

Lecture: 1

Temperature, ideal gas, Equipartition theorem, non –ideal gas

Our experience tells us that all physical bodies around us including our own body can be characterized by certain degree of “hotness and coolness”. We use word temperature to name the concept. If we connect two bodies or mix them and wait long enough the temperature becomes the same as our finger senses it.

Examples:

- (1) Cup of coffee gets cold after half an hour.
- (2) Mixing coffee and milk.

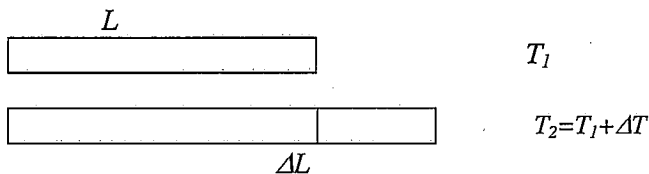
In example (1) “**half an hour**” is relaxation time, the time needed to reach the situation when T (temperature) is the same in all parts of the system. This final situation is called thermal equilibrium.

Physics is quantitative science. To find a way to measure “hotness” we look for other parameters affected by T .

Thermal expansion:

The length of a solid bar increases with temperature, $\Delta L = L(T_2) - L(T_1)$

$\Delta L = f(L, T, \Delta T) \approx L\alpha\Delta T$ Where, L – length, α – coefficient of linear expansion

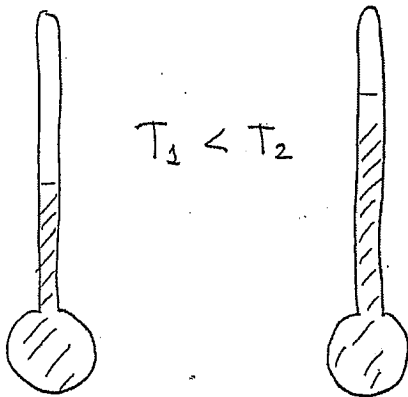


Volume expansion upon T increase:

$\Delta V = V\beta\Delta T$ Volume expansion of gases and liquids is convenient to calibrate temperature.

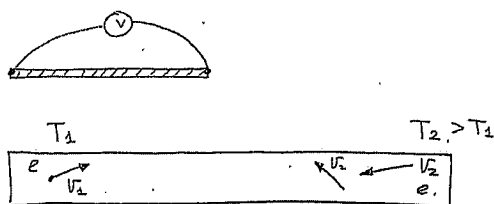
Two most popular liquid thermometers: Mercury (Hg) and alcohol thermometers.

	Freezing point	boiling point
Hg	-39°C	357°C
Alcohol	-112°C	78°C



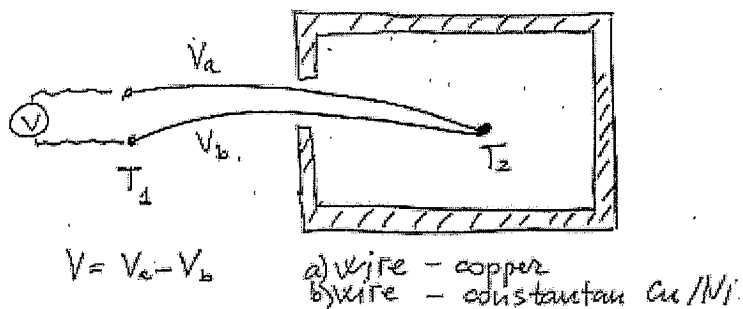
Thermocouple

When ends of a wire are kept at distinct temperature electrical potential difference occurs between them. Because the average velocity of electrons in the hot end of the wire (v_2) is larger than in the cold end, there is initial net flux of electrons from T_2 to T_1 . The initial flux is compensated by electric field that occurs inside of the wire.



Q. What is the direction of the field?

Thermocouple – two connected wires of different materials. Popular thermocouples: Cu-constantan (Cu-Ni alloy), Pt-Rd.



To determine the temperature in above examples, we need to perform calibration of thermometers that is to make correspondence between say voltage and temperature.

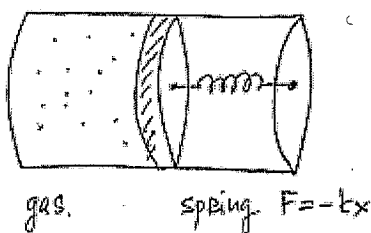
First principle thermometers -- > no calibration needed.

