

## Chapter 3

# First Law of Thermodynamics

1. What state functions correspond to the heat absorbed at constant P and the heat absorbed at constant V?  
 $\Delta H$  is the heat absorbed at constant pressure.  $\Delta E$  is the heat absorbed at a constant volume.

3. Classify each of the following processes as endothermic or exothermic:

- |                                   |                                       |                                      |
|-----------------------------------|---------------------------------------|--------------------------------------|
| a) melting a solid<br>endothermic | b) combustion of butane<br>exothermic | c) condensing a liquid<br>exothermic |
| d) photosynthesis<br>endothermic  | e) a battery reaction<br>exothermic   |                                      |

5. What is the energy change of the system if the system:

- a) absorbs 50. J of heat and does 50. J of work?

System absorbs heat, so  $q = +50$  J. The system does work, so  $w = -50$  J,  $\Delta E = q + w = 50$  J + (-50 J) = 0 J

- b) releases 20. J of heat and has 415 J of work done on it?

The system releases heat, so  $q = -20$  J. Work is done on the system, so  $w = +415$  J.

$$\Delta E = q + w = -20 \text{ J} + 415 \text{ J} = 395 \text{ J}$$

7. What is  $\Delta E$  of a gas that gives off 312 J of heat while being compressed 862 ml by a pressure of 1.64 atm? What are  $\Delta E_{\text{surr}}$  and  $\Delta E_{\text{univ}}$  for the process?

The system is compressed, so  $\Delta V$  is negative and  $w = -P_{\text{op}} \Delta V = -(1.64 \text{ atm})(-0.862 \text{ L}) = 1.41 \text{ L}\cdot\text{atm}$ .

Convert L-atm to joules:

$$w = (1.41 \text{ L}\cdot\text{atm})(101.3 \text{ J}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}) = 143 \text{ J}$$

Heat is given off, so  $q = -312$  J. Use Equation 3.5 and the values of  $q$  and  $w$ :  $\Delta E = q + w = -312 + 143 = -169$  J

Therefore, the energy of the system decreases by 169 J. As shown in Equation 3.4,  $\Delta E_{\text{surr}} = -\Delta E = 169$  J

$\Delta E_{\text{univ}} = 0$  (The First Law of Thermodynamics, Eq. 3.3)

9. Determine the mass of octane ( $\text{C}_8\text{H}_{18}$ ,  $\Delta H_{\text{comb}} = -5500. \text{ kJ/mol}$ ) must be combusted to yield the amount of energy equivalent to:

$$\text{First, convert the heat of combustion for octane to kJ/g: } \frac{5500. \text{ kJ}}{\text{mol C}_8\text{H}_{18}} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} = 48.15 \frac{\text{ kJ}}{\text{ g C}_8\text{H}_{18}}$$

then, use the above to convert from the given energy into the mass of octane.

- a) 3.1 kJ, the kinetic energy of a 220. lb. linebacker running at a speed of 40. yd in 4.7 seconds.

$$3.1 \text{ kJ} \times \frac{1 \text{ g C}_8\text{H}_{18}}{48.15 \text{ kJ}} = 0.064 \text{ g C}_8\text{H}_{18}$$

- b) 17 J, the potential energy of a 5 lb bag of sugar on top of a 30. inch high counter, 17 J.

$$17 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{1 \text{ g C}_8\text{H}_{18}}{48.15 \text{ kJ}} = 3.5 \times 10^{-4} \text{ g C}_8\text{H}_{18}$$

- c) the heat required to raise the temperature of 1 quart of water from 25 °C to its boiling point, 320 kJ.

$$320. \text{ kJ} \times \frac{1 \text{ g C}_8\text{H}_{18}}{48.15 \text{ kJ}} = 6.65 \text{ g C}_8\text{H}_{18}$$

11. The heat of vaporization of  $\text{CS}_2$  at its normal boiling point of 46 °C is 26.7 kJ/mole. Calculate  $\Delta H$  for the condensing 41.2 g of  $\text{CS}_2$  gas to liquid at 46 °C.

Condensation is the reverse of vaporization, so the enthalpy of condensation has the same magnitude but is opposite in sign to the heat of vaporization. Consequently,  $\Delta H_{\text{cond}} = -26.7$  kJ/mol. We simply need to multiply the moles of  $\text{CS}_2$  by the heat of condensation to obtain the  $\Delta H$  for the process.

$$41.2 \text{ g CS}_2 \times \frac{1 \text{ mol CS}_2}{76.143 \text{ g CS}_2} = 0.541 \text{ mol CS}_2$$

Convert the moles to units of kJ using the given heat of condensation:  $0.541 \text{ mol CS}_2 \times \frac{-26.7 \text{ kJ}}{\text{mol CS}_2} = -14.4 \text{ kJ}$

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13. Use the information in the preceding exercise to answer the following:

a) What mass of ice could be melted at 0 °C by 35.0 kJ of heat?

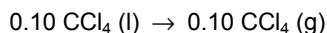
$$\frac{35.0 \text{ kJ}}{6.01 \text{ kJ/mol}} \times 18.0 \text{ g/mol} = 105 \text{ g ice}$$

b) What mass of water could be vaporized at 100 °C by 35.0 kJ of heat?

$$\frac{35.0 \text{ kJ}}{40.7 \text{ kJ/mol}} \times 18.0 \text{ g/mol} = 15.5 \text{ g water}$$

15. Determine  $\Delta H$ ,  $q$ ,  $w$ , and  $\Delta E$  for the evaporation of 0.10 mol  $\text{CCl}_4$  at 298K and 1atm pressure?

