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Ninth
Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 7: Thermochemistry

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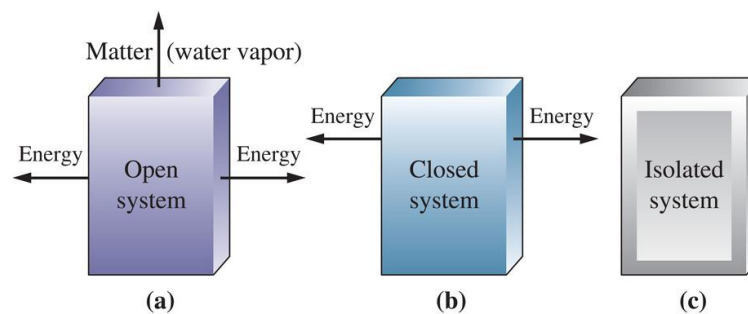
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➤ *Focus On Fats, Carbohydrates and Energy Storage*

7-1 Getting Started: Some Terminology

- ◆ System
- ◆ Surroundings



Terminology

◆ Energy, U

- The capacity to do work.

◆ Work

- Force acting through a distance.

◆ Kinetic Energy

- The energy of motion.

Energy

◆ Kinetic Energy

$$e_k = \frac{1}{2} mv^2 \quad [e_k] = \text{kg} \left(\frac{\text{m}}{\text{s}} \right)^2 = \text{J}$$

◆ Work

$$w = Fd \quad [w] = \left(\frac{\text{kg m}}{\text{s}^2} \right) \text{m} = \text{J}$$

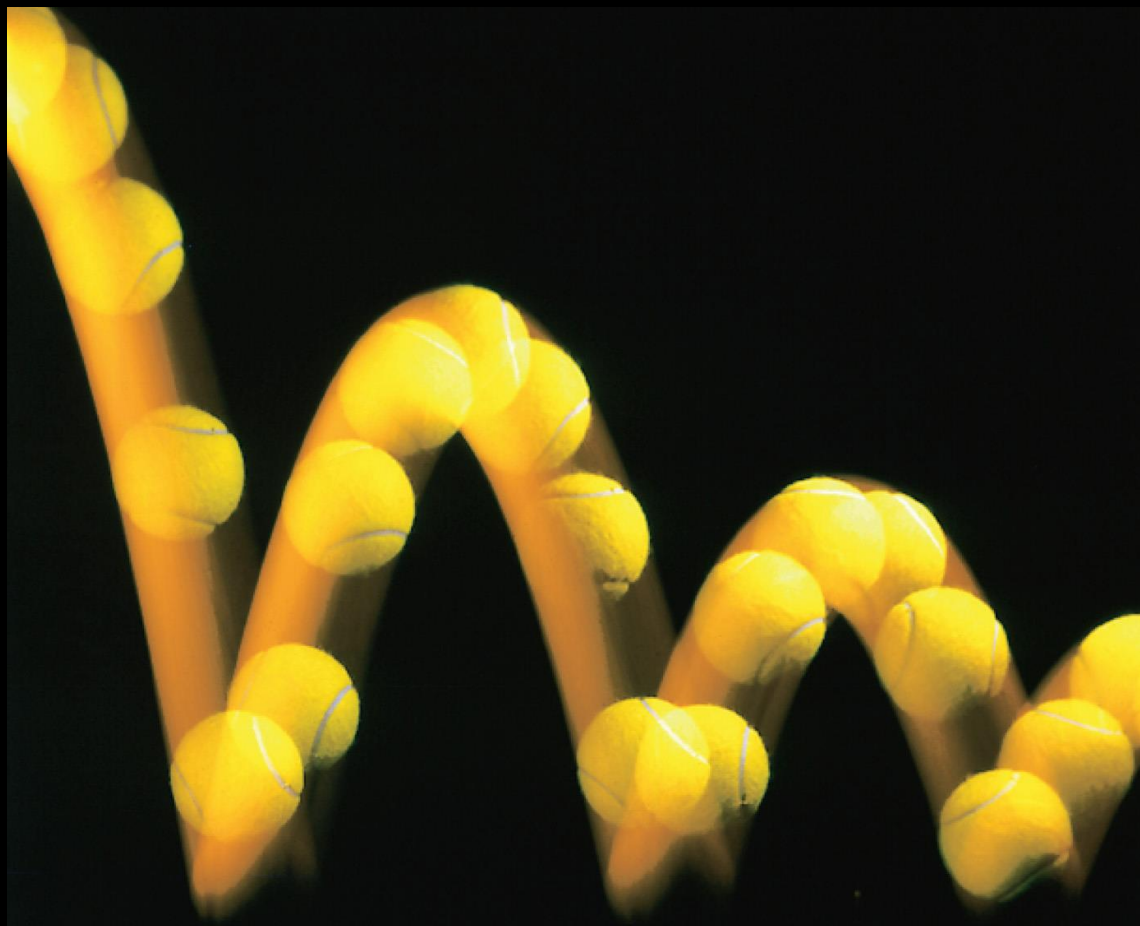
Energy

◆ Potential Energy

- Energy due to condition, position, or composition.
- Associated with forces of attraction or repulsion between objects.

◆ Energy can change from potential to kinetic.

Potential and Kinetic Energy



Energy and Temperature

◆ Thermal Energy

- Kinetic energy associated with random molecular motion.
- In general proportional to temperature.
- An intensive property.

◆ Heat and Work

- q and w .
- Energy changes.

Heat

Energy **transferred** between a system and its surroundings as a result of a temperature difference.

- ◆ Heat *flows* from hotter to colder.
 - Temperature may change.
 - Phase may change (an isothermal process).

Units of Heat

◆ Calorie (cal)

- The quantity of heat required to change the temperature of one gram of water by one degree Celsius.


◆ Joule (J)

- SI unit for heat

$$1 \text{ cal} = 4.184 \text{ J}$$

Heat Capacity

◆ The quantity of heat required to change the temperature of a system by one degree.

- Molar heat capacity.
 - System is one mole of substance.
- Specific heat capacity, c .
 - System is one gram of substance
- Heat capacity
 - Mass  specific heat.

$$q = mc\Delta T$$

$$q = C\Delta T$$

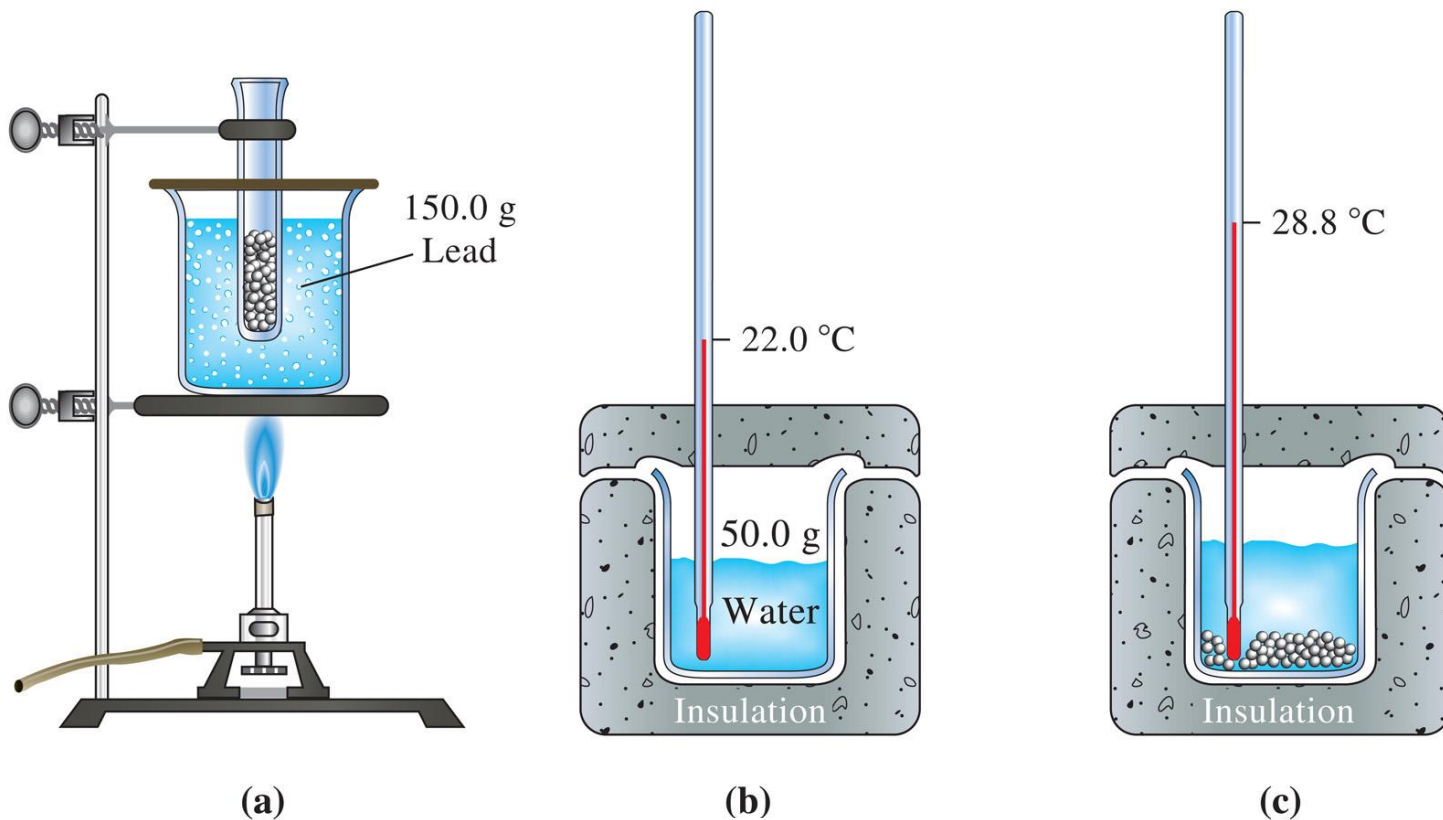
Conservation of Energy

- ◆ In interactions between a system and its surroundings the total energy remains *constant*—*energy is neither created nor destroyed*.

$$q_{\text{system}} + q_{\text{surroundings}} = 0$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$

