

Chapter 1

State of Matter. Properties of Gases

Chemistry deals with the *properties* of matter, the *changes* matter undergoes and the *energy* that accompanies the changes.

Physical Chemistry is concerned with the *principles* that underlie chemical behavior, the *structure* of matter, *forms* of energy and their interrelations and *interpretation of macroscopic* (bulk) properties of matter in terms of their *microscopic* (molecular) constituents.

Broad classification of Matter: A **gas** fills the container and takes on the shape of the container. A **liquid** has a well-defined surface and a fixed volume but no definite shape. A **solid** has a definite shape, a fixed volume, and is independent of constraints.

The foregoing classification is a macroscopic classification. From a microscopic (molecular) point of view — a **gas** consists of particles that interact with each other weakly; a **liquid** consists of particles that are in contact with each other but are able to move past each other; and a **solid** consists of particles that are in contact with each other but are unable to move past each other. For short, in a gas, particles have essentially no restriction on motion; in a solid, particles are locked together, mostly with fixed orientation; and in liquid, particles behave in a manner between gas and solid.

1.1. State of Matter

The above classification is often referred to as a classification into states of *aggregation*. In physical chemistry, the word **state** generally refers to another concept. A substance is described by its properties (pressure, volume, temperature, amount, composition, etc.). If all the properties

of a substance are specified, the *state* of the system is said to be specified. Actually, there is no need to specify *all* properties, because, as a rule, the properties are interdependent. For example, if you know the pressure, the volume and the number of moles n of an ideal gas, you can figure out the temperature from the equation of state: $[PV = nRT]$.

1.2. Description of Some States of Matter

- Volume, V : a measure of occupied space.
- Pressure: force per unit area.
- Temperature: hard to define rigorously,* but in simple language it is a measure of the degree of hotness or coolness for which all of us have an intuitive feeling.
- Amount of substance: a measure of the amount of matter.

*Comment: When two objects (bodies) are brought in contact with each other, the hotter body will cool, the colder body will heat up. This is interpreted that *heat (a form of energy) is flowing from the hotter body to the colder one*. This process will continue until no more heat is transferred. When that happens the two bodies are said to be in *thermal equilibrium* — and the temperatures of the two bodies will be the same.

1.3. Units

The recommended units are SI (Système Internationale) units:

Length	l	meter, m
Mass	m	kilogram, kg
Time	t	second, s
Electric current	I	ampere, A
Temperature	T	Kelvin, K
Amount	n	mole, mol

All other physical quantities that we use can be derived from these. For example, volume is length cube or m^3 . Some derived quantities have special names. For example,

- Force in SI units is $kg\ m\ s^{-2}$ or Newton, N.
- Pressure in SI units is $kg\ m^{-1}s^{-2}$ or pascal, Pa.
- Energy in SI units is $kg\ m^2\ s^{-2}$ or joule, J.

Other (non-SI) units frequently used are:

- Pressure: mmHg or Torr (1 Torr = 133.3 Pa) or atm (1 atm = 760 mmHg) or 101.325 kPa bar (1 bar = 10^5 Pa)
- Energy: electron volt, eV (1 eV = 1.602×10^{-19} J)

Equation of state is an algebraic relation between pressure, volume, temperature and quantity of substance.

1.4. Ideal or Perfect Gas Law

$$PV = nRT$$

This Law comprises three different Laws that preceded it.

1) Holding constant n and T gives $PV = \text{const}$ or

$$P_1V_1 = P_2V_2 \quad \text{Boyle's Law} \quad (1.1)$$

2) Holding constant P and n gives $V/T = \text{const}$ or

$$V_1/T_1 = V_2/T_2 \quad \text{Charles' Law} \quad (1.2)$$

3) Holding constant P and T gives $V/n = \text{const}$ or

$$V_1/n_1 = V_2/n_2 \quad \text{Avogadro's Law} \quad (1.3)$$

1.5. Evaluation of the Gas Constant, R

The gas constant can be expressed in various units, all having the dimension of energy per degree per mol.

