Chapter 6 Problems: 9, 19, 24, 25, 26, 27, 31-33, 37, 39, 43, 45, 47, 48, 53, 55, 57, 59, 65, 67, 73, 78-82, 85, 89, 93

Chapter 6 – Thermochemistry – The study of chemical reactions and the energy changes involved.

Energy – The capacity to do work or produce heat.

Many types of energy exist:

1) **Thermal – due to molecular motion.**

   Which has more thermal energy, 1 cup of 100 ^{o}C water or an ocean of water at 40 ^{o}C?

2) **Chemical – Energy stored within the chemical structure of a substance.**

   Which has more chemical energy, 1 gallon of gasoline or 1 gallon of water?

3) **Light, motion, nuclear, electrical,…**

Energy can be classified as either:

Potential Energy – Energy due to position or composition.

Kinetic Energy – Energy due to motion.

Is gasoline a form of Potential or Kinetic Energy? How about hot water?

Law of Conservation of Energy – Energy is transferred from 1 type to another, but never gained or lost.

Restated…The total amount of energy in the Universe is constant.

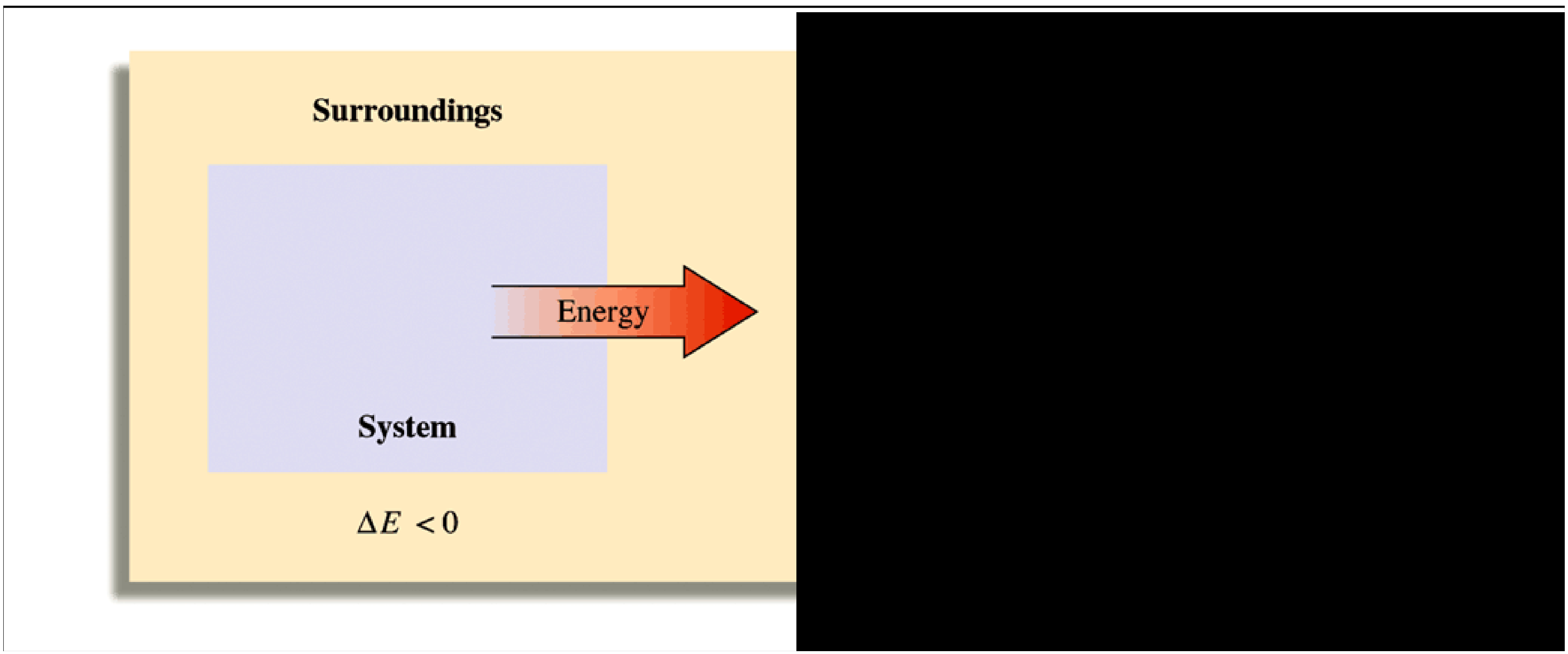
System – The reactants and products in a chemical reaction

Surroundings – Everything else.

