Unit 4

# First Law of Thermodynamics

This unit online, with its interactives:
science-playground.com/s/12f4

Pump up a bicycle tyre and feel the end of the pump: it gets warm. Press the button of a can of spray deodorant for a few seconds and the can turns cold in your hand. Leave a pressure cooker on the stove with its weight in place and the pressure inside climbs, though nothing is pushed into it but heat. In each case **heat**, **work** and the **energy stored inside a gas** are trading places.

This unit keeps the accounts of that trade. Its main rule, the **first law of thermodynamics**, is the law of conservation of energy written for heat engines: the heat you give a gas either stays inside it or comes out as work. With it you will see why squeezing a gas fast heats it, why a gas has two specific heat capacities, how to find the work a gas does from the area under a graph, and why the curve of a fast expansion is steeper than that of a slow one. The next unit asks the question this one can't answer: why can no engine turn all its heat into work?

## 4.1 Introduction

**Thermodynamics** is the branch of physics that deals with heat, work and the energy stored in matter, and with how they turn into one another. The word joins two Greek words: *thermē*, heat, and *dynamis*, power. It was born in the 1800s from a very practical question: how much work can a steam engine get from a tonne of coal?

The idea that work and heat are two forms of the same thing, energy, and can be changed into each other at a fixed rate, was proved by measurement in the 1840s, above all by the English brewer and physicist **James Prescott Joule** (Section 4.8). Thermodynamics has four laws:

- the **zeroth law**: two bodies each in thermal equilibrium with a third are in thermal equilibrium with each other. It makes temperature something that can be measured (Grade 11, Unit 9);
- the **first law**, this unit: energy is conserved, with heat counted as a form of energy;
- the **second law**, Unit 5: heat flows by itself only from hot to cold, and no engine can turn all its heat into work;
- the **third law**: absolute zero can be approached but never reached.

The first law says that the total energy of an **isolated system** stays constant. It brings in the three ideas of this unit, **heat**, **work** and **internal energy**, and it is the starting point for the study of gases, heat engines, refrigerators and many chemical and biological processes, down to what your body does with the dal bhat you eat.

A STORY FROM SCIENCE

### Maria Goeppert Mayer

**Maria Goeppert Mayer** (1906–1972) was born on 28 June 1906 in Kattowitz, then in Germany and now Katowice in Poland. She studied at the University of Göttingen, one of the great centers of the new quantum physics, and moved to the United States in 1930 with her husband, the chemist Joseph Mayer. Together they wrote *Statistical Mechanics* (1940), a textbook on how the laws of heat and temperature come from the motion of countless molecules, the subject of this unit and the next.

For most of the next thirty years universities would not give her a proper paid post, partly because her husband already worked there; much of the time she taught and researched without pay, for the love of the work. Her first full-time paid professorship came only in 1960, in San Diego. In 1948–49 she explained why nuclei with certain numbers of protons or neutrons (2, 8, 20, 28, 50, 82, 126, the "magic numbers") are especially stable: their particles fill shells, as electrons fill shells in an atom. For this **nuclear shell model** she shared the 1963 Nobel Prize in Physics, the second woman to win it, sixty years after Marie Curie. She died in San Diego, California, on 20 February 1972.



*Figure 4.1* *Maria Goeppert Mayer, who explained the "magic numbers" of nuclei, and with her husband wrote a textbook on the physics of heat.*
Photo: Nobel foundation, Public domain

## 4.2 Thermodynamic system

To keep accounts of energy you first have to say *whose* energy you are counting. A **thermodynamic system** is the particular part of matter or region of space we choose to study, separated from everything else by a **boundary**, real or imagined. Everything outside the boundary is the **surroundings**. The system together with its surroundings is sometimes called the *universe*.

A system is described by its large-scale (macroscopic) properties: its pressure, volume and temperature. It can interact with its surroundings in two ways: by exchanging **energy** (as heat or as work), and by exchanging **matter**. That gives three types of system (Figure 4.2):

1. **Open system:** exchanges both matter and energy with its surroundings. *Example:* water boiling in an open pot. Heat comes in from the flame, and steam (matter) leaves.
2. **Closed system:** exchanges energy but not matter. *Example:* a gas shut in a cylinder with a conducting wall and a movable piston. Heat can pass through the wall and the gas can do work on the piston, but no gas gets in or out. A pressure cooker with its weight in place is closed too, until the weight lifts and lets steam out.
3. **Isolated system:** exchanges neither energy nor matter. *Example:* hot water in a closed, insulated vacuum flask. No real system is perfectly isolated (a flask's tea does cool overnight), but a good flask comes close for a few hours.

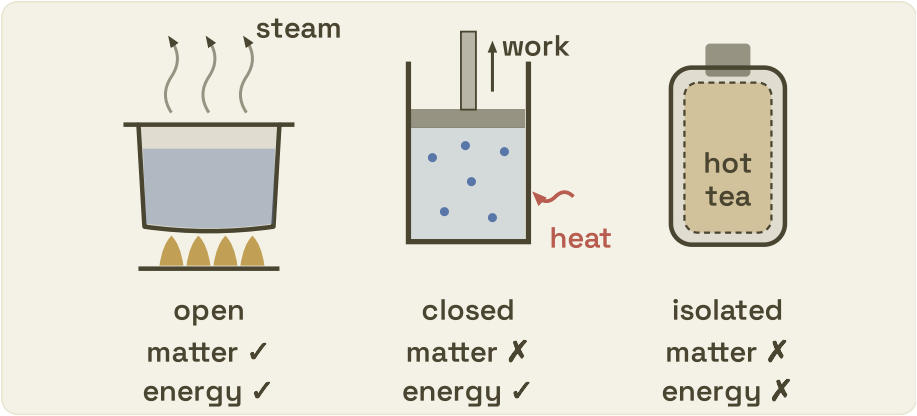



***Figure 4.2*** *The three kinds of system. An open pot on a flame takes in heat and lets steam out: matter and energy both cross its boundary. Gas in a cylinder with a piston can take in heat and push the piston, but no gas leaves. A stoppered vacuum flask lets neither through.*

**Check 1**

A sealed bottle of cold cold-drink is left on a table on a hot day. As a thermodynamic system, it is:

a open
b closed
c isolated
d none of these

## 4.3 Thermodynamic variables (thermodynamic coordinates)

When a system has settled down, so that nothing in it changes any more with time, it is in **thermodynamic equilibrium**: the same temperature everywhere (thermal equilibrium), no unbalanced forces, so the same pressure everywhere (mechanical equilibrium), and no chemical change going on. Its state can then be described by a few measurable quantities, the **thermodynamic variables** (or coordinates). They let us describe the system, and predict how it will behave.

They are of two kinds:

1. **State variables** (state functions) have a definite value in each equilibrium state, whatever happened to the system before: **pressure, volume, temperature, internal energy, entropy** (Unit 5) and **enthalpy** (chemistry's heat content, $U + PV$). A change in a state variable depends only on the starting and ending states.
2. **Process variables** describe something that happens *during* a change, and have no value in a state: **work** and **heat**. How much work is done or heat given depends on the path taken between the states.

An everyday picture: the height of the summit of Phulchoki above the Godavari road head is a state variable; it is the same whichever trail you take. The distance you walk and the sweat you lose are process variables: they depend on the trail. A gas "contains" internal energy, but it doesn't "contain" heat or work, any more than a hiker contains the trail.

**Check 2**

Which of these is **not** a state variable?

a temperature
b internal energy
c heat supplied
d volume

## 4.4 Work done

In mechanics, a force does work when its point of application moves: $W = Fs$ (Grade 11, Unit 5). In thermodynamics, the force usually comes from a **pressure**, and the movement is a **change of volume**: a gas pushing a piston out, or the air pushing a balloon's skin in. **Work done** is energy transferred because a force acts on a system and the system's boundary moves.

Work in thermodynamics is a **path function**: how much is done depends on the path the system takes from its first state to its last, not just on those two states (Section 4.7 shows why).

## 4.5 Positive and negative work

The work that matters is the work done **by the system on its surroundings**, and its sign is chosen so:

- **Positive work (work done by the system):** the system pushes its surroundings back. *Example:* a gas expanding and pushing a piston out, or the air in a bursting balloon pushing the room's air away. The gas gives energy to the surroundings.
- **Negative work (work done on the system):** the surroundings push the system in. *Example:* a gas being compressed by a piston, as in a bicycle pump. The surroundings give energy to the gas.

For a gas: **expansion**, $dV > 0$, work done by the gas positive; **compression**, $dV < 0$, work done by the gas negative.

> CAREFUL
> **Two sign conventions, one law**
>
> This unit, like most physics books, counts $W$ as the work done **by** the system, so the first law reads $dQ = dU + dW$. Chemistry books, and some physics books, count the work done **on** the system instead, and write $\Delta U = Q + W$. Both say the same thing: work done on the gas is minus the work done by it. Nepal's Grade 12 curriculum puts it the second way, "increase of internal energy = heat into the system + work done on the system". In an exam, either is right, as long as you say which work you mean and keep its sign consistent from start to finish.

## 4.6 Work done during the expansion of a gas

Take a gas in a cylinder closed by a piston of cross-sectional area $A$, which is light and moves without friction (Figure 4.3). The gas, at pressure $P$, pushes on the piston with a force

$$F = PA$$

Let the gas expand from its first state $(P_1, V_1)$ to its last $(P_2, V_2)$. Over a very small part of the expansion the piston moves out a tiny distance $dx$, so little that the pressure stays $P$ during it.

