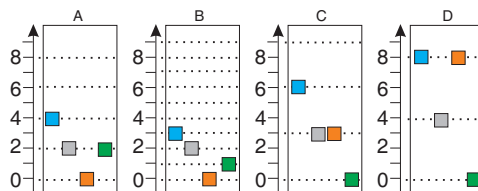# Chapter 4

Thermodynamics and Equilibrium

Refer to the following figures for Exercises 1-6. Each represents the energies of four molecules at a given instant, and the dotted lines represent the allowed energies. Assume constant spacing between levels to determine the energies of higher energy levels.

Use the letter 'U' for the energy unit.

1. **What are the energies of systems A and B? Which system is at the higher temperature?**

    $E_A = 4+2+0+2 = 8U$ $E_B = 3+2+0+1 = 6U$
    System A has the greater energy, so it is at the higher temperature.

3. **In how many ways can the energies of systems A and B be distributed? Which system has the greater entropy?**

    - System A has 8U of energy and A molecules have energy levels at 2, 4, 6, and 8U. The possible combinations that sum to 8U and the number of each are: one molecule with 8U {4}, One with 6U and one with 2U {12}, two molecules with 4U each {6}; one molecule with 4U and two with 2U each {12}, all four molecules with 2U each {1}. The total number of ways = 4 + 12 + 6 + 12 + 1 = 35.
    - System B has 6U of energy and B molecules have energy levels at 1, 2, 3, 4, 5, and 6U. The possible combinations that sum to 6U and the number of each are: one molecule with 6U {4}, One with 5U and one with 1U {12}, one molecule with 4U and one with 2U {12}; one molecule with 4U and two with 1U each {12}, two molecules with 3U each {6}; one molecule each with 3U, 2U, and 1U {20}; three molecules with 2U each {4}. The total number of ways = 4 + 12 + 12 + 12 + 6 + 20 + 4 = 70.
    - There are more ways to distribute the energy in System B, so it has the higher entropy. Note System A has more energy, but System B has the higher entropy because the energy levels are closer in System B.

5. **List the systems in order of increasing entropy at a temperature where they all had 12 U of energy.**

    The entropies of a group of systems at the same temperature increase as the spacing between their energy levels decreases. The energy levels are closest in System B, so it would have the highest energy at any given temperature.

7. **State the second law of thermodynamics.**

    The entropy of the universe must increase during a spontaneous process.

9. **What effect does the enthalpy change of a process have on the entropy of the universe in processes carried out at constant T and P?**

    The heat absorbed (or given off) by a system comes from (or enters) the surroundings. The heat flow causes an entropy in the surroundings: $\Delta S_{sur} = -\Delta H/T$, which impacts the entropy of the universe: $\Delta S_{univ} = \Delta S + \Delta S_{sur}$.

11. **Consider the reaction $H_2 + I_2 \rightarrow 2HI$ $\Delta G^o = 2.6$ kJ at 298 K. Criticize and correct the following statement: $\Delta G^o > 0$, so the reaction is not spontaneous and HI cannot be made from this reaction at 298 K. `**

    ΔG^o indicates the extent of the reaction, not the spontaneity. $\Delta G^o > 0$ means that K < 1, so the equilibrium concentration of HI will be less than at least one of the reactants, but it will not be zero.

13. **Explain why dissolving sugar in water always results in a homogeneous solution.**

    Dissolving sugar in water will result in a homogenous mixture because the water molecules have the highest entropy when they are farthest from each other.

15. **Indicate which member of each pair has the higher entropy and indicate the reason**

    a) **$PF_3(g)$ or $PF_5(g)$ at 75 ^{o}C**

    $PF_5(g)$ has higher entropy because it has more atoms and more degrees of freedom.

    b) **$I_2(s)$ or $I_2(g)$ at 300 K**

    $I_2(g)$ has higher entropy as entropy increases from solid to liquid to gas.

    c) **He(g) at 400 K or He(g) at 600 K**

    He(g) at 600K has higher entropy as entropy increases with increase in temperature.

    d) **A piece of tin or a piece of 60:40 solder (a solid solution that is 60% Pb and 40% Sn.**

    60:40 solder has higher entropy than a piece of tin as entropy decreases as perfection of crystal increases.

Thermodynamics and Equilibrium

17. What is an extensive process? What thermodynamic property indicates the extent of a reaction?

An Extensive Process is one which goes essentially to completion, i.e., a process in which K >> 1. The standard free energy change (ΔG°) indicates the extent of the reaction.

19. Indicate whether each of the following statements must be, can be, or cannot be true for a spontaneous endothermic reaction at constant pressure:

a) $\Delta H^\circ > 0$ This statement must be true because the reaction is endothermic.

b) $\Delta S_{univ} = 0$ This statement cannot be true because $\Delta S_{univ} > 0$ for a spontaneous process.

c) $\Delta G^\circ < 0$ This statement can be true, but it cannot be determined from the given information.

d) $\Delta G < 0$ Must be true because the reaction is spontaneous at constant T and P.

e) $\Delta S > 0$ Must be true. $\Delta G = \Delta H - T\Delta S$, so S must be positive 0 if $\Delta G < 0$ and $\Delta H > 0$.

f) $\Delta E_{univ} = 0$ Must be true; it is the first law of thermodynamics.

