

General Chemistry

Principles and Modern Applications

Petrucci • Harwood • Herring

8th Edition



Chapter 7: Thermochemistry

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Potassium reacts with water, liberating sufficient heat to ignite the hydrogen evolved. The transfer of heat between substances in chemical reactions is an important aspect of thermochemistry.

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Focus on Fats, Carbohydrates, and Energy Storage

7-1 Getting Started: Some Terminology

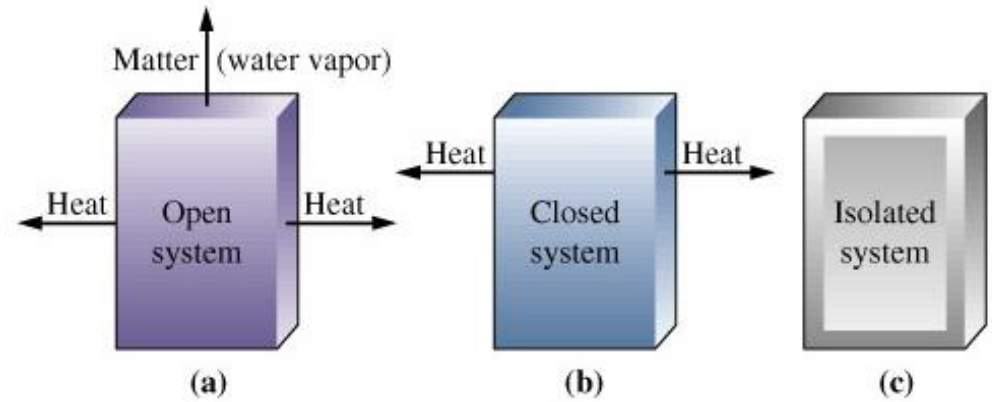
System and Surroundings

A **system** is the part of the universe chosen for study, and it can be as large as all the oceans on Earth or as small as the contents of a beaker.

Most of the systems we will examine will be small and we will look, particularly, at the transfer of energy (as heat and work) and matter between the system and its surroundings.

The **surroundings** are that part of the universe outside the system with which the system interacts.

7-1 Getting Started: Some Terminology



Open System

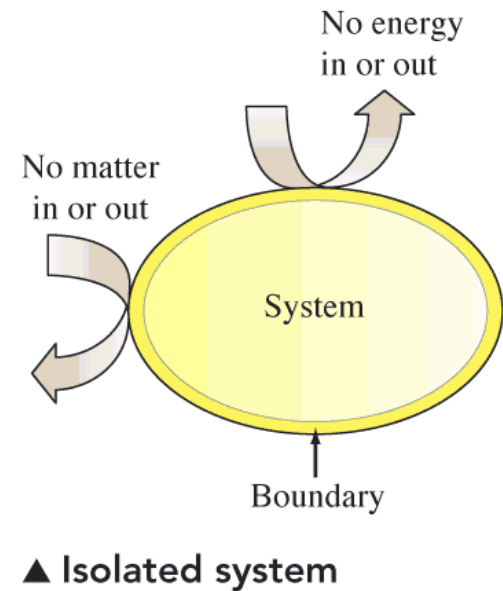
–exchanges energy and matter with its surroundings

Closed System

–exchange energy, but not matter, with its surround.

Isolated System

– doesnot interact with its surroundings



Terminology

- Energy, U Greek- “work within”
 - The capacity to do work.

➤ Work

- Force acting through a distance.

$$W = F \cdot d \quad W = m \cdot a \cdot d \quad W = \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = \text{J} = \text{Joule}$$

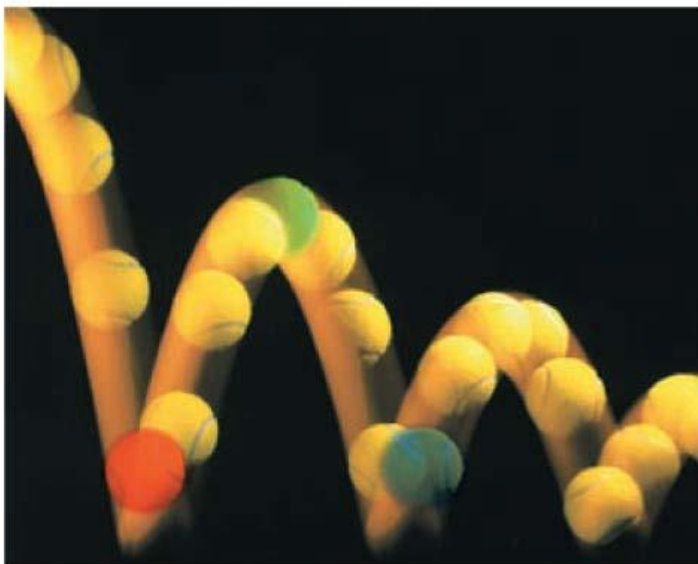
Moving objects do work when they slow down / stopped.

➤ Kinetic Energy

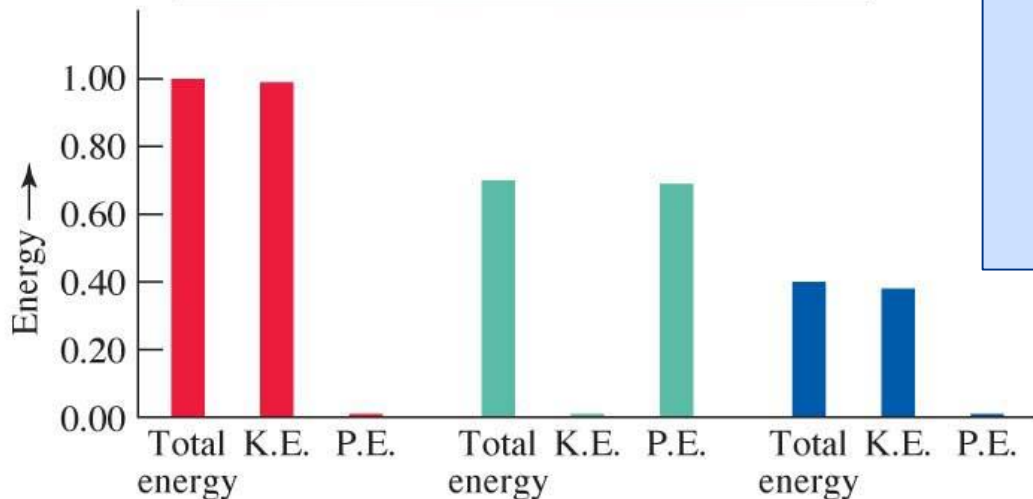
The energy of motion. Kinetic means “motion” in greek

$$e_k = \frac{1}{2} m v^2 \quad [e_k] = \frac{\text{kg m}^2}{\text{s}^2} = \text{Joule}$$

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
 - Energy is lost to the surroundings



Energy and Temperature:

- Thermal Energy

- Kinetic energy associated with random molecular motion.

- In general proportional to temperature of a system.

- The more vigorous the motion of the molecules in the system, the hotter the sample and the greater is its thermal energy.

- the thermal energy of a system also depends on the number of particles present,
 - cup of coffee at 75 C may have less thermal energy than swimming pool at 30 C therefore

- temperature and thermal energy needs to be carefully distinguished

we also need to distinguish between *work and heat* .

