Unit 4 · First Law of Thermodynamics

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Heat and Thermodynamics (Units 4–5 together): 7 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** an MCQ: which area of a P–V diagram is the work done in a cycle (the area enclosed by the loop)
- **MCQ (1 mark)**
  - not a type of system
  - first law conserves energy
  - adiabatic expansion: cools
  - constant in an isothermal process
  - $C_P - C_V = R$
  - isochoric work: zero
  - isothermal work $nRT \ln(V_f/V_i)$
  - adiabatic compression: hotter
  - work against a steady outside pressure
  - final T, P from $TV^{\gamma-1}, PV^{\gamma}$
- **Short (5 marks, in parts)**
  - systems with examples; work by vs on; indicator diagram
  - internal energy; $dU = -dW$; ideal vs real gas
  - state the first law; its limits
  - two specific heats; derive Mayer's relation; $C_P > C_V$; γ and atomicity
  - the four processes on P–V diagrams; derive $PV^{\gamma} =$ constant; isothermal and adiabatic work
  - reversible vs irreversible
  - numericals: $\Delta U = Q - W$; $nC_V \Delta T$; isobaric and isothermal work; adiabatic final T

Key terms

Thermodynamics: heat, work and the energy stored in matter, and how they change into one another.

System: the part of matter or space we study; the rest, across its **boundary**, is the **surroundings**.

Open / closed / isolated system: exchanges matter and energy (open pot) / energy only (gas behind a piston) / neither (closed vacuum flask).

Thermodynamic equilibrium: same T and P throughout, no chemical change; nothing changes with time.

State variables: one value in each state (P, V, T, U, entropy, enthalpy); **process variables**: depend on the path (work, heat).

Work done: energy transferred when a force acts and the boundary moves; a path function.

Indicator diagram: P–V graph of the working gas.

Internal energy U: sum of the KE and PE of all the molecules; a state function.

Mechanical equivalent of heat J: work that makes one unit of heat; 4.18 J/cal.

First law: heat given = rise in internal energy + external work done.

Molar specific heat capacity: heat to raise one mole by 1 K; C_V at constant volume, C_P at constant pressure.

Degrees of freedom: independent ways a molecule can store energy.

Equipartition: each degree of freedom gets $\frac{1}{2}k_BT$ per molecule ($\frac{1}{2}RT$ per mole).

Quasi-static: slow enough to pass through equilibrium states.

Isothermal / adiabatic / isobaric / isochoric: constant T / no heat exchanged / constant P / constant V.

Reversible process: can be run back so that system **and** surroundings return exactly; an ideal.

Formulas

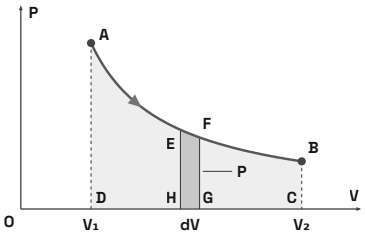
$dW = P\,dV$, $W = \int_{V_1}^{V_2} P\,dV$	area under the P–V curve **Use:** work by a gas
$dQ = dU + dW = dU + P\,dV$	Q in +, W by the gas + **Use:** first law
$W = JH$	$J = 4.18$ J/cal **Use:** work into heat
$C_P - C_V = R$; $c_P - c_V = r$	$r = R/M$ (air 287 J/(kg K)) **Use:** Mayer's relation
$U = \frac{f}{2}RT$, $C_V = \frac{f}{2}R$	per mole **Use:** degrees of freedom
$\gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$	1.67, 1.40, 1.33 **Use:** adiabatic index
$PV =$ constant	Boyle **Use:** isothermal
$W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$	$\ln x = 2.303 \log x$ **Use:** isothermal work
PV^γ, $TV^{\gamma-1}$, $T^\gamma/P^{\gamma-1}$ constant	ideal gas **Use:** adiabatic
$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{nR(T_1 - T_2)}{\gamma - 1}$	$= -\Delta U$ **Use:** adiabatic work
$W = P(V_2 - V_1) = nR\Delta T$	$Q = nC_P\Delta T$ **Use:** isobaric
$W = 0$, $Q = \Delta U = nC_V\Delta T$	P/T constant **Use:** isochoric

Systems, variables, work

- four laws: zeroth (temperature), first (energy conserved), second (direction of heat), third (0 K never reached)
- a sealed bottle on a table: closed (heat in, no matter)
- state vs process: Phulchoki's height vs the trail walked; a gas "contains" U, not heat or work
- **sign**: expansion $dV > 0$, work **by** the gas +; compression, work by the gas −
- chemistry's $\Delta U = Q + W$ counts work done **on** the gas: same law; say which you use

$dW = P\,dV$ (piston of area A)

1. $F = PA$; moves dx: $dW = PA\,dx$
2. $A\,dx = dV \rightarrow dW = P\,dV$; $W = \int P\,dV$
3. constant P only: $W = P\,\Delta V$



Strip EFGH under the step EF: area $P\,dV$; all strips fill ABCD.

