1 a.) $\Delta G_{rxn}^{\circ} = (\Delta_f G(25°C)_{CH_3CHO} + \Delta_f G(25°C)_{CO_2}) - (\Delta_f G(25°C)_{CH_3COOH})$

$= (-133 \frac{kJ}{mol} + (-394 \frac{kJ}{mol})) - (-463 \frac{kJ}{mol})$

$= -64 \frac{kJ}{mol}$

The reaction is spontaneous under standard state conditions because ΔG_{rxn} is negative.

b.) $\Delta H_{rxn}^{\circ} = (-166 \frac{kJ}{mol} + (-394 \frac{kJ}{mol})) - (-584 \frac{kJ}{mol}) = 24 \frac{kJ}{mol}$

$\Delta G_{rxn}^{\circ} = -64 \frac{kJ}{mol}$

$\ln K_p(T_f) = -\frac{\Delta G_{rxn}}{RT} - \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_f} - \frac{1}{298.15 K}\right)$

$\ln K_p(80.0K) = -\frac{-64 \times 10^3 \frac{J}{mol}}{8.314 \frac{J}{kmol} \times 298.15 K} - \frac{24 \times 10^3 \frac{J}{mol}}{8.314 \frac{J}{kmol}}\left(\frac{1}{80.0K} - \frac{1}{298.15K}\right)$

$\ln K_p(80.0K) = -0.58 \qquad K_p = e^{-0.58} = 0.56$

c.) At lower temperatures, the reaction favors the reactants because $K_p < 1$.

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

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

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

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{B}{k} \text{ so } \left(\frac{\partial S}{\partial V}\right)_T = \frac{B}{k}$

$\left(\frac{1}{n}\right)\left(\frac{\partial S}{\partial V}\right)_T = \frac{B}{k}\left(\frac{1}{n}\right) \quad \therefore \left(\frac{\partial S_m}{\partial V}\right)_T = \frac{B}{nk}$

b) The molar entropy increases when volume increases.

c) $G = H - TS \qquad dG = -SdT + VdP \qquad -S = \left(\frac{\partial G}{\partial T}\right)_P$

$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad dG = \left(\frac{\partial G}{\partial T}\right)dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad \nu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$

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

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

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

d)
$$\left(\frac{\partial N_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}} = \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T,P,n_{CO},n_{Cl_2}}$$

$$PV = nRT$$
$$V = \frac{nRT}{P}$$

$$= \left(\frac{\partial \frac{nRT}{P}}{\partial n_{COCl_2}}\right)_{T,P,n_{CO},n_{Cl_2}} = \left(\frac{RT}{P}\right)\left(\frac{\partial n_{COCl_2} + \partial n_{CO} + \partial n_{Cl_2}}{\partial n_{COCl_2}}\right)$$

$$= \left(\frac{RT}{P}\right)\left(\frac{\partial n_{COCl_2}}{\partial n_{COCl_2}} + \frac{\partial n_{CO}}{\partial n_{COCl_2}} + \frac{\partial n_{Cl_2}}{\partial n_{COCl_2}}\right)$$

• $dn_{COCl_2} = -dn_{CO}, \quad dn_{COCl_2} = -dn_{Cl_2}$

$$= \left(\frac{RT}{P}\right)\left(1 + (-1) + (-1)\right) = \left(\frac{RT}{P}\right)(-1)$$

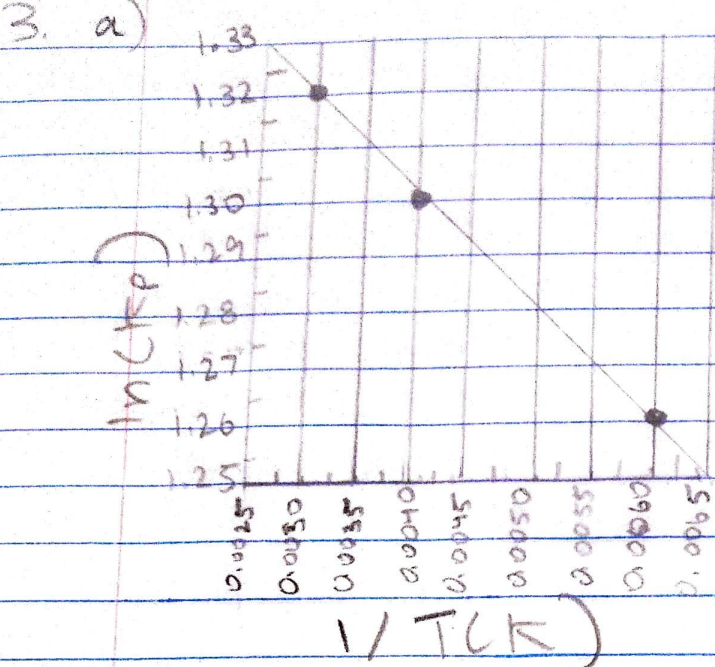$$\therefore \left(\frac{\partial N_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}} = -\frac{RT}{P}$$