- energy changes produced by the action of forces through distances, *work* , and those involving the transfer of thermal energy, *heat*

7.2. Heat, q ,

Heat

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

- At the molecular level, molecules of the warmer body, through collisions, lose kinetic energy to those of the colder body.
- Thermal energy is transferred. –” heat flows”- until the average molecular kinetic energies of the two bodies become the same, until the temperatures become equal.
- 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 is called the **heat capacity** of the system.
 - Molar heat capacity.
 - System is one mole of substance.
 - Specific heat capacity, **c**
 - System is one gram of substance
 - Heat capacity, **C**
 - Mass x specific heat.

Quantity of heat = mass of substance x spec. heat x temperature change

$$q = m \times c \times \Delta T$$

$$q = C\Delta T$$

EXAMPLE 7-1 Calculating a Quantity of Heat

How much heat is required to raise the temperature of 7.35 g of water from 21.0 to 98.0 °C? (Assume the specific heat of water is 4.18 J g⁻¹ °C⁻¹ throughout this temperature range.)

Analyze

To answer this question, we begin by multiplying the specific heat capacity by the mass of water to obtain the heat capacity of the system. To find the amount of heat required to produce the desired temperature change we multiply the heat capacity by the temperature difference.

Solve

The specific heat is the heat capacity of 1.00 g water:

$$\frac{4.18 \text{ J}}{\text{g water } ^\circ\text{C}}$$

The heat capacity of the system (7.35 g water) is

$$7.35 \text{ g water} \times \frac{4.18 \text{ J}}{\text{g water } ^\circ\text{C}} = 30.7 \frac{\text{J}}{^\circ\text{C}}$$

The required temperature change in the system is

$$(98.0 - 21.0) ^\circ\text{C} = 77.0 ^\circ\text{C}$$

The heat required to produce this temperature change is

$$30.7 \frac{\text{J}}{^\circ\text{C}} \times 77.0 ^\circ\text{C} = 2.36 \times 10^3 \text{ J}$$

Assess

Remember that specific heat is a quantity that depends on the amount of material. Also note that the change in temperature is determined by subtracting the initial temperature from the final temperature. This will be important in determining the sign on the value you determine for heat, as will become apparent in the next section.

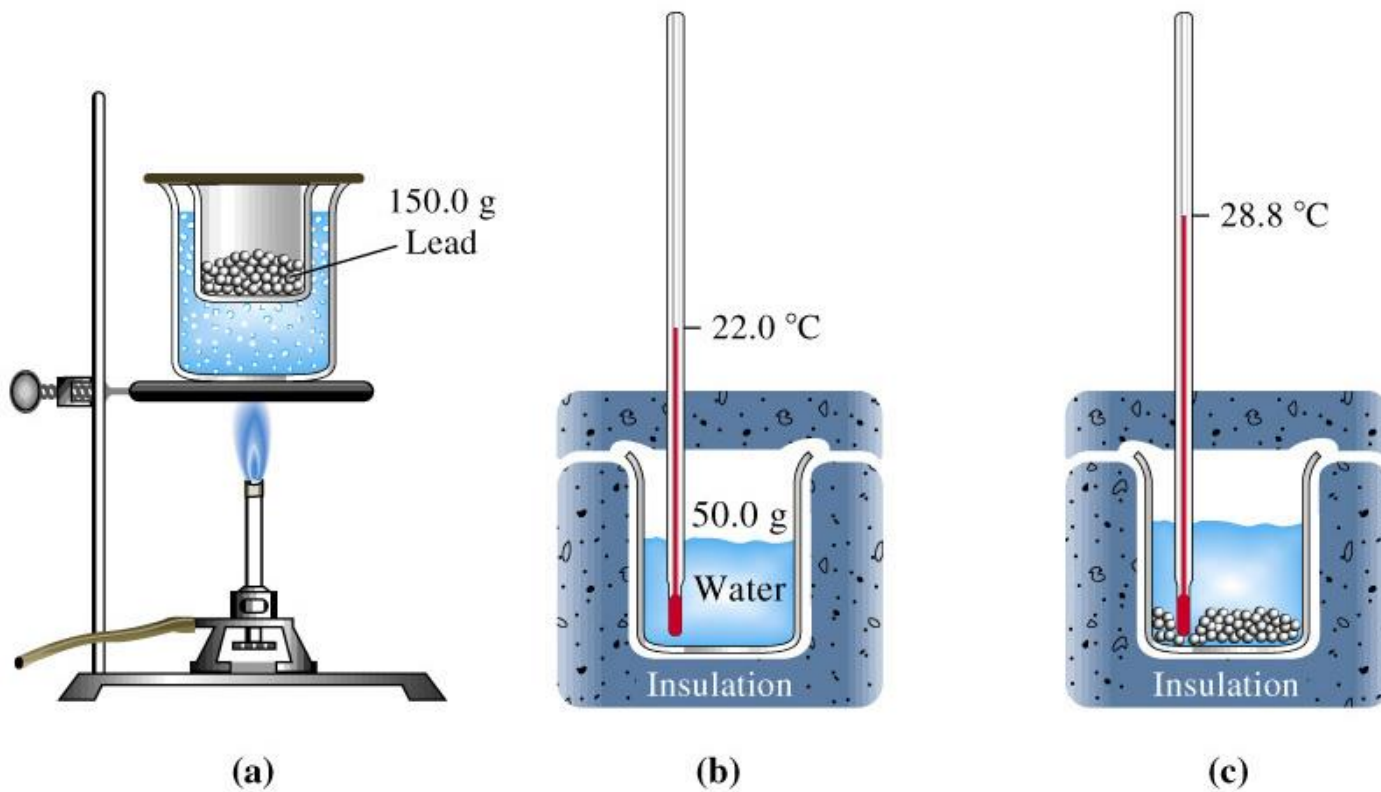
Conservation of Energy

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

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

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

Experimental Determination of Specific Heats



Example 7-2

Determining Specific Heat from Experimental Data.

Use the data presented on the last slide to calculate the specific heat of lead.

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

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

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

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

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

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.



(a)



(b)

Bomb Calorimeter

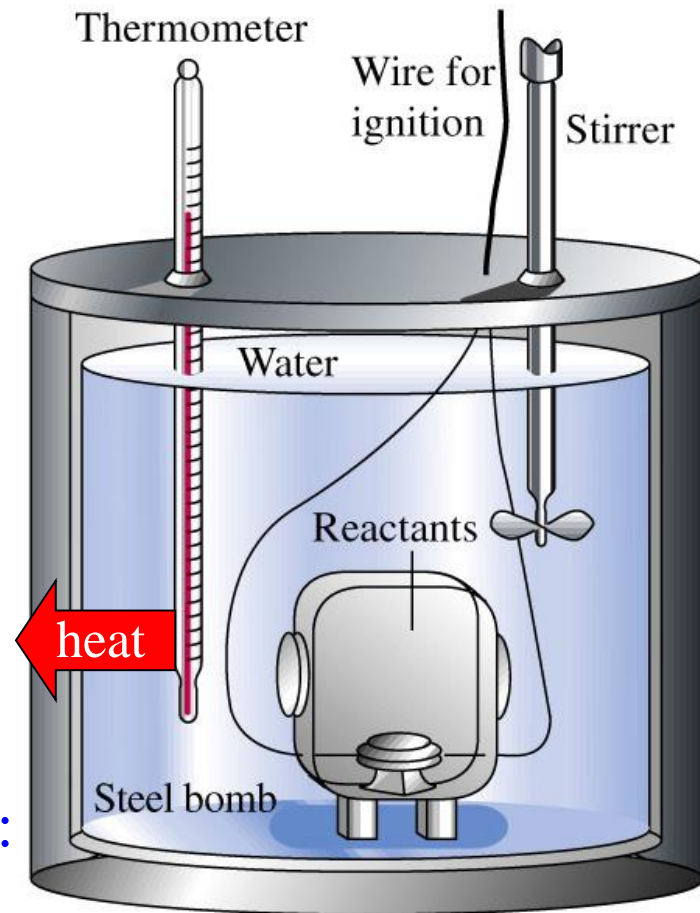
- System includes everything inside the double walled container. All the water, wires, stirrer, thermometer, and the reaction chamber.
- Bomb is filled with sample and assembled. Then pressurized with O_2 .
- A short pulse of electric current heats the sample and ignites it. The final temperature of the calorimeter assembly is determined after the combustion reaction.
- Because the reaction is carried out at a fixed volume we say that this is at *constant* volume.