1. The small work done by the gas is force × distance: $dW = F\,dx = PA\,dx$.
2. The piston sweeps out a volume $A\,dx$, which is the gas's increase in volume: $dV = A\,dx$.
3. So

$$\boxed{dW = P\,dV}$$

4. The total work done by the gas in the whole expansion is the sum of all these small pieces:

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

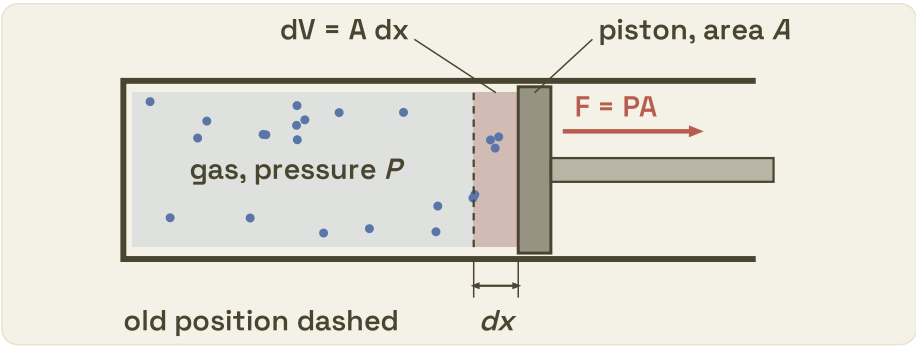



*Figure 4.3* *Gas at pressure $P$ pushes a piston of area $A$ with force $F = PA$. As the piston moves out a small distance $dx$, the gas's volume grows by $dV = A\,dx$, the shaded slice.*

To do the sum, you must know how $P$ changes with $V$ along the way, and that depends on the process: the pressure might stay the same, fall slowly (gas kept warm) or fall fast (gas cooling). Only if the pressure stays constant is it simply $W = P(V_2 - V_1) = P\,\Delta V$.

YOUR TURN

**Work at a constant pressure**

A gas at a steady pressure of $1.0 \times 10^5$ Pa is heated and expands from 2.0 L to 5.0 L. How much work does it do?

Answer

$\Delta V = 5.0 - 2.0 = 3.0$ L $= 3.0 \times 10^{-3}$ m³ (1 L = $10^{-3}$ m³).

$W = P\,\Delta V = 1.0 \times 10^5 \times 3.0 \times 10^{-3} =$ **300 J**, done by the gas.

## 4.7 Indicator diagram

An **indicator diagram** is a graph of the pressure of the working gas against its volume (a **P–V diagram**) as it expands or is compressed. The name comes from the steam age: in the 1790s James Watt's assistant John Southern made an "indicator", a pencil moved up and down by the pressure in an engine's cylinder while a card moved sideways with the piston, so that the engine drew its own P–V diagram as it ran. Engineers still use such diagrams to see how well an engine or a refrigerator works, and to find faults.

**Features of an indicator diagram:**

i. Volume is plotted across (the x-axis) and pressure up (the y-axis).

ii. The shape of the curve shows the kind of process (isothermal, adiabatic, isobaric, isochoric: Sections 4.11–4.13).

iii. The **area under the curve** is the work done in that process; for a cycle, a closed loop, the **area enclosed by the loop** is the net work done in one cycle.

Why the area? Let a gas expand from $A(P_1, V_1)$ to $B(P_2, V_2)$ along the curve AB (Figure 4.4). Cut the process into many tiny steps, like EF, in which the volume grows from $V$ to $V + dV$ while the pressure stays about $P$.

1. The strip under EF is (very nearly) a rectangle EFGH, with height $EH \approx FG = P$ and width $HG = dV$.
2. Its area is $EH \times HG = P\,dV$, which is the work done in going from $E(P, V)$ to $F(P, V + dV)$.
3. Adding all the strips from A to B, the total work done is the total area:

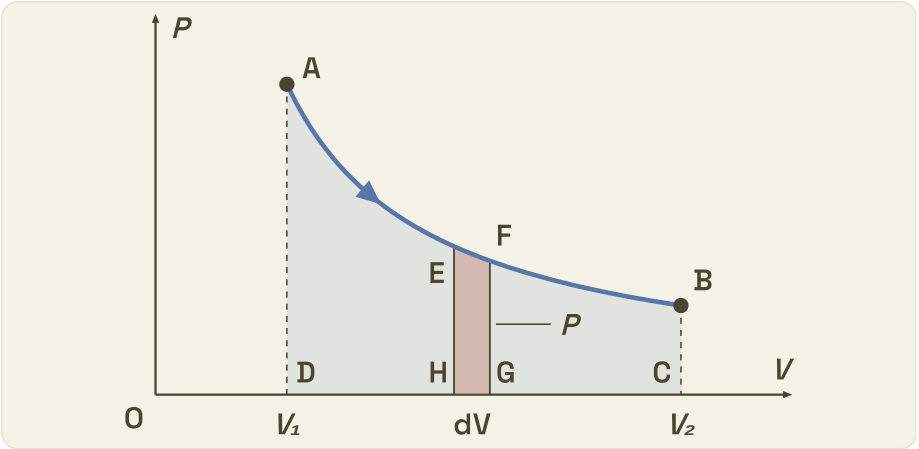



*Figure 4.4* *An indicator diagram: a gas expands from A to B. Under the small step EF, the thin strip EFGH has height P and width dV: its area, P dV, is the work done in that step. All such strips together fill the area ABCD under the curve.*

**Work depends on the path.** Two different curves between the same points A and B have different areas under them, so the gas does different amounts of work. That is what we meant by saying work is a **path function**. The widget shows it.

Two things to notice in the widget. The **work** is different for each path, but the **change in internal energy**, $\Delta U$, is always the same: it depends only on A and B. The **heat** taken in is the work plus $\Delta U$ (the first law, Section 4.9), so it depends on the path too.

**Cycles.** If the gas goes round a closed loop and returns to its first state, it does work on the parts of the loop where it expands (the area under the upper curve, positive) and has work done on it where it is compressed (the area under the lower curve, negative). What is left is the **area enclosed by the loop**. Going round **clockwise** on a P–V diagram, the expansion happens at the higher pressure, so the net work done by the gas is **positive**: this is what an engine does. Going round **anticlockwise**, the net work is negative: work is done on the gas, as in a refrigerator.

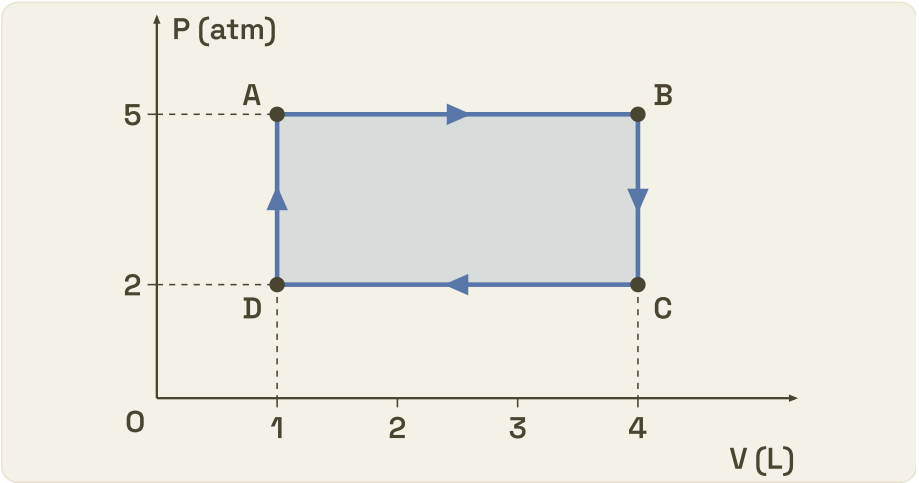



*Figure 4.5* *For Example 4.1: one mole of a gas goes round the rectangle ABCDA.*

WORKED EXAMPLE

### Example 4.1: a rectangular cycle

One mole of an ideal gas goes round the cycle ABCDA shown (Figure 4.5). Calculate the net work done in the cycle. (Take 1 atm = $10^6$ dyne/cm².)

**Answer**

The net work in a cycle is the area of the loop. The cycle goes A → B → C → D → A, clockwise, so the work done by the gas is positive.

Width of the loop: DC = 4 − 1 = 3 L = $3 \times 10^3$ cm³.

Height: AD = 5 − 2 = 3 atm = $3 \times 10^6$ dyne/cm².

$$W = +\text{area ABCD} = DC \times AD = 3 \times 10^3 \times 3 \times 10^6 = 9 \times 10^9 \text{ erg}$$

Since 1 J = $10^7$ erg, that is **900 J**. (With the exact value, 1 atm = $1.013 \times 10^6$ dyne/cm², it is 912 J.)

Check by parts: along AB the gas expands at 5 atm, doing 5 atm × 3 L of work; along CD it is compressed at 2 atm, having 2 atm × 3 L done on it; along BC and DA the volume doesn't change, so no work. Net: (5 − 2) atm × 3 L, the same.

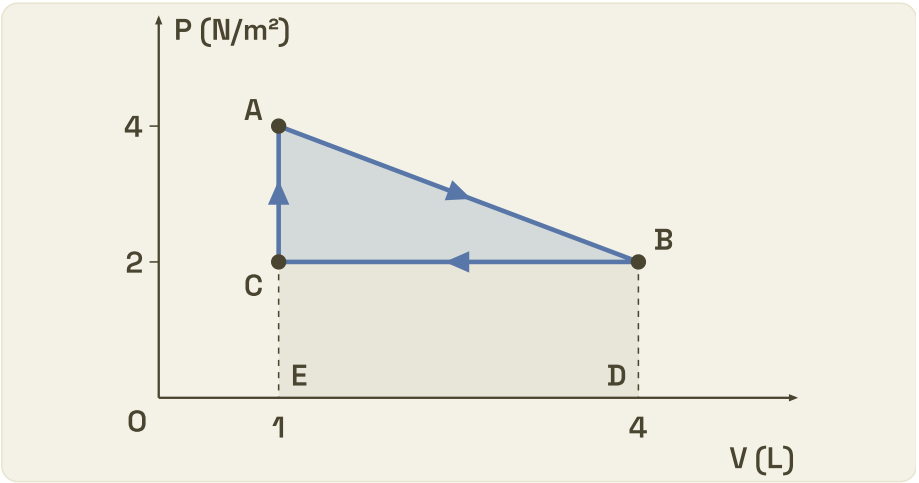



*Figure 4.6* For Example 4.2: the triangular cycle ABC, traced A → B → C → A.

