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CUET · CHEMISTRY · CLASS XI · CODE 306

Thermodynamics

CUET unit: Thermodynamics

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Establishes thermodynamics as the study of energy transformations in macroscopic systems at equilibrium — based only on initial and final states, not on rate or mechanism.
- Builds the toolkit: system/surroundings, state functions (U, H, S, G), first law ($\Delta U = q + w$), enthalpy ($H = U + pV$), heat capacities ($C_p - C_v = R$), Hess's law, and entropy-based criteria for spontaneity.
- Closes with the third law ($S = 0$ for a pure crystal at 0 K) and the link $\Delta G^\circ = -RT \ln K$ connecting thermodynamics to equilibrium.
- CUET tests this chapter heavily for sign conventions, $\Delta H \leftrightarrow \Delta U$ conversion via $\Delta n_g RT$, Hess-cycle arithmetic, and spontaneity prediction from $\Delta H/\Delta S/T$.

📖 Detailed Notes

2.1 Core concepts

- **System and surroundings.** System = part of universe under observation; surroundings = remaining universe that can interact with it; the wall between them is the boundary, real or imaginary (NCERT §5.1.1, p. 137).
- **Types of system.** Open = exchanges both matter and energy (open beaker); closed = exchanges only energy (sealed copper vessel); isolated = exchanges neither (thermos flask) (NCERT §5.1.2, p. 137–138).
- **State of a system.** Specified by state variables p, V, T, n; once a minimum set is fixed, all other macroscopic properties follow. State functions depend only on present state, not on path taken (NCERT §5.1.3, p. 138). The minimum set is independent of the choice of path used to reach that state.
- **Internal energy U as state function.** Sum of all forms of energy (chemical, mechanical, electrical, kinetic, potential, vibrational, rotational) of the system; can change by heat flow, work, or matter transfer. Joule's adiabatic experiments (1840–50) showed w_{ad} is path-independent, so $\Delta U = w_{ad}$ in an adiabatic process — a numerically equal amount of work whether performed mechanically, electrically or by friction (NCERT §5.1.4, p. 138–139).
- **Sign convention (IUPAC).** q positive when heat is absorbed by the system; w positive when work is done on the system; both negative when energy leaves the

system. $\Delta U > 0$ if the system gains energy and < 0 if it loses energy (NCERT §5.1.4, p. 139).

