

Chapter 10

Temperature and the behavior of gases

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COURSE TOPICS:

10.1 Temperature scales

10.3 Pressure

10.4 The ideal gas law

10.5 Gas mixtures

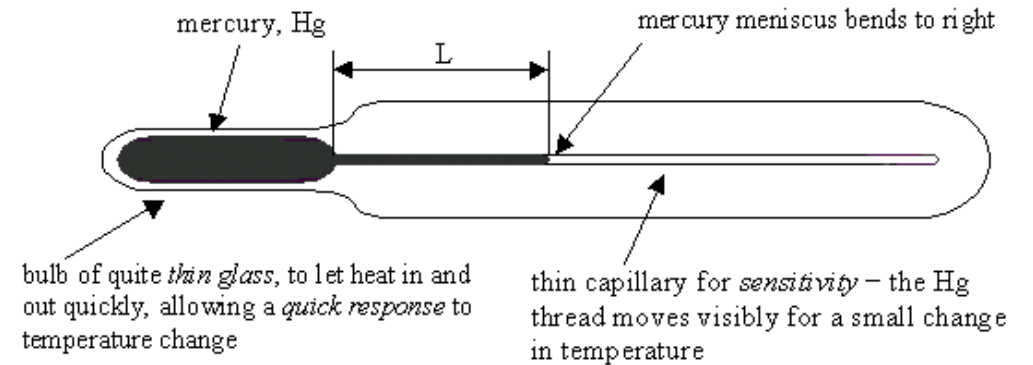
10.6 Temperature

Introduction:

- The concept of temperature plays an important role in the physical and biological sciences because the temperature of an object is directly related to the average kinetic energy of the atoms and molecules composing the object.
- Since natural processes often involve energy changes, the temperature plays the role of a label for these changes.
- Our perception of hot and cold is actually a measure of how rapidly energy exchange occurs between objects.
 - Touching something hot results in a rapid and sometimes damaging transfer of energy into our bodies.
- Dilute gases-those with average intermolecular separations that are very large compared to the molecular dimensions:
 - molecular forces are unimportant-
 - are sometimes used to measure temperature. This is because their pressure and temperature are related accurately by a simple expression called the **ideal gas law**.

10.1 Temperature scales:

- Many physical quantities always have the same value at a given temperature.
- One common thermometer uses the volume of a fixed mass of mercury to indicate the temperature.
- As the temperature increases, the volume of mercury increases faster than that of the bulb, so the mercury rises in the tube.
- To calibrate the thermometer, one usually chooses two reference temperatures and divides the interval between them into some number of equal steps.



- **Celsius ($^{\circ}\text{C}$) scale:**
 - The freezing and boiling points of water at normal atmospheric pressure are chosen as our reference temperatures and divide the interval between them into 100 equal steps.
 - We would then have the **Celsius (centigrade)** temperature scale if we set the **freezing temperature equal to 0°C** and **the boiling temperature equal to 100°C** .
- **The Fahrenheit ($^{\circ}\text{F}$) scale:**

The Fahrenheit scale was defined so that water freezes at 32°F and boils at 212°F .

10.1 Temperature scales:

- The relationship between the Celsius temperature T_C and the Fahrenheit temperature T_F is given exactly by the equation

$$T_C = \frac{5}{9}(T_F - 32^\circ \text{ F})$$

Example:

The normal body temperature is 98.6° F . On the Celsius scale, this is

$$\begin{aligned} T_C &= \frac{5}{9}(T_F - 32^\circ \text{ F}) \\ &= \frac{5}{9}(98.6^\circ \text{ F} - 32^\circ \text{ F}) \\ &= 37.0^\circ \text{ C} \end{aligned}$$

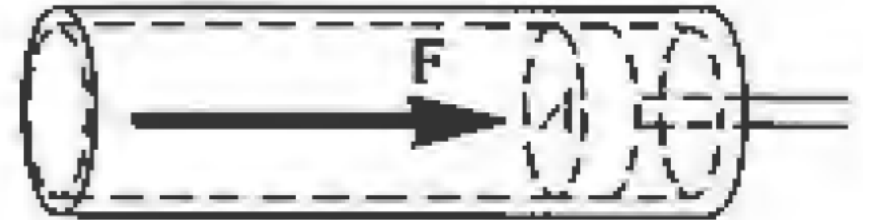
10.3 Pressure:

- In fact, the pressure of a fluid (a liquid or gas) is intimately related to but not the same as a force.
- The pressure is related to the magnitude of the forces a sample exerts in all directions on its surroundings. The surroundings may be the remainder of the sample or the walls of a container
- The **average pressure** \bar{P} is defined as the sum of the magnitudes of the normal forces divided by the surface area of the sphere:

$$\bar{P} = \frac{\text{magnetude of normal forces on a surface}}{\text{surface area}} = \frac{F_N}{A}$$

- The pressure exerted by a gas on its container walls is similarly defined.
 - The figure shows a gas in a cylinder fitted with a piston of area A . The magnitude of the force F the gas exerts on the piston divided by A is the pressure P :

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



10.3 Pressure:

- The S.I. unit of pressure is the pascal; 1 Pa :

$$1 \text{ Pa} = 1 \text{ N} \cdot \text{m}^{-2}.$$

- Normal atmospheric pressure is

$$\begin{aligned} 1 \text{ atmosphere} &= 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \\ &= 1.013 \text{ bars} \\ &= 760 \text{ torr} \\ &= 760 \text{ mm Hg} \end{aligned}$$

- The bar and millibar are used extensively in meteorology. The torr or the millimeter of mercury (mm Hg) is used in medicine and physiology. Normal atmospheric pressure will support a column of mercury of height $760 \text{ mm} = 0.76 \text{ m}$.

10.3 Pressure:

Example 10.3

A gas at a pressure of 10 atm is in a cubical container of side 0.1 m. If the pressure outside is atmospheric pressure, what is the net force on one wall of the container?

Answer:

The force due to the gas inside is

$$\begin{aligned} F_i &= P_i A = (10 \text{ atm})(1.013 \times 10^5 \text{ Pa atm}^{-1})(0.1 \text{ m})^2 \\ &= 1.013 \times 10^4 \text{ N} \end{aligned}$$

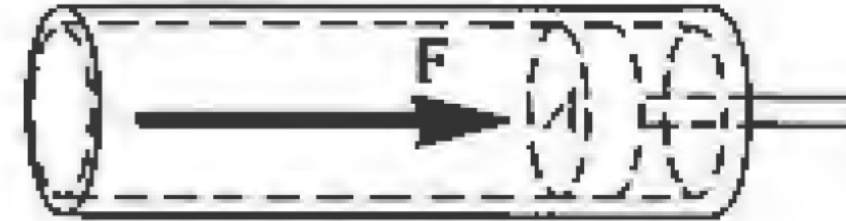
The force on the outside due to the atmosphere is

$$\begin{aligned} F_a &= P_a A = (1.013 \times 10^5 \text{ Pa})(0.1 \text{ m})^2 \\ &= 0.1013 \times 10^4 \text{ N} \end{aligned}$$

The net outward force is

$$\begin{aligned} F_i - F_a &= 1.013 \times 10^4 \text{ N} - 0.1013 \times 10^4 \text{ N} \\ &= 0.912 \times 10^4 \text{ N} \end{aligned}$$

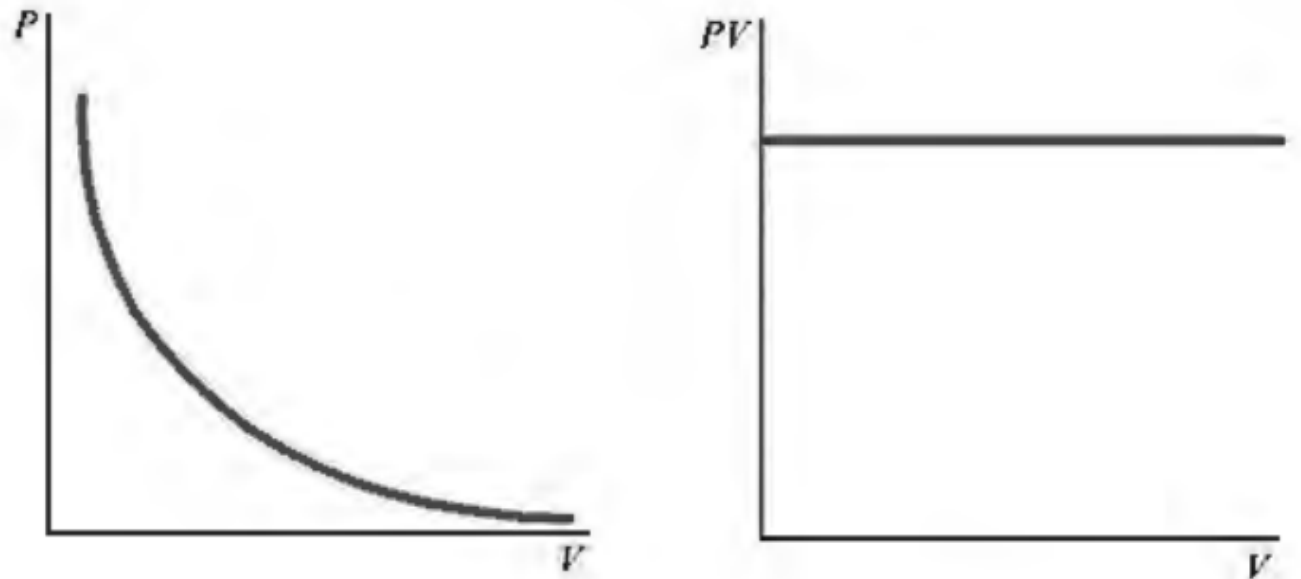
Note that the difference $P_i - P_o$ is called the gauge pressure of the gas