Determination of Specific Heat



EXAMPLE 7-2

Determining Specific Heat from Experimental Data. Use the data presented on the last slide to calculate the specific heat of lead.

$$q_{\text{lead}} = -q_{\text{water}}$$

$$q_{\text{water}} = mc\Delta T = (50.0 \text{ g})(4.184 \text{ J/g } ^\circ\text{C})(28.8 - 22.0)^\circ\text{C}$$

$$q_{\text{water}} = 1.4 \times 10^3 \text{ J}$$

$$q_{\text{lead}} = -1.4 \times 10^3 \text{ J} = mc\Delta T = (150.0 \text{ g})(c_{\text{lead}})(28.8 - 100.0)^\circ\text{C}$$

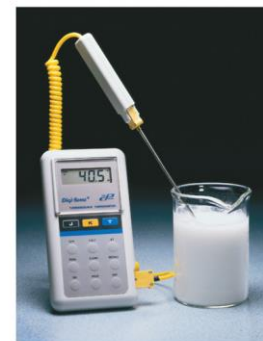
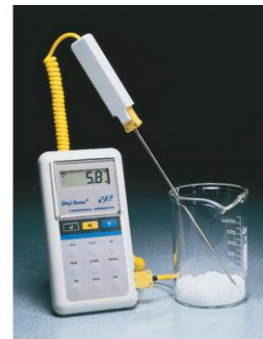
$$c_{\text{lead}} = 0.13 \text{ Jg}^{-1}\text{ }^\circ\text{C}^{-1}$$

7-3 Heats of Reaction and Calorimetry

- ◆ Chemical energy.
 - Contributes to the internal energy of a system.
- ◆ Heat of reaction, q_{rxn} .
 - The quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system, at *constant temperature*.

Heats of Reaction

- ◆ Exothermic reactions.
 - Produces heat, $q_{\text{rxn}} < 0$.
- ◆ Endothermic reactions.
 - Consumes heat, $q_{\text{rxn}} > 0$.
- ◆ Calorimeter
 - A device for measuring quantities of heat.



Add
water

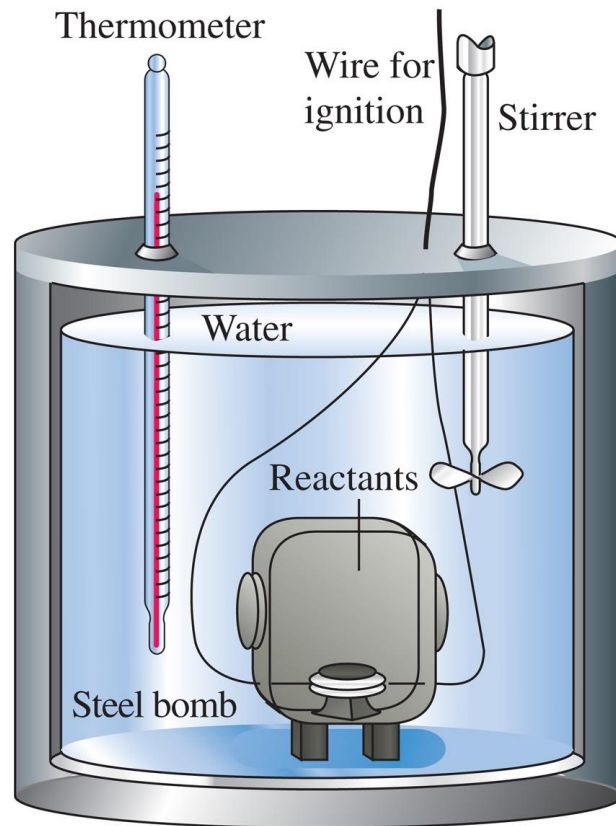
Bomb Calorimeter

$$q_{\text{rxn}} = -q_{\text{cal}}$$

$$q_{\text{cal}} = q_{\text{bomb}} + q_{\text{water}} + q_{\text{wires}} + \dots$$

Define the heat capacity of the calorimeter:

$$q_{\text{cal}} = \sum_{\text{all } i} m_i c_i \Delta T = C \Delta T$$



EXAMPLE 7-3

Using Bomb Calorimetry Data to Determine a Heat of Reaction. The combustion of 1.010 g sucrose, in a bomb calorimeter, causes the temperature to rise from 24.92 to 28.33°C. The heat capacity of the calorimeter assembly is 4.90 kJ/°C. (a) What is the heat of combustion of sucrose, expressed in kJ/mol $\text{C}_{12}\text{H}_{22}\text{O}_{11}$? (b) Verify the claim of sugar producers that one teaspoon of sugar (about 4.8 g) contains only 19 calories.

EXAMPLE 7-3

Calculate $q_{\text{calorimeter}}$:

$$\begin{aligned} q_{\text{cal}} &= C\Delta T = (4.90 \text{ kJ/}^{\circ}\text{C})(28.33-24.92)^{\circ}\text{C} = (4.90)(3.41) \text{ kJ} \\ &= 16.7 \text{ kJ} \end{aligned}$$

Calculate q_{rxn} :

$$q_{\text{rxn}} = -q_{\text{cal}} = -16.7 \text{ kJ} \quad \textit{per 1.010 g}$$

EXAMPLE 7-3

Calculate q_{rxn} in the required units:

$$q_{\text{rxn}} = -q_{\text{cal}} = \frac{-16.7 \text{ kJ}}{1.010 \text{ g}} = -16.5 \text{ kJ/g}$$

$$\begin{aligned} q_{\text{rxn}} &= -16.5 \text{ kJ/g} \frac{343.3 \text{ g}}{1.00 \text{ mol}} \\ &= -5.65 \times 10^3 \text{ kJ/mol} \end{aligned} \quad (\text{a})$$

Calculate q_{rxn} for one teaspoon:

$$q_{\text{rxn}} = (-16.5 \text{ kJ/g}) \left(\frac{4.8 \text{ g}}{1 \text{ tsp}} \right) \left(\frac{1.00 \text{ cal}}{4.184 \text{ J}} \right) = -19 \text{ kcal/tsp} \quad (\text{b})$$

Coffee Cup Calorimeter

- ◆ A simple calorimeter.
 - Well insulated and therefore *isolated*.
 - Measure temperature change.

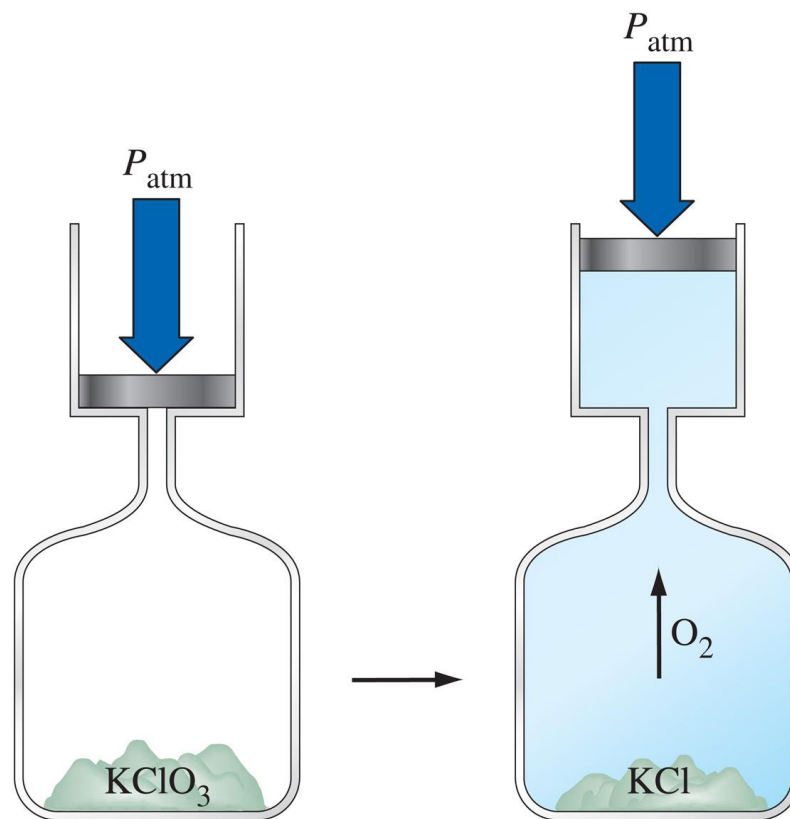
$$q_{\text{rxn}} = -q_{\text{cal}}$$

See example 7-4 for a sample calculation.

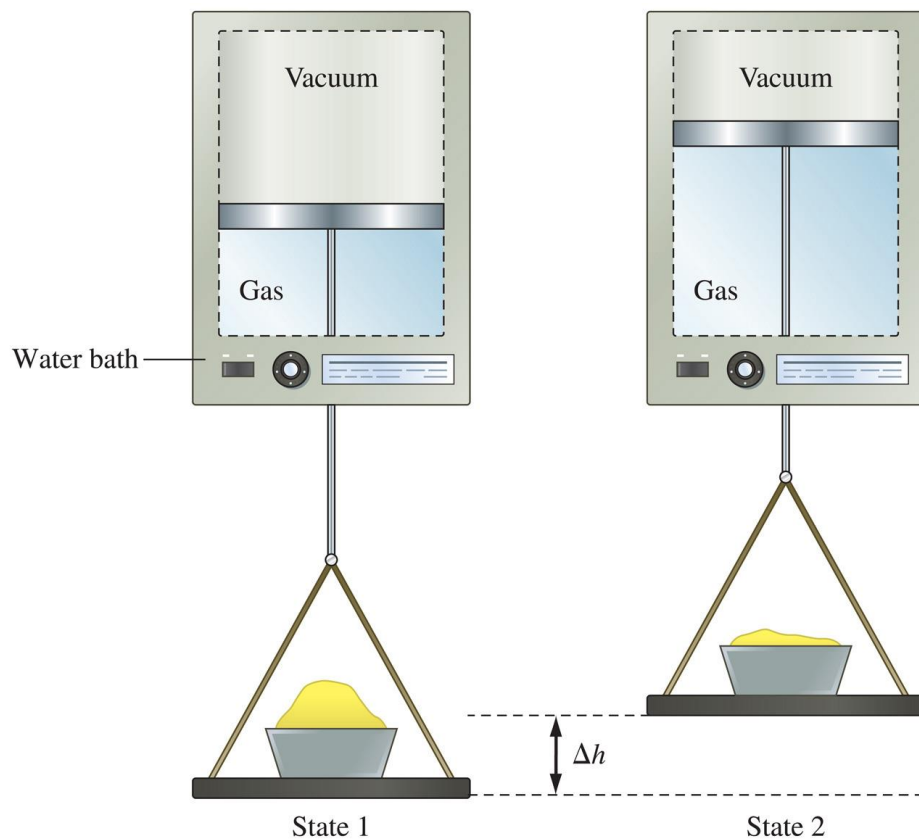


7-4 Work

- ◆ In addition to heat effects chemical reactions may also do *work*.
- ◆ Gas formed pushes against the atmosphere.
- ◆ Volume changes.
- ◆ *Pressure-volume work*.



