Chemical Thermodynamics

Thermochemistry

Recommended books

1. P. W. Atkins and J. D. Paula: Physical Chemistry (10th edition)
2. Ira N. Levine: Physical Chemistry (6th edition)
3. M. Mahbubul Huque and M. Yousuf Ali Mollah: Principles of Physical Chemistry

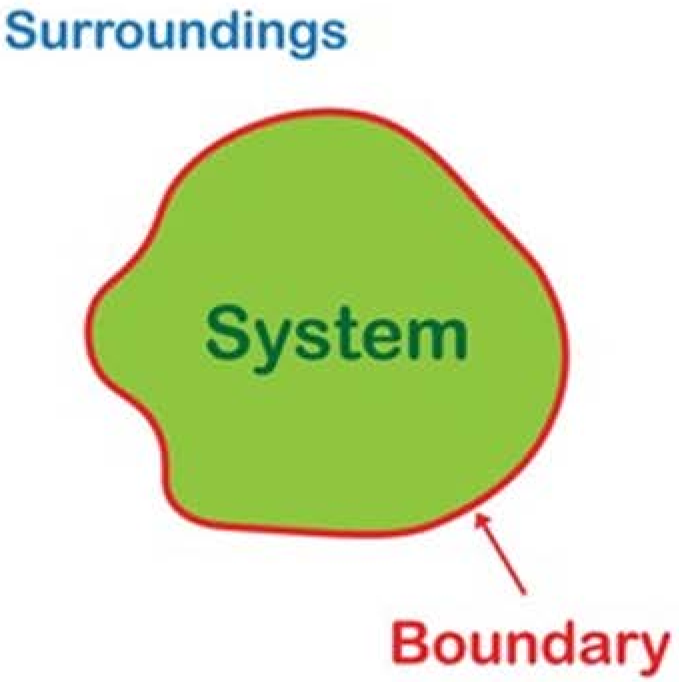
Thermochemistry

Standard states; thermochemical equations; enthalpy of reaction; Kirchhoff's equation; laws of thermochemistry; calorimetric measurements of bond activity and energies, enthalpy of reactions, formation, combustion, neutralization, solutions, dilution, fusion, vaporization, sublimation, hydrogenation.

Fundamental Concepts

System, surroundings and boundary

- ✓ **System:** The part of the universe we are interested in studying.
- ✓ **Surroundings:** Everything else in the universe outside the system.
- ✓ **Boundary**: a **boundary** is a real or imaginary surface that separates a thermodynamic system from its surroundings.
  - It defines the limits within which the system's properties are analyzed

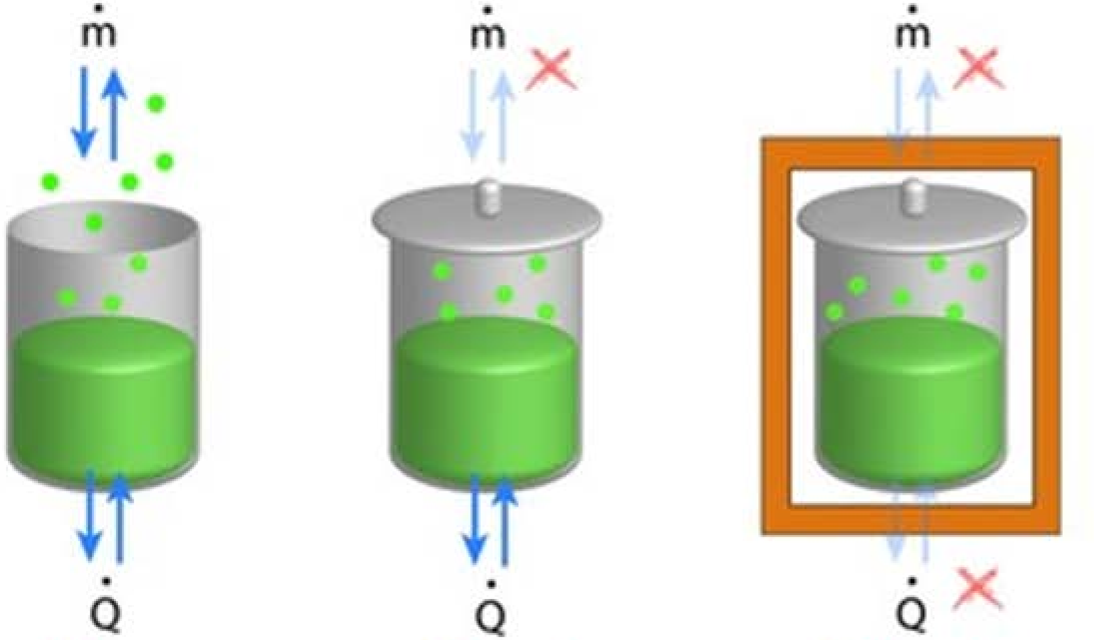


Fundamental Concepts

Types of systems

- **Open System**: Exchanges both matter and energy with the surroundings.
- **Closed System**: Exchanges only energy with the surroundings.
- **Isolated System**: Exchanges neither matter nor energy with the surroundings.

Thermodynamics
Systems



Open
Heat transfer
Mass Transfer

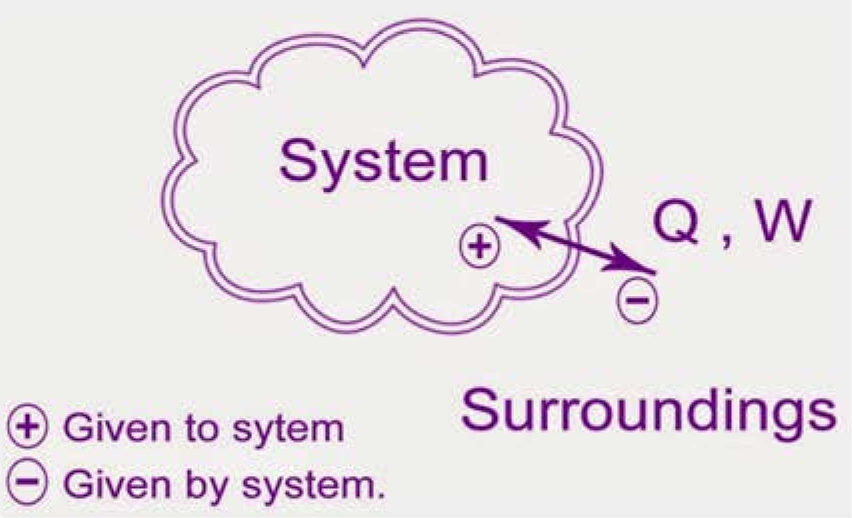
Closed
Heat transfer
No mass Transfer

Isolated
No heat transfer
No mass Transfer

Fundamental Concepts

Heat (q) and Work (w)

- **Heat (q)**: Energy transferred due to a temperature difference between the system and surroundings.
  - $q > 0$: Heat absorbed by the system (endothermic process).
  - $q < 0$: Heat released by the system (exothermic process).
- **Work (w)**: Energy transferred due to a change in the system's volume or other external parameters.
  - $w > 0$: Work done on the system by the surroundings.
  - $w < 0$: Work done by the system on the surroundings.



- **Note that**
  - → No heat and work are stored in the system and surroundings
  - → Energy is exchanged between system and surroundings through heat and work

Fundamental Concepts

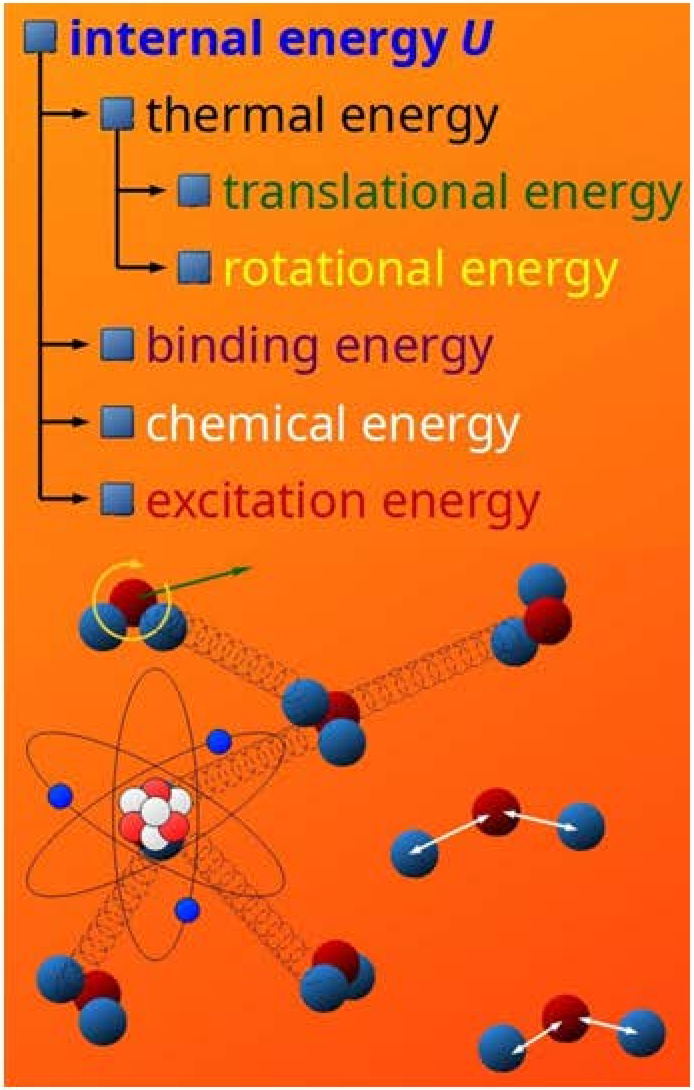
Internal energy (U)

Internal Energy (U): The sum of all kinetic and potential energies of all particles within a system.

- $\Delta U = q + w$
  (First Law of Thermodynamics)

$\Delta U = q + w$

1) Constant volume
   $w = 0$
   isochoric
2) Constant temperature
   $\Delta U = 0$
   isothermal
3) no heat transfer
   $q = 0$
   adiabatic
4) $q = 0$ and $w = 0$



Fundamental Concepts

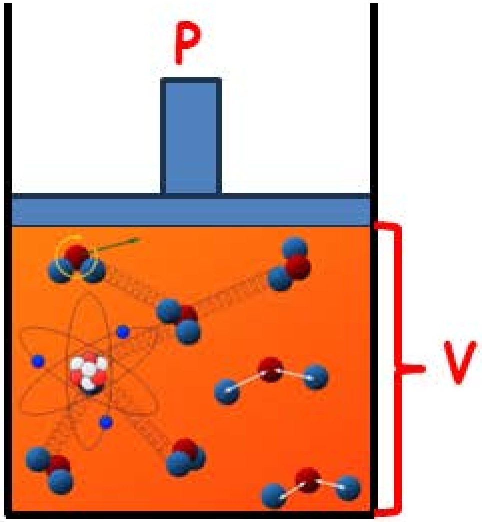
Enthalpy (H)

- **Enthalpy (H):** A state function related to the internal energy of a system at constant pressure. The definition of **enthalpy** (H) is:
- **Enthalpy is the total energy of a thermodynamic system, which includes its internal energy (U) and the energy required to displace its surroundings to make room for the system at constant pressure.**
- **This is mathematically expressed as**

$$H = U + PV,$$

where (PV) is the pressure-volume work.

- This definition captures the essence of enthalpy as a measure of the system's total energy, accounting for both the internal energy and the energy associated with maintaining the system's volume against external pressure.

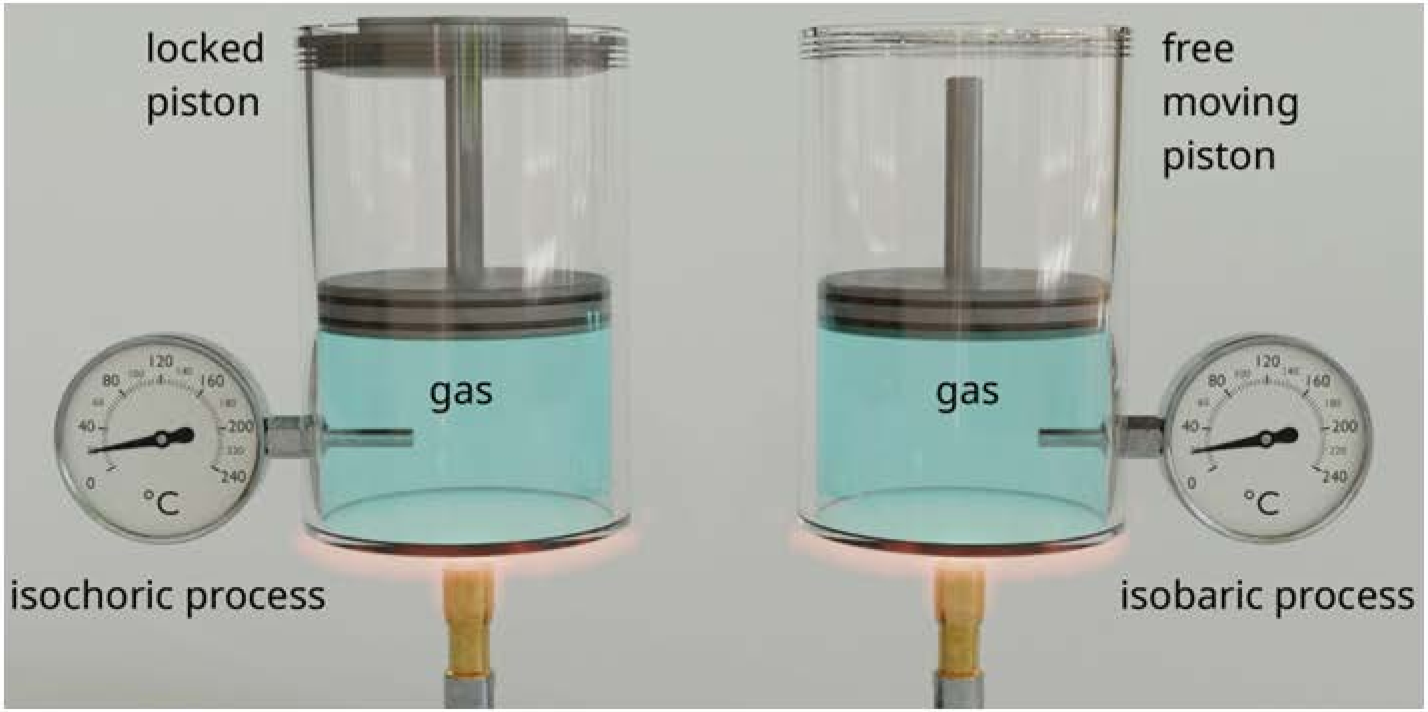


To maintain a fixed system's volume (V), energy is required to push the surroundings (such as a piston) against the external pressure (P). This energy is measured by the product (PV).