10.4 The ideal gas law:

- Suppose that we have a fixed quantity of a gas in a tank. We may vary the temperature T_C or the volume V of the gas:
- **Ideal (Dilute) gases** are those with average intermolecular separations that are very large compared to the molecular dimensions, so that molecular forces are unimportant.
 - Their **pressure** and **temperature** and **volume** are related accurately by a simple expression called the **ideal gas law**.
- The ideal gas law actually summarizes two kinds of experiments:
 - **First**, if the temperature of the gas is kept constant and its volume is decreased, then the pressure increases so that the product PV is constant. This is **Boyle's law**.

$$PV = \text{constant} \quad (T \text{ constant})$$



10.4 The ideal gas law:

- **Second:** Keeping the pressure fixed and changing the temperature. The temperature change and the volume change are proportional; each 1° temperature decrease produces the same volume decrease. This is **Charles's law**. Thus, the plot of the measured volumes versus T_c is a straight line.
- If we extend the line through the data points toward lower temperatures and pressures, it eventually reaches $V = 0$ at $T_c = -273.15^\circ\text{C}$.
- Since it is not possible to have a negative volume, this requires the existence of a minimum or absolute zero of temperature.
- It is convenient then to define a new temperature scale that measures temperatures from absolute zero.
 - Temperatures on this absolute or Kelvin scale are related to Celsius temperatures by

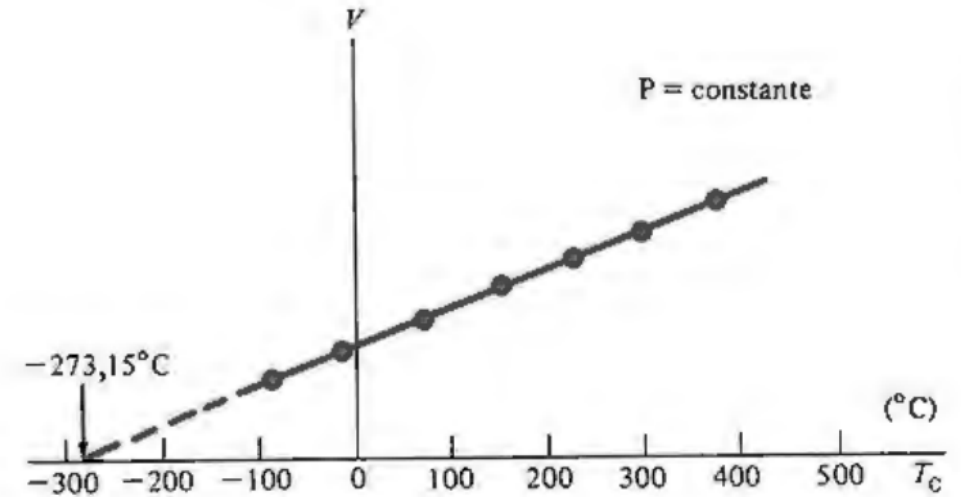
$$T = T_c + 273.15$$

Absolute or Kelvin scale

- Charles's law states

$$\frac{V}{T} = \text{constant} \quad (\text{P constant})$$

Charles's law



10.4 The ideal gas law:

- We can now state the **ideal gas law** that contains both Boyle's law and Charles's law:

$$\boxed{\frac{PV}{T} = \text{constant}} \quad \text{ideal gas law}$$

- If T is fixed, this gives $PV = \text{constant}$; when P is fixed, $\frac{V}{T} = \text{constant}$.
- Note that when we double the amount of the gas (the number of moles, n) while keeping the pressure and temperature the same, V doubles.
 - Hence, we may write the constant on the right side as nR , where R is found by experiment. Thus, the ideal gas law becomes

$$\boxed{PV = nRT} \quad (\text{ideal gas law})$$

- R is called the universal gas constant. For all dilute gases, real gases at low densities and pressures, it has the same value,

$$\begin{aligned} R &= 8.314 \text{ J mole}^{-1} \text{ K}^{-1} \\ &= 0.08207 \text{ litre atm mole}^{-1} \text{ K}^{-1} \\ & \quad (1 \text{ litre} = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3) \end{aligned}$$

- Standard conditions for a gas are defined to be $P = 1 \text{ atm}$ and $T = 0 \text{ }^\circ\text{C}$.

10.4 The ideal gas law:

Example 10.4

What is the volume of an ideal gas one mole of standard conditions

Answer

Standard conditions for a gas are defined to be $P = 1 \text{ atm}$ and $T = 0 \text{ }^\circ\text{C}$.

$$T = T_C + 273.15 = 273.15 \text{ K.}$$

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{1 \text{ mole}}{1 \text{ atm}} (0.08207 \text{ litre atm mole}^{-1} \text{ K}^{-1})(273.15 \text{ K}) \\ &= 22.4 \text{ litres} \end{aligned}$$

Thus under standard conditions, a mole of an ideal gas occupies 22.4 litres.

10.4 The ideal gas law:

Example 10.5

An ideal gas in a cylinder is initially at a temperature of 27 °C. It is heated and allowed to expand so that its volume is doubled and its temperature is increased to 127 °C. If it was originally at a pressure of 10 atm, what is its new pressure?

Answer

Since the amount of the gas is fixed, the initial value of PV/T equals the final value, $P'V'/T'$. Solving for P' , and converting to Kelvin temperatures, we have

$$\begin{aligned} P' &= P \left(\frac{T'}{T} \right) \left(\frac{V}{V'} \right) = (10 \text{ atm}) \left(\frac{400 \text{ K}}{300 \text{ K}} \right) \left(\frac{V}{2V} \right) \\ &= 6.67 \text{ atm} \end{aligned}$$

10.5 Gas mixtures:

- A **gas mixture** contains different amounts of different gases.
- For example, each mole of dry air contains 0.78 mole of nitrogen (N_2), 0.21 mole of oxygen (O_2), 0.009 mole of argon, 0.0004 mole of carbon dioxide, and traces of several other gases. These proportions are nearly constant up to an altitude of 80 km.
- Because in ideal gas model we assume that molecules do not interact with one another, Dilute gas mixtures are simplified by the fact that each constituent behaves as though the others were not present.

- **Example:**

suppose there are $n(O_2)$ moles of oxygen and $n(N_2)$ moles of nitrogen in a volume V of air at a temperature T . The partial pressures of oxygen and nitrogen, $P(O_2)$ and $P(N_2)$, will each satisfy an ideal gas law,

$$P(O_2)V = n(O_2)RT$$

$$P(N_2)V = n(N_2)RT$$

The total pressure P (ignoring the small amount of other gases present) of the air is the sum

$$P = P(O_2) + P(N_2)$$

The number of moles of air is

$$n = n(O_2) + n(N_2)$$

By adding, we recover

$$PV = nRT$$

10.5 Gas mixtures:

Example 10.6

What are the partial pressures of oxygen at sea level and at an altitude of 7000 m, where the air pressure is 0.45 atm?

Answer

Dividing $P(O_2) = n(O_2)RT$ by $PV = nRT$, we have at sea level, where $P = 1 \text{ atm}$,

$$\frac{P(O_2)}{P} = \frac{n(O_2)}{n} = \frac{0.21 \text{ mole}}{1 \text{ mole}} = 0.21$$

Thus, $P(O_2) = 0.21 \text{ atm}$

The ratio is the same at 7000 m, but $P = 0.45 \text{ atm}$, so

$$P(O_2) = (0.21)(0.45 \text{ atm}) = 0.096 \text{ atm}$$

Less than half of the pressure at sea level.