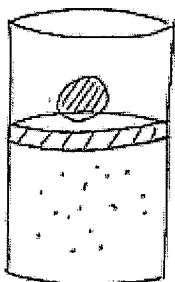
- Pyrometer deduces T from optical spectrum (high T , remote objects)
- Nuclear decay thermometer measures the width of the distribution of energies of γ - rays emitted by Co atoms in solids at low temperatures.

Historically for development of thermal physics, most important was a gas thermometer (GT). In GT pressure is used to calibrate temperature $P = F/S$

Where F – force, S – area (vector indicates normal to the surface).

Pressure can be easily measured





$$F = mg \quad P = F/S$$

Units of pressure Pa (Pascal)

$$1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/s}^2\text{m}$$

$$1 \text{ Bar} = 1 \text{ atmosphere} \approx 10^5 \text{ Pa}$$

10 meters of water approximately create the pressure of 1 atm.

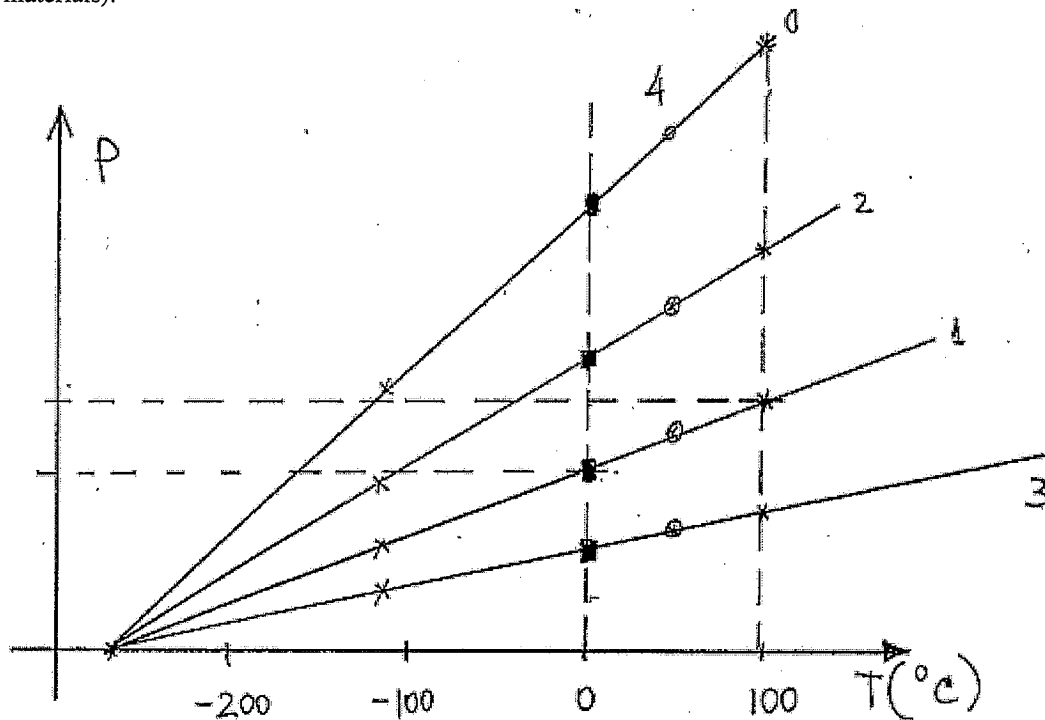
$$1 \text{ Bar} = 760 \text{ mmHg} = 760 \text{ Torr.}$$

$$1 \text{ Bar} = 14.7 \text{ Lb / inch square} = 14.7 \text{ psi (pounds per inch square)}$$

(Typical tire pressure is 30 psi \approx 2 atm)

Calibration of gas Thermometer (the way it was probably done in 18th century)

Imagine we are 18th century scientists who study ideal gases. We choose two reference temperature points. For example we assign 0°C to ice/water mixture (the temperature of the ice water mixture does not depend on relative content of water and ice) and we assign the temperature 100°C to boiling water. Then we take a container with some amount of gas, bring it in contact with our ice/water mixture and measure the pressure. We repeat the same procedure for boiling water. We assume that the pressure and temperature depends linearly on each other and determine the temperatures (by measuring the pressure and making linear extrapolation) corresponding to some other reference points (boiling, freezing or melting points of some materials).