Fundamental Concepts

Enthalpy Change (ΔH)

- $\Delta H = \Delta U + P\Delta V + V\Delta P = q + w + P\Delta V + V\Delta P = q - P\Delta V + P\Delta V + V\Delta P = q + V\Delta P$
- $\Delta H = q + V\Delta P = q_P$ (at constant pressure, $\Delta P = 0$)
- $\Delta H = q + V\Delta P = q_V + \Delta PV = q_V + \Delta nRT$ (at constant V, $V\Delta P = \Delta PV$)



Introduction to Thermochemistry

Definition

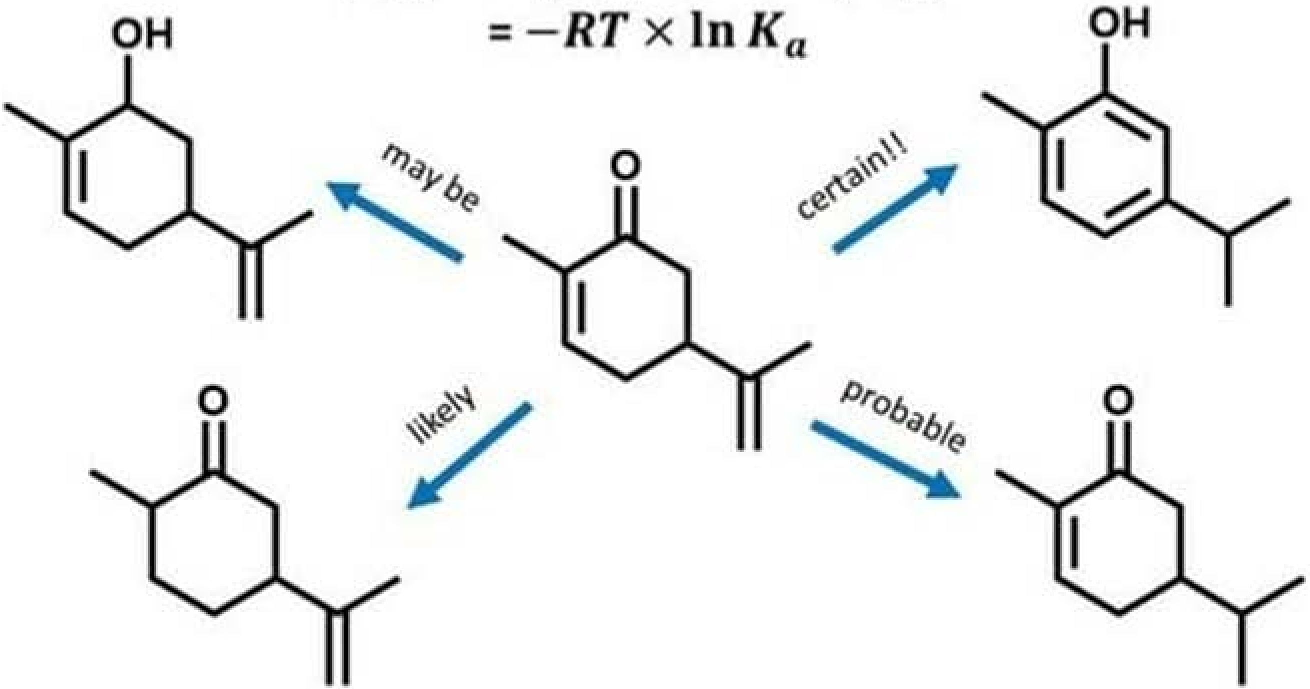
Thermochemistry is the study of the heat energy associated with chemical reactions and physical transformations. It involves measuring and analyzing the heat exchange between a system and its surroundings during chemical processes.

Introduction to Thermochemistry

Importance

- **Predicting Reaction Feasibility**: Helps determine whether a reaction will occur spontaneously based on enthalpy changes.

$$\Delta_r G^{o}_{m} = \Delta_r H^{o}_{m} - T \times \Delta_r S^{o}_{m} =$$
$$= -RT \times \ln K_a$$

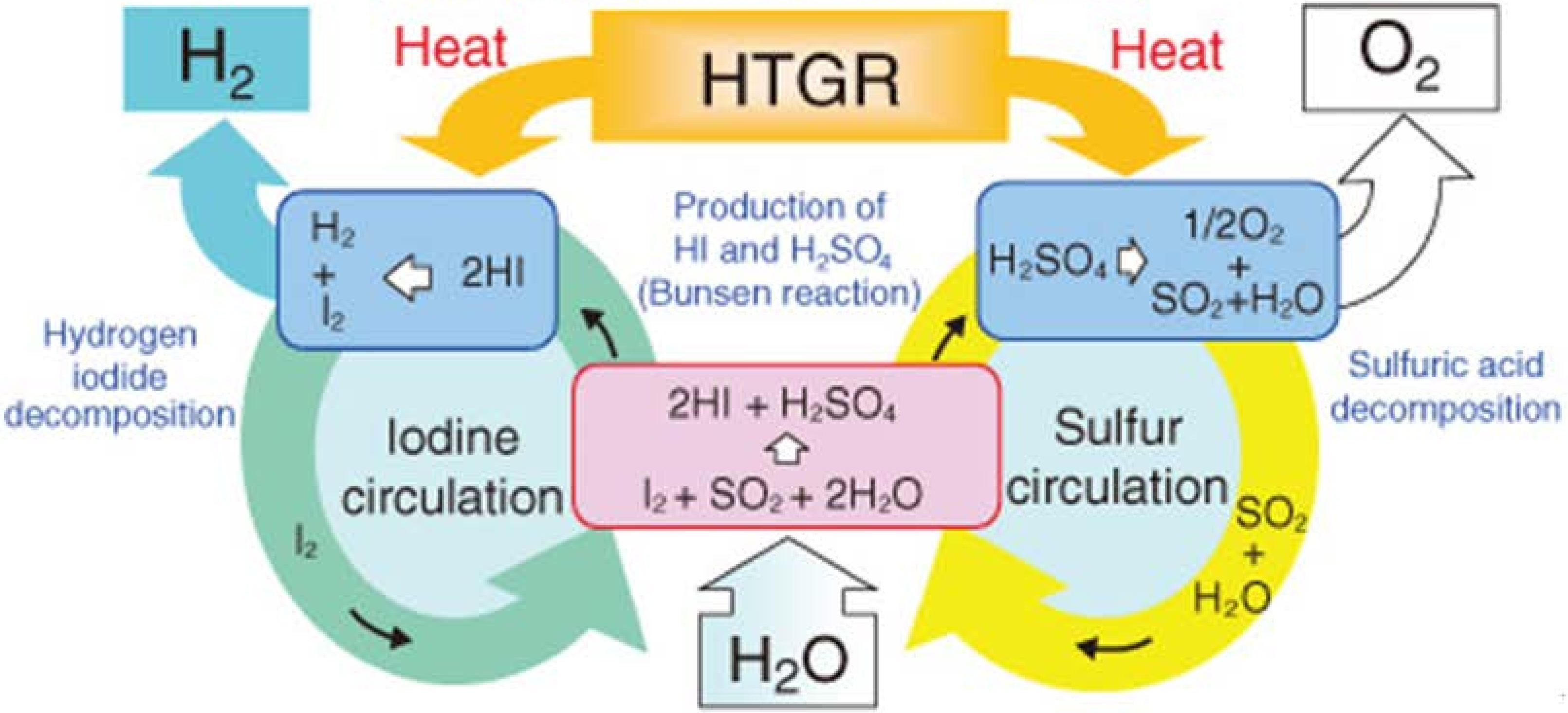


Introduction to Thermochemistry

Importance

- **Energy Efficiency**: Crucial for designing energy-efficient industrial processes, reducing costs, and improving sustainability.

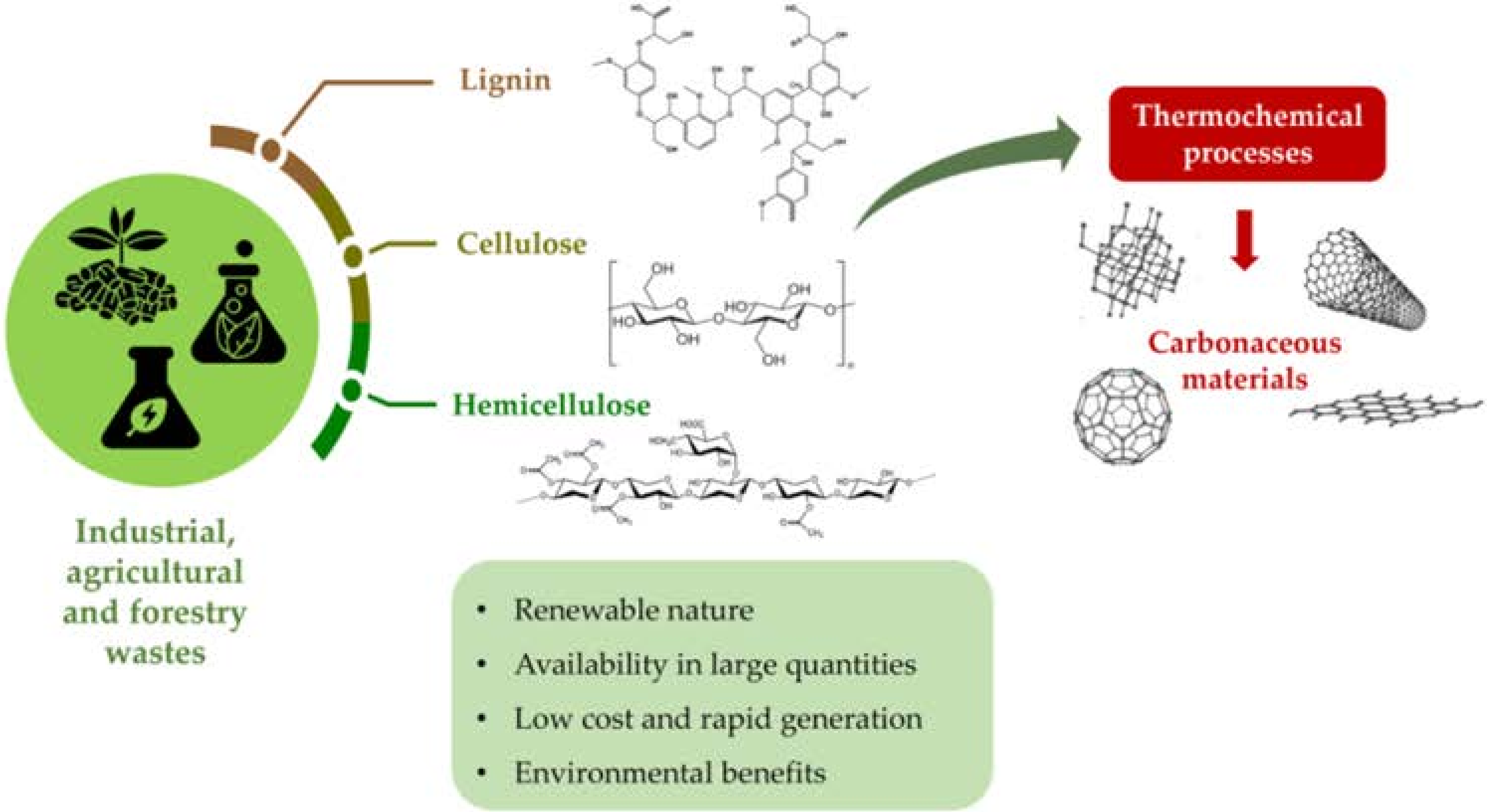
High-temperature gas-cooled reactor



Introduction to Thermochemistry

Importance

- **Environmental Impact**: Understanding heat changes can help minimize the environmental impact of chemical processes by optimizing energy use.



