FREE NOTES · NCERT + JEE/NEET LEVEL

Thermodynamics

System and surroundings, state functions, internal energy, work and heat, first law, enthalpy, ΔH and ΔU, heat capacity, calorimetry, enthalpies of reaction, Hess's law, Born-Haber idea, entropy, Gibbs energy and spontaneity, and equilibrium.

01 Basic terms
02 First law of thermodynamics
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01 Basic terms

- **System** = part we study; **surroundings** = everything else.
- **Open** (matter + energy exchange), **closed** (energy only), **isolated** (neither; e.g. ideal thermos).
- **State functions** depend only on initial and final states: U, H, S, G, p, V, T. **Path functions**: q, w.
- **Extensive** (depend on amount: mass, V, U, H, heat capacity) vs **intensive** (don't: T, p, density, molar heat capacity).
- Processes: isothermal (T const), adiabatic (q = 0), isobaric (p const), isochoric (V const), reversible (infinitely slow), irreversible.

02 First law of thermodynamics

$$\Delta U = q + w$$

Energy of an isolated system is constant. **IUPAC sign:** q positive when heat is absorbed by the system; w positive when work is done **on** the system.

- Isolated: ΔU = 0. Adiabatic: ΔU = w. Isochoric (no work): ΔU = q_V.
- For an ideal gas, U depends only on T ⇒ isothermal ΔU = 0 ⇒ q = -w.

03 Work of expansion

Process	Work done on the gas
Against constant external pressure (irreversible)	$w = -p_{ext}\,\Delta V$
Free expansion (into vacuum)	$w = 0$
Isothermal reversible	$w = -2.303\ nRT\log(V_2/V_1) = -2.303\ nRT\log(p_1/p_2)$

Expansion ⇒ w negative (system does work). Reversible expansion gives the maximum work.

04 Enthalpy; ΔH vs ΔU

$H = U + pV$, $\Delta H = q_p$ (heat at constant pressure)

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

Δn_g = moles of gaseous products − gaseous reactants. $\Delta n_g = 0 \Rightarrow \Delta H = \Delta U$ ($H_2 + Cl_2 \rightarrow 2HCl$).

$\Delta H < 0 \Rightarrow$ **exothermic**; $\Delta H > 0 \Rightarrow$ **endothermic**.

05 Heat capacity & calorimetry

- $q = C\,\Delta T = m\,c\,\Delta T$ (c = specific heat).
- For an ideal gas: $\mathbf{C_p - C_v = R}$.
- **Bomb calorimeter** (constant volume) measures ΔU; **coffee-cup calorimeter** (constant pressure) measures ΔH.

06 Types of enthalpy

Enthalpy of	Meaning
Formation $\Delta_f H°$	1 mol compound from elements in standard states ($\Delta_f H°$ of elements = 0)
Combustion $\Delta_c H°$	1 mol burns completely in O_2 (always negative)
Atomisation	1 mol of bonds/substance broken into gaseous atoms
Bond enthalpy	Break 1 mol of a bond in gas phase
Fusion / vaporisation / sublimation	Phase changes; $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$
Solution, lattice	Dissolving 1 mol; forming/breaking 1 mol ionic solid
Neutralisation	Strong acid + strong base ≈ −57.1 kJ/mol (less for weak)

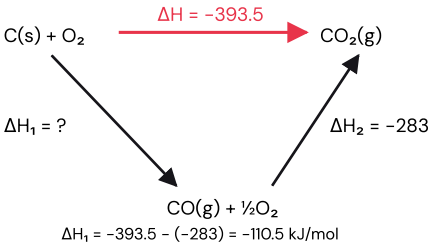
$$\Delta_r H° = \Sigma\,\Delta_f H°(\text{products}) - \Sigma\,\Delta_f H°(\text{reactants})$$

$$\Delta_r H° = \Sigma\,\text{bond enthalpies (reactants)} - \Sigma\,\text{bond enthalpies (products)}$$

07 Hess's law of constant heat summation

Since H is a state function, the total enthalpy change is the same whether a reaction happens in one step or many. We can add and subtract equations (and their ΔH) like algebra.

Born–Haber cycle uses Hess's law to find lattice enthalpy: sublimation + ionisation + dissociation + electron gain + lattice = $\Delta_f H$.