Use the heats of formation listed in Appendix G to calculate  $\Delta H$  for the evaporation.



$$\Delta H = c_{\text{gas}}\Delta H_f^\circ(\text{gas}) - c_{\text{liquid}}\Delta H_f^\circ(\text{liquid}) = (0.10 \text{ mol})(-103 \text{ kJ/mol}) - (0.10 \text{ mol})(-135 \text{ kJ/mol}) = 3.2 \text{ kJ}$$

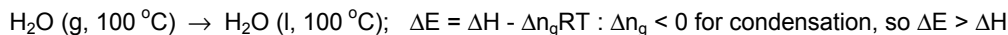
At constant pressure,  $q = \Delta H = 3.2 \text{ kJ}$

$$w = -\Delta n_g RT = -(0.10 - 0)(8.314 \text{ J/(mol}\cdot\text{K)})(298 \text{ K}) = -2.5 \times 10^2 \text{ J} = -0.25 \text{ kJ (work is done by the gas)}$$

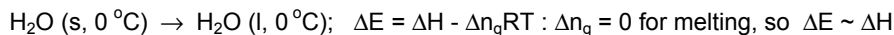
$$\Delta E = q + w = 3.2 - 0.2 = 3.0 \text{ kJ}$$

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

$$\Delta E = \Delta H - P\Delta V : \quad \Delta V > 0 \text{ for heating at constant P, so } \Delta E < \Delta H$$

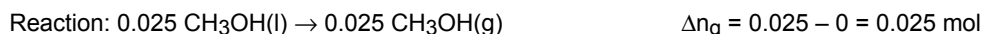
d) a solid decomposes into two gases at constant volume

$$\Delta E = \Delta H - P\Delta V : \quad \Delta V = 0, \text{ so } \Delta E = \Delta H.$$

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  $\text{CH}_3\text{OH}$

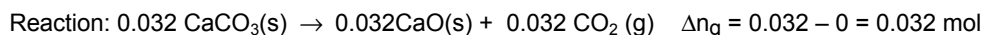
$$\text{moles of limiting reactant: } 0.80 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.042 \text{ g CH}_3\text{OH}} = 0.025 \text{ mol CH}_3\text{OH}$$



$$w = -(0.025 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = -62 \text{ J}. \quad 62 \text{ J of work is done by the gas.}$$

b) decomposition of 3.2 g of  $\text{CaCO}_3(\text{s})$  to  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$

$$\text{moles of limiting reactant: } 3.2 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} = 0.032 \text{ mol CaCO}_3$$



$$w = -(0.032 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = -79 \text{ J}. \quad 79 \text{ J of work is done by the gas.}$$

c) reaction of 4.0 g of  $\text{H}_2(\text{g})$  with excess  $\text{N}_2(\text{g})$  to produce  $\text{NH}_3(\text{g})$

$$\text{moles of limiting reactant: } 4.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} = 2.0 \text{ mol H}_2$$

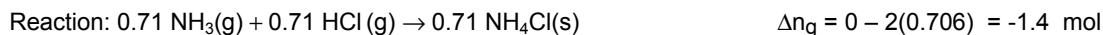


$$w = -(-1.3 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = 3.3 \times 10^3 \text{ J} = 3.3 \text{ kJ of work is done on the gas.}$$

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- d) reaction of 12 g of  $\text{NH}_3(\text{g})$  with excess  $\text{HCl}(\text{g})$  to produce  $\text{NH}_4\text{Cl}(\text{s})$

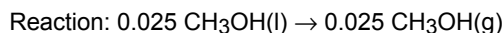
$$\text{moles of limiting reactant: } 12 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17 \text{ g NH}_3} = 0.706 \text{ mol NH}_3$$



$$w = -(-1.4 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) = 3.5 \times 10^3 \text{ J} = 3.5 \text{ kJ of work is done on the gas.}$$

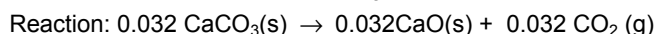
21. Determine the amount of heat given off or absorbed by each of processes in Exercise 19.

- a) evaporation of 0.80 g of  $\text{CH}_3\text{OH}$



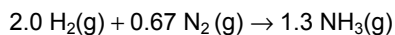
$$q = (0.025 \text{ mols gas})(-201.2 \text{ kJ/mol gas}) - (0.025 \text{ mols liquid})(-237.6 \text{ kJ/mol liquid}) = 0.91 \text{ kJ absorbed}$$

- b) decomposition of 3.2 g of  $\text{CaCO}_3(\text{s})$  to  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$



$$q = (0.032 \text{ mol CaO})(-635.1) + (0.032 \text{ mol CO}_2)(-393.51 \text{ kJ/mol}) - (0.032 \text{ mol CaO})(1206.9 \text{ kJ/mol}) = 5.7 \text{ kJ absorbed}$$

- c) reaction of 4.0 g of  $\text{H}_2(\text{g})$  with excess  $\text{N}_2(\text{g})$  to produce  $\text{NH}_3(\text{g})$



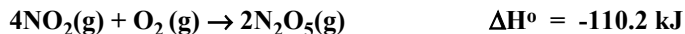
$$q = (1.3 \text{ mol NH}_3)(-46.11 \text{ kJ/mol}) = -61.48 \text{ kJ} \quad 61.48 \text{ kJ are released.}$$

- d) reaction of 12 g of  $\text{NH}_3(\text{g})$  with excess  $\text{HCl}(\text{g})$  to produce  $\text{NH}_4\text{Cl}(\text{s})$

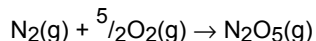


$$q = (0.71 \text{ mol})\{-314.4 - (-46.11) - (-92.30)\} \text{ kJ/mol} = -1.2 \times 10^2 \text{ kJ} \quad 120 \text{ kJ of heat are released.}$$

23. Write the chemical equation for the reaction corresponding to the standard enthalpy of formation of  $\text{N}_2\text{O}_5(\text{g})$ , and determine its value from the following thermochemical data:



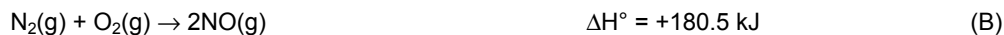
The formation reaction of  $\text{N}_2\text{O}_5$  is



Thus, our goal is to use the three equations above to generate the equation above. Rxn. 2 is an excellent place to start because it has  $\text{N}_2\text{O}_5$  as a product. The desired product is  $\text{N}_2\text{O}_5$ , rather than  $2\text{N}_2\text{O}_5$ , so Rxn. 2 and its  $\Delta H$  value are multiplied by  $\frac{1}{2}$  to obtain equation A:



The reactants must be  $\text{N}_2$  and  $\text{O}_2$ ; therefore, Rxn. 3 and its  $\Delta H$  value may be used as is.