For example we can get
 $+50^{\circ}\text{C}$ --- melting point of paraffin
 -39°C --- freezing point of mercury
 -112°C --- freezing point of alcohol

Then we without changing the volume of the container we add some extra amount of gas. Of course, the pressure changes and takes new values at 0 and 100 degree C. What is found that new points fall on a line 2 and that intersects the line 1 at temperature $T_0 = -273.15^{\circ}\text{C}$. We reduce the amount of gas in the container and find that all three lines intersects at the same temperature T_0 corresponding to zero pressure. And this is an amazing discovery. Experiments with different gases confirmed the value of T_0 .

We may introduce new temperature scale $^{\circ}\text{K}$ (Kelvin)
 $T(\text{K}) = T(^{\circ}\text{C}) + 273.15$

Experiments point on existence of the absolute zero temperature:

After manipulations with volume, pressure, temperature and gas amount, researchers came to important phenomenological law of ideal gas.

$$PV = nRT \quad T \text{ in Kelvin}$$

$R = 8.31 \text{ J/mole K}$ - gas constant, n - number of mole of a gas

1 mole = 6.02×10^{23} molecules = N_A - Avogadro number.

Definition of mole: Mole is the number of carbon -12 atoms in 12 grams of Carbon-12.

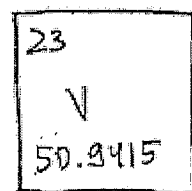
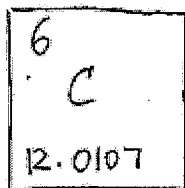
The atomic mass is the mass in grams of exactly one mole of that substance.

We look for atomic mass of an element in periodic table (textbook).

So we may rewrite ideal gas law in other forms.

$$PV = \frac{m}{\mu} RT = k_B NT$$

Where, μ - atomic mass, $n = m/\mu$ number of moles, N - total number of molecules and $k_B = 1.38 \times 10^{-23} \text{ J/K}$



Boltzmann constant.

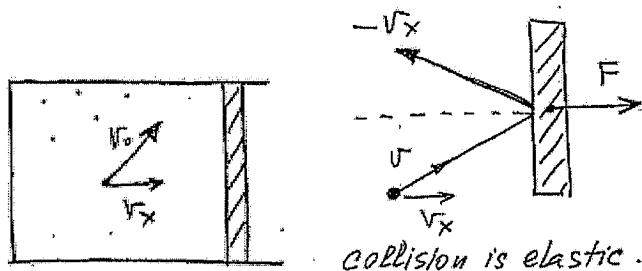
Problem 1 What is the volume of ideal gas at ambient conditions?

Problem 2 Find volume of 10g of water vapor at ambient conditions.

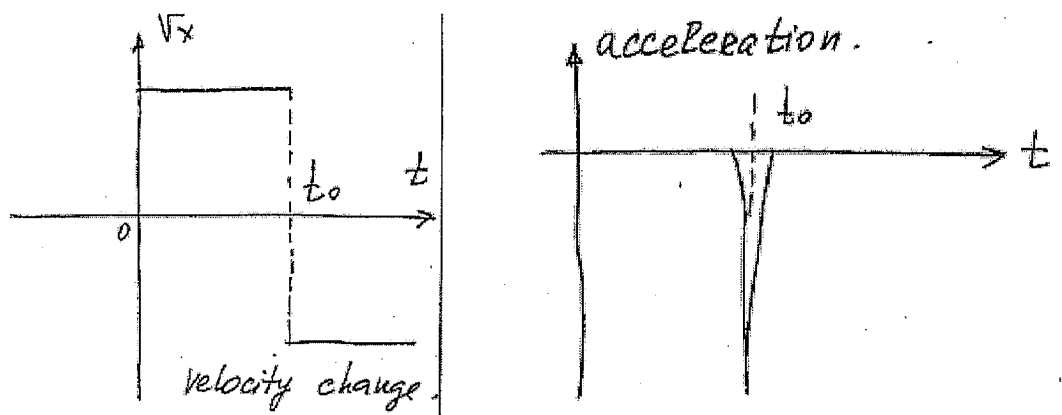
Microscopic model of ideal gas:

Temperature – result of mechanical motion of molecules (1650 Backon).

Pressure is a result of mechanical collision of the gas molecules with walls of a container.



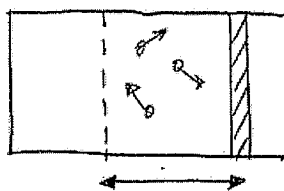
$F = ma = m \frac{dv}{dt}$. Each collision is very short event. It is hard to find out what is the acceleration of a molecule.



