JEE MAIN · PAPER 1 · CHEMISTRY

04 Chemical Thermodynamics

Formula & concept sheet

Energy accounting for chemical change: what a system is, how heat and work are counted, the first law and enthalpy, calorimetry and Hess's law, then entropy, Gibbs energy and the test for spontaneity and equilibrium. Each idea is explained first, then the formulas, shortcuts and traps.

INSIDE THIS SHEET

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READ ALONGSIDE NCERT XI · Thermodynamics

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 04

Chemical Thermodynamics

NCERT XI · Thermodynamics

Covers: system, surroundings and types of process · state and path functions · first law, work, heat, internal energy · enthalpy, heat capacities, calorimetry · Hess's law and the named enthalpies · bond enthalpy · entropy and the second law · Gibbs energy and spontaneity · ΔG° and the equilibrium constant.

1 System, surroundings and state functions

- The **system** is the part of the world we study; everything else is the **surroundings**; a boundary separates them. An **open** system exchanges matter and energy, a **closed** one only energy, an **isolated** one neither.
- A **state function** depends only on the present state, not on how it was reached: p, V, T, U, H, S, G. A **path function** depends on the route: heat q and work w. Over a cyclic process every state function returns to its start: $\Delta U = \Delta H = \Delta S = \Delta G = 0$ and $q = -w$.
- **Extensive** properties scale with the amount (mass, V, U, H, S, G, heat capacity); **intensive** ones do not (T, p, density, molar quantities, specific heat, emf). The ratio of two extensive properties is intensive.

NAMES OF PROCESSES

PROCESS	WHAT STAYS FIXED	CONSEQUENCE (IDEAL GAS)
isothermal	T	$\Delta U = 0$, $\Delta H = 0$, $q = -w$
isobaric	p	$q_p = \Delta H$, $w = -p\Delta V$
isochoric	V	$w = 0$, $q_V = \Delta U$
adiabatic	no heat exchange, $q = 0$	$\Delta U = w$; falls in T on expansion
reversible	system always at equilibrium; infinitely slow	maximum work; $\Delta S_{total} = 0$
free expansion	$p_{ext} = 0$ (into vacuum)	$w = 0$; $\Delta T = 0$ for an ideal gas

KEY IDEA

Only **changes** in U and H are measured. Whatever the route, the change in a state function between two states is the same; heat and work separately are not.

QUICK CHECK

Which are state functions: q, w, $q + w$, H, $T\Delta S$?

Answer: $q + w = \Delta U$ and H are. q and w separately depend on the path; $T\Delta S$ is a heat quantity, not a state function.

2 Work, heat and the first law

FIRST LAW (IUPAC SIGNS) Energy is conserved: $\Delta U = q + w$. $q > 0$ when heat flows **into** the system; $w > 0$ when work is done **on** the system (compression), so an expanding gas has $w < 0$. Older books write $\Delta U = q - w$; JEE uses the IUPAC form, so read the sign the question gives.

- **Heat** is energy that moves because of a temperature difference; **work** is energy that moves by any other means, in chemistry mainly pressure-volume work of a gas pushing a piston. Both are energy in transit, not stored: a system holds internal energy U, never "heat" or "work".
- A **reversible** change is carried out in infinitely small steps with the system always in equilibrium with the surroundings; it can be undone with no net change anywhere. Real changes are **irreversible**. Because the gas pushes against the largest possible opposing pressure, reversible expansion gives the maximum work, and reversible compression needs the minimum.
- For an expansion $w < 0$ (the system loses energy); for a compression $w > 0$. For an exothermic reaction $q < 0$.

IDEAL GAS, ANY PROCESS

$$\Delta U = nC_V\Delta T, \quad \Delta H = nC_p\Delta T$$

state functions: valid whatever the path, because U and H of an ideal gas depend on T alone

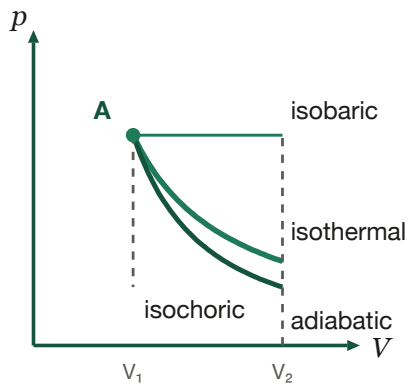
HEAT CAPACITIES

$$C_p - C_V = R, \quad \gamma = \frac{C_p}{C_V}$$

monatomic $C_V = \frac{3}{2}R, \gamma = \frac{5}{3}$; diatomic $C_V = \frac{5}{2}R, \gamma = \frac{7}{5}$; non-linear polyatomic $C_V = 3R, \gamma = \frac{4}{3}$