The unwanted components in Eq's A and B are the reactant  $2 \text{NO}_2$  (Eq. A) and the product  $2 \text{NO}$  (Eq. B). Therefore, Eq. 1 and its  $\Delta H$  value can be used as is to eliminate these unwanted components.



Adding Rxn's A, B, and C and their  $\Delta H$  values results in the desired equation and the numerical value of the standard heat of formation of  $\text{N}_2\text{O}_5$ .



The heat of formation of  $\text{N}_2\text{O}_5(\text{g})$  is 11.3 kJ/mol.

25. How are the heat of combustion of scandium and the heat of formation of  $\text{Sc}_2\text{O}_3$  related?

The heat of combustion is the heat absorbed when 1 mole of scandium reacts:  $1 \text{ Sc} + \frac{3}{4}\text{O}_2 \rightarrow \frac{1}{2} \text{ Sc}_2\text{O}_3$

The heat of formation is defined as the heat absorbed when 1 mole of  $\text{Sc}_2\text{O}_3$  forms:  $2 \text{ Sc} + \frac{3}{2} \text{ O}_2 \rightarrow \text{Sc}_2\text{O}_3$

Thus, the heat of formation of  $\text{Sc}_2\text{O}_3$  is twice the heat of combustion of Sc.

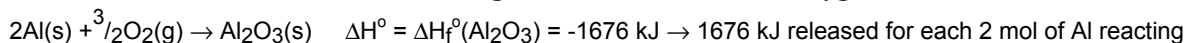
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27. Write the formation reaction for each of the following substances at 298 K. Refer to Appendix G to determine the standard states.

- a)  $\text{B}_2\text{H}_6(\text{g})$        $2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g})$   
b)  $\text{SO}_2(\text{g})$        $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$   
c)  $\text{PF}_3(\text{g})$        $\text{P}(\text{s}) + \frac{3}{2}\text{F}_2(\text{g}) \rightarrow \text{PF}_3(\text{g})$   
d)  $\text{NaCl}(\text{s})$        $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$

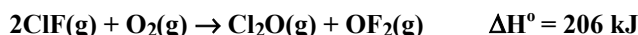
29. How much heat is liberated when a  $1.00 \times 10^3$  kg of aluminum reacts with oxygen at  $25^\circ\text{C}$  and 1atm?



$$\Delta H = 1.00 \times 10^3 \text{ kg Al} \times \frac{10^3 \text{ g Al}}{1 \text{ kg Al}} \times \frac{\text{mol Al}}{26.98 \text{ g Al}} \times \frac{1676 \text{ kJ released}}{2 \text{ mol Al}} = 3.11 \times 10^7 \text{ kJ released}$$

31. The heat of formation of  $\text{OF}_2(\text{g})$  is  $24.7 \text{ kJ/mol}$ , that of  $\text{Cl}_2\text{O}(\text{g})$  is  $80.3 \text{ kJ/mol}$ , and that of  $\text{ClF}_3(\text{l})$  is  $-189.5 \text{ kJ/mol}$ .

a) Determine the heat of formation of  $\text{ClF}$  given the following thermochemical equation:



$$\Delta H^\circ = \Delta H_f(\text{Cl}_2\text{O}) + \Delta H_f(\text{OF}_2) - 2\Delta H_f(\text{ClF})$$

$$206 \text{ kJ} = (1 \text{ mol})(80.3 \text{ kJ/mol}) + (1 \text{ mol})(24.7 \text{ kJ/mol}) - (2 \text{ mol})\Delta H_f$$

$$(2 \text{ mol})\Delta H_f = 80.3 + 24.7 - 206 = -101 \text{ kJ}, \text{ so } \Delta H_f = -51 \text{ kJ/mol}$$

b) What is the enthalpy of the following reaction?  $2\text{ClF}_3(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g}) + 3\text{OF}_2(\text{g})$

$$\Delta H = 1\Delta H_f(\text{Cl}_2\text{O}) + 3\Delta H_f(\text{OF}_2) - 2\Delta H_f(\text{ClF}_3) = (1 \text{ mol})(80.3 \text{ kJ/mol}) + (3 \text{ mol})(24.7 \text{ kJ/mol}) - (2 \text{ mol})(-189.5 \text{ kJ/mol})$$

$$\Delta H = 533.4 \text{ kJ}$$

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

a) What is the heat of reaction per gram of  $\text{CaO}$ ?

$\Delta H = -350 \text{ kJ}$  per mole of  $\text{CaO}$  that reacts, so we use molar mass of  $\text{CaO}$  to convert to a per gram basis.

$$\frac{-350. \text{ kJ}}{1 \text{ mol CaO}} \times \frac{1 \text{ mol CaO}}{56.077 \text{ g CaO}} = -6.24 \frac{\text{kJ}}{\text{g CaO}}$$

b) How much heat is released when  $25.0 \text{ kg}$  of slaked lime is produced?

Use the result of Part a to convert grams of slaked lime into kJ. Recall that the minus sign means that  $6.24 \text{ kJ}$  of heat are produced for each gram of  $\text{CaO}$  that reacts.

$$25.0 \text{ kg Ca}(\text{OH})_2 \times \frac{1000 \text{ g Ca}(\text{OH})_2}{1 \text{ kg Ca}(\text{OH})_2} \times \frac{6.24 \text{ kJ}}{\text{g Ca}(\text{OH})_2} = 1.18 \times 10^5 \text{ kJ produced}$$

35. Use the data in Appendix G to determine  $\Delta H^\circ$  of the following reactions.

a)  $\text{Pb}^{2+}(\text{aq}) + 2 \text{Br}^{-}(\text{aq}) \rightarrow \text{PbBr}_2(\text{s})$

$$\Delta H^\circ = 1\Delta H_f(\text{PbBr}_2) - 1\Delta H_f(\text{Pb}^{2+}) - 2\Delta H_f(\text{Br}^{-}) =$$

$$(1 \text{ mol})(-277.4 \text{ kJ/mol}) - (1 \text{ mol})(1.6 \text{ kJ/mol}) - (2 \text{ mol})(-120.0 \text{ kJ/mol}) = -37.2 \text{ kJ}$$