Lignin

Cellulose

Hemicellulose

Thermochemical processes

Carbonaceous materials

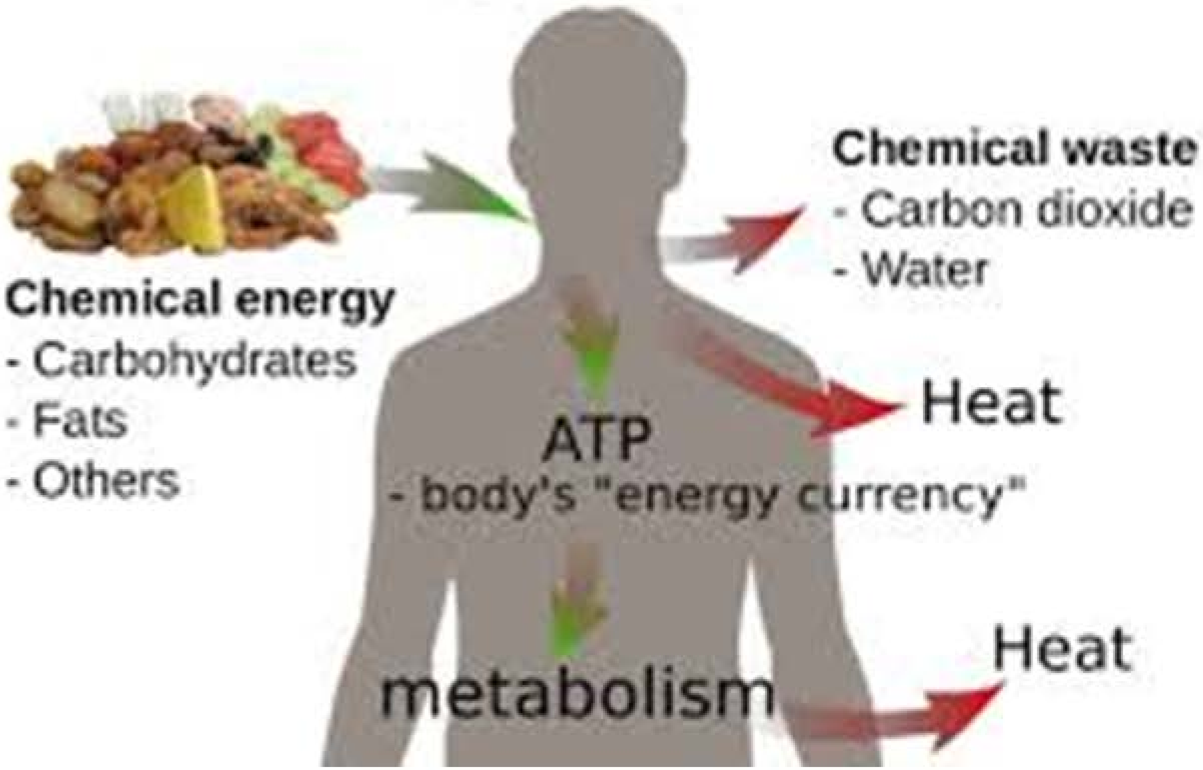
Industrial, agricultural and forestry wastes

- Renewable nature
- Availability in large quantities
- Low cost and rapid generation
- Environmental benefits

Introduction to Thermochemistry

Importance

- **Biological Processes**: Essential for understanding metabolic pathways and energy transfer in biological systems, such as ATP synthesis in cells.



Introduction to Thermochemistry

Historical Background

- **Antoine Lavoisier (1743-1794)**: Known as the father of modern chemistry, Lavoisier's work on the conservation of mass laid the groundwork for thermochemical studies. He demonstrated that mass is neither created nor destroyed in chemical reactions.
- **Germain Hess (1802-1850)**: Formulated Hess's Law, which states that the total enthalpy change of a reaction is the same, regardless of the number of steps in the reaction. This principle is fundamental in calculating enthalpy changes for complex reactions.

Antoine Lavoisier (1743-1794)

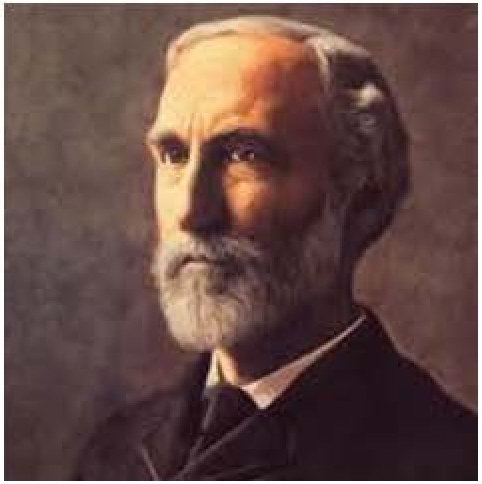
Germain Hess (1802-1850)

Introduction to Thermochemistry

Historical Background

- **Julius Robert Mayer (1814-1878)**: Contributed to the first law of thermodynamics, which states that energy cannot be created or destroyed, only transformed. His work helped establish the concept of energy conservation.
- **Josiah Willard Gibbs (1839-1903)**: Developed the concept of Gibbs free energy, which combines enthalpy and entropy to predict the spontaneity of reactions. Gibbs' work is crucial for understanding the thermodynamic favorability of reactions.

Julius Robert Mayer (1814-1878)



Josiah Willard Gibbs (1839-1903)

Standard States

Definition

- The **standard state** of a material (which can be a pure substance, mixture, or solution) serves as a reference point for calculating its thermodynamic properties under various conditions.
- The choice of standard state is somewhat arbitrary, but the **International Union of Pure and Applied Chemistry** **(IUPAC)** recommends specific conventions for general use.
- According to IUPAC convention, the standard state of a substance is its pure state at 1 bar (10^5 Pa). However, the temperature is not specified in this definition, allowing for flexibility in calculations involving different temperatures.
- It is denoted using a degree symbol (°) or a superscript Plimsoll symbol (⊖) to indicate thermodynamic quantities in the standard state, such as changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$), or Gibbs free energy ($\Delta G°$). The symbol (°) or ($^{\ominus}$) refers to 1 bar (10^5 Pa).
- It is important to note that the standard state should not be confused with standard temperature and pressure (STP), which is commonly used for gases.

Standard States

Standard State Definitions According to IUPAC

Ideal Gas	The standard state for an ideal gas is defined as the hypothetical state of the gas behaving ideally at 1 bar.
Real Gas	For real gases, the standard state is also defined at a pressure of 1 bar. However, real gases do not behave perfectly ideally, so corrections for non-ideality must be applied.
Solid	The standard state for solids is the pure substance in its most stable form at 1 bar. For elements, this is typically the most stable allotrope (e.g., graphite for carbon)
Liquid	Similar to solid, the standard state for liquids is the pure substance at 1 bar.
Solute	For solutes in a solution, the standard state is defined as the hypothetical state at infinite dilution, where solute-solute interactions are negligible, and only solute-solvent interactions are present. The standard state concentration is typically 1 mol/kg (molality) or 1 mol/dm^3 (molarity)
Solvent	The standard state for solvents is generally defined in the same way as for solutes, focusing on the behavior of the solvent at a standard concentration.

Standard States

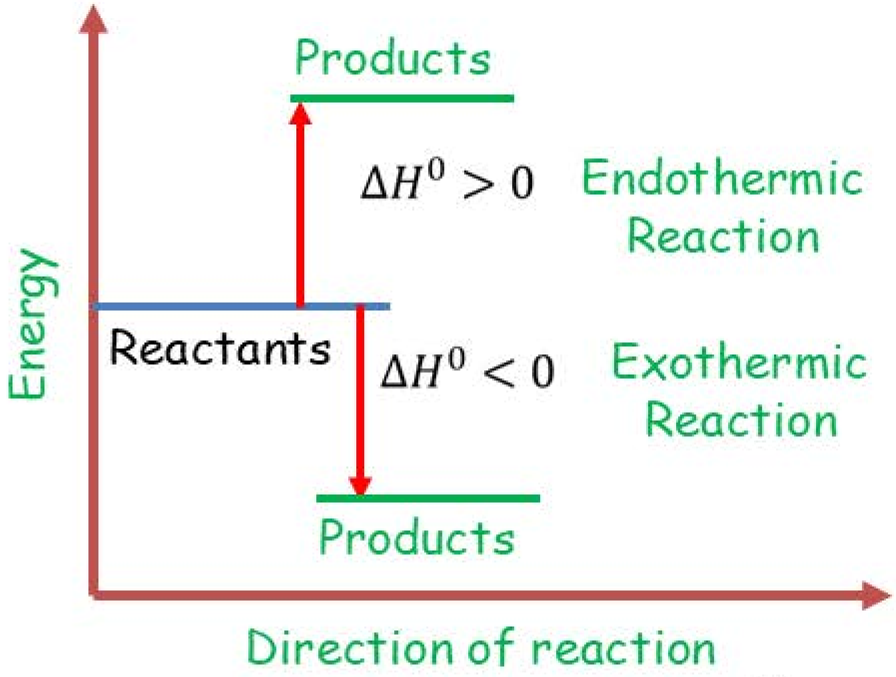
Standard Enthalpy Change, ΔH^0

- The **standard enthalpy change of a process** refers to the heat exchange that occurs during a specific process or reaction under standard conditions.
- This concept is crucial in thermodynamics and helps in understanding the energy changes associated with chemical reactions.
- The standard enthalpy change can be calculated using the formula
- Chemical reaction

$$\Delta_r H^0 = \underset{\text{Products}}{\sum\Delta_f H^0} - \underset{\text{Reactants}}{\sum\Delta_f H^0}$$

- Physical processes

$$\Delta_{\text{vap}} H^0 = \underset{H_2O(\text{vap})}{\sum\Delta_f H^0} - \underset{H_2O(\text{l})}{\sum\Delta_f H^0}$$



Standard States

Importance in Thermochemical Calculations

- **Consistency**: Provides a reference point for comparing enthalpy changes of different reactions, ensuring consistency in thermochemical data.
- **Simplification**: Simplifies the calculation of enthalpy changes by using standard enthalpies of formation, making it easier to predict reaction outcomes.
- **Predictability**: Helps in predicting the direction and extent of chemical reactions, aiding in the design of chemical processes and products.

Thermochemical Equations

What is a Thermochemical Equation?

- A **thermochemical equation** is a balanced chemical equation that includes the standard enthalpy change (ΔH^0) associated with the reaction.
- This equation not only shows the reactants and products but also indicates whether the reaction is exothermic (releases heat) or endothermic (absorbs heat).
- A positive ΔH^0 value indicates an endothermic process, while a negative ΔH^0 value indicates an exothermic process

Thermochemical Equations

Rules for Writing Thermochemical Equations

1. Sign of ΔH^0

- If heat is released during the reaction, the ΔH^0 value is negative. This value can be included as a product in the equation.

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)} \quad \Delta H^0 = -890.4\ \mathrm{kJ}$$

- If heat is absorbed, the ΔH^0 value is positive and can be included as a reactant.

$$\mathrm{H_2O(s) \rightarrow H_2O(l)} \quad \Delta H^0 = +6.10\ \mathrm{kJ}$$

2. Physical States

- All physical states (solid, liquid, gas) must be specified in the equation, as the ΔH^0 value can vary with different states.

$$\mathrm{H_2O(s) \rightarrow H_2O(l)} \quad \Delta H^0 = +6.10\ \mathrm{kJ}$$

3. Reversing Reactions:

- If the reaction is reversed, the sign of ΔH^0 also reverses.

$$\mathrm{H_2O(l) \rightarrow H_2O(s)} \quad \Delta H^0 = -6.10\ \mathrm{kJ}$$

4. Changing Stoichiometric Coefficients

- If the coefficients in the balanced equation are changed, the ΔH^0 value must also be adjusted proportionally. For example, doubling the coefficients will double the ΔH^0

$$\mathrm{2H_2O(s) \rightarrow 2H_2O(l)} \quad \Delta H^0 = +12.20\ \mathrm{kJ}$$

Thermochemical Equations

Differences Between Thermochemical Equations and Chemical Equations

- **Inclusion of Enthalpy:**
  - Thermochemical equations explicitly include the enthalpy change (ΔH), while standard chemical equations do not.
- **Heat Transfer Information:**
  - Thermochemical equations provide information about whether a reaction is exothermic or endothermic, which is not conveyed in regular chemical equations.
- **State of Matter:**
  - Thermochemical equations require the specification of the physical states of reactants and products, while chemical equations may not always include this information.

Thermochemical Equations

Importance of Thermochemical Equations

Energy Calculations	They allow chemists to calculate the energy changes associated with chemical reactions, which is essential for understanding reaction mechanisms and thermodynamics.
Predicting Reaction Feasibility	By knowing whether a reaction is exothermic or endothermic, chemists can predict the feasibility and spontaneity of reactions under certain conditions.
Industrial Applications	In industries, thermochemical equations help in designing processes that involve heat exchange, such as combustion engines, chemical reactors, and energy production systems.
Environmental Impact	Understanding the energy changes in reactions can aid in assessing the environmental impact of chemical processes, particularly in terms of energy efficiency and emissions.
Educational Value	They serve as a fundamental concept in chemistry education, helping students grasp the relationship between heat and chemical reactions.

