

# Thermodynamics Laws & Specific Heats of Gases

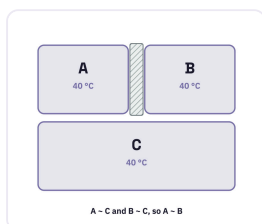
Last-minute revision: the key ideas, standard results and traps of every part. The formula sheet is the last page.

## If you only have five minutes

- 1 First law:  $\Delta Q = \Delta U + \Delta W$ , with  $Q$  in and  $W$  by the gas positive.
- 2  $\Delta U = nC_V \Delta T$  in every process;  $Q$  and  $W$  depend on the path.
- 3  $W$  = area under the  $P$ - $V$  curve; a cycle's net work is the loop area (+ clockwise).
- 4  $C_p - C_V = R$ ;  $\gamma = (f + 2)/f$ ; mixtures add  $n/(\gamma - 1)$ .
- 5 Isothermal  $W = nRT \ln(V_2/V_1)$ ; adiabatic  $PV^\gamma$ ,  $TV^{\gamma-1}$  constant,  $W = nR\Delta T/(\gamma - 1)$ .
- 6 Free expansion:  $Q = W = \Delta U = 0$ . Polytropic  $C = R/(\gamma - 1) + R/(1 - n)$ .
- 7 Engine  $\eta = 1 - Q_2/Q_1$ ; fridge  $\text{COP} = Q_2/W$ ; Carnot  $\eta = 1 - T_2/T_1$  in kelvin.

## 1 Thermal Equilibrium and the Zeroth Law

- Bodies in contact exchange heat until  $T$  is equal: thermal equilibrium.
- Zeroth law:  $A \sim C$  and  $B \sim C \Rightarrow A \sim B$ . It defines temperature (a thermometer is body  $C$ ).
- Equal temperature  $\neq$  equal heat content.

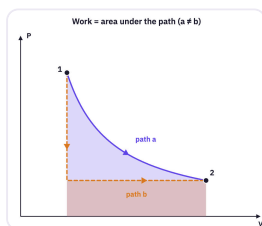


### TRAPS

- Thinking bodies in equilibrium have the same heat content** Only the temperature is equal; heat content depends on mass and material.
- Thinking A and B must touch to be in equilibrium** The zeroth law needs only that each is in equilibrium with a common third body.

## 2 First Law of Thermodynamics

- First law:  $\Delta Q = \Delta U + \Delta W$  ( $dQ = dU + dW$ ).  $Q$  in  $> 0$ ,  $W$  by gas  $> 0$ .
- $Q = nC \Delta T$ ;  $C$  depends on the process.
- $W = \int P dV$  = area under the  $P$ - $V$  curve; depends on the path.
- $\Delta U = \frac{f}{2} nR \Delta T$  for any process.



### STANDARD RESULTS

1 mol,  $0 \rightarrow 100^\circ\text{C}$  at 1 atm:  $W \approx 831 \text{ J}$ .

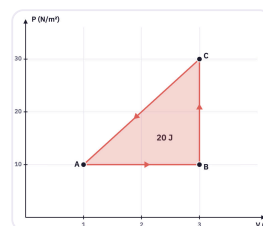
$\text{H}_2$  cooled 55 K at constant  $V$ :  $\Delta U = Q \approx -252 \text{ J}$ .

### TRAPS

- Assuming a gas has one fixed specific heat  $C$**  depends on the process:  $C_V$  at constant volume,  $C_p$  at constant pressure, others in between.
- Thinking  $\Delta U$  depends on the path**  $U$  depends only on  $T$ :  $\Delta U = \frac{f}{2} nR \Delta T$  for any path between the same temperatures.
- Mixing up signs** Heat given out is  $Q < 0$ ; work done on the gas is  $W < 0$ .

## 3 Indicator Diagrams, State Variables and Cycles

- Point = state, curve = process, area under it =  $W$ .
- $Q, W$ : path variables.  $U$ : state variable ( $\Delta U = Q - W$  same for every path).
- Cycle:  $\Delta U = 0$ ,  $Q_{\text{net}} = W_{\text{net}}$  = area enclosed.
- Clockwise:  $W$  by gas (engine). Anticlockwise:  $W$  on gas, heat out (fridge).



### STANDARD RESULTS

Triangle (1,10)(3,10)(3,30) anticlockwise:  $W = -20 \text{ J}$ .

$V$ - $T$  cycle ( $300 \rightarrow 500 \text{ K}$ ,  $\times 5/3$ ):  $Q_{\text{net}} \approx 461 \text{ J}$ .