The amount of a gas present in our bodies is directly proportional to the partial pressure of the gas in the air we breathe. Thus, any time the air pressure changes, so does the oxygen and nitrogen content of our bodies. This is of great importance to divers

10.6 Temperature and molecular energies:

- In the ideal gas model, we regard the molecules as particles that never collide with each other but that do collide with the container walls.
- These collisions are assumed to be elastic, so the molecules lose no energy, but they do change direction.
- The change in direction involves a change in momentum of the molecules, and this means that there is a reaction force on the container walls.
- The average force per unit area exerted by the molecules on the walls is the pressure of the gas.
- The average kinetic energy of the molecules $(K)_{\text{ave}}$ is

$$(K)_{\text{ave}} = \frac{m}{2} (v^2)_{\text{ave}}$$

The quantity $(v^2)_{\text{ave}}$ is called the mean square speed, and it represents the average value of v^2 .

- It can be shown that the average kinetic energy $(K)_{\text{ave}}$ is related to temperature as

$$(K)_{\text{ave}} = \frac{m}{2} (v^2)_{\text{ave}} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T$$

The ratio $k_B = R/N_A$ is called **Boltzmann's constant** and has the value

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

10.6 Temperature and molecular energies:

Example 10.7

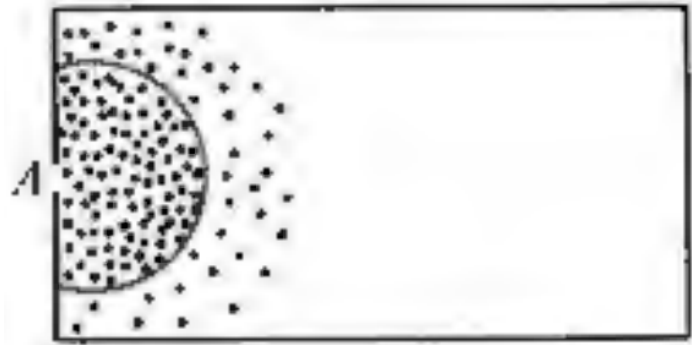
What is the average kinetic energy of a hydrogen molecule at $27\text{ }^\circ\text{C} = 300\text{ K}$?

From $(K)_{\text{ave}} = \frac{3}{2}k_B T$,

$$\begin{aligned}(K)_{\text{ave}} &= \frac{3}{2}k_B T \\ &= \frac{3}{2}(1.38 \times 10^{-23}\text{ J K}^{-1})(300\text{ K}) \\ &= 6.21 \times 10^{-21}\text{ J}\end{aligned}$$

10.7 Diffusion:

- **Diffusion:** The rather slow process by which the molecules spread out evenly.
- For example, When perfume is sprayed into still air, the scent eventually spreads to all parts of a room. Similarly, a drop of dye placed in a solvent will gradually spread throughout the container, even though we are careful not to disturb or stir the liquid.
- **In the diffusion process, the flow occurs from higher to lower concentrations.**
- To illustrate this, in the figure, a small amount of helium gas is released at point A in an air-filled container. At a given moment, we draw an imaginary hemispherical surface so that most of the helium atoms are inside the surface, but a few are outside. These helium atoms are in constant random motion, bouncing off air molecules, other helium atoms, and the walls. A certain number of helium atoms will cross the surface from the inside outward and some from the outside inward. Because most of the helium is inside, more helium atoms will pass outward than inward, increasing the number outside. We see that there is a net drift of helium atoms away from A into the remainder of the container



10.8 Dilute solutions, Osmotic pressure:

- **Osmotic pressure is the extra pressure that must be applied to stop the flow of water into the solution.**
- The figure (a) illustrates the meaning of osmotic pressure. The outer vessel contains water, and the inner one is filled initially to the same height with a solution of water and sugar. Water molecules can pass freely through the membrane separating the two vessels, but the larger sugar molecules cannot. Because the membrane is permeable to water molecules and impermeable to sugar molecules, it is called semipermeable.
- **Since the concentration of water molecules is greater in the outer vessel, there is a net diffusion of water molecules into the inner vessel raising the level of the solution until an equilibrium level is reached** (figure b).
- At this point equal numbers of water molecules cross the membrane in each direction.
- **The additional pressure in the solution just above the membrane due to the weight of the raised column of solution is called the osmotic pressure.**
- In general, a permeable fluid diffuse between regions of different concentrations if there is a difference in pressure between them.

