

Chapter 5

Thermochemistry

5.1 Energy and Energy Changes

- **Energy** is involved in all types of physical and chemical changes
- **Energy:** the capacity to do work or transfer heat
- forms of energy are either
 - Kinetic
 - Potential

- ***Kinetic energy*** - energy of motion
 - Defining equation

$$E_k = \frac{1}{2}mu^2$$

- Where m is mass and u is velocity
- Thermal - one form of kinetic energy associated with random motion
 - Monitor changes via changes in temperature

- *Potential energy*
 - *Chemical energy* is stored within structural units of chemical substances.
 - *Electrostatic energy* is energy resulting from the interaction of charged particles.
 - Dependent on charges and distance between charges (Q = charge and d = distance)
 - Defining equation
 - $+ E_{\text{el}}$: repulsive
 - $- E_{\text{el}}$: attractive

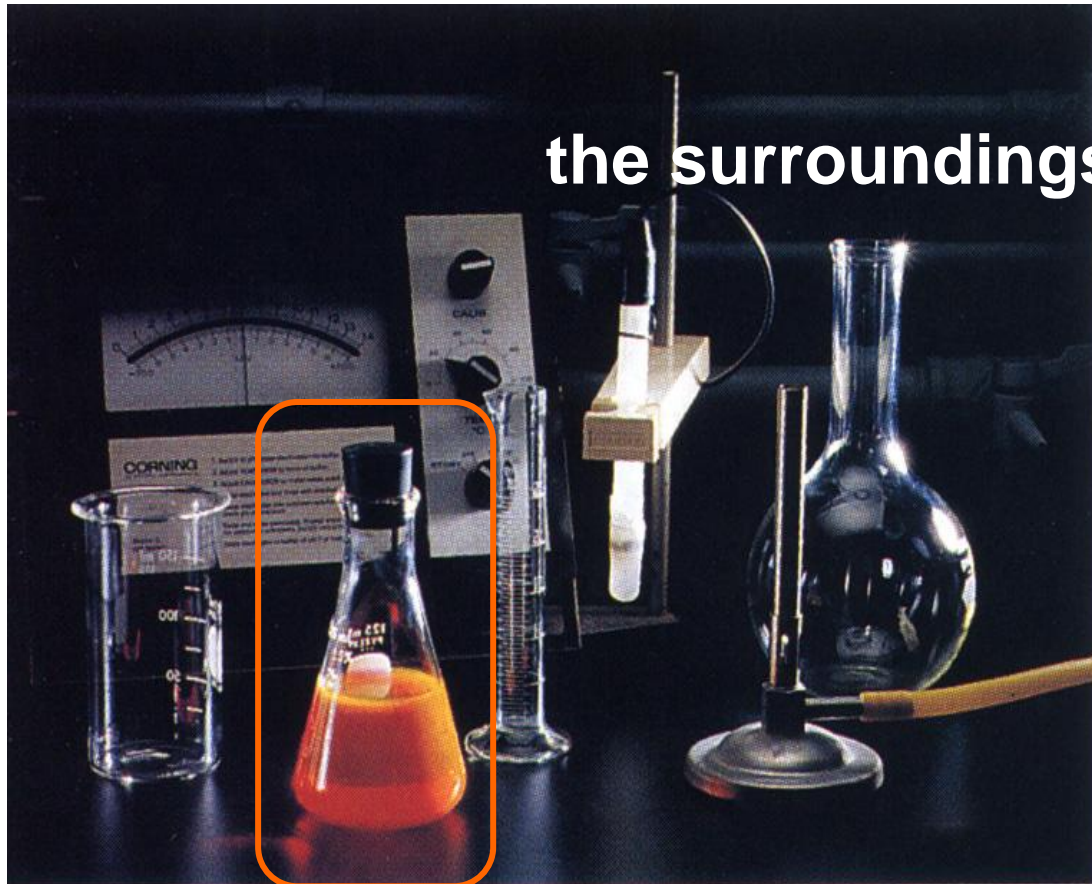
$$E_{\text{el}} \propto \frac{Q_1 Q_2}{d}$$

- **Law of conservation of energy**
 - Energy may be converted from one form to another.
 - The total amount of energy in the universe is constant.

$$(\Delta E_{\text{universe}} = 0)$$

- **Energy changes in chemical reactions**
 - *System* is the part of the universe of interest.
 - Example
 - The reactants NaOH and HCl
 - *Surroundings* are the rest of the universe.
 - Example
 - When heat is given off from the reaction of NaOH and HCl, the energy is transferred from the system to the surroundings.

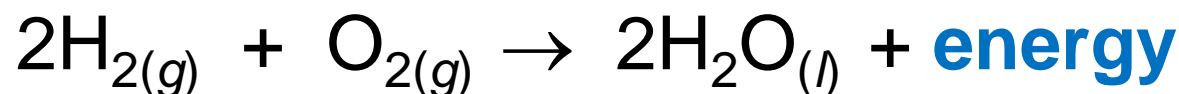
Chemical System and Surrounding



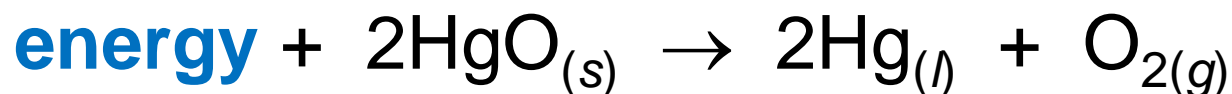
- ***Thermochemistry***

- The study of the transfer of heat (thermal energy) in chemical reactions.

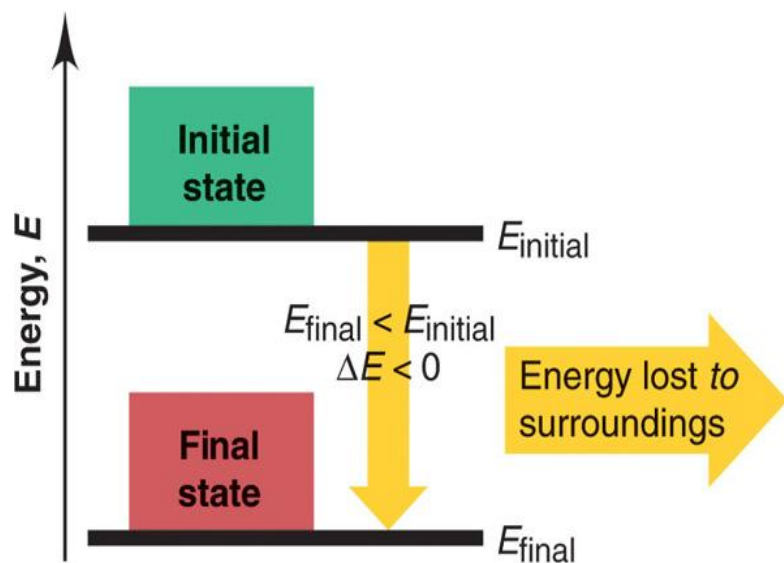
- ***Exothermic*** - transfer of heat from the system to the surroundings



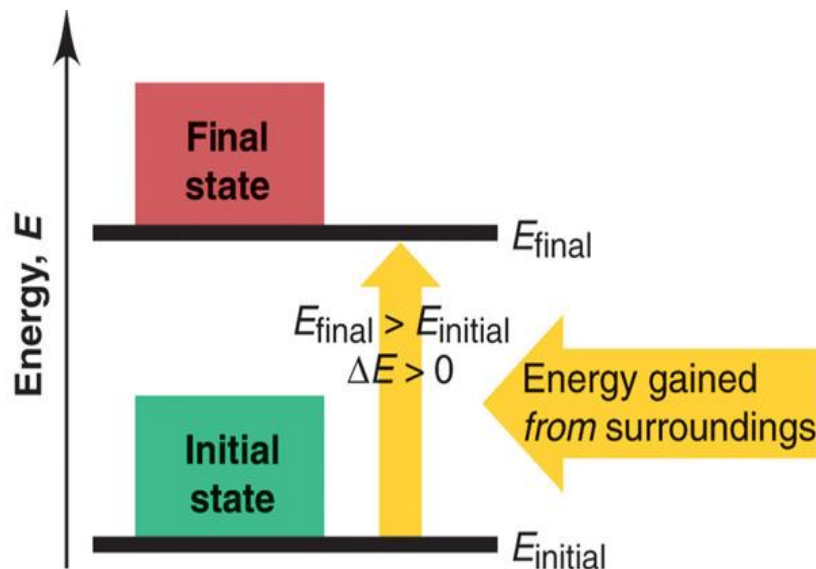
- ***Endothermic*** - the transfer of heat from the surroundings to the system