Kirchhoff's Equation

The Kirchhoff's equation is a fundamental relationship in thermodynamics that describes how the enthalpy change of a chemical reaction varies with temperature.

Derivation:

- Internal energy is a state function that deepens of state of the system. The change in internal energy, ΔU, can be expressed as

$$\Delta U = U_2 - U_1$$

- Differentiating with temperature at constant volume gives

$$\left(\frac{\partial \Delta U}{\partial T}\right)_V = \left(\frac{\partial U_2}{\partial T}\right)_V - \left(\frac{\partial U_1}{\partial T}\right)_V$$

$$\left(\frac{\partial \Delta U}{\partial T}\right)_V = (C_V)_2 - (C_V)_1 \quad \because \left[C_V = \left(\frac{\partial U}{\partial T}\right)_V\right]$$

$$\left(\frac{\partial \Delta U}{\partial T}\right)_V = \Delta C_V \Rightarrow d\Delta U = \Delta C_V dT$$

Kirchhoff's Equation

Derivation:

- Integrating between T_1 and T_2 gives

$$\int_{T_1}^{T_2} d\Delta U = \int_{T_1}^{T_2} \Delta C_V dT$$

- If ΔC_V is considered to be unaffected within a small range of temperature change, then integration gives

$$\Delta U(T_2) - \Delta U(T_1) = \Delta C_V(T_2 - T_1)$$

$$\Delta U(T_2) = \Delta U(T_1) + \Delta C_V(T_2 - T_1)$$

- Similarly, starting from enthalpy, H

$$\Delta H = H_2 - H_1$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \Longrightarrow d\Delta H = \Delta C_P dT$$

- Integrating between T_1 and T_2 gives

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$$

Kirchhoff's Equation

Kirchhoff's equation is a fundamental relationship in thermodynamics that describes how internal energy change or enthalpy change of a chemical reaction varies with temperature.

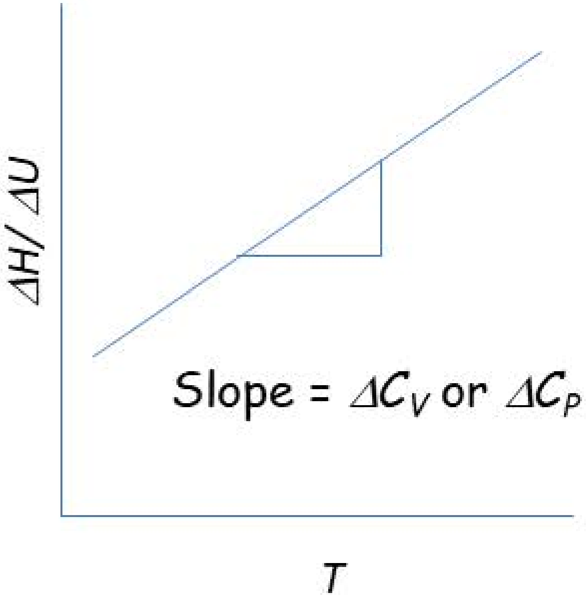
- It can be expressed as,

(1) $$\left(\frac{\partial \Delta U}{\partial T}\right)_V = \Delta C_V$$

(2) $$\Delta U(T_2) = \Delta U(T_1) + \Delta C_V(T_2 - T_1)$$

(3) $$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$$

(4) $$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$$



- Equations (1) & (3) are differential whereas (2) & (4) are integral Kirchhoff's equation.

Kirchhoff's Equation

SOLVED PROBLEM 1. The heat of reaction $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ at 27°C is -22.1 kcal. Calculate the heat of reaction at 77°C. The molar heat capacities at constant pressure at 27°C for hydrogen, chlorine and HCl are 6.82, 7.70 and 6.80 cal mol^{-1} respectively.

SOLUTION

Here,

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl \qquad \Delta H = -22.1 \text{ kcal}$$

ΔC_p = Heat capacities of products – Heat capacities of reactants

$$\begin{aligned} &= 6.80 - \left[\frac{1}{2}(6.82) + \frac{1}{2}(7.70)\right] \\ &= 6.80 - 7.26 = -0.46 \text{ cal} = -0.46 \times 10^{-3} \text{ kcal} \\ T_2 &= 273 + 77 = 350\text{ K}; T_1 = 273 + 27 = 300\text{ K} \\ T_2 - T_1 &= (350 - 300)\text{ K} = 50\text{ K} \end{aligned}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned} \Delta H_2 - \Delta H_1 &= \Delta C_p (T_2 - T_1) \\ &= -22.1 + (-0.46 \times 10^{-3}) \times 50 \\ &= -22.1 + (-0.023) \\ &= -22.123 \text{ kcal} \end{aligned}$$

$\therefore$ Heat of reaction at 77°C is – **22.123 kcal**

Kirchhoff's Equation

SOLVED PROBLEM 2. The heat of reaction $N_2 + 3H_2 \rightarrow 2NH_3$ at 27°C was found to be −21.976 kcal. What will be the heat of reaction at 50°C ?

The molar heat capacities at constant pressure and at 27°C for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.86 cal mol^{-1} degree^{-1}.

SOLUTION

Here,

$$\begin{aligned} \Delta H &= -21.976 \text{ kcal} \\ T_2 &= 273 + 50 = 323 \text{ K} \\ T_1 &= 273 + 27 = 300 \text{ K} \\ [T_2 - T_1] &= (323 - 300)\text{ K} = 23 \text{ K} \end{aligned}$$

ΔC_p = Heat capacities of products – Heat capacities of reactants

$$\begin{aligned} &= (2 \times 8.86) - [6.8 + (3 \times 6.77)] \\ &= 17.72 - (6.8 + 20.31) = -9.39 \text{ cal} \\ &= -9.39 \times 10^{-3} \text{ kcal} \end{aligned}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned} \Delta H_2 &= \Delta H_1 + (T_2 - T_1)\,\Delta C_p \\ &= -21.976 + [23 \times (-9.39 \times 10^{-3})] \\ &= -21.976 + (-0.216) = -22.192 \text{ kcal} \end{aligned}$$

∴ Heat of reaction at 50°C is = **22.192 kcal**

laws of thermochemistry

Lavoisier and Laplace Law

Together, Lavoisier and Laplace (1780) formulated a key principle in thermochemistry known as the Lavoisier and Laplace law.

- This law states that the energy change accompanying any transformation is equal and opposite to the energy change accompanying the reverse process.
- This principle is foundational in understanding the reversibility of chemical reactions.
- For example, if the reaction of sulfur dioxide to form sulfur and oxygen is represented as:

$$SO_2(g) \rightarrow S(s) + O_2(g) \quad \Delta H = +296.9\ kJ$$

Then the reverse reaction can be written as:

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H = -296.9\ kJ$$

Laws of thermochemistry

Hess's law of constant heat summation:

Hess's Law (1840), also known as the law of constant heat summation, states that

- The total enthalpy change during a chemical reaction is the same, regardless of whether the reaction occurs in one step or multiple steps.

Key Points of Hess's Law

- The law follows as more consequence of the first law of thermodynamics.
- State Function:
  - Enthalpy is a state function, which means that the change in enthalpy ΔH) for a reaction depends only on the initial and final states, not on the steps taken to reach the final state.
- Multiple Pathways:
  - Hess's Law allows us to calculate the enthalpy change for a reaction that may be difficult to measure directly by using known enthalpy changes of related reactions.
- Additivity of Enthalpy Changes:
  - The total enthalpy change for a reaction can be calculated by summing the enthalpy changes of individual steps.

laws of thermochemistry

Hess's law of constant heat summation:

- Let us suppose that a substance A can be changed to Z directly,

$$A \rightarrow Z + Q_1 \qquad \Delta H_1 = -Q_1$$

where Q_1 is the heat evolved in the direct change.

- When the same change is brought about in multiple steps

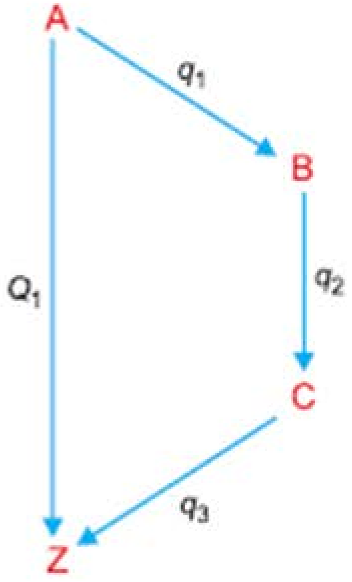
$$A \rightarrow B + q_1 \qquad \Delta H_2 = -q_1$$

$$B \rightarrow C + q_2 \qquad \Delta H_2 = -q_2$$

$$C \rightarrow Z + q_3 \qquad \Delta H_2 = -q_3$$

Total evolution of heat $= q_1 + q_2 + q_3 = Q_2$

- According to Hess's law: $Q_1 = Q_2$



laws of thermochemistry

Hess's law of constant heat summation:

Burning of carbon to CO_2

- Carbon can be burnt to CO_2 directly or it may first be changed to CO which may then oxidized to CO_2.
- 1st way:

  $C(s) + O_2\,(g) \rightarrow CO_2 \quad \Delta H = -94.05$ kcal

- 2nd way:

  $C(s) + \frac{1}{2}O_2\,(g) \rightarrow CO\,(g) \quad \Delta H = -26.42$ kcal

  $CO(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -67.71$ kcal

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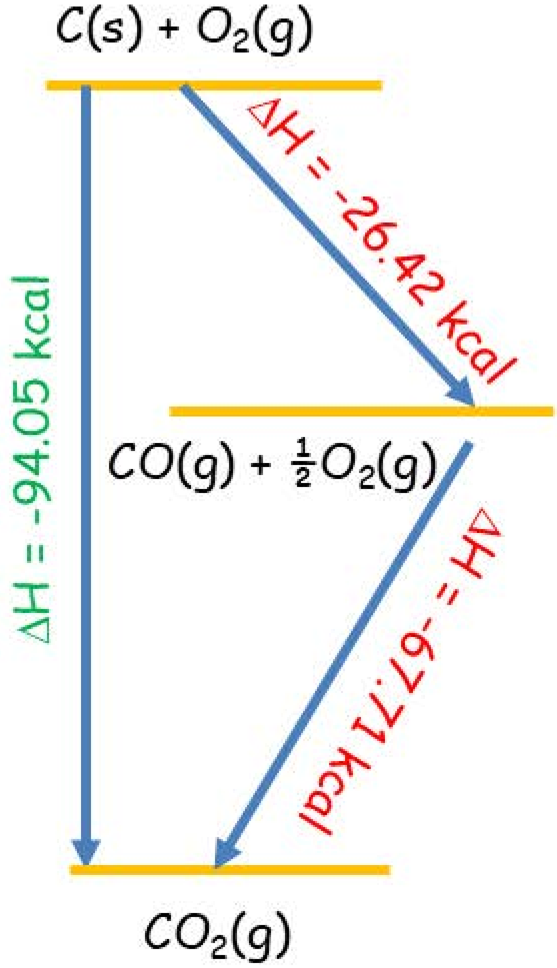
Total $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -94.13$ kcal



Heat Exchange and Quantification

- Heat is the exchange of thermal energy between the system and surroundings. It occurs when system and surroundings have a difference in temperature
- Heat flows from matter with high temperature to matter with low temperature until both objects reach the same temperature
  - thermal equilibrium
- When a system absorbs heat, its temperature increases and the increase in temperature is directly proportional to the amount of heat absorbed
- The proportionality constant is called the **heat capacity, *C***
  - units of *C* are J/°C or J/K

$$q = C \times \Delta T$$

- The heat capacity of an object depends on its mass
  - 200 g of water requires twice as much heat to raise its temperature by 1°C than 100 g of water
- The heat capacity of an object depends on the type of material
  - 1000 J of heat energy will raise the temperature of 100 g of sand 12°C, but only raise the temperature of 100 g of water by 2.4°C

Heat Exchange and Quantification

- Specific heat capacity (C_s) is the amount of heat required to raise the temperature of 1 g of a substance by 1°C, measured in J/(g·°C).
- Molar heat capacity refers to the heat needed to raise the temperature of 1 mole of a substance by 1°C.
- Water's high specific heat allows it to absorb large amounts of heat with minimal temperature change, helping cool coastal areas and making it an effective coolant.
- The heat absorbed or released by an object is proportional to its mass, specific heat, and temperature change, calculated by

$$q = m \cdot C_s \cdot \Delta T$$

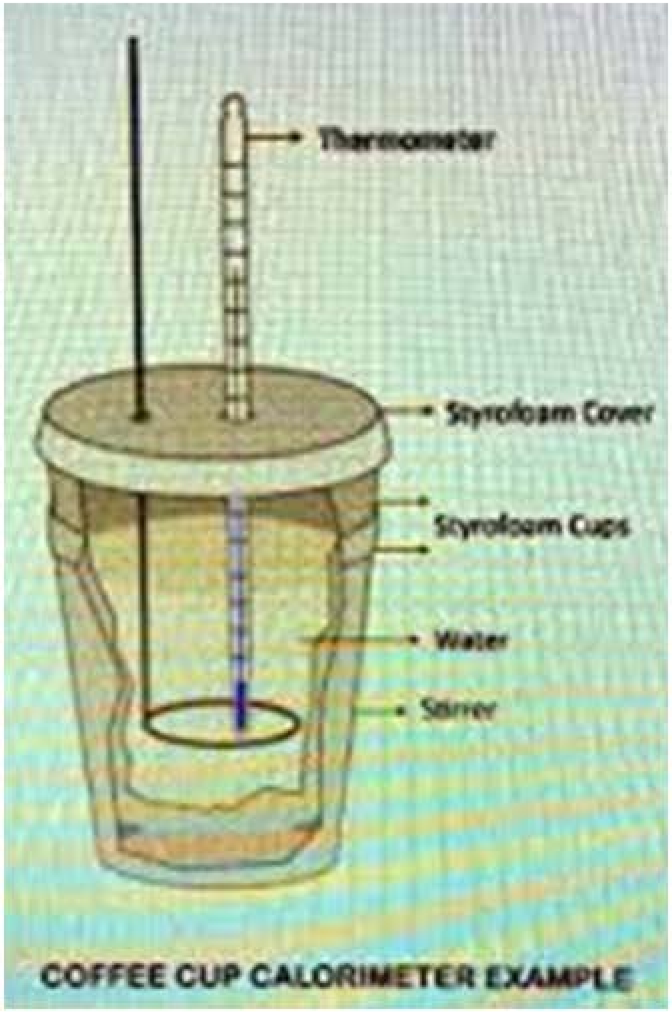
Table : Specific heat capacities of some common substances

Substance	Specific Heat Capacity, C_s (J/g · °C)*
Elements	
Lead	0.128
Gold	0.128
Silver	0.235
Copper	0.385
Iron	0.449
Aluminum	0.903
Compounds	
Ethanol	2.42
Water	4.18
Materials	
Glass (Pyrex)	0.75
Granite	0.79
Sand	0.84

*At 298 K.

