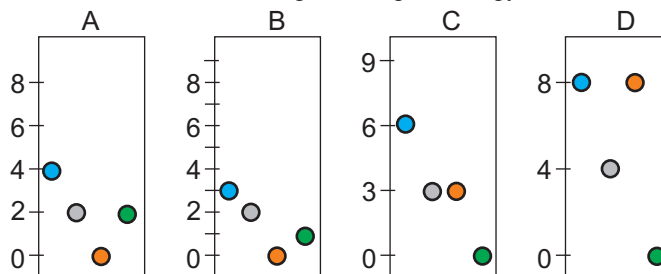## ENTHALPY, ENTROPY AND FREE ENERGY CHANGES

Refer to the following figures for Exercises 1-6.   The lines on the vertical axis 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?

2. What are the energies of systems C and D?   Which system 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?

4.   In how many ways can the energies of systems C and D be distributed? Which system has the greater entropy?

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

6. How many ways are there to distribute the energy of system B at 0 K? What is its entropy?

───

7. State the second law of thermodynamics.

8. Explain why the second law of thermodynamics is frequently stated as 'spontaneous processes increase the disorder of the universe'.

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?

10. What is ΔS_{sur} in a process that liberates 20 kJ of heat at 1 atm and 300 K?

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.

12. A large collection of cells is far more 'ordered' in an animal than as individual one-cell organisms. Does this mean that evolution is a violation of the second law? Explain.

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

14. Indicate which member of each pair has the higher entropy and indicate the reason:
    a) pure silicon wafer or one that has small amounts of germanium present
    b) water vapor at 25 ^{o}C or liquid water at 25 ^{o}C
    c) liquid water at 25 ^{o}C or liquid water at 50 ^{o}C
    d) $H_2O(l)$ or $H_2O_2(l)$ at the same temperature

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
    b) $I_2(s)$ or $I_2(g)$ at 300 K
    c) He(g) at 400 K or He(g) at 600 K
    d) A piece of tin or a piece of 60:40 solder (a solid solution that is 60% Pb and 40% Sn)

16. What is a *spontaneous process*? What thermodynamic property of the system indicates spontaneity at constant temperature and pressure?

17. What is an *extensive process*? What thermodynamic property of the system indicates the extent of a reaction at constant temperature and pressure?

18. What can be said about ΔS_{sur} if the entropy change of the system caused by a spontaneous process is -50 $J \cdot K^{-1}$?

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

    a) $\Delta H^o > 0$ **b)** $\Delta S_{univ} = 0$ **c)** $\Delta G^o < 0$

    d) $\Delta G < 0$ **e)** $\Delta S > 0$ **f)** $\Delta E_{univ} = 0$

20. Indicate whether each of the following statements must be true, can be true or false, or cannot be true for a reaction at *equilibrium*:

    a) $\Delta H^o = 0$ **b)** $\Delta S_{univ} = 0$ **c)** $\Delta G^o = 0$

    d) $\Delta G < 0$ **e)** $\Delta S = 0$ **f)** $\Delta E_{univ} = 0$

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

    a) Increasing the temperature of a pot of water from 18 ^oC to 23 ^oC.

    b) Condensing a liquid

    c) Clearing a field and planting rows of corn

    d) $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$

22. Use the data in Appendix B to calculate ΔH^o, ΔS^o and ΔG^o at 298 K for the following reactions:

    a) $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$

    b) $I_2(s) \rightarrow I_2(g)$

    c) $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

    d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

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

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

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

24. Consider the extraction of copper from the ore Cu_2S from the decomposition

        $Cu_2S(s) \rightarrow 2Cu(s) + S(s)$ (Rxn 1)

    a) Calculate ΔH^o, ΔS^o and ΔG^o at 298 K.

    b) Is the extraction of copper from Cu_2S extensive?

    c) Given the reaction

        $S(s) + O_2(g) \rightarrow SO_2(g)$ (Rxn 2)

        Calculate ΔH^o, ΔS^o and ΔG^o at 298 K.

    d) Adding Rxn 1 and Rxn 2 yields the equation for the overall reaction

        $Cu_2S(s) + O_2(g) \rightarrow 2Cu(s) + SO_2(g)$ (Rxn 3)

        Calculate ΔH^o and ΔG^o for the reaction above at 298 K.

    e) Is the overall process in Rxn 3 extensive?