Internal Energy Transfer



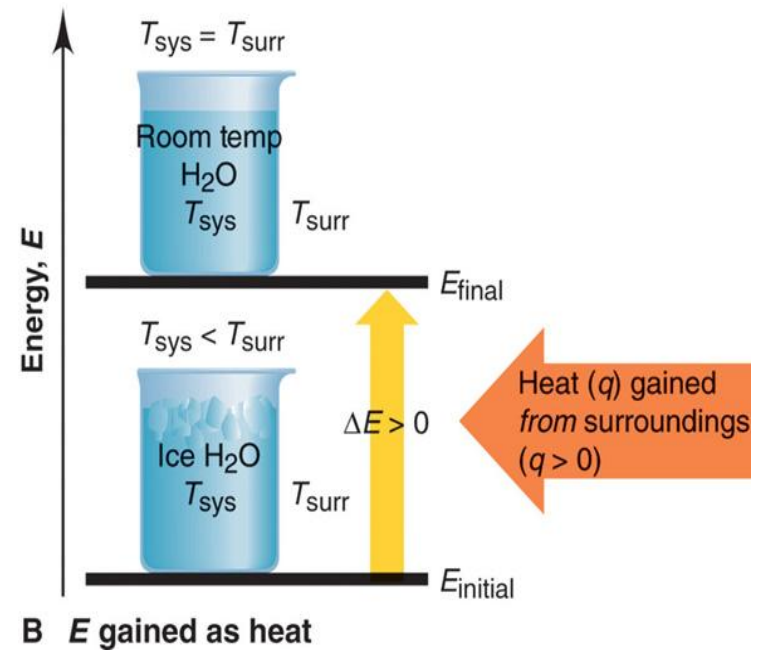
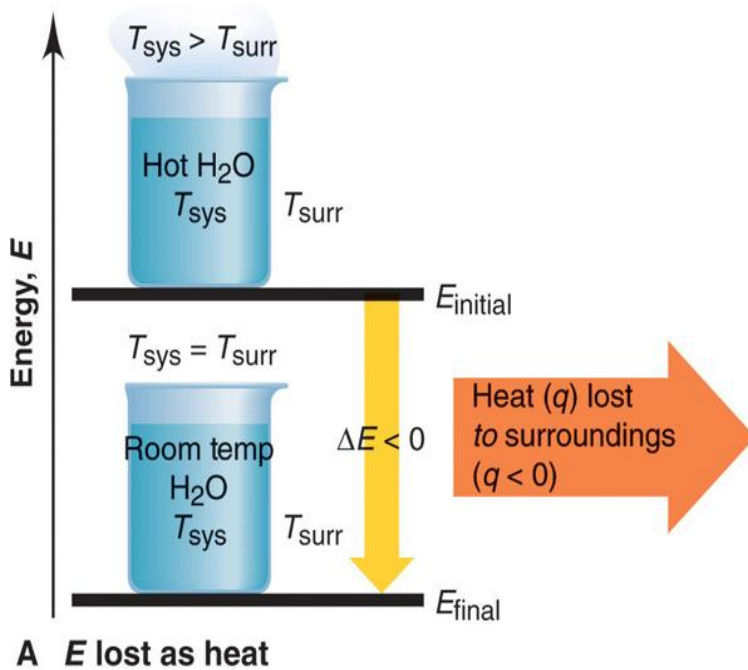
A E of system decreases



B E of system increases

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}}$$

Energy Transfer as heat



- Units of Energy
 - ***Joule (J)*** is the SI unit for energy.
 - The amount of energy possessed by a 2 kg mass moving at a speed of 1 m/s

$$E_k = \frac{1}{2}mu^2 = \frac{1}{2}(2 \text{ kg})(1 \text{ m/s})^2 = 1\text{kg} \cdot \text{m}^2/\text{s}^2 = 1 \text{ J}$$

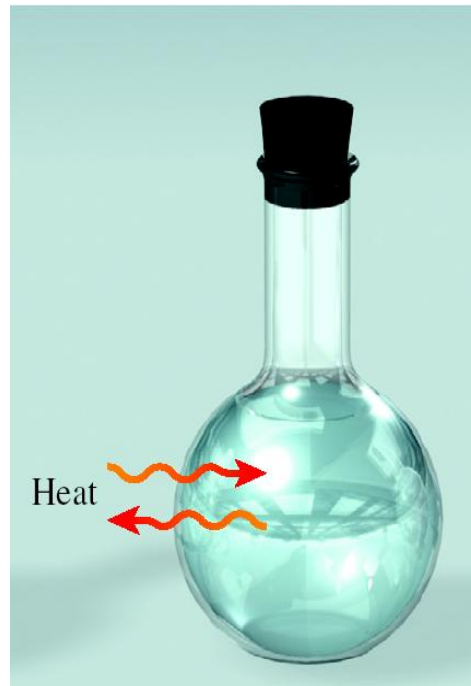
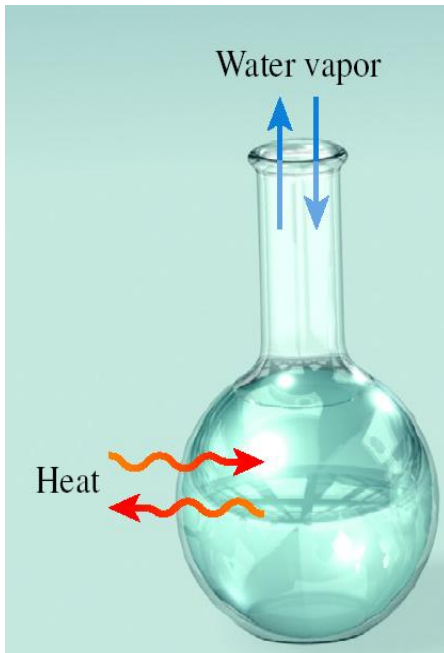
$$1 \text{ J} = 1 \text{ N} \cdot \text{m} \qquad 1 \text{ N} = 1 \text{ kg} \cdot \text{m}/\text{s}^2$$

$$1 \text{ kJ} = 1000 \text{ J}$$

- ***Calorie (cal)*** - commonly used on food labels
- 1 cal = 4.184 J
- 1000 cal = 1 Cal = 1 kcal

5.2 Introduction to Thermodynamics

- Types of systems:
 - **open** (exchange of mass and energy)
 - **closed** (exchange of energy)
 - **isolated** (no exchange)



- **State functions** depend only on initial and final states of the system and not on how the change was carried out.
 - Energy (E)
 - Pressure (P)
 - Volume (V)
 - Temperature (T)



First Law of Thermodynamics

- Energy can be converted from one form to another but cannot be created or destroyed.
 - Based on the law of conservation of energy

$$(\Delta E_{\text{universe}} = 0)$$

- *Internal energy (U)*
 - Kinetic energy - molecular motion
 - Potential energy - attractive/repulsive interactions

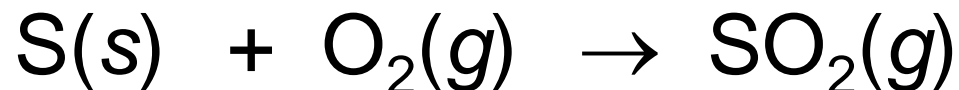
- The change in internal energy of a system between final (f) and initial (i) states is defined as:

$$\Delta U = U_f - U_i$$

- **For a chemical system**
 - Cannot calculate the total internal energy with any certainty
 - *Can* calculate the *change* in energy of the system experimentally

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

– Consider:



$$\Delta U = U(\text{product}) - U(\text{reactants})$$

= energy content of 1 mol $\text{SO}_2(g)$ – energy content of 1 mol $\text{S}(s)$ and 1 mol $\text{O}_2(g)$

– This reaction releases heat, therefore ΔU is negative.