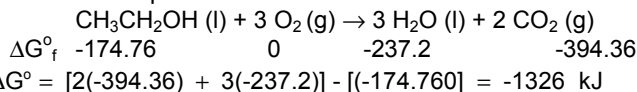**21. Indicate the sign of the entropy change for each of the following processes:**

a) **Increasing the temperature of a pot of water .**   Molecular motion (disorder) increases with thermal energy, S > 0.

b) **Condensing a gas**   The material becomes more ordered as it is condensed from a gas to a liquid; $\Delta S < 0$.

c) **Clearing a field and planting rows of corn**   This process results in more order; $\Delta S < 0$.

d) $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$ 3 moles of gas are produced per mole of solid that reacts; $\Delta S > 0$.

23. Use data in Appendix G to calculate the standard entropy change for

a) **the rusting of iron: $4\ Fe(s)\ +\ 3\ O_2(g)\ \rightarrow\ 2\ Fe_2O_3(s)$**

$\Delta S^\circ_{RXN} = 2 \times S^\circ(Fe_2O_3) - [4 \times S^\circ(Fe) + 3 \times S^\circ(O_2)]\ = 2(87.40) - [4(27.3) + 3(205.03)] = -549.5$ J/K

b) **the decomposition reaction: $CaCO_3(s)\ \rightarrow\ CaO(s)\ +\ CO_2(g)$**

$\Delta S^\circ_{RXN} =\ S^\circ(CO_2) + S^\circ(CaO) - S^\circ(CaCO_3)]\ = 38.2 + 213.6 - 92.9 = 158.9$ J/K

25. Gasohol is a mixture of ethanol (C_2H_5OH) and gasoline. Write the chemical equation for the combustion of ethanol and determine the maximum amount of work that can be obtained from the combustion of 1 gal of ethanol at 298 K and standard conditions. The density of ethanol is 0.789 g·mL^{-1}, and 1 gal is 3.79 L.

According to Equation 4.3, the maximum work done by a system = $-\Delta G$
The chemical equation for the combustion and the standard free energies are

$$CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightarrow 3\ H_2O\ (l) + 2\ CO_2\ (g)$$

ΔG°_f -174.76   0   -237.2   -394.36

$\Delta G^\circ =\ [2(-394.36)\ +\ 3(-237.2)] - [(-174.760]\ =\ -1326\ $ kJ

To calculate the free energy change, ΔG°, for 1 gallon of ethanol, convert to moles and multiply. The molecular weight of ethanol (C_2H_5OH) is 46.069 g mol^{-1}.

$$1\ \text{gal. } C_2H_5OH \times \frac{3.79\ \text{Liters}}{1\text{gallon}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{0.789\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{mol}}{46.069\ \text{g}} \times \frac{1326\ \text{kJ}}{\text{mol}} = 8.61 \times 10^4\ \text{kJ}$$

27. Determine the standard entropy of formation for each of the following substances at 298 K:

a) $H_2(g)$

$H_2\ (g)\ \rightarrow\ H_2\ (g);\ \ \Delta S^\circ = 0$; no change in products from reactants.

b) $H_2O(g)$

$H_2\ (g)$ + $^1/_2 O_2\ (g)$ $\rightarrow$ $H_2O\ (g)$
S° 130.57   205.03   188.7
$\Delta S^\circ = 188.7 - 1(130.57) - ^1/_2(205.03) = -44.4$ J/K for the above reaction, so $\Delta S^\circ_f = -44.4$ J·mol^{-1}·K^{-1}

c) $NH_3(g)$

$^1/_2N_2\ (g)$ + $^3/_2\ H_2\ (g)$ $\rightarrow$ $NH_3\ (g)$
S° 191.5   130.57   192.3   J·mol^{-1}·K^{-1}
$\Delta S^\circ = 192.3 - ^1/_2\ (191.5) - ^3/_2\ (130.57) = -99.3$ J/K for the above reaction, $\Delta S^\circ_f = -99.3$ J·mol^{-1}·K^{-1}

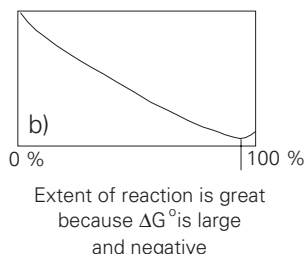**29. Which of the following is the most stable under standard conditions: $Al_2O_3(s)$, $NO(g)$ or $FeO(s)$?**

The more positive the value of ΔG°, the greater the tendency to decompose, and the less stable the compound is.
$Al_2O_3(s)$ -1582 kJ/mol $NO(g)$ 86.60 kJ/mol $FeO(s)$ -255.2 kJ/mol
$\therefore Al_2O_3(s)$ is the most stable.

