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1)

$$a) \Delta G_{rxn}^{\circ} = (-133 \text{ kJ/mol} + -394 \text{ kJ/mol}) - (-463 \text{ kJ/mol}) = -64 \text{ kJ/mol}$$

This reaction is spontaneous because ΔG is negative.

$$b) K_p = e^{\frac{-\Delta G^{\circ}}{RT}} = \exp(64 \text{ kJ/mol} / (10.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \cdot 80.0 \text{ K})) = 6.15 \times 10^4$$

c) Lowering temperature would cause the reaction to favor the products because decreasing T increases $-\Delta G^{\circ}/RT$, which increases K_p .

2)

$$a) A = U - TS \quad dA = dU - TdS - SdT \quad dU = TdS - PdV$$
$$dA = TdS - TdS - SdT - PdV$$

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

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

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T} \left(\frac{\partial V}{\partial T}\right)_P = \frac{\beta}{\kappa}$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{\kappa}$$

$$\frac{1}{n} \left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{n\kappa} \rightarrow \left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{n\kappa}$$

b) Because β , κ , and n are all positive, molar entropy must increase with increasing volume.

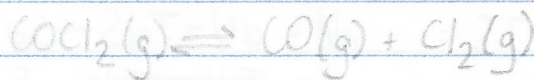
$$c) \mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

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

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

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

d)



$$\boxed{\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = \left(\frac{\partial V}{\partial n_{\text{COCl}_2}} \right)_{T, P, n_{j \neq i}} = \frac{RT}{P} = \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}}}$$

$$V = \frac{(n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2})RT}{P} = \frac{n_{\text{COCl}_2}RT}{P} + \frac{n_{\text{CO}}RT}{P} + \frac{n_{\text{Cl}_2}RT}{P}$$

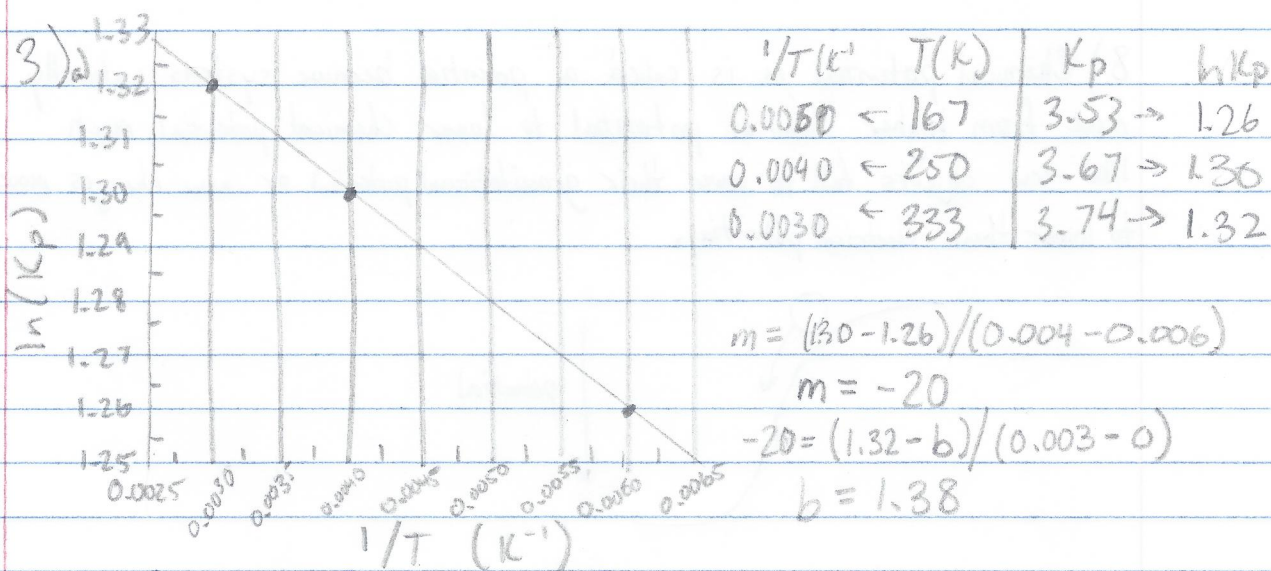
$$\left(\frac{\partial V}{\partial n_{\text{COCl}_2}} \right) = \frac{RT}{P}$$

The chemical potential would increase with increasing pressure.

