

Topic 10: Thermodynamics

Advanced Placement Physics 2

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Kinetic Theory of Gases

Assumptions for the kinetic theory of gases:

1. The gas consists of a large number of molecules that make *elastic* collisions with each other and with the walls of the container.
2. The molecules are separated, on average, by distances that are large compared to their diameters, and they exert no force (gravitational, electrostatic etc) on each other except when they collide.¹
3. In the absence of external forces, there is no preferred position for a molecules in the container, and there is no preferred velocity vector.

¹This means that the density of the gas is low, i.e. assume ideal gas behavior.

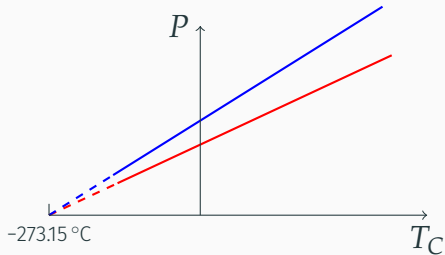
Properties of a Gas

- Volume
- Pressure
- Temperature

Thermodynamic Temperature

Thermodynamic Temperature

William Thomson (Lord Kelvin) and James Joule discovered that when a gas is heated/cooled at *constant volume*, the relationship between pressure and temperature is *linear*:



Regardless of the type of gas, amount of gas, or the volume of gas, pressure is always zero at $-273.15\text{ }^{\circ}\text{C}$. Since pressure cannot be negative; no temperature can exist below that value.

Thermodynamic Temperature

The **thermodynamic temperature** (or **absolute temperature**) T is obtained by shifting the “null point” (where temperature is zero) from the Celsius temperature T_C . The unit for thermodynamic is a **kelvin** (K). It is one of the 6 base units of the SI system.

$$T = T_C + 273.15$$

- A temperature of 0 K is called **absolute zero**, but it is impossible to obtain because of quantum-mechanic effects
- This temperature scale is more consistent with the physical and thermodynamic properties of gases
- Note: the temperature *change* of 1 K is the same as 1 °C, i.e.:

$$\Delta T = \Delta T_C$$

Ideal Gas Law

Ideal Gas Law for Low-Density Gases

Physicist Robert Boyle (1627-1691) discovered that, when a gas is allowed to expand or compress at *constant temperature*, the product of pressure P and V remain constant (**Boyle's law**), i.e.:

$$PV = \text{constant}$$

From the previous discussion on temperature scale, we also know that at *constant volume*, (thermodynamic) temperature is proportional to pressure. Combining the two discoveries yields this equation:

$$PV = CT$$

where “C” is some constant to be determined.

Ideal Gas Law

Thought experiment:

- Two identical containers with the same volume V , same amount of same kind of gas, at same pressure P and same temperature T
- When the containers are combined and the molecules are free to move, P and T remain the same, but volume and the number of molecules are both increased by factor of 2

Therefore C must scale with the number of molecules of gas N , which modifies the equation to this, the **ideal gas law**:

$$PV = NkT$$

The constant $k = 1.381 \times 10^{-23}$ J/K is called **Boltzmann's constant**. It is found experimentally to have the same value for any kind or amount of gas.

Ideal Gas Law

The ideal gas law is often expressed in a slightly different form in chemistry courses:

$$PV = nRT$$

where:

- $n = N/N_A$ is the number of moles of the gas
- $R = kN_A = 8.314 \text{ kg/mol K}$ is the **universal gas constant**, and
- $N_A = 6.022 \times 10^{23}$ is **Avagadro's number**, which is the number of molecules in one mole

Average Kinetic Energy of a Gas

We note that pressure is force of the gas molecules exerts when colliding with the container, given by

$$P = \frac{F}{A}$$

By Newton's second law of motion: the collision changes the momentum of the gases

$$\mathbf{F} = \frac{d\mathbf{p}}{dt}$$

We can then relate the change momentum, to force to pressure and to the ideal gas law. After some calculus...

Average Kinetic Energy of a Gas

We find the average kinetic energy $\langle K \rangle$ of a molecule of gas in a container, given by:

$$\langle K \rangle = \frac{3}{2}kT$$

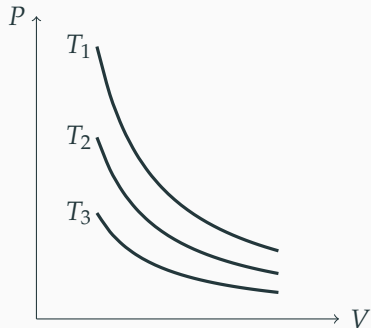
i.e. temperature is a measurement of the average kinetic energy.