REVERSIBLE ISOTHERMAL WORK OF AN IDEAL GAS

$w = -\int_{V_1}^{V_2} p\,dV$	in a reversible change p_{ext} differs from the gas pressure p by an infinitesimal amount
$p = \frac{nRT}{V}$	ideal gas, T constant so nRT comes out of the integral
$w = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$	$\ln x = 2.303\log x$; since $p_1V_1 = p_2V_2$ the ratio $V_2/V_1 = p_1/p_2$
$\Delta U = 0 \Rightarrow q = -w = +nRT\ln\frac{V_2}{V_1}$	internal energy of an ideal gas depends only on T



work = area under the curve

adiabatic falls faster than isothermal

work done by the gas is the area under the curve; isothermal is above adiabatic on expansion

CONSTANT EXTERNAL PRESSURE

$$w = -p_{ext}\,\Delta V$$

any path with a fixed p_{ext}; free expansion has $p_{ext} = 0$ so $w = 0$; convert: 1 L atm $= 101.3$ J, 1 L bar $= 100$ J

REVERSIBLE ISOTHERMAL

$$w = -2.303\,nRT\log\frac{V_2}{V_1}$$

$= -2.303\,nRT\log\frac{p_1}{p_2}$; $\Delta U = 0$ so $q = -w$; the maximum work an expansion can give

ISOCHORIC

$$w = 0, \quad q_V = \Delta U = nC_V\Delta T$$

a rigid vessel, as in a bomb calorimeter

REVERSIBLE ADIABATIC

$$pV^\gamma = \text{const}, \; TV^{\gamma-1} = \text{const}$$

$w = \Delta U = nC_V\Delta T = \frac{p_2V_2 - p_1V_1}{\gamma - 1}$; $q = 0$

IRREVERSIBLE ADIABATIC

$$w = \Delta U = -p_{ext}(V_2 - V_1)$$

$q = 0$; here $pV^\gamma = \text{const}$ does **not** hold

WHY IT WORKS

On the p-V diagram the work of expansion is the area under the curve. The isothermal curve lies above the adiabatic one because the gas also draws heat in to hold T; in an adiabatic expansion it spends its own internal energy, cools, and its pressure falls faster.

TRAP

Free expansion is not reversible: $w = -nRT\ln(V_2/V_1)$ does not apply and $w = 0$. For an ideal gas it has $q = w = \Delta U = \Delta T = 0$ but $\Delta S > 0$. The magnitude of irreversible expansion work is smaller than the reversible value.

QUICK CHECK

Work for 2 mol of an ideal gas expanding from 2 L to 10 L at 300 K (a) against 1 atm, (b) reversibly?

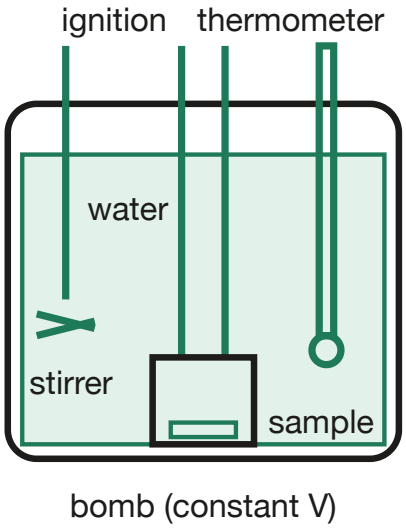
Answer: (a) $-1 \times 8 = -8$ L atm $= -810$ J. (b) $-2.303 \times 2 \times 8.314 \times 300 \log 5 = -8030$ J (magnitude $>$ (a)).

QUICK CHECK

1 mol of a monatomic ideal gas is heated at constant pressure from 300 K to 400 K. Find $q, \Delta U, w$.

Answer: $q = \Delta H = \frac{5}{2}R(100) = 2078$ J; $\Delta U = \frac{3}{2}R(100) = 1247$ J; $w = -R\Delta T = -831$ J; check $1247 = 2078 - 831$.