WORKED EXAMPLE

### Example 4.2: a triangular cycle

The P–V diagram of a cyclic process is the triangle ABC, traced in the order A → B → C → A (Figure 4.6). The coordinates (P, V) of A, B and C are (4, 1), (2, 4) and (2, 1), with the pressure in N/m² and the volume in liters. Calculate the work done from A to B, from B to C and from C to A, and in the whole cycle.

Answer

So A is at $V = 1$ L, $P = 4$ N/m²; B at $V = 4$ L, $P = 2$ N/m²; C at $V = 1$ L, $P = 2$ N/m². Let D and E be the points on the volume axis below B and C ($V = 4$ L and $V = 1$ L).

**A to B:** the gas expands, so the work is **positive**, the area under AB: the triangle ABC plus the rectangle under BC (BCED).

$$W_{AB} = \tfrac{1}{2} \times BC \times AC + BC \times CE$$

BC = $4 - 1 = 3$ L = $3 \times 10^{-3}$ m³; AC = $4 - 2 = 2$ N/m²; CE = 2 N/m².

$$W_{AB} = \tfrac{1}{2} \times 3 \times 10^{-3} \times 2 + 3 \times 10^{-3} \times 2 = 3 \times 10^{-3} + 6 \times 10^{-3} = \mathbf{9 \times 10^{-3}\ J}$$

**B to C:** the gas is compressed at 2 N/m², so the work done by it is **negative**, the area of the rectangle BCED:

$$W_{BC} = -\,BC \times CE = -\,3 \times 10^{-3} \times 2 = \mathbf{-6 \times 10^{-3}\ J}$$

**C to A:** the volume doesn't change, so $W_{CA} = \mathbf{0}$.

**Whole cycle:**

$$W = 9 \times 10^{-3} - 6 \times 10^{-3} + 0 = \mathbf{3 \times 10^{-3}\ J}$$

Check: the cycle is traced clockwise, so the net work is positive and equals the area of the triangle: $\tfrac{1}{2} \times 3 \times 10^{-3} \times 2 = 3 \times 10^{-3}$ J.

(These pressures are tiny, a few millionths of an atmosphere, to keep the arithmetic simple; the method is what matters.)

Check 3

A gas is taken round a cycle that appears as a loop traced **anticlockwise** on a P–V diagram. Over one cycle, the net work done **by** the gas is:

a positive, equal to the area of the loop
b negative, equal in size to the area of the loop
c zero, since the gas returns to its first state
d equal to the area under the upper curve

## 4.8 Internal energy and latent heat

The molecules of every body are in constant random motion, so they have **kinetic energy**. In a gas, their average kinetic energy depends only on the temperature: $\tfrac{1}{2}mc_{\text{rms}}^2 = \tfrac{3}{2}k_BT$ (Grade 11, Unit 13). The molecules also attract one another, so they have **potential energy**, which depends on how far apart they are, and so on the volume.

The **internal energy** $U$ of a system is the **sum of the kinetic and potential energies of all its molecules**, measured in the system's own frame (the motion of the whole body, like a gas in a moving bus, doesn't count). It depends on the temperature (through the kinetic energy) and the volume (through the potential energy): $U = f(V, T)$.

Internal energy is a **state function**: it has one value in each state, whatever path the system took to get there. So when a system goes round a cycle and returns to its first state, its change in internal energy is **zero**.

### Internal energy and latent heat

Internal energy can't be read off an instrument, as a speed or a height can: we can only measure how it **changes**. In that sense it is hidden, *latent*, energy. That is where **latent heat** goes. When ice melts at 0 °C, or water boils at 100 °C, heat goes in but the temperature doesn't rise: the molecules' kinetic energy doesn't change. The heat does work against the molecules' attraction, pulling them apart, and so raises their **potential energy**. The internal energy of a substance is therefore least in its solid state and greatest as a gas, at the same temperature.

The internal energy of a system changes in two ways: when **heat** flows in or out, and when **work** is done by or on it. Of the heat given to a system, part raises its internal energy and the rest is used to do work on the surroundings:

$$\text{change in internal energy } (dU) = \text{heat supplied } (dQ) - \text{work done by the system } (dW)$$

If the process happens without any exchange of heat ($dQ = 0$), then

$$dU = -\,dW$$

The work is done **at the expense of the internal energy**: a gas that expands without being heated cools, and a gas compressed without losing heat warms up. The bicycle pump's warm end and the deodorant can's cold one are both this equation.

### Internal energy of an ideal gas

In an **ideal gas** the molecules don't attract one another, so their potential energy is zero, and the internal energy is the kinetic energy alone. That depends only on the temperature, so **the internal energy of an ideal gas depends on its temperature only**, not on its volume or pressure. For $n$ moles of a monatomic ideal gas, whose molecules only move from place to place,

$$U = \tfrac{3}{2}nRT$$

(Section 4.10 shows what changes for molecules that can also spin.)

### Internal energy of a real gas

In a **real gas** the molecules do attract one another (weakly, but not negligibly), so its internal energy is kinetic **plus** potential energy. The kinetic part depends on the temperature, the potential part on the volume (how far apart the molecules are), so the internal energy of a real gas depends on **both its temperature and its volume**.

### The mechanical equivalent of heat

Rub your palms together hard and they warm up: work becomes heat. Before Joule, heat was measured in **calories** (the heat that warms 1 g of water by 1 °C) and work in joules, as if they were different things. If work $W$ is completely turned into heat $H$, then $W \propto H$, so

$$W = JH$$

where $J$ is **Joule's mechanical equivalent of heat**, the work that makes one unit of heat: $J = 4.18$ J/cal ≈ 4.2 J/cal (today the calorie is defined as exactly 4.184 J). It holds only when all the work becomes heat, or all the heat becomes work. Since heat is energy, it is now measured in joules like any other energy, and then $J = 1$: the equation simply says $W = H$.

A STORY FROM SCIENCE

#### The brewer who measured heat

**James Prescott Joule** (1818–1889) ran his family's brewery near Manchester in England and did his experiments at home. He first measured the exchange rate in 1843, and from 1845 to 1850 he refined it with falling weights turning a paddle wheel in an insulated can of water, measuring the tiny rise in the water's temperature, a fraction of a degree, with thermometers he could read to 1/200 of a degree. He found the same exchange rate every time: in 1850, about 4.16 J of work for each calorie of heat, close to today's 4.184. At first the scientific world was not interested in a brewer's claim, until the young William Thomson (later Lord Kelvin) heard him speak in 1847 and saw what it meant.

Thomson later told how, a few weeks after they met, he came upon Joule in the Alps near Chamonix, on his honeymoon, carrying a long thermometer: he meant to measure whether the water at the bottom of a waterfall was warmer than at the top. It should be, by about 0.23 °C for every 100 m of fall, as the water's falling energy becomes heat. The unit of energy is named after him.



*Figure 4.7* *A replica of Joule's paddle-wheel apparatus in the Science and Industry Museum, Manchester. In use the can is full of water and closed; strings from falling weights spin the spindle, the paddles churn the water between the fixed vanes, and the water warms up.*
Photo: Chris Allen, CC BY-SA 2.0

WORKED EXAMPLE

### Example 4.3: boiling water at 100 °C

1 g of water at 100 °C becomes 1650 cm³ of steam at 100 °C and atmospheric pressure. Calculate the change in its internal energy. (Specific latent heat of vaporization of water = 540 cal/g, $J = 4.2 \times 10^7$ erg/cal, $g = 981$ cm/s², density of mercury 13.6 g/cm³.)

Answer

The temperature stays at 100 °C, so all the heat is latent heat.
**Heat supplied:** $dQ = mL = 1 \times 540 = 540$ cal $= 540 \times 4.2 \times 10^7 = 2.268 \times 10^{10}$ erg.
**Work done by the steam** pushing the atmosphere back: the volume grows from 1 cm³ (1 g of water) to 1650 cm³, so $dV = 1650 - 1 = 1649$ cm³, at a pressure of 1 atmosphere, 76 cm of mercury:

$$P = h\rho g = 76 \times 13.6 \times 981 = 1.014 \times 10^6 \text{ dyne/cm}^2$$

$$P\,dV = 1.014 \times 10^6 \times 1649 = 1.67 \times 10^9 \text{ erg}$$

**Change in internal energy**, from $dQ = dU + P\,dV$:

$$dU = dQ - P\,dV = 22.68 \times 10^9 - 1.67 \times 10^9 = 21.0 \times 10^9 \text{ erg} = \mathbf{2.1 \times 10^{10}\ erg}$$

That is about **2100 J**. Of the 2268 J of heat, only 167 J (about 7%) goes into pushing the air back; the other 93% pulls the molecules apart, raising their potential energy.

## 4.9 First law of thermodynamics

The **first law of thermodynamics** is the law of conservation of energy for processes that involve heat. When an amount of heat $dQ$ is given to a system, it can raise the system's internal energy ($dU$), or let the system do external work ($dW$), or both, and nothing is lost:

$$\boxed{dQ = dU + dW} \tag{4.1}$$

For a gas whose only work is pushing its boundary out, $dW = P\,dV$:

$$\boxed{dQ = dU + P\,dV} \tag{4.2}$$

For a whole process, $Q = \Delta U + W$. The signs are the key:

| Quantity | Positive when | Negative when |
|---|---|---|
| $Q$ | heat flows **into** the system | heat flows **out** |
| $\Delta U$ | internal energy rises (an ideal gas warms up) | it falls (an ideal gas cools) |
| $W$ | the system does work (it expands) | work is done on it (it is compressed) |

In words: **heat in = rise in stored energy + work out**. The first law is the bookkeeping used for heat engines, refrigerators, the weather, chemical reactions and living bodies.