Finding $\Delta_f H$ of CO with Hess's law

08 Entropy, Gibbs energy & spontaneity

- **Entropy S** = measure of disorder/randomness. Gas > liquid > solid. $\Delta S = q_{rev}/T$. Phase change: $\Delta S = \Delta H/T$.
- **Second law:** for a spontaneous process $\Delta S_{total} > 0$. **Third law:** S of a perfect crystal at 0 K is zero.

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

$\Delta G < 0$ spontaneous; $\Delta G = 0$ equilibrium; $\Delta G > 0$ non-spontaneous. $\Delta G^\circ = -RT \ln K = -2.303\ RT \log K$. Also $\Delta G = W_{useful}$.

ΔH	ΔS	Spontaneous?
−	+	Always
+	−	Never
−	−	At low T
+	+	At high T (T > ΔH/ΔS)

09 JEE Extra + Tricks

JEE LEVEL

- Sign convention (IUPAC): $\Delta U = q + w$; work done **on** system positive. Free expansion: $w = 0$; ideal gas isothermal: $\Delta U = \Delta H = 0$.
- $\Delta H = \Delta U + \Delta n_g RT$ (Δn_g = gaseous moles of products − reactants).
- Spontaneity: $\Delta G = \Delta H - T\Delta S$. $\Delta H -$, $\Delta S +$ ⇒ always; $\Delta H +$, $\Delta S -$ ⇒ never; others depend on T ($T = \Delta H/\Delta S$ is the switch temperature).
- $\Delta G^\circ = -RT \ln K = -2.303RT \log K$; $\Delta G^\circ = -nFE^\circ$.
- Bond enthalpy method: $\Delta H = \Sigma$(bonds broken) − Σ(bonds formed).
- Extensive: U, H, S, G, V, mass. Intensive: T, P, density, molar properties.

10 Solved numericals

Q1. A gas absorbs 701 J of heat and does 394 J of work. ΔU?

q = +701, w = −394 ⇒ ΔU = **+307 J**.

Q2. For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, ΔU = −87.8 kJ at 298 K. ΔH?

$\Delta n_g = 2 - 4 = -2 \Rightarrow \Delta H = -87.8 + (-2)(8.314 \times 10^{-3})(298) =$ **−92.8 kJ**.

Q3. 2 mol ideal gas expands isothermally and reversibly at 300 K from 10 L to 20 L. Work?

$w = -2.303 \times 2 \times 8.314 \times 300 \times \log 2 =$ **−3458 J**.

Q4. ΔH = 30 kJ/mol, ΔS = 100 J/(K mol). Above what T is it spontaneous?

$T > \Delta H/\Delta S = 30000/100 =$ **300 K**.

11 Mistakes & practice

- Using the old sign convention ($w = +p\Delta V$). NCERT uses $w = -p_{ext}\Delta V$.
- Counting liquids/solids in Δn_g.
- Mixing kJ (ΔH) and J (ΔS) in $\Delta G = \Delta H - T\Delta S$.
- Saying every exothermic reaction is spontaneous.

1. Is heat a state function?
2. ΔU for isothermal expansion of an ideal gas?
3. $\Delta_f H°$ of $O_2(g)$?
4. Sign of ΔS when ice melts?
5. Relation between ΔG° and K?

ANSWERS

1) No (path function) · 2) 0 · 3) 0 · 4) Positive · 5) $\Delta G° = -2.303\ RT \log K$

12 Quick revision: 5 minutes before the exam

FIRST LAW

- $\Delta U = q + w$.
- $w = -p_{ext}\Delta V$.
- Reversible: $-2.303\ nRT \log(V_2/V_1)$.

ENTHALPY

- $\Delta H = \Delta U + \Delta n_g RT$.
- $C_p - C_v = R$.
- Hess: add equations.

ENTROPY

- Gas > liquid > solid.
- $\Delta S = q_{rev}/T$.
- S = 0 for perfect crystal at 0 K.

GIBBS

- $\Delta G = \Delta H - T\Delta S$.
- $\Delta G < 0$ spontaneous.
- $\Delta G^\circ = -2.303RT \log K$.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.