

- Chemical Thermodynamics
- Enthalpy Change
- Spontaneity
- Quick Reference Table
- Common Mistakes and Misconceptions
- Glossary

Chemical Thermodynamics

Introduction to Thermodynamics

Chemical thermodynamics is the branch of chemistry that deals with the quantitative study of energy changes, especially the interconversion of various forms of energy and the conversion of energy to work and vice versa during chemical and physical processes.

System and Surroundings

A **system** is the part of the universe selected for observation, while the **surroundings** include everything else outside the system. The **boundary** separates the system from its surroundings.

Types of Systems

- **Open system:** Can exchange both matter and energy with surroundings.
- **Closed system:** Can exchange only energy, not matter, with surroundings.
- **Isolated system:** Cannot exchange matter or energy with surroundings.

State and Properties of a System

The **state of a system** is defined by its macroscopic properties such as pressure, volume, and temperature. Properties are classified as:

- **State functions:** Depend only on the initial and final states (e.g., pressure, volume, temperature, enthalpy, internal energy, Gibbs free energy, entropy).
- **Path functions:** Depend on the path taken during the change (e.g., heat and work).

Thermodynamic Processes

- **Isothermal process:** Occurs at constant temperature.
- **Isobaric process:** Occurs at constant pressure.
- **Isochoric process:** Occurs at constant volume.
- **Adiabatic process:** No heat exchange with surroundings.
- **Reversible process:** Can be reversed by an infinitesimal change in conditions.
- **Cyclic process:** System returns to its initial state after the process.

Heat, Work, and Energy

Heat (q) is energy transferred due to temperature difference. It is positive when absorbed by the system and negative when released.

Work (w) is organized energy transfer. Work done on the system is positive; work done by the system is negative.

Internal energy (U) is the total energy (kinetic + potential) of the system.

Enthalpy (H) is the sum of internal energy and the product of pressure and volume: $H = U + pV$. It represents the heat content at constant pressure.

First Law of Thermodynamics

The law states that energy can neither be created nor destroyed, only transformed. Mathematically:

$$\Delta U = q + w$$

where ΔU is the change in internal energy, q is heat exchanged, and w is work done on the system.

Relation Between Enthalpy and Internal Energy

For gaseous reactions:

$$\Delta H = \Delta U + \Delta n_g RT$$

where Δn_g is the change in moles of gas, R is the gas constant, and T is temperature in Kelvin.

Heat Capacity and Specific Heat

Heat capacity (C) is the heat required to raise the temperature of a system by 1°C.

Specific heat capacity (C_s) is the heat required to raise the temperature of 1 gram of a substance by 1°C.

Heat absorbed or released is given by:

$$q = mC_s\Delta T$$

Calorimetry

Calorimetry is an experimental technique to measure heat changes during chemical or physical processes using a device called a calorimeter.

Solved Examples

Example 1: Calculating Work Done in Isothermal Expansion

An ideal gas expands isothermally and reversibly from volume 2 L to 5 L at 300 K. Calculate the work done by the gas. ($R = 8.314 \text{ J/mol}\cdot\text{K}$, $n = 1 \text{ mol}$)

Solution:

Work done in isothermal reversible expansion is:

$$W_{rev} = -nRT \ln \frac{V_f}{V_i}$$

Substituting values:

$$W_{rev} = -1 \times 8.314 \times 300 \times \ln \frac{5}{2}$$

$$= -2494.2 \times \ln 2.5$$

$$= -2494.2 \times 0.9163 = -2284.5 \text{ J}$$

Work done by the gas is -2284.5 J (work done by the system is negative).

Example 2: Calculating Enthalpy Change

Calculate the enthalpy change for the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ given that $\Delta U = -10 \text{ kJ}$ and $\Delta n_g = 0$ at 298 K.

Solution:

Since $\Delta n_g = 0$,

$$\Delta H = \Delta U + \Delta n_g RT = -10 + 0 = -10 \text{ kJ}$$

Therefore, enthalpy change is -10 kJ.