Define the heat capacity of the calorimeter:

$$q_{\text{cal}} = \sum m_i c_i \Delta T = C \Delta T$$

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

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



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 C₁₂H₂₂O₁₁**
- (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:

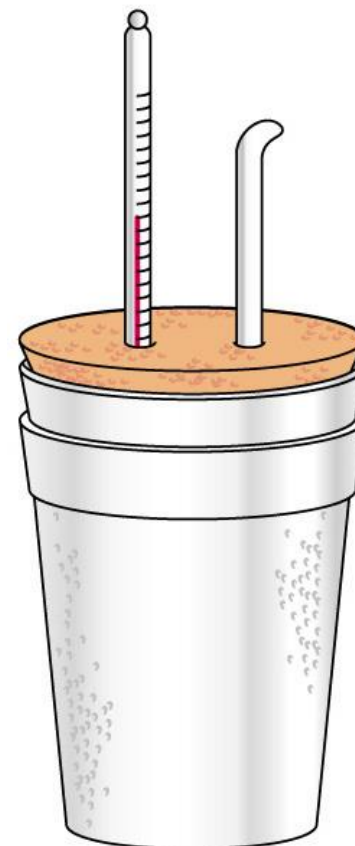
$$q_{\text{rxn}} = (-16.5 \text{ kJ/g}) \left(\frac{4.8 \text{ g}}{1 \text{ tsp}} \right) \left(\frac{1.00 \text{ cal}}{4.184 \text{ J}} \right) = -19 \text{ cal/tsp} \quad (\text{b})$$

Coffee Cup Calorimeter

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

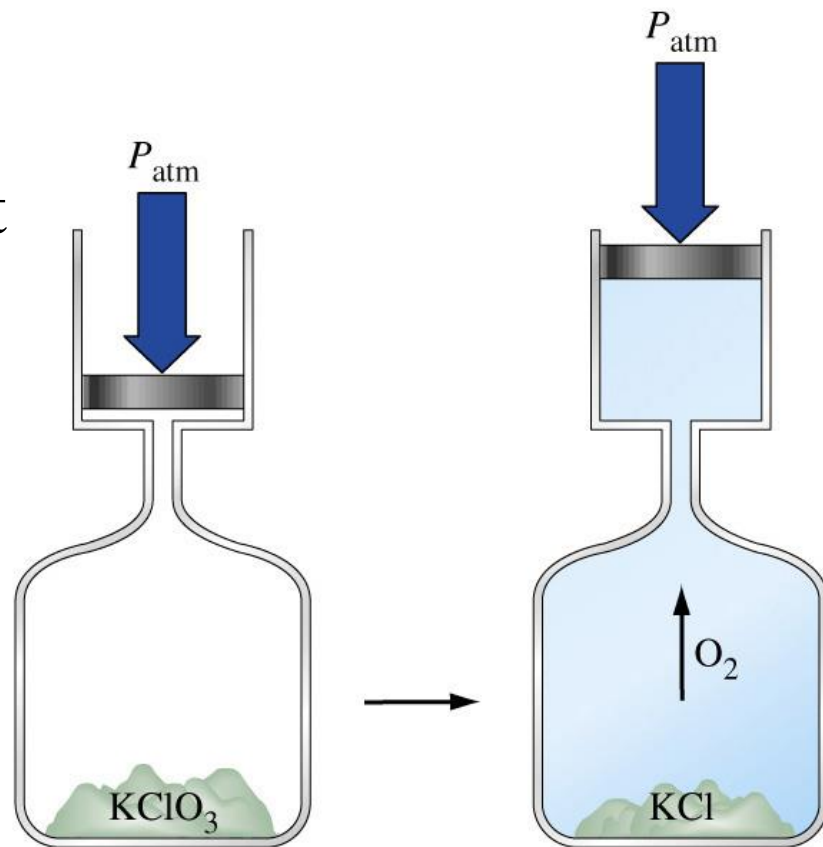
$$q_{\text{rxn}} = -q_{\text{cal}}$$

See example 7-4 for a sample calculation.

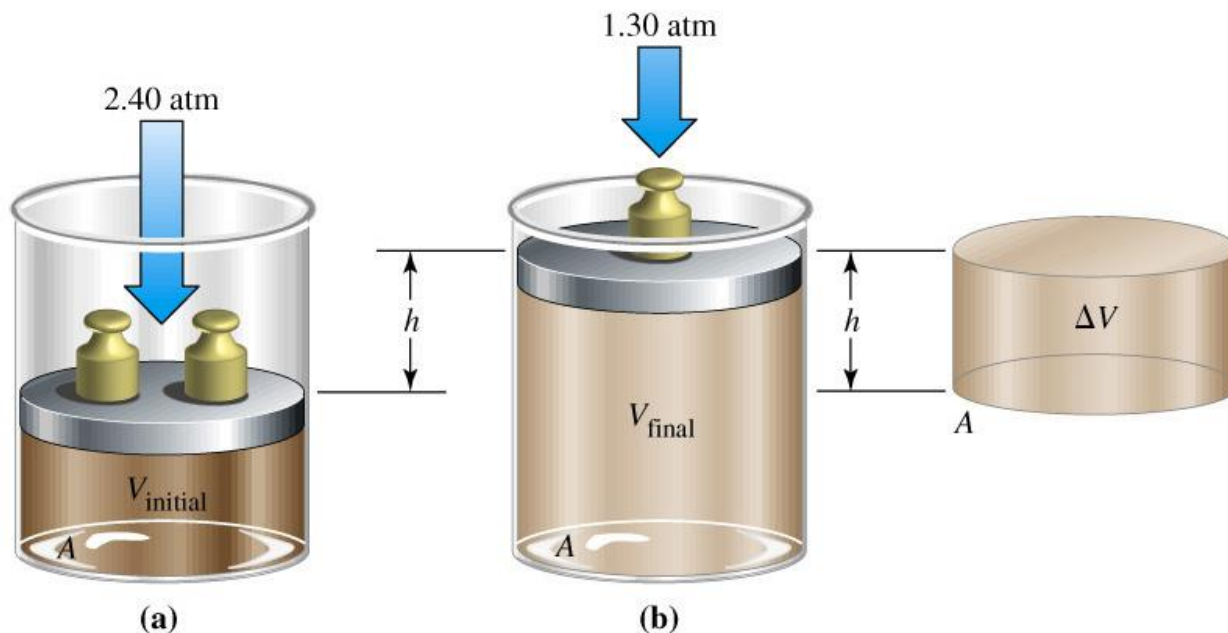


7-4 Work

- In addition to heat effects chemical reactions may also do *work*.
- Gas formed pushes against the atmosphere.
- Volume changes.
- *Pressure-volume work*.
- $KClO_3 \rightarrow KCl + O_2$



Pressure Volume Work



$$\begin{aligned}w &= F \times d \\&= (P \times A) \times h \\&= P\Delta V \\w &= -P_{\text{ext}}\Delta V\end{aligned}$$

- Negative sign is introduced for P_{ext} because the system does work ON the surroundings.
- When a gas expands ΔV is positive and w is negative.
- When a gas is compressed ΔV is negative and w is positive, indicating that energy (as work) enters the system.

