

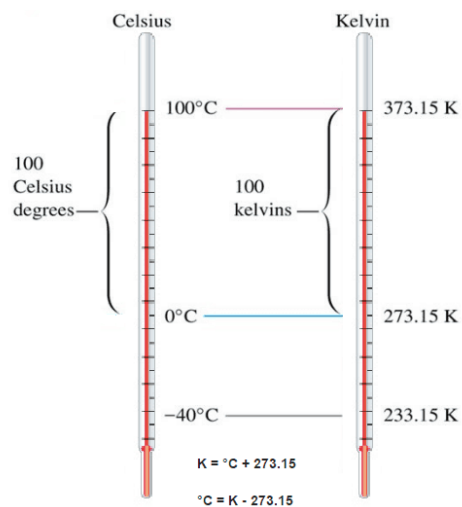
Thermal Equilibrium & Zeroth Law of Thermodynamics

Two objects are said to be in thermal equilibrium if there is no net exchange of thermal energy when they are in thermal contact.

Thermal equilibrium refers to no net transfer of thermal energy (heat) when in thermal contact.

Zeroth law of Thermodynamics states that if bodies A and B are separately in thermal equilibrium with a third body C, then A and B are also in thermal equilibrium with each other.

Thermodynamic Scale of Temperature



Absolute Zero: Temperature at which a substance has minimum internal energy.

Temperature and Heat:

Temperature is a measure of the average kinetic energy possessed by the particles of the system. The greater the average kinetic energy possessed per particle in the body, the greater its temperature.

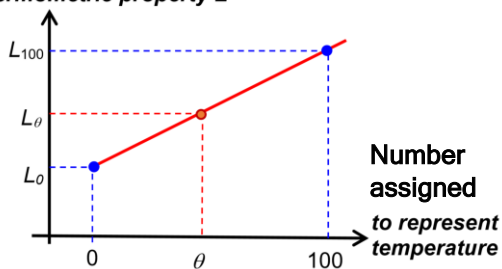
Heat is the thermal energy that flows naturally from a region of higher temperature to a region of lower temperature.

Centigrade Empirical Temperature Scale:

An empirical scale is one that is obtained through experiment and is dependent on the thermometric property chosen.

Let L be the thermometric property (e.g. length of mercury thread, resistance of platinum coil etc.) chosen.

Thermometric property L



By assuming that the thermometric property varies linearly with temperature, a scale of temperature based on the thermometric property L is defined by the equation:

$$\frac{t}{100} = \frac{L_\theta - L_0}{L_{100} - L_0}$$

Ideal Gas Equation or Equation of State:

An ideal gas is one which obeys the equation of state at all values of pressure, volume and temperature.

$pV = nRT$ where n = amount of substance (in terms of number of moles of gas)

$pV = NkT$ where N = amount of gas (in terms of number of gas molecules)

Important notes:

- T is the thermodynamic temperature expressed in Kelvin
- If the question asks for the ideal gas equation, quote $pV = nRT$ not $= NkT$. And n should be defined as the quantity amount of gas, not number of moles.

If a fixed mass of gas changes from state 1 to state 2 then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \rightarrow \frac{pV}{T} = nR$$

N_A : Avogadro constant = number of atoms in 0.012 kg of carbon-12.

R : Molar gas constant = $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

Boltzmann's constant = $R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Molar Mass of a substance M is the mass of one mole of the substance, $m = nM$

Molar volume of a gas V_m is the volume of one mole of the gas, $V = nV_m$

Internal Energy U

according to the kinetic theory of matter, matter is made up of many molecules in constant motion, hence they have **kinetic energy**. There may also be attractive and repulsive forces between the molecules, thus they have **potential energy** due to the interaction between them.

Definition: The internal energy of a system is the summation of microscopic kinetic energy due to the random motion and the microscopic potential energy due to the intermolecular forces of the molecules in the system.

$$U = KE_{micro} + PE_{micro}$$

Internal Energy U of an ideal gas:

For an ideal gas, it is assumed that there is no force of attraction between molecules, resulting in zero microscopic PE. The internal energy of an ideal gas is hence just the microscopic KE of the molecules.

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

NOTE: while the internal energy U of an ideal gas is proportional to T . This is not so for non-ideal gas, liquid and solids because of the PE component.

Using Kinetic Model to explain some Phenomenon

Why melting and boiling occurs without a change in temperature?

No change in average KE of the molecules. The energy supplied increases the potential energy among the particles of the system.

Why $L_{vaporization}$ is larger than L_{fusion} ?

In vaporization, there is an expansion of the gas against the environment and thus significant work done on the environment. In melting, there is little change in volume.

In vaporization, the intermolecular forces of attraction between molecules are completely broken and molecules are completely free. There is a huge increase in PE of the system. In melting, the increase in potential energy is not as much.

