

Name: Anas Saleh

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<https://acrobat.adobe.com/us/en/mobile/scanner-app.html>

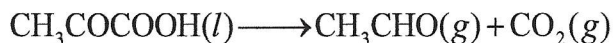
Who did you work with?

- a. Anas Saleh (Myself)
- b. Phuong Le
- c. Angela Tran
- d. Špela Kunstelj

Who else did you ask for help?

Name: Anas Saleh

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 $\Delta G^\circ_{\text{rxn}}$. Is this reaction spontaneous under standard state conditions? Justify your answer.

$$\Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_f(\text{CO}_2, g) + \Delta G^\circ_f(\text{CH}_3\text{CHO}, g)] - \Delta G^\circ_f(\text{CH}_3\text{COCOOH}, l)$$

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

$$\Delta G^\circ_{\text{rxn}} = -64\text{ kJ/mol}$$

↳ This reaction is spontaneous under standard state conditions because $\Delta G^\circ_{\text{rxn}} < 0$.

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

$$K_p(298.15\text{ K}) = e^{\frac{-\Delta G^\circ_{\text{rxn}}}{RT}} = e^{\left[\frac{-64 \times 10^3\text{ J mol}^{-1}}{(8.314\text{ J mol}^{-1}\text{ K}^{-1})(298.15\text{ K})} \right]} = 1.63 \times 10^{11}$$

$$\Delta H^\circ_{\text{rxn}} = [-394\text{ kJ mol}^{-1} + -166\text{ kJ mol}^{-1}] - (-584\text{ kJ/mol}) = 24\text{ kJ mol}^{-1}$$

$$K_p(80\text{ K}) = e^{\left[\ln K_p(298.15) - \frac{\Delta H^\circ_{\text{rxn}}}{R} \left(\frac{1}{80\text{ K}} - \frac{1}{298.15\text{ K}} \right) \right]}$$

$$K_p(80\text{ K}) = e^{\left[\ln(1.63 \times 10^{11}) - \left[(24 \times 10^3\text{ J/mol}) / 8.314\text{ J mol}^{-1}\text{ K}^{-1} \right] \left(\frac{1}{80\text{ K}} - \frac{1}{298.15\text{ K}} \right) \right]}$$

$$K_p(80\text{ K}) = 0.557 \approx 0.56$$

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

↳ The reaction favors the reactants at lower temperatures because $K < 1$.

2. For a pure substance

a. Derive the following expression

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

$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$
 Following Relationships are derived:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$
 Using these, three more relationships are derived:

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

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

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

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

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{nk}$$

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

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

→ With increasing volume the molar entropy also increases.

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

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

$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$
 $\left(\frac{\partial G}{\partial P}\right)_T = V$
 $\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}}$
 $\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_{j \neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_{j \neq i}}$
 $\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_{j \neq i}} = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_{j \neq i}} = \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_{j \neq i}}$

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

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

How does the chemical potential change with increasing pressure?

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

$$\begin{aligned} \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} &= \left(\frac{\partial V}{\partial n_{\text{COCl}_2}}\right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}} && \text{* As pressure increases,} \\ &= \left(\frac{\partial \left(\frac{nRT}{P}\right)}{\partial n_{\text{COCl}_2}}\right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}} && \text{Chemical potential decreases.} \\ &= \frac{RT}{P} \frac{\partial (n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2})}{\partial n_{\text{COCl}_2}} \\ &= \frac{RT}{P} \left(\frac{\partial n_{\text{COCl}_2}}{\partial n_{\text{COCl}_2}} + \frac{\partial n_{\text{CO}}}{\partial n_{\text{COCl}_2}} + \frac{\partial n_{\text{Cl}_2}}{\partial n_{\text{COCl}_2}} \right) = \frac{RT}{P} (1 - 1 - 1) = -\frac{RT}{P} \\ \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} &= -\frac{RT}{P} \end{aligned}$$

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

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

$$d\mu_{\text{COCl}_2} = -\frac{RT}{P} dP$$

$$\int d\mu_{\text{COCl}_2} = \int -\frac{RT}{P} dP$$

$$\begin{aligned} \mu_{\text{COCl}_2} - \mu_{\text{COCl}_2}^\circ &= -RT \ln \frac{P}{P^\circ} \\ + \mu_{\text{COCl}_2}^\circ &+ \mu_{\text{COCl}_2}^\circ \end{aligned}$$