Example 7-5

Calculating Pressure-Volume Work.

Suppose the gas in the previous figure is 0.100 mol He at 298 K. How much work, in Joules, is associated with its expansion at constant pressure.

Assume an ideal gas and calculate the volume change:

$$V_i = nRT/P$$

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

$$= 1.02 \text{ L}$$

$$V_f = 1.88 \text{ L}$$

$$\Delta V = 1.88 - 1.02 \text{ L} = 0.86 \text{ L}$$

Example 7-5

Calculate the work done by the system:

$$\begin{aligned}w &= -P\Delta V \\ &= -(1.30 \text{ atm})(0.86 \text{ L})\left(\frac{101 \text{ J}}{1 \text{ L atm}}\right) \\ &= -1.1 \text{ } \uparrow \text{ } 10^2 \text{ J}\end{aligned}$$

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

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.



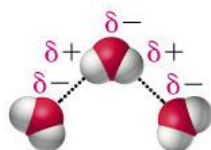
Translational



Rotational



Vibrational



Electrostatic
(Intermolecular attractions)

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

First Law of Thermodynamics

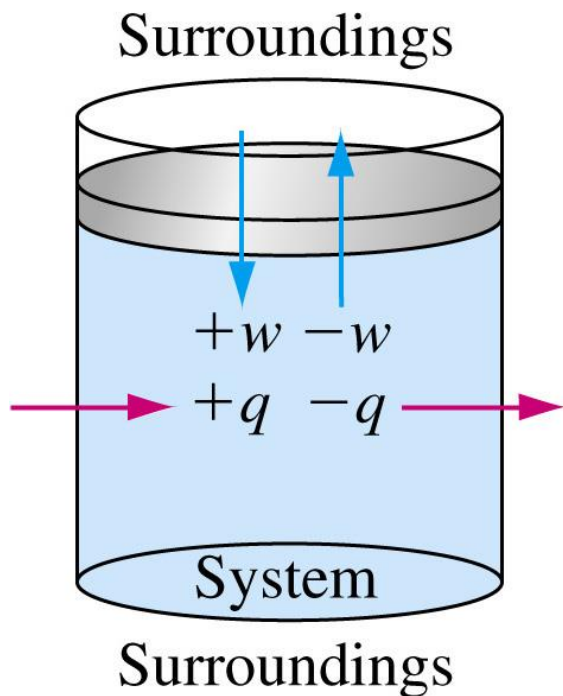
- A system contains *only* internal energy.
 - A system does not contain heat or work.
 - These only occur during a *change* in the system.

$$\Delta U = q + w$$

- The energy of an isolated system is constant

$$\Delta U_{\text{isolated system}} = 0$$

First Law of Thermodynamics



- Any energy entering the system carries a positive sign. Thus, if heat is absorbed by the system, $q > 0$.
If work is done on the system, $w > 0$

- Any energy leaving the system carries a negative sign. Thus, if heat is given off by the system, $q < 0$.
If work is done by the system, $w < 0$

- In general, the internal energy of a system changes as a result of energy entering or leaving the system as heat and/or work. If, on balance, more energy enters the system than leaves, ΔU is positive. If more energy leaves than enters, ΔU is negative.

-A consequence of ΔU (isolated system = 0) is that

$$\Delta U_{\text{system}} = - \Delta U_{\text{surroundings}}$$

EXAMPLE 7-6 Relating ΔU , q , and w Through the First Law of Thermodynamics

A gas, while expanding (recall Figure 7-8), absorbs 25 J of heat and does 243 J of work. What is ΔU for the gas?

Analyze

The key to problems of this type lies in assigning the correct signs to the quantities of heat and work. Because heat is absorbed by (enters) the system, q is *positive*. Because work done *by* the system represents energy *leaving* the system, w is *negative*. You may find it useful to represent the values of q and w , with their correct signs, within parentheses. Then complete the algebra.

Solve

$$\Delta U = q + w = (+25 \text{ J}) + (-243 \text{ J}) = 25 \text{ J} - 243 \text{ J} = -218 \text{ J}$$

Assess

The negative sign for the change in internal energy, ΔU , signifies that the system, in this case the gas, has lost energy.

PRACTICE EXAMPLE A: In compressing a gas, 355 J of work is done on the system. At the same time, 185 J of heat escapes from the system. What is ΔU for the system?

PRACTICE EXAMPLE B: If the internal energy of a system *decreases* by 125 J at the same time that the system *absorbs* 54 J of heat, does the system do work or have work done on it? How much?

State Functions

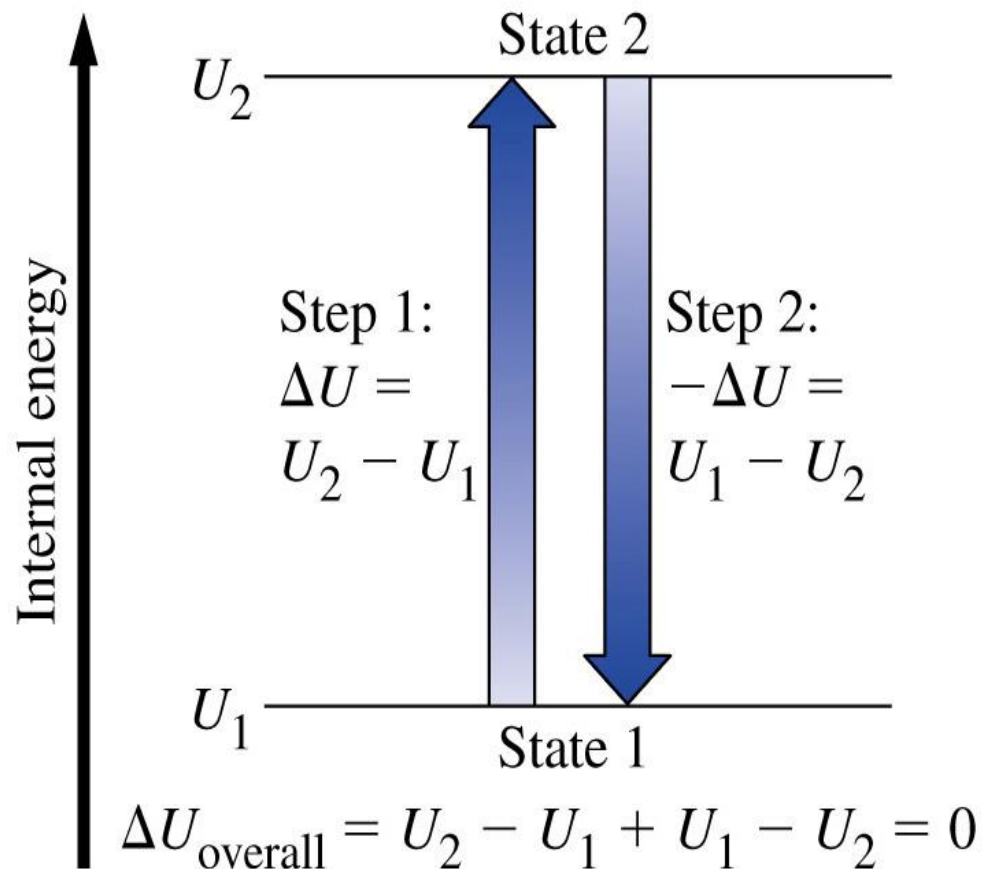
- Any property that has a unique value for a specified state of a system is said to be a *function of state*, or a *state function*.
 - Water at 293.15 K and 1.00 atm is in a specified state.
 - $d = 0.99820 \text{ g/mL}$, This density is a unique value-- function of the state.
- Obtain three different samples of water
 - one purified by extensive distillation of groundwater;
 - one synthesized by burning pure $\text{H}_2(\text{g})$ in pure $\text{O}_2(\text{g})$ and
 - one prepared by driving off the water of hydration from $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ and condensing the gaseous water to a liquid.