a) R is most easily calculated from the fact that the hypothetical volume of an ideal gas is 22.414 L at STP (273.1 K and 1 atm). Accordingly,

$$\begin{aligned} R &= (1 \text{ atm})(22.414 \text{ L mol}^{-1})/(273.16 \text{ K}) \\ &= 0.08206 \text{ atm L K}^{-1} \text{ mol}^{-1} \end{aligned} \quad (1.4)$$

b) If V is in cm^3 ,

$$\begin{aligned} R &= (1 \text{ atm})(22,414 \text{ cm}^3 \text{ mol}^{-1})/(273.16 \text{ K}) \\ &= 82.06 \text{ atm cm}^3 \text{ K}^{-1} \text{ mol}^{-1} \end{aligned} \quad (1.5)$$

c) In Pascal $\text{L K}^{-1} \text{mol}^{-1}$ [$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$; $1 \text{ L} = 10^{-3} \text{ m}^3$],

$$\begin{aligned} R &= 1.01325 \times 10^5 \text{ Pa} \times 22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} / 273.16 \text{ K} \\ &= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1} \end{aligned} \quad (1.6)$$

d) In $\text{JK}^{-1} \text{mol}^{-1}$,

$$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} [1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}] \quad (1.7)$$

e) In cgs units (V in cm^3 , P in dyne/cm^2 , $1 \text{ atm} = 1.013 \times 10^6 \text{ dyne cm}^{-2}$),

$$R = (1.013 \times 10^6 \text{ dyne cm}^{-2}) \times (22,414 \text{ cm}^3 \text{ mol}^{-1}) / 273.16 \text{ K}$$

Also $1 \text{ erg} = 10^7 \text{ J}$,

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \quad (1.8)$$

f) In $\text{cal K}^{-1} \text{mol}^{-1}$ ($1 \text{ cal} = 4.184 \text{ J}$),

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \quad (1.9)$$

Example 1.1. 50.0 g of N_2 ($M = 28.0 \text{ g}$) occupies a volume of 750 mL at 298.15 K. Assuming the gas behaves ideally, calculate the pressure of the gas in kPa.

Solution

$$\begin{aligned} P &= nRT/V \\ &= (50.0 \text{ g} / 28.0 \text{ g mol}^{-1}) \times (0.0826 \text{ atm L K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}) / 0.750 \text{ L} \\ &= 58.25 \text{ atm} = 58.25 \times 101.325 \text{ kPa/atm} = 5.90 \times 10^3 \text{ kPa} \end{aligned}$$

1.6. Mixtures of Gases

The partial pressure of a gas in a mixture is defined as the pressure the gas would exert if it *alone* occupied the whole volume of the mixture at the same temperature. *Dalton's Law* states that the total pressure is equal to

the sum of the partial pressures. That is,

$$P = \sum_i P_i = \sum_i n_i RT/V = RT \sum_i n_i/V = nRT/V \quad (1.10a)$$

where $n = \sum_i n_i$ is the total number of moles. Accordingly,

$$P_i/P = n_i/n = x_i \quad \text{or} \quad P_i = x_i P \quad (1.10b)$$

[This relation is strictly valid for ideal gases.]

1.7. The Kinetic Theory of Gases

The theory is based on the following assumptions:

1. There are N molecules, each of weight m .
2. Molecules are in constant motion. They collide with each other and with the walls of the container.
3. In ideal gases, molecules do not interact with each other.
4. The volume of molecules is negligible compared to the volume of container.

Consider one molecule in a cubic box colliding with a shaded wall parallel to the YZ direction. Before collision, the velocity of molecule in the X-direction is u_x . When the molecule collides with the shaded wall (see Fig. 1.1) of the cubic box, it is reflected in the opposite direction, having a velocity of $-u_x$ and a change of velocity of $2u_x$. If the distance between the shaded wall and

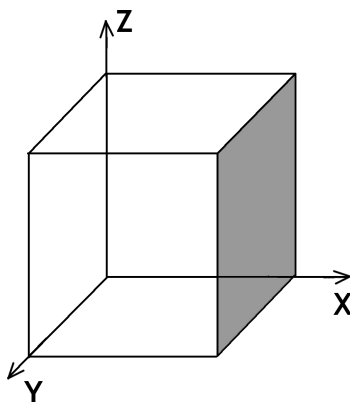


Fig. 1.1 Depicts a particle in a cubic box of sides L colliding with the shaded wall.

the opposite wall is L , the molecule is reflected in the opposite direction, having a velocity of $-u_x$. and a change of velocity of $2u_x$. The molecule will make $u_x/2L$ collisions per unit time with the shaded wall. Accordingly, the change in momentum per molecule per unit time at the shaded wall will be $(2mu_x) \times (u_x/2L) = mu_x^2/L$. For N molecules, the change in momentum per unit time will be $Nm\langle u_x^2 \rangle/L$ where $\langle \rangle$ stands for average.