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 $g \cdot mL^{-1}$, and 1 gal is 3.79 L.

26. The standard entropy of formation of stannane (SnH_4) is -84.64 $J \cdot mol^{-1} \cdot K^{-1}$ at 298 K. What is the absolute entropy of stannane at 298 K?

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

    a) $H_2(g)$ **b)** $H_2O(g)$ **c)** $NH_3(g)$

28. The free energies of formation of $SO_2(g)$, $H_2S(g)$, and $NO_2(g)$ are -300.2, -33.6, and +51.8 $kJ \cdot mol^{-1}$, respectively. Which of these gases has the greatest tendency to decompose to its elements at 298 K?

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

FREE ENERGY AND EQUILIBRIUM

30. Draw diagrams that indicate the relative positions of the free energy minima for reactions with the following ΔG^o values. Refer to Figure 4.9.

    a) large and positive   **b)** small and positive
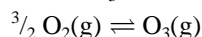
31. Draw diagrams that indicate the relative positions of the free energy minima for reactions with the following ΔG^o values. Refer to Figure 4.9.

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

32. Calculate the equilibrium constant at 298 K for the reaction
$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$
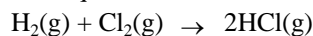
33. Gaseous ozone, O_3, is formed from O_2 by the following reaction:
$$^3/_2\, O_2(g) \rightleftharpoons O_3(g)$$

What is the equilibrium constant of this reaction at 298 K?

34. Write the expression for the reaction quotient for each of the following:

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

    b) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

    c) $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^{1-}(aq)$

    d) $2Al(s) + 6H^{1+}(aq) \rightleftharpoons 2Al^{3+}(aq) + 3H_2(g)$

    e) $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

35. Write the expression for the reaction quotient and use the data in Appendix B to determine the value of the equilibrium constant at 298 K for each of the following reactions:

    a) $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$

    b) $I_2(s) \rightarrow I_2(g)$

    c) $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

    d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

36. Write the equilibrium constant expression and use the data in Appendix B to determine the value of ΔG^o at 298 K for each of the following equilibria to be discussed in upcoming chapters.

    a) $AgCl(s) \rightleftharpoons Ag^{1+}(aq) + Cl^{1-}(aq)$ $K = 1.8 \times 10^{-10}$

    b) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{1+}(aq) + OH^{1-}(aq)$ $K = 1.8 \times 10^{-5}$

    c) $NH_4^{1+}(aq) + CN^{1-}(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$ $K = 1.4$

    d) $Pb^{2+}(aq) + Sn(s) \rightleftharpoons Pb(s) + Sn^{2+}(aq)$ $K = 2$

37. Indicate the activity of each of the following:

    a) NH_3 gas at 0.024 atm

    b) Cl^{1-} ion in a 0.11 M solution of NaCl

    c) A crystal of AgCl sitting in liquid water

    d) H_2 gas at 321 torr

38. Indicate the activity of each of the following:

    a) Liquid ammonia at -50 °C

    b) He gas that is 0.0376 M at 325 K

    c) NO_3^{1-} ion in a solution of 0.206 M $Mg(NO_3)_2$
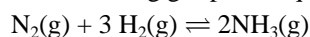
    d) Ar gas at 388 torr

39. What are the units of K_p for each of the following the reactions?

   a) $2ClF(g) + O_2(g) \rightleftharpoons Cl_2O(g) + OF_2(g)$

   b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

   c) $NH_4NO_3(s) \rightleftharpoons N_2O(g) + H_2O(g)$

40. What are the units of K_c for each of the following the reactions?

   a) $AgCl(s) \rightleftharpoons Ag^{1+}(aq) + Cl^{1-}(aq)$

   b) $Al(s) + 3Ag^{1+}(aq) \rightleftharpoons Al^{3+}(aq) + 3Ag(s)$

   c) $HNO_2(aq) + F^{1-}(aq) \rightleftharpoons HF(aq) + NO_2^{1-}(aq)$

41. Consider the following gas phase equilibrium at 298 K:

       $N_2(g) + 3\ H_2(g) \rightleftharpoons 2NH_3(g)$

   a) Use standard free energies of formation, calculate value of K at 298 K.