- **First law of thermodynamics.** $\Delta U = q + w$; energy of an isolated system is constant ($q = 0$, $w = 0 \Rightarrow \Delta U = 0$). Energy can neither be created nor destroyed, only converted from one form to another (NCERT §5.1.4(c), p. 140, Eq. 5.1).
- **Pressure–volume work.** $w = -p_{ext} \Delta V$ for a single-step (irreversible) compression; for reversible isothermal expansion of an ideal gas, $w_{rev} = -2.303\, nRT \log(V_2/V_1)$. The reversible work is the maximum work the gas can deliver because p_{ext} is set infinitesimally lower than p_{in} at every step (NCERT §5.2.1, p. 140–142, Eq. 5.2 & 5.5).
- **Free expansion.** $p_{ext} = 0$, so $w = 0$; for an isothermal ideal-gas free expansion $\Delta U = 0$ (no temperature change) and $q = 0$ too (NCERT §5.2.1, p. 142).
- **Special cases.** Constant volume: $\Delta U = q_V$ (because $w = 0$). Adiabatic: $q = 0$, so $\Delta U = w_{ad}$. Constant pressure: $\Delta H = q_p$ (NCERT §5.2.1, p. 142).
- **Enthalpy.** $H = U + pV$ is a state function; at constant pressure $\Delta H = q_p$ = heat absorbed. $\Delta H = \Delta U + \Delta n_g RT$ relates enthalpy and internal energy for gas-phase reactions; Δn_g = moles of gaseous products − moles of gaseous reactants (NCERT §5.2.2(a), p. 143, Eq. 5.7 & 5.10). For solids/liquids, $\Delta H \approx \Delta U$ because $p\Delta V$ is negligible.
- **Extensive vs intensive.** Extensive properties (mass, V, U, H, S, heat capacity) depend on amount; intensive properties (T, p, density, molar quantities, viscosity, refractive index) do not. Ratios of two extensive properties (density = m/V; molar volume V/n) are intensive (NCERT §5.2.2(b), p. 144).
- **Heat capacity.** $q = C\ \Delta T$; molar heat capacity $C_m = C/n$; specific heat $c = q/(m\ \Delta T)$. For an ideal gas, $C_p - C_v = R$; the extra heat at constant pressure goes into pV expansion work. For monatomic ideal gas $C_v = (3/2)R$, $C_p = (5/2)R$, $\gamma = 5/3$ (NCERT §5.2.2(c–d), p. 144–145, Eq. 5.13).
- **Calorimetry.** ΔU measured in a constant-volume bomb calorimeter (no work because $\Delta V = 0$; heat evolved heats the steel bomb + water bath); ΔH measured in a constant-pressure (coffee-cup) calorimeter, where $q_p = \Delta_r H$. Calorimeter constant must be known from a calibration run (NCERT §5.3, p. 145–146).
- **Reaction enthalpy and standard states.** $\Delta_r H = \sum a_i H_{products} - \sum b_i H_{reactants}$. Standard state of a substance = its pure form at 1 bar (and usually 298 K); denoted by superscript °. For solutes, standard state is hypothetical 1 mol kg^{-1} ideal solution (NCERT §5.4(a), p. 146–147, Eq. 5.14).
- **Phase-change enthalpies.** $\Delta_{fus}H^\circ$ (always positive, e.g., ice → water +6.00 kJ/mol at 273 K), $\Delta_{vap}H^\circ$ (water → steam +40.79 kJ/mol at 373 K), $\Delta_{sub}H^\circ$ (always positive) — all measured per mole at constant T and p (NCERT §5.4(b), p. 147–148).
- **Standard enthalpy of formation, $\Delta_f H^\circ$.** Enthalpy change when 1 mol of a compound forms from its elements in their reference (most stable) states at 1 bar and 298 K. $\Delta_f H^\circ$ of an element in its reference state = 0 by convention (NCERT §5.4(c), p. 149–150, Eq. 5.15).

