

CHE152
Chapter 20 - Entropy, Free Energy and Equilibrium

1. Predict the entropy change in each process below.

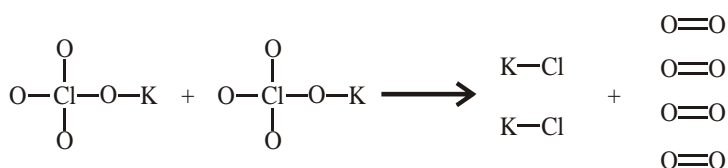
- (a) $2 \text{Fe}_2\text{O}_3 (\text{s}) \rightarrow 4 \text{Fe} (\text{s}) + 3 \text{O}_2 (\text{g})$ (ans. $\Delta S > 0$)
- (b) $\text{H}_2 (\text{g}) + \text{Cl}_2 (\text{g}) \rightarrow 2 \text{HCl} (\text{g})$ (ans. $\Delta S \approx 0$)
- (c) $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightarrow 2 \text{HI} (\text{s})$ (ans. $\Delta S < 0$)
- (d) $\text{NaCl} (\text{s}) \rightarrow \text{NaCl} (\text{aq})$ (ans. $\Delta S > 0$)
- (e) $2 \text{KClO}_4 (\text{s}) \rightarrow 2 \text{KCl} (\text{s}) + 4 \text{O}_2 (\text{g})$ (ans. $\Delta S > 0$)

2. Calculate the entropy (ΔS) for each reaction below.

- (a) $\text{C}_2\text{H}_5\text{OH} (\text{l}) + 3 \text{O}_2 (\text{g}) \rightarrow 2 \text{CO}_2 (\text{g}) + 3 \text{H}_2\text{O} (\text{l})$ (ans. -138.9 J/mol K)
- (b) $\text{H}_2 (\text{g}) + \text{Cl}_2 (\text{g}) \rightarrow 2 \text{HCl} (\text{g})$ (ans. 20.066 J/mol K)

3. Predict the conditions under which the following processes will be spontaneous.

- (a) $2 \text{Fe}_2\text{O}_3 (\text{s}) \rightarrow 4 \text{Fe} (\text{s}) + 3 \text{O}_2 (\text{g}) \Delta H = 2236.8 \text{ kJ/mol}$ (ans. spon. at high T)
- (b) $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightarrow 2 \text{HI} (\text{s}) \Delta H = 52.96 \text{ kJ/mol}$ (ans. not spon. at all T)
- (c) $2 \text{C}_2\text{H}_2 (\text{g}) + 5 \text{O}_2 (\text{g}) \rightarrow 4 \text{CO}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{l}) \Delta H = -2372.43 \text{ kJ/mol}$
(ans. spon. at low T)
- (d) $2 \text{KClO}_4 (\text{s}) \rightarrow 2 \text{KCl} (\text{s}) + 4 \text{O}_2 (\text{g})$ (ans. spon at all T)