3 Enthalpy, heat capacity and calorimetry



bomb (constant V)

constant volume gives $q_V = \Delta U$

ENTHALPY $H = U + pV$, a state function. At constant pressure the heat exchanged is exactly the enthalpy change, $q_p = \Delta H$; at constant volume it is the internal-energy change, $q_V = \Delta U$. Chemists use ΔH because reactions run in open vessels at fixed pressure.

ΔH AGAINST ΔU

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

Δn_g = moles of gaseous products − moles of gaseous reactants (solids and liquids do not count); $R = 8.314$ J K^{-1} mol^{-1}

CALORIMETRY

$$q = C\,\Delta T = m\,c\,\Delta T$$

C in J K^{-1}, c specific heat (water 4.18 J g^{-1} K^{-1}); heat gained by water = heat lost by the reaction

BOMB CALORIMETER

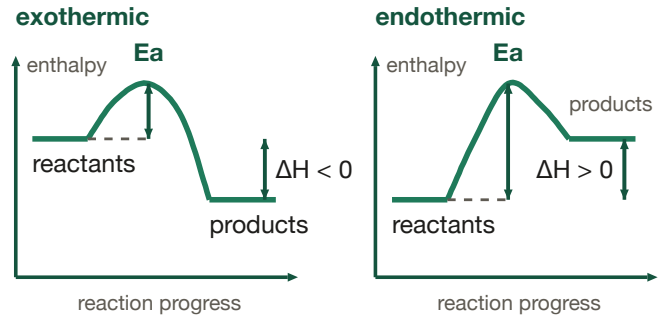
$$\Delta_c U = -\frac{C_{cal}\,\Delta T}{n}$$

constant V gives ΔU; then $\Delta_c H = \Delta_c U + \Delta n_g RT$

PER MOLE OF REACTION

$$\Delta_r H = \frac{q_p}{\xi}$$

divide the heat by the moles of reaction (the extent) the equation describes; scale if the equation is doubled



the activation energy E_a is the bump between reactants and the top of the barrier

READING AN ENTHALPY DIAGRAM

- ✓ Exothermic: products lower than reactants, $\Delta H < 0$, heat released.
- ✓ Endothermic: products higher, $\Delta H > 0$, heat absorbed.
- ✓ The barrier E_a governs the **rate**, not ΔH or ΔG.
- ✓ ΔH of the reverse reaction is the same number with the opposite sign.

TRAP

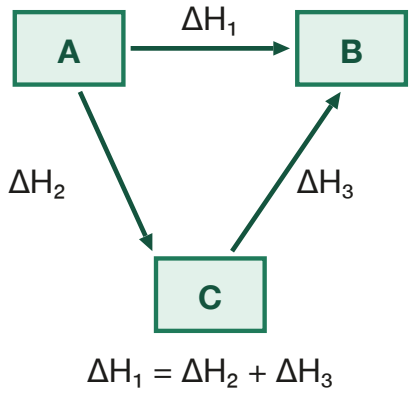
Δn_g counts **gases only**, taken from the balanced equation as written. For benzoic acid burning, $\mathrm{C_6H_5COOH\,(s)} + \frac{15}{2}\,\mathrm{O_2\,(g)} \longrightarrow 7\,\mathrm{CO_2\,(g)} + 3\,\mathrm{H_2O\,(l)}$: $\Delta n_g = 7 - \frac{15}{2} = -\frac{1}{2}$, so $\Delta H = \Delta U - \frac{1}{2}RT$ (at 300 K: $\Delta U - 150R$).

QUICK CHECK

Is $\Delta H > \Delta U$ or $<$ for $\mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{NH_3\,(g)}$?

Answer: $\Delta n_g = 2 - 4 = -2$, so $\Delta H = \Delta U - 2RT$: $\Delta H < \Delta U$.

4 Thermochemistry and Hess's law



enthalpy change is the same by any route

HESS'S LAW The enthalpy change of a reaction is the same whether it takes place in one step or several, because H is a state function. So equations and their ΔH can be added, reversed (flip the sign) and scaled (multiply). It is how ΔH of reactions that cannot be measured directly (C to CO) is found.

FROM FORMATION ENTHALPIES

$\Delta_r H^\circ = \sum \nu\, \Delta_f H^\circ(\text{prod}) - \sum \nu\, \Delta_f H^\circ(\text{react})$

$\Delta_f H^\circ = 0$ for an element in its standard state (graphite for carbon)

FROM BOND ENTHALPIES

$\Delta_r H = \sum BE(\text{broken}) - \sum BE(\text{formed})$

gas phase only; BE taken positive; cancel bonds that are unchanged

FROM COMBUSTION ENTHALPIES

$\Delta_r H = \sum \Delta_c H(\text{react}) - \sum \Delta_c H(\text{prod})$

reversed order compared with formation enthalpies

PHASE CHANGES

$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$

$\Delta_{fus} H(\text{ice}) \approx 6.0$, $\Delta_{vap} H(\text{water}) \approx 40.7$ kJ mol^{-1}

NAMED ENTHALPY CHANGES

NAME	DEFINITION	SIGN AND VALUES
formation	1 mol of compound from its elements in standard states	$\mathrm{H_2O\,(l)}$ -285.8; $\mathrm{CO_2}$ -393.5; CO -110.5; $\mathrm{CH_4}$ -74.8; $\mathrm{NH_3}$ -46.1 kJ mol^{-1}
combustion	1 mol burnt completely in excess $\mathrm{O_2}$	always negative; $\mathrm{CH_4}$ about -890 kJ mol^{-1}
neutralisation	strong acid + strong base giving 1 mol $\mathrm{H_2O}$	about -57 kJ mol^{-1}; smaller in size for a weak acid or base (part of the heat ionises it); $\mathrm{H_2SO_4}$ gives twice per mole of acid
atomisation, sublimation	1 mol of gaseous atoms from the element (or solid to gas)	always positive (bonds broken)
bond dissociation	breaking 1 mol of a gas-phase bond	positive: H−H 436, Cl−Cl 242, O=O 498, N≡N 945, C−H 414, C−C 347, C=C 614, O−H 463
hydration	gaseous ions to aqueous ions	always exothermic
solution	1 mol of solute dissolving in a large amount of solvent	either sign
lattice	1 mol of ionic solid from gaseous ions	negative as defined here; NaCl about -787 kJ mol^{-1} (as in Bonding)

HEAT OF HYDRATION FROM SOLUTION DATA

$$\Delta_{hyd}H = \Delta_{sol}H(\text{anhydrous}) - \Delta_{sol}H(\text{hydrate})$$

both dissolve to the same final solution, so the difference is the step anhydrous to hydrate

STANDARD STATE

1 bar, stated T (usually 298 K)

ΔH° refers to every species in its standard state; elements in the most stable form have $\Delta_f H^\circ = 0$

HESS IN THREE MOVES

1. Write the target equation and tick the species that appear in only one given equation.
2. Multiply or reverse the given equations (and their ΔH) so those species are on the correct side.
3. Add the equations, cancel intermediates, add the ΔH values, and check the final equation balances.

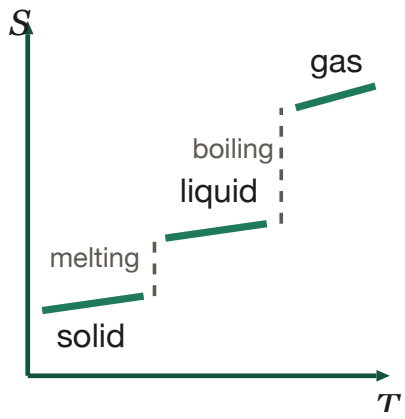
TRAP

Bond enthalpies apply to **gaseous** species: for a liquid or solid add the vaporisation or sublimation steps first. A formation enthalpy must make exactly **one** mole of the compound from elements in standard states: $\frac{1}{2}O_2$ appears with fractions, and diamond is not a standard state of carbon.

SYLLABUS NOTE

Kirchhoff's law, $\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$, is not in the chapter list recalled for the syllabus; it is here for completeness and for questions that give ΔC_p. Trouton's rule, $\Delta_{vap}H/T_b \approx 88$ J K^{-1} mol^{-1} for non-hydrogen-bonded liquids, is a shortcut only.

5 Entropy and the second law



S jumps at each phase change; $\Delta S = \Delta H/T$ at the transition

ENTROPY A measure of the dispersal of energy and matter, in J K^{-1}. For heat taken in reversibly at temperature T: $\Delta S = q_{rev}/T$. It is a state function, so it can be found for any process by choosing a reversible path between the same states.

