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PHYSICAL

CH 02

Thermodynamics — Gibbs Energy & Spontaneity

02

First law and work, enthalpy and Hess's law, bond enthalpies, entropy, Gibbs energy and its link to K and E°, plus the Joule–Thomson effect and the Gibbs–Helmholtz equation — with every numerical type solved, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Use the first law with the correct sign convention and calculate work for reversible and irreversible expansion
- Convert between ΔH and ΔU, and use Hess's law and bond enthalpies to find ΔH
- Predict the sign of ΔS and calculate entropy changes for phase changes
- Decide spontaneity from ΔH, ΔS and T, and find the crossover temperature
- Link ΔG° to K and to E°, and explain the Joule–Thomson effect

INSIDE

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HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One sign answers the chapter's main question.

IN ONE LINE

A process at constant temperature and pressure is spontaneous when $\Delta G = \Delta H - T\Delta S$ is negative; ΔG° also fixes the equilibrium constant through $\Delta G^\circ = -RT \ln K$.

1. **First law** — energy is conserved: $\Delta U = q + w$.
2. **Enthalpy** — heat at constant pressure; Hess's law lets you add reactions like equations.
3. **Entropy** — the universe's entropy rises in every spontaneous change.
4. **Gibbs energy** — combines both into one test that uses only the system.

THINK OF IT LIKE THIS

A ball rolls downhill on its own (energy falls, like negative ΔH). A drop of ink spreads through water on its own (disorder rises, like positive ΔS). Gibbs energy weighs both tendencies, with temperature deciding how much the spreading counts.

SECTION B

The language

B

Get these words right and the rest reads easily.

- **System** — the part you study. **Surroundings** — everything else.
- **Open** (exchanges matter and energy), **closed** (energy only), **isolated** (neither).
- **State functions** depend only on the initial and final states: U, H, S, G, p, V, T. **Path functions** depend on the route: q and w.
- **Extensive** properties depend on amount (U, H, S, G, V, heat capacity). **Intensive** do not (T, p, density, molar quantities).
- **Isothermal** (T constant), **isobaric** (p constant), **isochoric** (V constant), **adiabatic** (q = 0).

SECTION C

First law and work

C

Energy in, energy out — watch the signs.

$$\Delta U = q + w$$

IUPAC/NCERT sign convention: q and w are positive when energy enters the system

Process	Work done	Notes
Expansion against constant p_{ext} (irreversible)	$w = -p_{ext}\,\Delta V$	Gas does work → w negative
Free expansion ($p_{ext} = 0$)	$w = 0$	Ideal gas: q = 0, ΔU = 0 too
Reversible isothermal, ideal gas	$w = -2.303\ nRT \log(V_2/V_1)$	Maximum work for that expansion
Constant volume	$w = 0$	So $\Delta U = q_v$
Adiabatic	$q = 0$	$w = \Delta U = nC_v\Delta T$

KEY IDEA

For an ideal gas, U depends only on T. In any isothermal process of an ideal gas ΔU = 0, so q = −w: all the heat absorbed is turned into work.

SOLVED EXAMPLE 01 — REVERSIBLE VS IRREVERSIBLE WORK

2 mol of an ideal gas expand isothermally at 300 K from 10 L to 100 L. Find w, q and ΔU (R = 8.314 J K^{-1} mol^{-1}).

SOLUTION

1. $w = -2.303 \times 2 \times 8.314 \times 300 \times \log(100/10) = -2.303 \times 4988.4 \times 1$.
2. Isothermal ideal gas → ΔU = 0, so q = −w.

ANSWER w ≈ −11.5 kJ; q ≈ +11.5 kJ; ΔU = 0.

SOLVED EXAMPLE 02 — WORK AGAINST CONSTANT PRESSURE

1 mol of gas expands from 10 L to 20 L against a constant external pressure of 1 atm. Find w in joules (1 L atm = 101.3 J).

SOLUTION

1. $w = -p_{ext}\,\Delta V = -1\text{ atm} \times 10\text{ L} = -10\text{ L atm}$.
2. Convert: -10×101.3 J.

ANSWER $w = -1013$ J.

SECTION D

Enthalpy

D

Heat at constant pressure — the number in most thermochemical equations.

$$H = U + pV$$

$$\Delta H = \Delta U + \Delta n(g)\,RT$$

$\Delta n(g)$ = moles of gaseous products − moles of gaseous reactants

- $\Delta H = q_p$ (heat at constant pressure); $\Delta U = q_v$ (heat at constant volume, as in a bomb calorimeter).
- **Exothermic:** $\Delta H < 0$. **Endothermic:** $\Delta H > 0$.
- $C_p - C_v = R$ for one mole of ideal gas; heat $q = nC\Delta T$.
- The **standard enthalpy of formation** of an element in its most stable form is zero (graphite, O_2, H_2). Diamond and O_3 are not zero.
- **Enthalpy of neutralisation** of a strong acid by a strong base ≈ −57.1 kJ mol^{-1} (it is just $H^+ + OH^- \rightarrow H_2O$). With a weak acid or base it is less negative — some energy goes into ionising it.

SOLVED EXAMPLE 03 — ΔH FROM ΔU

For $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H = -92.4$ kJ at 298 K. Find ΔU.

SOLUTION

1. $\Delta n(g) = 2 - 4 = -2$.
2. $\Delta U = \Delta H - \Delta n(g)RT = -92.4 - (-2 \times 8.314 \times 298 / 1000)$.
3. $= -92.4 + 4.96$.

ANSWER $\Delta U \approx -87.4$ kJ.

SECTION E

Hess's law and bond enthalpy

E

Add equations, add their ΔH values.

Hess's law: because H is a state function, ΔH for a reaction is the same whatever route you take. Add or subtract equations, multiply them by numbers, and do exactly the same to their ΔH values. Reverse an equation → change the sign of ΔH.

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

$$\Delta_r H = \Sigma \text{ bond enthalpies (bonds broken)} - \Sigma \text{ bond enthalpies (bonds formed)}$$

Gas-phase reactions only; reactants minus products — the reverse of the formation-enthalpy formula

SOLVED EXAMPLE 04 — HESS'S LAW

Given C(graphite) + O_2 → CO_2, ΔH = −393.5 kJ and CO + ½O_2 → CO_2, ΔH = −283.0 kJ. Find ΔfH of CO.

SOLUTION

1. Target: C(graphite) + ½O_2 → CO.
2. Take equation 1 and subtract equation 2 (reverse it, so its ΔH becomes +283.0).
3. ΔH = −393.5 + 283.0.

ANSWER ΔfH(CO) = −110.5 kJ mol^{-1}.

SOLVED EXAMPLE 05 — BOND ENTHALPY

Find ΔH for H_2 + Cl_2 → 2HCl. Bond enthalpies: H–H 436, Cl–Cl 242, H–Cl 431 kJ mol^{-1}.

SOLUTION

1. Bonds broken: 436 + 242 = 678 kJ.
2. Bonds formed: 2 × 431 = 862 kJ.
3. ΔH = 678 − 862.

ANSWER ΔH = −184 kJ.

CHECK YOURSELF

C1 Which is larger in magnitude for the combustion of methane: ΔH or ΔU? (CH_4 + 2O_2 → CO_2 + 2H_2O(l))

C2 Why is the enthalpy of neutralisation of acetic acid with NaOH less than 57.1 kJ mol^{-1}?

Answers at the end of the chapter.

SECTION F

Entropy

F

The measure of how spread out energy and matter are.

$$\Delta S = q(rev) / T$$

$$\Delta S(total) = \Delta S(system) + \Delta S(surroundings) > 0$$

Second law: total entropy rises in every spontaneous process; = 0 at equilibrium

- **ΔS increases when:** a solid melts or a liquid boils; moles of gas increase; a solid dissolves; temperature rises; a molecule breaks into more pieces.
- **Entropy of a phase change:** ΔS = ΔH(transition) / T(transition).
- **Trouton's rule:** for many liquids ΔS(vap) ≈ 88 J K^{-1} mol^{-1}. Water is higher because of hydrogen bonding.
- **Third law:** the entropy of a perfectly crystalline substance at 0 K is zero, which allows absolute entropies.
- For the surroundings: ΔS(surr) = −ΔH(system) / T.

SOLVED EXAMPLE 06 — ENTROPY OF VAPORISATION

ΔvapH of water at 373 K is 40.79 kJ mol^{-1}. Find ΔvapS.

SOLUTION

1. ΔS = ΔH / T = 40 790 / 373.

ANSWER ΔvapS ≈ 109.4 J K^{-1} mol^{-1} (above Trouton's 88, because of hydrogen bonding).

SECTION G

Gibbs energy

G

The single test of spontaneity at constant T and p.

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

ΔG < 0 spontaneous; ΔG = 0 equilibrium; ΔG > 0 non-spontaneous (the reverse is spontaneous)

ΔH	ΔS	ΔG	Spontaneous?	Example
−	+	Always −	At all temperatures	Combustion; $2O_3 \rightarrow 3O_2$
−	−	− at low T	Below T = ΔH/ΔS	Freezing of water; NH_3 formation
+	+	− at high T	Above T = ΔH/ΔS	Melting of ice; $CaCO_3$ decomposition
+	−	Always +	Never	$3O_2 \rightarrow 2O_3$ on its own

KEY IDEA

Crossover temperature T = ΔH / ΔS. Put ΔH and ΔS in the same energy unit (both J or both kJ) — the commonest numerical error in this chapter. −ΔG also equals the maximum useful (non-expansion) work the system can do.

SOLVED EXAMPLE 07 — CROSSOVER TEMPERATURE

For a reaction ΔH = +30 kJ mol^{-1} and ΔS = +105 J K^{-1} mol^{-1}. Above what temperature is it spontaneous?

SOLUTION

1. Both signs positive → spontaneous at high T.
2. T = ΔH / ΔS = 30 000 J / 105 J K^{-1}.

ANSWER Above about 286 K.

CHECK YOURSELF

C3 At 0 °C, ice and water are at equilibrium. What is ΔG for melting?

C4 A reaction has ΔH < 0 and ΔS < 0. Is it spontaneous at high or low temperature?

Answers at the end of the chapter.

SECTION H

ΔG°, K and E°

H

The bridge from thermodynamics to equilibrium and electrochemistry.

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

$$\Delta G = \Delta G^\circ + 2.303\ RT \log Q$$

K > 1 ⇔ ΔG° < 0; K < 1 ⇔ ΔG° > 0

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

F = 96 500 C mol^{-1}; a positive E° means negative ΔG°

SOLVED EXAMPLE 08 — FROM K TO ΔG°

K = 10 for a reaction at 300 K. Find ΔG°.

SOLUTION

1. ΔG° = −2.303 × 8.314 × 300 × log 10.
2. = −5744 J mol^{-1}.

ANSWER ΔG° ≈ −5.74 kJ mol^{-1}.

SOLVED EXAMPLE 09 — FROM E° TO ΔG°

For the Daniell cell E° = 1.10 V and n = 2. Find ΔG°.

SOLUTION

1. ΔG° = −nFE° = −2 × 96 500 × 1.10.

ANSWER ΔG° = −212.3 kJ mol⁻¹.

SECTION I

Beyond the basics

I

Two ideas that appear in PGT and higher papers.

Joule–Thomson effect

- A real gas expanding adiabatically through a porous plug from high to low pressure: **enthalpy stays constant** (isenthalpic).
- Most gases **cool**, because work is done against intermolecular attractions. This is how gases are liquefied (Linde process).
- Every gas has an **inversion temperature**: below it the gas cools on expansion, above it the gas warms. H_2 and He have very low inversion temperatures, so they **warm** on expansion at room temperature and must be pre-cooled.
- An ideal gas shows no Joule–Thomson effect (no intermolecular forces).

Gibbs–Helmholtz equation

$$\Delta G = \Delta H + T\left(\partial \Delta G/\partial T\right)_p$$

Shows how ΔG changes with temperature; since $(\partial \Delta G/\partial T)_p = -\Delta S$, it is ΔG = ΔH − TΔS in another form

Combined with ΔG = −nFE it gives the enthalpy of a cell reaction from its EMF and the temperature coefficient of EMF: $\Delta H = -nF\left[E - T(\partial E/\partial T)_p\right]$.

SECTION J

Exam trap gallery

J

Where marks are lost in thermodynamics.

✗ TRAP 01 · WHAT STUDENTS WRITE

Work done by the gas on expansion is positive.

✓ WHAT IS ACTUALLY CORRECT

In the IUPAC/NCERT convention it is negative: $w = -p_{ext}\Delta V$.

WHY Energy leaves the system.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$\Delta H = \Delta U$ for every reaction.	$\Delta H = \Delta U + \Delta n(g)RT$; equal only when $\Delta n(g) = 0$.

WHY Count only gaseous moles.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
All exothermic reactions are spontaneous.	Spontaneity needs $\Delta G < 0$; $\Delta H < 0$ with large negative ΔS can be non-spontaneous at high T.

WHY Entropy matters too.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$\Delta_f H°$ of O_3 and diamond is zero.	Only for the most stable form: O_2, graphite.

WHY O_3 and diamond are not reference states.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$T = \Delta H/\Delta S$ with ΔH in kJ and ΔS in J K^{-1}.	Convert to the same unit first.

WHY Otherwise the answer is off by 1000.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$\Delta G° < 0$ means the reaction goes to completion.	It means $K > 1$ — products favoured at equilibrium.

WHY $\Delta G°$ tells position of equilibrium, not completeness.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Entropy of the system always increases in a spontaneous change.	The total (system + surroundings) increases.

WHY Freezing water below 0 °C: system $\Delta S < 0$, still spontaneous.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Hydrogen cools on Joule–Thomson expansion at room temperature.	H_2 warms — room temperature is above its inversion temperature.

WHY It must be pre-cooled before liquefaction.

MEMORY HOOK

"**Energy in is plus**" — q and w positive when energy enters.

"**H minus TS**" — $\Delta G = \Delta H - T\Delta S$.

"**Broken minus formed**" — bond enthalpy formula (opposite of products minus reactants).

"**Big K, negative G**" — $\Delta G^\circ = -RT \ln K$.

SECTION K

K

Practice MCQs

Levels: Easy, Moderate, Tough.

Q01 Which is a state function? [EASY]

(a) q
(b) w
(c) q + w
(d) q × w

Q02 For an isothermal process of an ideal gas: [EASY]

(a) q = 0
(b) w = 0
(c) $\Delta U = 0$
(d) $\Delta H \neq 0$

Q03 Which is intensive? [EASY]

(a) enthalpy
(b) volume
(c) temperature
(d) heat capacity

Q04 $\Delta f H^\circ$ is zero for: [EASY]

(a) C(diamond)
(b) $O_3(g)$
(c) $Br_2(l)$
(d) $H_2O(l)$

Q05 A process is at equilibrium when: [EASY]

(a) $\Delta G = 0$
(b) $\Delta H = 0$
(c) $\Delta S = 0$
(d) $\Delta U = 0$

Q06 For $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$: [MODERATE]

(a) $\Delta H = \Delta U$
(b) $\Delta H > \Delta U$
(c) $\Delta H < \Delta U$
(d) $\Delta H = 0$

Q07 ΔS is positive for: [MODERATE]

(a) $N_2 + 3H_2 \rightarrow 2NH_3$
(b) $H_2O(l) \rightarrow H_2O(s)$
(c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
(d) $2SO_2 + O_2 \rightarrow 2SO_3$

Q08 ΔH = +ve, ΔS = +ve. The reaction is spontaneous: [MODERATE]

(a) at all T
(b) at low T
(c) at high T
(d) never

Q09 If K < 1, then ΔG° is: [MODERATE]

(a) negative (b) positive
(c) zero (d) unpredictable

Q10 Enthalpy of neutralisation of HCl by NaOH is about: [MODERATE]

(a) −13.7 kJ mol^{-1} (b) −57.1 kJ mol^{-1}
(c) −100 kJ mol^{-1} (d) +57.1 kJ mol^{-1}

Q11 ΔH = −10 kJ and ΔS = −40 J K^{-1}. The reaction is spontaneous below: [MODERATE]

(a) 250 K (b) 400 K
(c) 25 K (d) 4 K

Q12 Free expansion of an ideal gas into vacuum under adiabatic conditions has: [MODERATE]

(a) q = 0, w = 0, ΔU = 0 (b) q = 0, w < 0
(c) ΔU < 0 (d) ΔT > 0

Q13 For a cell with positive E°, which is true? [TOUGH]

(a) ΔG° > 0, K < 1 (b) ΔG° < 0, K > 1
(c) ΔG° = 0, K = 1 (d) ΔG° < 0, K < 1

Q14 Which gas warms on Joule–Thomson expansion at room temperature? [TOUGH]

(a) N_2 (b) CO_2
(c) He (d) O_2

Q15 Molar entropy of vaporisation of a liquid boiling at 350 K with ΔvapH = 30.8 kJ mol^{-1} is: [TOUGH]

(a) 88 J K^{-1} mol^{-1} (b) 11.4 J K^{-1} mol^{-1}
(c) 0.088 J K^{-1} mol^{-1} (d) 880 J K^{-1} mol^{-1}

Answer key with explanations

Q01 **(c) q + w** — q + w = ΔU.

Q02 **(c) ΔU = 0** — U depends only on T.

Q03 **(c) temperature** — Independent of amount.

Q04 **(c) $Br_2(l)$** — Bromine is liquid in its standard state.

Q05 **(a) ΔG = 0** — No net driving force.

Q06 **(c) ΔH < ΔU** — Δn(g) = −1, so ΔH = ΔU − RT.

Q07 **(c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$** — A gas is produced.

Q08 **(c) at high T** — TΔS must exceed ΔH.

Q09 **(b) positive** — log K < 0.

Q10 **(b) −57.1 kJ mol^{-1}** — $H^+ + OH^- \rightarrow H_2O$.

Q11 **(a) 250 K** — T = 10 000/40.

Q12 **(a) q = 0, w = 0, ΔU = 0** — Nothing is pushed; no heat.

Q13 **(b)** $\Delta G^\circ < 0, K > 1$ — $\Delta G^\circ = -nFE^\circ$.

Q14 **(c) He** — Very low inversion temperature.

Q15 **(a) 88 J K^{-1} mol^{-1}** — 30 800/350 = 88 (Trouton's rule).

Check-yourself answers

C1 ΔH. $\Delta n(g) = 1 - 3 = -2$, so $\Delta H = \Delta U - 2RT$: ΔH is more negative.

C2 Part of the energy released is used to ionise the weak acid completely.

C3 $\Delta G = 0$ (equilibrium).

C4 Low temperature (below $T = \Delta H/\Delta S$).

QUICK REVISION

One-page revision

Read this page the night before the exam.

First law

- ΔU = q + w; energy in is +
- w = $-p_{ext}\Delta V$ (irreversible)
- w = $-2.303nRT \log(V_2/V_1)$ (reversible)
- Ideal gas isothermal: ΔU = 0, q = −w

Enthalpy

- ΔH = ΔU + Δn(g)RT
- $C_p - C_v = R$
- ΔfH° = 0 for stable elements
- Neutralisation (strong) = −57.1 kJ

Hess and bonds

- Reverse equation → reverse sign
- ΔrH = ΣΔfH(prod) − ΣΔfH(react)
- Bond: broken − formed
- ΔfH(CO) = −110.5 kJ

Entropy

- ΔS = q(rev)/T
- ΔS(total) > 0 spontaneous
- ΔS = ΔH/T at phase change
- Trouton: ≈ 88 J K^{-1} mol^{-1}

Gibbs

- ΔG = ΔH − TΔS
- T(crossover) = ΔH/ΔS (same units)
- −/+ always; +/− never
- −ΔG = max useful work

Links

- ΔG° = −2.303RT log K
- ΔG° = −nFE°
- J–T: isenthalpic; H_2, He warm
- $\Delta H = -nF[E - T(\partial E/\partial T)_p]$

END OF NOTES · RAMGOVINDYADAV.COM