Calorimetric measurements

- Calorimetry is the science of measuring the heat of chemical reactions or physical changes.
- The principle of calorimetry relies on the law of conservation of energy, which states that energy cannot be created or destroyed, only transferred.
- In a calorimetric experiment, the system (reaction or physical change) either absorbs or releases heat, and this heat is measured to determine various thermodynamic properties.



COFFEE CUP CALORIMETER EXAMPLE

Calorimetric measurements

Principles

- The main idea behind calorimetry is that the heat released or absorbed by the system is equal to the heat gained or lost by the surroundings.
- In practical terms, this means that when a reaction occurs in an insulated container (calorimeter), the heat change in the reaction is transferred to a substance in the calorimeter (usually water or another known material), which causes a change in temperature.
- The heat change (q) can be calculated using the formula:

$$q = mc\Delta T$$

where:

- m = mass of the substance (typically water) absorbing the heat,
- c = specific heat capacity of the substance,
- ΔT = change in temperature.

Calorimetric measurements

Example: Determining the Enthalpy of Neutralization

- In a neutralization reaction between a strong acid and a strong base (e.g., HCl + NaOH), the heat released during the reaction can be measured using a calorimeter.
- Suppose we mix 50 mL of 1 M HCl and 50 mL of 1 M NaOH in a calorimeter, and the temperature of the resulting solution increases by 5°C.
- Assuming the solution behaves like water and has a specific heat capacity of 4.18 J/g°C, we can calculate the heat released.

1. **Mass of solution**: Assuming the density of the solution is close to water (1 g/mL), the mass of the solution is 100 g (50 g from HCl and 50 g from NaOH).
2. **Change in temperature (ΔT)**: The temperature rise is 5°C.
3. **Heat absorbed by the solution**:

$$q = mc\Delta T = 100\ g \times 4.18\ J/(g\ {}^{\circ}C) \times 5\ {}^{\circ}C = 2090\ J$$

Thus, the heat released by the neutralization reaction is 2090 J. This value can be further used to calculate the enthalpy change per mole of reactants.

Calorimeter

A **calorimeter** is a device designed to measure the heat energy associated with a process.

- It allows scientists to quantify the heat transfer during chemical reactions, phase transitions, or other thermal events.
- By understanding the heat changes, researchers can optimize processes, study thermodynamic properties, and evaluate the efficiency of energy sources.

Key components of a Calorimeter:

- **Insulated Container**: Maintains a constant temperature during the reaction.
- **Temperature Sensor**: Measures the change in temperature.
- **Stirrer**: Ensures uniform mixing.
- **Calorimeter Vessel**: Holds the sample and reactants.
- **Water Jacket**: Surrounds the calorimeter vessel to regulate temperature.

Importance of Calorimeters in Chemistry:

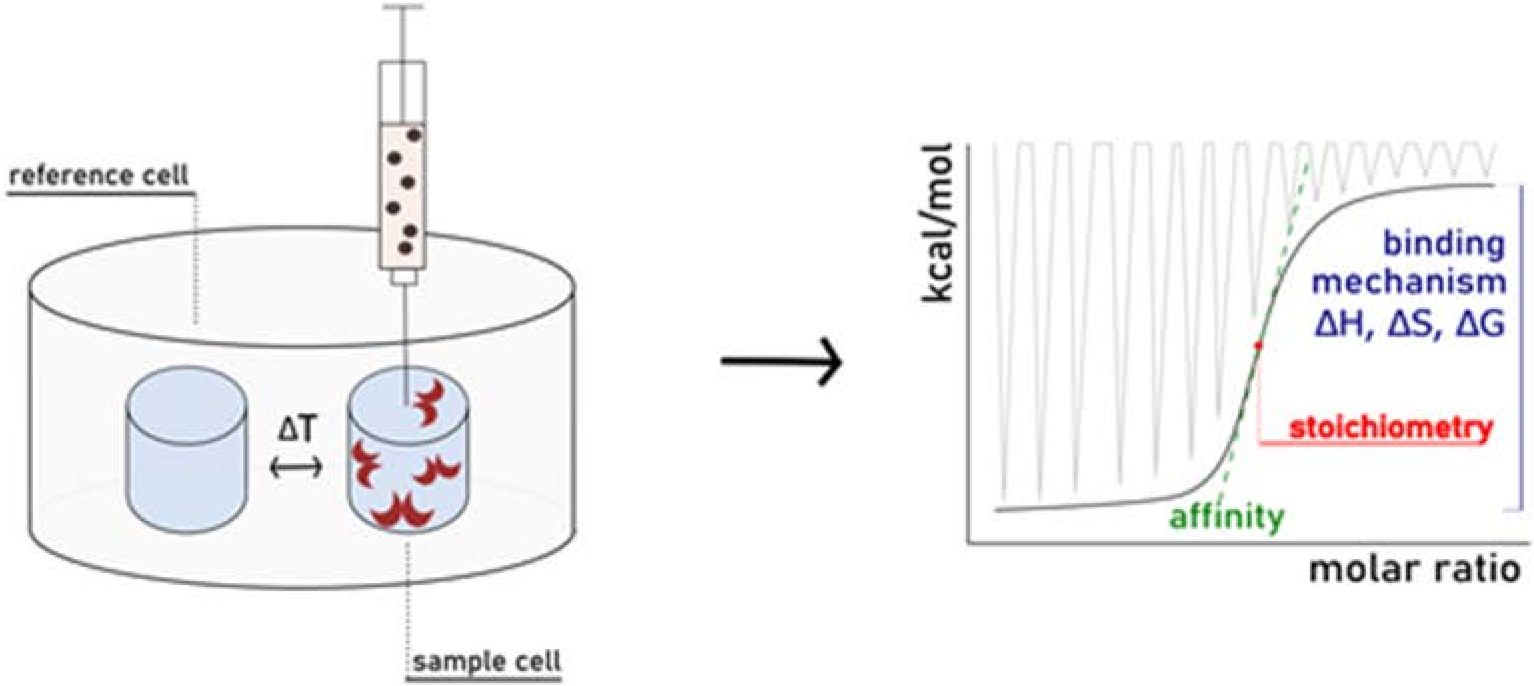
- Calorimeters play a crucial role in understanding thermodynamics. They allow scientists to:
  - Determine the heat energy involved in a reaction.
  - Optimize chemical processes.
  - Study thermochemical properties of substances (e.g., heat of formation, combustion, etc.).

Types of Calorimeter

1. **Isothermal Calorimeter**:
   - **Purpose**: Measures the heat of reaction at a constant temperature.
   - **Application**: Often used in biochemical studies (e.g., enzyme-catalyzed reactions).
   - **Key Feature**: Maintains a stable temperature throughout the experiment.
2. **Constant Pressure Calorimeter**:
   - **Purpose**: Measures the change in enthalpy (heat) of a reaction occurring at constant atmospheric pressure.
   - **Application**: Useful for solution-based reactions.
   - **Key Feature**: Operates under open conditions (constant pressure).
3. **Adiabatic Flame Calorimeter**:
   - **Purpose**: Measures the heat released by a combustion reaction without any heat exchange with the surroundings.
   - **Application**: Used for studying combustion reactions.
   - **Key Feature**: Maintains adiabatic (no heat transfer) conditions.
4. **Bomb Calorimeter**:
   - **Purpose**: Measures the energy released during combustion reactions under constant volume conditions.
   - **Application**: Commonly used for analyzing the calorific value of fuels.
   - **Key Feature**: Reaction occurs within a sealed container (the "bomb").
5. **Differential Scanning Calorimeter(DSC)**:
   - **Purpose**: Analyzes thermal transitions (e.g., melting, crystallization) in materials.
   - **Application**: Widely used in polymer science and material characterization.
   - **Key Feature**: Measures heat flow as a function of temperature.

Isothermal Calorimeter (ITC)

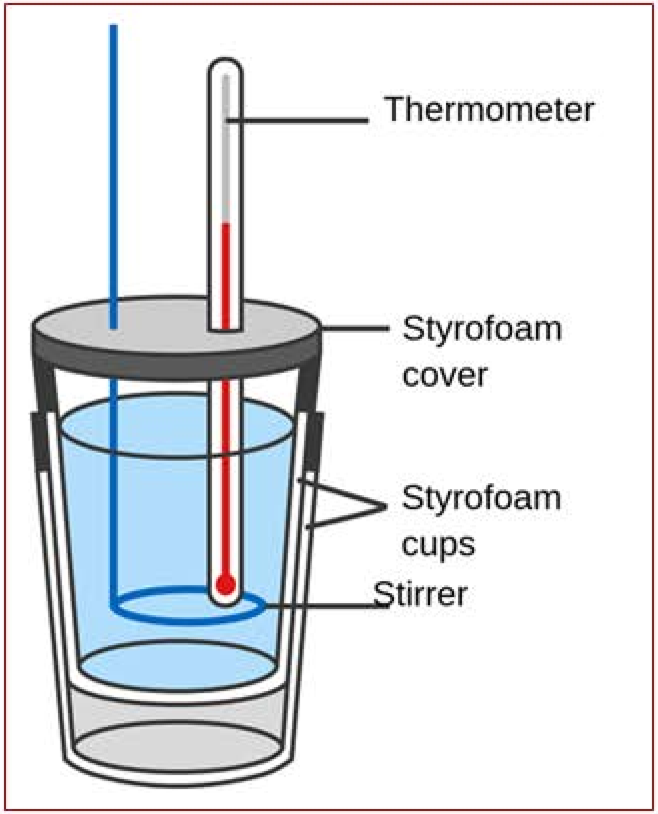
- Consisted of two identical cells—one containing the sample and the other serving as a reference—are enclosed in an adiabatic jacket.
- Sensitive thermopile or thermocouple circuits detect temperature differences between the cells.
- By injecting one molecule into the other cell and measuring enthalpies, we determine binding affinity, stoichiometry, and reaction enthalpy.



An ITC machine and the elaboration of detected signal

Constant Pressure Calorimeter CPC)

1. A **constant-pressure calorimeter** is a device used to measure enthalpy changes (ΔH) in chemical processes at a constant pressure.
2. In this calorimeter, the pressure remains constant throughout the experiment (usually at atmospheric pressure).
3. The heat exchange during a reaction at constant pressure is directly related to the enthalpy change (ΔH) of the system.
4. The calorimeter measures the heat absorbed or released during the reaction.



- Under thermal equilibrium,

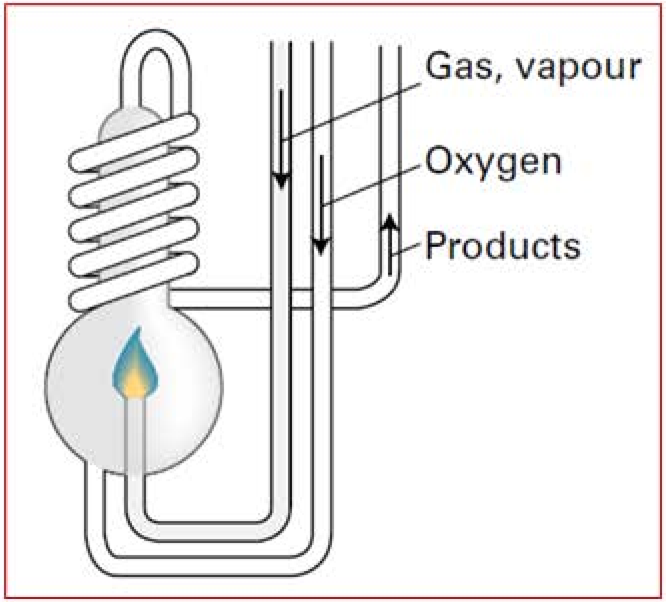
$$-q_{lost} = +q_{gained} + q_{calorimeter}$$

- Relating them to heat capacity

$$-mc_p\Delta T = +mc_p\Delta T + C\Delta T$$

Adiabatic Flame Calorimeter

1. **Construction**:
   - It typically consists of a combustion chamber (where reactions occur) and an insulating jacket to maintain adiabatic conditions.
   - The combustion chamber contains the reactants (usually a fuel and an oxidizer) and a temperature-sensing device.
2. **Principle**:
   - The key principle is adiabaticity—no heat exchange with the surroundings.
   - As the reaction occurs, the heat produced directly increases the temperature within the calorimeter.
   - By measuring this temperature rise, the heat of combustion or reaction is determined.

