Chapter 17
Temperature & Kinetic Theory of Gases
1. Thermal Equilibrium and Temperature

Any physical property that changes with temperature is called a thermometric property and can be used to measure temperature.

Heat flows from a hot object to a colder one until they get into thermal equilibrium with each other.

The zeroth law of thermodynamics:

If two objects are in thermal equilibrium with a third object, then all three are in thermal equilibrium with each other.

The objects in thermal equilibrium with each other are said to have the same temperature.
Centigrade (Celsius) and Fahrenheit temperature scales

The centigrade (Celsius) scale defines the ice-point temperature of water as zero degrees centigrade ($0^\circ$ C) and the steam-point temperature as $100^\circ$ C. The space between $0^\circ$ C and $100^\circ$ C is divided in 100 equal intervals (degrees).

If the temperature is measured using a mercury thermometer, then

$$ t_C = \frac{L_t - L_0}{L_{100} - L_0} \times 100^\circ $$

where $L$ stands for the length of the mercury column at the temperature indicated by the index after $L$.

The Fahrenheit scale defines the ice-point temperature of water as $32^\circ$ F and the steam-point temperature as $212^\circ$ F. The space between $32^\circ$ F and $212^\circ$ F is divided in 180 equal intervals (degrees).
Converting Fahrenheit and Celsius temperatures

\[ t_C = \frac{5}{9} (t_F - 32^0), \quad t_F = \frac{9}{5} t_C + 32^0. \]

**Example 1.** Suppose the body temperature measured with a Celsius thermometer is 40\(^0\) C. What is the temperature in \(^0\)F and is the patient running a fever?

\[ t_F = \frac{9}{5} t_C + 32^0 = \frac{9}{5} 40^0 + 32^0 = 104^0 \text{ F} \]

**Example 2.** What is the centigrade equivalent to 68\(^0\) F?

\[ t_C = \frac{5}{9} (t_F - 32^0) = \frac{5}{9} (68^0 - 32^0) = 20^0 \text{ C} \]

The thermometric properties most commonly used to make thermometers are the thermal expansion (mercury or bimetallic thermometers) and dependence of electric conductivity on temperature (various metal, semiconductor, and carbon thermometers).
Gas thermometers and the absolute temperature scale

The pressure $P$ of gas in tube $B_I$ is measured by the height $h$ of the column of mercury in tube $B_3$.

$$t_C = \frac{P_t - P_0}{P_{100} - P_0} \times 100^0$$

All properly calibrated gas thermometers provide identical results for the temperature irrespective of the nature of the gas in tube $B_I$ provided that the density of gas is low.

If one extrapolates temperature measured by the gas thermometer to zero gas pressure, the temperature approaches $-273.15^0 C$. This is, of course, an extrapolation: the real gas thermometers cannot measure temperatures that low.

Temperature $-273.15^0 C$ is called the **absolute zero**. It is used as a basis for the absolute or Kelvin temperature scale.
The absolute temperature scale (the Kelvin scale) is defined as

\[ T = t_c + 273.15 \text{ K} \]

**Example 2.** Converting temperature from kelvins to degrees Fahrenheit and back.

\[ T = t_c + 273.15 \text{ K} = \frac{5}{9} (t_F - 32^0) + 273.15 \text{ K} , \]

\[ t_F = \frac{9}{5} t_c + 32^0 = \frac{9}{5} (T - 273 \text{ K}) + 320 \]

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**Table 17-1: The Temperatures of Various Places and Phenomena**

- Supernova
- Hydrogen bomb
- Interior of the Sun
- Solar corona
- Surface of the Sun
- Copper melts
- Water freezes
- Liquid nitrogen
- Liquid hydrogen
- Liquid helium
- He\(^3\) goes superfluid
- Bose-Einstein condensate
- Lowest temperature achieved
The Ideal Gas Law

\[ PV = NkT \]

Where \( P \) is the pressure, \( V \) is the volume, \( N \) is the number of molecules in the gas, and the constant \( k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K} \) is called Boltzmann’s constant.

The gas law incorporates Boyle’s law,

\[ PV = \text{const} \quad \text{at constant temperature}, \]

Charles’ law

\[ T/V = \text{const} \quad \text{at constant pressure}, \]

And Gay-Lussac’s law,

\[ T/P = \text{const} \quad \text{at constant volume}. \]
An amount of gas is often expressed in moles. One mole contains Avogardo’s number of particles (atoms or molecules), \( N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \).

