1. What state functions correspond to the heat absorbed at constant pressure and the heat absorbed at constant volume?
2. Many devices are constructed to convert one type of energy to another. Give an example for each of the following energy conversions:
   a) thermal $\rightarrow$ mechanical **b)** mechanical $\rightarrow$ thermal
   c) electrical $\rightarrow$ light **d)** chemical $\rightarrow$ electrical
   e) electrical $\rightarrow$ thermal **f)** chemical $\rightarrow$ thermal
3. Classify each of the following processes as endothermic or exothermic:
   a) melting a solid **b)** combustion of butane
   c) condensing a liquid **d)** photosynthesis
   e) a battery reaction
4. Can all of the potential energy of the object described in Figure 3.3 be transferred to the mechanical surroundings by its fall? Explain.
5. What is the energy change of the system if the system:
   a) absorbs 50. J of heat and does 50. J of work?
   b) releases 20. J of heat and has 415 J of work done on it?
6. What is the energy change of the system if the system:
   a) absorbs no heat and does 125 J of work?
   b) releases 180. J of heat and has 825 J of work done on it?
7. What are ΔE, ΔE_{sur} and ΔE_{univ} for a gas that gives off 312 J of heat while being compressed 862 ml by a pressure of 1.64 atm?
8. How much heat is required to heat 1.0×10^3 kg of aluminum from room temperature (25 ^oC) to its melting point (660. ^oC)? $s_{Al} = 0.90\ J \cdot g^{-1} \cdot C^{-1}$
9. Determine the mass of octane (C_8H_{18}, $\Delta H_{comb} = -5500.\ kJ \cdot mol^{-1}$) must be combusted to yield the amount of energy equivalent to:
   a) 3.1 kJ, the kinetic energy of a 220. lb linebacker running at a speed of 40. yd in 4.7 seconds.
   b) 17 J, the potential energy of a 5 lb bag of sugar on top of a 30. inch high counter.
   c) 320 kJ, the amount of heat required to raise the temperature of 1 quart of water from 25 ^oC to its boiling point, .
10. How many joules of work must be done to inflate a balloon to a volume of 2.0 L if atmospheric pressure is 0.98 atm?
11. $\Delta H_{vap} = 26.7\ kJ \cdot mol^{-1}$ for CS_2 at its normal boiling point (46 ^oC). What is ΔH for the condensation 41.2 g of CS_2 gas to liquid at 46 ^oC.
12. How much heat must be supplied to 35 g of ice at -26 ^oC to convert it to steam at 148 ^oC? Specific heats: ice = $2.0\ J \cdot g^{-1} \cdot {}^oC^{-1}$; water = $4.2\ J \cdot g^{-1} \cdot {}^oC^{-1}$; steam = $2.0\ J \cdot g^{-1} \cdot {}^oC^{-1}$. The molar heat of fusion of water at 273 K is $\Delta H_{273} = 6.01\ kJ \cdot mol^{-1}$, and the molar heat of vaporization of water at 373 K is $\Delta H_{373} = 40.7\ kJ \cdot mol^{-1}$.
13. Use the information in the preceding exercise to answer the following:
   a) What mass of ice can be melted at 0 ^oC by 35.0 kJ of heat?
   b) What mass of water can be vaporized at 100 ^oC by 35.0 kJ of heat?
14. Mercury has the following physical properties: melting point = -39 ^oC, boiling point = 357 ^oC, heat of fusion = 2.33 $kJ \cdot mol^{-1}$, heat of vaporization = $284\ J \cdot g^{-1}$, specific heat of liquid = $0.139\ J \cdot g^{-1} \cdot {}^oC^{-1}$. Calculate ΔH for the conversion of 100. g of solid mercury at its freezing point to mercury vapor at its boiling point.
15. Determine ΔH, *q*, *w*, and ΔE for the evaporation of 0.10 mol CCl_4 at 298 K and 1atm pressure?
16. Determine ΔH, *q*, *w*, and ΔE at 298 K and 1 atm pressure for the reaction of 9.184 g of $NH_3(g)$ with excess HCl(g) to produce $NH_4Cl(s)$.