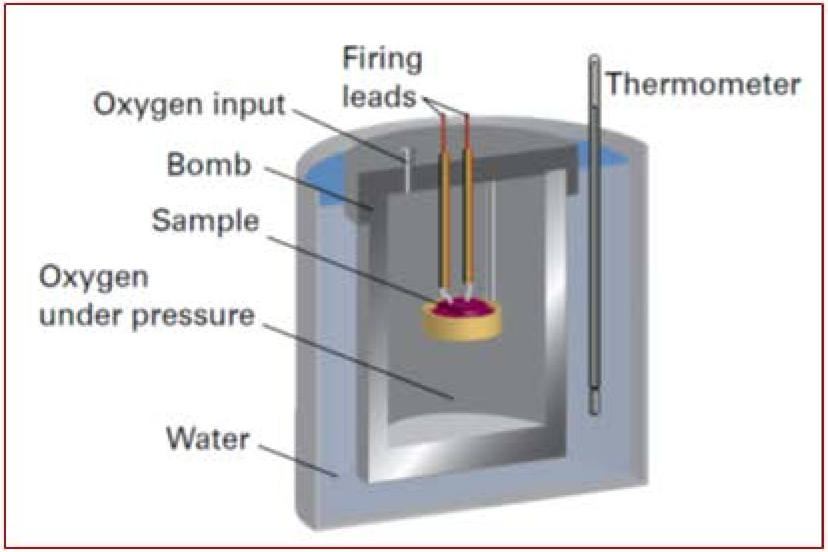


A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath.

Bomb Calorimeter

1. Construction:

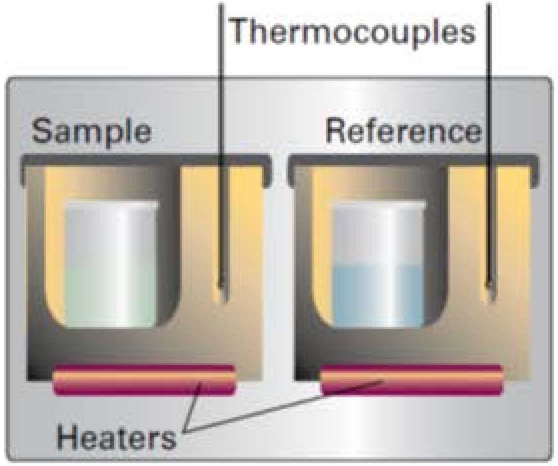
- A bomb calorimeter consists of a strong steel shell with withstand high pressures known as the "bomb."
- It has a base that supports a platinum crucible, which holds the sample to be tested.
- The top of the bomb includes an oxygen supply connection and a valve for releasing the reaction products.



2. Principle:

- The working principle involves the combustion of a substance within the bomb.
- The reaction occurs in an enclosed space under high pressure and constant volume conditions.
- By measuring the heat produced during combustion, we determine the calorific value of the sample.

Differential Scanning Calorimeter



DSC

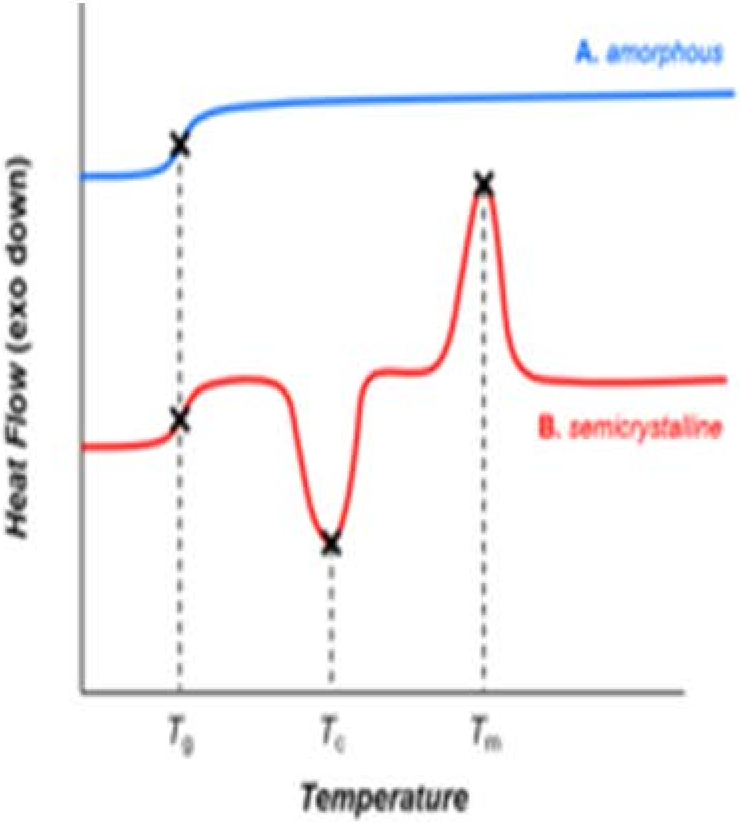
Construction:

1. A DSC typically consists of the following components:
    - **Sample Cell**: Holds the sample being analyzed.
    - **Reference Cell**: Contains a reference material (usually an inert substance).
    - **Heating Elements**: Raise the temperature of the cells.
    - **Temperature Sensors**: Measure the temperature difference between the sample and reference cells.
    - **Thermal Shield**: Minimizes heat exchange with the surroundings.
    - **Heating-Cooling Unit**: Controls the temperature program.
    - **Crystal Sensor**: Detects temperature differences.
    - **Auxiliary Heating Elements**: Ensure uniform heating.
2. The sample and reference cells are sealed within small aluminum pans.

Differential Scanning Calorimeter

Principle:

1. DSC measures the heat flow associated with temperature changes.
2. Two basic principles:
   - **Heat-Flux DSC**: Calculates changes in heat flow by integrating the temperature difference curve (ΔT_{ref}).
   - **Power-Compensated DSC**: Measures the difference in thermal energy applied to the sample and reference per unit of time while varying their temperature.
3. DSC quantitatively analyzes transitions (e.g., glass transition, melting) and chemical reactions (e.g., curing, heat history).



Thermal transitions in **(A)** amorphous and **(B)** semicrystalline polymers.

Enthalpies of chemical change

Standard Enthalpy of Reaction ($\Delta_r H^0$)

The **standard enthalpy of reaction** ($\Delta_r H^\circ$) is the enthalpy change when a reaction occurs under standard conditions with all reactants and products in their standard states.

- It is the heat absorbed or released when the stoichiometric quantities of reactants react to form products as written in a balanced chemical equation.
- The standard enthalpy change for a reaction can be calculated using the enthalpy of formation values of the reactants and products:

$$\Delta_r H^0 = \sum \Delta_f H^0\ (products) - \sum \Delta_f H^0\ (reactants)$$

where, $\Delta_f H^\circ$ is the **standard enthalpy of formation** of each compound

Enthalpies of chemical change

Standard Enthalpy of Reaction ($\Delta_r H^0$)

Example: The standard enthalpy of methane, carbon dioxide and water are -74.8, -393.5 and -285.8 kJ/mol, respectively. Calculate the standard enthalpy of the combustion of methane.

Combustion reaction of methane is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (l)$$

$$\sum \Delta_f H^0\ (products) = (-393.5 - 2 \times 285.8)\ kJ/mol$$

$$= -965.1\ kJ/mol$$

$$\sum \Delta_f H^0\ (reactants) = (-74.8 + 0)\ kJ/mol$$

$$= -74.8\ kJ/mol$$

$$\Delta_r H^0 = -965.1\ kJ/mol - (-74.8)\ kJ/mol$$

$$= -890.3\ kJ/mol$$

Enthalpies of chemical change

Standard Enthalpy of Formation ($\Delta_f H^0$)

The standard enthalpy of formation ($\Delta_f H^\circ$) is the heat change when one mole of a compound is formed from its constituent elements in their standard states.

- By definition, the standard enthalpy of formation of any element in its standard state is zero.
- The enthalpy of formation for compounds, however, can be positive (endothermic) or negative (exothermic).
- The standard enthalpy of formation is the standard enthalpy of reaction ($\Delta_r H^\circ$), which can be calculated as:

$$\Delta_r H^0 = \sum \Delta_f H^0\ (products) - \sum \Delta_f H^0\ (reactants)$$

where, $\Delta_f H^\circ$ is the standard enthalpy of formation of each compound

Enthalpies of chemical change

Standard Enthalpy of Formation ($\Delta_f H^0$)

Example: The standard enthalpies of reactions of propane, carbon and hydrogen with oxygen respectively, are -2220.2 kJ, -393.5 kJ and -571.6 kJ. Calculate the formation enthalpy of propane.

The reactions are:

(1) $C_3H_8(g) + 5O_2(g) \dashrightarrow 3CO_2(g) + 4H_2O\ (l) \quad \Delta H^0 = -2220.2\ kJ$

(2) $C(s) + O_2(g) \dashrightarrow CO_2(g) \quad \Delta H^0 = -393.5\ kJ$

(3) $2H_2(g) + O_2(g) \dashrightarrow 2H_2O(l) \quad \Delta H^0 = -571.6\ kJ$

3x(2) + 2x(3) – (1) results

$3C(s) + 4H_2(g) - C_3H_8(g) \dashrightarrow 0 \quad \Delta H^0 = -103.5\ kJ$

Or $3C(s) + 4H_2(g) \dashrightarrow C_3H_8(g) \quad \Delta H^0 = -103.5\ kJ$

Therefore, the standard formation enthalpy of propane is -103.5 kJ

Enthalpies of chemical change

Standard Enthalpy of Combustion ($\Delta_c H^0$)

The standard enthalpy of combustion ($\Delta_c H^\circ$) is the enthalpy change when one mole of a substance burns completely in oxygen under standard conditions with all reactants and products in their standard states.

- The standard enthalpy of combustion is usually negative because combustion reactions release energy (exothermic).
- The standard enthalpy of combustion is the standard enthalpy of reaction ($\Delta_r H^\circ$), which can be calculated as:

$$\Delta_c H^0 = \sum \Delta_f H^0\ (products) - \sum \Delta_f H^0\ (reactants)$$

where, $\Delta_f H^\circ$ is the standard enthalpy of formation of each compound

Enthalpies of chemical change

Standard Enthalpy of Combustion ($\Delta_c H^0$)

Example: The standard formation enthalpies of $C_3H_8(g)$, $CO_2(g)$ and $H_2O(g)$ respectively, are -103.5 kJ/mol, -393.5 kJ/mol and -285.8 kJ/mol. Calculate the combustion enthalpy of propane.

The reactions are:

(1) $3C(s) + 4H_2(g) \dashrightarrow C_3H_8(g) \quad \Delta H^0 = -103.5\ \text{kJ}$

(2) $C(s) + O_2(g) \dashrightarrow CO_2(g) \quad \Delta H^0 = -393.5\ \text{kJ}$

(3) $H_2(g) + \frac{1}{2} O_2(g) \dashrightarrow H_2O(l) \quad \Delta H^0 = -285.8\ \text{kJ}$

3x(2) + 4x(3) – (1) results

$5O_2(g) \dashrightarrow 3CO_2(g) + 4H_2O(l) - C_3H_8(g) \quad \Delta H^0 = -2220.2\ \text{kJ}$

Or $C_3H_8(g) + 5O_2(g) \dashrightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H^0 = -2220.2\ \text{kJ}$

Thus, the standard combustion enthalpy of propane is -2220.2 kJ

Enthalpies of chemical change

Applications of Combustion Enthalpy ($\Delta_c H^0$)

It is widely used in

- Calorific values of fuels and foods
- Fuel Efficiency and Energy Production
- Design of Combustion Systems
- Environmental Impact and Emissions Control
- Calorimetry and Energy Content Determination
- Energy Storage and Fuels Comparison
- Rocket Propulsion
- Material Safety and Fire Hazards

Calorific Value

The calorific value refers to the amount of energy released when a substance is completely burned or metabolized.

☞ It is typically expressed in units of energy per unit mass or volume, such as kJ/kg (kilojoules per kilogram), MJ/kg (megajoules per kilogram), or kcal/g (kilocalories per gram).

Enthalpies of chemical change

Applications of Combustion Enthalpy ($\Delta_c H^0$)

Calorific Value of Fuel

The calorific value of a fuel is the amount of heat energy released during the complete combustion of a specific quantity of the fuel.

- It is an important parameter for comparing the efficiency of different fuels.

Calorific Value of Food

The calorific value of food is the amount of energy obtained by the body when food is metabolized.