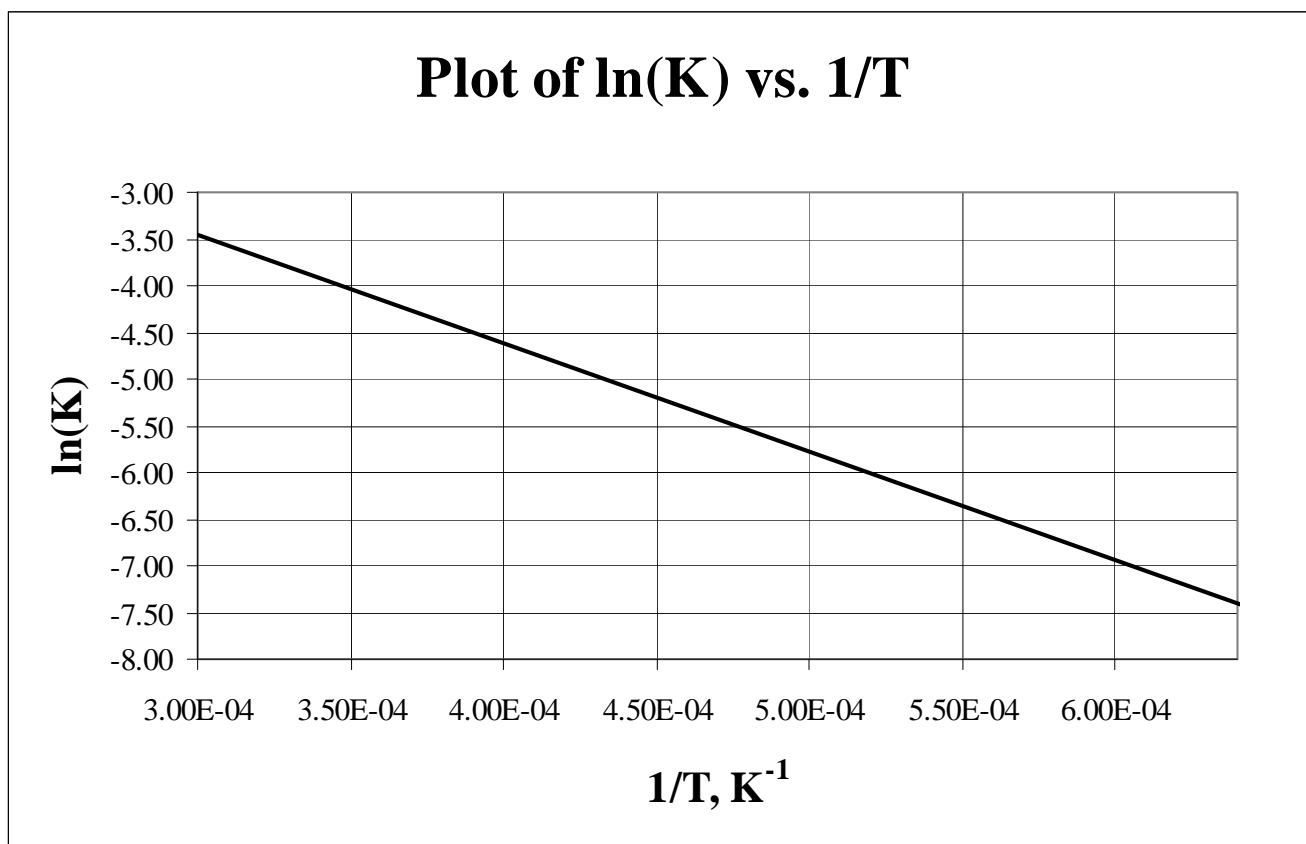


O-Cl 218 kJ/mol
K-Cl 423 kJ/mol
O=O 498 kJ/mol

4. Calculate ΔG_{298}° for the following reactions.

- (a) $2 \text{C}_2\text{H}_2 (\text{g}) + 5 \text{O}_2 \rightarrow 4 \text{CO}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{l})$ (ans. -2486.1 kJ/mol)
- (b) $2 \text{KClO}_4 (\text{s}) \rightarrow 2 \text{KCl} (\text{s}) + 4 \text{O}_2 (\text{g})$ (ans. -212.10 kJ/mol)
- (c) $2 \text{Cl}_2 (\text{g}) + 2 \text{NO} (\text{g}) \rightarrow 2 \text{NOCl} (\text{g})$ (ans. -40.94 kJ/mol)

5. If the boiling point of H_2O_2 is 150.2°C , what is $\Delta S_{\text{vap}}^\circ$ for hydrogen peroxide? What does this say about the polarity of H_2O_2 ?
(ans. 121.3 J/mol K ; polar liquid)
6. If the boiling point of CH_3OH is 64.7°C , what is $\Delta S_{\text{vap}}^\circ$ for methanol? What does this say about the polarity of CH_3OH ?
(ans. 112.5 J/mol K ; polar liquid)
7. Calculate ΔG at 625.0 K for the following process,
 $\text{H}_2\text{O}_2 (\text{l}, 0.2500 \text{ atm}) \rightleftharpoons \text{H}_2\text{O}_2 (\text{g}, 0.2500 \text{ atm})$ (ans. -32.73 kJ/mol)
8. Calculate ΔG at 375.0 K for the following process,
 $\text{CH}_3\text{OH} (\text{l}, 0.5000 \text{ atm}) \rightleftharpoons \text{CH}_3\text{OH} (\text{g}, 0.5000 \text{ atm})$ (ans. -6.50 kJ/mol)
9. Using the expression for ΔG determine the direction of the following reactions:
- (a) $\text{PCl}_3 (\text{g}, 0.00150 \text{ atm}) + \text{Cl}_2 (\text{g}, 0.0000250 \text{ atm}) \rightleftharpoons \text{PCl}_5 (\text{g}, 0.7500 \text{ atm})$
(ans. -48 kJ/mol)
- (b) $2 \text{N}_2\text{O} (\text{g}, 0.325 \text{ atm}) + 3 \text{O}_2 (\text{g}, 0.125 \text{ atm}) \rightleftharpoons 2 \text{N}_2\text{O}_4 (\text{g}, 0.0250 \text{ atm})$
(ans. -9.9 kJ/mol)



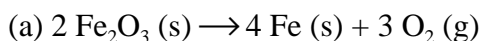
10. Determine ΔH° and ΔS° for the reaction plot above.