Practice Set

- **Level 1 (Easy):** Define an isolated system and give an example.
- **Level 2 (Moderate):** Explain the difference between state functions and path functions with examples.
- **Level 3 (Challenging):** Calculate the work done when 2 moles of an ideal gas expand isothermally and reversibly at 350 K from 3 L to 10 L. ($R = 8.314 \text{ J/mol}\cdot\text{K}$)

Answer Key

- **Level 1:** An isolated system cannot exchange matter or energy with its surroundings. Example: A perfectly insulated thermos flask.

- **Level 2:** State functions depend only on the initial and final states (e.g., pressure, volume, temperature), while path functions depend on the path taken (e.g., heat, work).
- **Level 3:** Work done, $W = -nRT \ln \frac{V_f}{V_i} = -2 \times 8.314 \times 350 \times \ln \frac{10}{3} \approx -2 \times 8.314 \times 350 \times 1.204 = -7009 \text{ J}$.

Enthalpy Change

Definition and Types

Enthalpy of reaction ($\Delta_r H$) is the enthalpy change when reactants convert to products as per stoichiometric coefficients.

Enthalpy of neutralisation ($\Delta_n H$) is the enthalpy change when 1 gram equivalent of acid reacts with 1 gram equivalent of base.

Standard enthalpy of fusion ($\Delta_{fusion} H^\circ$) is the enthalpy change when 1 mole of solid melts at its melting point.

Standard enthalpy of vaporisation ($\Delta_{vap} H^\circ$) is the enthalpy change when 1 mole of liquid vaporizes at its boiling point under standard pressure.

Standard enthalpy of sublimation ($\Delta_{sub} H^\circ$) is the enthalpy change when 1 mole of solid sublimates at constant temperature and pressure.

Standard enthalpy of formation ($\Delta_f H^\circ$) is the enthalpy change when 1 mole of a compound forms from its elements in their standard states.

Hess's Law

The enthalpy change of a reaction is the same whether it occurs in one step or multiple steps. The total enthalpy change is the sum of enthalpy changes of individual steps.

Applications include determining enthalpies of formation, slow reactions, allotropic transformations, bond energies, and resonance energy.

Other Important Enthalpy Terms

- **Standard enthalpy of combustion ($\Delta_c H^\circ$):** Enthalpy change when 1 mole of substance combusts completely in oxygen. It is always negative.
- **Enthalpy of atomisation ($\Delta_a H^\circ$):** Enthalpy change when 1 mole of substance dissociates into gaseous atoms.

- **Bond enthalpy** ($\Delta_{bond}H^\circ$): Average energy required to break 1 mole of a particular bond in gaseous molecules.
- **Enthalpy of solution** ($\Delta_{sol}H^\circ$): Enthalpy change when 1 mole of solute dissolves in a specified amount of solvent.
- **Enthalpy of hydration** ($\Delta_{hyd}H^\circ$): Enthalpy change when 1 mole of anhydrous salt combines with water molecules.
- **Lattice enthalpy** ($\Delta_{latt}H^\circ$): Enthalpy change when 1 mole of ionic compound dissociates into gaseous ions.

Solved Examples

Example 1: Calculating Enthalpy of Reaction

Given the enthalpies of formation: $\Delta_f H^\circ(CO_2) = -393.5 \text{ kJ/mol}$, $\Delta_f H^\circ(CH_4) = -74.8 \text{ kJ/mol}$, calculate the enthalpy change for combustion of methane:



Solution:

Using Hess's law:

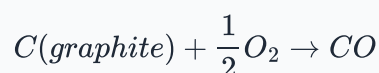
$$\Delta H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

Assuming $\Delta_f H^\circ(H_2O) = -285.8 \text{ kJ/mol}$,

$$\Delta H^\circ = [-393.5 + 2(-285.8)] - [-74.8 + 0] = (-393.5 - 571.6) + 74.8 = -890.3 \text{ kJ}$$

Example 2: Using Hess's Law

Calculate the enthalpy change for the reaction:

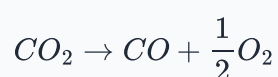


Given:

- $C(\text{graphite}) + O_2 \rightarrow CO_2, \Delta H = -393.5 \text{ kJ}$
- $CO + \frac{1}{2}O_2 \rightarrow CO_2, \Delta H = -283.0 \text{ kJ}$