Pressure Volume Work



$$w = F \times d$$

$$= (m \times g) \times \Delta h$$

$$= \frac{(m \times g)}{A} \times \Delta h \times A$$

$$= P\Delta V$$

$$w = -P_{\text{ext}}\Delta V$$

EXAMPLE 7-5

Calculating Pressure-Volume Work. Suppose the gas in the previous figure is 0.100 mol He at 298 K and the each mass in the figure corresponds to an external pressure of 1.20 atm. How much work, in Joules, is associated with its expansion at constant pressure.

Assume an ideal gas and calculate the volume change:

$$V_i = nRT/P$$

$$= (0.100 \text{ mol})(0.08201 \text{ L atm mol}^{-1} \text{ K}^{-1})(298\text{K})/(2.40 \text{ atm})$$

$$= 1.02 \text{ L}$$

$$V_f = 2.04 \text{ L}$$

$$\Delta V = 2.04 \text{ L} - 1.02 \text{ L} = 1.02 \text{ L}$$

EXAMPLE 7-5

Calculate the work done by the system:

$$\begin{aligned}w &= -P\Delta V \\&= -(1.20 \text{ atm})(1.02 \text{ L})\left(\frac{-101 \text{ J}}{1 \text{ L atm}}\right) \\&= -1.24 \times 10^2 \text{ J}\end{aligned}$$

*Hint: If you use
pressure in **kPa** you
get Joules directly.*

A negative value signifies that work is done ON the surroundings

Where did the conversion factor come from?

Compare two versions of the gas constant and calculate.

$$8.3145 \text{ J/mol K} \equiv 0.082057 \text{ L atm/mol K}$$

$$1 \equiv 101.33 \text{ J/L atm}$$

7-5 The First Law of Thermodynamics

◆ Internal Energy, U .

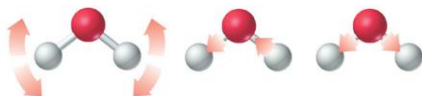
- Total energy (potential and kinetic) in a system.



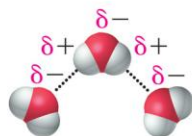
Translational



Rotational



Vibrational



Electrostatic
(Intermolecular attractions)

- Translational kinetic energy.
- Molecular rotation.
- Bond vibration.
- Intermolecular attractions.
- Chemical bonds.
- Electrons.

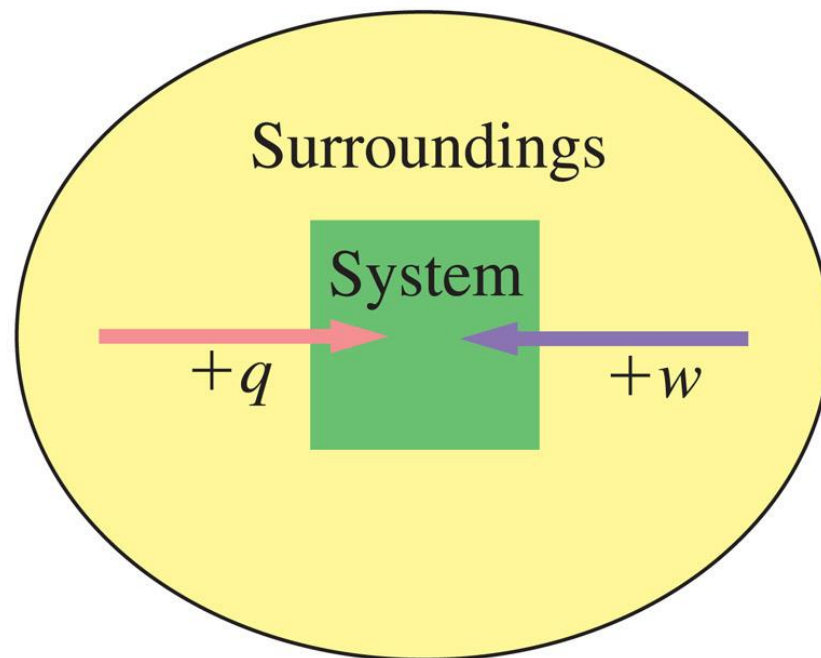
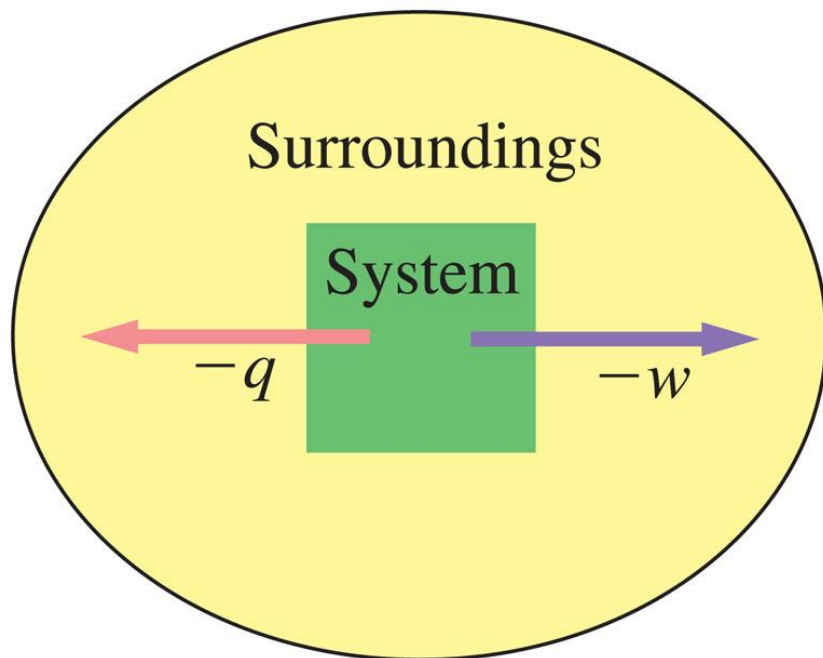
First Law of Thermodynamics

- ◆ A system contains *only* internal energy.
 - A system does not contain heat or work.
 - These only occur during a *change* in the system.

$$\Delta U = q + w$$

- ◆ Law of Conservation of Energy
 - The energy of an isolated system is constant

First Law of Thermodynamics

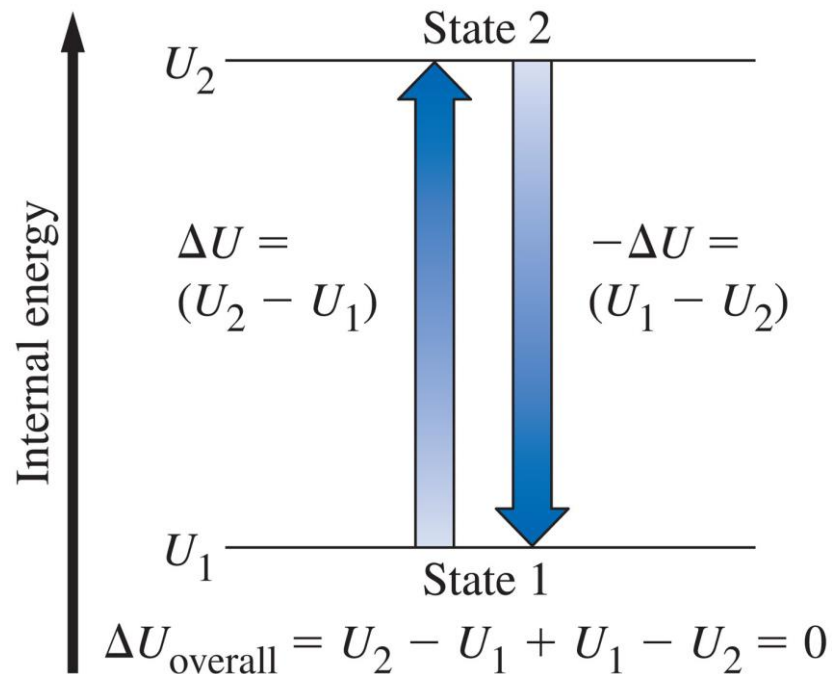


Functions of State

- ◆ Any property that has a unique value for a specified state of a system is said to be a State Function.
 - Water at 293.15 K and 1.00 atm is in a specified state.
 - $d = 0.99820 \text{ g/mL}$
 - This density is a unique function of the state.
 - It does not matter *how* the state was established.

Functions of State

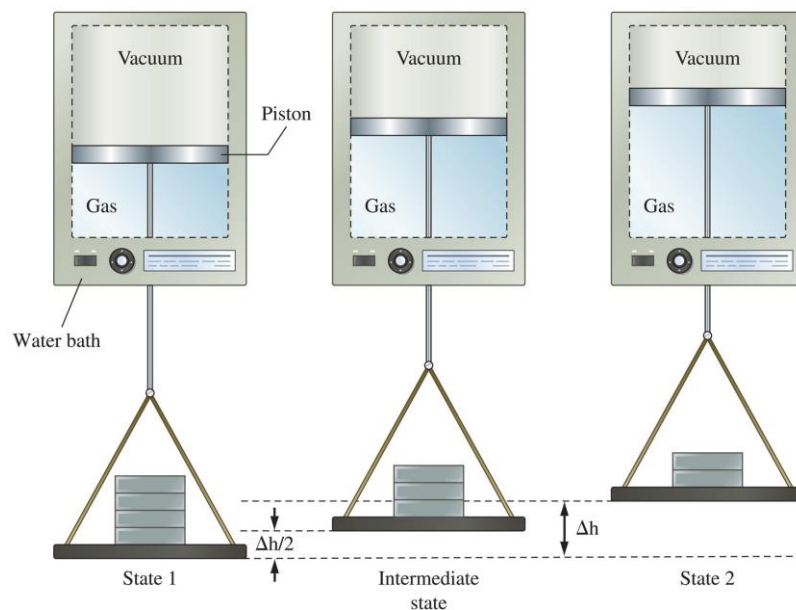
- ◆ U is a function of state.
 - Not easily measured.
- ◆ ΔU has a unique value between two states.
 - Is easily measured.



Path Dependent Functions

- ◆ Changes in heat and work are not functions of state.
 - Remember example 7-5, $w = -1.24 \times 10^2 \text{ J}$ in a one step expansion of gas:
 - Consider 2.40 atm to 1.80 atm and finally to 1.20 atm.

Path Dependent Functions



$$\begin{aligned}
 w &= (-1.80 \text{ atm})(1.36-1.02)\text{L} - (1.30 \text{ atm})(2.04-1.36)\text{L} \\
 &= -0.61 \text{ L atm} - 0.82 \text{ L atm} = -1.43 \text{ L atm} \\
 &= -1.44 \times 10^2 \text{ J}
 \end{aligned}$$

Compared $-1.24 \times 10^2 \text{ J}$ for the two stage process

7-6 Heats of Reaction: ΔU and ΔH

Reactants \rightarrow Products

$$U_i \qquad U_f$$

$$\Delta U = U_f - U_i$$

$$\Delta = q_{\text{rxn}} + w$$

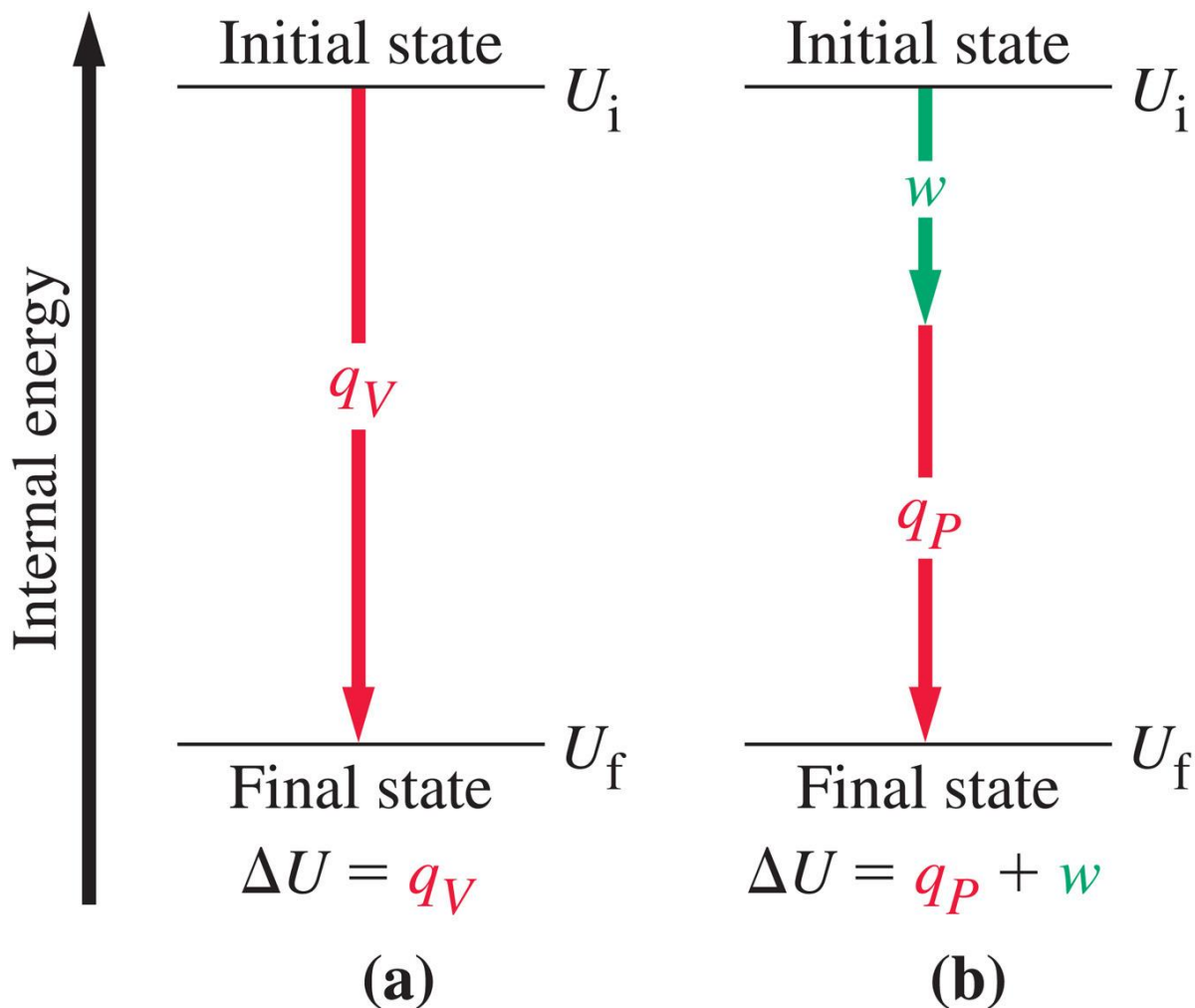
In a system at constant volume:

$$\Delta U = q_{\text{rxn}} + 0 = q_{\text{rxn}} = q_v$$

But we live in a constant pressure world!

How does q_p relate to q_v ?

Heats of Reaction



Heats of Reaction

$$q_V = q_P + w$$

We know that $w = -P\Delta V$ and $\Delta U = q_P$, therefore:

$$\Delta U = q_P - P\Delta V$$

$$q_P = \Delta U + P\Delta V$$

These are all state functions, so define a new function.

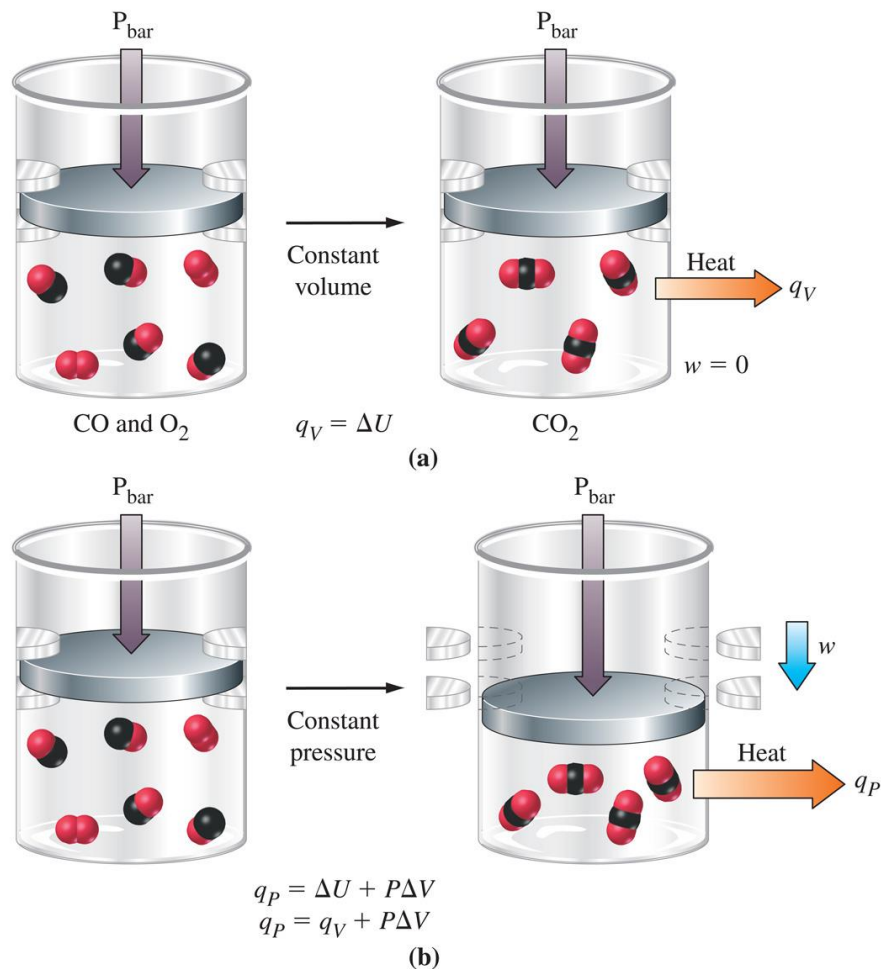
Let
$$H = U + PV$$

Then
$$\Delta H = H_f - H_i = \Delta U + \Delta PV$$

If we work at constant pressure and temperature:

$$\Delta H = \Delta U + P\Delta V = q_P$$

Comparing Heats of Reaction



$$q_P = -566 \text{ kJ/mol}$$

$$= \Delta H$$

$$P\Delta V = P(V_f - V_i)$$

$$= RT(n_f - n_i)$$

$$= -2.5 \text{ kJ}$$

$$\Delta U = \Delta H - P\Delta V$$

$$= -563.5 \text{ kJ/mol}$$

$$= q_V$$

Changes of State of Matter

Molar enthalpy of vaporization:



Molar enthalpy of fusion:



EXAMPLE 7-8

Enthalpy Changes Accompanying Changes in States of Matter. Calculate ΔH for the process in which 50.0 g of water is converted from liquid at 10.0°C to vapor at 25.0°C.

Break the problem into two steps: Raise the temperature of the liquid first then completely vaporize it. The total enthalpy change is the sum of the changes in each step.