However, we do not need it if we are interested in average value of the force. Average force on the wall of the container from one collision over the period of time T_1 is

$$\langle F \rangle = -\frac{1}{T_1} \int_0^{T_1} m \frac{dv}{dt} dt = -\frac{1}{T_1} \int_{\langle v_x \rangle}^{\langle -v_x \rangle} m dv = \frac{1}{T_1} 2m \langle v_x \rangle$$

The force from many molecules



$$L = \langle v_x \rangle \cdot T_1$$

$$\langle F \rangle = \frac{2mv_x}{T_1} \cdot \frac{1}{2} N = \frac{mv_x}{(L/v_x)} \cdot N = \frac{mv_x^2}{L} \cdot N = PS$$

S – area of the piston P – pressure. So we have $PV = Nmv_x^2$.

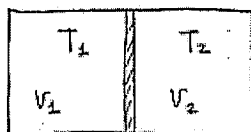
However from ideal gas law $P.V = Nk_B T$ and therefore we have

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T$$

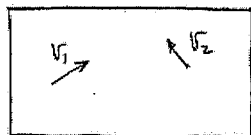
Because $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v^2 \rangle \quad \frac{1}{2} m \overline{v_{av}^2} = \frac{3}{2} k_B T$

Conclusion:

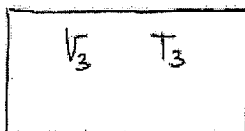
The average translational kinetic energy of a molecule in a gas is temperature times constant. Can we use the above expression as the definition of temperature? Yes in principle, but consider an example.



Wall is removed. T is undefined.



relaxation.



We need to be accurate when we deal with average values. Let's consider some averages for velocity.

$$v_{rms} = \sqrt{\frac{\sum_{i=1}^N v_i^2}{N}} \quad \text{average root-mean-square velocity}$$

$$v_{ave} = \frac{\sum_{i=1}^N |v_i|}{N} \quad \text{average speed}$$

The average kinetic K energy is

$$(2) \quad \overline{K} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m (\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{3}{2} k_B T$$

Because $\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} k_B T$ and average of a sum is a sum of averages. We may compute root-mean-square velocity (RMS).

$$V_{rms} = \sqrt{\overline{v^2}} = \sqrt{\langle v^2 \rangle} \quad \text{definition} \quad \langle v^2 \rangle = \frac{1}{T} \int_0^T v^2 dt$$

$$V_{rms} = \sqrt{\frac{3kT}{m}}$$

Note that average speed and v_{RMS} of molecules in a gas are not the same things.

Non-ideal gas, Van der Waals equation of state

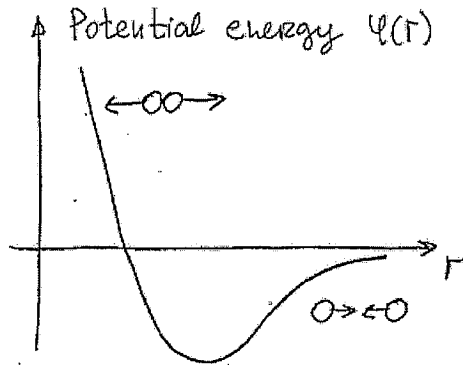
Ideal gas law $PV = nRT$ describes correctly very dilute gases. In more accurate model, we have to take into account two corrections.

- 1) Molecules have finite size.
- 2) Molecules (atoms) do interact with each other.

The simplest model that phenomenologically incorporates these two corrections is the Vander Waals model.

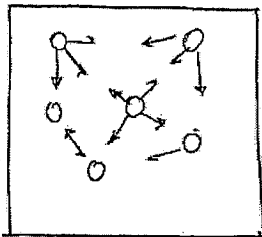
$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T$$

a, b constants to be determined from a comparison with experiments.



The interaction energy between two molecules or atoms normally consists of two terms – short-range repulsion plus long-range attraction. The short range can be approximately described assuming that each molecule has hard, impenetrable core. The addition of $(-Nb)$ term to (V) to form $(V - Nb)$ accounts for the fact that gas cannot be compressed all the way down to zero volume. The constant b represents the minimum volume occupied by a molecule when it is touching all its neighbors.

The aN^2/V^2 term accounts for the longer-range attractive forces between molecules when they are not “touching” each other. Direction of intermolecular forces that act on molecules near boundary of volume V is inward. The Van der Waals arguments suggest that these forces contribute and internal pressure aN^2/V^2 which is to be added to the external pressure P so that $P + aN^2/V^2$ should be used as the pressure in the gas law.



