

# Thermal Physics

Thermal physics is the combined study of **thermodynamics**, **statistical mechanics** and **kinetic theory of gases**.

## §0.1 Temperature

Heat is the transfer of energy between two bodies in **thermal contact** as a result of a temperature difference between them.

**Definition 0.1 (Thermal Equilibrium)** — Two bodies are in thermal equilibrium if when placed in **thermal contact** there is not net flow of heat energy between them.

Temperature is the property that determines whether an object is in thermal equilibrium with another object. Two objects at the same temperature are in thermal equilibrium with each other.

### §0.1.1 Internal Energy

**Definition 0.2 (Internal Energy)** — The sum of the random distribution of the kinetic and potential energies of a body's constituent microscopic particles.

Internal energy includes kinetic energy of **translation**, **rotation** and **vibration** of molecules, and potential energy within molecules and between molecules.

Increasing the internal energy of an object increases the kinetic and/or potential energy associated with the random motion of its constituent particles.

#### Formula 0.3 (Internal Energy of a System)

$$U = \sum \text{K.E.} + \sum \text{P.E.}$$

Notice that for an **ideal gas**,  $\sum \text{P.E.} = 0 \Rightarrow U_{\text{ideal}} = \sum KE$ .

### §0.1.2 Specific Heat Capacity

When energy is added to a substance and no work is done, the temperature of the substance usually rises - the exception is during a change of state.

**Definition 0.4 (Specific Heat Capacity)** — The energy required to raise the temperature of 1 kg of a substance by 1 K, without a change of state.

To raise the temperature of mass  $m$  of a substance by  $\Delta T$ , the energy required  $\Delta Q$  is

#### Formula 0.5 (Specific Heat Capacity)

$$\Delta Q = mc\Delta T$$

where  $c$  is the specific heat capacity. The 'specific' means per unit mass.

### §0.1.3 Specific Latent Heat

When the physical characteristics of a substance change from one form to another, we say that a phase change or change of state has occurred.

Such phase changes involve a **change in internal energy** of a substance without a change in temperature.

**Definition 0.6** (Specific Latent Heat of Fusion) — The energy required to change the state per unit mass of a substance from solid to liquid, without change of temperature.

**Definition 0.7** (Specific Latent Heat of Vaporisation) — The energy required to change the state per unit mass of a substance from liquid to gas, without change of temperature.

The energy required to change the state of mass  $m$  of a substance without change of temperature is

**Formula 0.8** (Specific Latent Heat)

$$Q = mL$$

where  $L$  is the specific latent heat of fusion/vaporisation.

### §0.1.4 Boiling vs Evaporation

In both boiling and evaporation, liquids become gases but there are important distinctions.

- Evaporation occurs only at the **surface** of the liquid and it occurs at **any temperature** (though occurs more quickly at higher temperatures).
- Boiling occurs only above the **boiling point**.
- Evaporation occurs because some particles possess more energy than others and may have sufficient energy to escape at the surface where they are held less tightly.
- Boiling occurs when the **average** energy of the particles is sufficient to overcome the forces of attraction between them.

### §0.1.5 Newton's Law of Cooling

*The rate of heat loss of a body is directly proportional to the difference in the temperatures between the body and its surroundings.*

By the specific heat capacity formula

$$\Delta Q = mc\Delta T \Rightarrow \frac{dQ}{dt} = mc \frac{dT}{dt}$$

For a body at temperature  $T$  with thermal conductance  $k$  in surroundings of temperature  $T_s$  at time  $t$ , the rate of thermal energy loss  $\frac{dQ}{dt}$  and rate of heat loss  $\frac{dT}{dt}$  is given by

**Formula 0.9** (Newton's Law of Cooling)

$$\frac{dQ}{dt} = -k(T - T_s)$$

$$\frac{dT}{dt} = -\frac{k}{mc}(T - T_s)$$

The following problem is far beyond the scope of A-Level, though is an elegant problem and intended as an extension.

**Example 0.10** Consider two vessels that are in thermal contact with one another, and nothing else - not even the room they are in. Vessel A is at a temperature ( $T_A$ ) of 373 K and has a heat capacity ( $C_A$ ) of 1000  $JK^{-1}$ , Vessel B is at a temperature ( $T_B$ ) of 273 K and has a heat capacity ( $C_B$ ) of 1500  $JK^{-1}$ .

Vessel A is transferring thermal energy to Vessel B according to Newton's Law of cooling.

Given the initial conditions above, find the time taken for Vessel A to reach a temperature of 323 K.

*Solution.* By conservation of energy, the total energy of the system,  $U$ , must remain constant.

$$U = c_A \cdot T_A + c_B \cdot T_B = 373 \times 1000 + 273 \times 1500$$

$$= 782500J$$

$$T_B = \frac{U - c_A \cdot T_A}{c_B} \quad (1)$$

By Newton's law of cooling:

$$\frac{dQ}{dt} = k(T_A - T_B)$$

But we also know:

$$Q = c\Delta T \Rightarrow \frac{dQ}{dt} = c \frac{dT}{dt}$$

N/B: we do not need to consider the mass of each vessel, since we are given the **heat capacity** and not the specific heat capacity.