- This energy is used to maintain body functions and perform physical activities.
- It is usually expressed in kilocalories (kcal) or kilojoules (kJ), where 1 kcal = 4.184 kJ.

Enthalpies of chemical change

Applications of Combustion Enthalpy ($\Delta_c H^0$)

Calorific values of some fuels and foods

Fuel	Value/(MJ/g)	Food	Value /(kCal/g)
Coal	24 - 35	**Carbohydrates**	4
Diesel	42 - 46	**Proteins**	4
Petrol (Gasoline)	43 - 47	**Fats**	9
Natural Gas	48 - 52	**Alcohol**	7
Wood	14 - 18	**Sugar**	3.87
Ethanol	26.8	**Butter**	7.17
		Rice (cooked)	1.3
		Chicken breast (cooked)	1.65
		Olive oil	8.84

Enthalpies of chemical change

Applications of Combustion Enthalpy ($\Delta_c H^0$)

Example: The heat of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ are -1409 kJ/mol, -1558.3 kJ/mol and - 285.645 kJ/mol, respectively. Calculate the calorific value of each fuel and compare fuel efficiency.

$$\Delta_c H^0 \text{ for } C_2H_4(g) = \frac{-1409\ kJ}{mol} \times \frac{1\ mol}{28\ g} = -50.32\ kJ/g$$

$$\Delta_c H^0 \text{ for } C_2H_6(g) = \frac{-1558\ kJ}{mol} \times \frac{1\ mol}{30\ g} = -51.93\ kJ/g$$

$$\Delta_c H^0 \text{ for } H_2(g) = \frac{-285.645\ kJ}{mol} \times \frac{1\ mol}{2\ g} = -142.82\ kJ/g$$

Since calorific value of $H_2(g)$ is greater than that of other two fuels, it is highly efficient followed by $C_2H_6(g)$ and $C_2H_4(g)$.

Enthalpies of chemical change

Standard Enthalpy of Hydrogenation ($\Delta_{hyd}H^0$)

The standard enthalpy of hydrogenation refers to the enthalpy change that occurs when one mole of an unsaturated compound reacts with hydrogen to form a saturated compound under standard conditions.

- This process is typically exothermic, meaning energy is released when the double or triple bonds in a compound are converted into single bonds by the addition of hydrogen.
- Hydrogenation is most commonly observed in organic compounds, especially alkenes and alkynes, where double or triple carbon-carbon bonds are reduced to single bonds.
- The hydrogenation enthalpy can be used to evaluate the stability of unsaturated compounds.

Example Reaction: Hydrogenation of Ethene

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

- The double bond between the carbon atoms in ethene is broken, and hydrogen atoms are added to each carbon atom, resulting in a single bond between the carbons.

Enthalpies of chemical change

Standard Enthalpy of Hydrogenation ($\Delta_{hyd}H^0$)

Example: The heat of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ are -1409 kJ, -1558.3 kJ and - 285.8 kJ, respectively. Calculate the heat of hydrogenation of ethylene.

The reactions are:

(1) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H^0 = -1409$ kJ

(2) $C_2H_6(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H^0 = -1558.3$ kJ

(3) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H^0 = -285.8$ kJ

(1) +(3) - (2) results

$C_2H_4(g) + H_2(g) - C_2H_6(g) \longrightarrow 0$ $\Delta H^0 = -136.5$ kJ

Or $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ $\Delta H^0 = -136.5$ kJ

Thus, the standard hydrogenation enthalpy of ethylene is -136.5 kJ

Enthalpies of chemical change

Standard Enthalpy of Neutralization ($\Delta_{nu}H^0$)

The standard enthalpy of neutralization is the change in enthalpy when one mole of water is formed from the reaction between an acid and a base under standard conditions. This reaction is typically exothermic, meaning heat is released.

Standard Enthalpy of Neutralization for Strong Acid and Strong Base

- When a **strong acid** (e.g., HCl) reacts with a **strong base** (e.g., NaOH), they fully dissociate in water:

$$HCl \rightarrow H^+ + Cl^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

- The neutralization reaction is essentially:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O\ (l)$$

- The standard enthalpy of neutralization for this reaction is about **-57.3 kJ/mol**.
- This value is constant for all strong acid-strong base combinations because in each case, the reaction involves only the formation of water from H^+ and OH^- ions.

Enthalpies of chemical change

Standard Enthalpy of Neutralization ($\Delta_{nu}H^0$)

Why Is It Constant for Strong Acids and Strong Bases?

- The enthalpy of neutralization is constant for strong acids and bases because both the acid and the base completely dissociate into their ions.
- The only significant process that occurs during neutralization is the combination of H^+ ions from the acid and OH^- ions from the base to form water, which consistently releases the same amount of energy.

Why Is It Not Constant for Weak Acids or Weak Bases?

- For weak acids or bases, the enthalpy of neutralization is not constant and is often less exothermic than -57.3 kJ/mol.
- This happens because weak acids and bases do not fully dissociate in water.
- Some of the energy released during neutralization is used to first ionize the weak acid or base, and this ionization requires energy (endothermic process).

Enthalpies of chemical change

Bond Enthalpy

Bond enthalpy (or bond dissociation energy) is the amount of energy required to break one mole of a specific bond in a gaseous molecule into its constituent atoms in their gaseous state.

- It is a measure of the strength of a chemical bond.
- The higher the bond enthalpy, the stronger the bond. Bond enthalpy values are usually positive because energy is absorbed to break bonds.

Calculation of Bond Enthalpy

- To calculate the overall bond enthalpy for a reaction, you can use the following formula:

$$\Delta H = \sum \begin{matrix}\text{(bond enthalpies} \\ \text{of bonds broken)}\end{matrix} - \sum \begin{matrix}\text{(bond enthalpies} \\ \text{of bonds formed)}\end{matrix}$$

Enthalpies of chemical change

Bond Enthalpy

Example: The combustion enthalpy of ethane is -1170 kJ/mol. Calculate bond enthalpy of C=O in $CO_2(g)$. Given that the bond enthalpy of C-H, C-C, O=O, O-H are 415, 345, 498 and 464 kJ/mol, respectively.

The combustion reaction of ethane is

$$C_2H_6(g) + \frac{7}{2} O_2(g) \text{---}\rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^0 = -1170 \text{ kJ}$$

The sum of enthalpies of bond broken

= (6 C-H bonds X 415 + 1 C-C X 345 + 7/2 O=O X 498) kJ

= 4578 kJ

Let the bond enthalpy of C=O in CO_2 is b kJ

Now, the sum of enthalpies of bond formed

= (4 C=O bonds X b + 6 O-H X 464) kJ = (4b + 2784) kJ

-1170 kJ = 4578 kJ –(4b+2784) kJ

Or b = 741 kJ/mol

Thus, the bond enthalpy of C=O in CO_2 is 741 kJ/mol.

Enthalpies of chemical change

Bond Enthalpy (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-H	436	C-O	350	N-Br	245	Si-Cl	359
H-C	415	C=O	741	O-O	140	Si-Br	290
H-N	390	C≡O	1080	O=O	498	Si-I	215
H-O	464	C-F	439	O-F	160	P-P	215
H-F	569	C-Si	360	O-Si	370	P-S	230
H-Si	395	C-P	265	O-P	350	P-Cl	330
H-P	320	C-S	260	O-Cl	205	P-Br	270
H-S	340	C-Cl	330	O-I	200	P-I	215
H-Cl	432	C-Br	275	F-F	160	S-S	215
H-Br	370	C-I	240	F-Si	540	S-Br	250
H-I	295	N-N	160	F-P	489	S-Br	215
C-C	345	N=N	418	F-S	285	Cl-Cl	243
C=C	611	N≡N	946	F-Cl	255	Cl-Br	220
C≡C	837	N-O	200	F-Br	235	Cl-I	210
C-N	290	N-F	270	Si-Si	230	Br-Br	190
C=N	615	N-P	210	Si-P	215		
C≡N	891	N-Cl	200	Si-S	225		

Enthalpies of chemical change

Bond Activity

Bond activity refers to the concept of how reactive or unstable certain bonds are in a given chemical context.

- Bonds can have different activities depending on their environment, hybridization, and the presence of other atoms or groups that might stabilize or destabilize them.

Example of Bond Activity:

Stability of Alkenes vs. Alkanes

- Ethane has only C-H and C-C single bonds.
- Ethene has a C=C double bond, making it more reactive than ethane.

Reactivity Comparison

Bond Strength:

- The C=C bond in ethene is weaker than the C-C single bond in ethane. This means ethene is more likely to undergo addition reactions.

Hydrogenation:

- Ethene can easily react with hydrogen (H_2) to become ethane through hydrogenation, showing the bond activity of the C=C bond.

Enthalpies of chemical change

Bond Activity

Example: The combustion enthalpies of ethane and ethene are -1170 kJ/mol and -1055 kJ/mol, respectively. Calculate bond enthalpy of C-C in ethane and C=C in ethene. Given that the bond enthalpy of C-H, C=O, O=O, O-H are 415, 741, 498 and 464 kJ/mol, respectively. Show that ethene is more active than ethane.

The combustion reactions are

$$C_2H_6(g) + \frac{7}{2}\,O_2(g) \dashrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^0 = -1170\text{ kJ}$$

$$C_2H_4(g) + 3\,O_2(g) \dashrightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H^0 = -1055\text{ kJ}$$

For ethane, (6 C-H x 415 + 1 C-C x b + 3.5 O=O x 498) - (4 C=O bonds x 741 + 6 O-H x 464) kJ = -1170 kJ

Or b = 345 kJ/mol

For ethene, (4 C-H x 415 + 1 C=C x d + 3 O=O x 498) - (4 C=O bonds x 741 + 4 O-H x 464) kJ = -1055 kJ

Or d = 611 kJ/mol

Since the bond enthalpy of C=C is for 1 σ and 1 π bond. Their average bond enthalpy is 305.5 kJ, which is lower than C-C bond enthalpy, thus ethene is more active than ethane.

Enthalpies of Physical change

Enthalpy of Solution ($\Delta_{sol}H$)

The standard enthalpy of solution ($\Delta_{sol}H$) refers to the change in enthalpy when one mole of a solute dissolves in a large quantity of solvent (typically water) under standard conditions.

- This process can either release energy (exothermic) or absorb energy (endothermic).
- The enthalpy of solution is a result of two opposing processes:
  - Breaking solute-solute interactions (endothermic).
  - Forming solute-solvent interactions (exothermic).
- The overall enthalpy change depends on the relative magnitudes of these processes.
- Enthalpy of solution are of two types
  - Integral enthalpy of solution
  - Differential enthalpy of solution

Enthalpies of Physical change

Integral enthalpy of solution

The integral enthalpy of solution refers to enthalpy change associated with dissolving a large or specific quantity of solute in a fixed amount of solvent.

- It is typically expressed as the total enthalpy change per mole of solute for the whole process of dissolving a given quantity of solute.
- Example: If 1 mole of NaCl is dissolved in 1 liter of water, integral enthalpy of solution would be +3.9 kJ for the entire process.

Differential enthalpy of solution

The differential enthalpy of solution is enthalpy change associated with dissolving an infinitesimal amount of solute in a very large amount of solvent.

- It measures how the enthalpy changes with respect to an incremental addition of solute, assuming that the solution remains very dilute.
- Example: If only a small amount of NaCl is added to a large volume of water, the differential enthalpy of solution would be close to +3.9 kJ/mol initially.
- However, as more NaCl is added, the interactions between NaCl and water molecules change slightly, and the differential enthalpy might deviate as concentration increases.

Enthalpies of Physical change

Relation between Integral and Differential enthalpy of solution

The integral enthalpy of solution, $\Delta_{sol}H$ depends upon the number moles of solvent and the solute;

$$\Delta_{sol}H = \Delta_{sol}H(n_1, n_2)$$

Differentiating at constant *T* and *p*

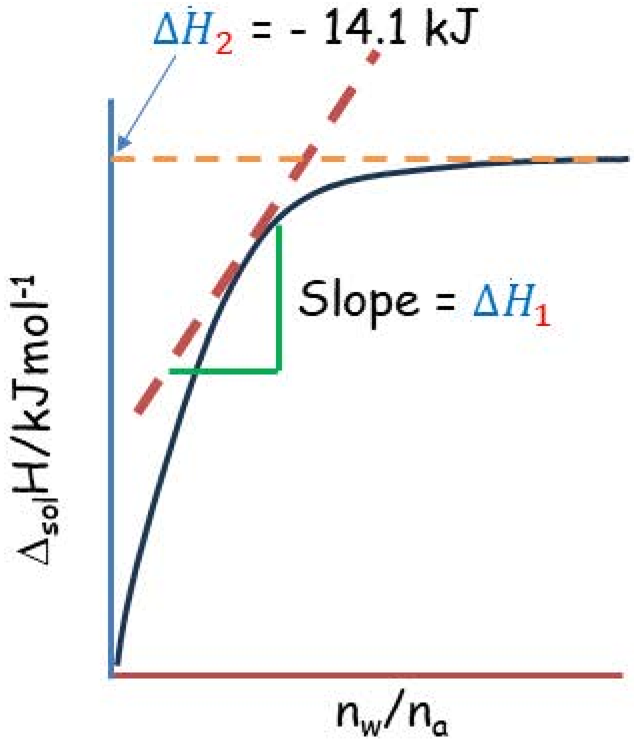
$$d(\Delta_{sol}H) = \left(\frac{\partial \Delta_{sol}H}{\partial n_1}\right)_{T,p} dn_1 + \left(\frac{\partial \Delta_{sol}H}{\partial n_2}\right)_{T,p} dn_2$$

$$d(\Delta_{sol}H) = \Delta\dot{H}_1 dn_1 + \Delta\dot{H}_2 dn_2$$

Integrating at constant composition,

$$\Delta_{sol}H = \Delta\dot{H}_1 n_1 + \Delta\dot{H}_2 n_2$$

$$\frac{\Delta_{sol}H}{n_2} = \Delta\dot{H}_1\left(\frac{n_1}{n_2}\right) + \Delta\dot{H}_2$$



Variation of integral enthalpy of solution for alcohol + water mixtures at 0ºC

Enthalpies of Physical change

Enthalpy of Dilution

The enthalpy of dilution is the change in enthalpy (or heat absorbed/ released) when a solution is diluted by adding more solvent to it.