The total number of molecules of the gas \( N \) and the number of moles \( n \) are related to each other as \( N = nN_A \)

The gas law can be rewritten using the number of moles instead of the number of molecules as

\[
P V = N k T = n N_A k T = n R T
\]

where \( R = N_A k = 8.314 \text{ J/(mol×K)} = 0.08206 \text{ L×atm/(mol×K)} \) is called the universal gas constant.
Mixtures of ideal gases and partial pressures

If one mixes several ideal gases with numbers of particles in each $N_i$ (numbers of moles $n_i$) in the same volume $V$, one can apply the gas law to each of the gases separately,

$$P_iV = N_i kT, \quad P_iV = n_i RT,$$

where the pressures of each component $P_i$ are called the partial pressures, and the overall pressure of the gas is equal to the sum of all these partial pressures $P_i$,

$$P = \sum P_i.$$

**Example 3.** One moves oxygen from a 50-L tank with pressure $P_1 = 2$ atm into a 100-L tank with nitrogen which initially had a pressure $P_{N2} = 1.5$ atm. Both gases are at room temperature, $T = 300$ K, and the temperature does not change. What is the final pressure in the tank?

1. Since the temperature and volume of nitrogen did not change, its partial pressure remained at $P_{N2} = 1.5$ atm.
2. The volume of the oxygen increased from $V_1 = 50$ L to $V_2 = 100$ L. Therefore, its pressure changed to $P_{O2} = P_1 V_1/V_2 = P_1/2 = 1$ atm.
3. The overall pressure in the tank now is the sum of these partial pressures,

\[ P = P_{N2} + P_{O2} = 2.5\text{atm} \]

**Example 4.** What is the volume of 1mol of an ideal gas at standard temperature and pressure (STP) - 0°C = 273 K and 1atm?

\[ PV = nRT \rightarrow V = \frac{nRT}{P} = 1\text{mol} \times 0.08206 \text{L} \times \text{atm/(mol} \times \text{K}) \times \frac{273}{1} = 22.4 \text{ L} \]

*This volume of 1mol of ideal gas at STP does not depend on the kind of the gas!*

If one knows the molar mass of the gas (mass of 1mol), one can easily obtain the atomic mass of particles.

**Example 5.** The molar mass of hydrogen is \( M = 1.008 \text{g} \). Since 1mol of the gas contains \( N_A \) atoms, the atomic mass is \( m_H = \frac{M}{N_A} = 1.008 \text{g} \times 6.022 \times 10^{23} = 1.674 \times 10^{-24} \text{g} \).
The kinetic theory of gases

The kinetic theory of gases provides a description of gases in terms of *averages* of microscopic quantities such as particle velocities, masses, etc. The molecules of a gas are separated by distances much larger than the molecule sizes. The fast moving molecules collide with each other and the walls.

**Pressure exerted by a gas.**

Number of molecules with velocities $v_x$ hitting the area $A$ of the all in time $\Delta t$ is

$$(1/2) \times (N/V) \times v_x \times \Delta t \times A$$

The change of momentum of all these particles is

$$\Delta p_x = (2mv_x) \times (1/2) \times (N/V) \times v_x \times \Delta t \times A$$

This change in momentum is equal to the impulse of the force exerted on the area,

$$\Delta p_x = F \Delta t$$

Thus, the pressure

$$P = F/A = Nmv_x^2 = \frac{2}{3} \times \frac{N}{V} \times \frac{1}{2} \, mv^2$$
Comparing this with the gas equation $PV = NkT$ we get the molecular interpretation of temperature via the average kinetic energy of the molecules, 

$$kT = \frac{2}{3} \times \left( \frac{1}{2} mv^2 \right)_{av}$$

The average of $v^2$ is $(v^2)_{av} = 3kT/m = 3RT/M$, where $M = N_A m$ is the molar mass.