So, considering vessel A only; since  $\frac{dT_A}{dt} < 0$

$$\frac{dQ_A}{dt} = -k(T_A - T_B) \Rightarrow \frac{dT_A}{dt} = \frac{-k}{c_A}(T_A - T_B)$$

Plugging in the expression for  $T_B$  from (1):

$$\frac{dT_A}{dt} = \frac{-k}{c_A} \left( T_A - \frac{U - c_A \cdot T_A}{c_B} \right)$$

This yields the 'friendly' first-order differential equation, which we can solve by separation of variables:

$$\begin{aligned} \frac{dT_A}{dt} &= \frac{k \cdot U}{c_A \cdot c_B} - \frac{k}{c_A} \left(1 + \frac{c_A}{c_B}\right) T_A \\ \Rightarrow \int_{373}^{323} \frac{dT_A}{\frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) T_A} &= \int_0^t \frac{k}{c_A} dt \\ -\frac{1}{1 + \frac{c_A}{c_B}} \ln \left( \frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) T_A \right) \Big|_{373}^{323} &= \frac{k}{c_A} t \\ \frac{1}{1 + \frac{c_A}{c_B}} \ln \left( \frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) 373 \right) - \frac{1}{1 + \frac{c_A}{c_B}} \ln \left( \frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) 323 \right) &= \frac{k}{c_A} t \\ \therefore t = \frac{c_A \cdot c_b}{k(c_A + c_B)} \ln \left( \frac{\frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) 373}{\frac{U}{c_B} - \left(1 + \frac{c_A}{c_B}\right) 323} \right) \end{aligned}$$

Chuckling in the values for all the constants on the right hand side of the equation gives:

$$t = 300 \cdot \ln(6) \text{ s} \approx \underline{538 \text{ s}}$$

This problem can also be solved without the need for applying conservation of energy, and instead solving a set of coupled differential equations.  $\square$

## §0.2 Laws of Thermodynamics

There are 4 laws of thermodynamics, although the ‘first’ law is referred to as the ‘zeroth’, and the ‘second’ as the ‘first’ *etc.*

### §0.2.1 Zeroth and First Laws

The zeroth law of thermodynamics states that:

*If objects A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other.*

The first law of thermodynamics concerns itself with the **internal energy** of a system. The internal energy of a system changes as a result of

- heat transfer to or from the system.
- work done on or by the system, including electrical work.

**Remark 0.11** Note that heat and work are ways of **changing** the energy of a system. We do not talk of the heat or work **of** a system.

The first law of thermodynamics states that:

*The change in internal energy of a system is equal to the heat added to the system plus the work done on the system.*

**Formula 0.12** (First Law of Thermodynamics)

$$\Delta U = \Delta Q + \Delta W$$

**§0.2.2 Second and Third Laws**

Both the second and third law are to do with the concept of **entropy**.

**Definition 0.13** (Entropy,  $S$ ) — The quantitative measure of **disorder** in a system.

Mathematically, the change in entropy can also be defined as the ‘area under the graph of heat capacity against temperature’. That is,

**Formula 0.14** (Entropy Definition)

$$\Delta S = \int C \, dT$$

The second law of thermodynamics states that:

*The state of entropy of the entire universe, as an isolated system<sup>1</sup>, will always increase over time, and the changes in the entropy in the universe can never be negative.*

The second law can also be thought of as the idea that ‘heat can never pass from a colder to a warmer body without some other change occurring at the same time (*e.g.* work done on the system).

The third law of thermodynamics states that:

*A system’s entropy approaches a constant value as the temperature approaches absolute zero.*

Essentially, to cool an object, energy must be drained from it into a colder object. As an object’s temperature becomes closer to absolute zero, this becomes an increasingly difficult task.

**§0.3 Ideal Gases**

**Definition 0.15** (Ideal Gas) — An ideal gas can be defined as a **monatomic** gas that obeys all gas laws at all conditions of pressure and temperature.

Ideal gases satisfy the following conditions:

- A very large number of particles in **constant random motion**.
- No forces between the particles, except during collisions.
- All collisions between particles or the wall are **elastic** *i.e.* KE is conserved.
- Gas molecules occupy negligible volume.

<sup>1</sup>A physical system without any external exchange - that is, neither mass nor energy can enter or exit.

