

# Topic 10: Thermodynamics

## Advanced Placement Physics 2

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Olympiads School

# Kinetic Theory of Gases

We begin the study of the thermodynamics of ideal gases using these assumptions:

1. The gas consists of a large number of identical molecules that are in high-speed random motion
2. Molecular motion and interaction obey Newtonian laws of motion
3. Collision between molecules and with the walls of the container are *elastic*
4. Molecules are separated, on average, by distances that are large compared to their diameters (i.e. the space occupied by the molecules are small compared to the space occupied by the gas as a whole)
5. The only forces that the molecules experience are *contact* forces (i.e. no gravitational, electrostatic etc forces on each other except when they collide)

# Properties of a Gas

- **Volume** is the space occupied by the gas, with a unit of **cubic meter** ( $\text{m}^3$ )
- **Pressure** is the force  $F$  that a gas exerts on the container, divided by the surface area of the container  $A$  when the molecules collide with it:

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

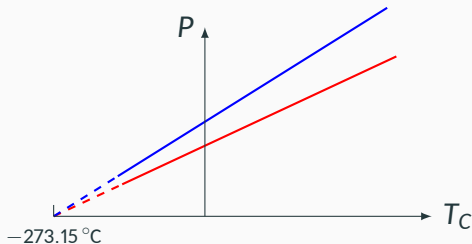
- Unit of pressure: **pascal** (Pa)
  - At thermal equilibrium, pressure is evenly distributed in the gas
- **Temperature** is a measure of the average kinetic energy of the gases.
  - It measures how “hot” an object is
  - SI Unit of temperature: **kelvin** (K)

# Thermodynamic Temperature

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# Thermodynamic Temperature

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



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

# Thermodynamic Temperature

The **thermodynamic temperature**<sup>1</sup>  $T$  is obtained by shifting the “null point” (where temperature is zero) from the Celsius temperature  $T_C$ .

$$T = T_C + 273.15$$

- A temperature of 0 K is called **absolute zero**<sup>2</sup>
- This temperature scale is consistent with the physical and thermodynamic properties of gases
- Note: the temperature *change* of 1 K is the same as 1 °C, i.e.:

$$\Delta T = \Delta T_C$$

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<sup>1</sup>or **absolute temperature**

<sup>2</sup>Absolute zero is impossible to obtain because of quantum-mechanic effects

# Ideal Gas Law

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## Ideal Gas Law for Low-Density Gases

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**):

$$PV = \text{constant}$$

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**:

$$PV = Nk_B T$$

The constant  $k_B = 1.381 \times 10^{-23}$  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 different form in chemistry courses:

$$PV = nRT$$

where:

- $n = N/N_A$  is the number of moles of the gas
- $R = kN_A = 8.314 \text{ kg/mol} \cdot \text{K}$  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

The ideal gas law is an **equation of state**, because it relates all the quantities that define the *state* of a gas: pressure  $P$ , volume  $V$  and temperature  $T$ .

# Maxwell-Boltzmann Distribution

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# Maxwell-Boltzmann Distribution

As gas molecules collide elastically with each other inside the container<sup>3</sup>:

- Some molecules *gain* kinetic energy (therefore moving faster), while
- Some molecules *lose* kinetic energy (therefore moving slower)
- Individual collisions are random occurrences (determined by statistical probabilities), but
- The overall behavior of the molecules at thermal equilibrium is very predictable

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<sup>3</sup>Recall the discussion on elastic collision from earlier in the course