Why cooling accompanies evaporation?

The molecules in the liquid have a range of KE. The ones with the most KE can overcome attraction with the other molecules, and overcome atmospheric pressure to escape from the surface, reducing the average KE per molecule of those remaining.

Molecular speeds in gas: in any gas, the molecules randomly collide with each other and some molecules gain energy (and therefore speed), while others lose it. As a result, at any instant, the moles have a range of speeds.

Root-mean-square (RMS): describes the 'average' speed of the molecules.

$$c_{rms} = \sqrt{\langle c^2 \rangle} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}}$$

Assumptions of an ideal gas:

- The gas consists of a very large number of molecules
- The gas molecules are moving randomly
- The collisions of the gas molecules with one another and with the walls of the container are perfectly elastic.
- There are no intermolecular forces of attraction except during collision.
- The volume of the gas molecules is negligible as compared to the volume of the container (volume of gas).
- The duration of collision is negligible compared to the time interval between collisions

This microscopic model of an ideal gas is in contrast with the macroscopic description using the ideal gas equation $pV = nRT$

Pressure of an Ideal Gas:

Consider the force exerted by one single molecule of mass m moving across a cube of sides L at velocity v_x .

$$\begin{aligned} f &= \Delta p \text{ per col.} \times \text{freq. of col.} \\ &= 2mv_x \times \frac{v_x}{2L} \\ &= \frac{mv_x^2}{L} \end{aligned}$$

The total force is thus

$$F = \frac{Nmv_x^2}{L} = \frac{Nm\langle c^2 \rangle}{3L}$$

The Pressure of an ideal gas is thus related to the microscopic random motion of the gas molecules

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

Linking Kinetic Energy and Temperature

In a gas, each molecule has kinetic energy because of translational motion. This is called translational kinetic energy. Its average value depends on the mean-square-speed.

$$\text{Average KE per molecule} = \frac{1}{2}m\langle c^2 \rangle$$

This can be linked to the Kelvin temperature as follows:

$$KE = \frac{3}{2}nRT = \frac{3}{2}NkT \rightarrow \text{kin. theory}$$

$$pV = NkT \rightarrow \text{ideal gas eqn}$$

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

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

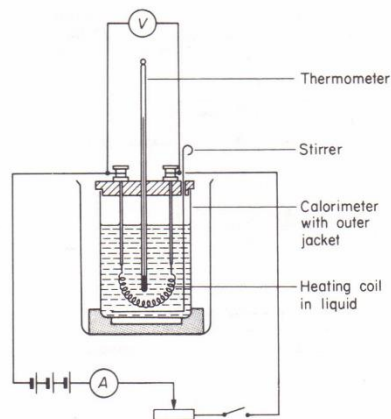
Heat Capacity C definition: Amount of energy required to raise the temperature of the substance by 1 unit of temperature. [SI unit is J kg^{-1}]

$$Q = c\Delta T$$

Specific Heat Capacity c definition: Amount of energy per unit mass required to raise the temperature of the substance by 1 unit of temperature. [SI unit is $\text{J kg}^{-1} \text{K}^{-1}$]

$$Q = mc\Delta T$$

How to find c for a liquid?



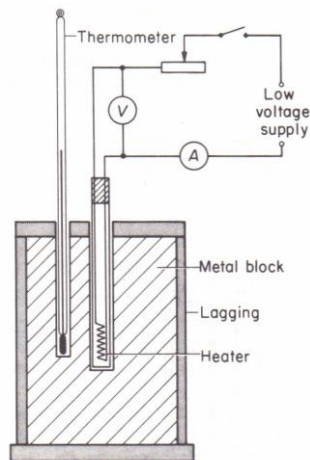
By principle of COE:
Electrical energy supplied = Heat gained by liquid

$$VIt = mc\Delta T$$

$$c = \frac{VIt}{m\Delta T}$$

How to find c for a solid?
(e.g. a metal)

The method is similar to the method for liquid, except the solid block is used instead of the liquid. The block has holes drilled in it for an electric heater and thermometer.

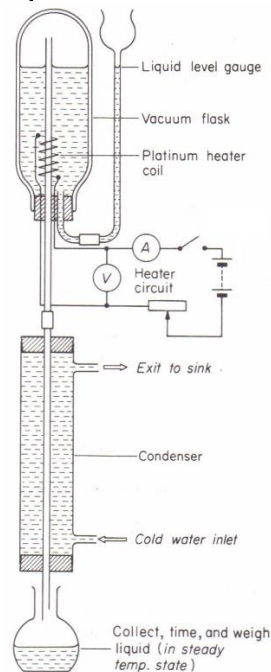


Specific Latent Heat of Vaporization. Definition: The specific latent heat of vaporization L_v of a substance is the energy per unit mass required to change the substance from the liquid to the gas without any change in temperature.