- When a system releases heat, some of the chemical energy is released as thermal energy to the surroundings but this does not change the total energy of the universe.

$$\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 = \Delta E_{\text{universe}}$$

or

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

- When a system undergoes a change in energy, the surroundings must undergo a change in energy equal in magnitude and opposite in sign.

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

- Work and heat

$$\Delta U_{\text{sys}} = q + w$$

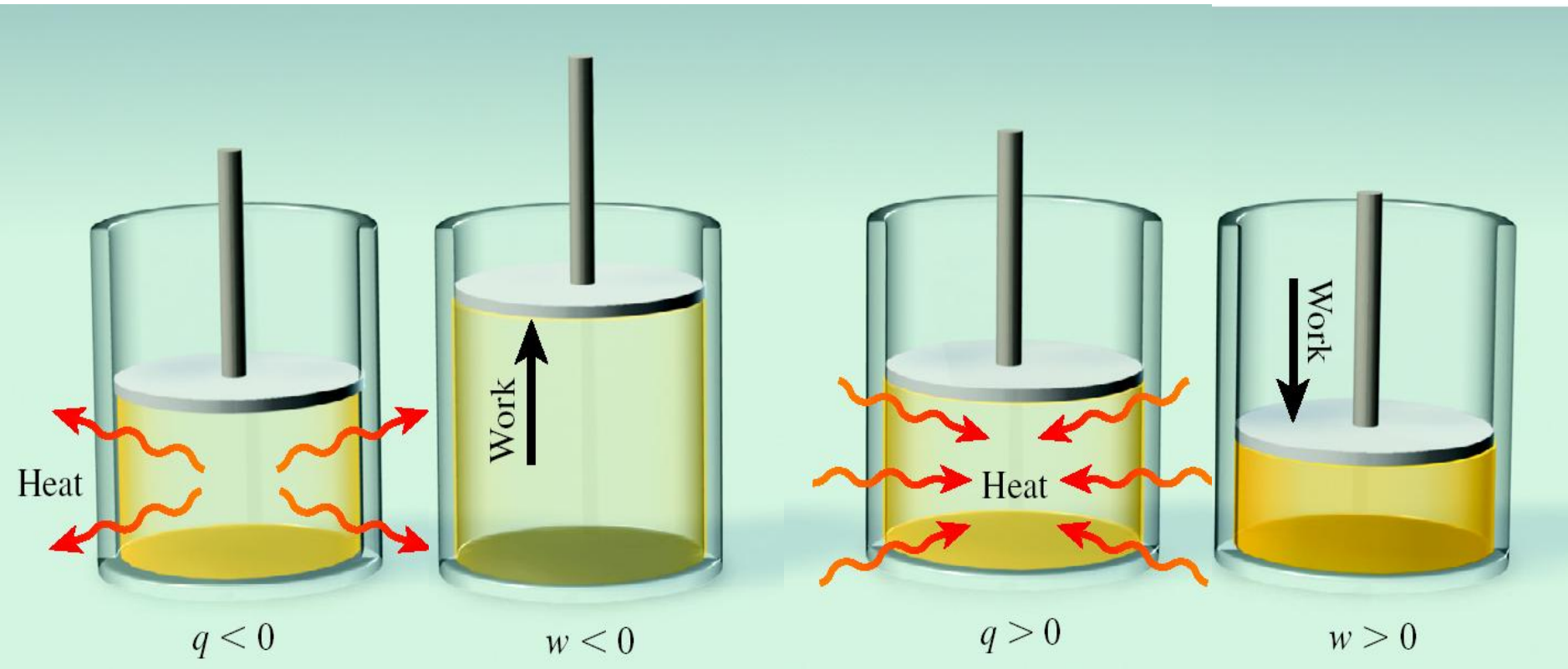
where q is heat w is work

TABLE 5.1

Sign Conventions for Heat (q) and Work (w)

Process	Sign
Heat absorbed by the system (endothermic process)	q is positive
Heat released by the system (exothermic process)	q is negative
Work done on the system by the surroundings (for example, a volume decrease)	w is positive
Work done by the system on the surroundings (for example, a volume increase)	w is negative

Sign Conventions of q and w



Calculate the overall change in internal energy for a system that absorbs 125 J of heat and does 141 J of work on the surroundings.

q is + (heat absorbed)

w is – (work done)

$$\begin{aligned}\Delta U_{\text{sys}} &= q + w = (+125 \text{ J}) + (-141 \text{ J}) \\ &= -16 \text{ J}\end{aligned}$$

- **Reactions carried out at constant volume**
 - Pressure-volume work, w , done by a system is

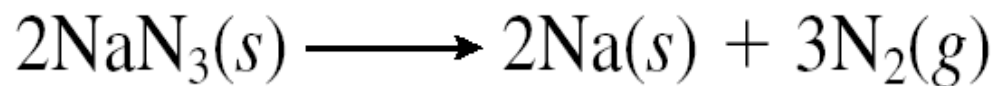
$$w = -P\Delta V$$

- Constant volume, $\Delta V = 0$

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

$$q_v = \Delta U$$

Decomposition of NaN_3 at Constant Volume

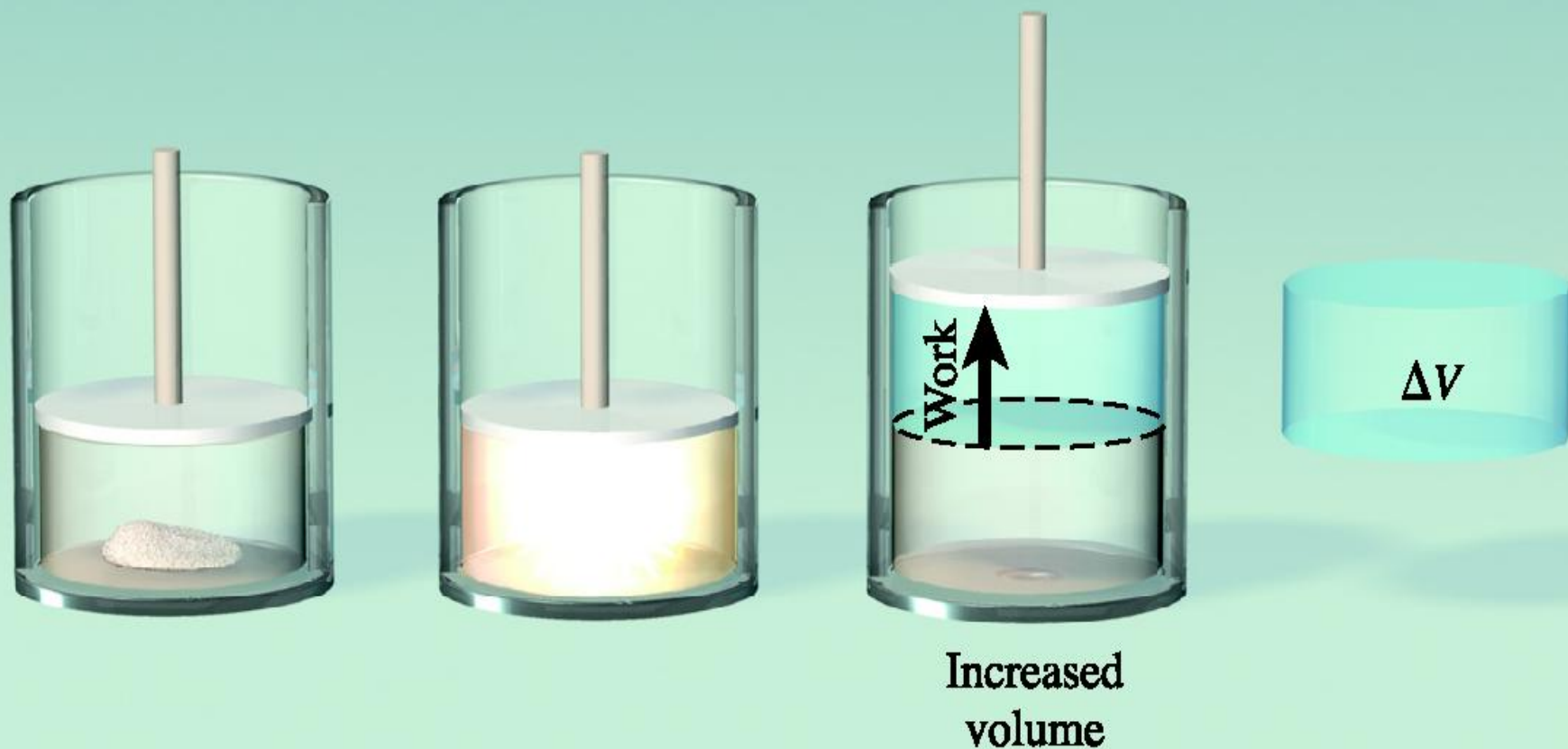
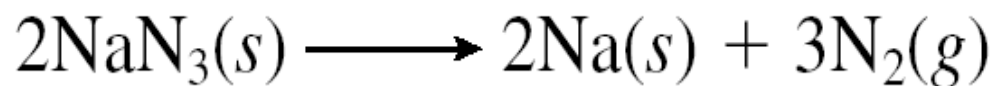