### TRAPS

- Assuming equal  $\Delta U$  means equal  $Q$  and  $W$**  Only  $Q - W$  is path-independent;  $Q$  and  $W$  separately change from path to path.
- Assuming every cycle does positive work** Clockwise: work by the gas. Anticlockwise: work on the gas, heat rejected.
- Forgetting  $\Delta U = 0$  over a full cycle** Back at the start means the same  $T$ , so  $\Delta U = 0$  and  $Q_{\text{net}} = W_{\text{net}}$ .

## 4 Molar Specific Heats: $C_V$ , $C_p$ and $\gamma$

- $C_V = \frac{f}{2} R$  (constant  $V$ :  $dQ = dU$ ).
- Mayer:  $C_p = C_V + R$ ; the extra  $R$  pays for the work.
- $\gamma = (f + 2)/f$ ;  $C_V = R/(\gamma - 1)$ .
- Mixture:  $\sum n_i/(\gamma_i - 1) = \sum n_i/(\gamma_{\text{mix}} - 1)$ .

| Heat capacities and $\gamma$          |     |                |                |              |
|---------------------------------------|-----|----------------|----------------|--------------|
| Gas                                   | $f$ | $C_V$          | $C_p$          | $\gamma$     |
| Monatomic (He)                        | 3   | $\frac{3}{2}R$ | $\frac{5}{2}R$ | $5/3 = 1.67$ |
| Diatomic ( $\text{N}_2, \text{O}_2$ ) | 5   | $\frac{5}{2}R$ | $\frac{7}{2}R$ | $7/5 = 1.4$  |
| Non-linear ( $\text{CH}_4$ )          | 6   | $3R$           | $4R$           | $4/3 = 1.33$ |

### STANDARD RESULTS

2 mol mono + 3 mol di:  $\gamma_{\text{mix}} \approx 1.48$  (not 1.51).

## TRAPS

- ✗ **Using  $C_V$  in a constant-pressure problem (or the reverse)** Constant volume:  $C_V$ . Constant pressure:  $C_p = C_V + R$ .
- ✗ **Averaging  $\gamma$  by moles for a mixture** Average  $C_V$  (equivalently add  $n/(\gamma - 1)$ ), then find  $\gamma$ .
- ✗ **Using  $f = 7$  for a diatomic gas at room temperature** Vibration is frozen at ordinary temperatures:  $f = 5$ ,  $\gamma = 1.4$ .

## 5 Isochoric, Isobaric and Isothermal Processes

- Isochoric:  $W = 0$ ,  $Q = \Delta U = nC_V \Delta T$ ,  $P/T$  constant.
- Isobaric:  $W = nR\Delta T$ ,  $Q = nC_p \Delta T$ .
- Isothermal:  $\Delta U = 0$ ,  $Q = W = nRT \ln(V_2/V_1)$ .
- Every process:  $\Delta U = nC_V \Delta T$ .

| Q, W and $\Delta U$ for n moles |                           |                 |                 |  |
|---------------------------------|---------------------------|-----------------|-----------------|--|
| Process                         | W                         | Q               | $\Delta U$      |  |
| Isochoric                       | 0                         | $nC_V \Delta T$ | $nC_V \Delta T$ |  |
| Isobaric                        | $nR\Delta T$              | $nC_p \Delta T$ | $nC_p \Delta T$ |  |
| Isothermal                      | $nRT \ln \frac{V_2}{V_1}$ | $= W$           | 0               |  |

## STANDARD RESULTS

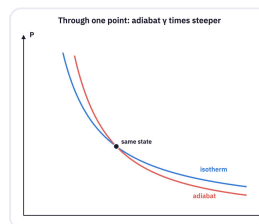
1 mol at 300 K, V doubled isothermally:  $W = Q \approx 1729$  J.

## TRAPS

- ✗ **Using  $\log_{10}$  in  $W = nRT \ln(V_2/V_1)$**  It is the natural log:  $\ln 2 = 0.693$ , not 0.301.
- ✗ **Writing  $\Delta U = nC_p \Delta T$  in an isobaric process**  $\Delta U$  is always  $nC_V \Delta T$ ;  $nC_p \Delta T$  is the heat  $Q$ .
- ✗ **Thinking an isothermal process has no heat**  $\Delta U = 0$ , but  $Q = W \neq 0$ : all the heat becomes work.

## 6 Adiabatic Process

- Adiabatic:  $Q = 0$ ,  $W = -\Delta U$ .
- $PV^\gamma$ ,  $TV^{\gamma-1}$ ,  $TP^{1-\gamma}$  constant.
- Adiabatic  $\gamma$  times steeper than the isotherm.
- $W = nR(T_1 - T_2)/(\gamma - 1)$ ;  
 $B_{adi} = \gamma P$ ,  $B_{iso} = P$ .



## STANDARD RESULTS

$\gamma = 1.5$ , 16 L  $\rightarrow$  12 L:  $P \times 1.54$ ,  $T \times 1.15$ .