WORKED EXAMPLE

### A gas in a cylinder

A gas in a cylinder is compressed by a piston, which does 300 J of work on it, while the gas gives out 120 J of heat to the cylinder's walls. Find the change in its internal energy.

Answer

Work done on the gas means the work done **by** it is negative: $W = -300$ J. Heat flows out: $Q = -120$ J.

$$\Delta U = Q - W = -120 - (-300) = +\mathbf{180\ J}$$

The internal energy rises by 180 J: the gas got 300 J as work and lost only 120 J as heat, so it warms up.

DID YOU KNOW?

### No energy from nothing

For centuries inventors tried to build a **perpetual motion machine**: a wheel with shifting weights, a water wheel that pumps its own water back up, that would keep running and give out work with no fuel. In a cycle the machine returns to its first state, so $\Delta U = 0$ and $W = Q$: with no heat in, there can be no work out. The first law rules out every such machine, and patent offices in many countries stopped examining them long ago, asking instead for a working model.

Check 4

A gas absorbs 500 J of heat and does 200 J of work on its surroundings. Its internal energy:

a falls by 300 J
b rises by 300 J
c rises by 700 J
d falls by 700 J

### Limitations of the first law

The first law only says that energy is conserved. It is silent on several things we see every day:

i. It doesn't say **which way** heat flows. By the first law alone, heat could just as well flow from a cold body to a hot one, if the energies balanced; it never does.

ii. It doesn't give the **conditions** under which heat can be turned into work.

iii. It treats heat and work as freely exchangeable, but they are not equally so: work can be turned **completely** into heat (the hands rubbed together), while heat can never be turned completely into work by an engine running in a cycle.

iv. It doesn't say **how much** of the heat an engine takes in can become work: the limit to the efficiency of a heat engine.

The **second law of thermodynamics** (Unit 5) was brought in to answer these.

## 4.10 Specific heat capacity of a gas

For solids and liquids (Grade 11, Unit 11) the heat needed to warm 1 kg by 1 K is a fixed number for each substance. For a gas it isn't: it depends on **how** the gas is heated, whether it is allowed to expand, because a gas that

expands does work. For gases we usually count the amount of gas in moles, and use **molar specific heat capacities** instead of the specific heat capacity per unit mass (the **principal** specific heat capacity).

The **molar specific heat capacity** of a gas is the heat needed to raise the temperature of **one mole** of it by **one degree Celsius (one kelvin)**:

$$C = \frac{dQ}{n\,dT}$$

where $dQ$ is the heat supplied to $n$ moles and $dT$ the rise in temperature. Its SI unit is J/(mol K).

A gas can be heated in many ways, and each gives a different heat capacity. Two are standard:

1. **Molar specific heat capacity at constant volume**, $C_V$: the heat needed to raise the temperature of one mole of gas by 1 K **at constant volume**.

$$C_V = \frac{dQ_V}{n\,dT}$$

The gas is heated in a closed rigid container. It can't expand, so it does no work: **all** the heat goes into its internal energy.

2. **Molar specific heat capacity at constant pressure**, $C_P$: the heat needed to raise the temperature of one mole of gas by 1 K **at constant pressure**.

$$C_P = \frac{dQ_P}{n\,dT}$$

The gas is heated in a cylinder with a free piston, so it expands as it warms, keeping its pressure the same. Its internal energy rises by the same amount as before, **and** it does work pushing the piston out, so it needs more heat.

### Mayer's relation: $C_P - C_V = R$

1. **At constant volume** no work is done ($dV = 0$), so for one mole the first law gives $dQ_V = dU$, that is,

$$dU = C_V\,dT$$

The internal energy of an ideal gas depends only on its temperature, so **any** process that changes its temperature by $dT$ changes its internal energy by this same $C_V\,dT$, however it happens.

2. **At constant pressure**, heating one mole by $dT$:

$$dQ_P = dU + P\,dV \quad \Rightarrow \quad C_P\,dT = C_V\,dT + P\,dV$$

3. For one mole of ideal gas $PV = RT$. At constant $P$, a change $dT$ in temperature makes a change $dV$ in volume with

$$P\,dV = R\,dT$$

4. Putting this into step 2: $C_P\,dT = C_V\,dT + R\,dT$. Dividing by $dT$:

$$\boxed{C_P - C_V = R}$$

This is **Mayer's relation** (also spelled Meyer's). The extra heat needed at constant pressure, per mole per kelvin, is exactly the work the gas does as it expands, $R = 8.31$ J. So $C_P$ **is always greater than** $C_V$.

For the **principal** specific heat capacities (per unit mass), divide by the molar mass $M$: $c_P = C_P/M$ and $c_V = C_V/M$, so

$$\frac{C_P}{M} - \frac{C_V}{M} = \frac{R}{M} \quad \Rightarrow \quad \boxed{c_P - c_V = r} \tag{4.3}$$

where $r = R/M$ is the gas constant per unit mass (for air, $r = 8.31 \div 0.029 = 287$ J/(kg K)).

### Why is $C_P$ greater than $C_V$?

When a gas is heated at constant volume, all the heat raises its internal energy, and so its temperature. When it is heated at constant pressure, it expands and does work on its surroundings, which takes extra energy. So more heat is needed for the same rise in temperature at constant pressure than at constant volume.

A STORY FROM SCIENCE

### The doctor who saw red

**Julius Robert Mayer** (1814–1878) was a German doctor. In 1840, as a ship's doctor in the hot East Indies, he bled sick sailors (a common treatment then) and was struck that the blood in their veins was bright red, almost like blood from an artery. He reasoned that in the heat the body needs to burn less food to keep warm, so less oxygen is taken from the blood. Food, heat and work, he decided, must be forms of one thing that is conserved. In 1842 he used the difference $c_P - c_V$ of air, already measured, to calculate the mechanical equivalent of heat, a year before Joule's first measurement. He got little credit for years, and only late in life was his share in the discovery of energy conservation recognized.

WORKED EXAMPLE

### Example 4.4: heating hydrogen

For hydrogen, the molar heat capacities at constant volume and at constant pressure are 20.5 J/(mol K) and 28.8 J/(mol K). Calculate i. the heat needed to raise the temperature of 8 g of hydrogen from 10 °C to 15 °C at constant pressure, ii. the increase in the internal energy of the gas, iii. the external work done. (Molar mass of hydrogen 2 g/mol.)

Answer

Number of moles: $n = \dfrac{m}{M} = \dfrac{8}{2} = 4$ mol. Rise in temperature: $dT = 15 - 10 = 5$ °C $= 5$ K.

i. $Q = nC_P\,dT = 4 \times 28.8 \times 5 = \mathbf{576\ J}$.

ii. $\Delta U = nC_V\,dT = 4 \times 20.5 \times 5 = \mathbf{410\ J}$ (the same whatever the process, for this rise in temperature).

iii. From the first law, $W = Q - \Delta U = 576 - 410 = \mathbf{166\ J}$.

Check: at constant pressure, $W = P\,\Delta V = nR\,dT = 4 \times 8.3 \times 5 = 166$ J, since here $C_P - C_V = 8.3$ J/(mol K) $= R$.

CAREFUL

### A heat capacity can be zero, or infinite

Since $C = \dfrac{dQ}{n\,dT}$, a gas has a different heat capacity for every way of heating it. If its temperature changes with **no** heat exchanged (an adiabatic process, Section 4.12), $dQ = 0$ and $C = 0$. If heat keeps flowing in while its temperature **doesn't** change (an isothermal expansion, Section 4.11), $dT = 0$ and $C$ is infinite. So the heat capacity of a gas can be anything from zero to infinity (and even negative, if it cools while being heated, by doing more work than the heat it takes in). That is why "the" heat capacity of a gas means nothing until you say how it is heated.

## Degrees of freedom, specific heat capacity and γ

The **degrees of freedom** of a body are the number of independent coordinates needed to describe its motion completely. In thermodynamics, they are the number of **independent ways in which a molecule can store energy**. There are three kinds (Figure 4.8):

- **Translational:** moving from place to place, along x, y and z. **Every** molecule has these 3.
- **Rotational:** spinning. A **linear** molecule (all its atoms in a line, like $N_2$, $O_2$, $CO_2$) has 2: it can spin about the two axes across it, but spinning about its own length stores almost no energy. A **non-linear** molecule (like $H_2O$ or $CH_4$) has 3. A single atom has none that count.
- **Vibrational:** the atoms moving towards and away from one another, as if joined by springs. Each way of vibrating (each **mode**) counts **2**, one for its kinetic energy and one for its potential energy. They come into play only at high temperatures.