# Maxwell-Boltzmann Distribution

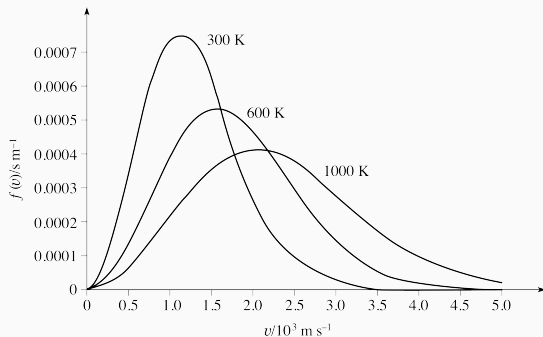
The distribution of particle velocities for a gas in a container is approximated by a probability distribution function called the **Maxwell-Boltzmann distribution**:

$$f(v) = 4\pi \left[ \frac{m}{2\pi k_B T} \right]^{\frac{3}{2}} v^2 \exp \left[ -\frac{mv^2}{2k_B T} \right]$$

Quantity	Symbol	SI Unit
Maxwell-Boltzmann dist. function	$f(v)$	s/m
Molecular mass	$m$	kg
Particle speed	$v$	m/s
Thermodynamic temperature	$T$	K
Boltzmann's constant	$k_B$	J/K

AP Physics 2 is not too concerned with the (difficult) mathematics, but rather, the overall concept.

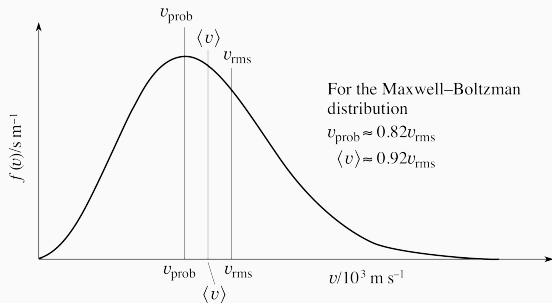
# Maxwell-Boltzmann Distribution



- The area under the distribution curve is 1 (all probabilities sum to 100 %)
- The peak of the distribution shifts to higher speeds as  $T$  increases
- The peak, which represents the most-probable speed  $v_{\text{prob}}$ , is lower at higher temperatures.

There are three particles speeds that are important: the most-probable speed  $v_{\text{prob}}$ , the mean (average) speed  $\langle v \rangle$  and the root-mean-square speed  $v_{\text{rms}}$ .

# Maxwell-Boltzmann Distribution



The **most probable speed**  $v_{\text{prob}}$  is the peak of the distribution function, where the speed is maximum (i.e. the mode of the function):

$$v_{\text{prob}} = \sqrt{\frac{2k_B T}{m}}$$

It is obtained through using basic (albeit not necessarily simple) calculus.<sup>4</sup>

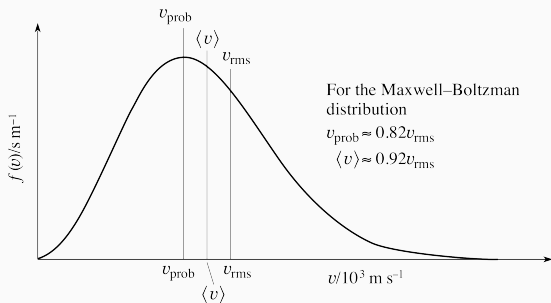
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<sup>4</sup>Finding the derivative of  $f(v)$  using chain rule and solving for  $f'(v) = 0$

# Maxwell-Boltzmann Distribution

The **mean speed**  $\langle v \rangle$  (or **average speed**) is calculated using the definition of an average using the weighted sum over  $N$  particles<sup>5</sup>:

$$\langle v \rangle = \frac{v_1 + v_2 + \cdots + v_N}{N}$$



This average speed is found to be:

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

<sup>5</sup>The proper calculus notation is the integral  $\int_0^\infty v f(v) dv$



# Root Mean Square Speed

When studying the behavior of gases, the quantity of interest is often the average *kinetic energy* of the molecules  $\langle K \rangle$ , which scales with  $v^2$ . The weighted average of kinetic energy:<sup>6</sup>

$$\langle K \rangle = \frac{\frac{1}{2}mv_1 + \cdots + \frac{1}{2}mv_N^2}{N} = \frac{1}{2}m \underbrace{\left[ \frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} \right]}_{v_{\text{rms}}^2}$$

The speed that gives the average kinetic energy is called the **root mean square speed**  $v_{\text{rms}}$ :

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

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<sup>6</sup>Again, the proper calculus notation is the integral  $\int_0^\infty v^2 f(v) dv$ .