Monatomic,  $V \rightarrow 8V$  adiabatically:  $T$  falls to  $T/4$ .

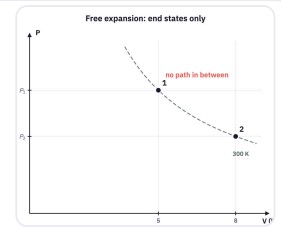
## TRAPS

- ✗ **Swapping  $\gamma$  and  $\gamma - 1$**   $PV^\gamma$  for pressure,  $TV^{\gamma-1}$  for temperature.
- ✗ **Thinking  $Q = 0$  means no temperature change** Adiabatic compression always heats the gas; expansion cools it.
- ✗ **Using  $B = P$  for sound** Sound compressions are adiabatic:  $B = \gamma P$ .

## 7 Free Expansion of a Gas

- Free expansion:  $W = 0$  (nothing to push),  $Q = 0$  (insulated),  $\Delta U = 0$ .

- Ideal gas:  $T$  unchanged; end states obey  $P_1 V_1 = P_2 V_2$ .
- Irreversible: no  $P$ - $V$  path, not isothermal, not  $PV^\gamma$ .



## STANDARD RESULTS

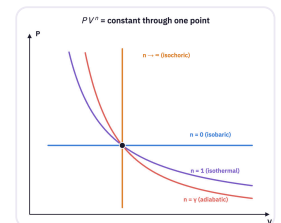
5 L  $\rightarrow$  8 L at 300 K:  $P_2 = 6.25 \times 10^4$  Pa.

## TRAPS

- ✗ **Assuming the gas does work because its volume grows** Work needs something to push against; a vacuum offers nothing.
- ✗ **Using  $PV^\gamma = \text{constant}$  because  $Q = 0$**  Free expansion isn't a slow, reversible adiabatic process; only  $P_1 V_1 = P_2 V_2$  holds for the end states.

## 8 Polytropic Process

- $PV^n = \text{constant}$ ;  $n$  is the polytropic index.
- $C = \frac{R}{\gamma - 1} + \frac{R}{1 - n}$ .
- $n = 0 \rightarrow C_p$ ,  $1 \rightarrow \infty$ ,  $\gamma \rightarrow 0$ ,  $\infty \rightarrow C_V$ .
- Slope  $dP/dV = -nP/V$ :  $n$  times the isotherm's.



## STANDARD RESULTS

Monatomic,  $PV^2 = \text{const}$ :  $C = 0.5R$ .

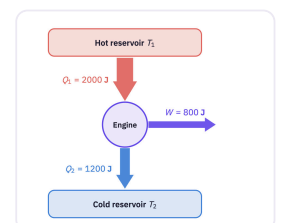
Diatomic,  $PV^3 = \text{const}$ :  $C = 2R$ .

## TRAPS

- ✗ **Confusing the polytropic index  $n$  with the number of moles** In  $PV^n$ ,  $n$  is a pure number; the moles are a separate quantity.
- ✗ **Flipping the sign of  $R/(1 - n)$**   $C = \frac{R}{\gamma - 1} + \frac{R}{1 - n}$ ; for  $n > 1$  the second term is negative.

## 9 Reversible Processes, Heat Engines and Refrigerators

- Reversible: system and surroundings restorable; quasi-static, no friction.
- Engine:  $W = Q_1 - Q_2$ ;  $\eta = W/Q_1 = 1 - Q_2/Q_1 < 1$ .
- Refrigerator:  $Q_1 = Q_2 + W$ ;  
 $\text{COP} = Q_2/W = Q_2/(Q_1 - Q_2)$ .



## STANDARD RESULTS

2000 J in, 1200 J out:  $W = 800$  J,  $\eta = 40\%$ .

Fridge 400 J out of cold with 100 J work:  $\text{COP} 4$ , 500 J rejected.

## TRAPS

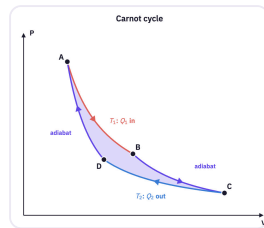
- ✗ **Calling COP an efficiency**  $\text{COP} = \text{heat removed per joule of work}$  and is usually more than 1.

✗ **Thinking an engine can reject no heat** Some heat must always go to the cold reservoir (Part 10: Kelvin–Planck).

✗ **Using  $\eta = Q_2/Q_1$**   $\eta = W/Q_1 = 1 - Q_2/Q_1$ .

## 10 Second Law and the Carnot Cycle

- Kelvin–Planck: no cyclic engine turns all heat into work.
- Clausius: heat doesn't flow cold  $\rightarrow$  hot by itself. Equivalent statements.
- Carnot: 2 isotherms + 2 adiabats;  $Q_2/Q_1 = T_2/T_1$ .
- $\eta_{Carnot} = 1 - T_2/T_1$  (kelvin): the upper limit.