(ans. $\Delta H^\circ = 97.3 \text{ kJ/mol}$ $\Delta S^\circ = 0.4_2 \text{ J/mol K}$)

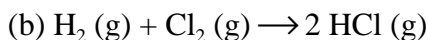
11. K_p for a reaction at 1500.0 K is 2.856. What is K_p at 2500.0 K? $\Delta H^\circ = 3.25 \times 10^2$ kJ/mol
(ans. 9.610×10^4)

12. K_p for a reaction at 750.0 K is 0.750. At what temperature is K_p 1.250?
 $\Delta H^\circ = 1.75 \times 10^2$ kJ/mol
(ans. 764 K)

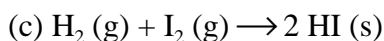
1. Predict the entropy change in each process below.



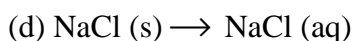
$\Delta S > 0$ (more disorder). Going from 2 moles of solid to 4 moles of a simpler solid and 3 moles of gas yields more disorder.



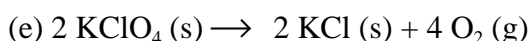
$\Delta S \approx 0$. 2 moles of gas going to 2 moles of gas. Note that the actual calculation of ΔS may not be zero, but should be a very small value (either positive or negative).



$\Delta S < 0$ (more order). Going from 2 moles of gas to 2 moles of solid yields more order.

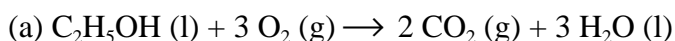


$\Delta S > 0$ (more disorder). Going from a solid state (s) to a solution (aq) yields more disorder.



$\Delta S > 0$ (more disorder). Going from 2 moles of solid to two moles of solid and 4 moles of gas yields more disorder.

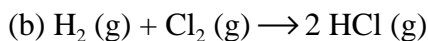
2. Calculate the entropy (ΔS) for each reaction below.



$$\Delta S^\circ = [2 \times S^\circ(\text{CO}_2 (\text{g})) + 3 \times S^\circ(\text{H}_2\text{O} (\text{l}))] - [S^\circ(\text{C}_2\text{H}_5\text{OH} (\text{l})) + 3 \times S^\circ(\text{O}_2 (\text{g}))]$$

$$\Delta S^\circ = [2 \times (213.74 \text{ J/mol K}) + 3 \times (69.91 \text{ J/mol K})] - [160.7 \text{ J/mol K} + 3 \times (205.138 \text{ J/mol K})]$$

$$\Delta S^\circ = -138.9 \text{ J/mol K}$$



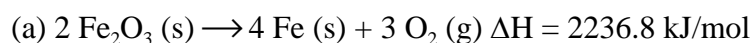
$$\Delta S^\circ = [2 \times S^\circ(\text{HCl} (\text{g}))] - [S^\circ(\text{H}_2 (\text{g})) + S^\circ(\text{Cl}_2 (\text{g}))]$$

$$\Delta S^\circ = [2 \times (186.908 \text{ J/mol K})] - [130.684 \text{ J/mol K} + 223.066 \text{ J/mol K}]$$

$$\Delta S^\circ = 20.066 \text{ J/mol K}$$

3. Predict the conditions under which the following processes will be spontaneous.

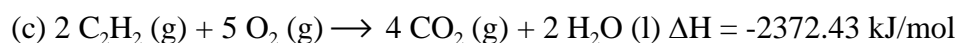
For a process to be spontaneous $\Delta G < 0$. Equation: $\Delta G = \Delta H - T \Delta S$.



