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Who did you work with?

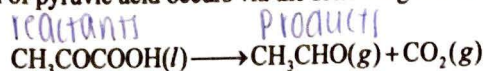
- a. Gabbie Singh
- b. Vic Savino
- c. David DeLuca
- d. Kylee McDonald

Who else did you ask for help?

Anas Saleh

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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.

$$\Delta G_{\text{rxn}}^\circ = \sum (\Delta G_f^\circ \text{ products}) - (\Delta G_f^\circ \text{ reactants})$$

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

$$\Delta G_{\text{rxn}}^\circ = -64 \frac{\text{kJ}}{\text{mol}} = \cancel{-64000 \text{ J/mol}} \quad \text{spontaneous!}$$

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

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

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

$$\ln K_p(T_f) = \frac{64000}{8.314(298)} - \frac{24000}{8.314} \left(\frac{1}{80\text{ K}} - \frac{1}{298\text{ K}} \right)$$

$$\ln K_p(T_f) = 25.832 - 26.3968$$

$$e^{\ln K_p(T_f)} = e^{-0.5648} \rightarrow K_p = 0.568$$

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

At a lower temperature (298 \rightarrow 80 K), the products are favored over the reactants since $K_p < 1$.

$$\Delta_f H_{\text{rxn}} = \sum \Delta_f H_f^\circ \text{ prod} - \sum \Delta_f H_f^\circ \text{ react}$$

$$\begin{aligned} \Delta_f H_{\text{rxn}} &= (-166 \frac{\text{kJ}}{\text{mol}} + \\ &\quad -394 \frac{\text{kJ}}{\text{mol}}) - \\ &\quad (-584 \text{ kJ/mol}) = 24 \frac{\text{kJ}}{\text{mol}} \\ &= 24000 \frac{\text{J}}{\text{mol}} \end{aligned}$$

2. For a pure substance

Start:

a. Derive the following expression

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial v}\right)_T dv$$

$$dS = \frac{1}{T} [C_v dT + (\partial U / \partial v)_T dv] + \frac{P}{T} dv - \frac{C_v}{T} dT + \frac{1}{T} [P + (\partial U / \partial v)_T] dv$$

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \text{ and } \left(\frac{\partial S}{\partial v}\right)_T = \frac{1}{T} [P + (\partial U / \partial v)_T]$$

$$dS = \left(\frac{C_v}{T} dT\right)_v$$

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

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial v}\right)_T\right)_v = \left(\frac{\partial}{\partial v} \left(\frac{\partial S}{\partial T}\right)_v\right)_T$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial v}\right)_T\right)_v = \frac{1}{T} \left(\frac{\partial P}{\partial T}\right)_v + \frac{1}{T^2} \left(\frac{\partial U}{\partial v}\right)_T$$

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

Molar entropy and volume are directly related meaning an increase of S_m is an increase in v because more interactions need more space to collide and that provides

For a mixture of substances, $n_1, n_2, n_3 \dots$ more ways of "organizing" molecules ($\uparrow S_m$)

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

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

$$\mu = v dP - s dT$$

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

$$\int_{\mu_0}^{\mu} d\mu = \int_{P_0}^P v dP$$

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



$$+ \left(\frac{\partial v}{\partial n_{\text{COCl}_2}}\right)_{T, P, n_1, n_2, n_3}$$

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?

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

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

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

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

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

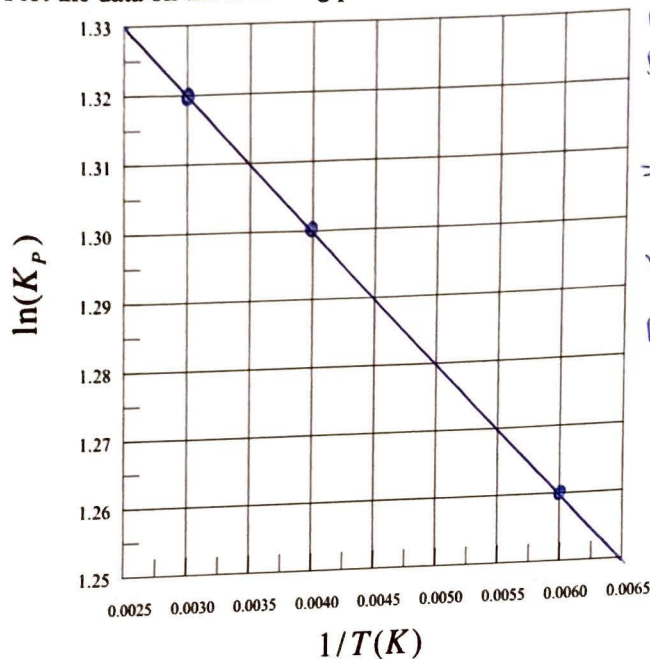
$$\mu_{\text{COCl}_2}^{\text{mix}}(T, P) = \mu_{\text{COCl}_2}^\circ(T) + nRT \ln(P/P^\circ) + RT \ln(x)_{\text{COCl}_2}$$