### STANDARD RESULTS

600 K / 300 K,  $Q_1 = 1000$  J:  $\eta = 50\%$ ,  $W = 500$  J.

### TRAPS

- ✗ **Using Celsius in  $\eta = 1 - T_2/T_1$**  Always use kelvin.
- ✗ **Expecting a real engine to reach Carnot efficiency** Carnot is the upper limit; real (irreversible) engines do worse.
- ✗ **Thinking a perfect engine breaks the first law** It conserves energy; it breaks the second law (Kelvin–Planck).

# Thermodynamics Laws & Specific Heats of Gases

R 8.314 J/mol·K

 1 atm  $1.013 \times 10^5$  Pa

Signs Q &gt; 0 heat in · W &gt; 0 work by gas

γ mono 5/3 · di 7/5

## 1 Thermal Equilibrium and the Zeroth Law

- Zeroth law: A ~ C and B ~ C ⇒ A ~ B. Equal T, not equal energy.

## 2 First Law of Thermodynamics

$$dQ = dU + dW$$

$$\Delta Q = \Delta U + \Delta W$$

$$dQ = nC dT$$

$$Q = nC(T_2 - T_1)$$

$$dW = P dV$$

$$W = \int_{V_1}^{V_2} P dV$$

$$dU = \frac{f}{2} nR dT$$

$$\Delta U = \frac{f}{2} nR(T_2 - T_1)$$

- Signs: Q > 0 heat in, W > 0 work by the gas. U depends only on T.

## 3 Indicator Diagrams, State Variables and Cycles

$$W = \int_{V_1}^{V_2} f(V) dV$$

$$\Delta U_{12} = Q - W \text{ (any path)}$$

$$\Delta U_{\text{cycle}} = 0$$

$$Q_{\text{net}} = W_{\text{net}} = \text{loop area}$$

- Point = state; area under path = W. Cycle: ΔU = 0, W<sub>net</sub> = loop area (+ clockwise, - anticlockwise).

## 4 Molar Specific Heats: C<sub>v</sub>, C<sub>p</sub> and γ

$$C_v = \frac{f}{2} R$$

$$C_p = C_v + R = \frac{f+2}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{f+2}{f}$$

$$\frac{n_1}{\gamma_1 - 1} + \frac{n_2}{\gamma_2 - 1} = \frac{n_1 + n_2}{\gamma_{\text{eq}} - 1}$$

- Mono: C<sub>v</sub> = 3R/2, γ = 5/3 · di: C<sub>v</sub> = 5R/2, γ = 7/5 · C<sub>v</sub> = R/(γ - 1).

## 5 Isochoric, Isobaric and Isothermal Processes

$$\text{isochoric: } W = 0$$

$$Q = \Delta U = nC_v \Delta T = \frac{nR \Delta T}{\gamma - 1}$$

$$\text{isobaric: } W = nR(T_2 - T_1)$$

$$Q = nC_p \Delta T$$

$$\Delta U = nC_v \Delta T \text{ (any process)}$$

$$\text{isothermal: } PV = \text{const}$$

$$W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

$$Q = W$$

- Always ΔU = nC<sub>v</sub>ΔT. Isothermal: W = nRT ln(V<sub>2</sub>/V<sub>1</sub>).

## 6 Adiabatic Process

$$\text{adiabatic: } PV^\gamma = \text{const}$$

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

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{nR(T_1 - T_2)}{\gamma - 1}$$

- Adiabatic slope = γ × isotherm slope. B<sub>iso</sub> = P, B<sub>adi</sub> = γP.

## 7 Free Expansion of a Gas

$$Q = 0, W = 0, \Delta U = 0$$

$$P_1 V_1 = P_2 V_2$$

- Free expansion: Q = W = ΔU = 0; T unchanged (ideal gas).

## 8 Polytropic Process

$$PV^n = \text{const}$$

$$C = \frac{R}{\gamma - 1} + \frac{R}{1 - n}$$

$$\frac{dP}{dV} = -n \frac{P}{V}$$

- n = 0, 1, γ, ∞ → isobaric, isothermal, adiabatic, isochoric.

## 9 Reversible Processes, Heat Engines and Refrigerators

$$W = Q_1 - Q_2$$

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

- Engine: W = Q<sub>1</sub> - Q<sub>2</sub>, η = 1 - Q<sub>2</sub>/Q<sub>1</sub>. Fridge: COP = Q<sub>2</sub>/W.

## 10 Second Law and the Carnot Cycle

$$\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1}$$

- Kelvin–Planck: no 100% engine. Clausius: no cold → hot without work.