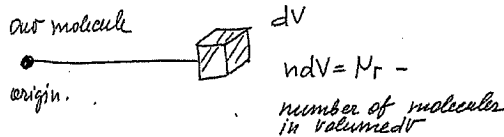
This can be shown from following arguments. When the concentration of atoms in the gas is n , the value of the interaction of an atom that is at $r = 0$ with all other atoms with is

$$u = \sum_{i=1}^N \phi(r_i) \text{ the sum is over all atoms (molecules) of the gas except the atom at the origin. } \phi(r) - \text{pair}$$

interaction potential between two atoms.

We may approximate the above sum by an integral.

$$\int_b^\infty dV \varphi(r) n = n \int_b^\infty dV \varphi(r) = -2na \quad (\text{Factor 2 is a useful convention}).$$



In writing the above equation we assume that the concentration n is constant throughout the volume accessible to molecules of the gas. That is we use mean value of n . In other words, we used so-called mean field approximation that ignores correlations in positions between interacting molecules.

$ndV = N_r$ - number of molecules in volume dV .

$\varphi(r)N_r$ - total energy of interaction between molecules in dV and our chosen molecule at origin.

n - doesn't depend on r . (It is our assumption, It often does depend on r in reality).

From the above arguments it follows that the interaction changes the internal energy and correspondingly the free energy of gas (we will learn what it is) of N molecules in volume V by

$$\Delta F = \Delta U = -\frac{1}{2}(2Nna) = -\frac{N^2 a}{V}$$

N appears in the above expression because we sum over all molecules, $\frac{1}{2}$ - appears because we count every bond between different pairs of atoms only once.

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -N^2 a \cdot \frac{1}{V^2} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,V} \quad \text{- the definition of pressure that we will soon learn in the}$$

course.

So we have

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_B T$$

+ sign in the pressure term appears because we have effective contribution to external pressure. It can also be checked from the fact that the volume of the system reduces when we "turn on" attractive interaction between molecules.

$$b \approx (4A^0)^3$$

$$a \approx 4 \times 10^{-49} \text{ J.m}^3 \text{ for } N_2$$

$$\approx 16 \times 10^{-49} \text{ J.m}^3 \text{ for } H_2O \text{ (H}_2\text{O is easy to polarize).}$$

$$\approx 1 \times 10^{-50} \text{ J.m}^3 \text{ for He.}$$

Equipartition of energy:

Equation $\frac{1}{2}mv_x^2 = \frac{1}{2}k_B T$ is a special case of more general result called equipartition theorem.

In our example a molecule can move along x axis and has the energy of this motion being proportional to the square of the velocity. We may say that the molecule has a degree of freedom to move along x axis.

Translational motion $\frac{1}{2}mv^2$

Rotational motion - $\bar{E} = \frac{1}{2}I\omega^2$, I - Moment of Inertia - $I = \sum m_i r_i^2$, ω - Angular velocity.

Vibrational motion, $E = \frac{1}{2}kx^2 + \frac{1}{2}mv^2$, k - spring constant.

Equipartition theorem:

At temperature T the average energy of quadratic degree of freedom is $\frac{1}{2}k_B T$.

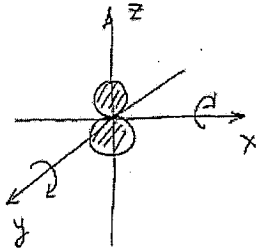
How to count d.o.f - f - number of degree of freedom.

→ Monoatomic molecule - x, y, z - Translational $f = f_T = 3$

→ Diatomic molecule (O_2 , N_2)

translational degrees of freedom $f_T = 3$

rotational degrees of freedom $f_R = 2$



vibrational degrees of freedom $f_V = 1$

Diatomic molecule can vibrate. The average energy that the excited vibrational degree of freedom carries is $k_B T$. One $\frac{1}{2}k_B T$ is for potential energy of the vibrating molecule and the other $\frac{1}{2}k_B T$ for kinetic energy.

(In Schroeder textbook a different convention is used - every vibration has two degrees of freedom, each carrying $\frac{1}{2}k_B T$ amount of energy)

- As a number of atoms in a molecule increases, counting of vibrational modes becomes tricky.
- For three-dimensional solid composed of N atoms total number of vibrational modes is $3N - 6$, where 6 represents three translation and three rotational degrees of freedom for the solid as a whole.

Equipartition theorem is a theorem of classical statistical mechanics, quantum mechanics dictates that some degree of freedom are frozen and therefore not in action at low T , where the energy quantization becomes important.