- area under the curve = work; different paths between A and B → different work and heat, **same** ΔU
- cycle: net work = **area enclosed**; clockwise → positive (engine); anticlockwise → negative (refrigerator)

Internal energy and the first law

- KE (depends on T) + PE of attraction (depends on V): $U = f(V, T)$
- latent heat: T steady, heat raises the molecules' **PE**; U least as a solid, most as a gas
- **ideal gas**: no attraction → U depends on T only; monatomic $U = \frac{3}{2}nRT$
- **real gas**: U depends on T **and** V
- cycle: $\Delta U = 0$
- no heat ($dQ = 0$): $dU = -dW$: expanding gas cools (deodorant can), compressed gas warms (bicycle pump)
- signs: Q + into the system; ΔU + when it warms; W + when it expands

Limits of the first law

1. doesn't say which way heat flows
2. doesn't give the conditions for heat → work
3. work → heat completely, but heat → work never completely in a cycle
4. doesn't limit an engine's efficiency

Specific heats of a gas

- heat needed depends on whether the gas may expand → two heat capacities
- C_V: rigid container, no work, all heat → U; C_P: free piston, U rises the same **and** work is done → more heat

Mayer's relation

1. constant V: $dQ_V = dU = C_V\,dT$ (true for any process of an ideal gas)
2. constant P: $C_P\,dT = C_V\,dT + P\,dV$
3. $PV = RT \rightarrow P\,dV = R\,dT$
4. $C_P - C_V = R$: the extra is the expansion work

- heat capacity zero (adiabatic, $dQ = 0$) to infinite (isothermal, $dT = 0$): say how the gas is heated

Gas	f	C_V	C_P	γ
monatomic (He, Ar)	3	$\frac{3}{2}R$	$\frac{5}{2}R$	1.67
diatomic (N_2, O_2, air)	5	$\frac{5}{2}R$	$\frac{7}{2}R$	1.40
non-linear (H_2O, CH_4)	6	$3R$	$4R$	1.33

- translational 3 (all); rotational 2 (linear) or 3 (non-linear); each vibration mode 2, only when hot
- more degrees of freedom $\rightarrow$ smaller γ; CO_2 measures 1.29 (vibrations begin)

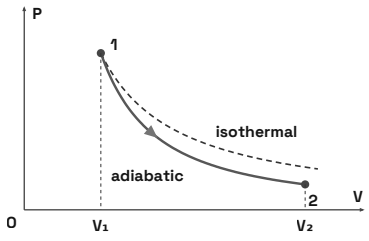
The four processes

- **isothermal**: thin conducting walls, a heat reservoir, slow; $dT = 0 \rightarrow \Delta U = 0$, $Q = W$
- isothermal work: $W = \int \frac{nRT}{V}dV = nRT \ln \frac{V_2}{V_1}$
- **adiabatic**: insulated, or fast (tyre bursting, engine stroke, sound, air over mountains); $Q = 0 \rightarrow W = -\Delta U$: expansion **cools**, compression **heats**

PV^γ = constant: derivation

1. $nC_V\,dT + P\,dV = 0$
2. $PV = nRT \rightarrow dT = \frac{P\,dV + V\,dP}{nR}$
3. substitute, $\times R$: $(C_V + R)P\,dV + C_V V\,dP = 0$
4. $C_V + R = C_P$; $\div C_V PV$: $\gamma\frac{dV}{V} + \frac{dP}{P} = 0$
5. integrate: $\ln(PV^\gamma) = \text{constant} \rightarrow PV^\gamma = \text{constant}$

- adiabatic work: $P = K/V^\gamma$, $W = \frac{K}{1-\gamma}(V_2^{1-\gamma} - V_1^{1-\gamma}) = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$
- quicker: $W = nC_V(T_1 - T_2)$, $C_V = \frac{R}{\gamma - 1}$



Adiabat from state 1 with the isotherm (dashed): the adiabat is steeper.

- slopes: isothermal $dP/dV = -P/V$; adiabatic $-\gamma P/V$: γ **times** steeper (the gas also cools)
- **isobaric**: horizontal line; V/T constant; boiling in an open pot
- **isochoric**: vertical line, no area $\rightarrow$ no work; P/T constant; pressure cooker heating up, the spark in a petrol engine

Process	Constant	W	Q	ΔU
isothermal	T	$nRT \ln \frac{V_2}{V_1}$	W	0
adiabatic	no heat	$\frac{nR(T_1 - T_2)}{\gamma - 1}$	0	$-W$
isobaric	P	$P\Delta V$	$nC_P\Delta T$	$nC_V\Delta T$
isochoric	V	0	$nC_V\Delta T$	Q

Reversible and irreversible

Reversible needs

1. infinitely slow (quasi-static)
2. no energy dissipated
3. system and surroundings in equilibrium at every step
4. no friction, viscosity or resistance

- near-reversible: slow frictionless expansion; a frictionless pendulum
- **irreversible**: permanent change, energy dissipated, entropy rises: rusting, rotting leaves, friction, tea cooling, a burst tyre, milk mixing into tea; every real process
- an irreversible change has no curve on a P–V diagram (only its end states)
- slow is not enough: a slow leak or slow friction is still irreversible

COMMON MISTAKES

✗ work is a state function
✓ a **path** function; U is the state function.

✗ isothermal: no heat flows
✓ $\Delta U = 0$, heat in = work out.

✗ adiabatic work $= P(V_2 - V_1)$
✓ $\frac{P_1V_1 - P_2V_2}{\gamma - 1}$; P isn't constant.

✗ $C_P = C_V$ for a gas
✓ $C_P - C_V = R$: expansion work.

✗ an ideal gas's U depends on volume
✓ on T only.

✗ the adiabat is flatter
✓ γ **times steeper**.

✗ any slow process is reversible
✓ also nothing dissipated.