The densities of the three different samples for the state that we specified will all be the same:

- Thus, the value of a function of state depends on the state of the system, and not on how that state was established.
 - 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.



Thus, the *overall change in internal energy is zero.*

Path Dependent Functions

- Changes in heat and work are not functions of state. Their values depend on the path followed when a system undergoes a change.
 - Remember example 7-5, $w = -1.1 \times 10^2 \text{ J}$ in a one step expansion of gas:
 - Consider 2.40 atm to 1.80 atm and finally to 1.30 atm.

$$\begin{aligned}w &= (-1.80 \text{ atm})(1.30-1.02)\text{L} - (1.30 \text{ atm})(1.88-1.36)\text{L} \\ &= -0.61 \text{ L atm} - 0.68 \text{ L atm} = -1.3 \text{ L atm} \\ &= 1.3 \times 10^2 \text{ J}\end{aligned}$$

7-6 Heats of Reaction: ΔU and ΔH

Reactants \rightarrow Products

$$U_i \qquad U_f$$

$$\Delta U = U_f - U_i$$

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

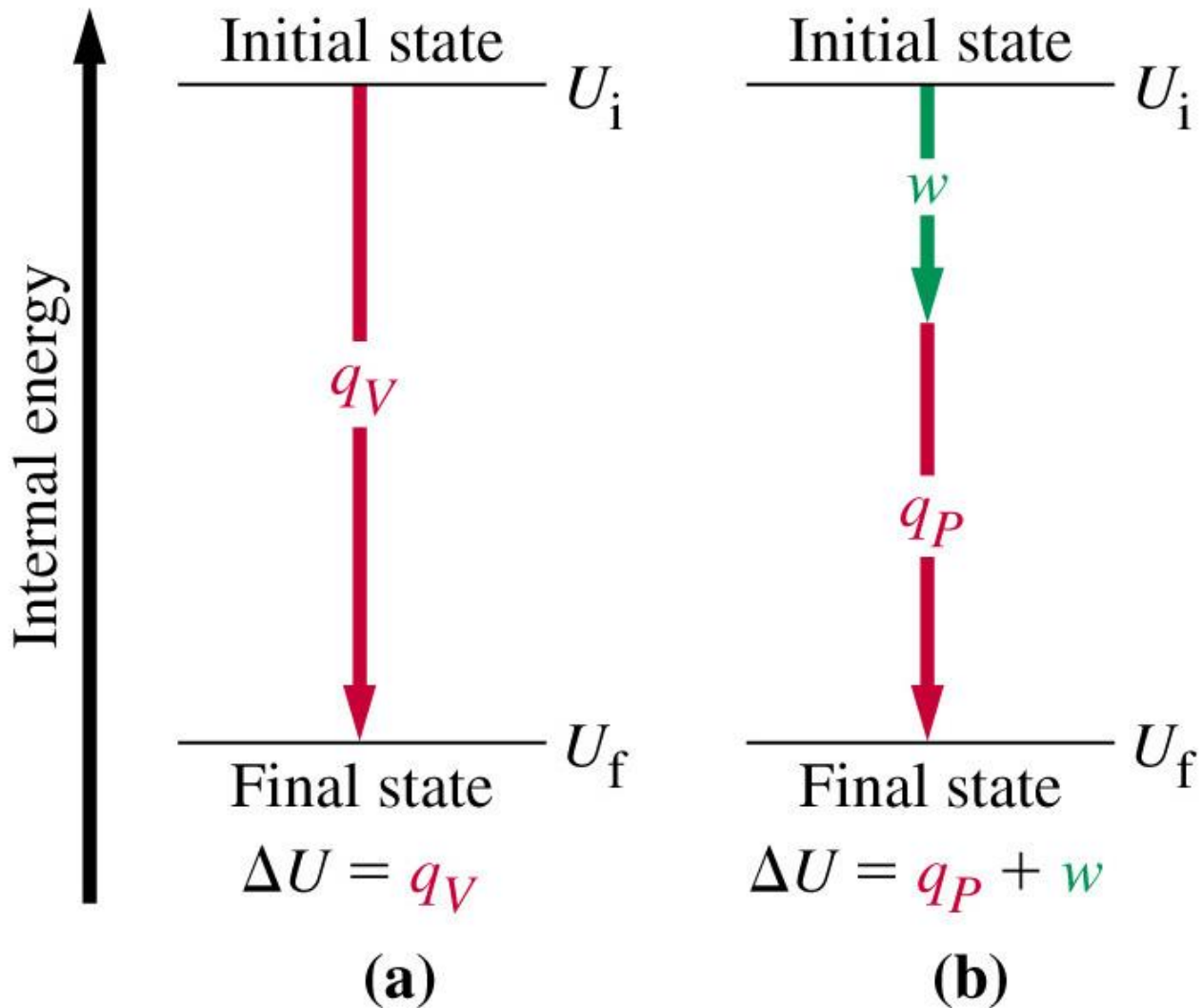
In a system at constant volume:

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

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.