17. Indicate $\Delta H > \Delta E$, $\Delta H \sim \Delta E$, or $\Delta H < \Delta E$ for each of the following processes:

a) condensing steam **b)** melting ice

c) heating a gas at constant pressure

d) a solid decomposes into two gases at constant volume

18. The combustion of one cubic foot of natural gas produces 1000 kJ of heat. Assume 60% efficiency for the heat transfer and determine how many cubic feet of natural gas must be burned to raise the temperature of 40 gallons of water from 20.0 ºC to 90.0 ºC. Note: 1 gal = 3.79 L = 4 qt

19. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.

a) evaporation of 0.80 g of CH_3OH

b) decomposition of 3.2 g of $CaCO_3(s)$ to $CaO(s)$ and $CO_2(g)$

c) reaction of 4.0 g of $H_2(g)$ with excess $N_2(g)$ to produce $NH_3(g)$

d) reaction of 12 g of $NH_3(g)$ with excess $HCl(g)$ to produce $NH_4Cl(s)$

20. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.

a) the condensation of 16.0 g of water

b) the reaction of 7.5 g $Na(s)$ and 12.0 g $Cl_2(g)$ to produce $NaCl(s)$

c) the decomposition of 12.6 g $KClO_3$ into $KCl(s)$ and $O_2(g)$

d) 6.0 g of $H_2(g)$ reacts with 4.0 g of $CO_2(g)$ to form $H_2O(g)$ and $CO(g)$.

ENTHALPY AND ENTHALPIES OF FORMATION

21. Determine the enthalpy change for each of the processes in Exercise 19.

22. Determine the enthalpy change for each of the processes in Exercise 20.

23. Write the chemical equation for the reaction corresponding to the standard enthalpy of formation of N_2O_5 (g), and determine its value from the following thermochemical data:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\quad \Delta H^o = -114.1$ kJ

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$ $\quad \Delta H^o = -110.2$ kJ

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\quad \Delta H^o = +180.5$ kJ

24. Given the following thermodynamic data:

$2Fe(s) + {}^3/_2O_2(g) \rightarrow Fe_2O_3(s)$ $\quad \Delta H^o = -823$ kJ

$3\,Fe(s) + 2\,O_2(g) \rightarrow Fe_3O_4(s)$ $\quad \Delta H^o = -1120.$ kJ

Calculate the ΔH^o for: $3Fe_2O_3(s) \rightarrow 2Fe_3O_4(s) + {}^1/_2O_2(g)$

25. How are the heat of combustion of scandium and the heat of formation of Sc_2O_3 related?

26. Write the formation reaction for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.

a) $NH_4NO_3(s)$ **b)** $CH_3I(g)$ **c)** $FeO(s)$ **d)** $Hg_2Cl_2(s)$

27. Write the formation reaction for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.

a) $B_2H_6(g)$ **b)** $SO_2(g)$ **c)** $PF_3(g)$ **d)** $NaCl(s)$

28. Magnesium burns with a brilliant white light. How much heat is released when a 0.75 g magnesium ribbon is burned?

29. How much heat is liberated when a 1.00×10^3 kg of aluminum reacts with oxygen at 25 ^oC and 1 atm?

30. The heat of combustion of toluene, $C_7H_8(l)$, is -3910.3 $kJ \cdot mol^{-1}$. What is the enthalpy of formation of toluene?

31. The heat of formation of $OF_2(g)$ is 24.7 kJ/mol, that of $Cl_2O(g)$ is 80.3 kJ/mol, and that of $ClF_3(l)$ is -189.5 kJ·mol^{-1}.

a) Determine the heat of formation of ClF(g) given the following thermochemical equation:
$2ClF(g) + O_2(g) \rightarrow Cl_2O(g) + OF_2(g) \quad \Delta H^o = 206$ kJ

b) Determine the standard enthalpy change for the following reaction.
$2ClF_3(l) + 2O_2(g) \rightarrow Cl_2O(g) + 3OF_2(g)$

32. Use the data in Appendix B and the following thermochemical equation to determine the enthalpy of formation of $MgCO_3(s)$.
$MgCO_3(s) + 2HCl(g) \rightarrow MgCl_2(s) + CO_2(g) + H_2O(l) \qquad \Delta H^o = -24$ kJ

33. The reaction of quicklime (CaO) with water produces slaked lime [$Ca(OH)_2$]. The reaction of quicklime with water is highly exothermic:
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s). \qquad \Delta H = -350.$ kJ

a) What is the heat of reaction per gram of CaO?

b) How much heat is released when 25.0 kg of slaked lime is produced?

34. C_2H_6 is ethane, a component of natural gas. All of the heat from the complete combustion of 8.506 mmol C_2H_6 gas at 298 K is transferred to 1.000 kg of water that is initially at 25.00 °C. Determine the final temperature of the water if the combustion is carried out at

a) constant pressure **b)** constant volume.