NaN_3



Increased
pressure

Decomposition of NaN_3 at Constant Pressure



Enthalpy

- **Enthalpy** is the internal energy plus the product of pressure and volume:

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P \Delta V \quad \textit{at constant pressure}$$

Enthalpy

$$\Delta H = \Delta E + P \Delta V$$

Since $\Delta E = q + w$, then

$$\Delta H = q + w + P \Delta V \qquad W = -P\Delta V$$

$$\Delta H = q - \cancel{P\Delta V} + \cancel{P\Delta V}$$

$$\Delta H = q$$

at constant pressure

- Enthalpy and enthalpy changes
 - Enthalpy (H) is a state function defined as
$$H = U + PV$$
 - At constant pressure
$$q_p = \Delta H$$
 - Enthalpy of reaction

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

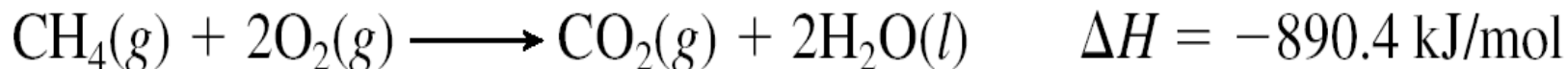
- **ΔH is +** for endothermic changes.
- **ΔH is –** for exothermic changes.

- **Thermochemical Equations**

- Equations that represent both mass and enthalpy changes

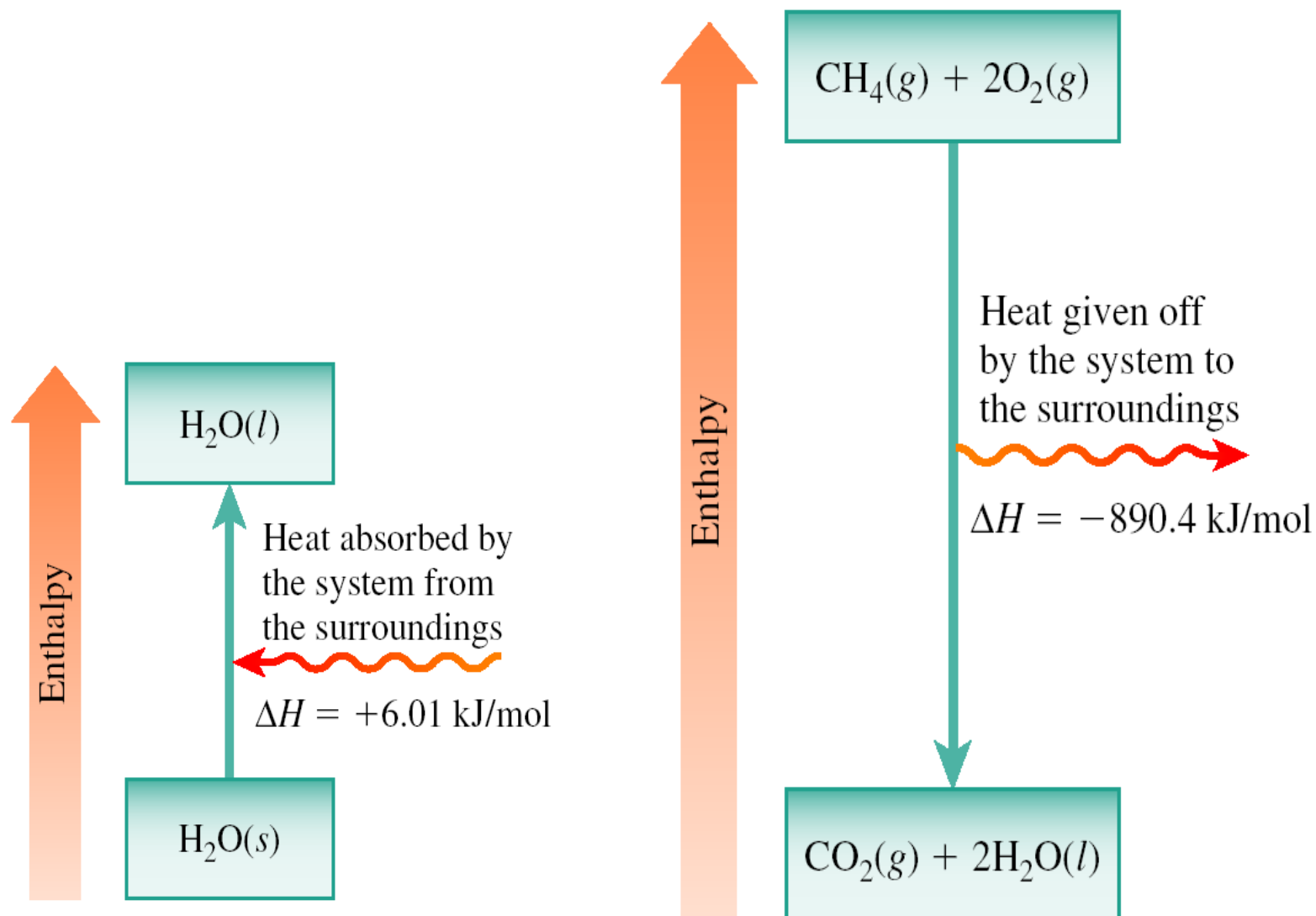


- This is an endothermic process. It requires 6.01 kJ to melt one mole of ice, $\text{H}_2\text{O}(\text{s})$.
- The enthalpy value will change if the number of moles varies from the 1:1 reaction stoichiometry.



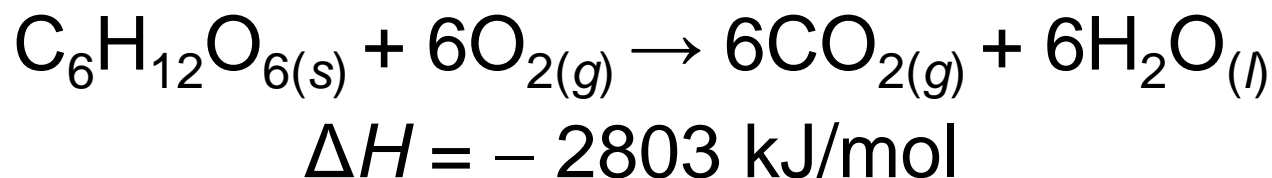
- This is an exothermic process. It releases 890.4 kJ when one mole of methane, CH_4 , reacts **or 2 moles of O_2 consumed or 1 mole of CO_2 produced or 2 moles of water produced.**
- The enthalpy value will change if the number of moles varies from the 1:2:1:2 reaction stoichiometry.

Comparison of Endothermic and Exothermic Changes



- Thermochemical equation guidelines
 - Always specify state of reactants and products.
 - When multiplying an equation by a factor (n), multiply the ΔH value by same factor.
 - Reversing an equation changes the sign but not the magnitude of the ΔH .