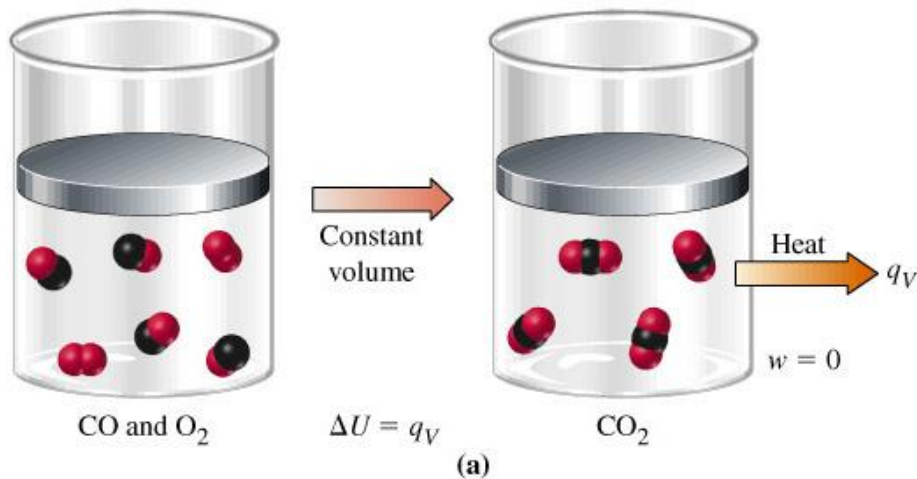
Let
$$H = U + PV$$

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



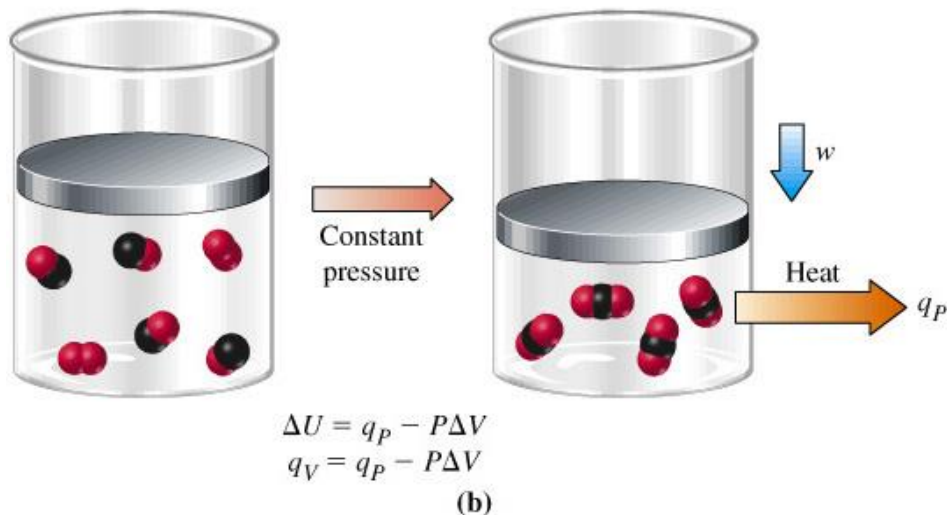
$$q_p = -566 \text{ kJ/mol}$$

$$= \Delta H$$

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

$$= RT(n_f - n_i)$$

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



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

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

$$= q_V$$

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.

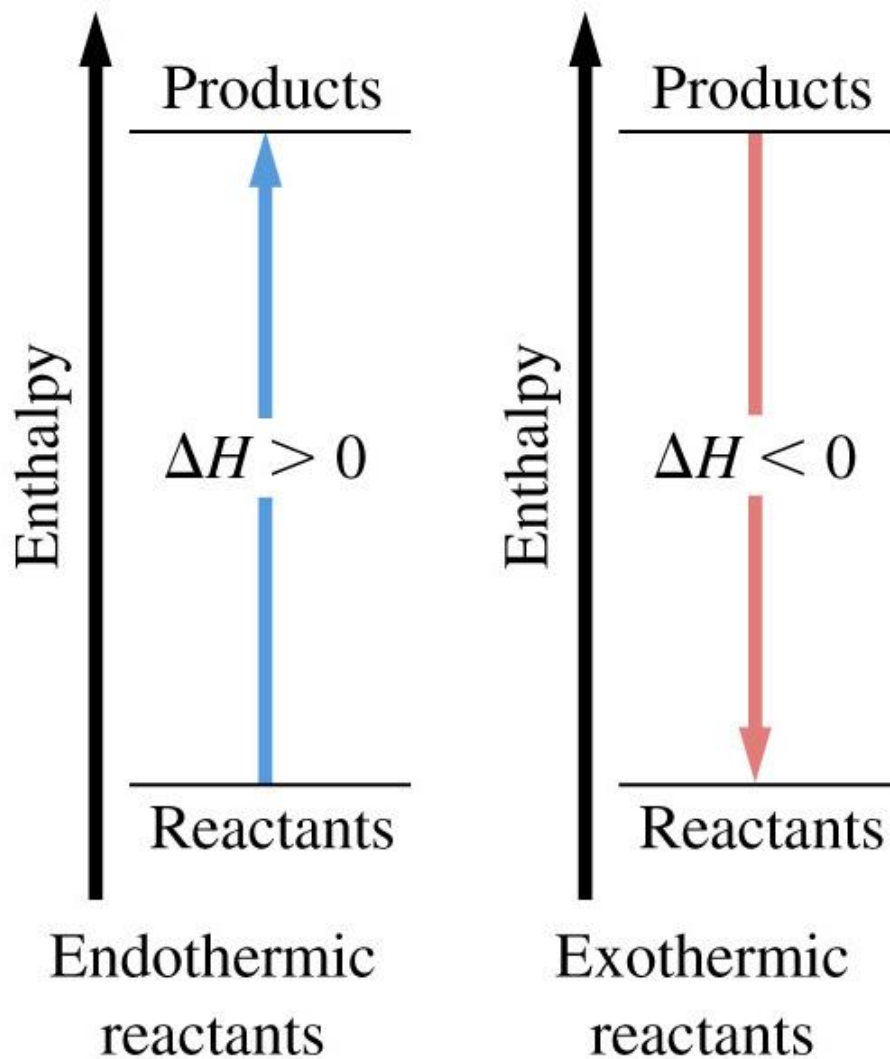
Set up the equation and calculate:

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

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.

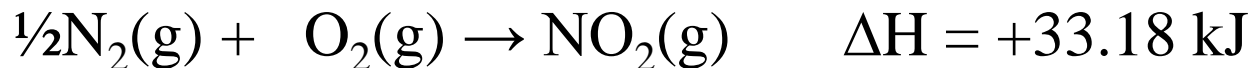
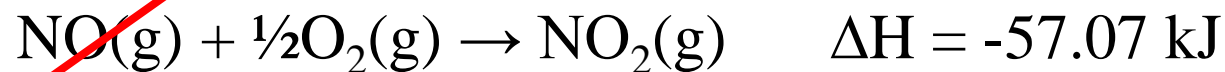


