CHAPTER 6 THERMOCHEMISTRY

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6. Thermochemistry

- Thermodynamics is the science of the relationships between heat and other forms of energy.

- Thermochemistry concerns the study of the quantity of heat absorbed or evolved (given off) by chemical reactions.

6.1 Energy and Its Units

- Energy: the potential or capacity to move matter

- Exist in different forms, including heat, light, and electrical energy, and these different forms can be interconverted.

- Focus on chemical energy

6.1 Energy and Its Units

- Kinetic Energy; Units of Energy
  - The energy associated with an object by virtue of its motion.

$$E_k = \tfrac{1}{2}mv^2$$

J (SI)

$$E_k = \tfrac{1}{2} \times (59.0 \text{ kg}) \times (26.8 \text{ m/s})^2 = 2.12 \times 10^4 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ cal} = 4.184 \text{ J} \qquad \text{(exact definition)}$$

6.1 Energy and Its Units

- Potential Energy
  - The energy an object has by virtue of its position in a field of force.

$E_\text{p} = mgh$

m: mass

g: the constant

acceleration of gravity

h: the height

potential energy converted to
kinetic energy

6.1 Energy and Its Units

- Internal Energy (U)

  The sum of the kinetic and potential energies of the particles making up of a substance (*U*).

- Total Energy

$$E_{tot} = \underline{E_k + E_p} + U$$

0 in the lab

6.1 Energy and Its Units

- Law of Conservation of Energy
  - Energy may be converted from one form to another, but the total quantity of energy remains constant.

6.2 Heat of Reaction

Surroundings

Surroundings

Surroundings

System
(solution of $Ba(OH)_2$ and NH_4NO_3)

- **Thermodynamic system**: the substance or mixture of substances under study in which a change occurs

- **Surroundings**: everything in the vicinity of the thermodynamic system.
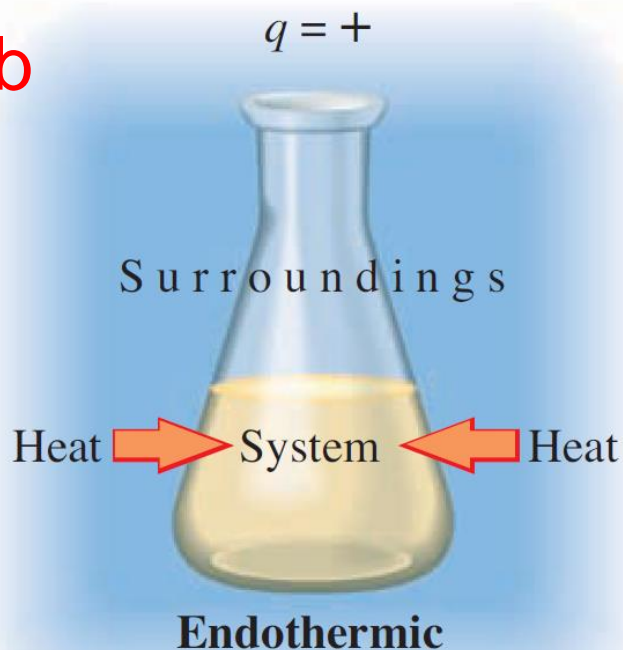
6.2 Heat of Reaction

- Definition of Heat
  - The energy that flows into or out of a system because of a difference in temperature between the thermodynamic system and its surroundings.
  - Heat is an energy flow.
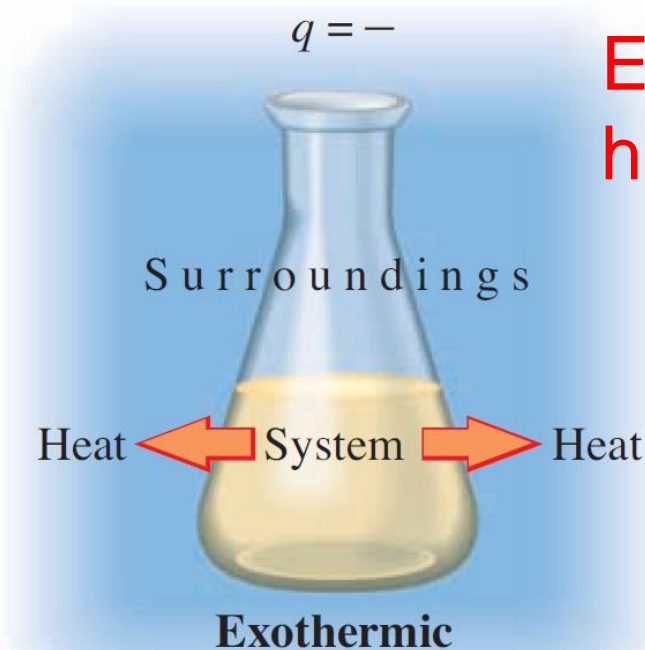 - Once the temperatures become equal, heat flow stops.
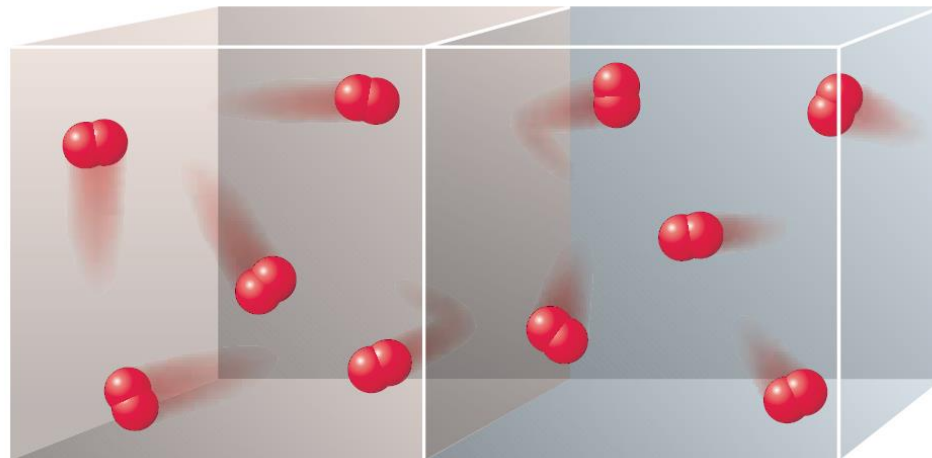
6.2 Heat of Reaction

- Heat is denoted by the symbol q: $+q$, $-q$.

- Heat of reaction: the value of q required to return a system to the given temperature at the completion of the reaction.