Given the following equation



calculate the energy released when 45.00 g of glucose is burned in oxygen.

$$45.00 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} \times \frac{2803 \text{ kJ}}{1 \text{ mol C}_6\text{H}_{12}\text{O}_6} = 700.0 \text{ kJ}$$

5.4 Calorimetry

- *Calorimetry* is the measurement of heat changes
- *Specific heat* (s) - the amount of heat required to raise the temp of 1 g of a substance by 1 °C.

– Units: J/g °C

– Relation to amount of heat (q)

where q is heat, m is mass, s is specific heat

$$q = ms\Delta T$$

and ΔT = change in temp ($\Delta T = T_{\text{final}} - T_{\text{initial}}$)

TABLE 5.2

Specific Heat Values of Some Common Substances

Substance	Specific Heat (J/g · °C)
Al(<i>s</i>)	0.900
Au(<i>s</i>)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu(<i>s</i>)	0.385
Fe(<i>s</i>)	0.444
Hg(<i>l</i>)	0.139
H ₂ O(<i>l</i>)	4.184
C ₂ H ₅ OH(<i>l</i>) (ethanol)	2.46

- ***Heat capacity (C)*** - the amount of heat required to raise the temp of an object by 1 °C.
 - Units: J/°C
 - Relation to amount of heat (q)

$$q = C\Delta T$$

where q is heat, m is mass, C is heat capacity

and ΔT = change in temp ($\Delta T = T_{\text{final}} - T_{\text{initial}}$)

Calculate the amount of energy required to heat 95.0 grams of water from 22.5°C to 95.5°C.

$$q = ms\Delta T$$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 95.5\text{ }^{\circ}\text{C} - 22.5\text{ }^{\circ}\text{C}$$

$$\Delta T = 73.0\text{ }^{\circ}\text{C}$$

$$q = (95.0\text{ g}) (4.184\text{ J/g}^{\circ}\text{C}) (73.0^{\circ}\text{C})$$

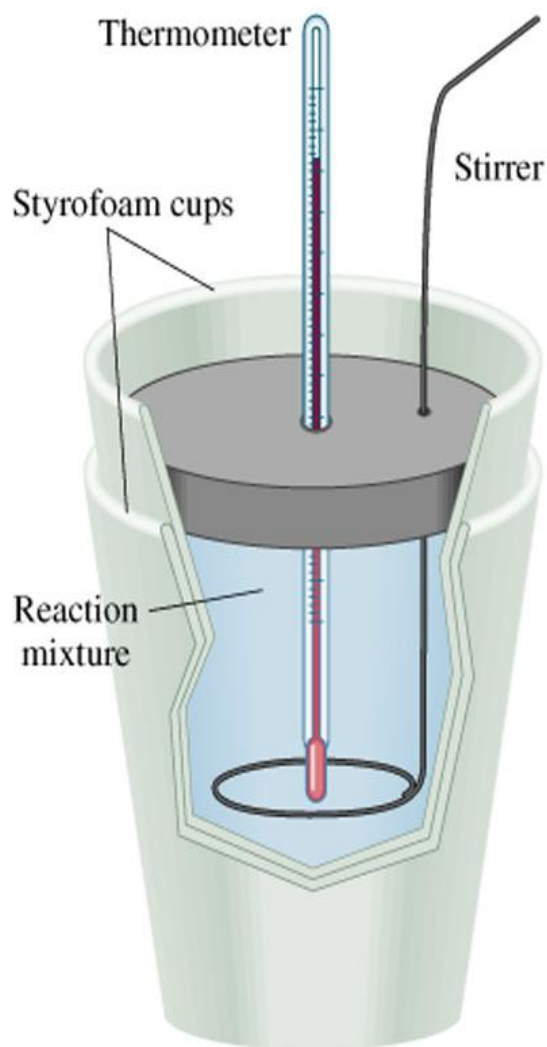
$$q = 2.90 \times 10^4\text{ J or } 29.0\text{ kJ}$$

How much heat is needed to raise the temperature of the copper layer from 25⁰C to 300.⁰C? The specific heat capacity (*c*) of Cu is 0.387 J/g*K.

Given the mass, specific heat capacity and change in temperature, we can use $q = c \times \text{mass} \times \Delta T$ to find the answer. ΔT in ⁰C is the same as for K.

$$q = \frac{0.387 \text{ J}}{\text{g} \cdot \text{K}} \times 125 \text{ g} \times (300 - 25)^{\circ}\text{C} = 1.33 \times 10^4 \text{ J}$$

Constant Pressure Calorimetry



By carrying out a reaction in aqueous solution in a simple calorimeter such as this one, one can indirectly measure the heat change for the system by measuring the heat change for the water in the calorimeter.

Constant Pressure Calorimetry

- If we assume that the calorimeter did not leak energy or absorb any itself (that all the energy was used to increase the T), we can find the energy released by the reaction

E released by rxn = - E absorbed by soln

$$\Delta H = q_p = s_p \times m \times \Delta T$$

TABLE 5.3

Heats of Some Typical Reactions and Physical Processes Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	+56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	+6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	+44.0*

*Measured at 25°C. At 100°C. the value is +40.79 kJ.

A metal with a mass of 85.00 grams at an original temperature of 92.5°C is dropped into a calorimeter with 150.00 grams of water at an original temperature of 23.1°C. The final temperature of the water and the metal is 26.8°C. Calculate the heat capacity and the specific heat for the metal.

$$\begin{aligned}
 q_{\text{water}} &= ms\Delta T \\
 &= (150.00 \text{ g}) (4.184 \text{ J/g}^\circ\text{C}) (3.7^\circ\text{C}) \\
 &= 2300 \text{ J (water gained energy)} \\
 &= -2300 \text{ J (metal released energy)}
 \end{aligned}$$

Heat capacity of metal: $q = C\Delta T$

$$\begin{aligned}
 C &= q/\Delta T \\
 &= -2300 \text{ J}/-65.7^\circ\text{C} = 35 \text{ J/}^\circ\text{C}
 \end{aligned}$$

Specific heat of pellet: $\text{J/g}^\circ\text{C}$

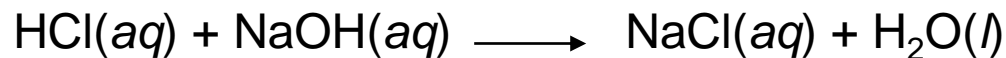
$$s = \frac{35 \text{ J/}^\circ\text{C}}{85.00 \text{ g}} = 0.41 \text{ J/g}^\circ\text{C}$$

Example

You place 50.0 mL of 0.500 M NaOH in a coffee-cup calorimeter at 25.00°C and carefully add 25.0 mL of 0.500 M HCl, also at 25.00°C. After stirring, the final temperature is 27.21°C. Calculate q_{soln} (in J) and ΔH_{rxn} (in kJ/mol of H₂O formed). (Assume the total volume is the sum of the individual volumes and that the final solution has the same density and specific heat capacity as water: $d = 1.00 \text{ g/mL}$ and $c = 4.18 \text{ J/g.K}$)

We need to determine the limiting reactant from the net ionic equation. The moles of NaOH and HCl as well as the total volume can be calculated. From the volume we use density to find the mass of the water formed. At this point q_{soln} can be calculated using the mass, c , and ΔT .