$$\frac{n_{\text{COCl}_2}}{n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}}$$

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

$1/T$	T (K)	K_p	$\ln(K_p)$
0.005988	167	3.53	1.26
0.004	250	3.67	1.30
0.003	333	3.74	1.32

a. Plot the data on the following plot



$\text{intercept} = \Delta S^\circ / R$
 $\text{slope} = -\Delta H^\circ / R$
 $= \Delta y / \Delta x$
 $= \frac{1.32 - 1.30}{0.003 - 0.004} = -20 (\text{slope})$
 $y = mx + b$
 $1.32 = (-20)(0.003) + b$
 $b = 1.38 (\text{intercept})$

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

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

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

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

$$\Delta G_r^\circ = -3,254.395 \text{ J/mol}$$

reaction is spontaneous because $\Delta G_r^\circ < 0$

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

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

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

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

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

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

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

$$\Delta H > 0$$

$$\Delta S > 0$$

$$\frac{1.38}{1} = \frac{\Delta S}{8.314}$$

$$\Delta S = 11.473$$

spontaneous @
high T
nonspontaneous @
low T

* entropically favorable
since $\Delta H > 0$ and
 $\Delta S > 0$.

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 + perform an equal amount of work.

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

The third law of thermodynamics is the entropy of a pure, perf. crystalline substance is zero at zero Kelvin. This makes entropy different than energy/enthalpy because it measures activity instead.

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

We cannot build a perpetual motion machine because it violates both the 1st and 2nd and 3rd law. There must be loss of heat and energy but not 100% EVER.

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


Gibbs free energy is usually more useful to chemists than Helmholtz energy because you can use it to determine how likely a reaction is to occur. Gibbs tends to be more

experimental than Helmholtz which is more of a calculated/general

8. Give the mathematical definition of chemical potential. Explain why it is called a potential. answer.

Include at least one drawing. $\mu = (\partial G / \partial n_i)_{T,P}$

Chemical potential is the change of free energy w/ respect to the no. of molecules at a constant temperature and pressure.

It shows absorbed/released ~~temperat~~ energy. Shows the natural direction of a rxn (stay prod, go to prod, rev?) Potential moves from high to low.  Helps allow activation energy to be found.

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

Mixing of different types of molecules in an ideal gas ~~spontaneous~~ is going to decrease the chemical potential. It will not react with the ideal gas and not interact. The overall entropy decreases and becomes unspontaneous due to a \uparrow denom. (\uparrow no. of molecules).

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.

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

$$\Delta H - T\Delta S = > 0 \text{ so } \dots \Delta H > T\Delta S$$

equilibrium is at in favor of reactants, no rxn.

meaning ΔS must be much smaller than ΔH . ΔS would have to be negative meaning more rxn can occur.

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 so far is the efficiency of the reversible Carnot cycle.

$$\varepsilon = \frac{-w_{\text{cycle}}}{q_{ab}} = \frac{q_{ab} + q_{cd}}{q_{ab}} = 1 - \frac{|q_{cd}|}{|q_{ab}|} < 1$$

This is my favorite equation so far because it tells us a lot about the ~~thermodynamic~~ engine ~~that~~ with an experimental mindset. It also showed / reminded me that systems ~~are~~ have an efficiency from 0% to 100% or 0 to 1. From my years studying chemistry, physics, biology, and calculus I have noticed the trend of everything being on a scale from 0 to 100 or 1-100 to 0 to 100%. Using the squeeze theorem from calculus and conditions placed onto a system, I believe it may be possible to continuously better engines until any change is insignificant. [If we have already gotten there using what we have available to us - great!]