Often it is advantageous to calculate the root mean square (“rms”) velocity of the molecules, which measures the speeds that the majority of the particles are below:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

P - V Diagram

Thermodynamic processes is usually plotted on a “ P - V diagram”.



- Under constant temperature, the relationship between pressure and volume is a hyperbolic curve.
- Each line is called an **isotherm**; it represents a different constant temperature
- $T_3 > T_2 > T_1$

Note: Aside from P - V diagrams, there are many similar diagrams in thermodynamics.

Real Gases

Most gases behave like ideal gas at most ordinary pressures, but the equation breaks down when the density of gas is high and molecules are not far apart:

- pressure is sufficiently high
- temperature is low

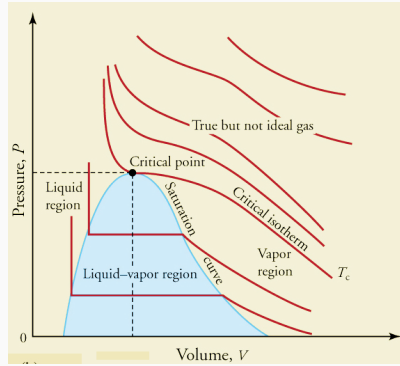
In these situations the **van der Waal equation** provides a more accurate description of the behavior of real gases:

$$\left(P + \frac{an^2}{V^2} \right) (V - bn) = nRT$$

- The term an^2/V^2 is from the attraction of the gas molecules to each other
- The term b is approximately the volume occupied by one mole of the gas

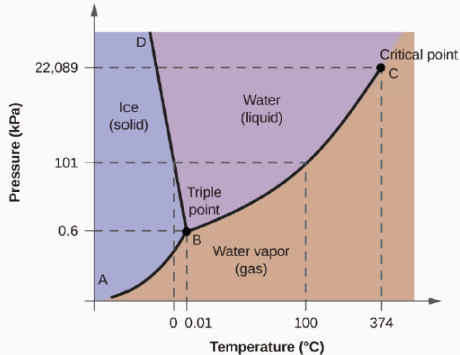
Real Substances

Neither the **ideal gas law** nor the **van der Waal equation** can capture the exact relationship between pressure and volume, because neither can account for phase changes. The P - V diagram of a real substance is like this:



Phase Diagrams

The phase diagram plots pressure against temperature to show when the different phases of matter exist. For water:



- At **triple point B**, all three phases of matter can exist in equilibrium
- At **critical point C**, liquid and vapour phases are indistinguishable, and the gas laws can model their behavior

First Law of Thermodynamics

In the **first law of thermodynamics**, the change in internal energy of a thermodynamic system (ΔU) is the difference between the heat added into the system and the sum of the work (W) *by* the system²:

$$\Delta U = Q - W$$

Quantity	Symbol	SI Unit
Change in internal energy of a system	ΔU	J
Work done <i>by</i> the system	W	J
Heat into the system	Q	J

²**VERY IMPORTANT NOTE:** Often the equation is written as $\Delta U = Q + W$, where W is the work done *to* the system. Since both conventions are commonly use, you must be very careful.

First Law of Thermodynamics

Internal energy U is the total kinetic & potential energies of the molecules. It is a linear function of temperature.

$$\Delta U = Q - W$$

For monatomic gases (including an ideal gas): there are 3 degrees of translational freedom, therefore the internal energy is

$$U = \frac{3}{2}NkT$$

For diatomic gases, there are 3 degrees of translational freedom and 2 degrees of rotational freedom:

$$U = \frac{5}{2}NkT$$

First Law of Thermodynamics

$$\Delta U = Q - W$$

For solids, there are 3 degrees of elastic compression freedom, therefore the internal energy is

$$U = 3NkT$$

Note that internal energy does not include:

- The bulk kinetic energy of the system, i.e. if the entire container of gas moves at speed v
- The potential energies caused by an external force field (e.g. gravitational, electric, magnetic)

First Law of Thermodynamics

Heat Q is the spontaneous transfer of energy *into* the system, through conduction, convection and radiation.

$$\Delta U = Q - W$$

- Heat transfer Q is:
 - + if thermal heat is added to the system
 - – if thermal heat leaves the system
- The net flow of energy is always from the higher temperature to low temperature
- Two objects are in thermal equilibrium if the temperatures are the same

First Law of Thermodynamics

W is the mechanical work³ done *by* the system to the surrounding.

$$\Delta U = Q - W$$

- Work is done iff⁴ the volume changes
- + done *by* the system, e.g. using steam pressure to push a piston or shaft
- – done *to* the system, e.g. pushing a piston to compress gas in an engine

³The full definition in calculus form is $W = \int P dV$ (i.e. pressure times change in volume) which is derived from the definition of mechanical work: $W = \int \mathbf{F} \cdot d\mathbf{x}$, i.e. force times distance.