In classical mechanics, the momentum change on an area represents the force exerted on that area. Denoting the force as f we can write $f = Nm\langle u_x^2 \rangle/L$ as the force exerted on the shaded wall. Pressure is force per unit area, $P = f/A$, and so $P = Nm\langle u_x^2 \rangle/V$, where V is the volume $V = A \times L$. This oversimplified analysis shows how a macroscopic (thermodynamic) property, i.e. pressure, can be related to the microscopic (mechanical) property, i.e. molecular velocity.

Thus,

$$P = f/A^2 = Nm\langle u_x^2 \rangle/L^3 \quad (1.11)$$

If c denotes the speed in 3-dimensions, $c^2 = u_x^2 + u_y^2 + u_z^2$, we can write $\langle u_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$, yielding

$$P = \frac{1}{3}Nm\langle c^2 \rangle/L^3 = \frac{1}{3}Nm\langle c^2 \rangle/V \quad (1.12a)$$

If N_A is Avogadro's number, then $Nm = nN_Am = nM$, where M is the molar mass. Thus,

$$PV = \frac{1}{3}nM\langle c^2 \rangle \quad (1.12b)$$

Equating this to the ideal gas law gives, for $n = 1$, the root-mean-square velocity:

$$c_{rms} = c = \sqrt{\langle c^2 \rangle} = \sqrt{(3RT/M)} \quad (1.12c)$$

Conclusion: *The root-mean square speed of a molecule in an ideal gas is proportional to the square-root of the temperature and inversely proportional to its mass.*

Example 1.2. What is the mean square speed of a N_2 molecule (treated as an ideal gas) at a temperature of 25°C and a pressure of 1 bar (10^5 Pa)?

Using $R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$ and observing that $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ and that the molar mass of N_2 is $M = 28.0 \text{ g/mol}$ or

$28.0 \times 10^{-3} \text{ kg/mol}$ gives

$$\begin{aligned} c_{\text{rms}} &= (3 \times 8.3145 \times \text{kg m}^2\text{s}^{-2} \text{K}^{-1}\text{mol}^{-1} \times 298 \text{ K} / 28 \times 10^{-3} \text{ kg mol}^{-1})^{1/2} \\ &= 515.2 \text{ ms}^{-1} \end{aligned}$$

We now have a relation between the macroscopic quantity T and the microscopic property, c . Since the average energy of molecule is $\langle \varepsilon \rangle = \frac{1}{2}m\langle c^2 \rangle$ we immediately obtain

$$PV = \frac{2}{3}N\langle \varepsilon \rangle \quad (1.13a)$$

and for one mole,

$$PV = RT = \frac{2}{3}N_A\langle \varepsilon \rangle \quad (1.13b)$$

where N_A is Avogadro's number. Finally,

$$\langle \varepsilon \rangle = \frac{3}{2}RT/N_A \quad (1.13c)$$

Defining R/N_A as Boltzmann's constant ($k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1}$) gives

$$\langle \varepsilon \rangle = \frac{3}{2}kT \quad (1.14)$$

Comment 1: Temperature is not associated with the kinetic energy of a single molecule, but with the average kinetic energy of a large number of molecules. It is a statistical concept.

Comment 2: So far we have dealt only with average speeds. Actually, the speeds of molecules vary enormously. Molecules slow down as they collide with one another, speed up afterwards, etc. An expression of the distribution of speeds was derived by *Maxwell*. A schematic diagram of the variation of speed with temperature is depicted in Fig. 1.2.

1.8. Molecular Collisions

The *mean free path*, λ , is the average distance (of molecules) between collisions. The *collision frequency*, z , is the rate at which single molecule



Fig. 1.2 Variation of the number of molecules with speed.

collides with other molecules (i.e. number of collisions/second). It is obvious that the root-mean-square speed is $c = \lambda z$.