The square root of $(v^2)_{av}$ is called the root-mean-square speed (rms):

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}.$$ 

Speed of sound in a gas $v_{ssound} = \sqrt{\frac{\gamma RT}{M}}$. For air, $\gamma = 1.4$

**Example 5.** Compare rms speeds of oxygen and hydrogen molecules at room temperature (300K).

The molecular weight of oxygen is 32g/mol, and the rms speed is 

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{3 \times (8.314 \frac{J}{mol K}) \times \frac{300K}{0.032 \frac{kg}{mol}}} = 484 \text{m/s}$$

For hydrogen with $M = 0.002 \text{kg/mol}$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{3 \times (8.314 \frac{J}{mol K}) \times \frac{300K}{0.002 \frac{kg}{mol}}} = 1.93 \text{km/s}$$
**Equipartition Theorem:**

*In equilibrium, there is an average energy of \((1/2)kT\) per molecule or \((1/2)RT\) per mole associated with each *quadratic degree of freedom*

**Mean Free Path**

Molecules of the gas do not travel in straight lines, but zigzag due to collisions with other molecules. The average distance between collisions is called the *mean free path* \(\lambda\).

If the molecule of radius moves with speed \(v\), then in time \(t\) such molecule collides with all the molecules in the cylinder of length \(vt\) and radius \(d\). The number of such molecules is \((N/V)(vt\pi d^2)\) and the average distance between individual collisions is

\[
\lambda = \frac{vt}{\frac{N}{V}\pi d^2 vt} = \frac{1}{n_v \pi d^2}
\]
When the motion of all molecules is taken into account, the correct result becomes

\[ \lambda = \frac{1}{\sqrt{2n_v \pi d^2}} \]

**Example 6.** Let us estimate the mean free path of CO molecule in air at 300K and pressure 1atm. Assume that diameter of a typical molecule \( d = 3.75 \times 10^{-10} \text{m} \).

According to the gas equation, the density of the gas \( N/V = P/kT \) and

\[ \lambda = \frac{kT}{\sqrt{2P \pi d^2}} = \frac{(1.381 \times 10^{-10} \text{J/K})(300 \text{K})}{\sqrt{2}(101.3 \times 10^3 \text{Pa}) \times 3.14 \times (3.75 \times 10^{-10} \text{m})^2} = 6.53 \times 10^{-8} \text{ m} \]
A distribution function of objects over some property shows the fraction of these objects exhibiting different values of this property. For example, the distribution of student grades shows the fraction of students receiving A, B, C, D or F on the test.

Particles in a gas have different velocities. The distribution of particles over velocities $f(v)$ shows the fraction of the particles with velocity $v$. This distribution is given by the Maxwell-Boltzmann distribution function

$$f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

(the Bell Curve). The most probable speed at which $f(v)$ is at maximum is $v_{max} = \sqrt{2kT/m} = \sqrt{2RT/M}$. The curve gets wider with increasing temperature.
Review of Chapter 17

Centigrade (Celsius) and Fahrenheit scales:

\[ t_F = \frac{9}{5} t_C + 32^0, \quad t_C = \frac{5}{9} (t_F - 32^0) \]

Temperature – 273.15°C is called the absolute zero.

The Kelvin scale is defined as \( T = t_c + 273.15 \) K

The Ideal Gas Law \( PV = NkT = nN_AkT = nRT \)

The Boltzmann constant \( k = 1.381 \times 10^{-23} \) J/K = 8.617 \( \times \) 10^{-5} eV/K

The universal gas constant \( R = N_Ak = 8.314 \) J/(mol×K) = 0.08206 L×atm/(mol×K)

In mixtures of several gases one can apply the gas law to each gas separately,

\( P_iV = N_i kT, \quad P_iV = n_iRT \)

The volume of 1mol of any ideal gas at standard temperature and pressure (STP) - 0°C = 273 K and 1atm is 22.4 L.

Pressure exerted by a gas on a wall \( P = \frac{2}{3} \times \frac{N}{V} \times \frac{1}{2} m(v^2)_{av} \)

Molecular interpretation of temperature \( kT = \frac{2}{3} \times (\frac{1}{2}mv^2)_{av} \)
In equilibrium, there is an average energy of $(1/2)kT$ per molecule or $(1/2)RT$ per mole associated with each **quadratic degree of freedom** – the equipartition theorem.

The mean free path of molecules in a gas $\lambda = \frac{1}{\sqrt{2n_v \pi d^2}}$

The Maxwell-Boltzmann distribution function

$$f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$