- ΔH changes sign when a process is reversed

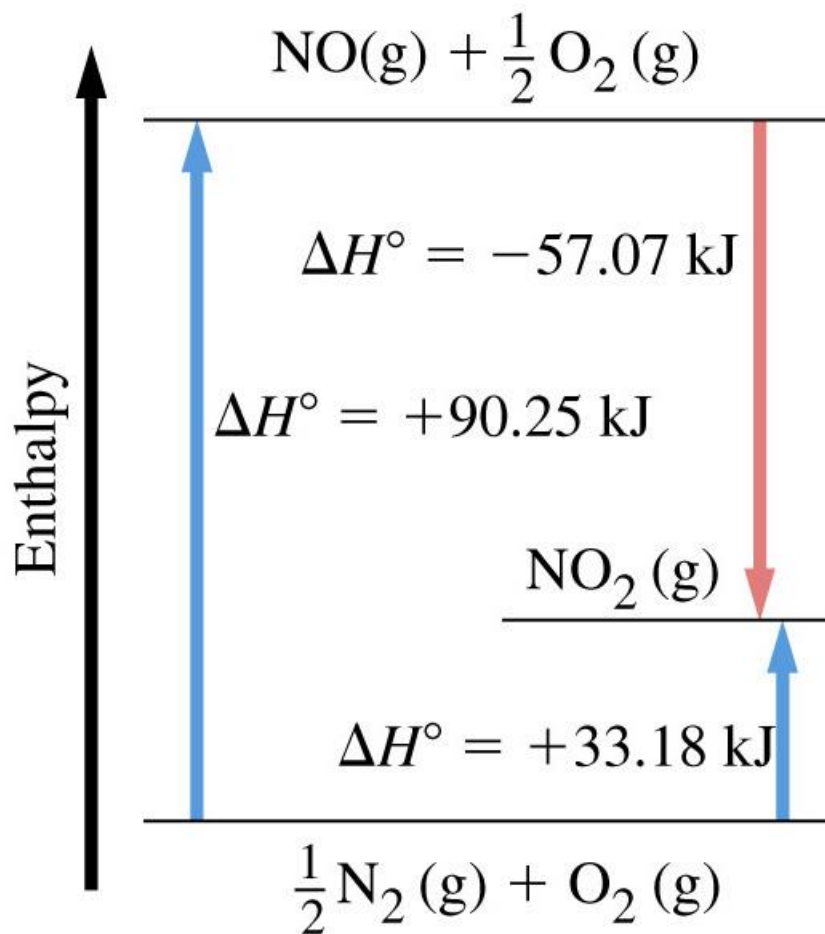


Hess's Law

- 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

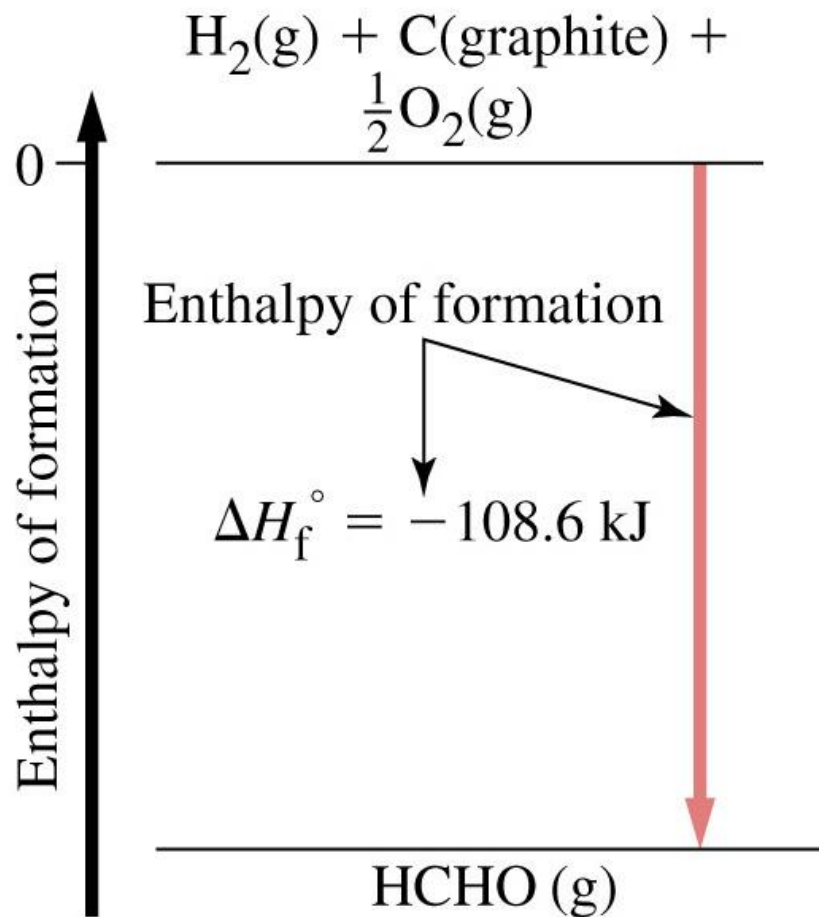


7-8 Standard Enthalpies of Formation

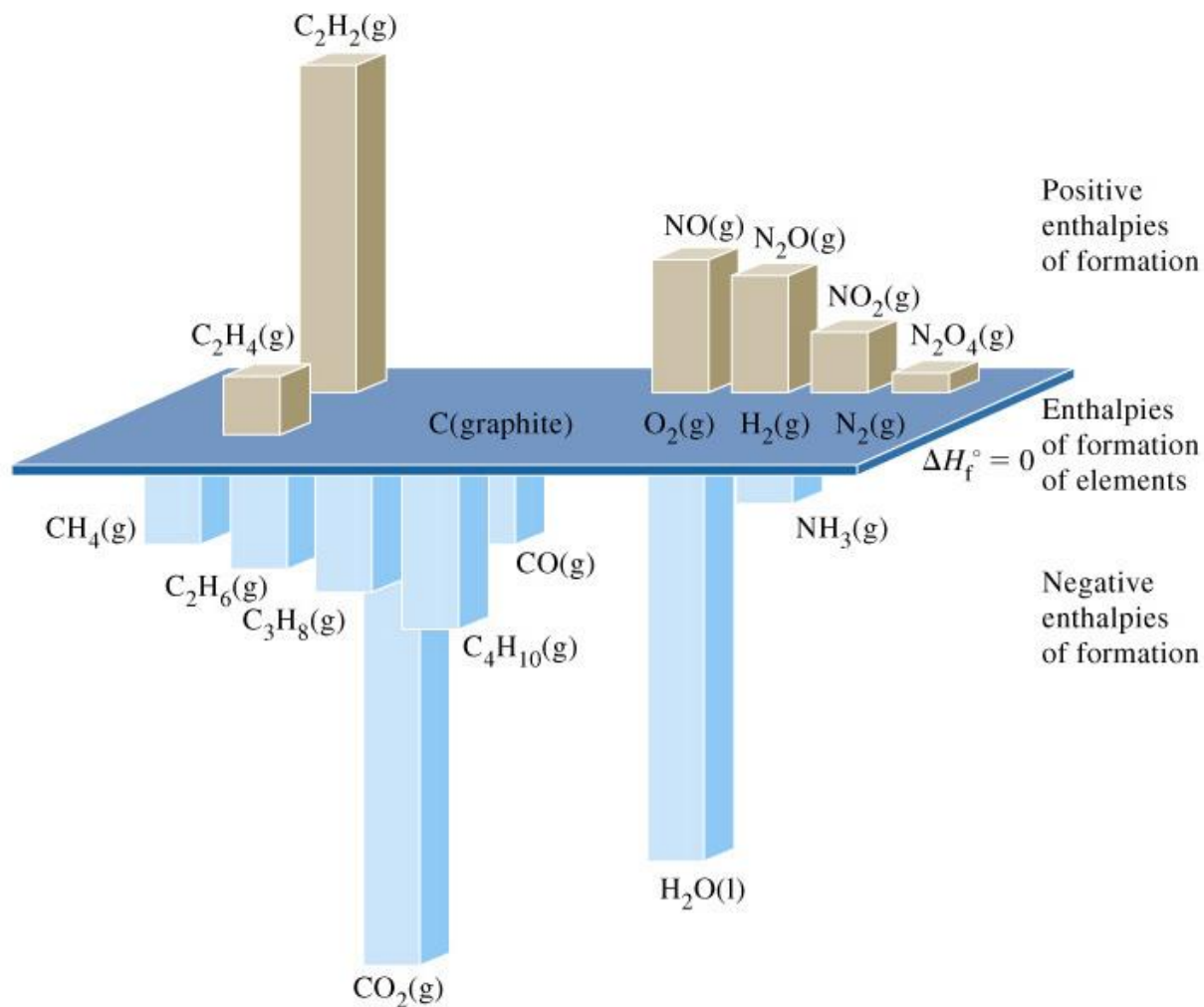
$$\Delta H_f^\circ$$

- 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.