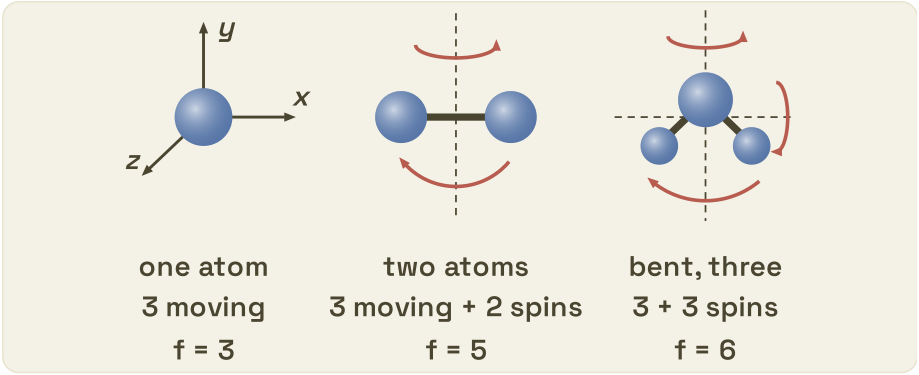



***Figure 4.8*** *The ways a molecule can store energy. A single atom can only move along x, y and z (3 degrees of freedom). A two-atom molecule can also spin about two axes across it (5). A bent three-atom molecule can spin about three axes (6). Spinning a dumbbell about its own length stores almost no energy, so it isn't counted.*

The **law of equipartition of energy** (from the kinetic theory) says that in thermal equilibrium the energy is shared equally among all the degrees of freedom: each gets, on average, $\frac{1}{2}k_BT$ per molecule, or $\frac{1}{2}RT$ per mole. (The $\frac{3}{2}RT$ of Grade 11's kinetic theory is $3 \times \frac{1}{2}RT$, the three translational degrees of freedom.) For a gas whose molecules have $f$ degrees of freedom:

1. Internal energy of one mole: $U = \dfrac{f}{2}RT$.
2. $C_V = \dfrac{dU}{dT} = \dfrac{f}{2}R$.
3. $C_P = C_V + R = \left(\dfrac{f}{2} + 1\right) R$.
4. The **ratio of the molar heat capacities** (the **adiabatic index**), $\gamma$:

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{(f/2+1)R}{(f/2)R} = 1 + \frac{2}{f}}$$

| Gas | Example | $f$ | $C_V$ | $C_P$ | $\gamma$ |
|---|---|---|---|---|---|
| monatomic | He, Ne, Ar | 3 | $\frac{3}{2}R = 12.5$ J/(mol K) | $\frac{5}{2}R = 20.8$ J/(mol K) | $\frac{5}{3} = 1.67$ |
| diatomic (translation and rotation) | $H_2$, $N_2$, $O_2$, air | 5 | $\frac{5}{2}R = 20.8$ J/(mol K) | $\frac{7}{2}R = 29.1$ J/(mol K) | $\frac{7}{5} = 1.40$ |
| non-linear polyatomic | $H_2O$ vapor, $CH_4$ | 6 | $3R = 24.9$ J/(mol K) | $4R = 33.3$ J/(mol K) | $\frac{4}{3} = 1.33$ |

So the more degrees of freedom, the smaller γ, always between 1 and 5/3. Measured values agree well: helium and argon 1.67, nitrogen, oxygen and air 1.40, steam about 1.33. Carbon dioxide (linear, $f = 5$ from translation and rotation) measures about 1.29 at room temperature, lower than 1.40, because some of its vibrations have already begun to take up energy.

DID YOU KNOW?

**Frozen degrees of freedom**

Why do $N_2$ and $O_2$ at room temperature behave as if their atoms were rigidly joined, when the bond is really springy? Quantum physics: a vibration can only take energy in steps, and for these molecules the smallest step is far larger than $k_B T$ at room temperature, so collisions almost never set them vibrating. The vibrations are "frozen". Heat the gas to a few thousand kelvin and they thaw: $C_V$ rises towards $\frac{7}{2}R$. Cool hydrogen far enough, below about 80 K, and even its rotations freeze: it then behaves like a monatomic gas, with $C_V = \frac{3}{2}R$. This puzzle, that the heat capacities of gases did not match equipartition, was one of the clues that led to quantum physics.

Check 5

For a diatomic ideal gas at room temperature, $\gamma$ is:

a 1.67
b 1.40
c 1.33
d 1.29

## 4.11 Thermodynamic processes

A **thermodynamic process** is any change of a system from one equilibrium state to another, in which energy is exchanged with the surroundings as heat, work or both, so that its state variables (pressure, volume, temperature, internal energy) take new values.

A process is like a journey. Where you start and where you finish don't fix how much fuel you use: a short steep road and a long gentle one use different amounts. In the same way, the heat and work exchanged depend on **how** the system gets from one state to the other. The study of these processes is what explains how heat engines and refrigerators work.

To draw a process as a line on a P–V diagram, every point along it must be an equilibrium state, with one pressure and one temperature throughout the gas. Such a process, slow enough to pass through equilibrium states all the way, is called **quasi-static**. The four standard processes below are each named for the quantity they hold constant.

### Isothermal process (constant temperature)

An **isothermal process** is one in which the **temperature** of the system stays constant throughout, while it expands or is compressed and heat flows in or out to keep the temperature steady. For that the gas must be in a container with **thin, well-conducting walls**, in contact with a large body at a steady temperature (a **heat reservoir**), and the change must be **slow**, so that heat has time to flow. Examples: the slow expansion or compression of a gas in a metal cylinder standing in a large water bath; melting and boiling, which also happen at a steady temperature.

Let $n$ moles of an ideal gas change isothermally from $A(P_1, V_1)$ to $B(P_2, V_2)$. By the first law,

$$dQ = dU + dW = nC_V\,dT + P\,dV = 0 + P\,dV = P\,dV \qquad [\,dT = 0\,]$$

The internal energy doesn't change (it depends only on $T$), so **all the heat given to the gas comes out as work**. In an isothermal expansion the gas takes in heat equal to the work it does; in an isothermal compression it gives out heat equal to the work done on it.

From the equation of state, $PV = nRT$. With $T$ constant, $nRT$ is constant, so

$$\boxed{PV = \text{constant}}, \qquad P_1V_1 = P_2V_2$$

which is Boyle's law. This is the **equation of state for an isothermal process**. Each temperature gives its own curve, a rectangular hyperbola, called an **isotherm**; a hotter isotherm lies farther from the axes (Figure 4.9).

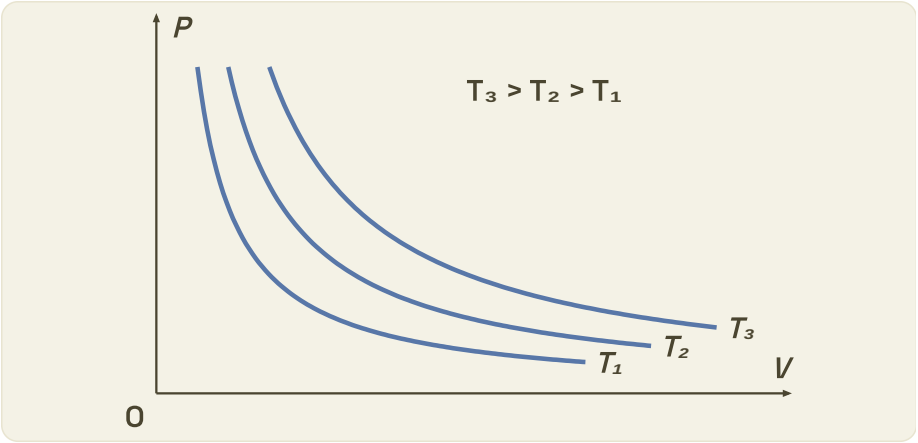



*Figure 4.9* *Isotherms of an ideal gas at three temperatures, $T_3 > T_2 > T_1$. Each is a curve $PV = \text{constant}$; the hotter, the farther out.*

### Work done during an isothermal expansion

Let $n$ moles of ideal gas expand isothermally at temperature $T$ from $(P_1, V_1)$ to $(P_2, V_2)$ (Figure 4.10).

1. In a small expansion $dV$, the pressure stays about $P$: $dW = P\,dV$.
2. The total work is

$$W = \int_{V_1}^{V_2} P\,dV \tag{4.4}$$

3. From $PV = nRT$, $P = \dfrac{nRT}{V}$, and $nRT$ is constant, so it comes out of the integral:

$$W = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT\Big[\ln V\Big]_{V_1}^{V_2} = nRT(\ln V_2 - \ln V_1)$$

4. So

$$\boxed{W = nRT \ln \frac{V_2}{V_1}}$$

where ln is the natural logarithm (to base e). For one mole, $W = RT \ln \dfrac{V_2}{V_1}$.

5. Since $P_1V_1 = P_2V_2$, $\dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$, so also

$$\boxed{W = nRT \ln \frac{P_1}{P_2}}$$

With common logarithms, $\ln x = 2.303 \log_{10} x$: $W = 2.303\, nRT \log_{10} \dfrac{V_2}{V_1}$.

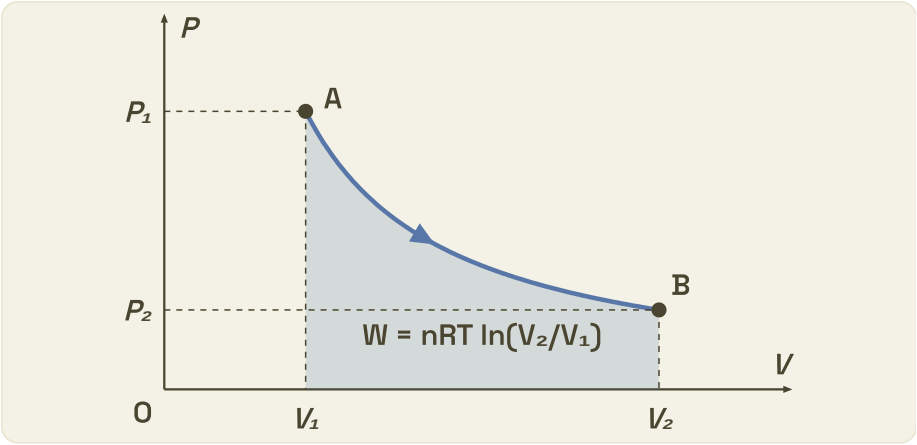



*Figure 4.10* Isothermal expansion from $A(P_1, V_1)$ to $B(P_2, V_2)$. The shaded area under the isotherm is the work done by the gas, $nRT\ln(V_2/V_1)$.

WORKED EXAMPLE

**Doubling the volume slowly**

One mole of an ideal gas at 27 °C expands isothermally to twice its volume. How much work does it do, and how much heat does it take in? ($R = 8.31$ J/(mol K))

Answer

$T = 27 + 273 = 300$ K.

$$W = nRT\ln\frac{V_2}{V_1} = 1 \times 8.31 \times 300 \times \ln 2 = 2493 \times 0.693 = \mathbf{1.73 \times 10^3\ J}$$

The temperature doesn't change, so $\Delta U = 0$ and the heat taken in equals the work: $Q = W = \mathbf{1.73\ kJ}$.