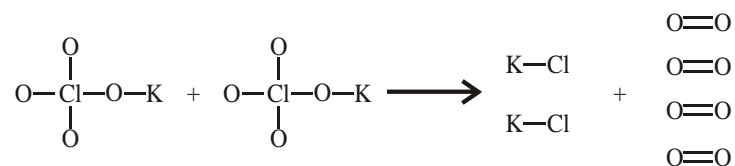
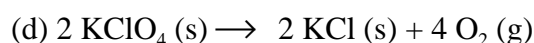
$\Delta H > 0$ and $\Delta S > 0$; ΔG will be less than 0 at high temperature.



$\Delta H > 0$ and $\Delta S < 0$; ΔG will always be greater than 0.



$\Delta H < 0$ and $\Delta S < 0$; ΔG will be less than 0 at low temperature.



O-Cl	218 kJ/mol
K-Cl	423 kJ/mol
O=O	498 kJ/mol
K-O	278 kJ/mol

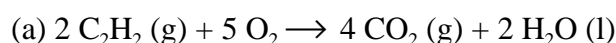
$$\Delta H = [4 \times \text{O-Cl} + 2 \times \text{O-K}] - [2 \times \text{K-Cl} + 4 \times \text{O=O}]$$

$$\Delta H = [4 \times (218 \text{ kJ/mol}) + 2 \times (278 \text{ kJ/mol})] - [2 \times (423 \text{ kJ/mol}) + 4 \times (498 \text{ kJ/mol})]$$

$$\Delta H = -1410 \text{ kJ/mol}$$

$\Delta H < 0$ and $\Delta S > 0$; ΔG will be less than 0 at all temperatures.

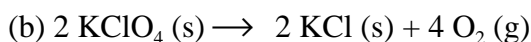
4. Calculate ΔG_{298}° for the following reactions.



$$\Delta G_{298}^\circ = [4 \times \Delta G^\circ(\text{CO}_2 (\text{g})) + 2 \times \Delta G^\circ(\text{H}_2\text{O} (\text{l}))] - [2 \times \Delta G^\circ(\text{C}_2\text{H}_2 (\text{g})) + 5 \times \Delta G^\circ(\text{O}_2 (\text{g}))]$$

$$\Delta G_{298}^\circ = [4 \times (-398.359 \text{ J/mol}) + 2 \times (-237.129 \text{ J/mol})] - [2 \times (209.2 \text{ J/mol}) + 5 \times (0 \text{ kJ/mol})]$$

$$\Delta G_{298}^\circ = -2486.1 \text{ kJ/mol}$$



$$\Delta G_{298}^{\circ} = [2 \times \Delta G^{\circ}(\text{KCl} (s)) + 4 \times \Delta G^{\circ}(\text{O}_2)] - [2 \times \Delta G^{\circ}(\text{KClO}_4 (s))]$$

$$\Delta G_{298}^{\circ} = [2 \times (-409.14 \text{ kJ/mol}) + 4 \times (0 \text{ kJ/mol})] - [2 \times (-303.09 \text{ kJ/mol})]$$

$$\Delta G_{298}^{\circ} = -212.10 \text{ kJ/mol}$$



$$\Delta G_{298}^{\circ} = [2 \times \Delta G^{\circ}(\text{NOCl})] - [2 \times \Delta G^{\circ}(\text{Cl}_2) + 2 \times \Delta G^{\circ}(\text{NO})]$$

$$\Delta G_{298}^{\circ} = [2 \times (66.08 \text{ kJ/mol})] - [2 \times (0 \text{ kJ/mol}) + 2 \times (86.55 \text{ kJ/mol})]$$

$$\Delta G_{298}^{\circ} = -40.94 \text{ kJ/mol}$$

5. If the boiling point of H_2O_2 is 150.2°C , what is $\Delta S_{\text{vap}}^{\circ}$ for hydrogen peroxide? What does this say about the polarity of H_2O_2 ?

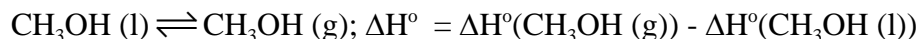


$$\Delta H^{\circ} = -136.31 \text{ kJ/mol} - (-187.78 \text{ kJ/mol}) = 51.41 \text{ kJ/mol}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ}}{T} = \frac{51.47 \text{ kJ/mol}}{423.3_5 \text{ K}} = \frac{0.1216 \text{ kJ}}{\text{mol K}} = \frac{121.3 \text{ J}}{\text{mol K}}$$

Since ΔS° is greater than $88 \text{ J mol}^{-1} \text{ K}^{-1}$ the order (entropy) of H_2O_2 must be high. This indicates that H_2O_2 is polar.