Absorb heat

$q = +$

Surroundings

Heat ⟶ System ⟵ Heat

Endothermic

$q = -$

Evolve heat

Surroundings

Heat ⟵ System ⟶ Heat

Exothermic

6.2 Heat of Reaction

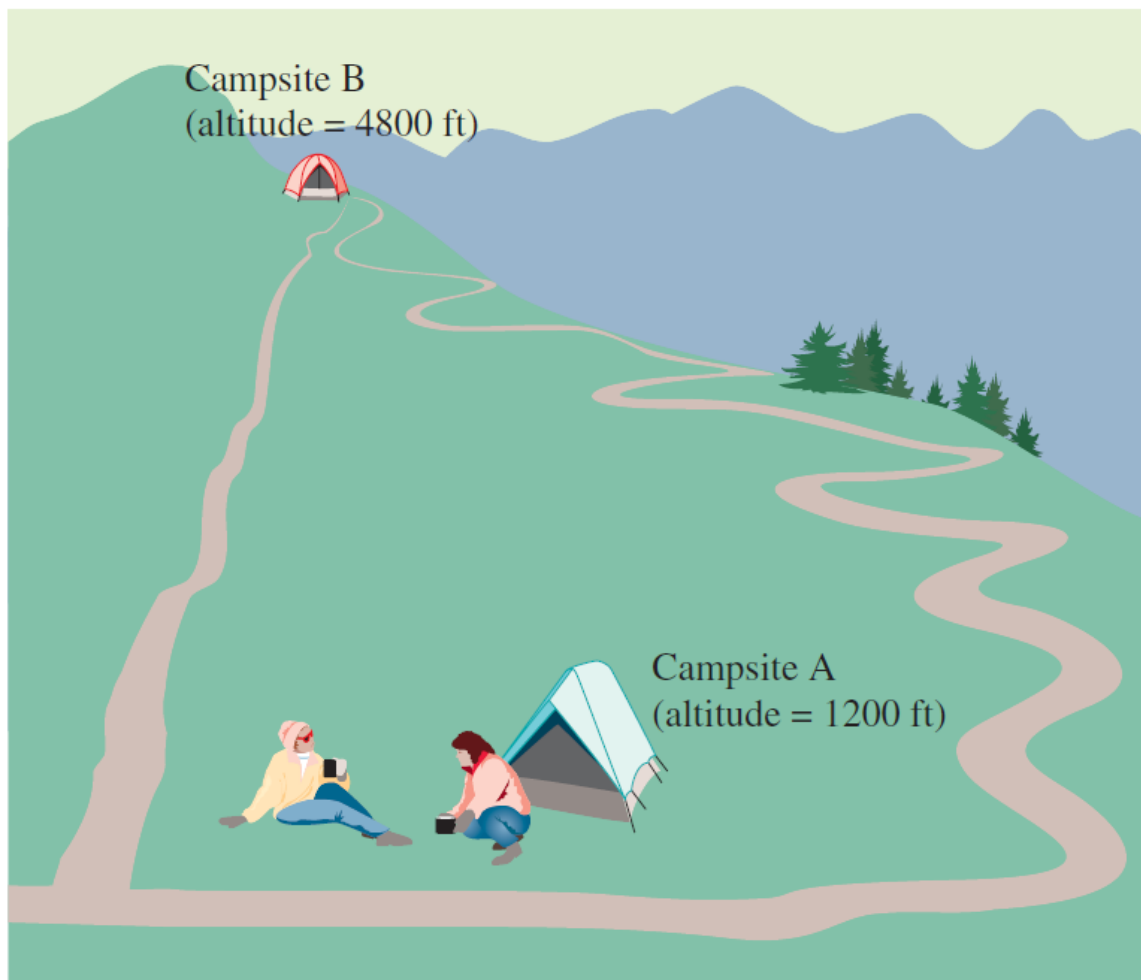| Type of Reaction	Experimental Effect Noted	Result on System	Sign of q
Endothermic	Reaction vessel cools (heat is absorbed)	Energy added	+
Exothermic	Reaction vessel warms (heat is evolved)	Energy subtracted	−

6.3 Enthalpy and Enthalpy Change

- Enthalpy: an extensive property of a substance that can be used to obtain the heat absorbed or evolved in a chemical reaction.

- An extensive property is a property that depends on the amount of substance.

- Denoted H

6.3 Enthalpy and Enthalpy Change

- Enthalpy
  - A state function: a property of a system that depends o   is determined   nd pressure, a   us history of th

Campsite B
(altitude = 4800 ft)

Campsite A
(altitude = 1200 ft)

6.3 Enthalpy and Enthalpy Change

- Enthalpy of Reaction
  - Obtained by subtracting the enthalpy of the reactants from the enthalpy of the products

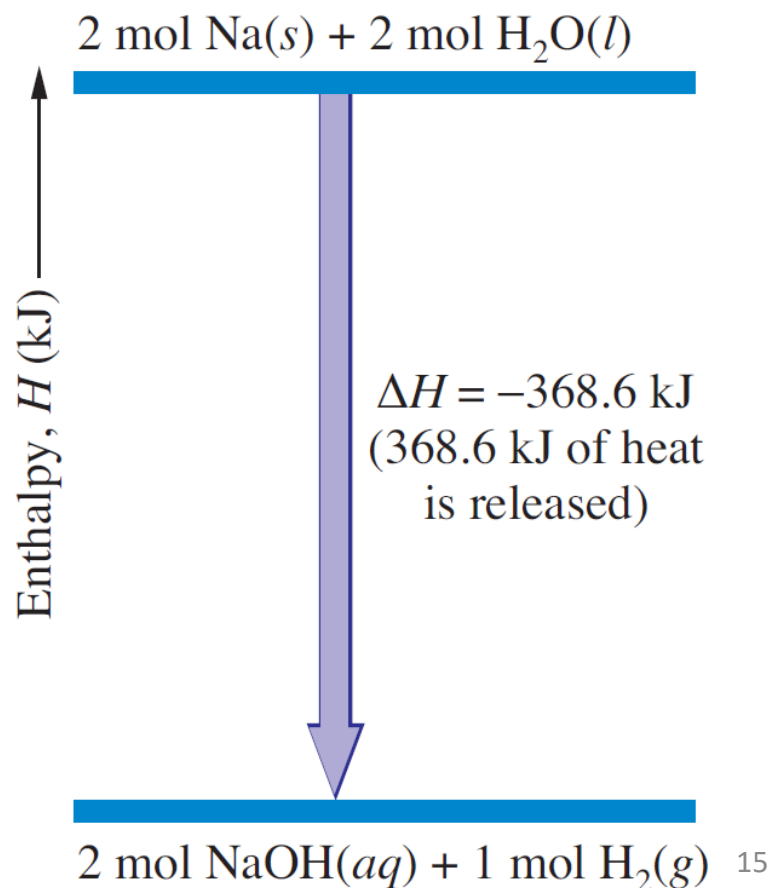$$\Delta H = H(\text{products}) - H(\text{reactants})$$

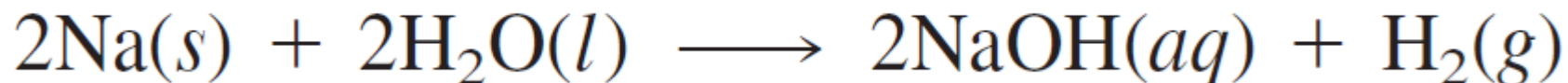 - Independent of the details of the reaction.

$$\Delta H = q_p$$

  - The enthalpy of reaction equals the heat of reaction at constant pressure.