31. **Draw diagrams that indicate the relative positions of the free energy minima for reactions with the following ΔG° values. Refer to Figure 4.3.**

    a) **small and negative**　　　　b) **large and negative**

    a)

    0 %　　　　　　100 %

    Extent of reaction is slightly
    greater than 50% because
    ΔG° is negative but small

    b)

    0 %　　　　　　100 %
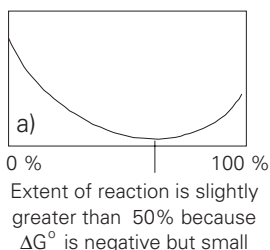
    Extent of reaction is great
   because ΔG° is large
    and negative

33. **When gaseous ozone, O_3, is formed from O_2 by the reaction $^3/_2 O_2(g) \rightarrow O_3(g)$. What is the equilibrium constant of this reaction at 298 K?**

    We must first find ΔG°_{RXN}, using Appendix G: ΔG°_{RXN} = 163 - 3/2(0) = 163 kJ/mol
    From equation 4.11, K= exp(-ΔG°/RT). Therefore, K = exp[-(163)/2.478)] = 2.68×10^{-29}.

35. **Write the expression for the reaction quotient and determine the value of the equilibrium constant at 298 K for each of the following reactions:**
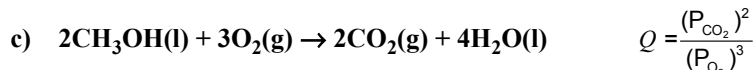
    a) **$H_2(g) + Br_2(l) \rightarrow 2HBr(g)$**　　　　　　$Q = \dfrac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})}$
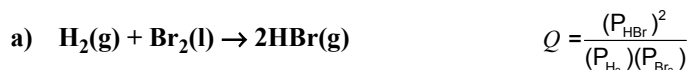
    The chemical equation is for the formation of 2HBr, so ΔG° = $2\Delta G_f^\circ$(HBr) = (2 mol)(-53.5 kJ/mol) = -107.0 kJ

    From Eqn 4.11:   K= exp(-ΔG°/RT);　　　　RT = (0.008314 kJ/mol·K)(298 K) = 2.48 kJ/mol

    K = exp[-(-107.0 kJ/mol)/(2.48/mol)] = $e^{43.15}$ = 5.66×10^{18}

    b) **$I_2(s) \rightarrow I_2(g)$**　　　　　　　　　$Q = P_{I_2}$;

    ΔG° = 19.36 – 0 = 19.36 kJ/mol;　　K = exp[-(19.36)/(2.48)] = 4.0×10^{-4}

    c) **$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$**　　$Q = \dfrac{(P_{CO_2})^2}{(P_{O_2})^3}$

    ΔG°_{RXN} = 2(-394.36) + 4(-237.2) - [0 + 2(-166.23)] = -1405.1 kJ/mol

    $K = \exp\left\{\dfrac{[-(-1405.1)]}{2.478}\right\} = e^{567.0} = 10^{246}$. If your calculator does not give this result, try solving for the log K

    log K = 567/2.303 = 246, which means that K = 10^{246}

    d) **$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$**　　　　　　$Q = \dfrac{1}{(P_{NH_3})(P_{HCl})}$
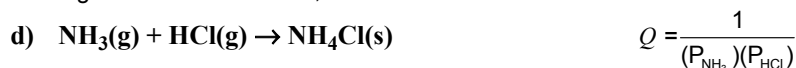
    ΔG°_{RXN} = -203.0 – [-16.5 + -95.31] = -91.2 kJ/mol, so K = exp [-(-91.2)/2.48] = $e^{36.8}$ = 9.6×10^{15}

37. **Indicate the activity of each of the following:**

    The activity of a species is the ratio of the concentration of the species to its concentration in its standard state. For pure solids and liquids in their standard state, their activity is unity (1). The activity of a gas in its standard state is 1 atm and for a solute it is 1 M. Thus, the activity of solute A is [A]/1M, which is unitless but numerically equal to the molarity of A. Similarly, the activity of gas B is P_B /1atm, which is also unitless but numerically equal its partial pressure in atmospheres.
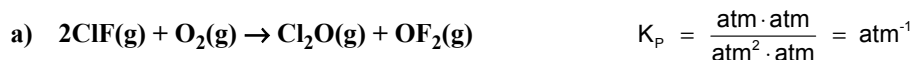
    a) **NH_3 gas at 0.024 atm**
    a = (0.024 atm)/(1 atm) = 0.024.

    b) **Cl^{1-} ion in a 0.11-M solution of NaCl**　　　a = 0.11 M / 1 M = 0.11**.**
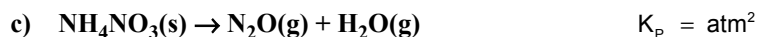
    c) **A crystal of AgCl sitting in liquid water**　　　Pure solids in their standard states have an activity of 1 (unity).

    d) **H_2 gas at 321 torr**　　　Change torr to atm: (321 torr)(760 torr/1 atm) = 0.422 atm. a = 0.422 atm/1 atm = 0.422.