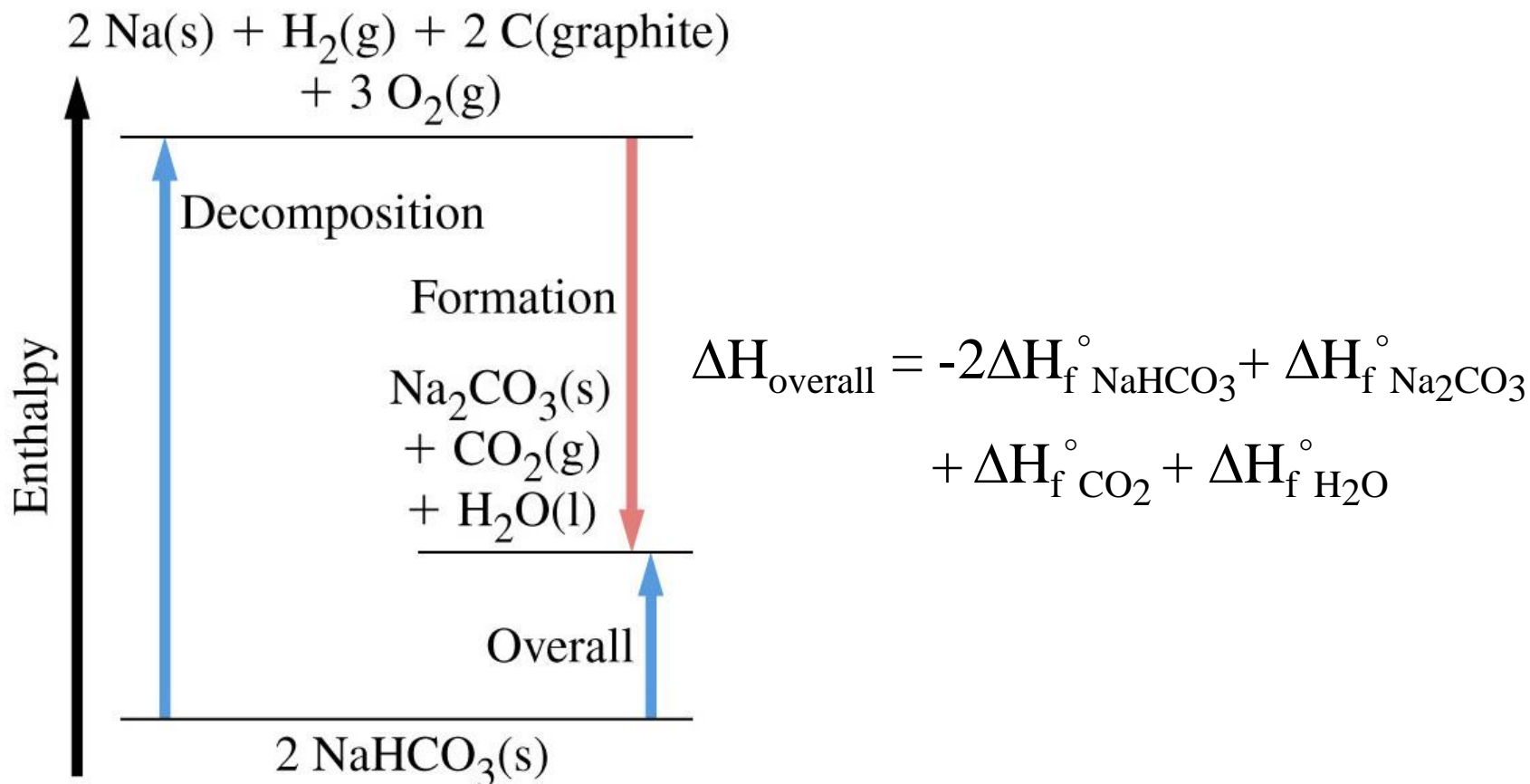
Standard Enthalpies of Formation



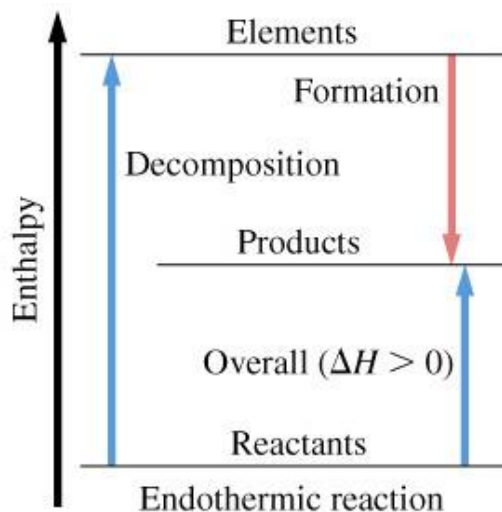
Standard Enthalpies of Formation



Standard Enthalpies of Reaction



Enthalpy of Reaction



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

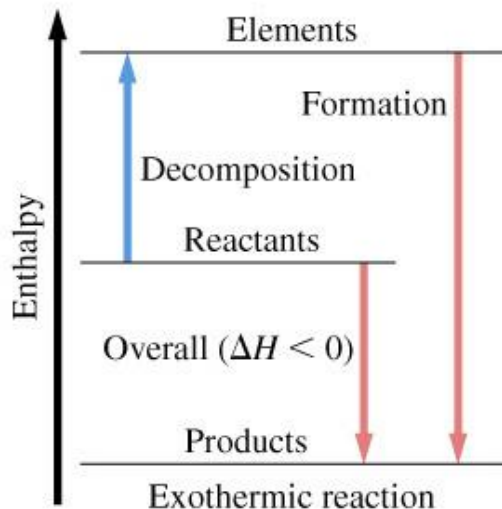


TABLE 7.3 Some Standard Enthalpies of Formation of Ions in Aqueous Solution

Ion	$\Delta H_{f, 298}^{\circ}$, kJ /mol	Ion	$\Delta H_{f, 298}^{\circ}$, kJ /mol
H ⁺	0	OH ⁻	-230.0
Li ⁺	-278.5	Cl ⁻	-167.2
Na ⁺	-240.1	Br ⁻	-121.6
K ⁺	-252.4	I ⁻	-55.19
NH ₄ ⁺	-132.5	NO ₃ ⁻	-205.0
Ag ⁺	+105.6	CO ₃ ²⁻	-677.1
Mg ²⁺	-466.9	S ²⁻	+33.05
Ca ²⁺	-542.8	SO ₄ ²⁻	-909.3
Ba ²⁺	-537.6	S ₂ O ₃ ²⁻	-648.5
Cu ²⁺	+64.77	PO ₄ ³⁻	-1277
Al ³⁺	-531		

7-9 Fuels as Sources of Energy

TABLE 7.4 Approximate Heats of Combustion of Some Fuels

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

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

Chapter 7 Questions

1, 2, 3, 11, 14, 16,
22, 24, 29, 37, 49,
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