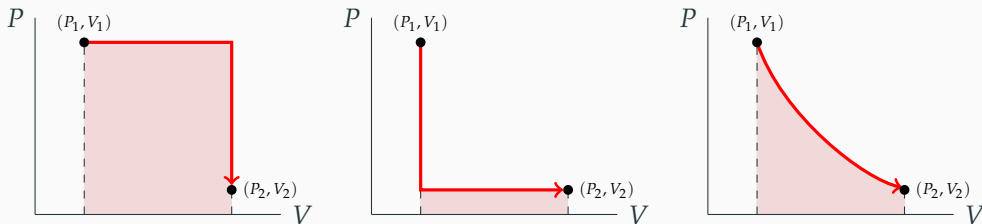
⁴“if and only if”

Work Done By a Gas

On the P - V diagram, W is the area under the curve.

- W is $+$ (by the system) if the path moves right
- W is $-$ (to the system) if the path moves left

In the example below, the gas is changed from points 1 to 2, but the work done is different.



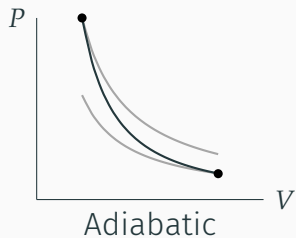
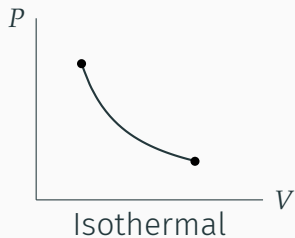
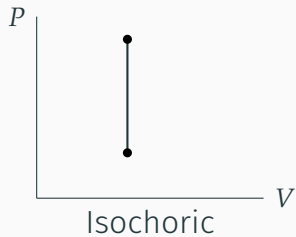
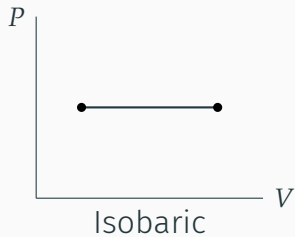
The fact that W is *path dependent* means that the pressure force is non-conservative.

Quasi-Static Processes

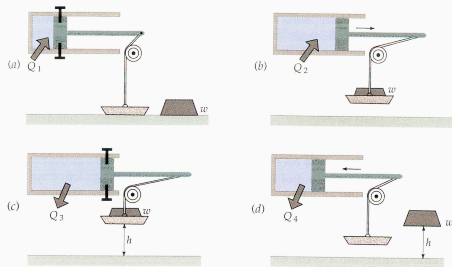
A **quasi-static process** is a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium. We are concerned with four of these processes:

- **Isobaric process** - constant pressure
- **Isochoric process** - constant volume
- **Isothermal process** - constant temperature
- **Adiabatic process** - “isolated”, no heat exchanged with surrounding

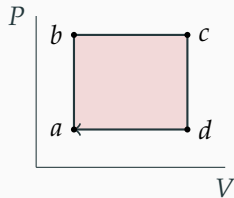
Quasi-Static Processes



A Simple Heat Engine Cycle



1. Heat is added at constant volume; no work done.
2. Heat is added as gas expands at constant pressure; work is done by the gas to lift the weight.
3. Heat is extracted at constant volume; no work done.
4. Heat is extracted at constant pressure; work is done on the gas to compress it.



P - V diagram of the simple heat engine shown on the left.

Efficiency of Heat Engine

In a heat engine, the internal energy at the beginning and end of the cycle are the same (same point on the P - V diagram), so the work done is just the difference between heat added and taken out:

$$W = Q_{\text{in}} - Q_{\text{out}}$$

Efficiency is defined as the ratio between work done and heat added:

$$\eta = \frac{W}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

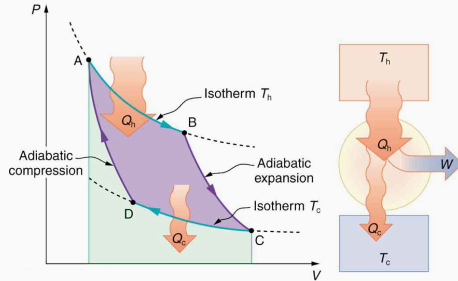
Second Law of Thermodynamics

Kelvin-Planck Statement

It is impossible for heat engine working in a cycle to produce no other effect than that of extracting heat from a reservoir and performing an equivalent amount of work.

Carnot Engine

The Carnot engine cycle is the most efficient.



The efficiency of a Carnot engine is:

$$\eta_C = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_c}{T_h}$$