

Introduction to Chemical Thermodynamics

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Fundamental concepts, key laws, and practical applications

1. What Is Thermodynamics?

- Definition:** The branch of physical chemistry that studies the relationship between energy, work, and heat in chemical systems.
- Scope:** Predicts the direction of chemical reactions, equilibrium positions, and the amount of energy that can be harnessed or released.

2. Core Concepts

Concept	Symbol	Units	Typical Use
System	–	–	Portion of the universe under study (e.g., a reaction flask).
Surroundings	–	–	Everything external to the system.
State Function	–	–	Property that depends only on the current state (e.g., internal energy, enthalpy, entropy).
Path Function	–	–	Property that depends on the process path (e.g., heat q , work w).
Enthalpy (H)	(H)	J (or kJ)	Heat content at constant pressure.
Entropy (S)	(S)	J/K ¹	Measure of disorder or the number of accessible microstates.
Gibbs Free Energy (G)	(G)	J (or kJ)	Predicts spontaneity at constant T and P .
Internal Energy (U)	(U)	J	Total microscopic energy of a system.

3. The Four Laws of Thermodynamics (Chemistry-focused)

Law	Statement (Chemistry Emphasis)	Practical Implication

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Zeroth	If two systems are each in thermal equilibrium with a third, they are in equilibrium with each other.	Enables the definition of temperature.
First (Energy Conservation)	$\Delta U = q + w$. Energy cannot be created or destroyed; it only changes form.	Balances heat and work in reactions; basis for calorimetry.
Second	For any spontaneous process, $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$.	Predicts directionality; introduces entropy.
Third	As $T \rightarrow 0\text{K}$, the entropy of a perfect crystal approaches zero.	Provides an absolute entropy reference point.

4. Key Equations

1. First Law (Differential Form)

$$[dU = \delta q + \delta w]$$

2. Enthalpy Change at Constant Pressure

$$[\Delta H = \Delta U + P\Delta V]$$

3. Entropy Change (Reversible Process)

$$[\Delta S = \int_{i}^f \frac{\delta q_{\text{rev}}}{T}]$$

4. Gibbs Free Energy

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

○ Spontaneity criterion:

- $\Delta G < 0$? spontaneous
- $\Delta G = 0$? equilibrium
- $\Delta G > 0$? non-spontaneous

5. Relationship to Equilibrium Constant

$$[\Delta G^\circ = -RT \ln K]$$

$$(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, (K \text{ is dimensionless}))$$