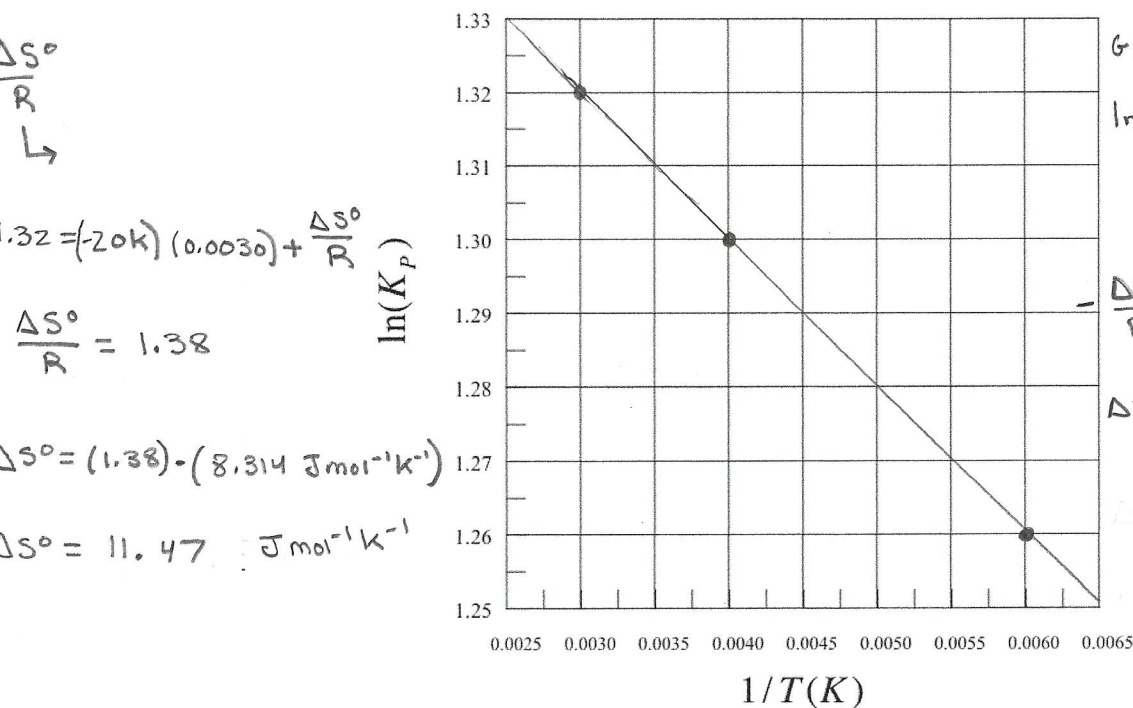
$$\mu_{\text{COCl}_2} = \mu_{\text{COCl}_2}^\circ - RT \ln \frac{P}{P^\circ}$$

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

T (K)	K _P
167	3.53
250	3.67
333	3.74

1/T (K)	ln(K _P)
6.00×10^{-3}	1.26
4.00×10^{-3}	1.30
3.00×10^{-3}	1.32

a. Plot the data on the following plot



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

$$\Delta G_r^\circ = (166.28 \text{ J/mol}) - (298.15 \text{ K})(11.47 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta G_r^\circ = -3253.5 \text{ J/mol}$$

This reaction is spontaneous because the Gibbs free energy is very negative.

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

H S

Reaction is entropically driven because the reaction is spontaneous as $\Delta S^\circ > 0$ and $\Delta H^\circ < 0$.

Short Answers:

4. What is the second law of thermodynamics?

- ~ The total entropy of an isolated system can never decrease over time and is constant if all processes are reversible.
- ~ For any reversible process in an isolated system, there is a unique direction of spontaneous change: $\Delta S > 0 \rightarrow$ spontaneous, $\Delta S < 0 \rightarrow$ nonspontaneous, $\Delta S = 0 \rightarrow$ reversible process @ equilibrium.

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 is zero at 0K. Entropy can have an absolute value, while energy and enthalpy only have relative values.

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

- ~ We can't build a perpetual motion machine because the work exerted by any machine is always smaller than the heat absorbed \rightarrow second law of thermodynamics.

Recall equation: $E = \frac{W_{\text{cycle}}}{Q_{\text{ab}}} = \frac{T_h - T_c}{T_h}$ will always be less than 1.

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

Gibb's free energy is $\Delta G = \Delta(H - TS)$. Helmholtz energy is $\Delta A = \Delta(U - TS)$.

The Gibb's free energy is usually more useful to chemists than Helmholtz energy because it's easier to measure H through heat than U (internal energy).

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

Include at least one drawing.



$dn_I \rightarrow$

$\Delta T, \Delta P = 0$

System is setup so that

$\mu_I^I > \mu_I^{II}$

Region I loses molecules

$$dG = -\mu_I^I dn_I + \mu_I^{II} dn_I = (\mu_I^{II} - \mu_I^I) dn_I < 0$$

Always negative

Region II gains molecules

Gains molecules

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

The natural direction of change dictated by chemical potential from high to low. Every chemical species are trying to lower its chemical potential as much as possible. This relates to the gravitational plot.



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

$$\Delta S_{\text{mixing}} = - \left(\frac{\partial \Delta G_{\text{mixing}}}{\partial T} \right)_P = -nR \sum_i X_i \ln X_i$$

$$\Delta G_{\text{mixing}} = nRT \sum_i X_i \ln X_i$$

$$X_i < 1 \rightarrow \ln X_i < 0 \rightarrow \Delta G_{\text{mixing}} < 0$$

So gasses will always mix.

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

$K = e^{-\frac{\Delta G}{RT}} \rightarrow$ More reactants would be formed because the larger the $\Delta G_{\text{rxn}}^\circ$ value the smaller the K value. The reaction wouldn't be spontaneous.

$$K = e^{-\frac{100000}{(8.314)(298.15K)}} = 2.02 \times 10^{-18}$$

Extra Credit (5 pts)

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

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

$$\varepsilon = 1 - \frac{|q_{cd}|}{|q_{ab}|} < 1 \text{ because } |q_{ab}| > |q_{cd}|, q_{ab} > 0, \text{ and } q_{cd} < 0.$$

→ The efficiency equation of the reversible Carnot engine defines the ratio of the work output to the heat withdrawn from the hot reservoir. The equation which we derived in class shows that the efficiency of a heat engine operating in a reversible Carnot cycle is always less than one. These conclusions led to the formation of the second law of thermodynamics: where 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.