SECOND LAW A process is spontaneous if the entropy of the **universe** rises: $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$. At constant T, p the surroundings receive the heat the system gives out: $\Delta S_{surr} = -\Delta H_{sys}/T$.

PHASE CHANGE

$$\Delta S = \frac{\Delta H_{trans}}{T_{trans}}$$

ice at 273 K: $6010/273 = 22.0$; water at 373 K: $40700/373 = 109$ J K^{-1} mol^{-1}

IDEAL GAS, ISOTHERMAL

$$\Delta S = 2.303\, nR \log \frac{V_2}{V_1}$$

also free expansion: $\Delta S > 0$ even though $q = 0$

IDEAL GAS, GENERAL

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

or $nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1}$

WHEN DOES ENTROPY INCREASE?

CHANGE	REASON
solid → liquid → gas	more freedom of motion; the biggest jump is vaporisation
dissolving a solid; mixing gases	more dispersal of particles
increase in the number of gas moles ($\Delta n_g > 0$)	more gas particles; $CaCO_3 \longrightarrow CaO + CO_2$
heating	more thermal states are reached; S rises with T
a perfect crystal at 0 K	$S = 0$ (third law); S° of elements at 298 K is positive

KEY IDEA

The system's entropy can fall in a spontaneous process (freezing, a precipitate forming) if the surroundings gain more: freezing of water is spontaneous below 273 K because the heat given out raises ΔS_{surr} by more than the fall in ΔS_{sys}.

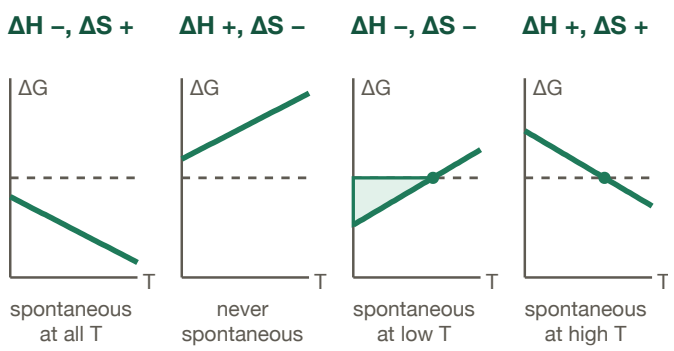
QUICK CHECK

2 mol of an ideal gas doubles its volume isothermally. ΔS_{sys}?

Answer: $2 \times 8.314 \times \ln 2 = 11.5$ J K^{-1}, whether reversible or a free expansion.

6 Gibbs energy, spontaneity and equilibrium

Tracking the surroundings is awkward, so everything is folded into the system: **Gibbs energy** $G = H - TS$. At constant T and p, $\Delta G = \Delta H - T\Delta S = -T\Delta S_{total}$, so the process is spontaneous when $\Delta G < 0$, at equilibrium when $\Delta G = 0$. ΔG says whether, never how fast.



$\Delta G = \Delta H - T\Delta S$; $\Delta G < 0$ means spontaneous, and each line crosses zero at $T = \Delta H/\Delta S$

READING THE FOUR LINES

- Each line is $\Delta G = \Delta H - T\Delta S$ against T: the intercept is ΔH, the slope is $-\Delta S$.
- Where the line crosses $\Delta G = 0$ the temperature is $T = \Delta H/\Delta S$: above it the sign of ΔG flips.
- Same signs of ΔH and ΔS give a crossover, so the temperature decides; opposite signs never change.

SIGN OF ΔG FROM ΔH AND ΔS

ΔH	ΔS	ΔG	SPONTANEOUS?	EXAMPLE
$-$	$+$	always $-$	at all temperatures	$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$
$+$	$-$	always $+$	never (the reverse always is)	$3\,O_2 \longrightarrow 2\,O_3$
$-$	$-$	$-$ at low T	below $T = \Delta H/\Delta S$	freezing of water; $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$
$+$	$+$	$-$ at high T	above $T = \Delta H/\Delta S$	$CaCO_3 \longrightarrow CaO + CO_2$; melting

LINK TO EQUILIBRIUM

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

$K > 1$ when $\Delta G^\circ < 0$; for gases $K = K_p$ with pressures in bar; $RT \times 2.303 = 5.71$ kJ mol^{-1} at 298 K