### §0.3.1 Ideal Gas Law

Boyle's Law:

*For a fixed mass of gas at **constant temperature**, the pressure and volume of a gas are inversely proportional.*

#### Formula 0.16 (Boyle's Law)

$$PV = \text{constant}, \quad P_1V_1 = P_2V_2$$

Charles' Law:

*For a fixed mass of gas at **constant pressure**, the volume of a gas is directly proportional to its **absolute** temperature.*

#### Formula 0.17 (Charles' Law)

$$\frac{V}{T} = \text{constant}, \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The Pressure Law:

*For a fixed mass of gas at **constant volume**, the pressure of a gas is directly proportional to the absolute temperature.*

#### Formula 0.18 (The Pressure Law)

$$\frac{P}{T} = \text{constant}, \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Combining all these three laws, gives us that  $\frac{PV}{T} = \text{constant}$ , and this can be formalised into the ideal gas equation.

#### Formula 0.19 (Ideal Gas Equation)

$$PV = nRT$$

where  $n$  is the number of moles of gas (1 mole =  $6.022 \times 10^{23}$  particles) and  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$  - the **molar gas constant**.

Sometimes, however, we may want to deal with only a few particles. If we have one particle, the constant is  $1.38 \times 10^{-23} \text{ J K}^{-1}$ . This number is known as the **Boltzmann's constant**  $k_B$ . It is defined as the molar gas constant divided by **Avogadro's constant** ( $6.022 \times 10^{23}$ ).

#### Formula 0.20 (Boltzmann's Constant)

$$k_B = \frac{R}{N_A}$$

From this, we find the following second form of the ideal gas equation.

**Formula 0.21** (Ideal Gas Equation)

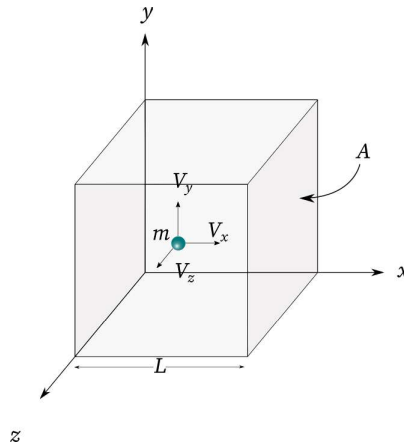
$$PV = Nk_B T$$

where  $N$  (instead of  $n$ ) is the number of particles.

**Remark 0.22** Note that  $n = \frac{N}{N_A}$ .

**§0.3.2 Pressure in an ideal gas**

Consider a sealed cube ‘container’ filled with particles of an ideal gas in random **Brownian motion**. The gas particles exert pressure on the walls of the cube.



We will focus on a single particle, as shown above, of mass  $m$  and velocity in the  $x$ -direction only  $v_x$ . The cube container has sides of length  $L$  and the particle hits the surface of the wall at right angles.

Since this is an ideal gas, the particle has **elastic collisions** with the wall so the change in momentum has magnitude  $\Delta p = mv_x - (-mv_x) = 2mv_x$ . Furthermore, the time  $t$  between collisions is the total distance covered divided by its speed, so  $t = \frac{2L}{v_x}$ .

By Newton's Second Law, force is the rate of change of momentum, hence

$$F = \frac{\Delta p}{\Delta t} = 2mv_x \times \frac{v_x}{2L} = \frac{mv_x^2}{L}$$

But, this is the force for only one molecule. So the force for  $N$  molecules of gas moving in the  $x$ -direction is

$$\begin{aligned} F &= \frac{mv_{x1}^2}{L} + \frac{mv_{x2}^2}{L} + \dots + \frac{mv_{xN}^2}{L} \\ &= \frac{m}{L} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) \\ &= \frac{m}{L} \cdot \sum_{i=1}^N v_{xi}^2 \end{aligned}$$

The **mean-square** velocity  $\bar{v}^2$  is given by the mean of the squares of the velocities,  $\frac{1}{N} \cdot \sum_{i=1}^N v_{xi}^2$ , and the **root-mean-square** velocity  $v_{RMS} = \sqrt{\bar{v}^2}$ . So we get

$$F = \frac{Nm\bar{v}_x^2}{L}$$

$$\therefore P = \frac{F}{A} = \frac{Nm\bar{v}_x^2}{L \times L^2} = \frac{Nm\bar{v}_x^2}{V}$$

But, now if we consider the total velocity of the  $y$  and  $z$  directions also, we have  $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$ . And, the magnitudes in each direction are equal so  $\bar{v}^2 = 3\bar{v}_x^2$ , which gives us

$$P = \frac{Nm\bar{v}^2}{3V} \Rightarrow PV = \frac{1}{3}Nm\bar{v}^2$$

**Formula 0.23** (Pressure in an Ideal Gas)

$$PV = \frac{1}{3}Nm\bar{v}^2$$

We can also use this to find an expression for the kinetic energy of a particle in an ideal gas.

$$E_K = \frac{1}{2}m\bar{v}^2 = \frac{3}{2} \cdot \frac{PV}{N}$$

But from the [ideal gas equation](#),  $\frac{PV}{N} = k_B T$  where  $T$  is the absolute temperature.

$$\therefore E_K = \frac{3}{2}k_B T$$

**Formula 0.24** (Kinetic Energy of an Ideal Gas Particle)

$$E_K = \frac{3}{2}k_B T$$