39. **K and K_p have the same value for the following. However, K has no units, while K_p does. What are the units of K_c for each of the following the reactions?**

    a) **$2ClF(g) + O_2(g) \rightarrow Cl_2O(g) + OF_2(g)$**　　　　$K_P = \dfrac{atm \cdot atm}{atm^2 \cdot atm} = atm^{-1}$

b) $2HI(g) \rightarrow H_2(g) + I_2(g)$ $\qquad\qquad K_P = \dfrac{atm \cdot atm}{atm^2} = $ no units

c) $NH_4NO_3(s) \rightarrow N_2O(g) + H_2O(g)$ $\qquad\qquad K_P = atm^2$

41. **Consider the following gas phase equilibrium at 298 K:** $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

a) **From standard free energies of formation, calculate the equilibrium constant K at 298 K.**

This is the formation reaction for ammonia. $\Delta G° = 2\Delta G_f°(NH_3) = (2\ mol)(-16.5\ kJ/mol) = -33.0\ kJ$

Use Eq. 4.11 to solve for K: $K = e^{-\frac{\Delta G°}{RT}} = \exp\left(-\dfrac{-33.0\ kJ/mol}{(8.314\times10^{-3}\ kJ/mol \cdot K)(298\ K)}\right) = 6.09 \times 10^5$

b) **Calculate ΔG when a reaction mixture consists of 10 atm N_2, 10 atm H_2, and 1 atm NH_3.**

Determine the reaction quotient with the given pressures: $\qquad Q = \dfrac{P_{NH_3}^2}{P_{H_2}^3 \times P_{N_2}} = \dfrac{1^2}{10^3 \times 10} = 1.0 \times 10^{-4}$

Use Eq. 4.12 to calculate ΔG: $\Delta G = RT\ \ln\left(\dfrac{Q}{K}\right) = (0.008314\ kJ/mol \cdot K)(298\ K)(\ln\dfrac{1.0 \times 10^{-4}}{6.09 \times 10^5}) = $ -55.8 kJ/mol

43. **Consider the following acid-base reaction:** $NH_4^{1+}(aq) + CN^{1-}(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$ **K = 1.7**

a) **What is the value of $\Delta G°$?** $\qquad \Delta G° = -RT\ln K = -(8.314\ x\ 10^{-3}\ kJ.mol^{-1}.K^{-1})(298\ K)(\ln 1.7) = $ -1.3 kJ/mol

What are the values of Q and ΔG at 298 K and in which directionis the reaction proceeding?

$[NH_4^{1+}]$	$[CN^{1-}]$	$[NH_3]$	$[HCN]$

b) **0.10** $\qquad$ **0.10** $\qquad$ **0.10** $\qquad$ **0.10**

$\Delta G = RT\ln\dfrac{Q}{K} \qquad Q = \dfrac{[NH_3][HCN]}{[NH_4^{1+}][CN^{1-}]} = \dfrac{(0.01)(0.01)}{(0.01)(0.01)} = 1$

$\Delta G = (8.314\ J \cdot mol^{-1} \cdot K^{-1})(298\ K)(\ln\dfrac{1}{1.7}) = $ -1.3 kJ $\quad (\Delta G < 0$, so Rxn $\rightarrow)$

c) **0.12** $\qquad$ **0.10** $\qquad$ **0.17** $\qquad$ **0.12**

$Q = \dfrac{(0.17)(0.12)}{(0.12)(0.10)} = 1.7; \qquad \Delta G = (8.314\ J \cdot mol^{-1} \cdot K^{-1})(298\ K)(\ln\dfrac{1.7}{1.7}) = 0\ (\Delta G = 0$, so Rxn $\rightleftharpoons)$

d) **0.18** $\qquad$ **0.18** $\qquad$ **0.10** $\qquad$ **0.10**

$Q = \dfrac{(0.10)(0.10)}{(0.18)(0.18)} = 0.31; \qquad \Delta G = (8.314\ J \cdot mol^{-1} \cdot K^{-1})(298\ K)(\ln\dfrac{0.31}{1.7}) = $ -4.2kJ $\ (\Delta G < 0$, so Rxn $\rightarrow)$

45. **The process of dissolving a gas in a liquid is exothermic because of solvent-solute interactions. Consider the process of making carbonated water,** $CO_2(g) \rightarrow CO_2(aq)$ $\Delta H° = $ **-19.4 kJ**

a) **Write the equilibrium constant expression for the carbonation process and solve it for the equilibrium concentration of CO_2 in solution in terms of the partial pressure of the gas in equilibrium with it.**

$K = \dfrac{[CO_2(aq)]}{P_{CO_2}} \quad \Rightarrow \quad [CO_2(aq)] = KP_{CO_2}$

b) **Use Equation 4.19 and the expression for the equilibrium constant for the carbonation process to explain why a carbonated drink gets flat when it is allowed to warm.**

According to Eq 4.13, the equilibrium constant for an exothermic reaction decreases as the temperature increases. Thus, warming the drink decreases the equilibrium constant, which means that the pressure of the gas increases while the concentration of the gas in the solution decreases. Loss of gas from the solution into the vapor causes the drink to go flat.

c) **Explain why a carbonated drink gets flat when allowed to sit in an open container.**

For an open container, P_{CO_2} is lower than in a closed container (P_{CO_2} is quite low in the atmosphere). As a result, the equilibrium will shift to the left reducing the concentration of CO_2 in solution. This can also be determined by rearranging the expression from Part b: $[CO_2(aq)] = K \times P_{CO_2}$. From this equation, one can see that $[CO_2(aq)]$ decreases with P_{CO_2}.