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

$$\Delta H^\circ = 1\Delta H_f(\text{Na}^{+}) + 1\Delta H_f(\text{Cl}^{-}) - 1\Delta H_f(\text{NaCl}) = 1(-240.1) + 1(-167.2) - 1(411.1) = 3.8 \text{ kJ}$$

c)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$$\Delta H^\circ = 1\Delta H_f(\text{CO}_2) + 1\Delta H_f(\text{CaO}) - 1\Delta H_f(\text{CaCO}_3) = 1(-393.51) + 1(-635.1) - 1(-1206.9) = 178.3 \text{ kJ}$$

d)  $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

$$\Delta H^\circ = 1\Delta H_f(\text{HCl}) + 1\Delta H_f(\text{NH}_3) - 1\Delta H_f(\text{NH}_4\text{Cl}) = 1(-92.30) + 1(-46.11) - 1(-314.4) = 176.0 \text{ kJ}$$

e)  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

$$\Delta H^\circ = 3\Delta H_f(\text{H}_2\text{O}) + 2\Delta H_f(\text{CO}_2) - \Delta H_f(\text{C}_2\text{H}_5\text{OH}) - 2\Delta H_f(\text{O}_2) = 3(-285.83) + 2(-393.51) - 1(-277.7) = -1366.8 \text{ kJ}$$

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37. Thermite is a mixture of Al and Fe<sub>2</sub>O<sub>3</sub> that can be ignited with a magnesium ribbon fuse to form Fe and Al<sub>2</sub>O<sub>3</sub>. The thermite reaction is so exothermic that the iron is produced in the molten state. At one time, this reaction was used to weld railroad tracks. How much heat is liberated in the reaction of 5.0 g of Al and 20.0 g of Fe<sub>2</sub>O<sub>3</sub> at 25 °C?

Set up a balanced equation:  $2 \text{Al}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow 2 \text{Fe}(s) + \text{Al}_2\text{O}_3(s)$

Next, use heats of formation to obtain the enthalpy change for the reaction. Note that we are told that heat is liberated, so the enthalpy change is negative.

$$\Delta H = 2\Delta H_f^\circ(\text{Fe}) + 1\Delta H_f^\circ(\text{Al}_2\text{O}_3) - 2\Delta H_f^\circ(\text{Al}) - 1\Delta H_f^\circ(\text{Fe}_2\text{O}_3) = 2(0) + 1(-1676) - 2(0) - 1(-824.2) = -852 \text{ kJ}$$

Determine the limiting reactant by determining the number of moles of a product that each reactant could produce. We choose heat as the product.

$$5.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.982 \text{ g Al}} \times \frac{852 \text{ kJ}}{2 \text{ mol Al}} = 79 \text{ kJ} \quad 20.0 \text{ g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g Fe}_2\text{O}_3} \times \frac{852 \text{ kJ}}{1 \text{ mol Fe}_2\text{O}_3} = 107 \text{ kJ}$$

Aluminum is the limiting reactant because the reaction of 5.0 g Al results in less product than does 20.0 g Fe<sub>2</sub>O<sub>3</sub>, so 79 kJ of heat would be produced.

39. Determine the Ti-Cl bond energy and NaCl bond energies.

Use heats of formation to determine the atomization energy of the compound that contains only Ti-Cl bonds  
 $\text{TiCl}_4(g) \rightarrow \text{Ti}(g) + 4\text{Cl}(g) \quad \Delta H_{\text{atom}} = 468 + 4(121.7) - (-763.4) = 1718 \text{ kJ}$

Atomization of TiCl<sub>4</sub> requires breaking four Ti-Cl bonds, so  $\Delta H_{\text{atom}} = 1718 \text{ kJ} = 4D_{\text{Ti-Cl}}$

$$D_{\text{Ti-Cl}} = 1718/4 = 430 \text{ kJ/mol}$$

Use heats of formation to determine the atomization energy of the compound that contains only NaCl bonds  
 $\text{NaCl}(g) \rightarrow \text{Na}(g) + \text{Cl}(g) \quad \Delta H_{\text{atom}} = 107.7 + 121.7 - (-181.4) = 410.8 \text{ kJ}$

Atomization of NaCl requires breaking one Na-Cl bond, so  $\Delta H_{\text{atom}} = 410.8 \text{ kJ} = 4D_{\text{Na-Cl}}$

$$D_{\text{Na-Cl}} = 410.8 \text{ kJ/mol}$$

41. What is the O-O bond energy in H<sub>2</sub>O<sub>2</sub>. What can you conclude about the O-O bond order in H<sub>2</sub>O<sub>2</sub> based on its bond energy?

Use heats of formation from Appendix B to determine the atomization energy of gas phase HNO<sub>3</sub>.

$$\text{H}_2\text{O}_2 \rightarrow 2\text{H} + 2\text{O} \quad \Delta H_{\text{atom}} = 2(217.97) + 2(249.17) - (-136.10) = 1070.4 \text{ kJ}$$

Atomization of H<sub>2</sub>O<sub>2</sub> requires breaking two O-H bonds and one O-O bond. The O-H bond energy from Table 3.2 is 463 kJ, so  $1070.4 = 2(463) + D_{\text{O-O}}$ .

$$D_{\text{O-O}} = 1070 - 2(463) = 144 \text{ kJ/mol.}$$

The O-O bond strength reported in Table 3.2 is 142 kJ/mol, so the O-O bond in H<sub>2</sub>O<sub>2</sub> is a single bond.

43. What is the N-N bond energy in N<sub>2</sub>O<sub>4</sub>, which is two NO<sub>2</sub> units bound through the N-N bond?

Although atomization energies can be used, it is simpler to note that  $\Delta H$  for the reaction  $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$  is equal to the N-N bond energy. Thus,  $D_{\text{NN}} = 2\Delta H_f(\text{NO}_2) - \Delta H_f(\text{N}_2\text{O}_4) = 2(33.84) - 9.66 = 58.02 \text{ kJ/mol}$ .