– This process typically involves interactions between solute and solvent molecules, and the enthalpy change depends on the extent to which these interactions change as the solution becomes more dilute.

Why Does Enthalpy of Dilution Occur?

Ion-Solvent Interactions:

- When a solute like sulfuric acid is diluted, the ions (H^+ and SO_4^{2-}) interact more with water molecules.
- The hydration of these ions (the formation of ion-dipole bonds between ions and water) releases energy.
- As the solution becomes more dilute, more solvent molecules are available to interact with the solute particles, releasing or absorbing energy.

Entropy Effects:

- Dilution also increases the randomness of the system, and the process of mixing solute with solvent affects the overall energy balance.

Enthalpies of Physical change

Enthalpy of Dilution

Dilution Enthalpy of Acids (H_2SO_4, HNO_3, HCl):

- H_2SO_4, HNO_3, and HCl: When these strong acids are diluted, they dissociate into ions (H^+, SO_4^{2-}, NO_3^-, Cl^-) and undergo strong exothermic hydration.
- The energy released from hydration is greater than the energy required for breaking bonds, making the dilution process exothermic.

Dilution Enthalpy of Salts (NH_4NO_3):

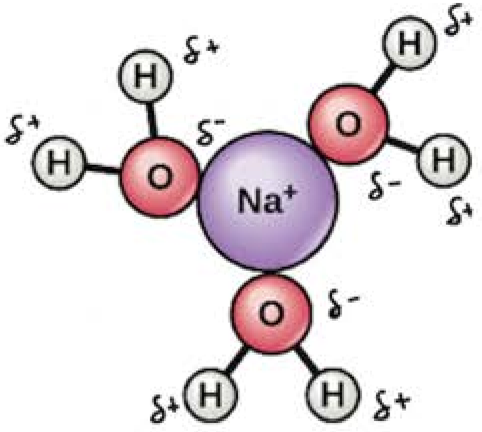
- NH_4NO_3: Dissolving salts like NH_4NO_3 is endothermic because the energy required to break the ionic lattice (NH_4^+ and NO_3^-) is greater than the energy released by hydration.
- This results in an overall absorption of heat, making the process endothermic.

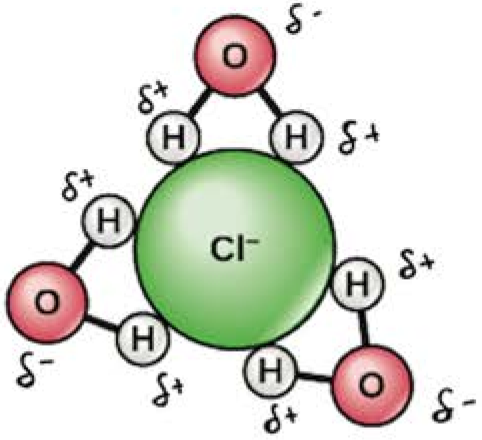
Enthalpies of Physical change

Enthalpy of Hydration

The enthalpy of hydration is the energy change when 1 mole of gaseous ions dissolves in water, forming hydrated ions.

- It is typically an exothermic process because energy is released when the ions interact with water molecules.
- In water, ions become surrounded by water molecules due to the strong ion-dipole interactions that form between the ion and the polar water molecules.
- These interactions release energy, lowering the system's energy.





Enthalpies of Physical change

Factors Affecting Enthalpy of Hydration:

Ionic Charge:

- Higher charge ions (e.g., Al3$^+$) have stronger electrostatic attractions with water molecules, leading to a more negative (more exothermic) enthalpy of hydration.

Ionic Radius:

- Smaller ions (e.g., Li$^+$) have stronger interactions with water molecules because the charge is more concentrated, resulting in a more negative enthalpy of hydration.

Example:

- For sodium ion (Na^+) and chloride ion (Cl^-):

$$Na^+(g) + H_2O \rightarrow Na+(aq) \quad \Delta_{hyd}H = -406 \text{ kJ/mol}$$

$$Cl^-(g) + H_2O \rightarrow Cl^-(aq) \quad \Delta_{hyd}H = -364 \text{ kJ/mol}$$

Enthalpies of Physical change

Enthalpy of Transition

The enthalpy of transition refers to the heat absorbed or released when a substance undergoes a phase transition from one form to another form without undergoing a change in its physical state.

S (rhombic) ---→ S (monoclinic) $\Delta H = 297.1$ J

C (graphite) ---→ C (diamond) $\Delta H = 2008.3$ J

- This enthalpy change is associated with breaking or forming intermolecular forces and depends on the specific nature of the transition.
- The enthalpy change is positive for transitions that require energy input (endothermic), such as melting and vaporization, and negative for exothermic transitions like condensation or freezing.
- The magnitude of enthalpy of transition depends on the strength of intermolecular forces, with stronger forces resulting in higher enthalpy changes.

Enthalpies of Physical change

- **Fusion enthalpy ($\Delta_{fus}H$):** The heat required to convert a solid into a liquid at its melting point.

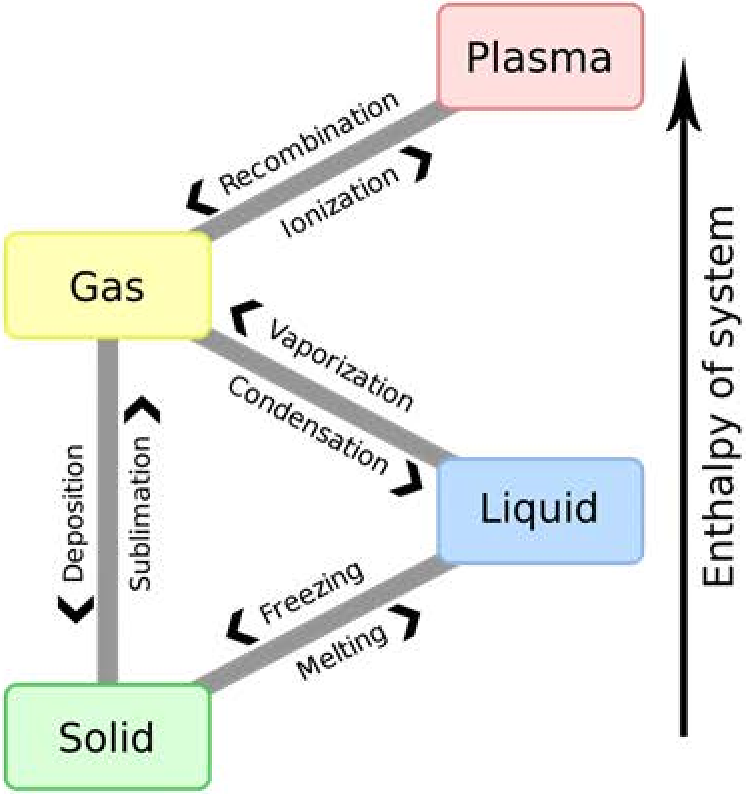
$$\text{Ice } (s) \xrightarrow{0^oC} H_2O\ (l) \quad \Delta H = 6.0\ \text{kJ}$$

- **Vaporization enthalpy ($\Delta_{vap}H$):** The heat required to convert a liquid into a gas at its boiling point.

$$H_2O\ (l) \xrightarrow{100^oC} H_2O\ (v) \quad \Delta H = 40.7\ \text{kJ}$$

- **Sublimation enthalpy ($\Delta_{sub}H$):** The heat required to convert a solid directly into a gas.

$I_2\ (s)$ ---→ $I_2\ (v)$ $\Delta H = 62.0\ \text{kJ}$



Enthalpies of Physical change

Crystal or Lattice Enthalpy

Lattice Enthalpy (or lattice energy) is the amount of energy released when one mole of an ionic crystalline compound forms from its constituent gaseous ions.

It can also be defined as the energy required to break the ionic bonds and completely separate one mole of a solid ionic compound into its gaseous ions.

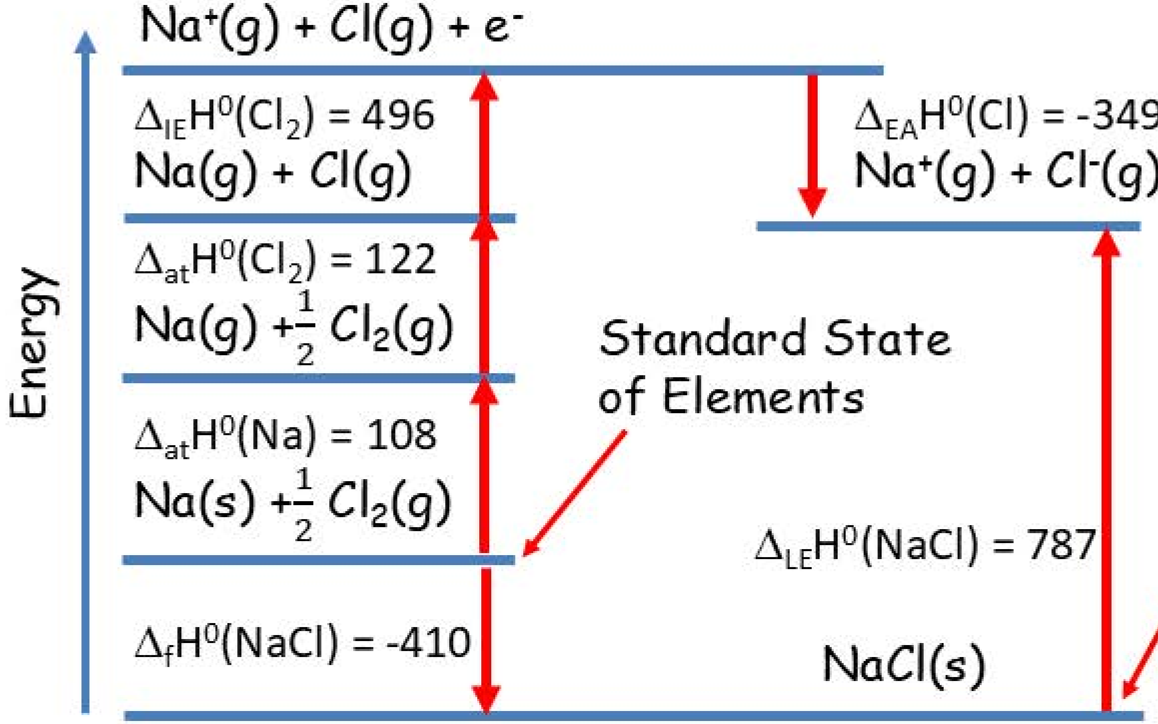
- For ionic compounds, lattice enthalpy is a measure of the strength of the electrostatic forces between the cations and anions in the crystal lattice.
- Exothermic process: When the ions combine to form the ionic lattice, energy is released, and the lattice enthalpy is negative.
- Endothermic process: When the lattice breaks into individual ions (i.e., to dissociate the compound), energy is required, and the lattice enthalpy is positive.
- Lattice enthalpy plays an essential role in determining the stability and solubility of ionic compounds, where higher lattice enthalpy usually corresponds to stronger ionic bonds, leading to less solubility and higher melting points.

Enthalpies of Physical change

Born-Haber Cycle for Calculating Lattice Enthalpy

- The Born-Haber cycle is a thermodynamic cycle that allows the calculation of the lattice enthalpy of an ionic solid using Hess's law.
- **Steps in the Born-Haber Cycle**
  - **Formation of gaseous atoms**
    - Sublimation energy
    - Bond dissociation enthalpy
  - Ionization of gaseous atoms
  - Electron gain by gaseous atoms
  - Formation of the ionic lattice

Born-Haber Cycle for Sodium Chloride (NaCl)



Energy

$Na^+(g) + Cl(g) + e^-$

$\Delta_{IE}H^0(Cl_2) = 496$

$Na(g) + Cl(g)$

$\Delta_{at}H^0(Cl_2) = 122$

$Na(g) + \frac{1}{2} Cl_2(g)$

$\Delta_{at}H^0(Na) = 108$

$Na(s) + \frac{1}{2} Cl_2(g)$

$\Delta_f H^0(NaCl) = -410$

$\Delta_{EA}H^0(Cl) = -349$

$Na^+(g) + Cl^-(g)$

Standard State of Elements

$\Delta_{LE}H^0(NaCl) = 787$

NaCl(s)

Figure: Born-Haber Cycle for Sodium Chloride (NaCl)

Crystal States