47. The pressure of water vapor in a closed container is 0.3 atm. If the vapor pressure of water at this temperature is 1.5 atm, what are the signs of ΔG and ΔG° for $H_2O(l) \rightarrow H_2O(g)$?

$P^o_{H_2O}$ = 1.5 atm, so K = 1.5 P_{H_2O} = 0.3 atm, so Q = 0.3

K > 1, so ΔG° < 0. Q < K so ΔG < 0

49. Use the data in Appendix G to estimate the vapor pressure of water at 50. °C. Express your answer in torr.

Recall that the vapor pressure is equal to the equilibrium constant (K) in atmospheres. Therefore, we need to calculate ΔG_{vap} at 50°C. Apply equation 4.2 to the vaporization process: $\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$

First, we need to calculate the ΔH_{vap} and ΔS_{vap} by taking the difference between the values for $H_2O(l)$ and $H_2O(g)$ using the data found in Appendix G (See Example 4.2 for a similar problem)

ΔH_{vap} = -241.82 kJ/mol - (-285.83 kJ/mol) = 44.01 kJ/mol

ΔS_{vap} = 188.7 J/mol·K - 69.01 J/mol·K = 118.8 J/mol·K

Substituting into Eq. 4.2, we get: ΔG_{vap} = 44.01 kJ/mol - (323 K)(0.1188 kJ/mol·K) = 5.64 kJ/mol

Then, use eqn. 4.6 to calculate the equilibrium constant (See Example 4.3 for a similar problem):

$$K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{5{,}640 \text{ J/mol}}{(8.314 \text{ J/mol K})(323 \text{ K})}\right) = e^{-2.10} = 0.122$$

K has no units as derived above, but is equal to the pressure in atmospheres, which can be converted to torr by multiplying by 760 torr/atm: (0.122 atm)(760 torr/atm) = 93.0 torr

51. The heat of vaporization of $SiCl_4$ at 300. K is 29.7 kJ/mol and its vapor pressure is 34.0 torr.

a)   What are ΔG° and ΔS° of vaporization of $SiCl_4$ at 300 K?

$\Delta G° = $ -RT ln K $K = \dfrac{(34/760)}{1}$

$\Delta G° = (-8.314 \text{J/mol} \cdot \text{ K})(300\text{K})(\ln 0.045)$ K = 0.045

$\Delta G° = 7.75 \text{ kJ} = \Delta H° - T\Delta S$

$\Delta S° = \dfrac{-\Delta G° + \Delta H°}{T} = \dfrac{-(7.75 \text{ kJ}) + 29.7 \text{ kJ}}{300 \text{ K}} \times \dfrac{1000J}{1 \text{ kJ}} = 73.2 \text{ J/K}$

b)   Assume ΔH° and ΔS° are temperature independent and estimate the boiling point of $SiCl_4$.

$\Delta G°_{vap} = \Delta H°_{vap} - T\Delta S°_{vap} = 0$ $\Rightarrow$ $T_{bp} = \dfrac{\Delta H°_{vap}}{\Delta S°_{vap}} = \dfrac{29.7 \text{ kJ/mol}}{0.0732 \text{ kJ/mol} \cdot \text{K}} = 406K$ or 133°C

53. The enthalpy of vaporization of H_2S at 212.8 K is 18.67 kJ/mol.   Calculate the molar entropy of vaporization of 2.50 moles of H_2S at this temperature.

To solve this problem, rearrange Eq. 4.11: $\Delta S = \dfrac{\Delta H}{T} = \dfrac{18670 \frac{J}{mol}}{212.8 \text{ K}} = 87.73 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

Taking into account the number of moles: ΔS = (2.50 mol)(87.73 J·mol^{-1}·K^{-1}) = 219 J·K^{-1}.

55. The equilibrium constant of a reaction is 3.2×10^3 at 358 K and 1.7×10^2 at 456K. What are ΔH° and ΔS° for the reaction?

Solve two equations in two unknowns as follows. Note extra sig figs are used in intermediate steps.

$\Delta G° = $ -RT ln K = $\Delta H° - T\Delta S°$

$\Delta G°_1 = -(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(358 \text{ K})(\ln 3200) = -2.402 \times 10^4 \text{ J} = \Delta H° - 358\Delta S°$

$\Delta G°_2 = -(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(456 \text{ K})(\ln 170) = -1.947 \times 10^4 \text{ J} = \Delta H° - 456\Delta S°$

Subtract the two standard free energies to eliminate the standard enthalpy then solve for the entropy.