## Average Kinetic Energy of a Gas

From the expression of  $v_{\text{rms}}$ , and relating to the average kinetic energy, it is easy to show that:

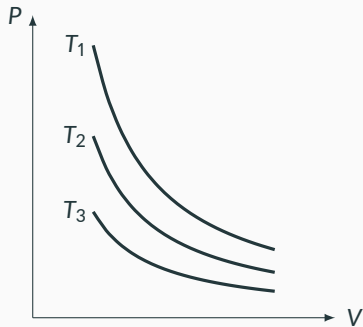
$$\langle K \rangle = \frac{1}{2} v_{\text{rms}}^2 = \frac{1}{2} \left( \sqrt{\frac{3k_B T}{m}} \right)^2 \rightarrow \boxed{\langle K \rangle = \frac{3}{2} k_B T}$$

i.e. thermodynamic temperature represents the average kinetic energy. If the number of gas molecules is known (which is usually not the case), then the *total* kinetic energy is just:

$$K = N \langle K \rangle = \frac{3}{2} N k_B T$$

# 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

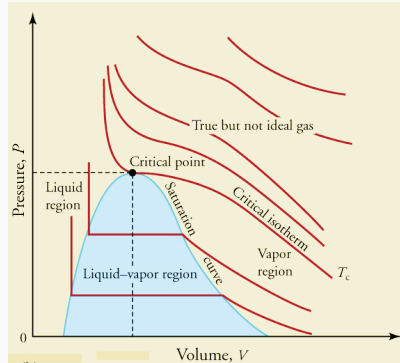
In these situations the **van der Waal equation** provides a more accurate description of the behavior of real gases:

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

- 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

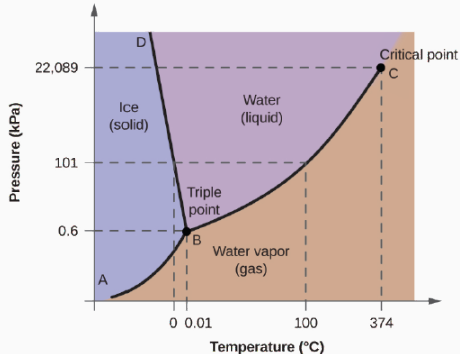
# Real Substances

Neither the ideal gas law nor the van der Waal equation capture the exact relationship between pressure and volume, because neither accounts 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 ( $\Delta U$ ) is the difference between the heat added into the system and the sum of the work ( $W$ ) *by* the system<sup>7</sup>:

$$\Delta U = Q - W$$

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

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<sup>7</sup>**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 proportional to thermodynamic temperature.

$$\Delta U = Q - W$$

For monatomic gases and ideal gas: there are 3 degrees of translational freedom, therefore the internal energy is the total kinetic energy, shown a few slides ago:

$$U = \frac{3}{2} N k_B T$$

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

$$U = \frac{5}{2} N k_B T$$



# First Law of Thermodynamics

$$\Delta U = Q - W$$

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

$$U = 3Nk_B T$$

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

# Heat Required for a Temperature Change

Heat  $Q$  required to change the temperature  $\Delta T$  is defined as:

$$Q = mc\Delta T$$

Quantity	Symbol	SI Unit
Amount of heat transferred	$Q$	J
Mass	$m$	kg
Specific heat capacity	$c$	J/kg · K
Temperature change	$\Delta T$	K

# Specific Heat Capacity

**Specific heat capacity**  $c$  is the amount of energy needed to raise 1 kg of a substance by 1 K. For gases,  $c$  is either measured at constant volume or pressure

- **Constant volume**  $c_v$ : no work is done; all the heat transfer goes to changing the temperature
- **Constant pressure**  $c_p$ : work  $P\Delta V$  is done at constant pressure while temperature also changes