AWAY FROM EQUILIBRIUM

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$Q < K$ gives $\Delta G < 0$: the reaction runs forward; $\Delta G = 0$ at $Q = K$

CROSSOVER TEMPERATURE

$$T = \frac{\Delta H}{\Delta S}$$

ΔH in J and ΔS in J K^{-1}; meaningful only when both have the same sign

ELECTROCHEMICAL LINK

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$F = 96500$ C mol^{-1}; Daniell cell: $-2 \times 96500 \times 1.10 = -212$ kJ mol^{-1}

TEMPERATURE DEPENDENCE OF K

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

van 't Hoff: exothermic reactions have smaller K at higher T; endothermic ones larger

TRAP

$\Delta G < 0$ gives no rate: diamond turning to graphite is spontaneous and does not happen. $\Delta G^\circ = 0$ means $K = 1$, **not** equilibrium; equilibrium is $\Delta G = 0$. Convert kJ to J before using $T = \Delta H / \Delta S$.

QUICK CHECK

$\mathrm{CaCO_3 \longrightarrow CaO + CO_2}$ has $\Delta H = +178$ kJ and $\Delta S = +161$ J K^{-1}. Above what temperature is it spontaneous?

Answer: $T = \dfrac{178000}{161} = 1106$ K ($\approx 833^\circ$C).

7 Worked examples

REVERSIBLE ISOTHERMAL WORK

5 mol of an ideal gas expands from 10 L to 100 L at 300 K, reversibly and isothermally. Work done?

$w = -2.303 \times 5 \times 8.314 \times 300 \times \log 10 = -28.7$ kJ; the gas does about 28.7×10^3 J of work

ΔH FROM ΔU

The heat of combustion of benzoic acid at constant volume is -321.30 kJ mol^{-1} at 27°C. At constant pressure?

$\Delta n_g = -\frac{1}{2}$; $\Delta H = \Delta U - \frac{1}{2}RT = -321.30 - 150R$ kJ mol^{-1} (R in kJ); $x = 150$

HEAT OF HYDRATION

$\Delta_{sol}H$ of anhydrous $\mathrm{CuSO_4}$ is -70 and of $\mathrm{CuSO_4 \cdot 5\,H_2O}$ is $+12$ kJ mol^{-1}. Heat of hydration?

$-70 - (+12) = -82$ kJ mol^{-1}

BOND ENTHALPIES

$\mathrm{C_2H_4 + H_2 \longrightarrow C_2H_6}$ using C=C 614, C−C 347, C−H 414, H−H 436.

broken: $614 + 436 = 1050$; formed: $347 + 2 \times 414 = 1175$ (two new C−H); $\Delta H = 1050 - 1175 = -125$ kJ mol^{-1}

FORMATION ENTHALPIES

$\Delta_c H$ of methane from $\Delta_f H$ of $\mathrm{CH_4, CO_2, H_2O\,(l)} = -74.8, -393.5, -285.8$.

$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O\,(l)}$: $-393.5 + 2(-285.8) - (-74.8) = -890.3$ kJ mol^{-1}

HESS

ΔH for $\mathrm{C\,(s) + \frac{1}{2}\,O_2 \longrightarrow CO}$ given $\mathrm{C + O_2 \longrightarrow CO_2}$ (-393.5) and $\mathrm{CO + \frac{1}{2}\,O_2 \longrightarrow CO_2}$ (-283.0).

first equation minus the second: $-393.5 - (-283.0) = -110.5$ kJ mol^{-1}

ΔU OF METHANE

$\Delta_c H(\mathrm{CH_4}) = -890$ kJ mol^{-1} at 298 K. $\Delta_c U$?

$\Delta n_g = 1 - 3 = -2$; $\Delta U = \Delta H - \Delta n_g RT = -890 + 2 \times 8.314 \times 298/1000 = -885.0$ kJ mol^{-1}

CALORIMETER

100 mL of 1 M HCl is mixed with 100 mL of 1 M NaOH ($\Delta_{neut}H = -57.1$ kJ mol^{-1}). Temperature rise ($c = 4.18$ J g^{-1} K^{-1}, 200 g)?

$q = 0.1 \times 57100 = 5710$ J; $\Delta T = \dfrac{5710}{200 \times 4.18} = 6.8$ K

REVERSIBLE ADIABATIC

1 mol of a monatomic ideal gas at 300 K is compressed reversibly and adiabatically to half its volume. Final T and work?

$T_2 = 300 \times 2^{2/3} = 476$ K; $w = \Delta U = \frac{3}{2}R(176.2) = 2198$ J on the gas

ENTROPY OF FUSION

$\Delta_{fus}H$ of ice is 6010 J mol^{-1} at 273 K. ΔS_{fus}?

$\dfrac{6010}{273} = 22.0$ J K^{-1} mol^{-1}

AMMONIA SYNTHESIS

$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$: $\Delta H^\circ = -92.2$ kJ, $\Delta S^\circ = -198.7$ J K^{-1}. ΔG° and K at 298 K, and the crossover T ?

$\Delta G^\circ = -92200 + 298 \times 198.7 = -33.0$ kJ; $\ln K = 32987/(8.314 \times 298) = 13.3$, $K \approx 6 \times 10^5$; $T = 92200/198.7 = 464$ K (spontaneous below it)

K FROM ΔG°

$\Delta G^\circ = -5.7$ kJ mol^{-1} at 298 K. K?

$\log K = \dfrac{5700}{5706} \approx 1.0$, so $K \approx 10$ (since $2.303RT = 5.71$ kJ)

BOMB CALORIMETER

Burning 0.5 mol of a fuel in a bomb calorimeter of heat capacity 20 kJ K^{-1} raises the temperature by 2.5 K. $\Delta_c U$ per mole?

$\Delta_c U = -\dfrac{20 \times 2.5}{0.5} = -100$ kJ mol^{-1} (constant V, so this is ΔU, not ΔH)

CROSSOVER TEMPERATURE

A reaction has $\Delta H = -10$ kJ and $\Delta S = -35$ J K^{-1}. When is it spontaneous?

both negative: $T = \dfrac{10000}{35} = 286$ K; spontaneous below 286 K ($\Delta G = -10000 + 35T < 0$)

SURROUNDINGS

A reaction at 300 K has $\Delta H = -60$ kJ and $\Delta S_{sys} = -100$ J K^{-1}. Is it spontaneous?

$\Delta S_{surr} = +60000/300 = +200$; $\Delta S_{total} = -100 + 200 = +100 > 0$; also $\Delta G = -60000 + 30000 = -30$ kJ: spontaneous

HEAT IN A PROCESS

An ideal gas expands isothermally against a constant external pressure, doing 300 J of work. ΔU, q, w?

isothermal: $\Delta U = 0$; $w = -300$ J; $q = +300$ J (heat absorbed equals work done)

8 Last-minute checklist

BEFORE YOU ANSWER

Which sign convention (IUPAC: w on the system > 0)? Constant V or constant p? Which units, J or kJ, L atm or J? Gases only in Δn_g?

- $\Delta U = q + w$; $w = -p_{ext}\Delta V$; reversible isothermal $w = -2.303\,nRT\log(V_2/V_1)$; free expansion $w = q = 0$; adiabatic $q = 0$.
- $\Delta H = \Delta U + \Delta n_g RT$; $q_V = \Delta U$, $q_p = \Delta H$; $C_p - C_V = R$; $\Delta U = nC_V\Delta T$ and $\Delta H = nC_p\Delta T$ for any ideal-gas process.
- $\Delta_r H = \sum \Delta_f H(\text{prod}) - \sum \Delta_f H(\text{react}) = \sum BE(\text{broken}) - \sum BE(\text{formed})$; Hess: add, reverse (sign), scale; hydration $= \Delta_{sol}H(\text{anhydrous}) - \Delta_{sol}H(\text{hydrate})$.
- $\Delta S = q_{rev}/T$; $\Delta S_{surr} = -\Delta H/T$; $\Delta S_{total} > 0$ spontaneous; third law $S = 0$ for a perfect crystal at 0 K.
- $\Delta G = \Delta H - T\Delta S$; $\Delta G < 0$ spontaneous; $\Delta G^\circ = -2.303RT\log K$; $\Delta G = \Delta G^\circ + RT\ln Q$; $T = \Delta H/\Delta S$ in matching units.
- State functions: U, H, S, G, p, V, T; path functions: q, w; neutralisation about -57 kJ mol^{-1}; 1 L atm $= 101.3$ J.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**