45. Use the data in Appendix B and C-H bond energy in Table 3.2 to determine the average C-C bond energy in benzene (C<sub>6</sub>H<sub>6</sub>, see text for structure).

$$\text{C}_6\text{H}_6 \rightarrow 6\text{C}(g) + 6\text{H}(g) \quad \Delta H_{\text{atom}} = 6\Delta H_f^\circ[\text{C}] + 6\Delta H_f^\circ[\text{H}] - \Delta H_f^\circ[\text{C}_6\text{H}_6] = 6D_{\text{C-C}} + 6D_{\text{C-H}}$$

$$\Delta H_{\text{atom}} = 6(716.681) + 6(217.97) - 82.927 = 5525 \text{ kJ} = 6D_{\text{C-C}} + (6 \text{ mol})(413 \text{ kJ.mol})$$

$$6D_{\text{C-C}} = 5525 - 6(413) = 3045 \text{ kJ}; \quad D_{\text{C-C}} = (3045 \text{ kJ})/(6 \text{ mol}) = 508 \text{ kJ/mol}$$

How does this compare to the average of a single bond and a double bond?

$$\text{Average} = \frac{1}{2}(D_{\text{C-C}} + D_{\text{C=C}}) = \frac{1}{2}(347 + 612) = 480 \text{ kJ, which is 6\% lower.}$$

# First Law of Thermodynamics

## 47. Use the data in Table 3.2 and Exercise 31 to determine values for the O-Cl and O-F bond energies.

Exercise 31 gives the enthalpies of formation of  $\text{OF}_2$  as 24.7 kJ/mol. Applying bond energies to this reaction we obtain

$$\frac{1}{2}\text{O}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{OF}_2 \quad \Delta H = 24.7 \text{ kJ} = \frac{1}{2}D_{\text{O}=\text{O}} + D_{\text{F}-\text{F}} - 2D_{\text{O}-\text{F}} = 0.5(495) + 159 - 2D_{\text{O}-\text{F}} = 406.5 - 2D_{\text{O}-\text{F}}$$

$$2D_{\text{O}-\text{F}} = 24.7 - 406.5 = -381.8 \text{ kJ} \quad \rightarrow \quad D_{\text{O}-\text{F}} = 191 \text{ kJ/mol}$$

Proceed as above with  $\text{OCl}_2$ ,

$$\frac{1}{2}\text{O}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{OCl}_2 \quad \Delta H = 80.37 \text{ kJ} = \frac{1}{2}D_{\text{O}=\text{O}} + D_{\text{Cl}-\text{Cl}} - 2D_{\text{O}-\text{Cl}} = 0.5(495) + 243 - 2D_{\text{O}-\text{Cl}} = 490.5 - 2D_{\text{O}-\text{Cl}}$$

$$2D_{\text{O}-\text{Cl}} = 80.3 - 490.5 = -410.2 \text{ kJ} \quad \rightarrow \quad D_{\text{O}-\text{Cl}} = 205 \text{ kJ/mol}$$

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

Write the formation reaction and then use bond energies to estimate the enthalpy of the reaction.

### a) $\text{NF}_3(\text{g})$

$$\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{F}_2(\text{g}) \rightarrow \text{NF}_3(\text{g}) \quad \Delta H = 0.5 D_{\text{N}=\text{N}} + 1.5D_{\text{F}-\text{F}} - 3D_{\text{N}-\text{F}} = 0.5(941) + 1.5(159) - 3(272) = -107 \text{ kJ}$$

### b) $\text{H}_2\text{N}-\text{NH}_2(\text{g})$

$$\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{H}_2\text{N}-\text{NH}_2(\text{g}) \quad \Delta H = D_{\text{N}=\text{N}} + 2D_{\text{H}-\text{H}} - 4D_{\text{N}-\text{H}} - D_{\text{N}-\text{N}} = 941 + 2(436) - 4(391) - 163 = +86 \text{ kJ}$$

## 51. What is the final temperature of a system prepared by adding 12.4 g of Fe at 89.4 °C to 25.6 mL of water at 18.6 °C? Assume that the density of water is 1.00 g/mL and that the mixture is in an insulated container.

As the system comes to thermal equilibrium, the heat lost by the hot mass (the Fe) will be gained by the cool one (the water):

$$q_{\text{Fe}} = q_{\text{water}}$$

Each heat term can be expressed using specific heats and temperature differences.

$$-ms\Delta T_{\text{Fe}} = ms\Delta T_{\text{water}}$$

$$-(12.4 \text{ g})(0.44 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(T_{\text{final}} - 89.4 \text{ }^\circ\text{C}) = (25.6 \text{ mL})(1.00 \text{ g mL}^{-1})(4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(T_{\text{final}} - 18.6 \text{ }^\circ\text{C})$$

$$5.456(89.4 - T_{\text{final}}) = 107.008(T_{\text{final}} - 18.6)$$

$$487.7664 - 5.456 T_{\text{final}} = 107.008 T_{\text{final}} - 1990.3488$$

$$2478.1152 = 112.464 T_{\text{final}}; \quad T_{\text{final}} = 22.0 \text{ }^\circ\text{C}$$

## 53. At what temperature would thermal equilibrium be reached in a mixture prepared by adding 1.00 g of $\text{N}_2$ at 0 °C to 1.00 g of Kr at 200 °C in an insulated container? See Table 3.1 for specific heats.

The container is insulated, so the heat absorbed by the cooler gas equals the heat given off by the warmer gas.

$$q_{\text{N}_2} = -q_{\text{Kr}} \Rightarrow m_{\text{N}_2} s_{\text{N}_2} \Delta T_{\text{N}_2} = -m_{\text{Kr}} s_{\text{Kr}} \Delta T_{\text{Kr}}$$

At thermal equilibrium, the two gases are at the same temperature,  $T_f$ .

$$\Delta T_{\text{N}_2} = (T_f - T_i)_{\text{N}_2} = T_f - 0 \text{ }^\circ\text{C} \quad \& \quad \Delta T_{\text{Kr}} = (T_f - T_i)_{\text{Kr}} = T_f - 200 \text{ }^\circ\text{C}$$

$$\text{Therefore, } 1.00 \text{ g N}_2 \times \frac{1.04 \text{ J}}{\text{ }^\circ\text{C} \cdot \text{g N}_2} \times (T_f - 0 \text{ }^\circ\text{C}) = -1.00 \text{ g Kr} \times \frac{0.25 \text{ J}}{\text{ }^\circ\text{C} \cdot \text{g Kr}} \times (T_f - 200 \text{ }^\circ\text{C})$$

$$1.04 T_f = -0.25 T_f + 50 \text{ }^\circ\text{C}. \text{ Solving for } T_f, \text{ we obtain } T_f = \frac{50 \text{ }^\circ\text{C}}{1.29} = 39 \text{ }^\circ\text{C}$$

## 55. A 35.4-g metal bar at 97.6 °C is placed into an insulated flask containing 75.0 g of ice at 0 °C. What is the specific heat of the metal if cooling the bar to 0 °C melted 2.36 g of the ice? The $\Delta H_{\text{fus}}$ = 6.01 kJ/mol for water.