6.3 Enthalpy and Enthalpy Change

- Enthalpy of Reaction

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

2 mol Na(s) + 2 mol H_2O(l)

Enthalpy, H (kJ)

$\Delta H = -368.6$ kJ
(368.6 kJ of heat is released)

2 mol NaOH(aq) + 1 mol H_2(g)

6.3 Enthalpy and Enthalpy Change

- Enthalpy and Internal Energy

$$H = U + PV$$

$$\Delta H = H_f - H_i = (U_f + PV_f) - (U_i + PV_i)$$

$$\Delta H = (U_f - U_i) + P(V_f - V_i) = \Delta U + P\Delta V$$

$$\Delta U = \Delta H - \underline{P\Delta V}$$
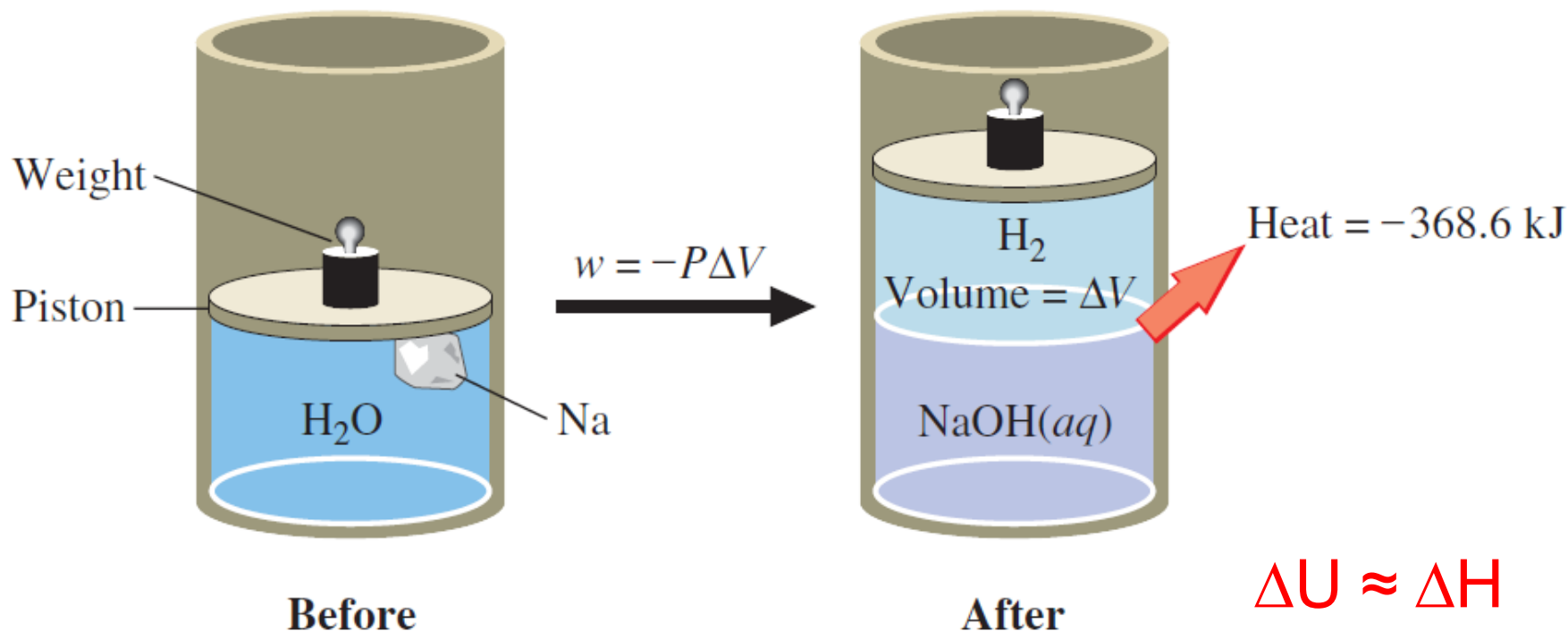
The pressure-volume work

  - The internal energy of the system changes in two ways: 1) energy leaves or enters the system as heat ($\triangle H$); 2) the system increases or decreases in volume against the constant pressure of the atmosphere.

- Enthalpy and Internal Energy

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$

Weight

Piston

H_2O

Na

$w = -P\Delta V$

H_2

Volume $= \Delta V$

Heat $= -368.6$ kJ

$\text{NaOH}(aq)$

Before

After

ΔU ≈ ΔH
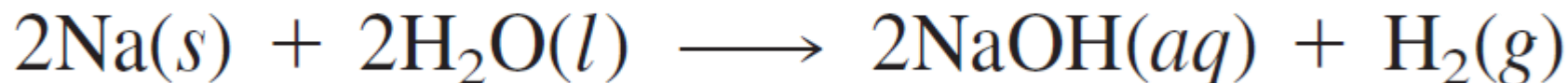
$$\Delta U = \Delta H - P\Delta V = -368.6 \text{ kJ} - 2.5 \text{ kJ} = -371.1 \text{ kJ}$$