6. If the boiling point of CH_3OH is 64.7°C , what is $\Delta S_{\text{vap}}^{\circ}$ for methanol? What does this say about the polarity of CH_3OH ?

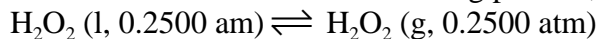


$$\Delta H^{\circ} = -200.66 \text{ kJ/mol} - (-238.66 \text{ kJ/mol}) = 38.00 \text{ kJ/mol}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ}}{T} = \frac{38.00 \text{ kJ/mol}}{337.8_5 \text{ K}} = \frac{0.1125 \text{ kJ}}{\text{mol K}} = \frac{112.5 \text{ J}}{\text{mol K}}$$

Since ΔS° is greater than $88 \text{ J mol}^{-1} \text{ K}^{-1}$ the order (entropy) of CH_3OH must be high. This indicates that CH_3OH is polar.

7. Calculate ΔG at 625.0 K for the following process,



$$\Delta H^\circ = \Delta H^\circ(\text{H}_2\text{O}_2 (\text{g})) - \Delta H^\circ(\text{H}_2\text{O}_2 (\text{l}))$$

$$\Delta H^\circ = -136.31 \text{ kJ/mol} - (-187.78 \text{ kJ/mol}) = 51.41 \text{ kJ/mol}$$

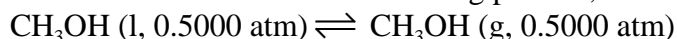
$$\Delta S^\circ = S^\circ(\text{H}_2\text{O}_2 (\text{g})) - S^\circ(\text{H}_2\text{O}_2 (\text{l}))$$

$$\Delta S^\circ = 232.7 \text{ J/mol K} - 109.6 \text{ J/mol K} = 123.1 \text{ J/mol K} = 0.1231 \text{ kJ/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 51.41 \text{ kJ/mol} - 625.0 \text{ K} \times 0.1231 \text{ kJ/mol K} = -25.53 \text{ kJ/mol}$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln(Q) = -25.53 \text{ kJ/mol} + 0.008314472 \text{ kJ/mol K} \times 625.0 \text{ K} \times \ln(0.2500) \\ &= -25.53 \text{ kJ/mol} - 7.2039 \text{ kJ/mol} = -32.73 \text{ kJ/mol} \end{aligned}$$

8. Calculate ΔG at 375.0 K for the following process,



$$\Delta H^\circ = \Delta H^\circ(\text{CH}_3\text{OH} (\text{g})) - \Delta H^\circ(\text{CH}_3\text{OH} (\text{l}))$$

$$\Delta H^\circ = -200.66 \text{ kJ/mol} - (-238.66 \text{ kJ/mol}) = 38.00 \text{ kJ/mol}$$

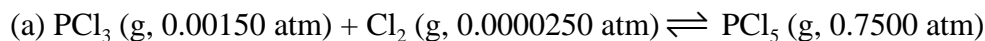
$$\Delta S^\circ = S^\circ(\text{CH}_3\text{OH} (\text{g})) - S^\circ(\text{CH}_3\text{OH} (\text{l}))$$

$$\Delta S^\circ = 282.7 \text{ J/mol K} - 126.8 \text{ J/mol K} = 112.9 \text{ J/mol K} = 0.1129 \text{ kJ/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 38.00 \text{ kJ/mol} - 375.0 \text{ K} \times 0.1129 \text{ kJ/mol K} = -4.34 \text{ kJ/mol}$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln(Q) = -4.34 \text{ kJ/mol} + 0.008314472 \text{ kJ/mol K} \times 375.0 \text{ K} \times \ln(0.5000) \\ &= -4.34 \text{ kJ/mol} - 2.161 \text{ kJ/mol} = -6.50 \text{ kJ/mol} \end{aligned}$$

9. Using the expression for ΔG determine the direction of the following reactions at 298.15 K:



$$\Delta G_{298}^\circ = \Delta G^\circ(\text{PCl}_5 (\text{g})) - [\Delta G^\circ(\text{PCl}_3 (\text{g})) + \Delta G^\circ(\text{Cl}_2 (\text{g}))]$$

$$\Delta G_{298}^\circ = -305 \text{ kJ/mol} - [-267.8 \text{ kJ/mol} + 0 \text{ kJ/mol}] = -37.2 \text{ kJ/mol}$$