Determine the amount of heat required to melt 2.36 g of ice:

$$q_{\text{H}_2\text{O}} = 2.36 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0148 \text{ g H}_2\text{O}} \times \frac{6.01 \text{ kJ}}{\text{mol}} = 0.787 \text{ kJ}$$

$$q_{\text{metal}} = m_{\text{metal}} s_{\text{metal}} \Delta T_{\text{metal}} = -q_{\text{H}_2\text{O}} = -0.787 \text{ kJ}$$

$$s_{\text{metal}} = -\frac{q_{\text{water}}}{m_{\text{metal}} \Delta T_{\text{metal}}} = \frac{0.787 \text{ kJ}}{(35.4 \text{ g})(-97.6 \text{ }^\circ\text{C})} = 2.28 \cdot 10^{-4} \text{ kJ} \cdot \text{g}^{-1} \cdot \text{ }^\circ\text{C}^{-1} = 0.228 \text{ J} \cdot \text{g}^{-1} \cdot \text{ }^\circ\text{C}^{-1}$$

# First Law of Thermodynamics

57. 25.0 mL of 0.12 M HX(aq) at 22.0 °C and 25.0 mL of 0.12 M NaOH(aq) at 22.0 °C are mixed. After reaction, the temperature of the mixture is 27.6 °C. What is the heat of neutralization:  $\text{HX(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{NaX(aq)}$ ? Assume that the specific heat of the solution is 4.18 J/g·°C and the densities of all solutions are 1.00 g/mL.

$$q = -m\Delta T = -50(4.18)(5.6) = 1.17 \times 10^3 \text{ J}; \quad \Delta H = -1.17 \text{ kJ} / (0.025 \text{ L})(0.12 \text{ mol/L}) = -3900 \text{ kJ}$$

59. The combustion of 0.3268 g of oleic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2(\text{l})$ , resulted in a temperature rise of 3.462 °C in a constant pressure calorimeter with a heat capacity of 3.715 kJ/°C.

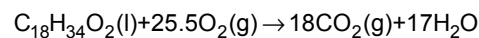
- a) What is the standard molar enthalpy of combustion of oleic at 298 K?

$$q_p = -C_{\text{cal}}\Delta T_{\text{cal}} = -(3.715 \text{ kJ/}^\circ\text{C})(3.462^\circ\text{C}) = -12.861 \text{ kJ}; \quad n = \frac{0.3268 \text{ g } \text{C}_{18}\text{H}_{34}\text{O}_2}{282.4646 \text{ g/mol}} = 1.157 \times 10^{-3} \text{ mol } \text{C}_{18}\text{H}_{34}\text{O}_2$$

$$\Delta H = q_p = \frac{-12.861 \text{ kJ}}{1.157 \times 10^{-3} \text{ mol}} = -1.112 \times 10^4 \text{ kJ}$$

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

Use the coefficients of the balanced equation and the heats of formation.



$$1.112 \times 10^4 \text{ kJ} = 18 \times \Delta H_f^\circ[\text{CO}_2(\text{g})] + 17 \times \Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - 25.5 \times \Delta H_f^\circ[\text{O}_2(\text{g})] - 1\Delta H_f^\circ[\text{C}_{18}\text{H}_{34}\text{O}_2(\text{l})]$$

$$1\Delta H_f^\circ[\text{C}_{18}\text{H}_{34}\text{O}_2(\text{l})] = 1.112 \times 10^4 + 18(-393.5) + 17(-285.8) - 0 = -830 \text{ kJ}$$

$$\Delta H_f^\circ[\text{C}_{18}\text{H}_{34}\text{O}_2(\text{l})] = -830 \text{ kJ/mol}$$

61. Burning 117.7 mg of naphthalene,  $\text{C}_{10}\text{H}_8(\text{s})$ , the active ingredient in mothballs, results in a temperature rise of 3.275 °C in a bomb calorimeter with a heat capacity of 1.444 kJ·°C<sup>-1</sup>.

- a) Write the balanced equation for the combustion at 25 °C.

Combustion is the reaction of a substance with  $\text{O}_2$  to produce the oxides of the elements. The oxides of carbon and hydrogen are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Therefore, the combustion of naphthalene ( $\text{C}_{10}\text{H}_8$ ) is



- b) What is  $\Delta E_{\text{comb}}$  of  $\text{C}_{10}\text{H}_8(\text{s})$  in kJ/mol?

To calculate the  $\Delta E_{\text{comb}}$  of  $\text{C}_{10}\text{H}_8(\text{s})$  in kJ/mol, it is first necessary to determine the amount of heat ( $q$ ) that the reaction generated using Eq. 3.13:  $q_{\text{rxn}} = -C\Delta T = -(1.444 \text{ kJ}\cdot^\circ\text{C}^{-1})(3.275^\circ\text{C}) = -4.729 \text{ kJ}$

The reaction is carried out at constant volume (a bomb) so  $q_{\text{rxn}} = \Delta E$ . Thus, to obtain the molar energy of combustion, we need only divide the above by the number of moles of  $\text{C}_{10}\text{H}_8$ . The number of moles in 117.2 mg of naphthalene is

$$0.1177 \text{ g } \text{C}_{10}\text{H}_8 \times \frac{1 \text{ mol } \text{C}_{10}\text{H}_8}{128.173 \text{ g } \text{C}_{10}\text{H}_8} = 9.183 \times 10^{-4} \text{ mol } \text{C}_{10}\text{H}_8$$

$$\text{and the molar energy of combustion is } \Delta E_{\text{comb}} = \frac{\Delta q_{\text{rxn}}}{\text{mols } \text{C}_{10}\text{H}_8} = \frac{-4.729 \text{ kJ}}{9.183 \times 10^{-4} \text{ mol } \text{C}_{10}\text{H}_8} = -5150 \text{ kJ}\cdot\text{mol}^{-1}$$

- c) What is  $\Delta H_{\text{comb}}$  of  $\text{C}_{10}\text{H}_8(\text{s})$  at 298 K?