Substance	$c$ (J/kg · K)
ethyl alcohol	2450
glycerine	2410
mercury	139
water (at 15 °C)	4186
aluminum	900
copper	387
glass	840
human body (37 °C)	3500
ice (−15 °C)	2000
steel	452
lead	128
silver	235

# First Law of Thermodynamics

$W$  is the mechanical work<sup>8</sup> done *by* the system to the surrounding.

$$\Delta U = Q - W$$

- Work is done iff<sup>9</sup> the volume changes
- At constant pressure:

$$W = P\Delta V$$

- + 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

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<sup>8</sup>The 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:  $W = \int \mathbf{F} \cdot d\mathbf{x}$  (force times distance).

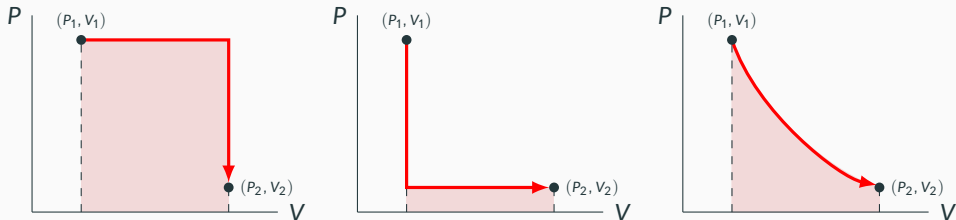
<sup>9</sup>“if and only if”

# 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.



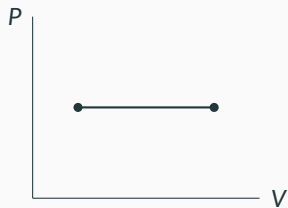
The fact that  $W$  is *path dependent* means that the pressure force  $F = P \cdot A$  is non-conservative.

# Quasi-Static Processes

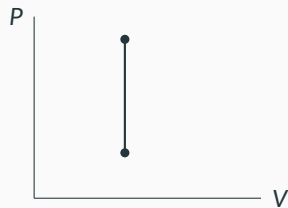
A **quasi-static process** is a thermodynamic process that happens slowly enough for the system to remain in internal equilibrium. We are concerned with four of these processes:

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

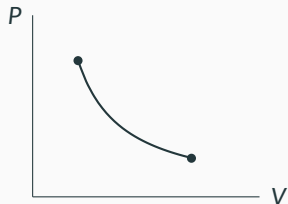
# Quasi-Static Processes



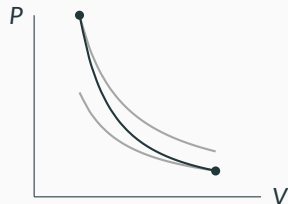
Isobaric



Isochoric



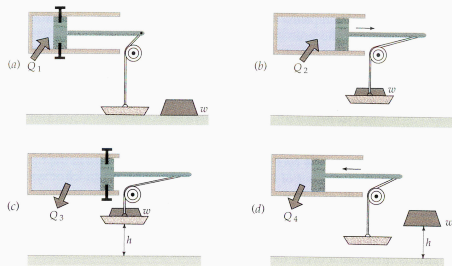
Isothermal



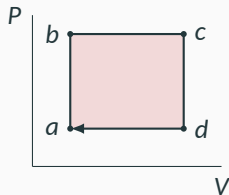
Adiabatic



# 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:

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

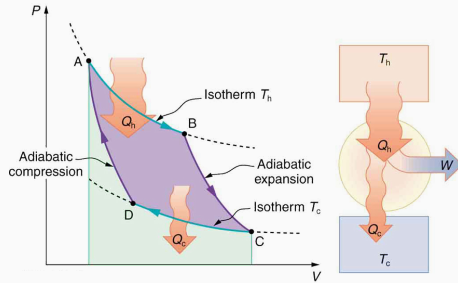
## Second Law of Thermodynamics

### **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:

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