6.4 Thermochemical Equations

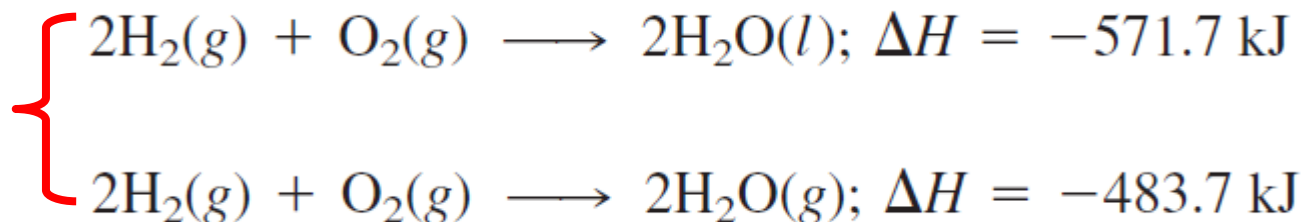- Thermochemical Equations: The chemical equation for a reaction (including phase labels) in which the equation is given a molar interpretation, and the enthalpy of reaction for these molar amounts is written directly after the equation.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g); \; \Delta H = -368.6 \, kJ$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l); \; \Delta H = -571.7 \, kJ$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \; \Delta H = -483.7 \, kJ$$
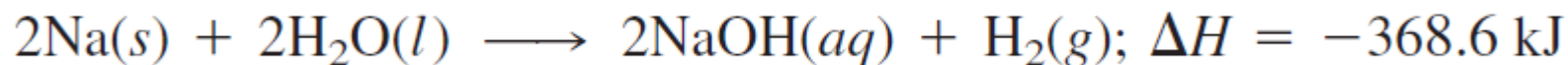
6.4 Thermochemical Equations

- Two important rules:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \Delta H = -91.8 \text{ kJ}$$

$$2N_2(g) + 6H_2(g) \longrightarrow 4NH_3(g); \Delta H = -184 \text{ kJ}$$

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g); \Delta H = +91.8 \text{ kJ}$$
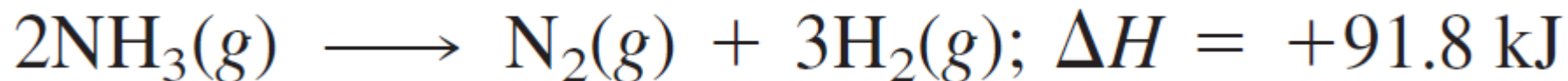
P234 Example 6.3

When 2 mol $H_2(g)$ and 1 mol $O_2(g)$ react to give liquid water, 572 kJ of heat evolves.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \Delta H = -572 \text{ kJ}$$
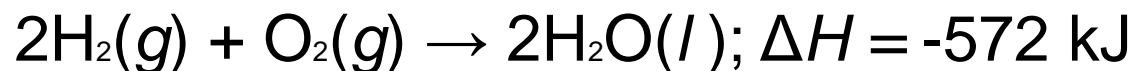
Write this equation for 1 mol of liquid water. Give the reverse equation, in which 1 mol of liquid water dissociates into hydrogen and oxygen.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H = -286 \text{ kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g); \Delta H = +286 \text{ kJ}$$

6.5 Applying Stoichiometry to Heats of Reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta H = -890.3 \text{ kJ}$$
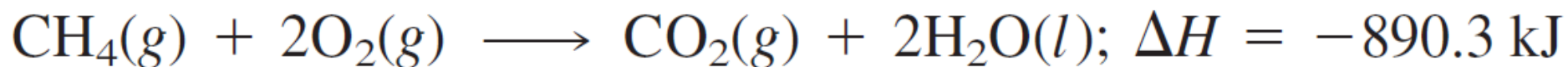
Grams of CH_4 $\longrightarrow$ moles of CH_4 $\longrightarrow$ kilojoules of heat

$$10.0 \text{ g } \cancel{CH_4} \times \frac{1 \text{ mol } \cancel{CH_4}}{16.0 \text{ g } \cancel{CH_4}} \times \frac{-890.3 \text{ kJ}}{1 \text{ mol } \cancel{CH_4}} = -556 \text{ kJ}$$

P236 Example 6.4

How much heat is evolved when 9.07×10^5 g of ammonia is produced according to the following equation? (Assume that the reaction occurs at constant pressure.)

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \Delta H = \text{-91.8 kJ}$$

$$9.07 \times 10^5 \text{ g } \cancel{NH_3} \times \frac{1 \text{ mol } \cancel{NH_3}}{17.0 \text{ g } \cancel{NH_3}} \times \frac{-91.8 \text{ kJ}}{2 \text{ mol } \cancel{NH_3}} = -2.45 \times 10^6 \text{ kJ}$$

6.6 Measurement of Heat of Reaction

- Heat capacity (*C*) of a sample of substance is the quantity of heat needed to raise the temperature of the sample of substance one degree Celsius (or one kelvin).

$$q = \underline{C}\Delta t$$

heat capacity

6.6 Measurement of Heat of Reaction

- Specific heat capacity: the quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (or one kelvin) at constant pressure.

$$q = s \times m \times \Delta t$$

TABLE 6.1	Specific Heats and Molar Heat Capacities of Some Substances*	
Substance	Specific Heat J/(g·°C)	Molar Heat Capacity J/(mol·°C)
Aluminum, Al	0.901	24.3
Copper, Cu	0.384	24.4
Ethanol, C_2H_5OH	2.43	112.2
Iron, Fe	0.449	25.1
Water, H_2O	4.18	75.3

*Values are for 25°C.

P237 Example 6.5

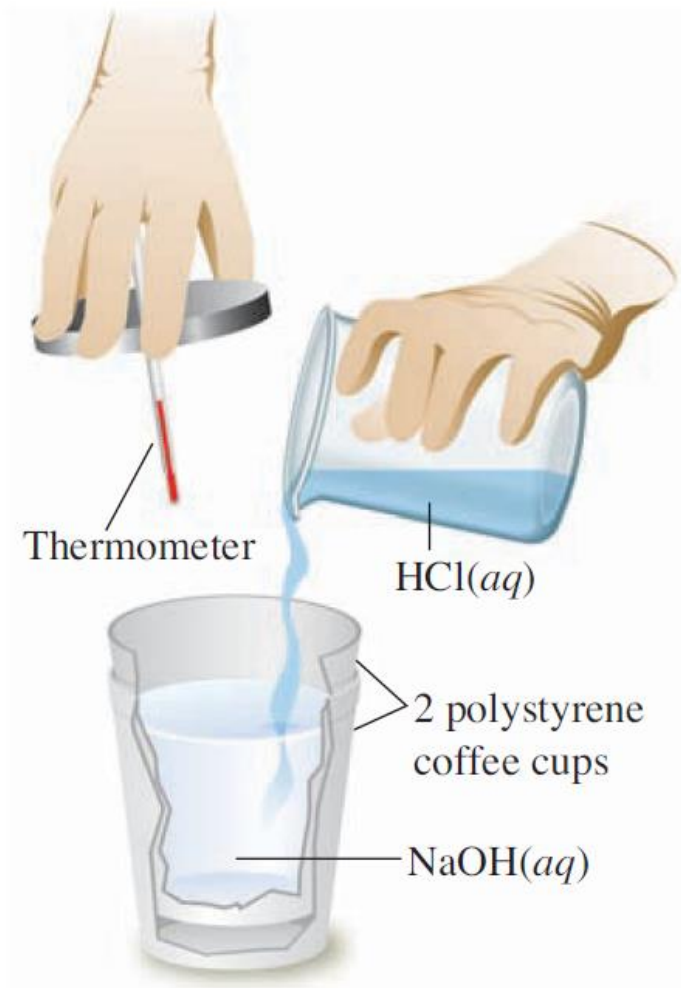Calculate the heat absorbed by 15.0 g of water to raise its temperature from 20.0 °C to 50.0 °C (at constant pressure). The specific heat of water is 4.18 J/(g °C).

