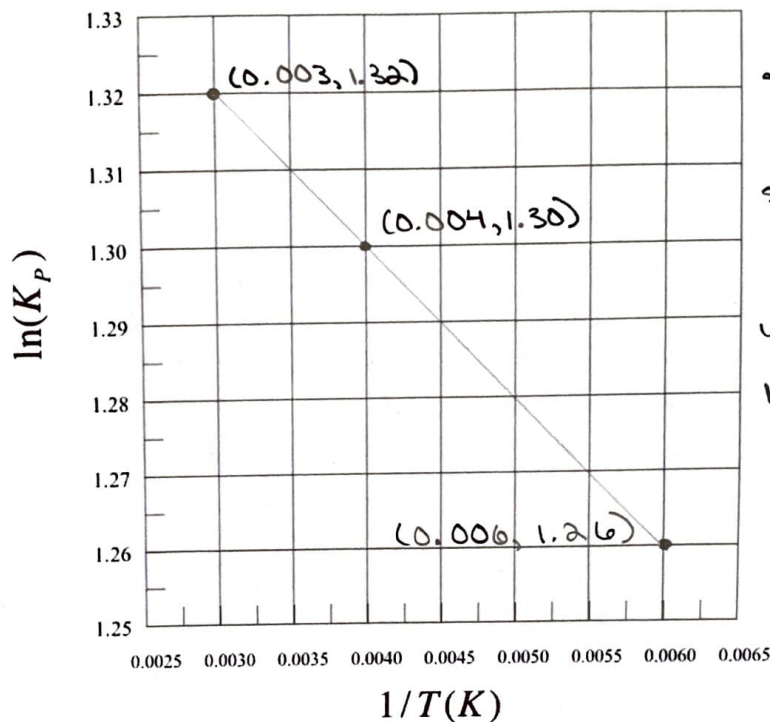
3. The following thermodynamic data was measured for a chemical reaction:

points on graph

	x	y
	T (K)	K _P
$\frac{1}{167} = 0.005988 \approx 0.006$	167	point 1 3.53
$\frac{1}{250} = 0.004$	250	point 2 3.67
$\frac{1}{333} = 0.003$	333	point 3 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



$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x}$$

$$\text{slope} = \frac{1.32 - 1.30}{0.003 - 0.004} = -20.0$$

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

$$y = mx + b$$

$$1.32 = (-20.0)(0.003) + b$$

$$b = 1.38$$

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

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

$$\Delta G = -RT \ln K_P$$

$$\text{average } \Delta G = \frac{\Delta G_1 + \Delta G_2 + \Delta G_3}{3}$$

$$\text{average } \Delta G^\circ = -2701.884 \text{ J/mol}$$

Since ΔG is negative at high T it is spontaneous, but since ΔG is positive at lower T it is also nonspontaneous.

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

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

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

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

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

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

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

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

$$\Delta S^\circ = 1.38(8.314 \text{ J/mol}\cdot\text{K})$$

$$\Delta S^\circ = 11.473 \text{ J/mol}\cdot\text{K}$$

The reaction is entropically favorable.

$$\Delta G^\circ = -RT \ln K_{eq} \rightarrow -RT \ln K_{eq} = \Delta H^\circ - T \Delta S^\circ$$

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \leftarrow \text{substitute from part a}$$

$$\ln K_{eq} = -20.0 + 1.38$$

$$\ln K_{eq} = -18.62$$

$$K_{eq} = 8.193 \times 10^{-9}$$

$$\Delta G^\circ = (-8.314 \text{ J/mol}\cdot\text{K})(250 \text{ K})$$

$$\ln(8.193 \times 10^{-9})$$

$$\Delta G^\circ = -38701.640 \text{ J/mol}$$

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

$\Delta H > 0$

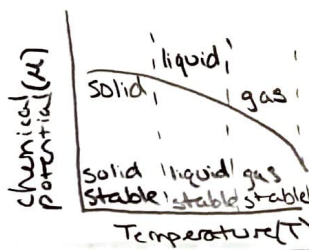
$\Delta S > 0$

Short Answers:

4. What is the second law of thermodynamics?
The second law of thermodynamics states that there is a quantity (entropy) that can never decrease over time in an isolated system. Entropy always increases or stays constant (at equilibrium) for an isolated system. $\Delta S \geq 0$ for any process in an isolated system.
5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.
The third law of thermodynamics states that the entropy of a pure, perfectly crystalline substance (element or compound) is zero at Kelvin [$S = k \ln(\omega)$]. This proves that when entropy (measure of random activity) is zero, then it is in equilibrium/order. Enthalpy, on the other hand, is a measure of the overall amount of energy.
6. Why can't we build a perpetual motion machine?
We can't build a perpetual motion machine because it violates the first and second laws of thermodynamics. It violates the first because it produces mechanical work without any energy being input; so the conservation of energy is not being upheld. The second law is violated because it converts thermal energy into mechanical work with no heat being rejected. This does not follow the rule of production of entropy which states that entropy of a system must always increase.
7. Why is Gibb's free energy usually more useful to chemists than Helmholtz energy?
Gibb's energy is usually more useful because it is more straight forward when manipulating variables. Helmholtz energy is more useful when dealing with mechanical systems.
8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing.

$$\left(\frac{dG}{dn_i} \right)_{T,P,\dots,n_j} = G = \mu_i \rightarrow \mu \frac{U_c}{N}$$

It is called a potential as it is under constant temperature, pressure, and a constant number of moles for all species except species "i." It is potential because it's the rate of increase in Gibb's free energy of a system in respect to the increase in the number of moles of species "i."



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 chemical potential is the change of free energy with respect to the number of molecules added. When a molecule is added in an ideal gas, it will not react with it. Therefore, the number of molecules increase and entropy increases because of an increase in particles. Chemical potential is inversely proportional to the number of molecules added. Chemical potential decreases as the number of particles increases. Mixing in an ideal gas is spontaneous. $dU = \left(\frac{dG}{dn}\right)_{T, A, n}$ \uparrow change = entropy

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.

Free energy of the reaction is positive, therefore it is not spontaneous and there is no product formed, but more reactants are produced.

$$\Delta G_{rxn}^{\circ} = -RT \ln K_{eq} \rightarrow K_{eq} = \frac{\text{products}}{\text{reactants}} \rightarrow K_{eq} < 1 \rightarrow \text{forms more reactants than products.}$$

$$\Delta G_{rxn}^{\circ} > 0 \quad K_{eq} < 1$$

Extra Credit (5 pts)

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

$$H = U + PV$$

This has been my favorite equation from this semester because it has been used numerous times throughout multiple chapters. In chapter 2, we first examined this state function when attempting to calculate internal pressure heat. This definition of enthalpy was utilized not only in these calculations, but could also determine if the reaction is endothermic or exothermic. In chapter 4, we studied how this equation could be applied to real and ideal gases. By simply applying the ideal gas law $PV = nRT$, we were able to calculate a whole new set of problems by transforming the equation into $\Delta H = \Delta U + \Delta(nRT)$. In chapter 6, this state function comes up again when we learn about natural variables. We can see how state functions depend on natural variables and how Maxwell Relations are derived from these differential expressions. I enjoyed this equation the most because it taught us new lessons with every chapter we learn.