Topic 8 - Temperature and ideal gases

1 Temperature and thermal equilibrium

1.1 Heat

Heat is the energy transferred between objects because of the temperature difference between them

- when 2 objects are ni thermal contact, heat flows from an object of higher temperature to an object at a lower temperature until their temperatures equalize at some intermediate value

1.2 Thermal equilibrium

Two objects are in a state of **thermal equilibrium** when there is **no net flow of heat** between them
Two objects are in thermal equilibrium if and only if they are at the **same temperature**

1.3 Zeroth law of thermal dynamics

if object A and B are each separately in thermal equilibrium with object C, then A and B are also in thermal equilibrium with each other

2 Temperature scales

A temperature scale is a system of measuring temperature based on some thermometric property of a substance.
Criteria for a suitable thermometric property

1. Property **varies continuously and uniquely** with temperature

2. Change in property must be **large** enough to enable accurate measurements of temperature (ensure sensitivity of thermometer)

3. The value of thermometric property at any temperature within its working range must be **reproducible**

2.1 Centigrade scale

Empirical centigrade scale

- lower fixed point, 0°C : **ice point** (temperature of pure ice in equilibrium with water at standard atmospheric pressure of 101.3kPa)

- upper fixed point, 100°C : **steam point** (temperature of steam in equilibrium with boiling water at standard atmospheric pressure of 101.3kPa)

- divide the range into 100 degrees

An empirical scale is established by

1. taking the value of a thermometric property, X, at a ice and steam fizxed points, X_0 and X_{100}

2. dividing the range of values $(X_{100} - X_0)$ into a number of equal steps / degrees

3. assume that the thermometric property X vaies linearly with temperature, draw a calibration graph of X against temperature, θ

4. Measure thermometric property at unknown temperature θ and call it X_θ the unknown temperature θ in $°C$ is then computed from
$$\theta = \frac{(X_\theta - X_0)}{(X_{100} - X_0)} \times 100°C$$

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2.2 Thermodynamic temperature scale

Absolute zero

the absolute zero is defined as the zero pint (0K) of the thermodynamic temperature scale

Thermodynamic temperature scale Kelvin scale

- lower point: absolute zero

- upper point: triple point of water, (0.01°C, or 275.16K)

The kelvin is defined as $\frac{1}{275.16}$ of the thermodynamic temperature of the triple point of water

3 Ideal gas equation

Ideal gas is an idealization of the real gas in which potential energy of intermolecular interaction is 0.

An **ideal gas** is a gas which obeys the equation of state $pV = nRT$ at all pressures, volume, temperatures

3.1 equation of state / ideal gas equation

The ideal gas equation can be derived from

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$p_1 V_1 = p_2 V_2$$

Hence,

$$pV = nRT$$

where R is a molar gas constant $R = 8.314 JK^{-1}mol^{-1}$
Avogadro's constant, N_A is defined as the number of atoms in a 12 grams of a carbon-12 sample

$$N_A = 6.023 \times 10^{23}$$

Alternative forms of the ideal gas equation

$$pV = \frac{N}{N_A} RT$$

$$pV = NkT$$

where $k = \frac{R}{N_A}$ is the Boltzmann constant, $k = 1.38 \times 10^{23}$

4 Kinetic theory of gases

Molecular model of an ideal gas makes the following assumptions

1. molecules have **negligible volume**

2. molecules exert **no intermolecular forces** on one another, except during collisions

3. molecules move about in random motion in straight lines at constant speed

4. all collisions are completely elastic

5. the molecules of a particular gas are identical

6. there are sufficiently large number of molecules, so only average behaviour need to be considered

Derivation of model

For an ideal gas in a cubic container with lenght d
Let mass of each molecule be m. For one molecule with velocity c_X in the x-direction, upon colliding with the wall, its velocity changes from c_X to $-c_X$, the change in momentum is given by

$$\Delta p = (-mc_X) - mc_X = -2mc_X$$

Assuming no intermolecular collision, when the particle collides with the wall it would have travelled a distance of $2d$ in the x-direction. the time interval between collisions is thus given by

$$\Delta t = \frac{2d}{c_X}$$

By Newton's second law, the rate of change of momentum is given by

$$F_{\text{on molecule}} = \frac{\Delta P}{\Delta t} = -2mc_X \times \frac{c_X}{2d} = -\frac{mc_X^2}{d}$$

By Newton's third law, the force that the molecule acts on the wall is

$$F_{\text{on wall}} = -F_{\text{on molecule}} = \frac{mc_X^2}{d}$$

Total force is thus

$$F_{tot} = \frac{m}{d}(c_{X1}^2 + c_{X2}^2 + c_{X3}^2 ... c_{XN}^2)$$

The mean-square-speed in the x direction is defined as

$$\langle c_x^2 \angle = \frac{c_{X1}^2 + c_{X2}^2 + c_{X3}^2 ... c_{XN}^2}{N}$$

Hence

$$F_{tot} = \frac{Nm}{d}\langle c_x^2 \rangle$$

Total pressure p on the wall is thus

$$p = \frac{F}{A} = \frac{F_{tot}}{d^2} = \frac{Nm}{d^3}\langle c_x^2 \rangle = \frac{Nm}{V}\langle c_x^2 \rangle$$

By pythagoras' theorem

$$c^2 = c_x^2 + c_y^2 + c_z^2$$

Taking the average

$$\langle c^2 \rangle = \langle c_x^2 \rangle + \langle c_y^2 \rangle + \langle c_z^2 \rangle$$

$$\langle c_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$$

Substituting,

$$pV = \frac{1}{3}Nm\langle c^2 \rangle$$

where N is the number of gas molecules
m is the mass of one molecule
$\langle c^2 \rangle$ is the mean-square-speed of the gas

Define **root-mean-square** speed as

$$c_{rms} = \sqrt{\langle c^2 \rangle} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2...c_N^2}{N}}$$

Combining $pV = NkT$ and $pV = \frac{1}{3}Nm\langle c^2 \rangle$

$$pV = NkT = \frac{1}{3}Nm\langle c^2 \rangle$$

$$\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$$

The LHS is the average translational KE of one gas molecule

$$\langle E_k \rangle = \frac{1}{2}m\langle c^2 \rangle = \frac{1}{2}mc_{rms}^2 = \frac{3}{2}kT$$

$$\sqrt{\frac{c_1^2 + c_2^2 + c_3^2...c_N^2}{N}}$$