Use Eq. 3.9b to obtain  $\Delta H_{\text{comb}}$ .  $\Delta n_g$  is defined as the number of moles of gaseous products (10 moles  $\text{CO}_2$ ) minus the number of moles of gaseous reactants (12 moles  $\text{O}_2$ ), so  $\Delta n_g = -2$  mol. Substitution into Equation 3.9b yields

$$\Delta H_{\text{comb}} = \Delta E_{\text{comb}} + \Delta n_g RT = -5150 \text{ kJ} + (-2 \text{ mol})(8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = -5155 \text{ kJ}$$

- d) What is  $\Delta H_f^\circ$  of  $\text{C}_{10}\text{H}_8(\text{s})$  at 298 K?

Use the above heat of combustion and heats of formation in Equation 3.10

$$\Delta H_{\text{rxn}} = [10\Delta H_f^\circ[\text{CO}_2] + 4\Delta H_f^\circ[\text{H}_2\text{O}]] - [1\Delta H_f^\circ[\text{C}_{10}\text{H}_8] + 12\Delta H_f^\circ[\text{O}_2]]$$

$$\Delta H_f^\circ[\text{C}_{10}\text{H}_8] = -\Delta H_{\text{rxn}} + 10\Delta H_f^\circ[\text{CO}_2] + 7\Delta H_f^\circ[\text{H}_2\text{O}] - 12\Delta H_f^\circ[\text{O}_2]$$

$$\Delta H_f^\circ[\text{C}_{10}\text{H}_8] = -(-5155) + 10(-393.5) + 4(-285.8) - 12(0) = 77 \text{ kJ/mol}$$

# First Law of Thermodynamics

63. When 2.000 g of propane (C<sub>3</sub>H<sub>8</sub>) was burned in excess oxygen in a bomb calorimeter, 105.0 kJ of heat was obtained at 25 °C. Find ΔH for the reaction.

The balanced equation for the combustion of propane is C<sub>3</sub>H<sub>8</sub>(g) + 5 O<sub>2</sub>(g) → 3 CO<sub>2</sub>(g) + 4 H<sub>2</sub>O(l)

The heat liberated in the reaction, *q*, can be expressed per mole of C<sub>3</sub>H<sub>8</sub> using the given information.

$$\frac{105.0 \text{ kJ}}{2.000 \text{ g C}_3\text{H}_8} \times \frac{44.097 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} = \frac{-2315. \text{ kJ}}{\text{mol C}_3\text{H}_8}$$

The reaction was carried out in a bomb calorimeter, so  $q = \Delta E = -2315. \text{ kJ}$ .

To find ΔH, use Eq. 3.9b and the fact that Δn<sub>g</sub> = 3 – 6 = -3 mol gas per mole of propane that reacts.

$$\Delta H = -2315 \text{ kJ} + (-3 \text{ mol})(8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) = -2322 \text{ kJ}$$

65. When 0.8681 g of cetyl palmitate (C<sub>32</sub>H<sub>64</sub>O(s), (M<sub>m</sub> = 464.86 g/mol) was burned in a calorimeter having a heat capacity of 9.535 kJ/°C, the temperature rose by 3.99 °C. Calculate the standard enthalpy change per mole, ΔH° at 298 K for the combustion of cetyl palmitate.

Balanced equation: C<sub>32</sub>H<sub>64</sub>O(s) + 47.5 O<sub>2</sub>(g) → 32 CO<sub>2</sub>(g) + 32 H<sub>2</sub>O(l) (Δn<sub>g</sub> = 32 – 47.5 = -15.5 mol)

$$q = -C_{\text{cal}}\Delta T = -9.535 \frac{\text{kJ}}{^\circ\text{C}} \times 3.99 \text{ }^\circ\text{C} = -38.0 \text{ kJ}$$

$$\Delta E = \frac{-38.0 \text{ kJ}}{0.8681 \text{ g C}_{32}\text{H}_{64}\text{O}} \times \frac{464.86 \text{ g C}_{32}\text{H}_{64}\text{O}}{1 \text{ mol C}_{32}\text{H}_{64}\text{O}} = -2.03 \times 10^4 \frac{\text{kJ}}{\text{mol C}_{32}\text{H}_{64}\text{O}}$$

$$\Delta H = \Delta E + \Delta n_{\text{g}}RT; \quad \Delta n_{\text{g}}RT = (-15.5 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) = -3.84 \times 10^4 \text{ J} = -38.4 \text{ kJ}$$

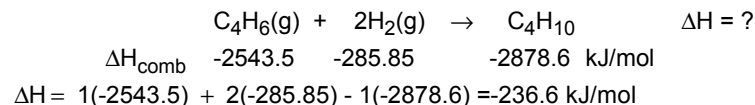
$$\Delta H = -2.03 \times 10^4 - 38.4 = -2.03 \times 10^4 \text{ kJ}; \text{ As is often the case, } w \text{ is negligible compared to } \Delta H.$$

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?

Use the conversions at the beginning of Section 3.7.

$$10 \text{ g fat} \times \frac{9. \text{ Cal}}{1 \text{ g fat}} + 25 \text{ g carbohydrates} \times \frac{4. \text{ Cal}}{1 \text{ g carbohydrate}} + 6 \text{ g protein} \times \frac{4. \text{ Cal}}{1 \text{ g protein}} = 200 \text{ Cal}$$

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<sub>4</sub>H<sub>6</sub>)?