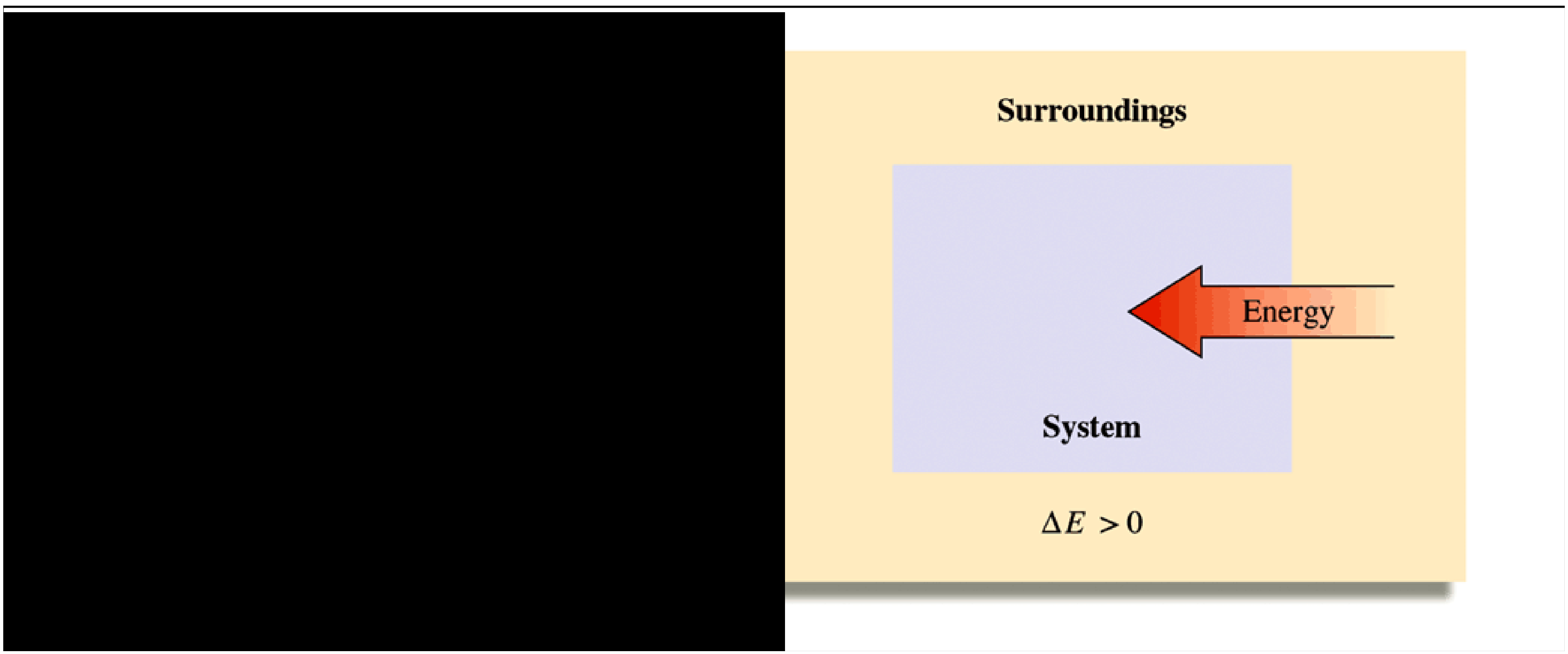
Universe = System + Surroundings

Exothermic Reaction – Energy flows out of the system and into the surroundings.

The system loses energy, and the surroundings gain that energy.



Endothermic Reaction – Energy flows out of the surroundings and into the system…the surroundings lose energy, and the system gains energy.



q = heat, as measured in joules, kJ, calories and Calories.

Heat is a measure of the energy contained in a substance. Temperature is a measure of how hot or cold a substance is. Heat and Temperature are not the same.

Heat always flow from a warm to a cold object.

w = Work (also measured in joules, kJ, calories and Calories) is a form of energy

Sign Conventions:

(-) energy means that energy is released by the system, gained by surroundings.

(+) energy indicates that energy is lost by the surroundings, and gained by the system.