Continue



$$\text{For NaOH} \quad 0.500 \text{ M} \times 0.0500 \text{ L} = 0.0250 \text{ mol OH}^-$$

$$\text{For HCl} \quad 0.500 \text{ M} \times 0.0250 \text{ L} = 0.0125 \text{ mol H}^+$$

HCl is the limiting reactant

0.0125 mol of H₂O will form during the rxn

$$\text{total volume after mixing} = 0.0750 \text{ L} = 75.0 \text{ ml}$$

$$75.0 \text{ ml} \times 1.00 \text{ g/mL} = 75.0 \text{ g of water}$$

$$q = \text{mass} \times \text{specific heat} \times \Delta T$$

$$= 75.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times (27.21 - 25.00)^\circ\text{C}$$

$$= 693$$

$$693 \text{ J} / 0.0125 \text{ mol H}_2\text{O} = 55.4 \text{ kJ/mol H}_2\text{O formed}$$

• Constant-volume Calorimetry

$$\Delta E = q + w$$

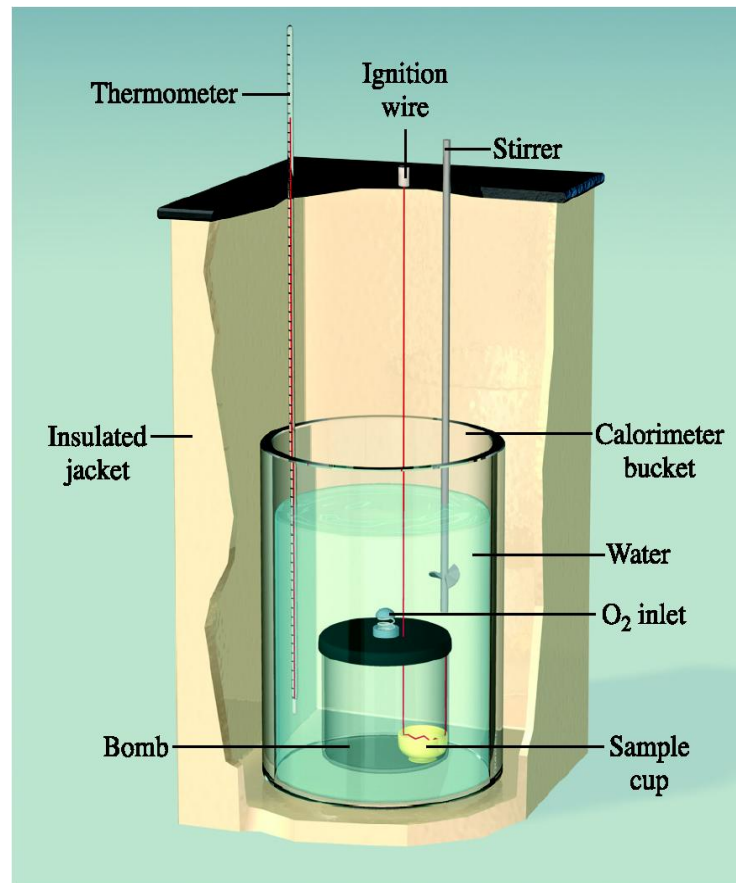
Here, the $\Delta V = 0$, So **$W=0$**

$$\Delta E = q \quad \text{at constant volume}$$

$E_{\text{released by rxn}} = -E_{\text{absorbed by calorimeter}}$

$$q_{\text{cal}} = C_{\text{cal}}\Delta T$$

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T$$



bomb calorimeter

- Typical procedure used in a bomb calorimeter
 - Known amount of sample placed in steel container and then filled with oxygen gas
 - Steel chamber submerged in known amount of water
 - Sample ignited electrically
 - Temperature increase of water is determined

A snack chip with a mass of 2.36 g was burned in a bomb calorimeter. The heat capacity of the calorimeter 38.57 kJ/°C. During the combustion the water temp rose by 2.70°C. Calculate the energy in kJ/g for the chip.

$$\begin{aligned}q_{\text{rxn}} &= - C_{\text{cal}} \Delta T \\&= -(38.57 \text{ kJ/}^{\circ}\text{C}) (2.70^{\circ}\text{C}) \\&= - 104 \text{ kJ}\end{aligned}$$

Energy content is a positive quantity.

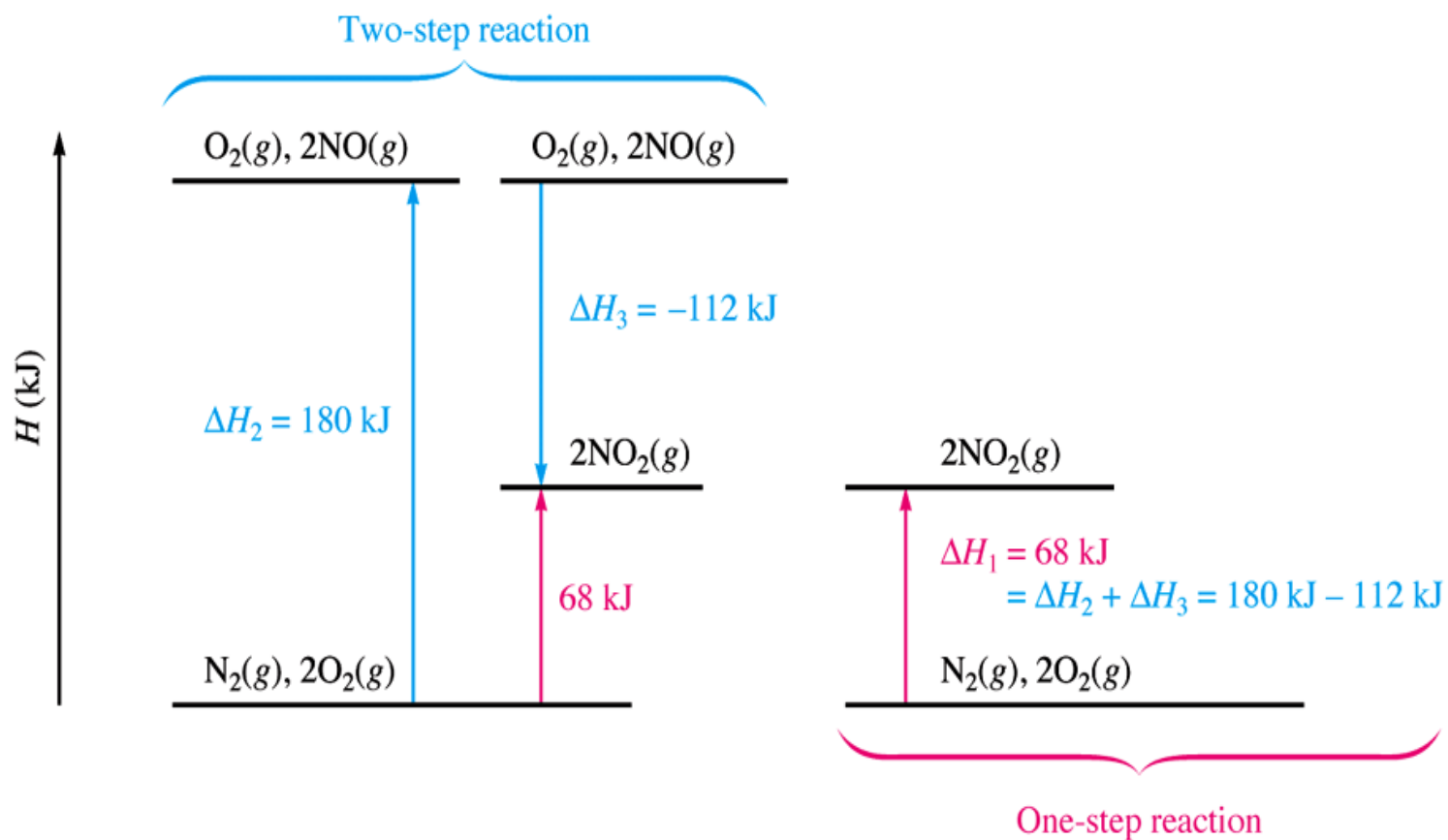
$$\begin{aligned}&= 104 \text{ kJ}/2.36 \text{ g} \\&= 44.1 \text{ kJ/g}\end{aligned}$$

Food Calories: 10.5 Cal/g

5.5 Hess's Law

- ***Hess's Law***: The change in enthalpy that occurs when reactants are converted to products is the same whether the reaction occurs in one step or a series of steps.
- Used for calculating enthalpy for a reaction that cannot be determined directly.