## 4.12 Adiabatic process

An **adiabatic process** is one in which **no heat** is exchanged between the system and its surroundings, while its pressure, volume and temperature change because work is done by or on it. (*Adiabatic* is Greek for "not passable".) It needs either a perfectly **insulated** container, or a change so **fast** that heat has no time to flow. Examples: the sudden bursting of a vehicle's tyre or of a balloon; the expansion of the hot gases in a petrol engine's cylinder; the squeezing and stretching of air as sound passes through it; air rising and sinking over mountains.

By the first law, with $dQ = 0$:

$$dQ = dU + P\,dV \quad\Rightarrow\quad 0 = nC_V\,dT + P\,dV \quad\Rightarrow\quad P\,dV = -nC_V\,dT \tag{4.5}$$

The work is done **at the expense of the internal energy**. Over the whole process, $W = \int P\,dV = -nC_V(T_2 - T_1)$:

- In an **adiabatic expansion** ($W > 0$), $T_2 < T_1$: the gas **cools**.
- In an **adiabatic compression** ($W < 0$), $T_2 > T_1$: the gas **heats up**.

### Equation of state for an adiabatic process

Let $n$ moles of ideal gas expand adiabatically from $(P_1, V_1, T_1)$ to $(P_2, V_2, T_2)$. Take a small step in which the volume and temperature change by $dV$ and $dT$, at nearly constant pressure $P$.

1. First law, with $dQ = 0$:

$$nC_V\,dT + P\,dV = 0 \tag{4.6}$$

2. Differentiate the ideal gas equation $PV = nRT$: $P\,dV + V\,dP = nR\,dT$, so

$$dT = \frac{P\,dV + V\,dP}{nR} \tag{4.7}$$

3. Put (4.7) into (4.6):

$$nC_V\left(\frac{P\,dV + V\,dP}{nR}\right) + P\,dV = 0$$

4. Multiply by $R$ and collect the $P\,dV$ terms:

$$C_V P\,dV + C_V V\,dP + RP\,dV = 0 \quad \Rightarrow \quad (C_V + R)P\,dV + C_V V\,dP = 0$$

5. By Mayer's relation $C_V + R = C_P$:

$$C_P P\,dV + C_V V\,dP = 0$$

6. Divide by $C_V PV$ and write $\gamma = C_P/C_V$:

$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0$$

7. Integrate both sides:

$$\gamma\ln V + \ln P = \text{constant} \quad \Rightarrow \quad \ln V^\gamma + \ln P = \text{constant} \quad \Rightarrow \quad \ln(PV^\gamma) = \text{constant}$$

8. So

$$\boxed{PV^\gamma = \text{constant}}, \qquad P_1V_1^\gamma = P_2V_2^\gamma \tag{4.8}$$

This is the **equation of state for an adiabatic process**. Using $P = nRT/V$, it can also be written with the temperature:

$$TV^{\gamma-1} = \text{constant}, \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

and, using $V = nRT/P$,

$$\frac{T^\gamma}{P^{\gamma-1}} = \text{constant}, \qquad \frac{T_1^\gamma}{P_1^{\gamma-1}} = \frac{T_2^\gamma}{P_2^{\gamma-1}}$$

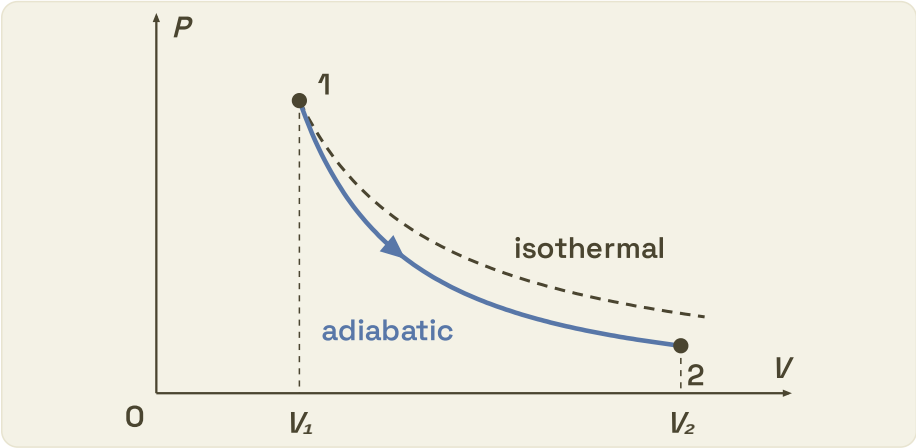



*Figure 4.11* *An adiabatic expansion from state 1 $(P_1, V_1, T_1)$ to state 2 $(P_2, V_2, T_2)$, along $PV^\gamma = \text{constant}$, with the isotherm through state 1 dashed for comparison. The adiabat falls more steeply: the gas cools as it expands.*

### Work done during an adiabatic process

Let $n$ moles of ideal gas with ratio $\gamma$ expand adiabatically from $(P_1, V_1, T_1)$ to $(P_2, V_2, T_2)$.

1. The work done is $W = \int_{V_1}^{V_2} P\,dV$.
2. Along the adiabat $PV^\gamma = K$ (a constant), so $P = \dfrac{K}{V^\gamma}$:

$$W = \int_{V_1}^{V_2} \frac{K}{V^\gamma}\,dV = K\int_{V_1}^{V_2} V^{-\gamma}\,dV = K\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2} = \frac{K}{1-\gamma}\left(V_2^{1-\gamma} - V_1^{1-\gamma}\right)$$

3. Change the sign of both factors:

$$W = \frac{1}{\gamma - 1}\left(KV_1^{1-\gamma} - KV_2^{1-\gamma}\right)$$

4. Put $K = P_1V_1^\gamma$ in the first term and $K = P_2V_2^\gamma$ in the second (they are equal): $KV_1^{1-\gamma} = P_1V_1^\gamma V_1^{1-\gamma} = P_1V_1$, and likewise for state 2. So

$$\boxed{W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}} \tag{4.9}$$

5. With $P_1V_1 = nRT_1$ and $P_2V_2 = nRT_2$:

$$\boxed{W = \frac{nR(T_1 - T_2)}{\gamma - 1}} \tag{4.10}$$

The work done in an adiabatic process depends only on the first and last temperatures. A quicker way to the same result: $W = -\Delta U = -nC_V(T_2 - T_1) = nC_V(T_1 - T_2)$, and from $C_P - C_V = R$ and $C_P = \gamma C_V$, $C_V = \dfrac{R}{\gamma - 1}$.

### The adiabat is steeper than the isotherm

At any point, the slope of an adiabatic curve is **γ times** the slope of the isothermal curve through the same point, so the adiabat is the **steeper** of the two ($\gamma > 1$) (Figure 4.11).

1. **Isothermal:** $PV =$ constant. Differentiate: $P\,dV + V\,dP = 0$, so the slope is

$$\left(\frac{dP}{dV}\right)_{\text{iso}} = -\frac{P}{V}$$

2. **Adiabatic:** $PV^\gamma =$ constant. Differentiate: $\gamma PV^{\gamma-1}\,dV + V^\gamma\,dP = 0$. Divide by $V^\gamma$: $\gamma\dfrac{P}{V}\,dV + dP = 0$, so

$$\left(\frac{dP}{dV}\right)_{\text{adia}} = -\gamma\frac{P}{V}$$

3. So

$$\boxed{\left(\frac{dP}{dV}\right)_{\text{adia}} = \gamma\left(\frac{dP}{dV}\right)_{\text{iso}}}$$

Physically: in an adiabatic expansion the pressure falls for two reasons, the gas spreading out (as in the isothermal case) and the gas cooling, so it falls faster. In a compression it rises faster, because the gas also heats up.

DID YOU KNOW?

**Fire from a squeeze**

A **fire piston** is a tube closed at one end with a tight piston and a pinch of cotton or tinder at the bottom. Slam the piston in and the tinder glows. Squeezing air quickly to a tenth of its volume heats it, by $TV^{\gamma-1} =$ constant, from 300 K to $300 \times 10^{0.4} \approx 750$ K, about 480 °C: hot enough to set a wisp of cotton or tinder glowing. Fire pistons were used in Southeast Asia long before matches. A diesel engine (Unit 5) lights its fuel in exactly this way, with no spark plug.

DID YOU KNOW?

**Why the air on the mountains is cold**

Air that rises up the slopes of the Himalaya moves into lower pressure, expands, and does work on the air around it. Air is a poor conductor of heat, so it hardly takes in any: the expansion is nearly adiabatic, and the rising air cools by about 10 °C for every kilometer it climbs (less once its water vapor starts to condense into cloud, which gives out latent heat). That is why clouds form over the hills on a summer afternoon, and why dry air sinking down the far side of a range warms up as it is squeezed. Sound waves are adiabatic too: the squeezes and stretches are too quick for heat to flow between them.

Check 6

An ideal gas is compressed adiabatically to half its volume. Its temperature:

a stays the same, since no heat enters
b halves
c rises
d falls

## 4.13 Isobaric and isochoric processes

### Isobaric process (constant pressure)

An **isobaric process** is one in which the **pressure** of the system stays constant throughout, while heat is given to it or taken from it; its volume, temperature and internal energy change. Examples: heating or cooling a gas in a cylinder with a freely moving piston (the piston's weight and the air above keep the pressure steady); boiling water in an open pot, or melting ice, at atmospheric pressure; much of what happens in the atmosphere.

It is carried out in a container that can expand. By the first law, $dQ = dU + dW$: part of the heat raises the internal energy (and the temperature), and the rest is used to do external work.