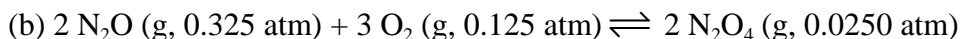
$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = -37.2 \text{ kJ/mol} + \frac{0.008314472 \text{ J}}{\text{mol K}} \times 298.15 \text{ K} \times \ln\left(\frac{(0.7500)}{(0.0000250 \times 0.00150)}\right)$$

$$\Delta G = -37.2 \text{ kJ/mol} + \frac{0.008314472 \text{ J}}{\text{mol K}} \times 298.15 \text{ K} \times -16.8_{112}$$

$$\Delta G = -37.2 \text{ kJ/mol} - 14.3_{32} \text{ kJ/mol} = -52 \text{ kJ/mol}$$

Since $\Delta G < 0$ the reaction will go to the right.



$$\Delta G_{298}^{\circ} = 2 \times \Delta G^{\circ}(\text{N}_2\text{O}_4 (\text{g})) - [2 \times \Delta G^{\circ}(\text{N}_2\text{O} (\text{g})) + 3 \Delta G^{\circ}(\text{O}_2 (\text{g}))]$$

$$\Delta G_{298}^{\circ} = 2(97.89 \text{ kJ/mol}) - [2(104.2 \text{ kJ/mol}) + 3(0 \text{ kJ/mol})] = -12.6_2 \text{ kJ/mol}$$

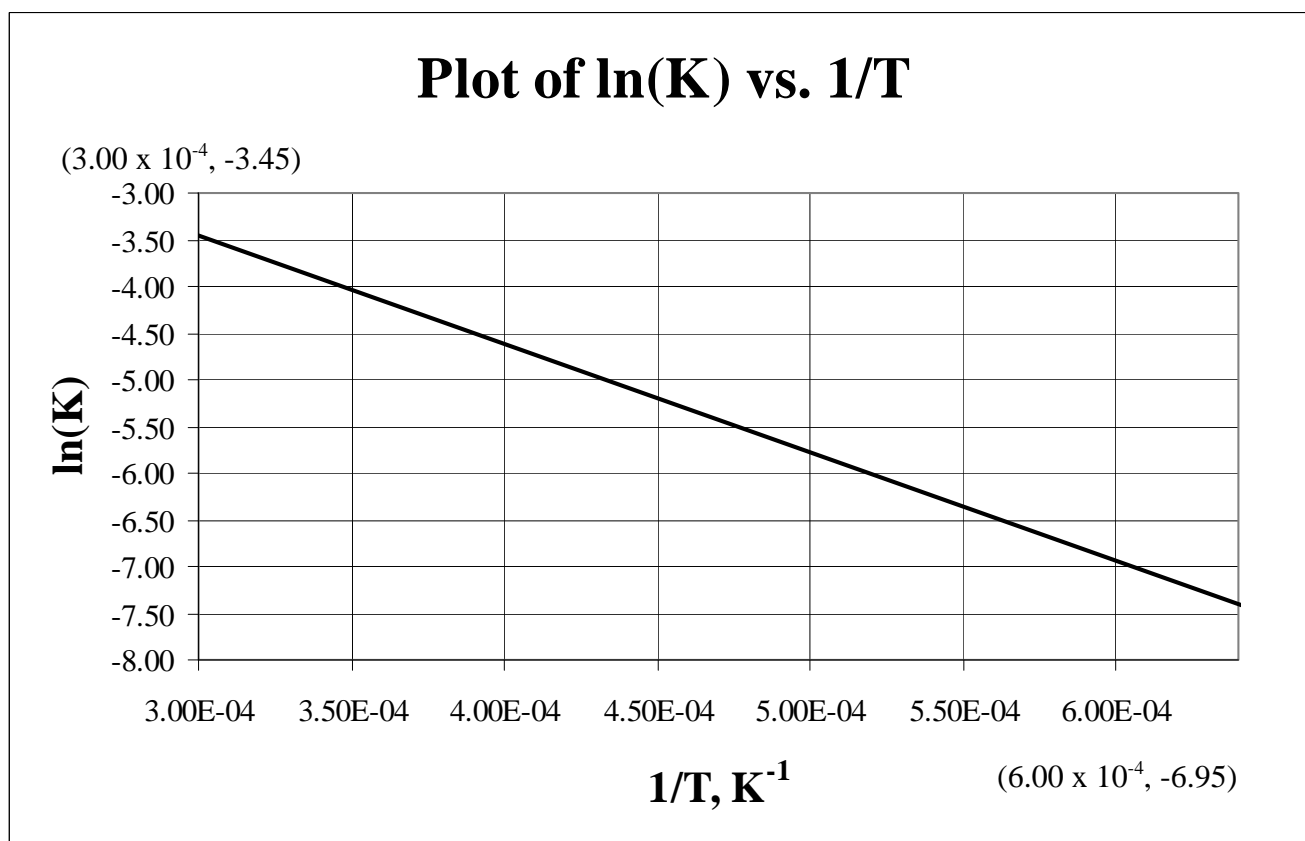
$$\Delta G = \Delta G^{\circ} + RT \ln(Q)$$