35. Use the data in Appendix B to determine ΔH^o of the following reactions.

a) $Pb^{2+}(aq) + 2Br^{1-}(aq) \rightarrow PbBr_2(s)$

b) $NaCl(s) \rightarrow Na^{1+}(aq) + Cl^{1-}(aq)$

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

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

e) $C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

36. Use the data in Appendix B to determine ΔH^o for each of the following reactions:

a) $Ag_2O(s) + H_2(g) \rightarrow 2Ag(s) + H_2O(l)$

b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

c) $2Ag^{1+}(aq) + Pb(s) \rightarrow 2Ag(s) + Pb^{2+}(aq)$

d) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

e) $CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

37. Determine the heat liberated in the reaction of 5.0 g of Al and 20.0 g of Fe_2O_3 at 25 °C to produce Fe and Al_2O_3. The reaction, which is known as the thermite reaction, is so exothermic that it was used to weld railroad ties because the iron is produced in the molten state.

BOND ENERGIES

Use the data in Appendix B in Exercises 38-44.

38. Determine the P-H and Si-H bond energies.

39. Determine the Ti-Cl and Na-Cl bond energies.

40. What is the average O-O bond energy in O_3? How does it compare to the O-O and O=O bond energies in Table 3.3?

41. What is the O-O bond energy in H_2O_2. What can you conclude about the O-O bond order in H_2O_2 based on its bond energy?

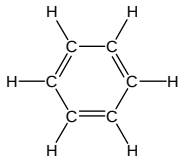
42. Determine N-O bond energy in NOCl (O is central atom). Based on your answer and the tabulated bond energies in Table 3.2, what is the bond order of the N-O bond in NOCl?

43. What is the N-N bond energy in N_2O_4, which is two NO_2 units bound through the N-N bond?

44. What is the C-H bond energy in HCN?

45. Use the data in Appendix B and the C-H bond energy in Table 3.3 to determine the average C-C bond energy in benzene (structure given below). How does this value compare to the average of a single bond and a double bond, the result expected from the Lewis structure? The difference is due to the fact that the pi system is delocalized that makes it more stable.

Benzene (C_6H_6) :



46. Use the bond energies given in Table 3.3 to estimate the enthalpy of combustion at 298 K for each of the following organic compounds. Remember that water is a liquid at 298 K.

a) $H_3C\text{-}CH_3(g)$ **b)** $H_2C{=}CH_2(g)$ **c)** $HC{\equiv}CH(g)$

47. Use the data in Appendix B and the information given in Exercise 31 to determine values for the O-Cl and O-F bond energies.

48. Use bond energies to estimate the enthalpy change of each of the following gas-phase reactions:

a) $H_2C{=}CH_2(g) + HC{\equiv}N(g) \rightarrow H_3C\text{-}CH_2\text{-}C{\equiv}N(g)$

b) $2NO_2(g) \rightarrow N_2O_4(g)$

c) $CH_3F(g) + HCl(g) \rightarrow CH_3Cl(g) + HF(g)$

49. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances:

a) $NF_3(g)$ **b)** $H_2N\text{-}NH_2(g)$

50. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances. Note that the standard state of C is graphite not a gas.

a) $F_2C{=}CH_2(g)$ **b)** $CH_3Cl(g)$

CALORIMETRY

51. What is the final temperature of a mixture prepared by adding 12.4 g of Fe at 89.4 ^oC to 25.6 mL of water in an insulated container at 18.6 ^oC? The density of water is 1.00 $g{\cdot}mL^{-1}$ and s_{Fe} = 0.44 $J{\cdot}g^{-1}{\cdot}C^{-1}$.

52. What is the specific heat of tin if a mixture of 100.0 g of Cu at 10.0 ^oC and 200.0 g of Sn at 120.0 ^oC reach thermal equilibrium at a temperature of 69.0 ^oC? The specific heat of copper is 0.38 $J{\cdot}g^{-1}{\cdot}{}^oC^{-1}$.

53. At what temperature would thermal equilibrium be reached in a mixture prepared by adding 1.00 g of N_2 at 0 ^oC to 1.00 g of Kr at 200 ^oC in an insulated container? See Table 3.1 for specific heats.