For $n$ moles of ideal gas going from $V_1$ to $V_2$ at pressure $P$:

$$W = P(V_2 - V_1) = nR(T_2 - T_1), \qquad \Delta U = nC_V(T_2 - T_1), \qquad Q = nC_P(T_2 - T_1)$$

and $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ (Charles's law). On a P–V diagram it is a **horizontal line**, and the work is the rectangle under it (Figure 4.12).

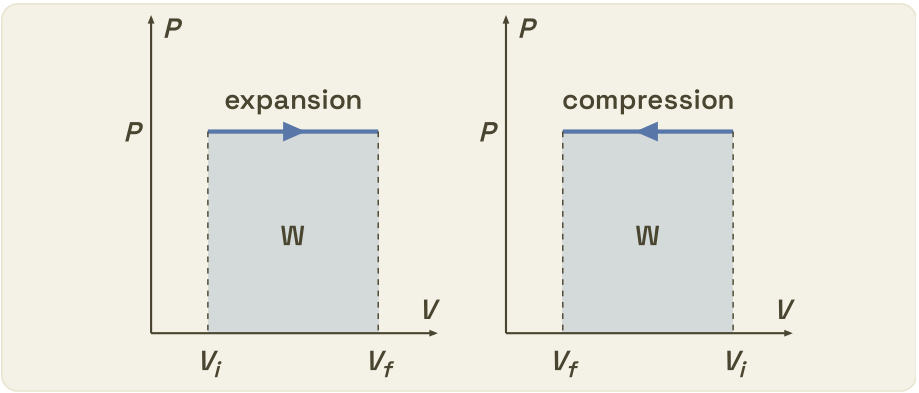



*Figure 4.12* *Isobaric processes are horizontal lines. In an expansion from $V_i$ to $V_f$ (left), the gas does work $P(V_f - V_i)$, the shaded rectangle; in a compression (right), the same area is work done on the gas.*

### Isochoric process (constant volume)

An **isochoric** (or isometric) **process** is one in which the **volume** stays constant throughout, while the pressure, temperature and internal energy change. Examples: heating a gas in a closed rigid container; the burning of a fuel–air mixture in a sealed chamber, as in a petrol engine at the instant of the spark (Unit 5); a pressure cooker heating up with its weight in place, until the weight lifts.

It is carried out in a container that can't expand. With no change of volume, the system does **no work**, and **all** the heat supplied goes into its internal energy:

$$W = 0, \qquad Q = \Delta U = nC_V(T_2 - T_1), \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

On a P–V diagram it is a **vertical line**, with no area under it (Figure 4.13).

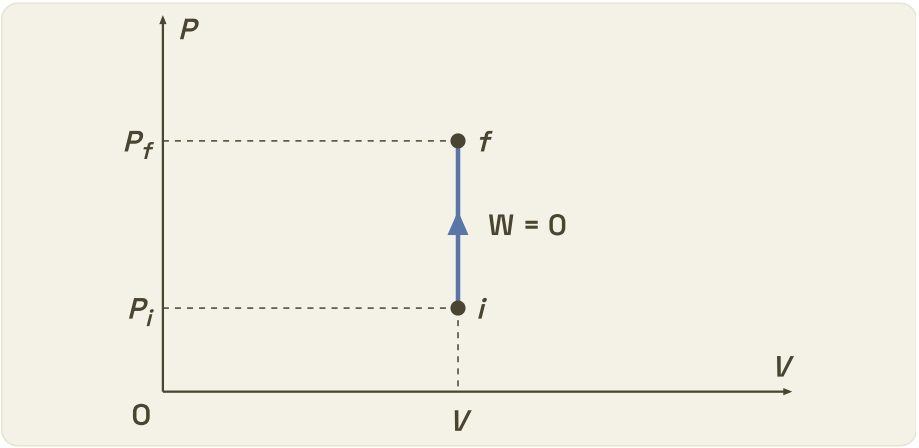



***Figure 4.13*** *An isochoric process is a vertical line: the pressure changes from $P_i$ to $P_f$ at the same volume. There is no area under it, so no work is done.*



***Figure 4.14*** *A pressure cooker of the kind used in kitchens all over Nepal. Until its weight lifts, the water and steam inside are heated at constant volume: the heat goes into the internal energy, and the pressure rises, which raises the boiling point (Grade 11, Unit 11).*

Photo: Cantons-de-l'Est, CC BY-SA 4.0

### The four processes compared

| Process | Constant | Equation of state | Work done by the gas, $W$ | Heat in, $Q$ | $\Delta U$ |
|---|---|---|---|---|---|
| isothermal | $T$ | $PV = \text{constant}$ | $nRT \ln \dfrac{V_2}{V_1}$ | $Q = W$ | $0$ |
| adiabatic | no heat flow | $PV^{\gamma} = \text{constant}$ | $\dfrac{nR(T_1 - T_2)}{\gamma - 1}$ | $0$ | $-W$ |
| isobaric | $P$ | $\dfrac{V}{T} = \text{constant}$ | $P(V_2 - V_1)$ | $nC_P\,\Delta T$ | $nC_V\,\Delta T$ |
| isochoric | $V$ | $\dfrac{P}{T} = \text{constant}$ | $0$ | $nC_V\,\Delta T$ | $Q$ |

WORKED EXAMPLE

#### Example 4.5: out fast, back slowly

A mass of air at first occupies $2 \times 10^{-3}$ m³ at a pressure of 760 mm of mercury and a temperature of 20 °C. It is expanded adiabatically and reversibly to twice its volume, then compressed isothermally and reversibly to a volume of $3 \times 10^{-3}$ m³. Find its final temperature and pressure ($\gamma$ for air = 1.4).

Answer

State 1: $V_1 = 2 \times 10^{-3}$ m³, $P_1 = 760$ mm of Hg, $T_1 = 20 + 273 = 293$ K.

**Adiabatic expansion** to $V_2 = 2V_1 = 4 \times 10^{-3}$ m³:

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{\gamma} = 760 \times \left(\frac{1}{2}\right)^{1.4} = 760 \times 0.379 = 288 \text{ mm of Hg}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma - 1} = 293 \times \left(\frac{1}{2}\right)^{0.4} = 293 \times 0.758 = 222 \text{ K}$$

**Isothermal compression** to $V_3 = 3 \times 10^{-3}$ m³: the temperature stays $T_3 = T_2 = \mathbf{222\ K}$ (−51 °C), and $P_2V_2 = P_3V_3$:

$$P_3 = \frac{P_2V_2}{V_3} = \frac{288 \times 4 \times 10^{-3}}{3 \times 10^{-3}} = \mathbf{384\ mm\ of\ Hg}$$

WORKED EXAMPLE

#### Example 4.6: in slowly, out fast

Air at first at 27 °C and 750 mm of mercury is compressed isothermally until its volume is halved. It is then expanded adiabatically until its original volume is restored. Assuming the changes are reversible, find its final temperature and pressure ($\gamma$ for air = 1.4).

Answer

State 1: $T_1 = 27 + 273 = 300$ K, $P_1 = 750$ mm of Hg; call the volume $V$.

**Isothermal compression** to $V_2 = V/2$, at $T_2 = 300$ K:

$$P_2 = \frac{P_1V_1}{V_2} = \frac{750 \times V}{V/2} = 1500 \text{ mm of Hg}$$

**Adiabatic expansion** back to $V_3 = V$:

$$P_3 = P_2 \left(\frac{V_2}{V_3}\right)^{\gamma} = 1500 \times \left(\frac{1}{2}\right)^{1.4} = \mathbf{568.4\ mm\ of\ Hg}$$

$$T_3 = T_2 \left(\frac{V_2}{V_3}\right)^{\gamma - 1} = 300 \times \left(\frac{1}{2}\right)^{0.4} = \mathbf{227.4\ K}$$

The air is back at its first volume but colder (−46 °C) and at a lower pressure than it began (568 instead of 750 mm). It gave out heat while it was squeezed slowly, then did work out of its own internal energy while it expanded fast.

## 4.14 Reversible process

A **reversible process** is one that can be run backwards so that the system **and** its surroundings both return exactly to their first states, leaving no change anywhere. At every step, a tiny change in the conditions (pressure a whisker higher instead of lower) would send it the other way. It is an **idealization**: no real process is perfectly reversible, but some come close. Examples: a very slow, frictionless expansion or compression of a gas; the slow isothermal and adiabatic changes of Section 4.11–4.12; the swing of a pendulum with no friction or air resistance (motion under conservative forces only).

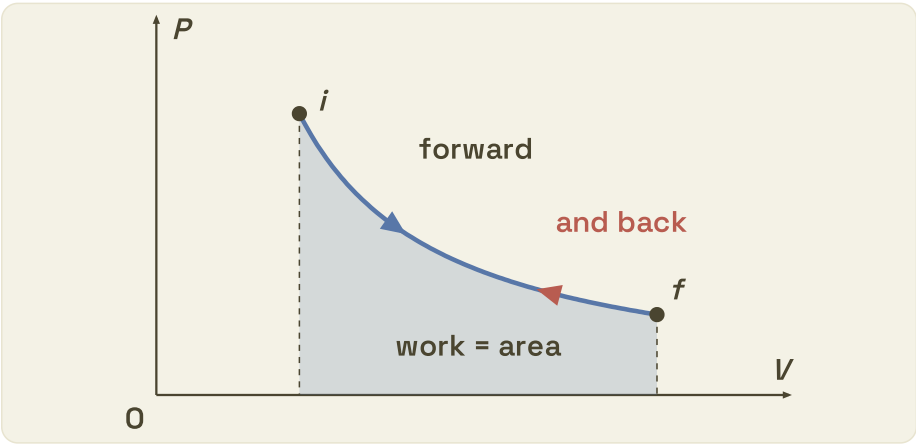



*Figure 4.15* *A reversible expansion from i to f passes through equilibrium states, so it can be drawn as a curve and retraced exactly in reverse. The area under it is the work done.*

**Conditions for a reversible process:**

1. It must be carried out infinitely slowly (quasi-statically).
2. No energy may be dissipated (turned into waste heat) during it.
3. The system and its surroundings must be in thermodynamic equilibrium with each other at every step: the same temperature where heat flows, the same pressure where the boundary moves.
4. There must be no dissipative forces: no friction, viscosity, electrical resistance or the like.