$$e) \left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right) = \frac{RT}{P} \rightarrow \int_{P^0}^P d\mu_{\text{COCl}_2} = \int_{P^0}^P \frac{RT}{P} dP$$

$$\mu_{\text{COCl}_2}(P) - \mu_{\text{COCl}_2}(P^0) = RT \ln \frac{P}{P^0}$$

$$\mu_{\text{COCl}_2}(P) = \mu_{\text{COCl}_2}^0 + RT \ln \frac{P}{P^0}$$



b) $\ln K = \frac{-\Delta H}{R} \left(\frac{1}{T} \right) + \frac{\Delta S}{R}$

$\frac{-\Delta H}{R} = -20$
 $\Delta H = 166 \text{ J/mol}$

$\Delta G^\circ = 166 \text{ J/mol} - 298 \text{ K} (11.5 \text{ J/mol}\cdot\text{K})$

$\Delta G^\circ = -3.26 \text{ kJ/mol}$

$\frac{\Delta S}{R} = 1.38 \Rightarrow \Delta S = 11.5 \text{ J/mol}\cdot\text{K}$

The reaction is spontaneous because $\Delta G^\circ < 0$.

c) The reaction is entropically driven because it is endothermic, so it cannot be driven by enthalpy.

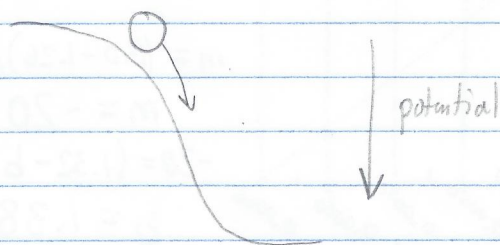
4) The entropy of an isolated system must always increase.

5) The entropy of a pure substance at 0K is 0. This makes entropy different from energy and enthalpy in that it has an absolute zero.

6) We cannot build perpetual motion machines because heat cannot be converted to work with 100% efficiency.

7) Gibbs free energy is more useful to chemists because it describes spontaneous processes if $\Delta G < 0$ in constant-pressure conditions instead of constant-volume conditions as Helmholtz energy does.

8) Chemical potential μ is called a potential because systems naturally move from higher chemical potential to lower chemical potential, much like how objects fall to lower their gravitational potential or how charges move to lower their electrical potential.



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

9) Mixing molecules in an ideal gas is spontaneous because:

State i: All gasses are separate.

$$G_i = G_A + G_B + G_C + \dots = n_A G_{m,A} + n_B G_{m,B} + n_C G_{m,C} + \dots$$

State f: All gasses are mixed

$$\begin{aligned} G_f &= n_A (G_{m,A} + RT \ln \chi_A) + n_B (G_{m,B} + RT \ln \chi_B) + \dots \\ &= n_A G_{m,A} + n_B G_{m,B} + \dots + n_A RT \ln \chi_A + n_B RT \ln \chi_B + \dots \end{aligned}$$

$$G_f - G_i = \Delta G = n_A RT \ln \chi_A + n_B RT \ln \chi_B + n_C RT \ln \chi_C + \dots$$

$$= RT \sum_i n_i \ln \chi_i = n RT \sum_i \chi_i \ln \chi_i$$

$$\chi_i \in [0, 1] \rightarrow \ln \chi_i < 0 \rightarrow \Delta G < 0$$

\therefore Mixing is spontaneous

10) If $\Delta G_r^\circ > 0$, then $K_p < 1$ because $K_p = e^{\frac{-\Delta G^\circ}{RT}}$. Because the system is at equilibrium, we have

$$K = \frac{\left(\frac{P_A}{P^\circ}\right)^\alpha \left(\frac{P_B}{P^\circ}\right)^\beta \dots}{\left(\frac{P_C}{P^\circ}\right)^\gamma \left(\frac{P_D}{P^\circ}\right)^\delta \dots} \quad \text{for the reaction}$$
$$\gamma C + \delta D + \dots \rightleftharpoons \alpha A + \beta B + \dots$$

Therefore, if $K_p < 1$, there will be more reactants than products.

Extra Credit:

My favorite equation from the semester so far is the Second Law of Thermodynamics, $\Delta S \geq 0$ for an isolated system. It is extremely useful in determining spontaneity and can be used with other equations to relate types of energy and other natural variables to it.

The variable was derived from inspecting a cycle and did not require any theory to find. This implies that many relationships and useful metrics do not need to be understood completely to be useful to people.