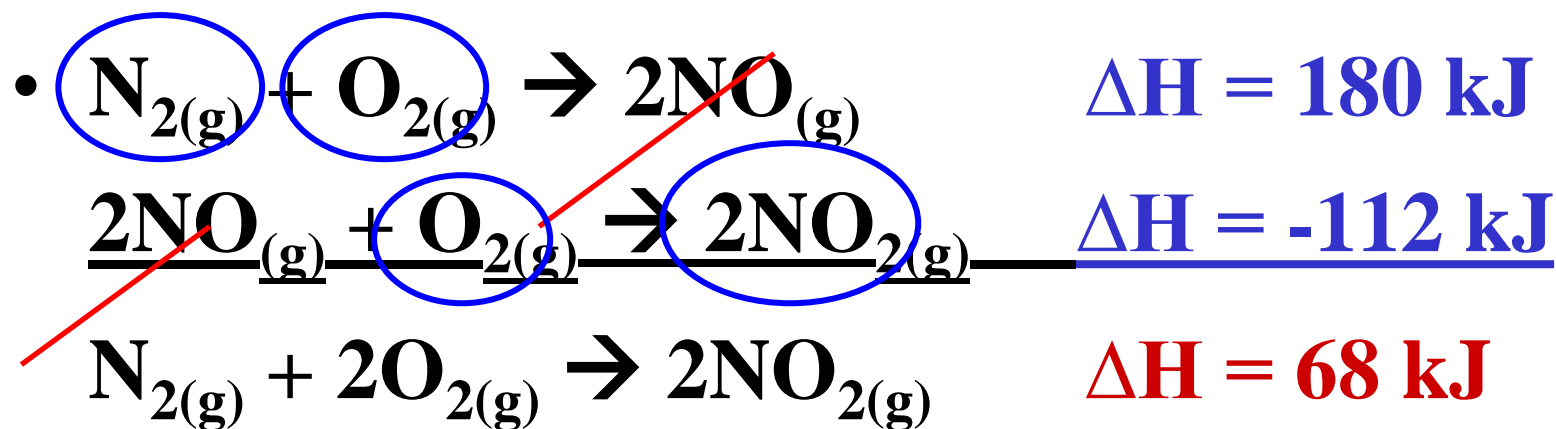
Consider the following reaction



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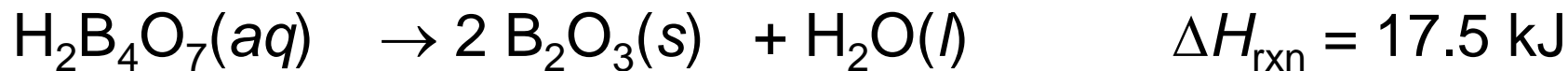


OR

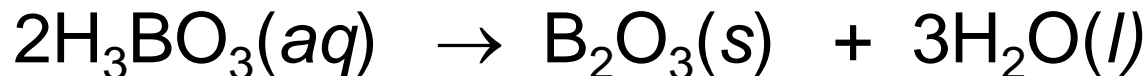


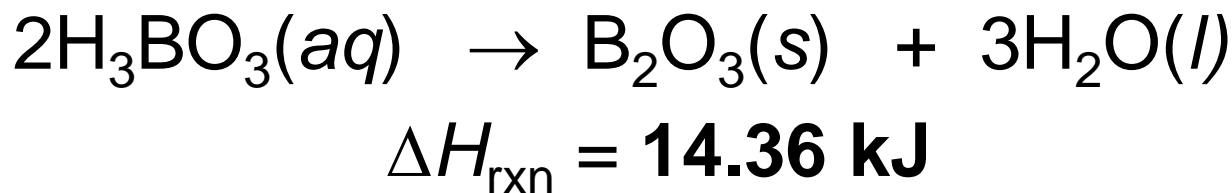
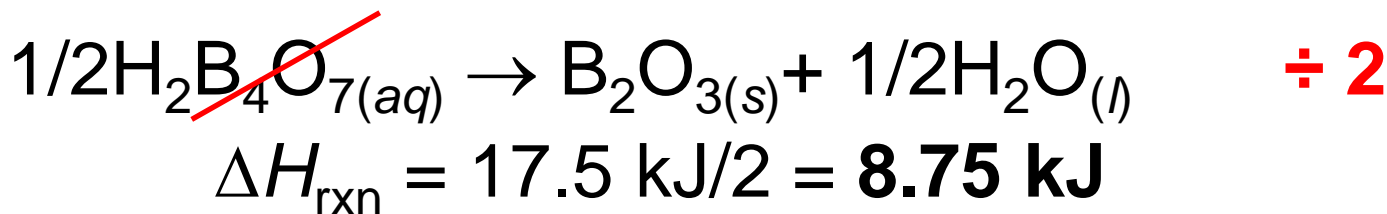
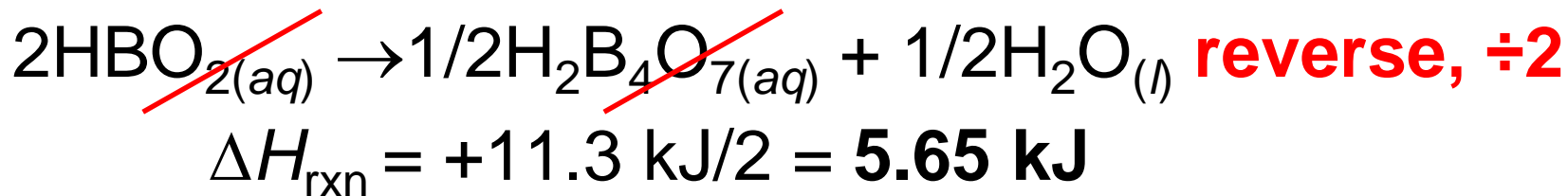
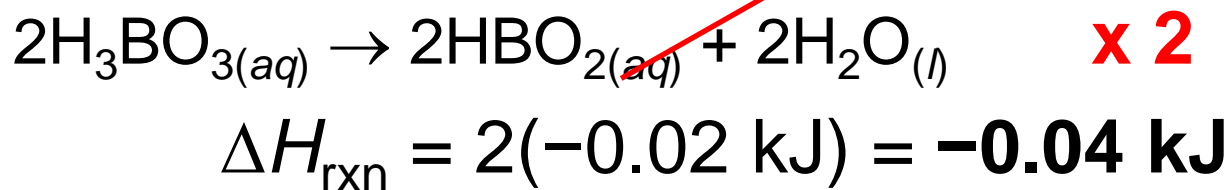
- In using stepwise reactions to determine an overall reaction
 - Remember the rules for manipulating equations.
 - Add the ΔH values for each step together after proper manipulation to obtain the overall enthalpy for the desired reaction.

Given the following equations:



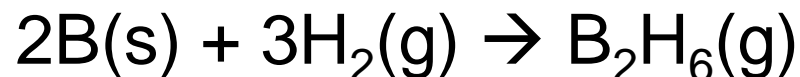
Find the ΔH for this overall reaction.



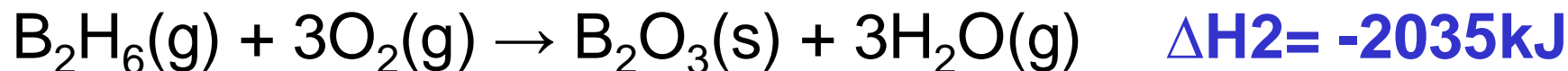
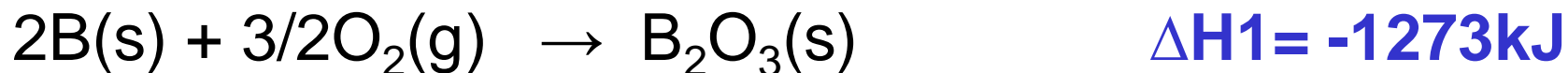


Example

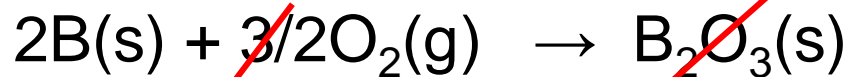
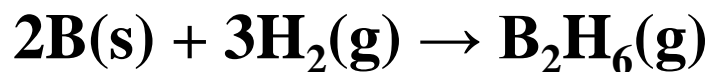
Find ΔH for the following reaction



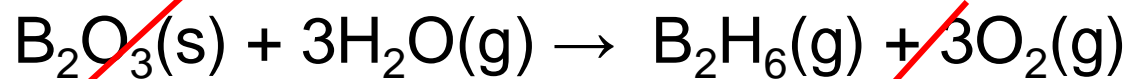
Given:



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$$\Delta\text{H}_1 = -1273\text{kJ}$$



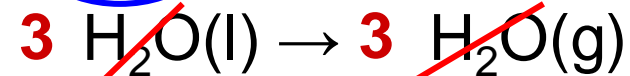
$$-\Delta\text{H}_2 = -(-2035\text{kJ})$$



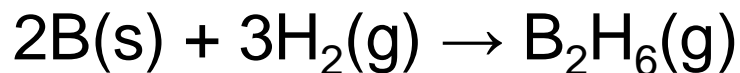
$$\Delta\text{H} = 762\text{ kJ}$$



$$3\text{x } \Delta\text{H}_3 = -286\text{kJ}$$



$$3\text{x } \Delta\text{H}_4 = 44\text{ kJ}$$

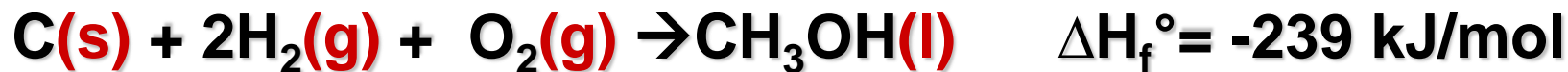


$$\Delta\text{H}_f = 3\text{x}(-286) + 3\text{x}44 + 762$$

$$= 36\text{ kJ}$$

5.6 Standard Enthalpies of Formation

- *Standard enthalpy of formation*
 - Symbol: ΔH_f°
 - The enthalpy change that results when 1 mole of a compound is formed from its elements in their standard states.
 - ΔH_f° for an element in its standard state is defined as zero.
 - Standard state: 1 atm, 25°C



Enthalpy of Formation

- The standard enthalpy of formation of any element in its most stable form is zero.

$$\Delta H_f^\circ (\text{C, graphite}) = 0$$

$$\Delta H_f^\circ (\text{O}_{2(\text{g})}) = 0$$

$$\Delta H_f^\circ (\text{Br}_{2(\text{l})}) = 0$$

$$\Delta H_f^\circ (\text{Cl}_{2(\text{g})}) = 0$$

$$\Delta H_f^\circ (\text{H}_{2(\text{g})}) = 0$$

$$\Delta H_f^\circ (\text{H}_{(\text{g})}) = 218 \text{ kJ/mole} \neq 0$$

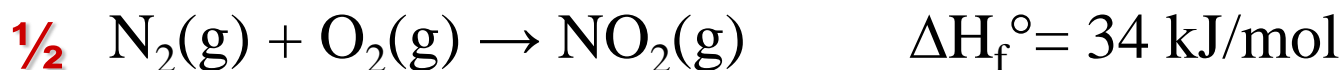
Selected Standard Heats of Formation at 25°C(298K)

Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$	Formula	$\Delta H_f^\circ(\text{kJ/mol})$
calcium				silver	
Ca(s)	0	Cl ₂ (g)	0	Ag(s)	0
CaO(s)	-635.1	HCl(g)	-92.3	AgCl(s)	-127.0
CaCO ₃ (s)	-1206.9	hydrogen		sodium	
carbon		H(g)	218	Na(s)	0
C(graphite)	0	H ₂ (g)	0	Na(g)	107.8
C(diamond)	1.9	nitrogen		NaCl(s)	-411.1
CO(g)	-110.5	N ₂ (g)	0	sulfur	
CO ₂ (g)	-393.5	NH ₃ (g)	-45.9	S ₈ (rhombic)	0
CH ₄ (g)	-74.9	NO(g)	90.3	S ₈ (monoclinic)	2
CH ₃ OH(l)	-238.6	oxygen		SO ₂ (g)	-296.8
HCN(g)	135	O ₂ (g)	0	SO ₃ (g)	-396.0
CS ₅ (l)	87.9	O ₃ (g)	143		
chlorine		H ₂ O(g)	-241.8		
Cl(g)	121.0	H ₂ O(l)	-285.8		

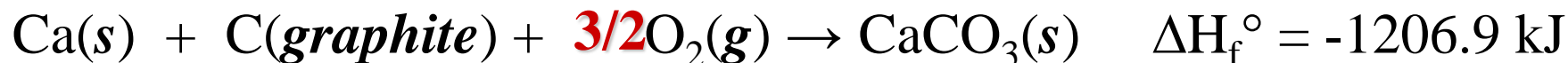
Writing Formation Equation

- Write equation where 1 mole of compound is formed (*Even if you must use non-integer coefficients*)

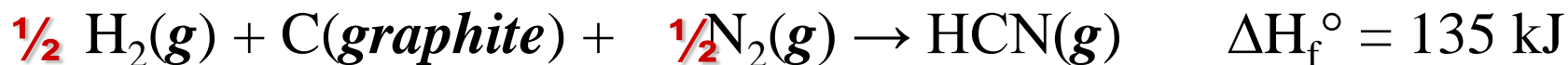
$\text{NO}_{2(g)}$:



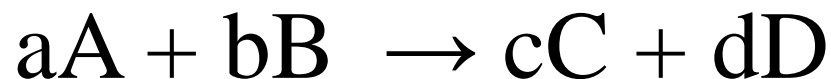
$\text{CaCO}_{3(s)}$:



$\text{HCN}_{(g)}$:



Using Enthalpy of Formation



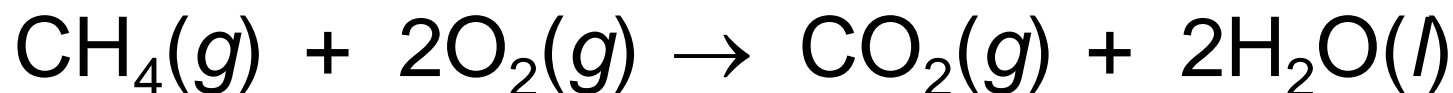
$$\Delta H_{\text{reaction}}^{\circ} = \sum n_p \Delta H_{\text{f}(\text{products})}^{\circ} - \sum n_r \Delta H_{\text{f}(\text{reactants})}^{\circ}$$

n = equation coefficient of products/reactants

Σ means “sum of”

$\Delta H_{\text{f}}^{\circ}$ is the standard enthalpy of formation for reactants or products

Calculate the $\Delta H^\circ_{\text{rxn}}$ for the following reaction from the table of standard values.

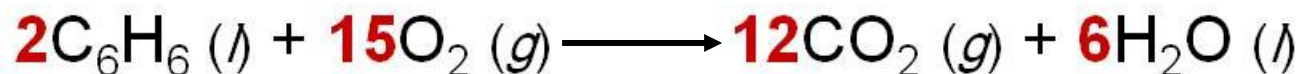


$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_{\text{f}} (\text{products}) - \sum m \Delta H^\circ_{\text{f}} (\text{reactants})$$

$$= [1(-393.5) + 2(-285.8)] - [1(-74.8) + 2(0)]$$

$$= -890.3 \text{ kJ/mol (exothermic)}$$

Benzene (C₆H₆) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted?



$$\Delta H_{\text{rxn}}^0 = \Sigma n\Delta H_{\text{f}}^0 (\text{products}) - \Sigma m\Delta H_{\text{f}}^0 (\text{reactants})$$

$$\Delta H_{\text{rxn}}^0 = [12\Delta H_{\text{f}}^0 (\text{CO}_2) + 6\Delta H_{\text{f}}^0 (\text{H}_2\text{O})] - [2\Delta H_{\text{f}}^0 (\text{C}_6\text{H}_6) + 0]$$

$$\Delta H_{\text{rxn}}^0 = [12 \times -393.5 + 6 \times -187.6] - [2 \times 49.04] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mole}} = -2973 \text{ kJ/mol C}_6\text{H}_6$$

Key Points

- Energy and energy types
- Law of conservation of energy
- Energy associated with reactions
- System and surroundings
- Exothermic and endothermic
- Thermochemistry
- Systems - open, closed, isolated

Key Points

- First law of thermodynamics
- Enthalpy (heat of formation; heat of reaction)
- State function
- Calorimetry
- Specific heat
- Hess's law
- Calculations involving enthalpy, specific heat, energy