- **Thermochemical equations.** Must specify physical state; coefficients refer to moles; reversing the equation reverses the sign of ΔrH; multiplying by a factor multiplies ΔrH by the same factor (NCERT §5.4(d), p. 150–151).
- **Hess's law of constant heat summation.** Total ΔrH for a reaction is the sum of ΔrH of the steps into which it can be divided; allows indirect calculation of unmeasurable enthalpies, e.g. $C + ½O_2 \rightarrow CO$ via $C \rightarrow CO_2$ and $CO \rightarrow CO_2$ (NCERT §5.4(e), p. 151–152, Eq. 5.16). Direct measurement of $C + ½O_2 \rightarrow CO$ is impossible because some CO_2 always forms.
- **Enthalpies of various reactions.** Combustion $\Delta cH°$ (always exothermic, e.g. butane –2658, glucose –2802 kJ/mol); atomization $\Delta aH°$ (= bond dissociation enthalpy for diatomics); bond enthalpy $\Delta bondH°$; mean bond enthalpy (e.g. $\Delta C–HH°$ = ¼·1665 = 416 kJ/mol in CH_4); $\Delta rH° = \Sigma$ bond enthalpies(reactants) – Σ bond enthalpies(products) for gas-phase reactions (NCERT §5.5(a–c), p. 152–155, Eq. 5.17).
- **Lattice enthalpy and Born–Haber cycle.** $\Delta latticeH°$ = enthalpy change when 1 mol of ionic solid dissociates into gaseous ions; computed indirectly via Born–Haber cycle using sublimation + ionization + dissociation + electron-gain + lattice steps. $\Delta solH° = \Delta latticeH° + \Delta hydH°$ — most ionic solids dissolve in water because hydration enthalpy is exothermic and large enough to overcome lattice enthalpy (NCERT §5.5(d–e), p. 155–156).
- **Spontaneity.** A spontaneous process has the potential to proceed without external help; it is irreversible. Decrease in enthalpy is **not** a sufficient criterion — endothermic reactions like $½N_2 + O_2 \rightarrow NO_2$ ($\Delta rH = +33.2$ kJ/mol) are also spontaneous. Mixing of two gases is spontaneous with $\Delta H \approx 0$ (NCERT §5.6 & §5.6(a), p. 157–158).
- **Entropy S.** A state function and measure of disorder/randomness; $\Delta S = qrev/T$. Gaseous state has highest S, crystalline solid lowest. For a spontaneous process in an isolated system, $\Delta Stotal = \Delta Ssys + \Delta Ssurr > 0$; $\Delta Stotal = 0$ at equilibrium (NCERT §5.6(b), p. 158–159, Eq. 5.18 & 5.19).
- **Gibbs energy.** $G = H – TS$; at constant T, $\Delta G = \Delta H – T\Delta S$. $\Delta G < 0 \Rightarrow$ spontaneous; $\Delta G > 0 \Rightarrow$ non-spontaneous; $\Delta G = 0 \Rightarrow$ equilibrium. ΔG is the "free" (useful work) energy of the reaction; ΔG also equals the maximum non-pV work available from the system at constant T, p (NCERT §5.6(c), p. 160–161, Eq. 5.20 & 5.21).
- **Second law of thermodynamics.** Entropy of an isolated system increases for a spontaneous process; explains why exothermic reactions tend to be spontaneous (heat released raises Ssurr, $\Delta Ssurr = –\Delta Hsys/T$) (NCERT §5.6(d), p. 161).
- **Third law of thermodynamics.** Entropy of a pure crystalline substance approaches zero as T → 0 K; lets us calculate absolute entropies by integrating qrev/T from 0 K to T. Allows tabulation of standard absolute entropies S° at 298 K (NCERT §5.6(e), p. 161–162).

- **ΔG° and equilibrium constant.** At equilibrium $\Delta_r G = 0$; $\Delta_r G^\circ = -RT \ln K = -2.303\ RT \log K$. Large negative $\Delta_r G^\circ \Rightarrow K >> 1$ (reaction near completion); large positive $\Rightarrow K << 1$; $\Delta_r G^\circ \approx 0 \Rightarrow K \approx 1$ (NCERT §5.7, p. 162, Eq. 5.23).

2.2 Definitions to memorise

Term	Definition	Page
System	Part of the universe chosen for study	137
Surroundings	Remainder of the universe in contact with the system	137
Open system	Exchanges both matter and energy with surroundings	137
Closed system	Exchanges only energy (not matter) with surroundings	137
Isolated system	Exchanges neither matter nor energy with surroundings	138
State function	Property whose value depends only on the present state, not on path (e.g. U, H, S, G, p, V, T)	138–139
Path function	Property dependent on the route taken between states (q, w)	139
Adiabatic process	Process with no heat exchange between system and surroundings ($q = 0$)	138
Isothermal process	Process at constant temperature ($\Delta T = 0$)	141
Isobaric process	Process at constant pressure	142
Isochoric process	Process at constant volume ($w = 0$)	142
Internal energy U	Sum of all forms of energy of the system; a state function	138
First law	$\Delta U = q + w$; energy of an isolated system is constant	140
Enthalpy H	$H = U + pV$; $\Delta H = q_p$ at constant pressure	143
Extensive property	Depends on amount/size of matter (m, V, U, H, C)	144
Intensive property	Independent of amount (T, p, density, molar quantities)	144
Heat capacity C	$q = C\ \Delta T$; $C_p - C_v = R$ for an ideal gas	144–145
Reversible process	Process carried out infinitely slowly through equilibrium states; $p_{ext} = p_{in} \pm dp$	141
Irreversible process	Sudden, finite-step process; usually $p_{ext} \neq p_{in}$	141
Hess's law	$\Delta_r H$ for a reaction is independent of the path — equals sum of $\Delta_r H$ of the steps	151
Standard enthalpy of formation $\Delta_f H^\circ$	ΔH when 1 mol of a compound forms from its elements in their reference states at 1 bar	149
Bond dissociation enthalpy	ΔH to break 1 mol of covalent bonds in a gaseous compound to give gaseous products	153