[SI unit is J kg^{-1}]

$$Q = mL_v$$

How to find latent heat of vaporization?



COE: Electrical energy supplied = Heat gained by liquid

$$VIt = mL_v$$

$$L_v = \frac{VIt}{m}$$

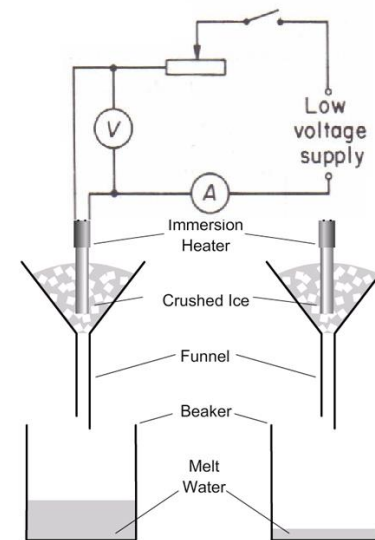
Specific Latent Heat of Fusion.

Definition: The specific latent heat of fusion L_f of a substance is the energy per unit mass required to change the substance from the solid to the liquid without any change in temperature.

[SI unit is J kg^{-1}]

$$Q = mL_f$$

How to find latent heat of Fusion?



Mass of ice melted due to electric heater = $m_2 - m_1$

COE: Electrical energy supplied = Heat gained by liquid

$$VIt = (m_2 - m_1)L_v$$

$$L_v = \frac{VIt}{m_2 - m_1}$$

First Law of Thermodynamics: By COE:

$$\Delta U = Q + W$$

Definition: The increase in the internal energy of the system is the sum of the heat supplied to the system and the work done on the system (note that the law applies to any system)

ΔU : *increase in the internal energy if the system*

- System gains internal energy: positive
- System loses internal energy: negative

Q : *amount of heat supplied to the system*

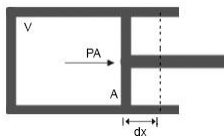
- Heat flows into the system: positive
- Heat flows out of the system: negative

W : *work done on the system*

- Work done ON the system (compression): positive
- Work done BY the system (expansion): negative

Work Done by Gas, W

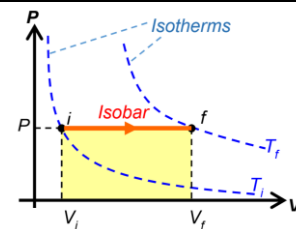
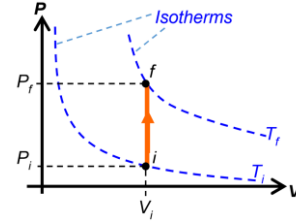
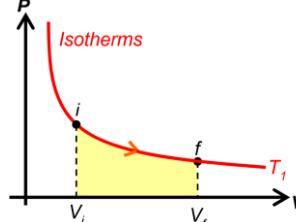
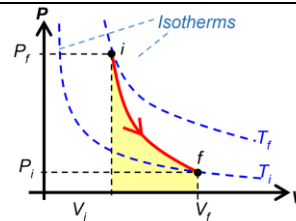
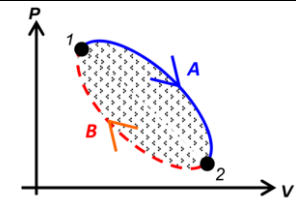
When a gas expands, it does work. In the diagram above, a gas at pressure p exerts a force on the piston, and moves it a short distance Δx . If the expansion of the gas is so small that the pressure does not change,



$$\text{work done by gas} = \text{force} \times \text{displacement} = p\Delta x = p\Delta V$$

- If the volume of the gas is decreased by ΔV , then $p\Delta V$ is the work done on the gas.
- Work done ON the gas = work done BY the gas
- In general, the area under the graph of a p - V diagram gives the work done on a gas (decreasing volume) or work done by a gas (increasing Volume)

Indicator Diagrams (Pressure-Volume graphs for an ideal gas)

Process	Indicator Diagram	Application of First Law
Isobaric (Constant pressure)		$W = -ve$ $\Delta U = +ve$ $\therefore Q = +ve$
Isochoric (Constant volume)		$W = 0$ $\Delta U = +ve$ $\therefore Q = +ve$
Isothermal (Constant temperature)		$W = -ve$ $\Delta U = 0$ $\therefore Q = +ve$
Adiabatic (no heat exchange with surroundings)		$W = -ve$ $Q = 0$ $\therefore \Delta U = -ve$
Cyclic (Start and end at same position)		$W_A = - \text{area under the graph} $ $W_B = + \text{area under the graph} $ $\therefore W_{AB} = - \text{area enclosed in the cycle} $ $\Delta U = 0$ $W = -ve$ $\therefore Q = +ve$