54. A 14.6-g sample of beryllium at 96.7 ^oC is placed into 35.0 mL of water at 20.2 ^oC in an insulated container. The temperature of the water at thermal equilibrium is 32.0 ^oC. What is the specific heat of beryllium? Assume a density of 1.00 $g{\cdot}mL^{-1}$ for water.

55. A 35.4-g metal bar at 97.6 ^oC is placed into an insulated flask containing 75.0 g of ice at 0 ^oC. What is the specific heat of the metal if cooling the bar to 0 ^oC melted 2.36 g of the ice? The heat of fusion of water at 0 ^oC is 6.01 $kJ{\cdot}mol^{-1}$.

56. A 0.186-mole sample of NaX is dissolved in 275 mL of water in an insulated container at 23.7 ^oC. After the solid dissolves, the temperature of the water is 19.2 ^oC. What is the heat of solution of NaX? The solution process is $NaX(s) \rightarrow NaX(aq)$.

57. 25.0 mL of 0.12 M HX(aq) at 22.0 ^oC and 25.0 mL of 0.12 M NaOH(aq) at 22.0 ^oC are mixed. After reaction, the temperature of the mixture is 27.6 ^oC. What is the heat of neutralization; $HX(aq) + NaOH(aq) \rightarrow H_2O(l) + NaX(aq)$? Assume a specific heat of 4.18 $J{\cdot}g^{-1}{\cdot}{}^oC^{-1}$ and a density of 1.00 $g{\cdot}mL^{-1}$ for all solutions.

58. What is the heat of combustion of the sugar D-sorbose ($C_6H_{12}O_6$) at 298 K if combustion of 0.0187 moles of the solid caused a 6.56 ^oC rise in temperature in a bomb calorimeter with a heat capacity of 7.97 $kJ{\cdot}{}^oC^{-1}$?

59. The combustion of 0.3268 g of oleic acid, $C_{18}H_{34}O_2(l)$, resulted in a temperature rise of 3.462 ^oC in a constant pressure calorimeter with a heat capacity of 3.715 $kJ \cdot {}^oC^{-1}$.

a) What is the standard enthalpy of combustion of oleic acid at 298 K?

b) What is the standard heat of formation of oleic acid at 298 K?

60. What is the heat capacity of a bomb calorimeter if the combustion of 2.360 mmol of salicylic acid ($C_7H_6O_3(s)$, ΔH_{comb} = -3022 $kJ \cdot mol^{-1}$) increases the temperature of the calorimeter by 2.612 ^oC?

61. Burning 117.7 mg of naphthalene, $C_{10}H_8(s)$, the active ingredient in mothballs, results in a temperature rise of 3.275 ^oC in a bomb calorimeter with a heat capacity of 1.444 $kJ \cdot {}^oC^{-1}$.

a) Write the balanced equation for the combustion at 25 ^oC.

b) What is ΔE_{comb} of $C_{10}H_8(s)$ in $kJ \cdot mol^{-1}$?

c) What is ΔH_{comb} of $C_{10}H_8(s)$ at 298 K?

d) What is ΔH_f of $C_{10}H_8(s)$ at 298 K?

62. When 1.020 g of ethanol was burned in oxygen in a bomb calorimeter containing 2400. g of water, the temperature of the water rose from 22.46 ^oC to 25.52 ^oC. What is the enthalpy change, ΔH, for the combustion of 1 mol of ethanol?
$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

63. Combustion of 2.000 g of propane (C_3H_8) in a bomb calorimeter produces 105.0 kJ of heat at 25 ^oC. What is the heat of combustion of propane?

64. ΔE_{comb} = -8942.6 $kJ \cdot mol^{-1}$ for chrysene, $C_{18}H_{12}(s)$, at 25 ^oC. When any hydrocarbon (such as chrysene) is burned completely, the products are CO_2 and H_2O.

a) Write and balance a chemical equation for the combustion of chrysene and determine the value of Δn_g for the combustion reaction.

b) Determine the value of ΔH per mole for the combustion of chrysene at 298 K.

c) When 1.1492 g of chrysene, $C_{18}H_{12}(s)$ (M_m= 228.29 $g \cdot mol^{-1}$), was burned in a bomb calorimeter, the temperature of the water rose from 23.00 ^oC to 27.72 ^oC. What is the heat capacity of this calorimeter.