E = internal energy of a system

$$\Delta E = q + w$$

Problem: Calculate ΔE of a system if the reaction is endothermic, and absorbs 15.6 kJ of heat, and 1.4 kJ of work are done on the system.

The most common type of work done by a chemical reaction is expansion or compression of gases.

i.e. Dynamite blows up

gasoline engine

What type of work (+ or -) are done in each?

$w = -p\Delta V$ where p = atm.
$\Delta V = V_2 - V_1$ (Liters)

units? Atm · Liter where 1 Atm · Liter = 101.3 Joules

Problem: Calculate the work done when gas expands from 46 L to 64 L against:

a) 0 atm pressure

b) 15 atm pressure

c) Is the system in b) higher or lower in energy?

To determine the total energy undergone by a system:

$$\Delta E = q + w$$

Problem: a balloon is inflated from 2L to 4L against 1 atmosphere, and is warmed by the addition of 200 Joules of heat. Calculate ΔE for the gas molecules in the balloon.

Is the system (the balloon gases) higher or lower in energy?

Enthalpy (H) – A measure of the amount of energy in a system that is available for conversion to heat.

$\Delta H = H_{products} - H_{reactants}$ **(also called the heat of reaction)**

Exothermic reaction – heat is lost by the system, the surroundings gain the heat.

ΔH **= negative number**

Endothermic reaction – a reaction that absorbs heat from the surroundings. Often, the surroundings immediately around the reaction will become cold.

ΔH **= positive number**

Problem: Methane burns giving up 890 kJ/mole. What is ΔH when 5.8 g methane burns?

Thermochemical equations:

1) Physical

$$6.01\ kJ + H_2O_{(s)} \rightarrow H_2O_{(l)}$$

or

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad \Delta H = 6.01\ kJ$$

The system is higher in energy as a result of this physical change.

2) Chemical

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} + 890.4\ kJ$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890.4\ kJ$$

Rules for writing thermochemical equations:

1) Stoichiometric coefficients refer to the number of moles of each substance. If the coefficients are changed, ΔH changes by the same factor.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -890.4 \text{ kJ}$$

$$2CH_{4(g)} + 4O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)} \qquad \Delta H = ??$$

2) When an equation is reversed, the sign of ΔH changes.

$$CO_{2(g)} + 2H_2O_{(l)} \rightarrow CH_{4(g)} + 2O_{2(g)} \qquad \Delta H = ?? \text{ kJ}$$

3) Thermochemical equations are always specific of state of matter.

$$H_2O_{(g)} \rightarrow H_2O_{(l)} \qquad \Delta H = -44 \text{ kJ}$$

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -802.4 \text{ kJ}$$

$$CH_{4\ (g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = ??$$

4) The enthalpy of a substance increases with temperature, therefore most reactions are expressed at a temperature of 25 ^{o}C

Calorimetry – measurement of heat changes between a system and the surroundings based on the law of conservation of energy

heat lost by system = heat gained by surroundings

Specific Heat (s) – The amount of heat (energy) required to raise the temperature of <u>1 g of a substance</u> by 1 ^oC. (J/g^oC)

Heat Capacity (C) - The amount of heat required to raise the temperature of an <u>object</u> by 1 ^oC.

$$C = ms$$

$$= (g)\left(\frac{J}{g^oC}\right)$$

$$= \frac{J}{^oC}$$

TABLE 6.1 p. 251

The Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity (J/°C · g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71

To determine heat (q) gained or lost by a system:

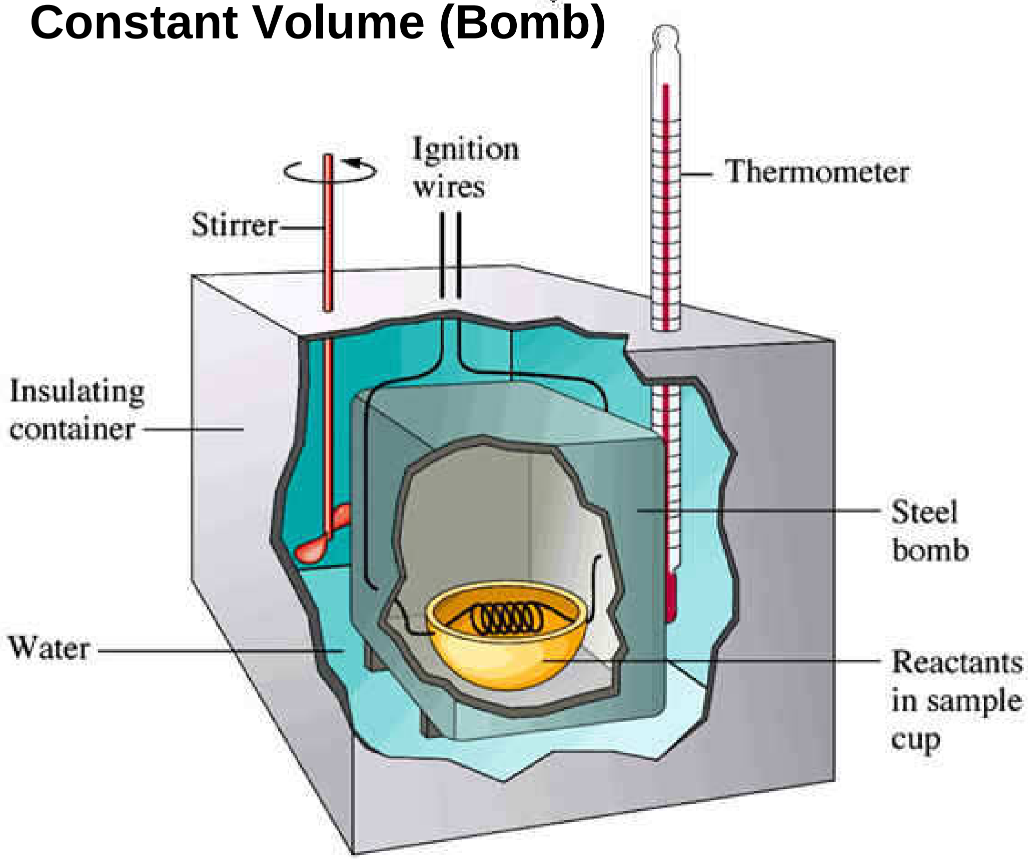
$q = m\,s\,\Delta t$	$m =$	mass (g)
	$s =$	specific heat $J/g^{o}C$
	$\Delta t =$	$(t_2 - t_1)$ ^{o}C or K

Problem: 466 g H_2O is heated from 8.5 ^{o}C to 74.6 ^{o}C. Calculate the heat gained by the system.

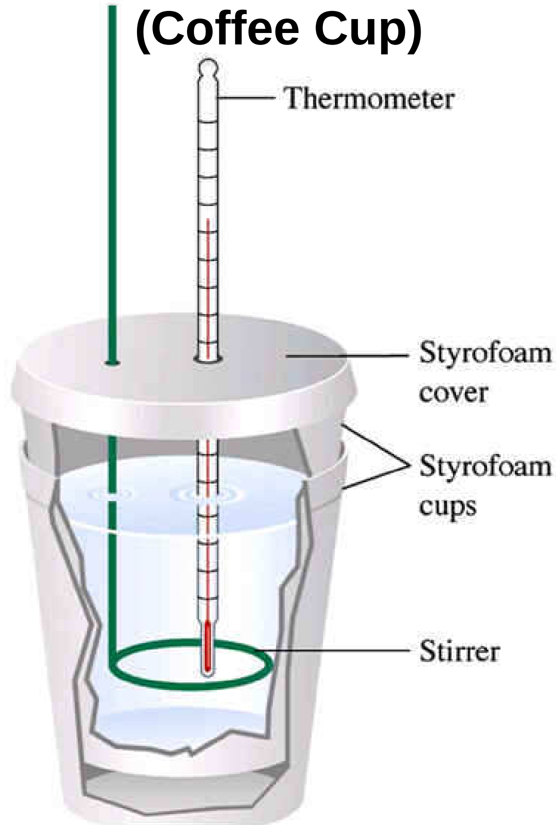
Calorimeter: device that measures ΔH of a reaction by simulating the surroundings.

2 Types:

1) Constant Volume (Bomb)



2) Constant Pressure (Coffee Cup)



ΔH of combustion reactions use constant volume, most others use constant pressure.