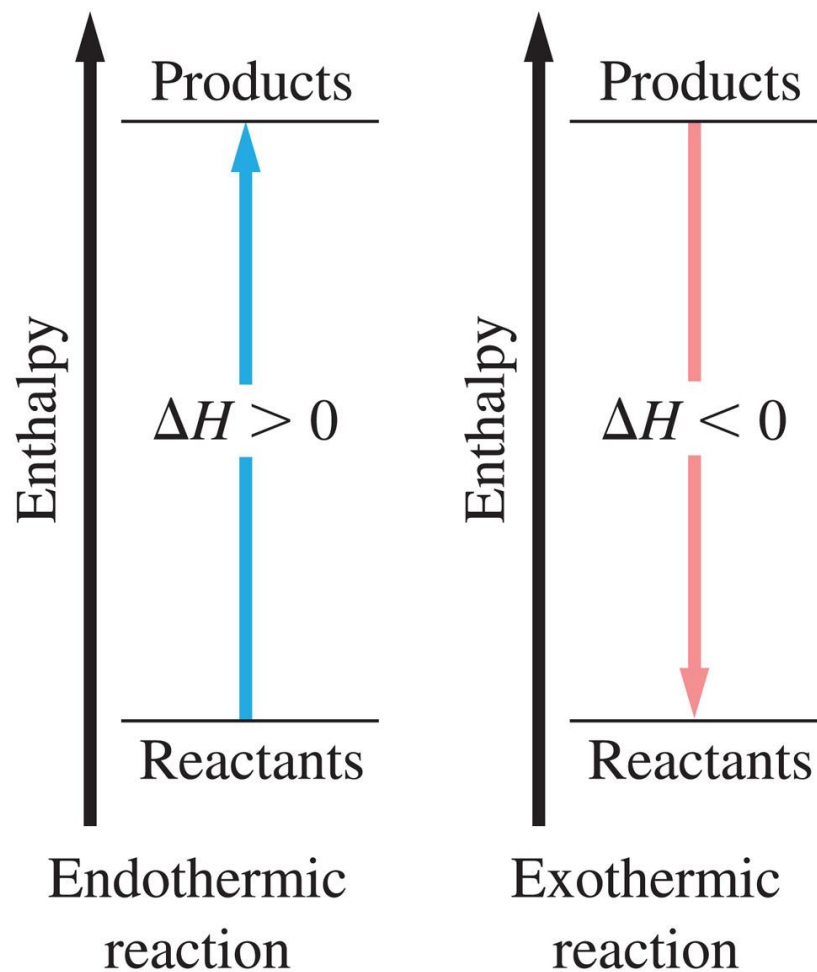
Set up the equation and calculate:

$$\begin{aligned} q_P &= mc_{\text{H}_2\text{O}}\Delta T + n\Delta H_{\text{vap}} \\ &= (50.0 \text{ g})(4.184 \text{ J/g } ^\circ\text{C})(25.0-10.0)^\circ\text{C} + \frac{50.0 \text{ g}}{18.0 \text{ g/mol}} 44.0 \text{ kJ/mol} \\ &= 3.14 \text{ kJ} + 122 \text{ kJ} = 125 \text{ kJ} \end{aligned}$$

Standard States and Standard Enthalpy Changes

- ◆ Define a particular state as a standard state.
- ◆ Standard enthalpy of reaction, ΔH°
 - The enthalpy change of a reaction in which all reactants and products are in their standard states.
- ◆ Standard State
 - The pure element or compound at a pressure of 1 bar and at the temperature of interest.

Enthalpy Diagrams

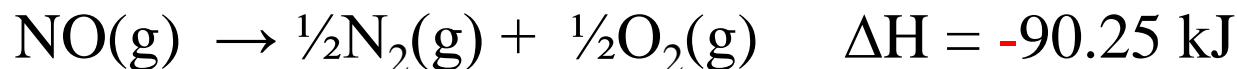


7-7 Indirect Determination of ΔH : Hess's Law

- ◆ ΔH is an extensive property.
 - Enthalpy change is directly proportional to the amount of substance in a system.



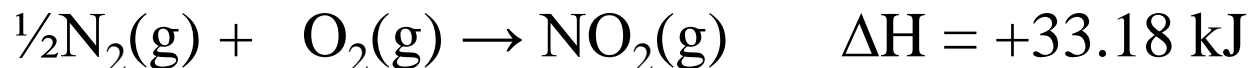
- ◆ ΔH changes sign when a process is reversed



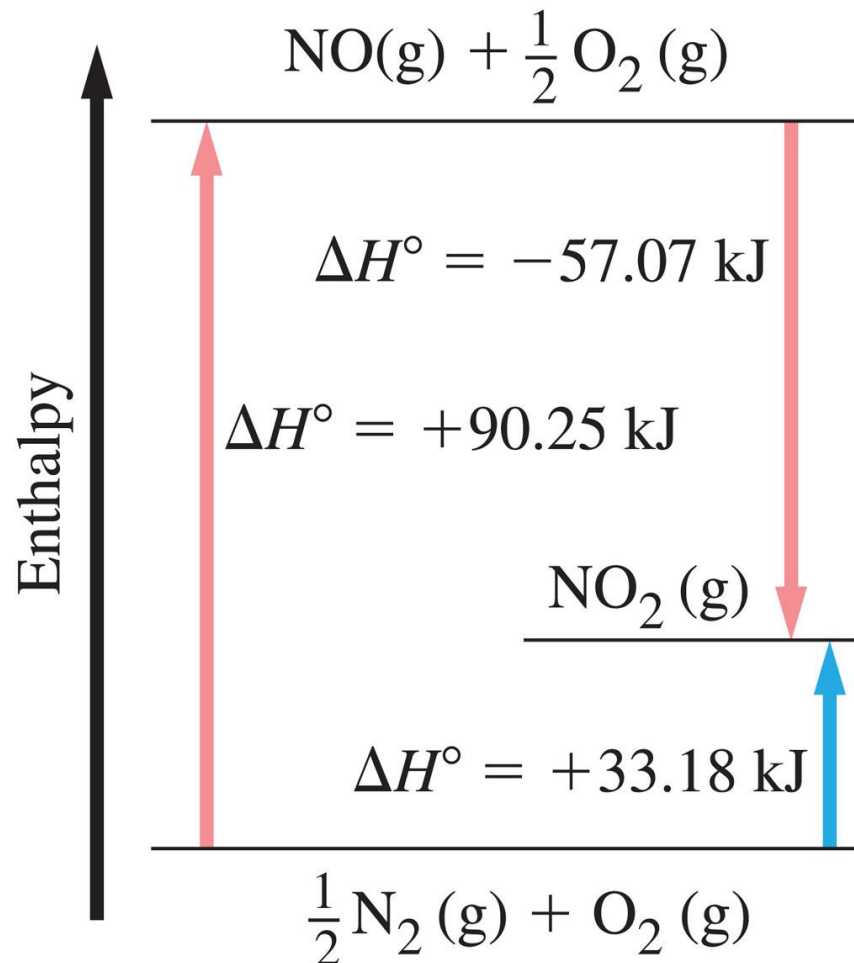
Hess's Law

◆ Hess's law of constant heat summation

- If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.



Hess's Law Schematically



7-8 Standard Enthalpies of Formation

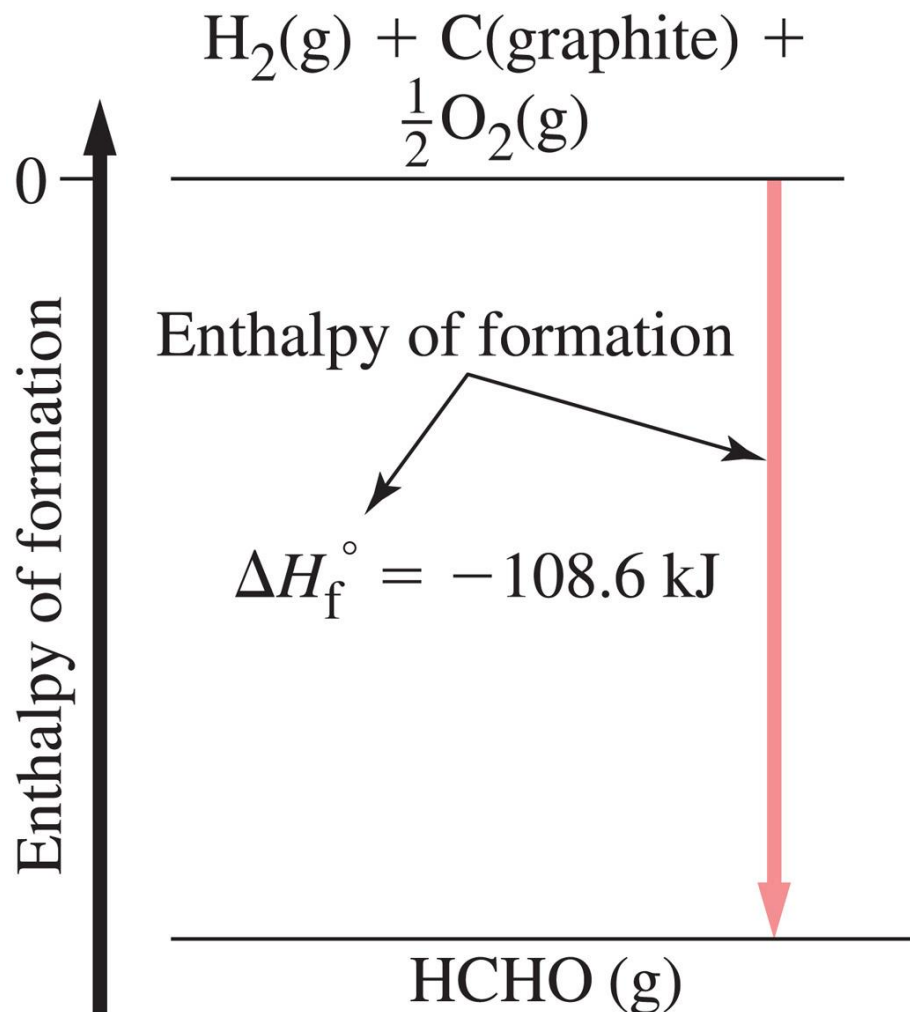


- ◆ The enthalpy change that occurs in the formation of one mole of a substance in the standard state from the reference forms of the elements in their standard states.
- ◆ The standard enthalpy of formation of a pure element in its reference state is 0.