$$q = 4.18 \text{ J/(g}\cdot°\text{C)} \times 15.0 \text{ g} \times (+30.0°\text{C}) = \mathbf{1.88 \times 10^3 \text{ J}}$$

6.6 Measurement of Heat of Reaction

- Calorimeter

Thermometer

HCl(aq)

2 polystyrene coffee cups

NaOH(aq)

P236 Example 6.6

Suppose 0.562 g of graphite is placed in a calorimeter with an excess of oxygen at 25.00 °C and 1 atm pressure. Excess O_2 ensures that all carbon burns to form CO_2. The graphite is ignited, and it burns according to the equation

$$C(graphite) + O_2(g) \rightarrow CO_2(g)$$
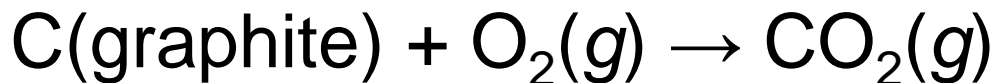
On reaction, the calorimeter temperature rises from 25.00 °C to 25.89 °C. The heat capacity of the calorimeter and its contents was determined in a separate experiment to be 20.7 kJ/°C. What is the heat of reaction at 25.00 °C and 1 atm pressure? Express the answer as a thermochemical equation.

P236 Example 6.6

$$q_{rxn} = -C_{cal}\Delta t = -20.7 \text{ kJ/°C} \times (25.89°\text{C} - 25.00°\text{C})$$

$$= -20.7 \text{ kJ/°C} \times 0.89°\text{C} = -18.4 \text{ kJ}$$

$$1 \text{ mol C} \times \frac{12 \text{ g C}}{1 \text{ mol C}} \times \frac{-18.4 \text{ kJ}}{0.562 \text{ g C}} = -3.9 \times 10^2 \text{ kJ}$$

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \Delta H = -3.9 \times 10^2 \text{ kJ}$$

6.7 Hess's Law

- For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of enthalpy changes for the individual steps.

- To obtain the enthalpy change for a reaction that is difficult to determine by direct

expe $2C(graphite) + O_2(g) \longrightarrow 2CO(g)$

$2C(graphite) + 2O_2(g) \longrightarrow 2CO_2(g)$ (first step)

$2CO_2(g) \longrightarrow 2CO(g) + O_2(g)$ (second step)

6.7 Hess's Law

$$2C(graphite) + 2O_2(g) \longrightarrow 2CO_2(g); \Delta H = (-393.5 \text{ kJ}) \times (2)$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g); \Delta H = -566.0 \text{ kJ}$$

$$2CO_2(g) \longrightarrow 2CO(g) + O_2(g); \Delta H = (-566.0 \text{ kJ}) \times (-1)$$

$$2C(graphite) + 2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H_1 = (-393.5 \text{ kJ}) \times (2)$$
$$2CO_2(g) \longrightarrow 2CO(g) + O_2(g) \qquad \Delta H_2 = (-566.0 \text{ kJ}) \times (-1)$$
$$\overline{2C(graphite) + O_2(g) \longrightarrow 2CO(g) \qquad \Delta H_3 = -221.0 \text{ kJ}}$$
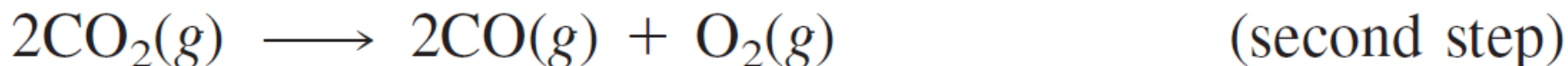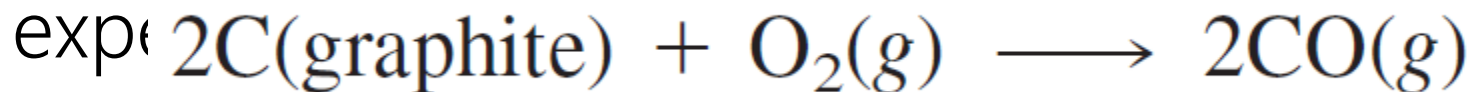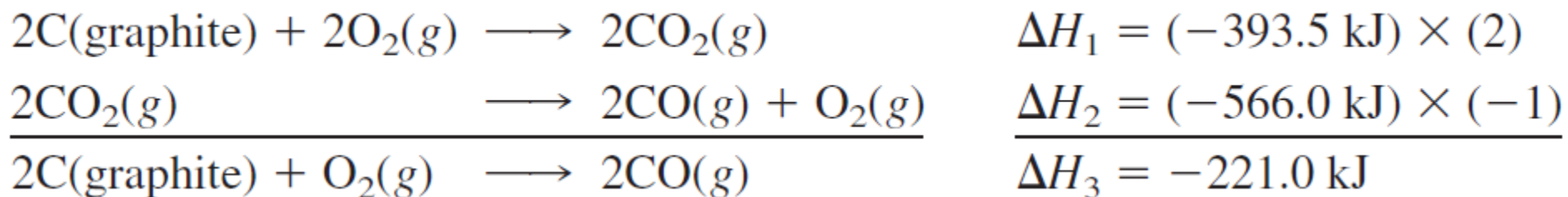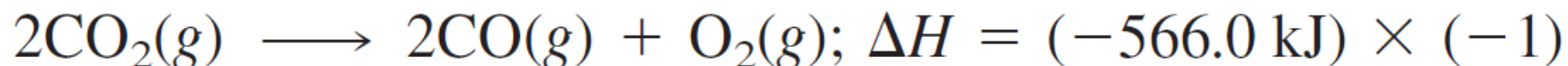
P243 Example 6.7

What is the enthalpy of reaction, ΔH, for the formation of tungsten carbide, WC, from the elements?

$$W(s) + C(graphite) \rightarrow WC(s)$$

The enthalpy change for this reaction is difficult to measure directly, because the reaction occurs at 1400 °C. However, the heats of combustion of the elements and of tungsten carbide can be measured easily:

$2W(s) + 3O_2(g) \rightarrow 2WO_3(s); \Delta H = -1685.8 \text{ kJ}$ (1)

$C(graphite) + O_2(g) \rightarrow CO_2(g); \Delta H = -393.5 \text{ kJ}$ (2)

$2WC(s) + 5O_2(g) \rightarrow 2WO_3(s) + 2CO_2(g); \Delta H = -2391.8 \text{ kJ}$ (3)

P243 Example 6.7

$$\text{W}(s) + \tfrac{3}{2}\cancel{\text{O}_2(g)} \longrightarrow \cancel{\text{WO}_3(s)} \qquad \Delta H = -842.9\ \text{kJ}$$

$$\text{C(graphite)} + \cancel{\text{O}_2(g)} \longrightarrow \cancel{\text{CO}_2(g)} \qquad \Delta H = -393.5\ \text{kJ}$$

$$\underline{\cancel{\text{WO}_3(s)} + \cancel{\text{CO}_2(g)} \longrightarrow \text{WC}(s) + \tfrac{5}{2}\cancel{\text{O}_2(g)}} \qquad \underline{\Delta H = 1195.9\ \text{kJ}}$$

$$\text{W}(s) + \text{C(graphite)} \longrightarrow \text{WC}(s) \qquad \boldsymbol{\Delta H = -40.5\ \text{kJ}}$$
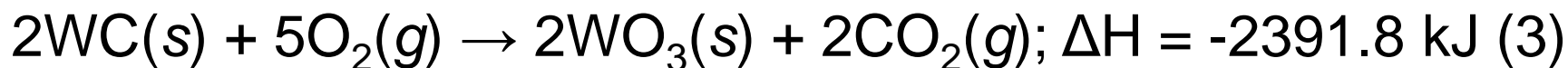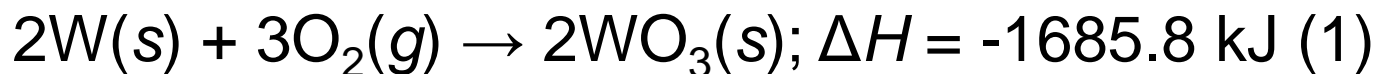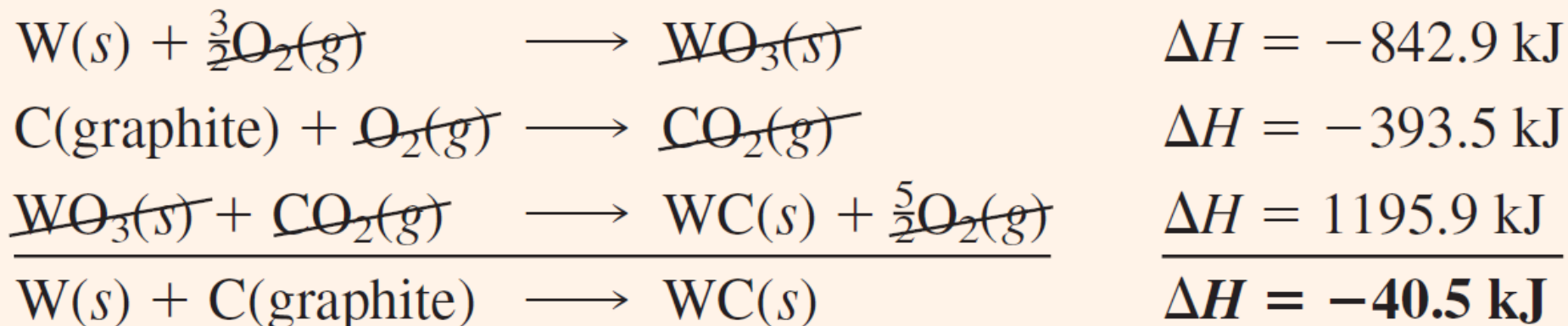
6.8 Standard Enthalpies of Formation

- Standard state: the standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: 1 atm pressure and the specified temperature (usually 25 °C). Indicated by °

- Allotrope: one of two or more distinct forms of an element in the same physical state.

  e.g., O_2 & O_3; graphite & crystal

- The reference form: the stablest form of the element under standard thermodynamic conditions.

6.8 Standard Enthalpies of Formation

- Standard Enthalpies of Formation ($\triangle H^{o}_{f}$)
  - The enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l); \; \Delta H^{\circ}_f = -285.8 \text{ kJ}$$
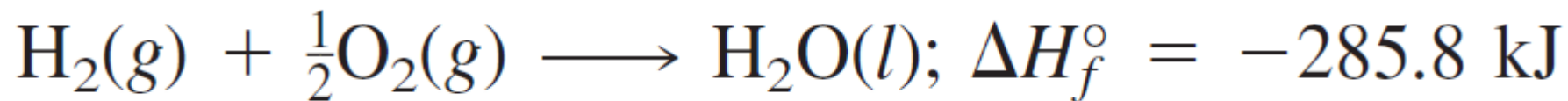
  - The values of $\triangle H^{o}_{f}$ for the elements in reference forms have zero values.

$$C(\text{graphite}) \longrightarrow C(\text{diamond}); \; \Delta H^{\circ}_f = 1.9 \text{ kJ}$$
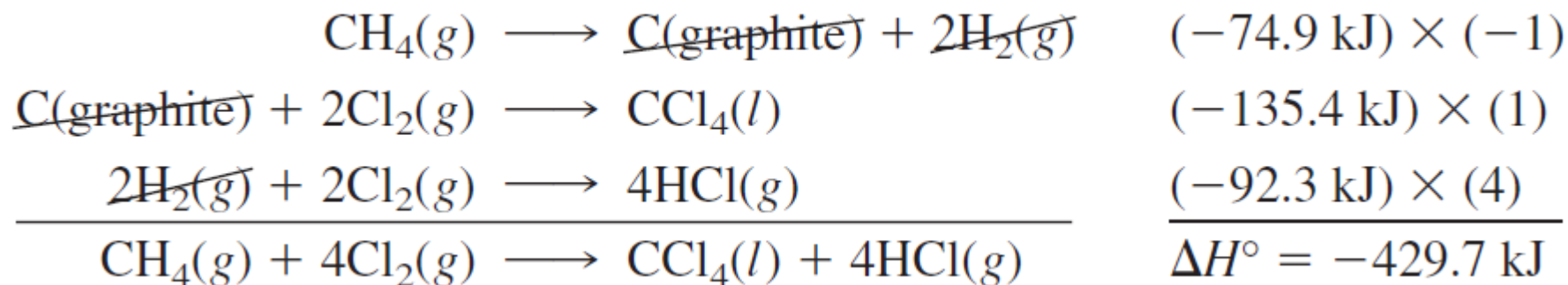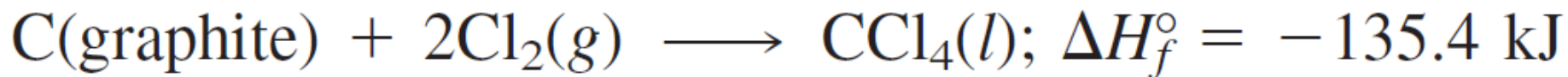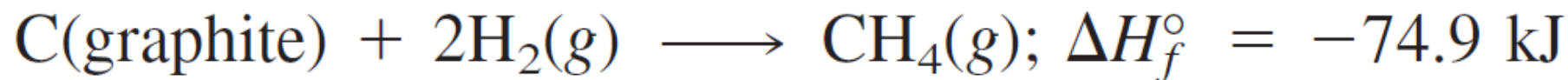
TABLE 6.2 — Standard Enthalpies of Formation (at 25°C)*

Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0	$CH_3CHO(g)$	−166.1	$NO_2(g)$	33.10
Bromine		$CH_3CHO(l)$	−191.8	$HNO_3(aq)$	−207.4
$Br(g)$	111.9	**Chlorine**		**Oxygen**	
$Br^-(aq)$	−121.5	$Cl(g)$	121.3	$O(g)$	249.2
$Br^-(g)$	−219.0	$Cl^-(aq)$	−167.2	$O_2(g)$	0
$Br_2(g)$	30.91	$Cl^-(g)$	−234.0	$O_3(g)$	142.7
$Br_2(l)$	0	$Cl_2(g)$	0	$OH^-(aq)$	−230.0
$HBr(g)$	−36.44	$HCl(g)$	−92.31	$H_2O(g)$	−241.8
Calcium		**Fluorine**		$H_2O(l)$	−285.8
$Ca(s)$	0	$F(g)$	79.39	**Silicon**	
$Ca^{2+}(aq)$	−542.8	$F^-(g)$	−255.1	$Si(s)$	0
$CaCO_3(s, \text{calcite})$	−1206.9	$F^-(aq)$	−332.6	$SiCl_4(l)$	−687.0
$CaO(s)$	−635.1	$F_2(g)$	0	$SiF_4(g)$	−1614.9
Carbon		$HF(g)$	−272.5	$SiO_2(s, \text{quartz})$	−910.9
$C(g)$	716.7	**Hydrogen**		**Silver**	
$C(s, \text{diamond})$	1.897	$H(g)$	218.0	$Ag(s)$	0
$C(s, \text{graphite})$	0	$H^+(aq)$	0	$Ag^+(aq)$	105.6
$CCl_4(g)$	−95.98	$H^+(g)$	1536.2	$AgBr(s)$	−100.4
$CCl_4(l)$	−135.4	$H_2(g)$	0	$AgCl(s)$	−127.1
$CO(g)$	−110.5	**Iodine**		$AgF(s)$	−204.6
$CO_2(g)$	−393.5	$I(g)$	106.8	$AgI(s)$	−61.84
$CO_3^{2-}(aq)$	−677.1	$I^-(aq)$	−55.19	**Sodium**	
$CS_2(g)$	116.9	$I^-(g)$	−194.6	$Na(g)$	107.3
$CS_2(l)$	89.70	$I_2(s)$	0	$Na(s)$	0
$HCN(g)$	135.1	$HI(g)$	26.36	$Na^+(aq)$	−240.1

6.8 Standard Enthalpies of Formation

- Standard Enthalpies of Formation ($\triangle H^{\circ}_f$)

$$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(l) + 4HCl(g); \Delta H^{\circ} = \,?$$

$$C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g); \Delta H^{\circ}_f = -74.9 \text{ kJ}$$

$$C(\text{graphite}) + 2Cl_2(g) \longrightarrow CCl_4(l); \Delta H^{\circ}_f = -135.4 \text{ kJ}$$

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow HCl(g); \Delta H^{\circ}_f = -92.3 \text{ kJ}$$

$CH_4(g) \longrightarrow \cancel{C(\text{graphite})} + \cancel{2H_2(g)}$	$(-74.9 \text{ kJ}) \times (-1)$
$\cancel{C(\text{graphite})} + 2Cl_2(g) \longrightarrow CCl_4(l)$	$(-135.4 \text{ kJ}) \times (1)$
$\cancel{2H_2(g)} + 2Cl_2(g) \longrightarrow 4HCl(g)$	$(-92.3 \text{ kJ}) \times (4)$
$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(l) + 4HCl(g)$	$\Delta H^{\circ} = -429.7 \text{ kJ}$

6.8 Standard Enthalpies of Formation

- Standard Enthalpies of Formation ($\triangle H^{\circ}_f$)

$$\Delta H^{\circ} = \Sigma\, n\, \Delta H^{\circ}_f(\text{products}) - \Sigma\, m\, \Delta H^{\circ}_f(\text{reactants})$$

$\Delta H^{\circ} = [\Delta H^{\circ}_f(CCl_4) + 4\,\Delta H^{\circ}_f(HCl)] - [\Delta H^{\circ}_f(CH_4) + 4\,\Delta H^{\circ}_f(Cl_2)]$

$\qquad = [(-135.4) + 4(-92.3)]\,\text{kJ} - [(-74.9) + 4(0)]\,\text{kJ} = -429.7\,\text{kJ}$

P247 Example 6.8

Use values of ΔH°_f to calculate the heat of vaporization, ΔH°_{vap}, of carbon disulfide at 25 °C. The vaporization process is
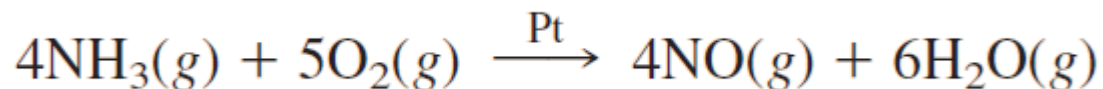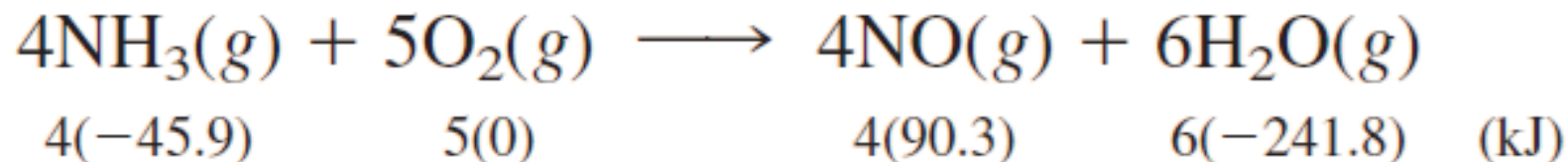
$$CS_2(l) \rightarrow CS_2(g)$$

89.7   116.9   kJ/mol
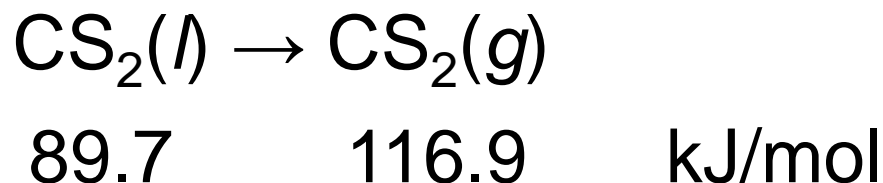
$$\Delta H^{\circ}_{vap} = \Sigma\, n\, \Delta H^{\circ}_f(\text{products}) - \Sigma\, m\, \Delta H^{\circ}_f(\text{reactants})$$
$$= \Delta H^{\circ}_f[CS_2(g)] - \Delta H^{\circ}_f[CS_2(l)]$$
$$= (116.9 - 89.7)\ \text{kJ} = \textbf{27.2 kJ}$$

P247 Example 6.9

Large quantities of ammonia are used to prepare nitric acid. The first step consists of the catalytic oxidation of ammonia to nitric oxide, NO.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt} 4NO(g) + 6H_2O(g)$$

What is the standard enthalpy change for this reaction?

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$
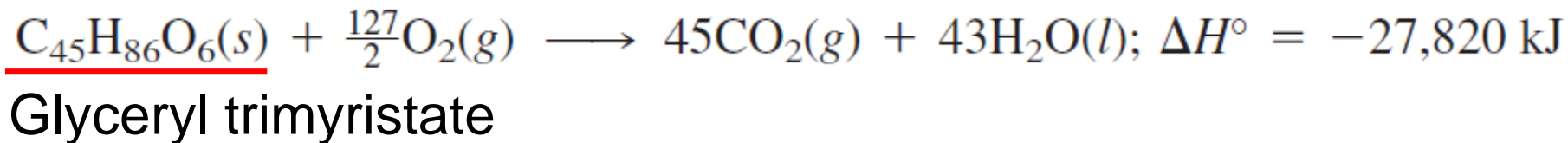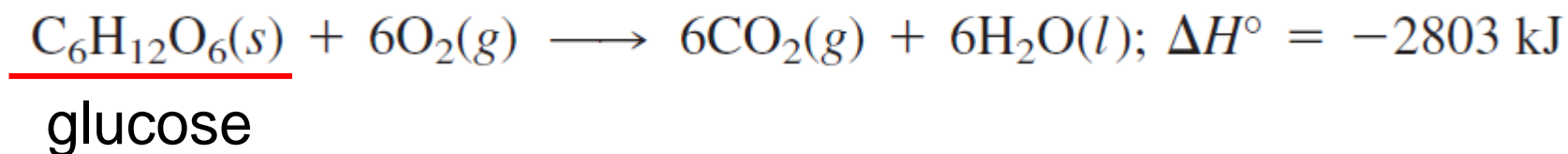$$4(-45.9) \qquad 5(0) \qquad\qquad 4(90.3) \qquad 6(-241.8) \quad (kJ)$$

P247 Example 6.9

$$\Delta H^\circ = \Sigma\, n\, \Delta H_f^\circ(\text{products}) - \Sigma\, m\, \Delta H_f^\circ(\text{reactants})$$

$$= [4\, \Delta H_f^\circ(\text{NO}) + 6\, \Delta H_f^\circ(\text{H}_2\text{O})] - [4\, \Delta H_f^\circ(\text{NH}_3) + 5\, \Delta H_f^\circ(\text{O}_2)]$$

$$= [4(90.3) + 6(-241.8)]\ \text{kJ} - [4(-45.9) + 5(0)]\ \text{kJ}$$

$$= \mathbf{-906\ kJ}$$

6. Thermochemistry

- Fuels-Foods, Commercial Fuels, and Rocket Fuels
  - Foods as Fuels
    - ➢ Carbohydrates: 4.0 kcal/g
    - ➢ Fats: 9.0 kcal/g
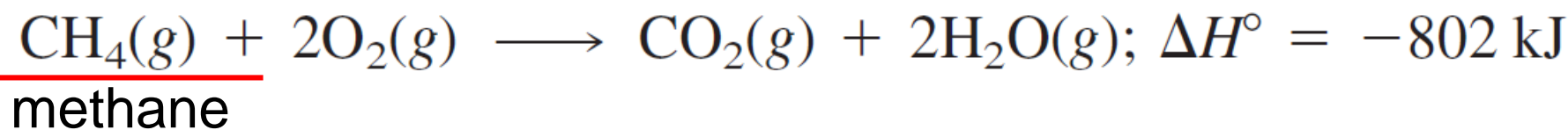
$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l); \Delta H° = -2803 \text{ kJ}$$

glucose

$$C_{45}H_{86}O_6(s) + \frac{127}{2}O_2(g) \longrightarrow 45CO_2(g) + 43H_2O(l); \Delta H° = -27,820 \text{ kJ}$$

Glyceryl trimyristate

6.9 Fuels-Foods, Commercial Fuels, and Rocket Fuels

- Fossil Fuels

  ➢ Coal: 30.6 kJ/g

$$C(graphite) + O_2(g) \longrightarrow CO_2(g); \Delta H° = -393.5 \text{ kJ}$$

  ➢ Natural gas: 50.1 kJ/g

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g); \Delta H° = -802 \text{ kJ}$$

methane

  ➢ Gasoline: 44.4 kJ/g

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g); \Delta H° = -5074 \text{ kJ}$$

octane

- Rocket Fuels

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g); \ \Delta H^\circ = -242 \text{ kJ}$$

$$C_{12}H_{26}(l) + \tfrac{37}{2}O_2(g) \longrightarrow 12CO_2(g) + 13H_2O(g); \ \Delta H^\circ = -7513 \text{ kJ}$$

kerosene

$$2N_2H_4(l) + N_2O_4(l) \longrightarrow 3N_2(g) + 4H_2O(g); \ \Delta H^\circ = -1049 \text{ kJ}$$

hydrazine