$$\Delta G = -12.6_2 \text{ kJ/mol} + \frac{0.008314472 \text{ J}}{\text{mol K}} \times 298.15 \text{ K} \times \ln\left(\frac{(0.0250)^2}{(0.325)^2 (0.125)^3}\right)$$

$$\Delta G = -12.6_2 \text{ kJ/mol} + \frac{0.008314472 \text{ J}}{\text{mol K}} \times 298.15 \text{ K} \times 1.108$$

$$\Delta G = -12.6_2 \text{ kJ/mol} + 2.75 \text{ kJ/mol} = -9.9 \text{ kJ/mol}$$

Since $\Delta G < 0$ the reaction will go to the right.



10. Determine ΔH° and ΔS° for the reaction plot above.

$$m = \frac{(-6.95 - (-3.45))}{(6.00 \times 10^{-4} - 3.00 \times 10^{-4}) \text{ K}^{-1}} = -1.17 \times 10^4 \text{ K}$$

$$-6.95 = 1.17 \times 10^4 \text{ K} \times 6.00 \times 10^{-4} \text{ K}^{-1} + b; b = 0.05$$

$$\frac{-\Delta H^\circ}{R} = m; \frac{-\Delta H^\circ}{0.008314472 \text{ kJ/mol K}} = -1.17 \times 10^4 \text{ K}$$

$$\Delta H^\circ = 97.3 \text{ kJ/mol}$$

$$\frac{\Delta S^\circ}{R} = b; \frac{\Delta S^\circ}{8.314472 \text{ kJ/mol K}} = 0.05$$

$$\Delta S^\circ = 0.4_2 \text{ J/mol K}$$

$$\Delta H^\circ = \underline{\quad 97.3 \text{ kJ/mol} \quad} \quad \Delta S^\circ = \underline{\quad 0.4_2 \text{ J/mol K} \quad}$$

11. K_p for a reaction at 1500.0 K is 2.856. What is K_p at 2500.0 K? $\Delta H^\circ = 3.25 \times 10^3$ kJ/mol

$$\ln\left(\frac{2.856}{K_1}\right) = \frac{3.25 \times 10^2 \text{ kJ/mol}}{0.008314472 \text{ kJ/mol K}} \left(\frac{1}{2500.0 \text{ K}} - \frac{1}{1500.0 \text{ K}} \right)$$

$$\ln\left(\frac{2.856}{K_1}\right) = 3.91 \times 10^4 \text{ K} \left(0.00040000 \text{ K}^{-1} - 0.00066667 \text{ K}^{-1} \right)$$

$$\ln\left(\frac{2.856}{K_1}\right) = -10.4; \frac{2.856}{K_1} = 2.972 \times 10^{-5}; 9.610 \times 10^4$$

12. K_p for a reaction at 750.0 K is 0.750. At what temperature is K_p 1.250? $\Delta H^\circ = 1.75 \times 10^2$ kJ/mol

$$\ln\left(\frac{0.750}{1.250}\right) = \frac{1.75 \times 10^2 \text{ kJ/mol}}{0.008314472 \text{ kJ/mol K}} \left(\frac{1}{T} - \frac{1}{750.0 \text{ K}} \right)$$

$$-0.511 = 2.10 \times 10^4 \text{ K} \left(\frac{1}{T} - 0.001333 \text{ K}^{-1} \right)$$

$$-0.0000243 \text{ K}^{-1} = \frac{1}{T} - 0.001333 \text{ K}^{-1}$$

$$\frac{1}{T} = 0.00131 \text{ K}^{-1}; T = 764 \text{ K}$$