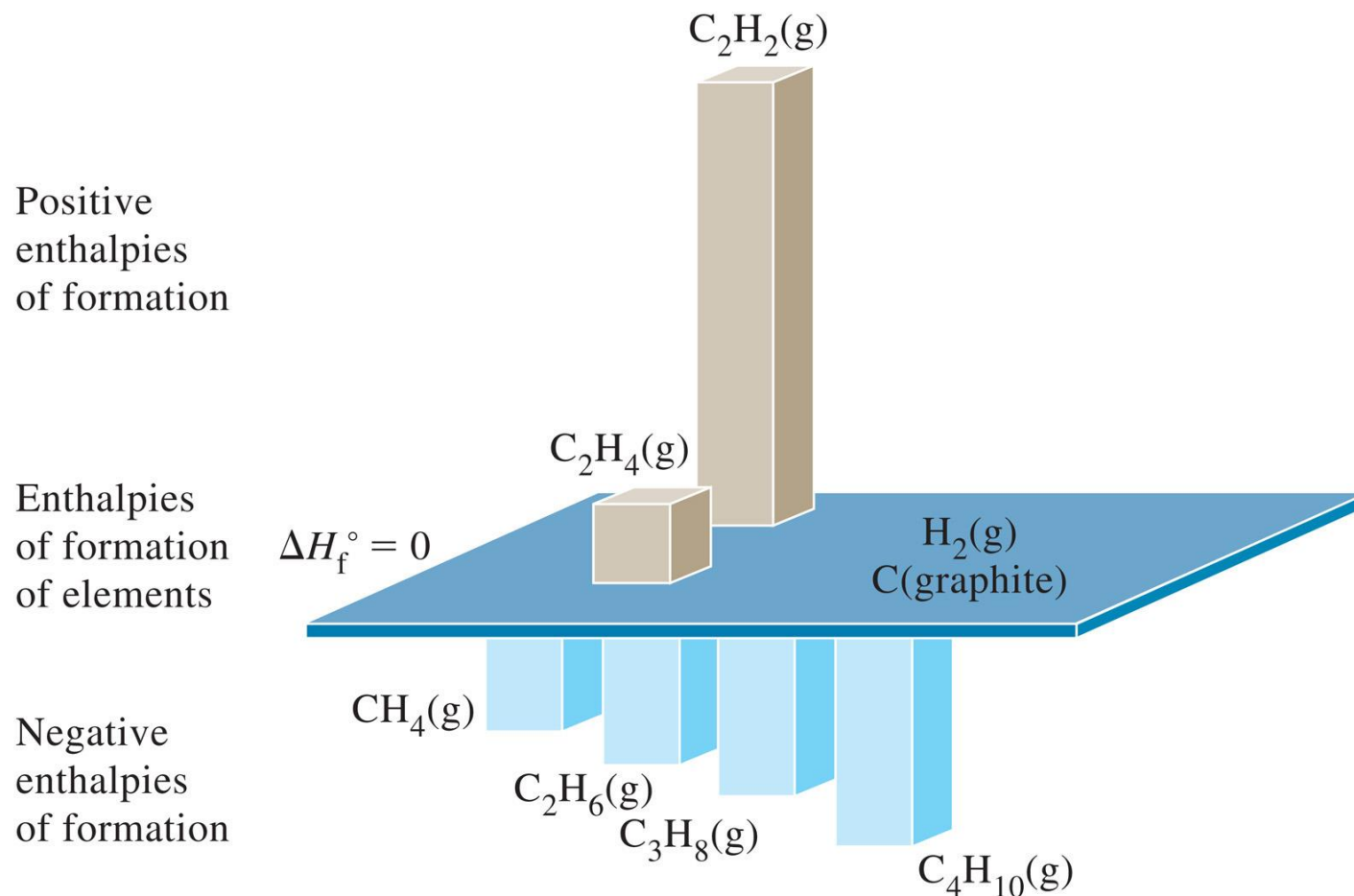
Standard States



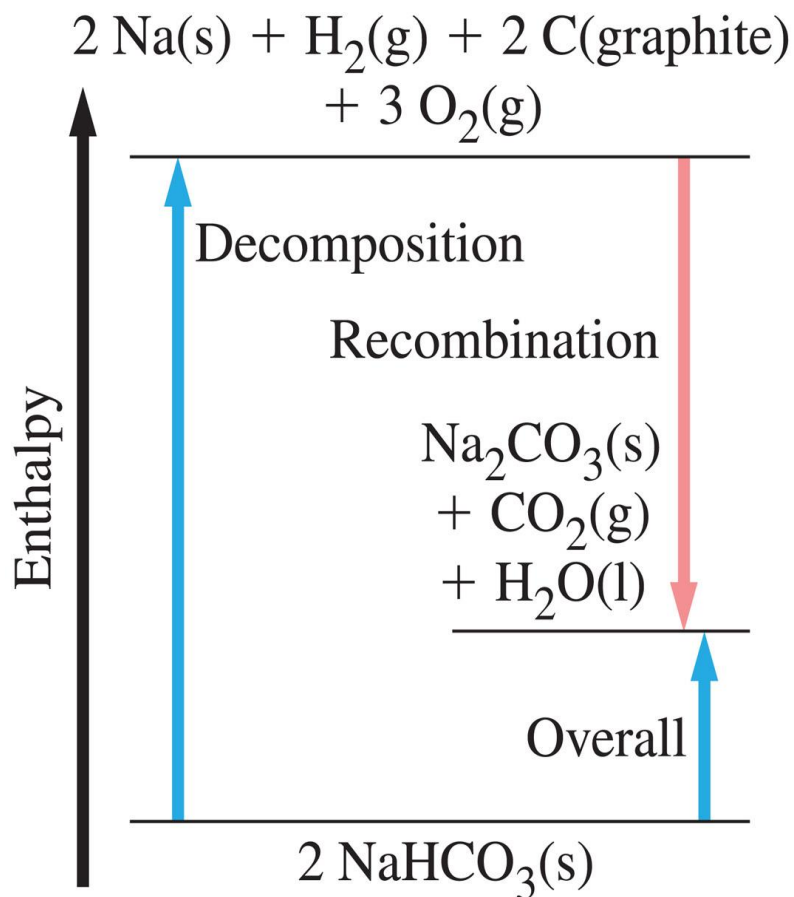
Standard Enthalpy of Formation



Standard Enthalpies of Formation



Standard Enthalpies of Reaction



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$$\Delta H_{\text{overall}} = -2\Delta H_{\text{f}}^{\circ} \text{NaHCO}_3 + \Delta H_{\text{f}}^{\circ} \text{Na}_2\text{CO}_3 + \Delta H_{\text{f}}^{\circ} \text{CO}_2 + \Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}$$

Enthalpy of Reaction

$$\Delta H_{\text{rxn}} = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

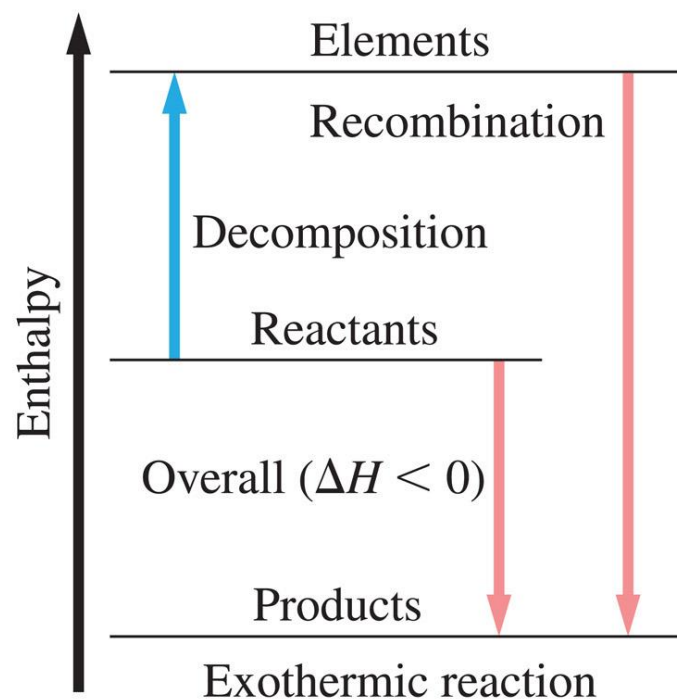
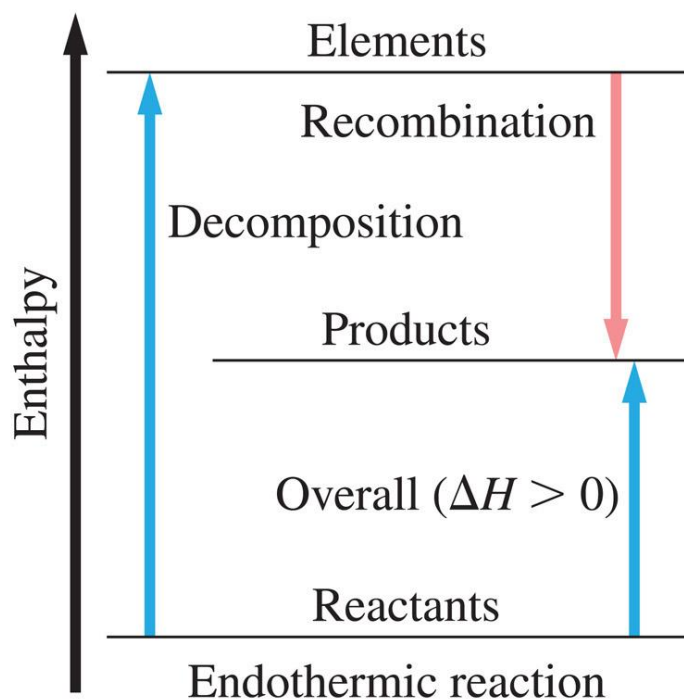


TABLE 7.2 Some Standard Molar Enthalpies of Formation at 298.15 K, ΔH_f°

Substance	kJ/mol ^a	Substance	kJ/mol ^a
CO(g)	−110.5	HBr(g)	−36.40
CO ₂ (g)	−393.5	HI(g)	26.48
CH ₄ (g)	−74.81	H ₂ O(g)	−241.8
C ₂ H ₂ (g)	226.7	H ₂ O(l)	−285.8
C ₂ H ₄ (g)	52.26	H ₂ S(g)	−20.63
C ₂ H ₆ (g)	−84.68	NH ₃ (g)	−46.11
C ₃ H ₈ (g)	−103.8	NO(g)	90.25
C ₄ H ₁₀ (g)	−125.6	N ₂ O(g)	82.05
CH ₃ OH(l)	−238.7	NO ₂ (g)	33.18
C ₂ H ₅ OH(l)	−277.7	N ₂ O ₄ (g)	9.16
HF(g)	−271.1	SO ₂ (g)	−296.8
HCl(g)	−92.31	SO ₃ (g)	−395.7

^aValues are for reactions in which one mole of substance is formed. Most of the data have been rounded off to four significant figures.