$\Delta G°_1 - \Delta G°_2 = (-2.402 + 1.947) \times 10^4 = (-358 + 456)\Delta S° \Rightarrow \Delta S° = \dfrac{-4550 \text{ J}}{98 \text{ K}} = -46 \text{ J} \cdot \text{K}^{-1}$

Substitute this value into the expression for $\Delta G°_2$ to obtain $-1.947 \times 10^4 \text{ J} = \Delta H° - (456 \text{ K})(-46.4 \text{ J} \cdot \text{K}^{-1})$

so $\Delta H° = -1.947 \times 10^4 \text{ J} - 2.116 \times 10^4 \text{ J} = -4.1 \times 10^4 \text{ J} = -41 \text{ kJ}$

Thermodynamics and Equilibrium

57. The vapor pressure of solid CO_2 (dry ice) is 280. torr at -90. °C and 105 torr at -100. °C.

a) What is the value of ΔG^o for the reaction $CO_2(s) \rightleftharpoons CO_2(g)$ at each temperature?

The first step is to convert mm Hg to atm.

$$280 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.368 \text{ atm} \qquad\qquad 105 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.138 \text{ atm}$$

Thus, K = 0.368 at –90 °C and K = 0.138 at –100 °C. Use Eq. 4.8 with these values of K and T.

At -90°C: $\Delta G^\circ = -RT\ln K = -(0.008314 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(183 \text{ K})(\ln 0.368) = 1.52 \text{ kJ} \cdot \text{mol}^{-1}$

At -100°C: $\Delta G^\circ = -RT\ln K = -(0.008314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(173 \text{ K})(\ln 0.138) = 2.85 \text{ kJ} \cdot \text{mol}^{-1}$

b) What are ΔH^o and ΔS^o for the reaction $CO_2(s) \rightleftharpoons CO_2(g)$ at these temperatures? Assume that ΔH^o and ΔS^o are constant over this temperature range.

Use Eq. 4.2 for each temperature to produce two equations with two unknowns (ΔH° and ΔS°).

At -90 °C: $1.52 \text{J} \cdot \text{mol}^{-1} = \Delta H^\circ - 183 \text{ K} \times \Delta S^\circ$ at -100 °C: $2.85 \text{ J} \cdot \text{mol}^{-1} = \Delta H^\circ - 173 \text{ K} \times \Delta S^\circ$

Subtract the equation on the left from the one on the right and solve for ΔS°.

$$1.33 \text{ kJ} \cdot \text{mol}^{-1} = (10 K)\Delta S^\circ \text{ so } \Delta S^\circ = \frac{1.330 \text{ kJ} \cdot \text{mol}^{-1}}{10 \text{ K}} = 0.13 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Substitute ΔS° into either of the original equations. $\Delta H^\circ = 1.52 \text{ kJ} \cdot \text{mol}^{-1} + (183 \text{ K})(0.13 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 26 \text{ kJ} \cdot \text{mol}^{-1}$

c) A dry ice bath is used routinely in the laboratory to keep things cold. It is made by making a powder of the dry ice and then mixing the powder with a solvent to make a slurry. Estimate the temperature of a dry ice bath by determining the temperature at which the vapor pressure of CO_2 is 1 atm.

Apply Equation 4.11 to the sublimation of dry ice. $T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{25.9 \frac{kJ}{mol}}{0.133 \frac{kJ}{mol \cdot K}} = 195 \text{ K} = -78 \text{ °C}$

59. Write the reaction that would result when the oxidation of S to SO_2 is coupled to each of the following reactions. Calculate ΔG^o at 298 for each coupled reaction and indicate whether it is extensive.

The oxidation of S to SO_2 is shown as follows: $S(g) + O_2(g) \rightarrow SO_2(g)$ $\Delta G^\circ = -300 \text{ kJ/mol}$
Each reaction is the reverse of the formation reaction of the substance, so use Appendix G to find ΔG.

a) $Cr_2O_3(s) \rightarrow 2Cr(s) + \frac{3}{2}O_2(g)$

$Cr_2O_3(s) \rightarrow 2Cr(s) + \frac{3}{2}O_2(g)$ $\Delta G^\circ = -(-1059 \text{ kJ}) = +1059 \text{ kJ}$

$\frac{3}{2}S(s) + \frac{3}{2}O_2(g) \rightarrow \frac{3}{2}SO_2(g)$ $\Delta G^\circ = \frac{3}{2}(-300) = -450 \text{ kJ}$

$Cr_2O_3(s) + \frac{3}{2}S \rightarrow 2Cr(s) + \frac{3}{2}SO_2(g)$ $\Delta G^\circ = 1059 - 450 = +609 \text{ kJ}$ $\Delta G^\circ > 0$, so reaction is not extensive.

b) $SiO_2(s) \rightarrow Si(s) + O_2(g)$

$SiO_2(s) \rightarrow Si(s) + O_2(g)$ $\Delta G^\circ = -(-857 \text{ kJ}) = +857 \text{ kJ}$

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta G^\circ = -300 \text{ kJ}$

$Cr_2O_3(s) + \frac{3}{2}S \rightarrow 2Cr(s) + \frac{3}{2}SO_2(g)$ $\Delta G^\circ = 857 - 300 = +557 \text{ kJ}$ $\Delta G^\circ > 0$, so reaction is not extensive.