Term	Definition	Page
Lattice enthalpy $\Delta_{lattice}H^\circ$	ΔH when 1 mol of ionic solid dissociates into its gaseous ions	155
Entropy S	Measure of disorder; $\Delta S = q_{rev}/T$; state function	158–159
Second law	Entropy of an isolated system increases in a spontaneous process	161
Gibbs energy G	$G = H - TS$; $\Delta G < 0 \Rightarrow$ spontaneous at constant T, p	160
Third law	Entropy of a pure crystalline substance is zero at 0 K	161

2.3 Diagrams / processes to remember

- **Fig. 5.2 (p. 137):** Open, closed and isolated systems — three labelled containers showing matter/energy exchange. Open beaker shows arrows for both matter (vapour) and heat; closed system shows only heat arrows through a sealed lid; isolated system (thermos) has neither.
- **Fig. 5.5(a–c) (p. 140–141):** pV-plots of work done — single-step (rectangle of area $p_{ext}\cdot\Delta V$), finite-step (staircase whose total area is the sum of rectangles), and infinite-step reversible (smooth hyperbola whose shaded area equals $nRT \ln(V_2/V_1)$, the maximum possible work). The diagrams visually illustrate why $w_{rev} > w_{irrev}$ for expansion.
- **Fig. 5.7 (p. 145):** Bomb calorimeter — steel bomb in a water bath; constant-volume ΔU measurement. The bomb is filled with O_2 at high pressure, electrical ignition burns the sample, and the temperature rise of the surrounding water gives q_V which equals ΔU directly. Used for combustion enthalpies of food, fuels.
- **Fig. 5.8 (p. 146):** Coffee-cup / constant-pressure calorimeter for ΔH measurement of dissolution and neutralisation reactions in aqueous solution. Polystyrene cup acts as adiabatic shield; measured $q_p = \Delta H$ directly.
- **Fig. 5.9 (p. 155):** Born–Haber enthalpy diagram for NaCl — sublimation (+108.4 kJ/mol) + ionization (+496) + ½ bond dissociation (+121) + electron-gain (–348.6) + lattice (–788) = –411.2 kJ/mol formation enthalpy. The vertical-arrow construction shows how an indirect cycle gives the otherwise unmeasurable $\Delta_{lattice}H^\circ$.
- **Fig. 5.10(a) & (b) (p. 158):** Enthalpy diagrams for exothermic (products below reactants) and endothermic (products above reactants) reactions; the vertical arrow downwards/upwards represents $-\Delta H$ or $+\Delta H$ respectively.
- **Fig. 5.11 (p. 158):** Diffusion of two gases A and B before and after partition removal — visual for entropy increase. The number of accessible microstates rises sharply on mixing, so $\Delta S_{mix} > 0$ even though $\Delta H_{mix} \approx 0$ for ideal gases.
- **Table 5.4 (p. 162):** Effect of ΔH, ΔS and T on the sign of ΔG (spontaneity matrix): $\Delta H<0$, $\Delta S>0$ → spontaneous at all T; $\Delta H>0$, $\Delta S<0$ → non-spontaneous at all T; $\Delta H<0$,

$\Delta S<0$ → spontaneous at low T; $\Delta H>0$, $\Delta S>0$ → spontaneous at high T. A four-row table that summarises every spontaneity case.

- **PE diagram of catalysed vs uncatalysed reaction (implicit, p. 158):** identical reactants and products, but the activation barrier lowered by the catalyst; the overall ΔH (and ΔG) is unchanged because state functions depend only on initial/final states.