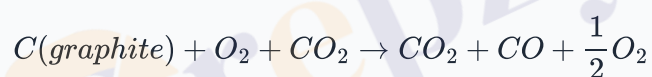
Solution:

Reverse the second reaction:

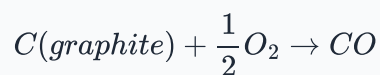


, $\Delta H = +283.0 \text{ kJ}$

Add to first reaction:



Cancel CO_2 and O_2 terms:



Enthalpy change:

$$-393.5 + 283.0 = -110.5 \text{ kJ}$$

Practice Set

- **Level 1 (Easy):** Define enthalpy of fusion and give its unit.
- **Level 2 (Moderate):** State Hess's law and mention two applications.
- **Level 3 (Challenging):** Calculate the enthalpy change for the reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ given $\Delta H_f^\circ(NH_3) = -46 \text{ kJ/mol}$, and elements in standard state have zero enthalpy.

Answer Key

- **Level 1:** Enthalpy of fusion is the enthalpy change when 1 mole of solid melts at its melting point. Unit: kJ/mol.
- **Level 2:** Hess's law states that the total enthalpy change for a reaction is the same whether it occurs in one step or multiple steps. Applications: determining enthalpies of formation and bond energies.
- **Level 3:** $\Delta H = 2 \times (-46) - 0 = -92$ kJ.

Spontaneity

Spontaneous Processes

A spontaneous process occurs naturally in a given direction without external influence once initiated.

Entropy (S)

Entropy is a measure of disorder or randomness in an isolated system. For a reversible process at constant temperature:

$$\Delta S = \frac{q_{rev}}{T}$$

For a spontaneous process, the total entropy change of the universe is positive:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Second Law of Thermodynamics

The entropy of the universe always increases in a spontaneous process.

Third Law of Thermodynamics

At absolute zero (0 K), the entropy of a perfect crystalline substance is zero.

Gibbs Free Energy (G)

Gibbs free energy is the maximum useful work obtainable from a process at constant temperature and pressure. It is given by:

$$\Delta G = \Delta H - T\Delta S$$

Criteria for spontaneity:

- $\Delta G < 0$: Spontaneous process
- $\Delta G > 0$: Non-spontaneous process
- $\Delta G = 0$: Equilibrium

Relation with equilibrium constant (K):

$$\Delta G^\circ = -RT \ln K = -2.303RT \log K$$

Solved Examples

Example 1: Calculating Entropy Change

Calculate the entropy change when 100 J of heat is absorbed reversibly at 400 K.

Solution:

$$\Delta S = \frac{q_{rev}}{T} = \frac{100}{400} = 0.25 \text{ J/K}$$

Example 2: Gibbs Free Energy and Spontaneity

Given $\Delta H = -50 \text{ kJ}$, $\Delta S = -100 \text{ J/K}$, calculate ΔG at 300 K and state if the process is spontaneous.

Solution:

Convert entropy to kJ/k: $-100 \text{ J/K} = -0.1 \text{ kJ/K}$

$$\Delta G = \Delta H - T\Delta S = -50 - 300 \times (-0.1) = -50 + 30 = -20 \text{ kJ}$$

Since $\Delta G < 0$, the process is spontaneous.

Practice Set

- **Level 1 (Easy):** Define entropy and state its unit.
- **Level 2 (Moderate):** State the second law of thermodynamics.
- **Level 3 (Challenging):** Calculate the Gibbs free energy change for a reaction with $\Delta H = 40 \text{ kJ}$ and $\Delta S = 150 \text{ J/K}$ at 350 K. Is the reaction spontaneous?

Answer Key

- **Level 1:** Entropy is a measure of disorder or randomness. Unit: J/K.
- **Level 2:** The entropy of the universe always increases in a spontaneous process.
- **Level 3:** Convert entropy: $150 \text{ J/K} = 0.15 \text{ kJ/K}$.
 $\Delta G = 40 - 350 \times 0.15 = 40 - 52.5 = -12.5 \text{ kJ}$.
Since $\Delta G < 0$, the reaction is spontaneous.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary
