Unit 4 · Chemical Thermodynamics

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Physical Chemistry (Units 1–5 together): 22 of 75 marks; 4 MCQs, 2 short and 1 long question
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: water freezing, from ΔH and S° data: ΔS of the system, surroundings and universe, is it spontaneous at 0 °C, *K* for melting at 10 °C; long (OR): enthalpy of formation of ethanol from enthalpies of combustion (Hess)
- **MCQ (1 mark)**
  - what thermodynamics is; a fridge with its door open; ΔH vs ΔE; adsorption spontaneous and exothermic; ΔH of C(s) → C(g) from data; diamond and graphite
  - first law sums (ΔE = 50 J, w = 20 J); violates the first law; −393.5 kJ is both ΔH°f(CO_2) and ΔH°c(C); Hess; Lavoisier–Laplace
  - entropy up and enthalpy down; second law; ΔG for spontaneity; turning temperature; sign of ΔG° when K > 1; isobaric on a P–V diagram
- **Short (5 marks, in parts)**
  - define with units: E, H, S, G; differences: exo/endo, extensive/intensive, formation/combustion, state/path function, isobaric/isochoric
  - state with maths: first and second laws, Lavoisier–Laplace, Hess; ΔH and ΔE with Δn_g; $N_2 + O_2 \rightarrow 2NO$ (+180 kJ): reverse, ΔH°f(NO)
  - changes of state (endo/exo, entropy, spontaneous when); Hess sums ($C_4H_{10}O$, hydroquinone, $KClO_3$, $BaCl_2$ hydration, graphite → diamond, NO + O)
  - sign of ΔS; boiling point from ΔH and ΔS; bond enthalpies (methane); four processes on a P–V diagram
- **Long (8 marks)**: methane's −890 kJ/mol (equation, calorific value, entropy of the universe); signs of ΔS; ethane from combustion data; graphite's ΔH°, ΔS° and ΔG°; stability from ΔH°f, calorific values; ethene + H_2 by Hess; ΔH from bond enthalpies

Key terms

System: the part studied; **surroundings**: everything outside it; **boundary**: the surface between.

Open system: matter and energy cross (tea in a cup); **closed**: only energy (sealed cylinder); **isolated**: neither (vacuum flask).

Intensive property: not on the amount (T, P, density, boiling point); **extensive**: on the amount (mass, V, E, H, S, G).

State function: depends only on the start and end states (P, V, T, E, H, S, G); **path function**: on the path (q, w).

Isothermal (ΔT = 0), **adiabatic** (q = 0), **isobaric** (ΔP = 0), **isochoric** (ΔV = 0), **cyclic** (back to the start).

Reversible process: through equilibrium states, in tiny steps; **irreversible**: every real process.

Internal energy (E or U): total energy inside a system, kinetic and potential, J.

Enthalpy (H): heat content, $H = E + PV$; ΔH = heat at constant pressure.

ΔH°f: one mole of a compound **from its elements** in their standard states (1 bar, 298 K).

ΔH°c: one mole burned **completely** in oxygen; always negative.

Enthalpy of solution: one mole dissolved to infinite dilution.

Calorific value: heat from burning **1 g** (or 1 kg) completely, kJ/g.

Bond enthalpy: energy to break one mole of a bond, gas phase, kJ/mol.

Spontaneous process: goes by itself once started; **non-spontaneous**: only while energy is supplied.

Entropy (S): measure of disorder, of how spread out the energy is; J K^{-1} (J K^{-1} mol^{-1}).

Gibbs free energy (G): energy available for useful work at constant T and P, $G = H - TS$; J (kJ/mol).

Formulas

$\Delta E = q + w$	w on the system + **Use:** first law
$w = -P\Delta V$	expansion: $w < 0$ **Use:** constant P
$\Delta H = \Delta E + \Delta n_g RT$	Δn_g: gas moles **Use:** ΔH and ΔE
$\Delta S = q_{\text{rev}}/T$	J K^{-1} **Use:** entropy
$\Delta G = \Delta H - T\Delta S$	ΔH, ΔS in J **Use:** Gibbs
$T = \Delta H/\Delta S$	where ΔG = 0 **Use:** turning point
$\Delta G^\circ = -2.303RT \log K$	R = 8.314 **Use:** ΔG° and K

- reversible, isothermal: $w_{\text{rev}} = -2.303\, nRT \log(V_2/V_1)$; $\Delta H = q_P$, $\Delta E = q_V$
- $\Delta H_r^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$, × coefficients, elements 0
- from combustion: $\Delta H_f^\circ = \sum \Delta H_c^\circ(\text{elements}) - \Delta H_c^\circ(\text{compound})$
- from bonds (gases): ΔH = Σ broken − Σ formed
- $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_m$, $\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T_b$; $\Delta S_r^\circ = \sum S^\circ(\text{p}) - \sum S^\circ(\text{r})$, S° of an element **not** zero
- $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$; $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$; $\Delta G = -T\Delta S_{\text{univ}}$; $-\Delta G = w_{\text{max}}$

Systems and processes (4.1)

- system + surroundings = universe; open beaker (open), bomb calorimeter (closed), the universe (isolated)
- cut in half: intensive same, extensive halved; ratio of two extensive = intensive (density)
- **heat is not a property**: energy in transit; a system has E, H, S, not heat
- water 25 → 100 °C: ΔT the same by any flame; gas burnt and heat lost depend on the path
- isothermal: slow, in a bath; adiabatic: fast or insulated (bicycle pump warms); isobaric: open beaker; isochoric: sealed rigid vessel, bomb
- cyclic: every state function back, ΔE = 0; engines, refrigerators
- reversible: a curve on a P–V diagram, retraced exactly; irreversible: no curve, only its ends

First law, enthalpy (4.2–4.5)

- bond breaking endothermic, bond making exothermic
- E = translational + rotational + vibrational KE + intermolecular, bond, electronic, nuclear PE; only ΔE measurable
- isolated: ΔE = 0; 100 kg iron has twice the E of 50 kg at the same T
- first law: energy neither created nor destroyed; physics writes $\Delta E = Q - W$ (W by the gas): don't mix the two
- 600 J in, 200 J of work done by the gas: ΔE = +400 J; 200 J released, 100 J done: ΔE = −300 J
- 2.00 mol, 300 K, 10.0 → 20.0 L reversibly: $w = -3.46$ kJ, $q = +3.46$ kJ (ΔE = 0)

Process	First law
isolated	$q = 0$, $w = 0$, ΔE = 0
cyclic	ΔE = 0, $q = -w$
isothermal, ideal gas	ΔE = 0, $q = -w$
adiabatic	ΔE = w (compression heats)
isochoric	$w = 0$, ΔE = q_V
isobaric	ΔE = $q_P - P\Delta V$ (work is done)

- ΔH = ΔE + PΔV at constant P; with $\Delta E = q_P - P\Delta V$ → **ΔH = q_P**
- $\Delta n_g = 0$ ($H_2 + Cl_2 \rightarrow 2HCl$): ΔH = ΔE; $N_2 + 3H_2 \rightarrow 2NH_3$ (−91.8 kJ): $\Delta n_g = -2$, ΔE = −91.8 + 4.96 = −86.8 kJ
- exothermic (ΔH < 0): burning, respiration, neutralization, freezing, condensation; surroundings warm
- endothermic (ΔH > 0): photosynthesis, melting, evaporation, NH_4NO_3 dissolving, $CaCO_3$ decomposing
- reversing a process changes the sign: ice melting +6.01, freezing −6.01 kJ/mol
- standard state: pure, most stable form at 1 bar (1 atm in older books, ~1%)

Enthalpies of reaction (4.6)

- solution: NH_4NO_3 +25.7 (cold pack), NaOH −44.5, $CaCl_2$ −82.8 kJ/mol
- $N_2 + O_2 \longrightarrow 2\,NO$ +181 kJ; $2\,NO + O_2 \longrightarrow 2\,NO_2$ −114 kJ
- formation: $H_2O(l)$ −285.8, CO_2 −393.5, CO −110.5 kJ/mol; C(diamond) +1.9 (not zero)
- more negative ΔH°f, more stable relative to the elements
- not formation: $2H_2 + O_2 \rightarrow 2H_2O$ (2 mol); $CO + \frac{1}{2}O_2 \rightarrow CO_2$ (CO not an element)
- combustion: CH_4 −890.3, C_2H_5OH −1367; each CH_2 adds ~660 (ethane −1560, propane −2219, butane −2877)
- calorific value: CH_4 890.3/16.04 = **55.5 kJ/g**; ethane 1560/30.07 = 51.9; ethanol 29.7; dry wood ~18
- fossil fuels: high, add ancient CO_2; biofuels lower (contain O), renewable

Thermochemistry (4.7)

- **Lavoisier–Laplace**: heat to split a compound into its elements = heat of forming it, opposite sign ($S + O_2 \rightarrow SO_2$ −296.8; reverse +296.8)

- **Hess**: same ΔH by one step or several (ΔH a state function)
- C → CO (−110.5) → CO_2 (−283.0): −393.5 kJ, as burned directly
- CH_4 to H_2O(g) −802, condensing −88: −890 kJ
- rules: add and subtract equations and ΔH; reverse → change sign; × n → ΔH × n; states must match
- uses: ΔH that can't be measured (benzene, graphite → diamond, hydration of salts, lattice energies)
- benzene: 6(−394) + 3(−286) − (−3268) = **+46 kJ/mol**
- ethanol: 2(−393.5) + 3(−285.8) − (−1367) = **−277 kJ/mol**; model paper in kcal: 2(−94) + 3(−68.5) − (−330) = −63.5 kcal
- graphite → diamond: −393.5 − (−395.4) = +1.9 kJ; graphite more stable

Bond	kJ/mol	Bond	kJ/mol
H–H	436	C=O (CO_2)	805
C–H	413	O–H	464
C–C, C=C, C≡C	347, 612, 837	O=O	498
C–F, C–Cl, C–I	485, 339, 240	N≡N	945

- bond enthalpy rises with **bond order**, shorter **length**, smaller atoms, electronegativity difference; N≡N 945: air's N_2 unreactive
- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$(g): broken 4(413) + 2(498) = 2648; formed 2(805) + 4(464) = 3466; ΔH = **−818 kJ** (averages, gas: not −890)

Entropy, second law (4.8–4.9)

- spontaneous: water downhill, ice melting at room T, rusting, gas spreading, heat hot → cold; reverse needs outside help (pumping, electrolysis, fridge)
- spontaneous ≠ fast (rusting; diamond → graphite)
- S: solid < liquid < gas; perfect crystal at 0 K has S = 0 (third law)
- ice melting: 6010/273 = **+22.0 J mol^{-1} K^{-1}**; water boiling: 40 700/373 = **+109**
- ΔS > 0: melting, boiling, sublimation, more gas moles, dissolving, splitting; ΔS < 0: freezing, condensing, gas used, precipitating
- $CaCO_3 \rightarrow CaO + CO_2$: (38.1 + 213.8) − 91.7 = +160.2 J K^{-1} mol^{-1}
- first law's limits: no direction, nothing on entropy, any efficiency allowed, can't predict feasibility
- 1000 J from 353 K to 293 K: −2.83 + 3.41 = **+0.58 J/K**
- second law: $\Delta S_{univ} > 0$ spontaneous, = 0 equilibrium; a system's S may fall (freezing, a tree) if the surroundings' rises more
- uses: no engine 100% efficient; fridges need work; photosynthesis

Gibbs energy and K (4.10–4.11)

- $\Delta G = -T\Delta S_{univ}$: spontaneous ⇔ ΔG < 0; = 0 equilibrium; > 0 the reverse is spontaneous

ΔH	ΔS	Spontaneous	Example
−	+	always	$2O_3 \rightarrow 3O_2$
+	−	never	$3O_2 \rightarrow 2O_3$
−	−	low T	freezing, condensing
+	+	high T	melting, boiling

- $CaCO_3$: ΔH° 179.2 kJ, ΔS° 160.2 J/K: T = 179 200/160.2 = **1119 K** (~846 °C)
- water ⇌ ice at 0 °C: ΔG = 0, ΔS_{univ} = 0, equilibrium; ice melts above, water freezes below
- ΔG° < 0 → K > 1 (products); = 0 → K = 1; > 0 → K < 1
- every 5.7 kJ/mol of ΔG° at 298 K: K × 10
- $N_2 + 3H_2 \rightleftharpoons 2NH_3$: ΔG° = −91.8 − 298(−0.1981) = −32.8 kJ; log K = 5.75, K = 5.6 × 10^5
- ΔG° (standard states) fixes K; ΔG (the mixture now) is 0 at equilibrium

COMMON MISTAKES

✗ ΔE = q + w and ΔE = q − w in one answer
✓ one convention: *w* on the system +.

✗ isobaric: no work
✓ isochoric: no work; isobaric does PΔV.

✗ isochoric: ΔE = q + PΔV
✓ $\Delta E = q_V$.

✗ isolated: q = w
✓ q = 0, w = 0, ΔE = 0.

✗ heat is an extensive property
✓ a path function.

✗ calorific value of CH_4 222.5 kJ/g
✓ 890.3 ÷ 16.04 = 55.5.

✗ ice melting ΔH negative
✓ +6.01 kJ/mol.

✗ ΔG > 0 spontaneous
✓ ΔG < 0.

✗ ΔG° = 0 at equilibrium
✓ ΔG = 0; ΔG° = 0 means K = 1.

✗ $\Delta S_{univ} > 0$ is the first law
✓ the second.

✗ S° of O_2 = 0
✓ 205.2 J K^{-1} mol^{-1} (only ΔH°f is 0).

✗ T = ΔH/ΔS with kJ over J
✓ convert first.