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

42. Consider the following acid-base equilibrium at 25 ^oC:

    $CH_3COOH(aq)\ +\ NO_2^{1-}(aq) \rightleftharpoons CH_3COO^{1-}(aq)\ +\ HNO_2(aq)\ \ K = 0.045$
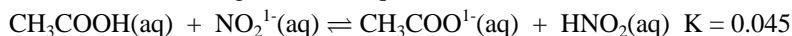
   a) What would be the sign of ΔG immediately after the addition of NO_2^{1-} to an equilibrium mixture? How would the reaction mixture respond?

   b) What effect would the addition of CH_3COO^{1-} to an equilibrium mixture have on the sign of ΔG? How would the reaction mixture respond?

   c) State a general rule that summarizes what happens when you add a reactant or product to an equilibrium mixture. This effect is known as Le Châtelier's principle.

43. Consider the following acid-base reaction at 25 ^oC:
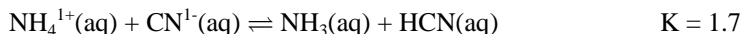
    $NH_4^{1+}(aq) + CN^{1-}(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$ $K = 1.7$

   a) What is the value of ΔG^o?

What are the values of Q and ΔG at 298 K under the following conditions, and in which direction ($\rightarrow$, $\leftarrow$, or $\rightleftharpoons$) is the reaction proceeding?

	$[NH_4^{1+}]$	$[CN^{1-}]$	$[\ NH_3]$	$[HCN]$
b)	0.10 M	0.10 M	0.10 M	0.10M
c)	0.12 M	0.10 M	0.17 M	0.12 M
d)	0.18 M	0.18 M	0.10 M	0.10 M

44. Consider the acid-base reaction at 25 ^oC

    $CH_3COOH(aq)\ +\ NO_2^{1-}(aq) \rightleftharpoons CH_3COO^{1-}(aq)\ +\ HNO_2(aq)$ $K = 0.045$

   a) What is the value of ΔG^o at 298 K?

What are the values of Q and ΔG at 298 K under the following conditions, and in which direction ($\rightarrow$, $\leftarrow$, or $\rightleftharpoons$) is the reaction proceeding?

	$[\ CH_3COOH]$	$[\ NO_2^{1-}]$	$[CH_3COO^{1-}]$	$[HNO_2]$
b)	0.10 M	0.10 M	3.0 M	0
c)	0.010 M	0.10 M	1.0 M	0.50 M
d)	0.088 M	0.10 M	0.021 M	0.019 M
e)	0.12 M	0.12 M	0.15 M	0.15 M

45. The process of dissolving a gas in a liquid is exothermic due to solvent-solute interactions. Consider the process of making carbonated water,

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad\qquad \Delta H^\circ = -19.4 \text{ kJ}$$

   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. This expression is known as Henry's Law.

   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.

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

46. CO_2 is pumped into a container at -70 °C until its pressure is 1800 torr. If the vapor pressure of CO_2 is 1486 torr at -70 °C, what are the signs of ΔG and ΔG° for $CO_2(s) \rightarrow CO_2(g)$ under these conditions?

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 $H_2O(l) \rightarrow H_2O(g)$?

TEMPERATURE DEPENDENCE OF ΔG° AND K

48. The amount of product in an equilibrium mixture increases when the temperature is raised. Is the reaction exothermic or endothermic? Explain.

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

50. The standard enthalpy of vaporization of methanol is 36.4 $kJ \cdot mol^{-1}$ and the standard entropy of vaporization is 110.8 $J \cdot mol^{-1} \cdot K^{-1}$. What is the normal boiling point of methanol in degrees Celsius?