e)
$$\left(\frac{\partial N_{COCl_2}}{\partial P}\right)_{T,n_{CO},n_{Cl_2}} = \frac{-RT}{P}$$

$$\left(\partial N_{COCl_2}\right) = \left(\frac{-RT}{P}\right)\left(\partial P\right)$$

$$\int_{P^0}^{P} \partial N_{COCl_2} = \int_{P^0}^{P} \frac{-RT}{P} dP$$

$$N_{COCl_2}(P) - N_{COCl_2}(P^0) = -RT \ln(P/P^0)$$

$$N_{COCl_2}(P) = -RT \ln(P/P^0) + N_{COCl_2}(P^0)$$

3. a)

T(K)	Kp
167	3.53
250	3.67
333	3.74

1/T(K)	ln(Kp)
0.006	1.26
0.004	1.30
0.003	1.32

b)
$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

slope $= -\Delta H / R$

y intercept $\Delta S / R$

$$\text{slope} = \frac{1.32 - 1.30}{.003 - .004} = \frac{.02}{-.001} = -20$$

$\Delta H = -R \times$ slope

$\Delta S = R \times$ intercept

$1.32 = -20(.003) + b$ $b = 1.38$

$\Delta H = -8.314 \times -20 = 166.28 \frac{J}{mol}$

$\Delta S = 8.314 \times 1.38 = 11.47 \frac{J}{mol\cdot K}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 166.28 \frac{J}{mol} - (298.15 K)(11.47 \frac{J}{mol\cdot K})$

$= -3353.5$ J/mol

The reaction is spontaneous because ΔG_r° is negative.

c) The reaction is entropically driven because both ΔH and ΔS is positive.

4. The second law of thermodynamics states that it is impossible for a system to have a cyclic process where the heat conversion to work is at 100% efficiency. It also

states that for an irreversible process in an isolated system, $\Delta S > 0$ for a spontaneous process, $\Delta S < 0$ for a nonspontaneous direction, and $\Delta S = 0$ for a reversible process.

5. The third law of thermodynamics states that the entropy of a pure, perfectly crystalline substance is 0 at 0 kelvin. This makes entropy different than energy or enthalpy. Since the entropy of a substance is compared to a perfect crystalline substance at 0 kelvin, it makes entropy have absolute values. However enthalpy is compared as relative since there is no absolute zero.

6. We can't build a perpetual perfect machine because it would violate the first or second law of thermodynamics. The perpetual perfect machine would be able to produce an unlimited amount of work and have 100% efficiency for its heat conversion to work.

7. Gibbs free energy is more useful to chemists than Helmholtz energy. This is because they usually carry out reactions under constant pressure, rather than constant volume conditions.

8. The chemical potential is defined as $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq n_i}}$. It is also defined in terms of an infinitesimal change in the amount of dn_i for species i, and is the change in Gibbs energy per mole of substance i added at constant concentration.

higher region
lower region
(gravitational potential)
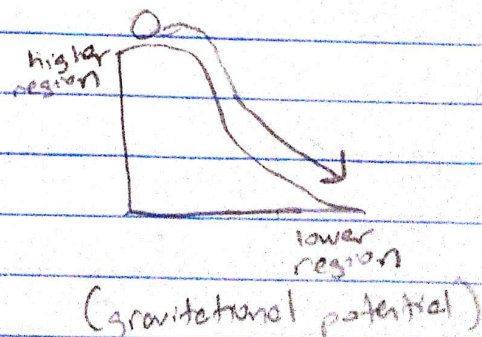
It's called a potential because there's a flow of material from a higher region to a lower region, analogous to a flow of mass for gravitational potential.

9. The mixing of different types of molecules in an ideal gas is spontaneous.

$$\Delta G_{mixing} = nRT \sum x_i \ln x_i \qquad x_i < 1 \quad \ln x_i < 0$$

$\Delta G_{mixing} < 0$ so mixing is a spontaneous process.

10. There will be more reactants formed in this reaction.

$$\Delta G^{\circ}_{rxn} = -RT \ln k_p \qquad k_p = e^{(-\Delta G_{rxn})/RT}$$

If $\Delta G^{\circ}_{rxn} > 0$, $k_p < 1$ and more reactants form.

My favorite equation from this semester was $\Delta G = \Delta H - T\Delta S$. This formula is able to show whether the chemical transformation is spontaneous or not spontaneous based on if ΔH and ΔS are either positive or negative. It also shows if the reaction is at equilibrium if ΔG is equal to 0.

I worked individually.
I did not ask for help.