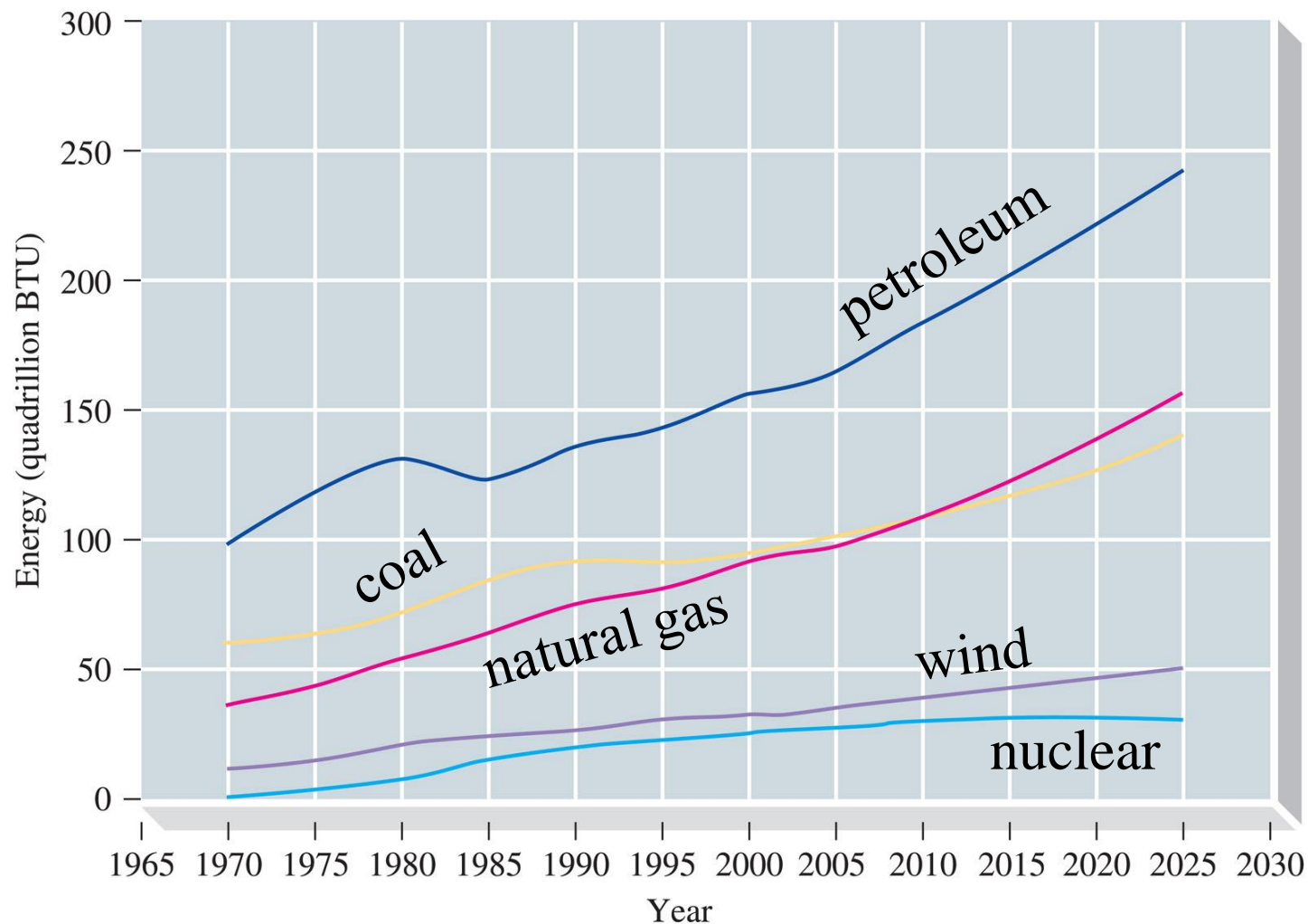
7-9 Fuels as Sources of Energy

- ◆ Fossil fuels.
 - Combustion is exothermic.
 - Non-renewable resource.
 - Environmental impact.

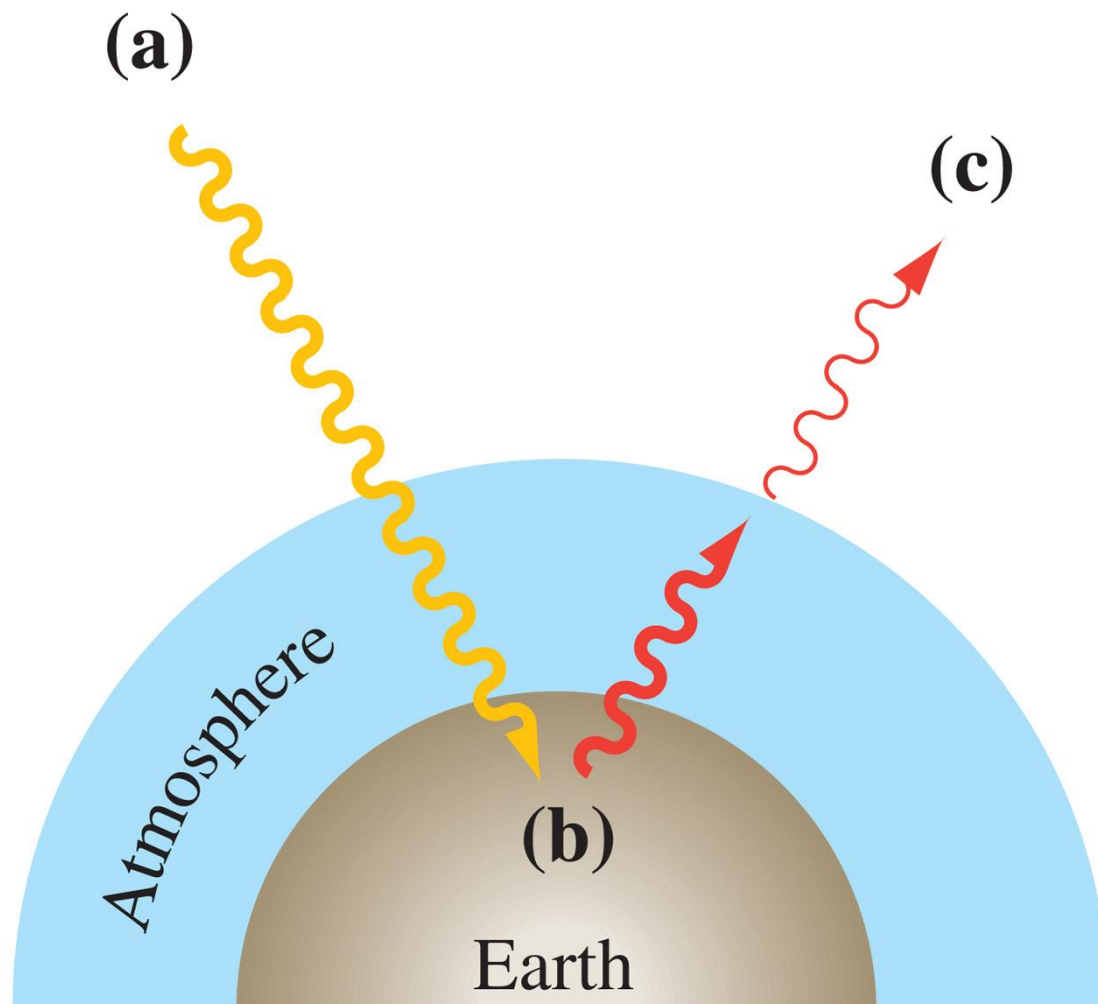
TABLE 7.4 Approximate Heats of Combustion of Some Fuels

Heat of Combustion	
Fuel	kJ/g
Municipal waste	−12.7
Cellulose	−17.5
Pinewood	−21.2
Methanol	−22.7
Peat	−20.8
Bituminous coal	−28.3
Isooctane	−47.8
(a component of gasoline)	
Natural gas	−49.5