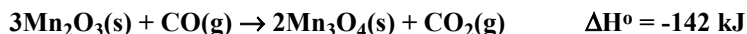
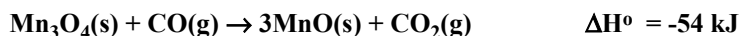


71. Bicycle riding at 13 mph consumes 2800 kJ per hour for a 150 lb. person. How many miles must this person ride to lose 1 lb. of body fat? Hint: body fat contains 39 kJ/g of stored energy?

$$2800 \text{ kJ/h} \times X(\text{hours}) = (39 \text{ kJ/g}) \times \frac{1 \text{ g}}{.0022 \text{ lb}} \times 1 \text{ lb}$$

$$X = 6.3 \text{ hours, which is } 6.3 \text{ hr} \times 13 \text{ miles/hr} = 82 \text{ miles}$$

73. Use the following thermochemical equations:



and any of the answers to preceding parts to determine ΔH° for each of the following reactions:

- a) 2MnO<sub>2</sub>(s) + CO(g) → Mn<sub>2</sub>O<sub>3</sub>(s) + CO<sub>2</sub>(g)

$$2\text{MnO}_2 + 2\text{CO} \rightarrow 2\text{MnO} + 2\text{CO}_2 \quad \Delta H_A = 2\Delta H_1 = 2(-151) = -302 \text{ kJ}$$

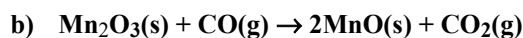
$$2\text{MnO} + \frac{2}{3}\text{CO}_2 \rightarrow \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{2}{3}\text{CO} \quad \Delta H_B = -\frac{2}{3}\Delta H_2 = -\frac{2}{3}(-54) = +36 \text{ kJ}$$

$$\frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{CO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \frac{1}{3}\text{CO}_2 \quad \Delta H_C = -\frac{1}{3}\Delta H_3 = -\frac{1}{3}(-142) = +47 \text{ kJ}$$

$$2\text{MnO}_2 + \text{CO} \rightarrow \text{Mn}_2\text{O}_3 + \text{CO}_2 \quad \Delta H = \Delta H_A + \Delta H_B + \Delta H_C = -302 + 36 + 47 = -219 \text{ kJ}$$



# First Law of Thermodynamics



$$\begin{array}{l} \text{Mn}_2\text{O}_3 + \frac{1}{3}\text{CO} \rightarrow \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{CO}_2 \quad \Delta H_A = \frac{1}{3}\Delta H_3 = \frac{1}{3}(-142) = -47 \text{ kJ} \\ \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{2}{3}\text{CO} \rightarrow 2\text{MnO} + \frac{2}{3}\text{CO}_2 \quad \Delta H_B = \frac{2}{3}\Delta H_2 = \frac{2}{3}(-54) = -36 \text{ kJ} \\ \hline \text{Mn}_2\text{O}_3 + \text{CO} \rightarrow 2\text{MnO} + \text{CO}_2 \quad \Delta H = \Delta H_A + \Delta H_B = -47 - 36 = -83 \text{ kJ} \end{array}$$



$$\begin{array}{l} \text{MnO}_2 + \text{CO} \rightarrow \text{MnO} + \text{CO}_2 \quad \Delta H_A = \Delta H_1 = -151 \text{ kJ} \\ 2\text{MnO} + \frac{2}{3}\text{CO}_2 \rightarrow \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{2}{3}\text{CO} \quad \Delta H_B = -\frac{2}{3}\Delta H_2 = -\frac{2}{3}(-54) = +36 \text{ kJ} \\ \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{CO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \frac{1}{3}\text{CO} \quad \Delta H_C = -\frac{1}{3}\Delta H_3 = -\frac{1}{3}(-142) = +47 \text{ kJ} \\ \hline \text{MnO} + \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \quad \Delta H = \Delta H_A + \Delta H_B + \Delta H_C = -151 + 36 + 47 = -68 \text{ kJ} \end{array}$$



$$\begin{array}{l} \text{Mn}_2\text{O}_3 + \frac{1}{3}\text{CO} \rightarrow \frac{2}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{CO}_2 \quad \Delta H_A = \frac{1}{3}\Delta H_3 = \frac{1}{3}(-142) = -47 \text{ kJ} \\ \text{MnO} + \frac{1}{3}\text{CO}_2 \rightarrow \frac{1}{3}\text{Mn}_3\text{O}_4 + \frac{1}{3}\text{CO} \quad \Delta H_B = -\frac{1}{3}\Delta H_2 = -\frac{1}{3}(-54) = +18 \text{ kJ} \\ \hline \text{Mn}_2\text{O}_3 + \text{MnO} \rightarrow \text{Mn}_3\text{O}_4 \quad \Delta H = \Delta H_A + \Delta H_B = -47 + 18 = -29 \text{ kJ} \end{array}$$

**75. Ammonium nitrate is a common ingredient in fertilizers that can also be used to make explosives because it decomposes as follows:  $2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$   $\Delta H = -236 \text{ kJ}$**

The following questions deal with the decomposition of 12.0 g of  $\text{NH}_4\text{NO}_3$  at  $300^\circ\text{C}$ ?

**a) How much heat is liberated?**

$$12.0 \text{ g NH}_4\text{NO}_3 \times \frac{1 \text{ mol NH}_4\text{NO}_3}{80.05 \text{ g}} \times \frac{236 \text{ kJ liberated}}{2 \text{ mol NH}_4\text{NO}_3} = 17.7 \text{ kJ of heat liberated}$$

**b) How much work would be done by the gases at  $300^\circ\text{C}$ ?**

Work done by the gases is  $\Delta n_g RT$  (plus sign is used in Eq 3.8 because it is the work done by the gas).  
Construct the reaction table to determine  $\Delta n_g$

	$2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$			
initial moles	0.15	0	0	0
$\Delta$	-0.15	+0.15	+0.30	+0.075
final moles	0	0.15	0.30	0.075

$$\Delta n_g = (0.15 + 0 + 30 + 0.075) - 0 = 0.525 \text{ mol,}$$

$$\text{so work done by the gas is } (0.525 \text{ mol})(8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(573) = 2.5 \text{ kJ}$$

**c) What volume of gas would be produced at 1.00 atm and  $300^\circ\text{C}$ ?**

Using the ideal gas law:  $PV = nRT$  we find,

$$V = \frac{nRT}{P} = \frac{(0.525 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{K mol}})(573 \text{ K})}{1 \text{ atm}} = 25 \text{ L}$$

# First Law of Thermodynamics

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