2.4 Common confusions / NTA trap points

- **Sign convention.** IUPAC: w is positive when work is done on the system. Older physics books use the opposite sign — NTA distractors exploit this. If the gas expands ($V_2 > V_1$), $w < 0$ (work done by gas).
- **ΔH vs ΔU.** They are equal only when $\Delta n_g = 0$ (no change in moles of gas) or for solids/liquids; otherwise $\Delta H = \Delta U + \Delta n_g RT$. For $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$, $\Delta n_g = -1.5$, so $\Delta H < \Delta U$.
- **q is path-dependent, but $q_V = \Delta U$ and $q_p = \Delta H$** make them appear like state functions only under those specific constraints.
- **Free expansion of an ideal gas.** $w = 0$ (because $p_{ext} = 0$) and $q = 0$ and $\Delta U = 0$ — students often write $w \neq 0$ because volume changes. No work because external pressure is zero, no heat because temperature does not change.
- **$\Delta_f H^\circ$ of an element in its reference state is zero**, not "unity" or "different for each element" — a frequent NCERT exercise trap (Ex. 5.3). But $\Delta_f H^\circ$ of an element in a non-reference state (e.g., O_3 from O_2, or C(diamond) instead of C(graphite)) is NOT zero.
- **Spontaneity ≠ fast.** A reaction can be spontaneous ($\Delta G < 0$) yet extremely slow ($H_2 + O_2$ mixture at room T). Thermodynamics is silent on rate; kinetics handles speed.
- **Entropy of surroundings.** $\Delta S_{surr} = -\Delta H_{sys}/T$ (heat lost by system at temperature T is gained by surroundings). Negative ΔS_{sys} can still give $\Delta S_{total} > 0$ if ΔH_{sys} is sufficiently negative.
- **Bond enthalpy method gives $\Delta_r H$ for gas-phase reactions only.** If any reactant/product is in solid or liquid state, you must add appropriate phase-change enthalpies; otherwise the calculated $\Delta_r H$ is wrong.
- **Reversible work is the maximum** the system can deliver; irreversible work is always smaller in magnitude. Students sometimes use the same w for both — wrong.
- **ΔG° is a standard-state quantity at 1 bar (and the chosen T).** $\Delta_r G$ itself depends on actual concentrations: $\Delta_r G = \Delta_r G^\circ + RT \ln Q$; equilibrium reached when $Q = K$ and $\Delta_r G = 0$, giving $\Delta_r G^\circ = -RT \ln K$.
- **Heat capacity is extensive; specific heat and molar heat capacity are intensive.** A common slip in MCQ definitions.

🎯 Practice MCQs

Q1. A thermos flask containing hot coffee, sealed with its lid, is best classified as which kind of thermodynamic system?

A. Open system

B. Closed system

C. Isolated system

D. Adiabatic system but not isolated

Q2. Which one of the following sets contains only state functions?

A. q, w, U

B. U, H, q

C. U, H, S

D. w, q, S

Q3. For the isothermal reversible expansion of one mole of an ideal gas, the work done is given by:

A. $w = -p_{ext}(V_2 - V_1)$

B. $w = -2.303\ nRT \log(V_2/V_1)$

C. $w = -nR(T_2 - T_1)$

D. $w = +2.303\ nRT \log(V_1/V_2)$

📊 PYQ Alignment

Thermodynamics is one of the most heavily tested CUET Chemistry units — typically 8–10 MCQs per year. Recurring themes include identifying state functions vs path functions, applying the first law to special processes (adiabatic, isothermal, free expansion), ΔH vs ΔU conversions using $\Delta n_g RT$, Hess's-law arithmetic for unknown enthalpies of formation/combustion, predicting the sign of ΔG from ΔH and ΔS at a stated temperature (Table 5.4 patterns), and the $\Delta G^\circ = -RT \ln K$ relation for equilibrium yield problems.

CUET 2023 — Actual PYQs from this chapter

Q.23 (CUET 2023) Which of the following is not an expression of Dalton’s law of partial pressures?

- A) (P = P_1 + P_2) B) (P = P_1^0 x_1) C) (P = P_1^0 + (P_2^0 – P_1^0)x_2) D) (P_1 = P – P_2)

Tests: Dalton's law of partial pressures (states/thermo crossover) **Answer:** Not in extracted key