The difference between the 2 calorimeters:

<u>at constant volume:</u>

$2NH_{3(g)} + 87.26\ kJ \rightarrow N_{2(g)} + 3H_{2(g)}$ $\Delta E = 87.26\ kJ$

<u>at constant pressure:</u>

$2NH_{3(g)} + 92.22\ kJ \rightarrow N_{2(g)} + 3H_{2(g)}$ $\Delta E = 92.22\ kJ$

A calorimeter is only capable of measuring q or ΔH. It cannot measure the work done when gas expansion takes place.

When an exothermic reaction occurs in a calorimeter, the calorimeter temporarily absorbs all of the heat given off by the system.

$$q_{(system)} = -q_{(surroundings)}$$

where $q_{(surroundings)} = q_{(calorimeter)}$

Problem: 1.435 g napthalene (m.w. = 128.2 g/mole) is burned in a bomb calorimeter. The temperature of the calorimeter and 2000. g water within the calorimeter increases from 20.17 ^oC to 25.84 ^oC. The heat capacity (C) of the calorimeter is 1.80 kJ/^oC.

Calculate ΔE

Problem: 1.00 L of 1.00 M $Ba(NO_3)_2$ at 25.0°C is mixed with 1.00 L 1.00M Na_2SO_4 at 25 °C in a constant pressure calorimeter. A white solid forms and the temperature of the solution rises to 28.1 °C. Assume that the specific heat of the solution is 4.18 J/g°C and the density of the final solution is 1.0 g/mL. The heat capacity of the calorimeter is 5.0 J/°C.

Write a thermochemical equation for this reaction.

How would this problem change if .30 mole Ba^{+2} and .40 mole SO_4^{-2} were added, and the heat from the calorimeter measured 7.77 kJ?

Problem: Some people think that $H_{2(g)}$ would be a good substitute for methane (natural) gas in heating homes. To compare:

1.50 g sample CH_4 is combusted in a bomb calorimeter (C = 11.3 kJ/^oC, which includes water) and the temperature rose by 7.3 ^oC.

1.15 g sample H_2 is combusted in the same calorimeter, and the temperature rose by 14.3 ^oC.

Calculate the energy of combustion for each fuel in terms of kJ/gram.

Second method for determining ΔH of a reaction: Hess' Law of Heat Summation:

Given the following Equations:

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.5$ kJ

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -285.8$ kJ

$2C_2H_{2(g)} + 5\ O_2 \rightarrow 4CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H = -2598.8$ kJ

Calculate ΔH for:

$2C_{(graphite)} + H_{2(g)} \rightarrow C_2H_{2(g)}$

Problem: Determine ΔH_{rxn} for $C_{(graphite)} + 2H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow CH_3OH_{(l)}$

Given:

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$	$\Delta H = -393.5\ kJ$
$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$	$\Delta H = -285.8\ kJ$
$2C_2H_{2(g)} + 5\ O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -2598.8\ kJ$
$CH_3OH_{(l)} + 3/2\ O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -726.4\ kJ$

Third method of determining ΔH of a reaction:

Standard Enthalpy of Formation ΔH^o_f

- **Standard State (not conditions)** → o
- **Formation from elements in their standard state** → f

Standard State – 1 atmosphere
pure liquid or solid
solutions are 1 Molar
25 °C

defined – the change in enthalpy that accompanies the formation of 1 mole of a substance from its elements at standard state.

See p. A21 – A24, note ΔH^o_f of all elemental substances = 0

TABLE 6.2
Standard Enthalpies of Formation for Several Compounds at 25°C

Compound	ΔH°_f (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

Problem: Write an equation that produces $H_2O_{(l)}$ from its elements.

What is ΔH for this reaction?

Problem: Write an equation that produces $CH_3OH_{(l)}$ from its elements.

What is ΔH for this reaction?

TABLE 6.2
Standard Enthalpies of Formation for Several Compounds at 25°C

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$C_8H_{18}(l)$	−269

Problem: Calculate ΔH_{rxn} using the addition of <u>heat of formation summation</u> for:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Use Appendix pages a21 – a24

Calculate ΔH_{rxn} for : $2H_2S_{(g)} + 3O_{2(g)} \rightarrow 2H_2O_{(l)} + 2SO_{2(g)}$

Determine ΔH_{rxn} for one of the most exothermic chemical reactions known, the <u>Thermite Reaction:</u>

$$2Al_{(s)} + Fe_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)}$$

Problem: Which produces more energy per gram when combusted, gasoline (C_8H_{18}) or methanol (CH_3OH)?

Read p. 267-280 regarding energy sources, present and future.