65. When 0.8681 g of cetyl palmitate ($C_{32}H_{64}O(s)$, (M_m= 464.86 $g \cdot mol^{-1}$) was burned in a calorimeter having a heat capacity of 9.535 $kJ \cdot {}^oC^{-1}$, the temperature rose by 3.99 ^oC. Calculate the standard enthalpy change per mole, ΔH^o at 298 K for the combustion of cetyl palmitate.

FOOD AS FUEL

66. The serving size listed on a bag of tortilla chips is 1 oz (28 g or ~ 6 chips), which contains 6 g or fat, 19 g of carbohydrates and 2 g of protein. What are the total number of dietary calories in one serving of chips?

67. A package of cookies from the vending machine has the following dietary information for a serving size of 6 cookies: 10. g of fat, 25 g of carbohydrates, and 6 g of protein. What are the total number of dietary calories in a serving?

68. The nutrition label on a jar of maple syrup indicates that a serving (60 mL) contains 200 Calories. Assume that all of the calories come from sugars (carbohydrates) and determine the number of grams of sugar that are in one serving of maple syrup.

MISCELLANEOUS PROBLEMS

69. Use Hess' law of heat summation and the heats of *combustion* given below to determine the heat of hydrogenation of 1,3-butadiene (C_4H_6)?

$C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}$ $\Delta H = ?$

ΔH_{comb} -2543.5 -285.85 -2878.6 $kJ \cdot mol^{-1}$

70. What are ΔE, q, w and ΔH for the evaporation of 10.0 g of $Br_2(l)$ at 298 K and 1 atm?

71. Bicycle riding at 13 mph consumes 2800 kJ per hour for a 150 lb. person. How many miles must this person ride to lose 1 lb. of body fat? Hint: body fat contains 39 $kJ \cdot g^{-1}$ of stored energy?

72. Kerosene is a mixture of organic compounds that has a density of 0.749 g/mL and a heat of combustion of -88 $kJ \cdot g^{-1}$. Note that 1 gal = 3.79 L = 4 qt.

a) How much heat is liberated when 0.75 gal of kerosene is burned?

b) Assume that all of the heat of the combustion is transferred to the water and determine how many quarts of kerosene must be burned to take 1.0 gal of water from 25 °C to its boiling point. Give two reasons why the actual amount of heat required on a stove is much higher than the calculated value.

73. Use the following thermochemical equations:

i) $MnO_2(s) + CO(g) \rightarrow MnO(s) + CO_2(g)$ $\Delta H^o = -151$ kJ

ii) $Mn_3O_4(s) + CO(g) \rightarrow 3MnO(s) + CO_2(g)$ $\Delta H^o = -54$ kJ

iii) $3Mn_2O_3(s) + CO(g) \rightarrow 2Mn_3O_4(s) + CO_2(g)$ $\Delta H^o = -142$ kJ

to determine ΔH^o for each of the following reactions:

a) $2MnO_2(s) + CO(g) \rightarrow 2Mn_2O_3(s) + CO_2(g)$

b) $Mn_2O_3(s) + CO(g) \rightarrow 2MnO(s) + CO_2(g)$

c) $MnO(s) + MnO_2(s) \rightarrow Mn_2O_3(s)$

d) $Mn_2O_3(s) + MnO(s) \rightarrow Mn_3O_4(s)$

74. Dissolving 8.65 g NH_4NO_3 in 50.0 mL water in an insulated container resulted in a temperature drop of 13.3 °C. What is the heat of solution of ammonium nitrate?

75. Ammonium nitrate is a common ingredient in fertilizers that can also be used to make explosives because it decomposes as follows:

$2NH_4NO_3(s) \rightarrow 2N_2(g) + O_2(g) + 4H_2O(g)$ $\Delta H = -236$ kJ.

The following questions deal with the decomposition of 12.0 g of NH_4NO_3.

a) How much heat is liberated under standard conditions?

b) How much work would be done by the gases at 300. °C?

c) What volume of gas would be produced at 1.00 atm and 300. °C?

76. Benzoic acid ($HC_7H_5O_2$, $\Delta E_{comb} = -26.38$ $kJ \cdot g^{-1}$) is a common standard used to determine the heat capacities of bomb calorimeters. The following combustion data were collected in an experiment.

1. Combustion of 1.066 g of solid benzoic acid resulted in a rise of 2.860 °C in a bomb calorimeter.
2. Combustion of 0.7832 g of liquid toluene (C_7H_8) caused the temperature of the same bomb calorimeter to rise by 3.376 °C

Use the above data and 25 °C as the temperature of the experiment to determine the heat of formation of liquid toluene at 298 K.