## 4.15 Irreversible process

An **irreversible process** is one that can't be retraced: once it has happened, the system and its surroundings can't both be returned to their first states. It brings a permanent change, with energy **dissipated** as waste heat and an increase in **entropy** (Unit 5). Examples: the rusting of iron; the decay of dead leaves; heat produced by friction; heat flowing from a hot cup of tea to the air; gas rushing out of a burst tyre; mixing milk into tea. Almost all processes in nature are irreversible.

During a fast, irreversible change the gas is not in equilibrium: it swirls, one part is hotter or at a higher pressure than another, so it has no single pressure or temperature. Only its first and last states can be marked on a P–V diagram, and the change between them can't be drawn as a curve (Figure 4.16).

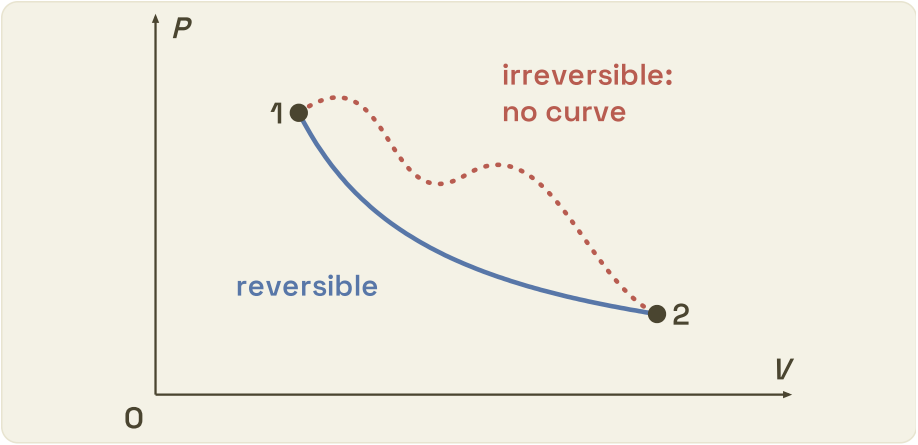



*Figure 4.16* *An irreversible change from state 1 to state 2 (dotted) passes through states that are not in equilibrium, so it has no curve on the P–V diagram and can't be retraced. A reversible process between the same states (solid) could be.*

CAREFUL

**Slow is not enough**

A process can be slow and still irreversible. A gas leaking slowly out of a balloon through a pinhole, or a slow process with friction, can never be undone without leaving a change somewhere else. Reversible needs both: slow, **and** nothing dissipated.

Check 7

Which of these processes is closest to reversible?

a a car braking to a stop

b ice melting in a glass of warm water

c a gas compressed very slowly by a frictionless piston in an insulated cylinder

d a balloon bursting

IN SHORT

### Key ideas of Unit 4

- A **system** is the part we study; its **surroundings** are the rest. Open: matter and energy cross; closed: energy only; isolated: neither.
- **State variables** (P, V, T, U, S) have one value in each state; **work and heat** depend on the path.
- Work done **by** a gas: $dW = P\,dV$, $W = \int P\,dV$, the area under the P–V curve; positive in expansion, negative in compression. Net work in a cycle = area of the loop (positive if clockwise).
- **Internal energy** = kinetic + potential energy of the molecules; a state function. Ideal gas: $U$ depends on $T$ only; real gas: on $T$ and $V$. Latent heat raises the potential energy.
- **First law:** $dQ = dU + dW = dU + P\,dV$. Adiabatic: $dU = -dW$.
- $C_P - C_V = R$ (Mayer), $c_P - c_V = r$; $\gamma = C_P/C_V = 1 + 2/f$: 1.67 monatomic, 1.40 diatomic, 1.33 non-linear polyatomic.
- Isothermal: $PV = \text{const}$, $W = nRT\ln(V_2/V_1) = nRT\ln(P_1/P_2)$, $Q = W$, $\Delta U = 0$.
- Adiabatic: $PV^\gamma = \text{const}$, $TV^{\gamma-1} = \text{const}$, $W = \dfrac{P_1V_1 - P_2V_2}{\gamma - 1} = \dfrac{nR(T_1 - T_2)}{\gamma - 1}$; expansion cools, compression heats; slope $\gamma$ times the isotherm's.
- Isobaric: $W = P\,\Delta V$, $Q = nC_P\,\Delta T$. Isochoric: $W = 0$, $Q = \Delta U = nC_V\,\Delta T$.
- **Reversible:** infinitely slow, in equilibrium throughout, nothing dissipated; an ideal. **Irreversible:** every real process.

## Exercise

### Choose the correct option

Check 8

1. Which of the following is **not** a type of thermodynamic system?

a open system
b closed system
c isolated system
d static system

Check 9

2. The first law of thermodynamics is a statement of the conservation of:

a mass
b momentum
c energy
d entropy

Check 10

3. If a gas expands adiabatically, which of these statements is true?

a the internal energy of the gas remains constant
b the gas absorbs heat
c the work done by the gas is equal to the decrease in its internal energy
d the temperature of the gas remains unchanged

Check 11

4. In an isothermal process, which of the following remains constant?

*The textbook's fourth option, "internal energy", also stays constant in an isothermal process of an ideal gas, so the question had two right answers; it is replaced below.*

a pressure
b temperature
c volume
d entropy

**Check 12**

5. Which of these correctly relates the molar heat capacities at constant pressure and at constant volume?

a $C_P = C_V$ b $C_P < C_V$
c $C_P - C_V = R$ d $C_P - C_V = \gamma$

**Check 13**

6. A gas undergoes an isochoric (constant volume) process. The work done during it is:

a positive b negative
c zero d cannot be determined

**Check 14**

7. A gas expands isothermally at 300 K from 2 L to 6 L. If the work done is $W = nRT\ln(V_f/V_i)$, the work done is:

a positive b negative
c zero d infinite

**Check 15**

8. A gas undergoes an adiabatic compression. What happens to its temperature?

a it increases b it decreases
c it remains constant d it becomes zero

**Check 16**

9. A gas at 27 °C, kept at that temperature, expands from 1 L to 4 L against a constant external pressure of 2 atm. The work done by the gas is closest to:

*The textbook's options (1384 J, 1725 J, 1845 J, 2100 J) don't include the answer, 608 J, so the book's numbers don't work; the options below are corrected.*

a 304 J b 608 J
c 1216 J d 3458 J

**Check 17**

10. 2 moles of an ideal gas ($\gamma = 1.4$) are compressed adiabatically from 5 L to 1 L. If the first temperature is 300 K, the final temperature is:

*None of the textbook's options (750 K, 820 K, 900 K, 1050 K) is right: the answer is 571 K, so the book's numbers don't work. The options below are corrected.*

a 571 K b 750 K
c 900 K d 1500 K

**Check 18**

11. A gas expands so that $PV^{1.4} =$ constant. Its first pressure and volume are 2 atm and 3 L. The final pressure when its volume becomes 6 L is:

*The textbook's nearest option is 0.78 atm, but the answer is 0.76 atm; the option is corrected below.*

a 0.57 atm b 0.63 atm
c 0.76 atm d 1.2 atm

## Answer these questions

12. a. Define a thermodynamic system. Give one example of each type, and differentiate between open,

closed and isolated systems with examples.

b. How does work done on the system differ from work done by the system?

c. A gas at a pressure of $2 \times 10^5$ Pa and a volume of 0.01 $m^3$ expands isobarically to 0.03 $m^3$. Find the work done.

d. Define an indicator diagram and explain how the work done by an expanding gas can be found from it.

**13.**

a. Explain the concept of internal energy and its relation with heat and work. What does the equation $dU = -dW$ signify? How does the internal energy of a real gas differ from that of an ideal gas?

b. Calculate the change in internal energy of 2 moles of a monatomic ideal gas whose temperature changes from 300 K to 500 K. ($C_V = \frac{3}{2}R$)

**14.**

a. State and explain the first law of thermodynamics. Discuss its significance.

b. Does it follow the law of conservation of energy?

c. A gas absorbs 600 J of heat and does 150 J of work. Find the change in its internal energy.

d. List the limitations of the first law of thermodynamics.

**15.**

a. Why does a gas have two specific heat capacities?

b. Derive Mayer's relation, $C_P - C_V = R$.

c. Why is $C_P$ always greater than $C_V$?

d. If $C_P = 29.1$ J/(mol K) and $C_V = 20.8$ J/(mol K), find the gas constant $R$ and γ.

**16.**

a. Explain the isothermal, adiabatic, isobaric and isochoric processes with the help of P–V diagrams.

b. Differentiate between the types of thermodynamic process, and compare their P–V diagrams.

**17.**

a. Define an adiabatic process. Derive the equation $PV^\gamma =$ constant.

b. In an adiabatic expansion, a gas does 1200 J of work. Find the change in its internal energy.

c. Find the final temperature and the work done when 1 mole of ideal gas expands adiabatically from 1 L to 5 L. Take $\gamma = 1.4$, $T_1 = 300$ K, $R = 8.314$ J/(mol K).

**18.**

a. Derive expressions for the work done in isothermal and adiabatic processes.

b. A gas expands isothermally from 2 L to 8 L at a temperature of 300 K. Calculate the work done. ($R = 8.314$ J/(mol K), $n = 1$ mol)

**19.**

a. Define the heat capacity ratio (γ).

b. How does γ vary with the atomicity of a gas? Explain using degrees of freedom.

c. Differentiate between reversible and irreversible processes.

A companion to your textbook, not a replacement for it: study from the book your school uses, and where the two differ, follow your teacher. Found a mistake? Please tell us.