51. The heat of vaporization of $SiCl_4$ at 300. K is 29.7 $kJ \cdot mol^{-1}$ and its vapor pressure is 34.0 torr.

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

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

52. What are the vapor pressure at 298 K in torr and the normal boiling point in degree Celsius of CS_2?

53. The enthalpy of vaporization of H_2S at 212.8 K is 18.67 $kJ \cdot mol^{-1}$. What is the molar entropy of vaporization of 2.50 moles of H_2S at this temperature?

54. The equilibrium constant of a reaction is 6.0 at 326 K and 9.0 at 412 K. What are ΔH° and ΔS° for the reaction?

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

56. Iodine sublimes, and a closed jar of iodine at room conditions consists of both the solid and the vapor.

   a) What is the pressure of iodine gas in equilibrium with the solid at 25 °C and 1 atm?

   b) At what temperature is the pressure of the gas at 1 atm?

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 ΔG° for the reaction $CO_2(s) \rightleftharpoons CO_2(g)$ at each temperature?

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

   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.

COUPLED REACTIONS

58. Write the reaction that would result when the oxidation of CO is coupled to each of the following reactions. Calculate ΔG° at 298 K for each coupled reaction and indicate whether it is extensive.

   a) $Al_2O_3(s) \rightarrow 2Al(s) + \frac{3}{2}O_2(g)$

   b) $2PbO(s) \rightarrow 2Pb(s) + O_2(g)$

   c) $Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g)$

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° at 298 K for each coupled reaction and indicate whether it is extensive.

   a) $Cr_2O_3(s) \rightarrow 2Cr(s) + \frac{3}{2}O_2(g)$ **b)** $SiO_2(s) \rightarrow Si(s) + O_2(g)$

60. How many moles of ATP ions must be converted to ADP to drive a biochemical reaction in which $\Delta G^\circ = 350$ kJ?

MISCELLANEOUS PROBLEMS

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

   $Al_2O_3(s) + 3C(s,graphite) + 3Cl_2(g) \rightarrow 2AlCl_3(s) + 3CO(g)$

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

   b) Write the expression for K and calculate its value at 298 K.

   c) Estimate the value of K at 600 K.

62. Calculate ΔH°, ΔS° and ΔG° at 298 K for the following reaction:

   $S(s,rhombic) + 2CH_3COOH(l) \rightarrow 2CH_3CHO(g) + SO_2(g)$

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

   b) What are the equilibrium constant expression and value at 298 K?

   c) Estimate the equilibrium constant at 600. K.

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

   $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{1-}(aq)$ $K = 1.7 \times 10^{-5}$

   a) What is the value of ΔG° for the reaction at 25 $^\circ$C?

   Determine Q and ΔG for the above reaction given the solutions described in Parts b and c and indicate whether more solid could dissolve or more solid would precipitate.

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

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

64. Indicate whether each of the following must be true, must be false, or can be either true or false for an *exothermic* process that is *extensive* but *not spontaneous*.

   a) $\Delta H^\circ > 0$ **b)** $\Delta S_{univ} = 0$ **c)** $\Delta G^\circ < 0$

   d) $\Delta G < 0$ **e)** $\Delta S > 0$ **f)** $\Delta E_{univ} = 0$

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

   a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

   b) $CO_2(g) \rightarrow CO_2(s)$

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

66. Use the data in Appendix B to determine the value of the equilibrium constant for the following reaction at 298 K:

   $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ Estimate the value of the equilibrium constant at 500 K.

67. When both driving forces in a reaction are favorable ($\Delta H^\circ < 0$ and $\Delta S^\circ > 0$) 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.

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

   b) $SO_3(g) \rightleftharpoons \frac{1}{2}O_2(g) + SO_2(g)$

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

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

68. What are the values of ΔS^o and ΔH^o for the reaction $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ if $K_{600} = 381$ and $K_{700} = 2.69 \times 10^3$. What would be the value of the equilibrium constant at 400 K? Assume that enthalpy and entropy are temperature independent.

69. Determine ΔS^o and ΔH^o from the following equilibrium constant/ temperature data. Note the use of the Celsius scale for temperature.

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

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

T (°C)	20	60	90	110	125
K	2.31×10^4	8.97×10^4	2.09×10^5	3.92×10^5	5.03×10^5

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