61. Calculate ΔH^o, ΔS^o, and ΔG^o at 298 K for the following reaction:

$Al_2O_3(s) + 3C(s,graphite) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g)$
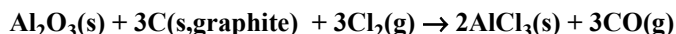
$\Delta H^\circ = 2(-704.2) + 3(110.52) - [-1676 + 3(0) + 3(0)] = -63.96 \text{ kJ/mol}$
$\Delta S^\circ = 2(110.7) + 3(197.56) - [50.92 + 3(5.740) + 3(223.0)] = 76.94 \text{ J/mol·K}$
$\Delta G^\circ = 2(-628.8) + 3(-137.15) - [-1582 + 3(0) + 3(0)] = -87.05 \text{ kJ/mol}$

a) Is the reaction extensive at standard conditions and 298 K?

The reaction is extensive at standard conditions and 298 K because $\Delta G^\circ < 0$.
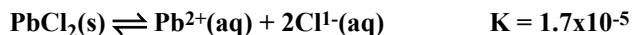
b) Write the expression for K and calculate its value at 298 K.

$$K = \frac{(P_{CO})^3}{(P_{Cl_2})^3} = \exp\left\{\frac{\Delta G^\circ}{RT}\right\} = \exp\left\{\frac{87.05}{2.478}\right\} = e^{35.13} = 1.8 \times 10^{15}$$

c) **Estimate the value of K at 600 K.**

$\Delta G° = \Delta H° - T\Delta S° = $ -63.96 kJ/mol – (600K)(0.07694kJ/mol·K) = -110.1 kJ/mol·K
Then, K = exp-($\Delta G°$/RT) = exp-(-110.1/4.988) = 3.9 x 10^9

63. **Consider the following equilibrium, which defines the solubility of lead chloride in water at 25 $^{\circ}$C:**

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{1-}(aq) \qquad K = 1.7x10^{-5}$$

a) **What is the value of $\Delta G°$ for the reaction at 25 $^{\circ}$C?**

use Eq. 4.8 to calculate $\Delta G°$: $\qquad \Delta G° = $ -RTln(K) = -(8.314 J/mol·K)(298K)ln(1.7x10^{-5}) = 27.2 kJ/mol

Determine Q and ΔG for the solubility of lead chloride under each of the following circumstances and indicate whether more solid could dissolve or more solid would precipitate:

b) **$[Pb^{2+}]$ = 1.2 mM and $[Cl^{1-}]$ = 15.2 mM**

$Q = [Pb^{2+}][Cl^{1-}]^2 = $[0.0012 M][0.0152 M]^2 = 2.8x10^{-7}
Use Eqn. 4.10 to calculate ΔG for this process:
$\Delta G = $ RTln(Q/K) = (8.314 J/mol·K)(298)ln(2.8x10^{-7}/1.7x10^{-5}) = -10.1 kJ/mol
Because ΔG < 0, more solid will dissolve.

c) **$[Pb^{2+}]$ = 0.075 M and $[Cl^{1-}]$ = 0.040 M**

$Q = [Pb^{2+}][Cl^{1-}]^2 = $[0.075 M][0.04 M]^2 = 1.2x10^{-4}
ΔG = 4.8 kJ/mol
ΔG > 0, so no more solid will dissolve.

65. **Indicate whether ΔG increases, decreases, or remains the same as the partial pressure of CO_2 is increased in each of the following.**

If CO_2 is a product then increasing its partial pressure increases Q, but if it is a reactant then the increase in pressure decreases Q. Using that logic and $\Delta G = $ RTln(Q/K), we conclude that ΔG becomes more negative (decreases) if the CO_2 is a reactant, but it gets more positve (increases) if CO_2 is a product.

a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\qquad$ decreases

b) $CO_2(g) \rightleftharpoons CO_2(s)$ $\qquad$ increases

c) $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(l)$ increases

67. **When both driving forces in a reacton are favorable ($\Delta H° < 0$ and $\Delta S° > 0$) the reaction is extensive (K > 1) at all temperatures, and when both are unfavorable, the reaction is never extensive (K < 1). However, when one driving force is favorable and the other is not, the reaction can be either extensive or not depending upon the temperature. Determine the temperature at which K ~ 1 for each of the following reactions and discuss the conditions at which the reaction is likely to be extensive.**

K = 1 when $\Delta G° = \Delta H° - T\Delta S° = 0$, so we determine $\Delta H°$ and $\Delta S°$ at 298. If they have the same sign, one is favorable ane the other is not, so there is a temperature at which $\Delta G° = 0$. We obtain the temperature by setting $\Delta H° = T\Delta S°$ and solve for T ~ $\Delta H°/\Delta S°$. We use the approximately equals sign because we are assuming that $\Delta H°$ and $\Delta S°$ are temperature independent. The effect of temperature is determined by the sign of ΔSo. When the entropy term is favorable ($\Delta S° > 0$), the extent of reaction is increased by increasing the temperature, so the reaction is extensive at temperatures above the one at which K ~ 1. When the entropy term is unfavorable ($\Delta S° < 0$), reducing the temperature increases the extent of reaction.

a) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

$\Delta H° = $ 9.66 – 2(33.84) = -58.02 kJ; $\quad \Delta S° = $ 304.3 – 2(240.45) = -176.6 J·K^{-1}
T ~ $\Delta H°/\Delta S° = $ -58.02/-0.1766 = 329K.
The entropy term is unfavorable ($\Delta S° < 0$), so the reaction is extensive at temperatures below ~300 K.

b) $SO_3(g) \rightleftharpoons {}^1/_2O_2(g) + SO_2(g)$

$\Delta H° = (^1/_2)(0) - $ 296.83 + 395.72 = +98.89 kJ; $\qquad \Delta S° = (^1/_2)$(205.03) + 248.1 – 256.6 = 94.0 J·K^{-1}
T ~ $\Delta H°/\Delta S° = $ 98.89/0.0940 = 1.05x10^3 K.
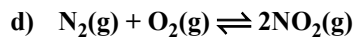The entropy term is favorable ($\Delta S° > 0$), so the reaction is extensive at temperatures above ~1100 K.

c) $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

ΔH^o = -314.4 + 46.11 + 92.30 = -175.99 kJ; ΔS^o = 94.6 – 192.3 – 186.8 = -284.5 J·K^{-1}

T ~ $\Delta H^o/\Delta S^o$ = -175.99/-0.2845 = 618 K.

ΔS^o < 0, so the reaction is extensive at temperatures below ~600 K

d) $N_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

ΔH^o = 2(33.84) – 0 - 0 = 67.74 kJ; ΔS^o = 2(240.45) – 191.5 – 205.03 = 84.4 J·K^{-1}

T ~ $\Delta H^o/\Delta S^o$ = 67.74/0.0844= 803 K.

ΔS^o > 0, so the reaction is extensive at temperatures above ~800 K

69. Determine ΔS^o and ΔH^o from the following equilibrium constant/temperature data:

T(°C)	200	225	230	250	260
K	19.6	10.9	11.6	7.8	5.6

To use all of the data, we must plot RlnK versus 1/T and determine the slope (ΔS^o) and intercept (-ΔH^o) of the best straight line through the data. First, convert then plot the data. Recall the T must always be on the Kelvin scale.

t (°C)	T (K)	1/T (x10³)	R ln K
200	473	2.114	24.74
225	498	2.008	19.86
230	503	1.988	20.38
250	523	1.912	17.08
260	533	1.876	14.32
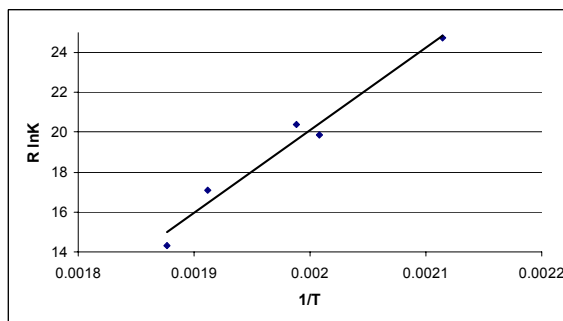
The slope and intercept of the best line (shown in plot) are 41513 J·mol^{-1} and -62.9 J·mol^{-1}·K^{-1}. Therefore, ΔH^o = -41.5 kJ·mol^{-1} and ΔS^o = -62.9 J·mol^{-1}·K^{-1}

71. Use the following equilibrium constant-temperature data to determine ΔH^o and ΔS^o for the reaction.

T (K)	300	350	375	400	460
K	2000.0	87.7	33.2	7.0	1.8

Convert the given data to that required in Equation 4.18. The resulting table of 1/T and R ln K values is

1/T x 10³	R ln K
3.33	63.19
2.86	37.20
2.67	29.12
2.50	16.18
2.17	4.89
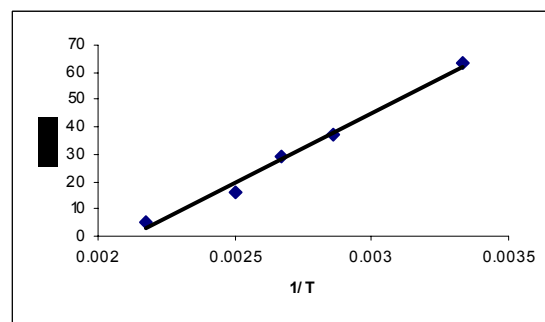
Linear regression yields an intercept of -109 and a slope of 5.13x10⁴, so **ΔS^o = -109 J·K^{-1}** and **ΔH^o = -51.3 kJ.**

If only the last two data points are used, the slope = 3.42x104 J.K-1, which which differs from the best fit slope by 33%. Such large deviations can occur when one or both points are not on the best fit line.