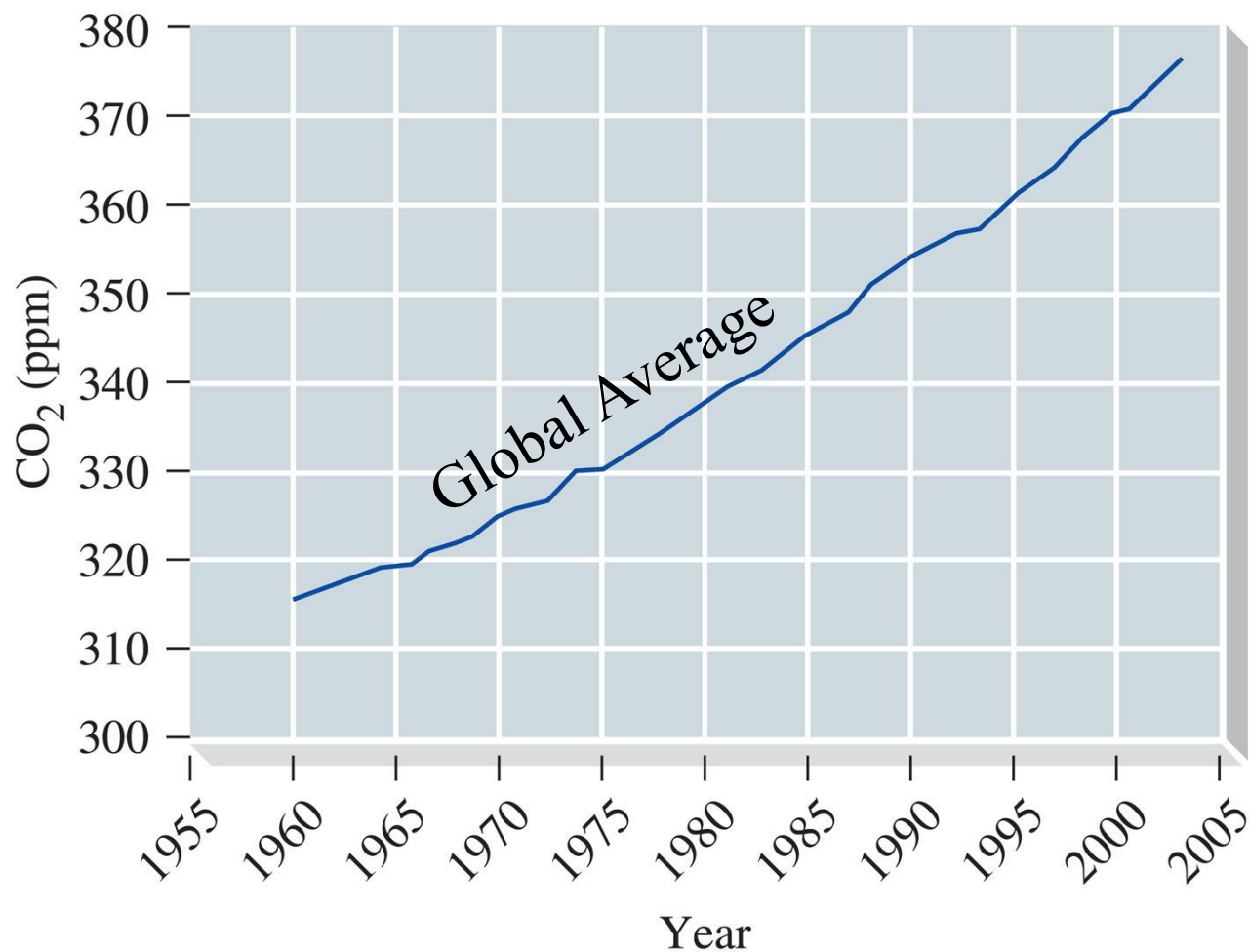
World Primary Energy Consumption



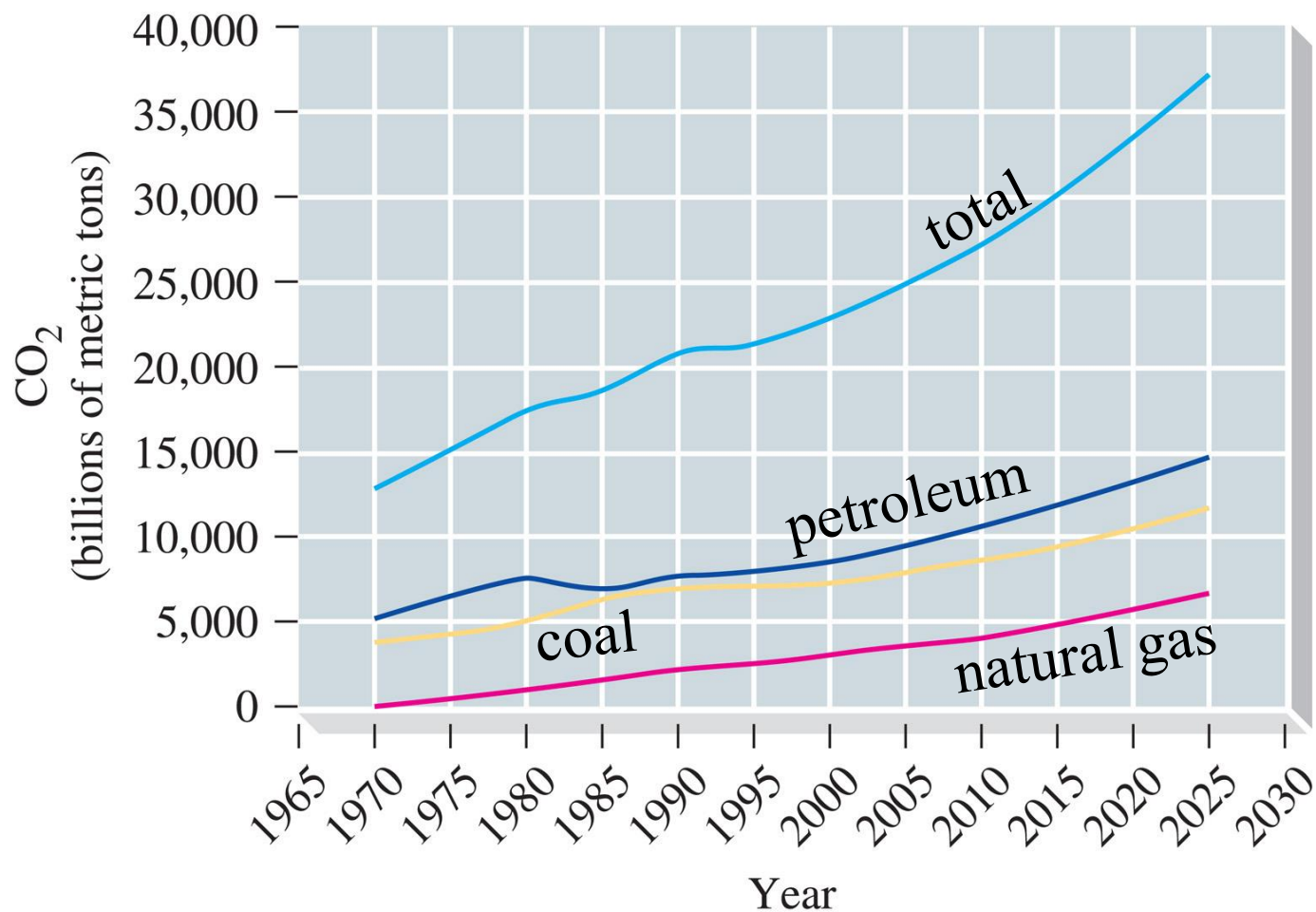
Greenhouse Effect



CO₂ in the Atmosphere



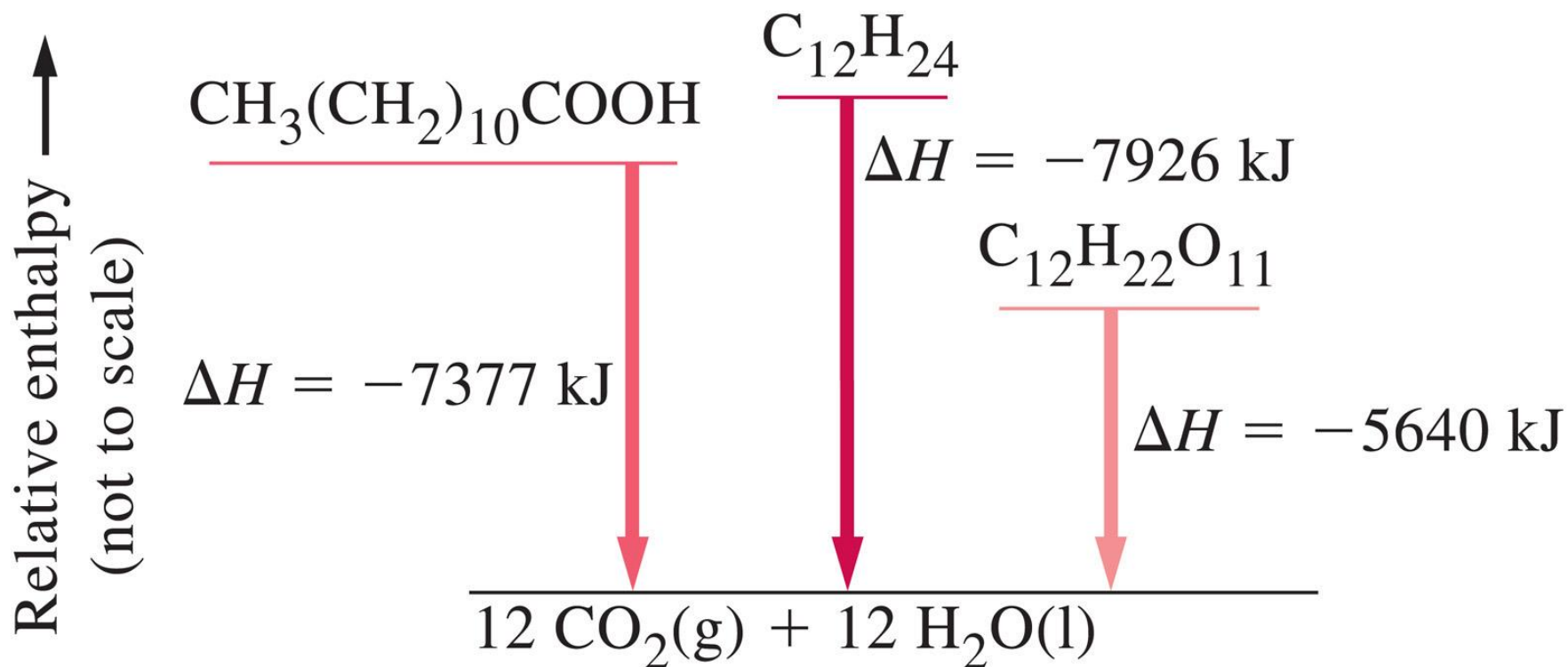
Actual and Predicted Emission of CO₂



Focus on: Fats Carbohydrates and Energy Storage



Energy Values of Fats and Carbohydrates



$$1 \text{ cal} = 4.184 \text{ J}$$

End of Chapter Questions

- ◆ Seek help with problems
 - But only after struggling with them.
- ◆ The initial effort pays off
 - Understanding occurs when solutions are explained by peers, tutors or professors.
- ◆ Do *not* go straight to the solution manual
 - You only *think* that you understand the solution if you have not worked hard on it first. The struggle to solve the problem is a key part of the memory and understanding process.