The kinetic theory developed so far cannot be used to derive λ . We must take into account the finite size of the particles. The result (not derived here) is

$$\lambda = RT/(\sqrt{2}N_A\sigma P) \quad (1.15)$$

$$z = \sqrt{2}N_A\sigma cP/(RT) \quad (1.16)$$

where σ is the area, $\sigma = \pi d^2$, and d the diameter.

Note:

- 1) $\lambda z = c$.
- 2) When P increases, λ increases and z increases.
- 3) Gases with larger σ have smaller λ and greater z .

1.9. Diffusion of Gases. Graham's Law

Diffusion is the tendency of a substance to spread uniformly through space available to it. Effusion is escape of a gas through a small hole.

The rate at which gases diffuse depends on the density. Graham's Law states that the rate of diffusion is inversely proportional to the square root of the density. If D_1 and D_2 represent the rate of diffusion of Gas 1 and of Gas 2, Graham's Law suggests that the rate of diffusion is inversely

proportional to the square root of the density, ρ . That is

$$D_1/D_2 = \sqrt{(\rho_2/\rho_1)} \quad (1.17)$$

Since for an ideal gas $PV = (m/M)RT$, where m is the total mass of the gas and M its molecular weight, we can write

$$P = (m/V)(RT/M) = (\rho/M)RT \quad (1.18)$$

It follows that for two gases at a given P and T ,

$$\rho_2/\rho_1 = M_2/M_1 \quad (1.19)$$

and thus

$$D_1/D_2 = \sqrt{(M_2/M_1)} \quad (1.20)$$

1.10. Molecular Basis of Graham's Law

It is natural to suppose that the rate of diffusion is proportional to the root-mean-square velocity, that is, D is proportional to $\sqrt{\langle c^2 \rangle}$ or to c . Accordingly,

$$\begin{aligned} D_1/D_2 &= c_1/c_2 \\ &= \{ \sqrt{(3RT/M_1)} / \sqrt{(3RT/M_2)} \} \\ &= \sqrt{M_2/M_1} \end{aligned} \quad (1.21a)$$

It follows also that for the same gas at different temperatures,

$$D_1/D_2 = \sqrt{(T_1/T_2)} \quad (1.21b)$$

and for different gases at the same P and T ,

$$D_1/D_2 = \sqrt{(M_2/M_1)} \quad (1.21c)$$

in accordance with the kinetic theory of gases.

Example 1.3.

- a) Calculate the root-mean-square speed (in ms^{-1}) of a H_2 molecule at $T = 298.15 \text{ K}$. The root-mean-square speed is $c = \sqrt{(3RT/M)}$. Taking R in Joule ($1 \text{ J} = \text{kg m}^2\text{s}^{-2}$) and M in kg mol^{-1} , we get

$$c = \sqrt{(3 \times 8.3145 \text{ kg m}^2\text{s}^{-2} \times 298.15 \text{ K} / 0.028 \text{ kg mol}^{-1})} = 515.4 \text{ m s}^{-1}$$

b) Calculate the ratio of the rate of diffusion of



The ratio is proportional to the ratio of the speeds of the molecules, and if P and T are the same for both molecules,

$$\begin{aligned} (D \text{ of } \text{O}_2 / D \text{ of } \text{N}_2) &= c(\text{O}_2) / c(\text{N}_2) = \sqrt{[3RT/M(\text{O}_2)] / [3RT/M(\text{N}_2)]} \\ &= \sqrt{[M(\text{N}_2) / M(\text{O}_2)]} = \sqrt{(28.0 / 32.0)} = 0.95 \end{aligned}$$

1.11. Real Gases

So far attention was focused on ideal gases. From a molecular point of view, ideal gases consist of molecules that do not attract or repel each other. This is obviously unrealistic. In a real gas (even if the molecules have no dipoles, quadrupoles, etc. or electrical charges), there are short-range repulsive forces and long-range attractive forces, which invalidates the ideal equation of state.

An equation of state that takes into account these interactions is the

a) **van der Waals equation of state**

$$(P + an^2/V^2)(V - nb) = nRT \quad (1.22)$$

where a and b are constants.

Another equation of state is the

b) **Virial equation of state**

$$PV_m = RT[1 + B/V_m + C/V_m^2 + \dots] \quad (1.23)$$

where V_m is the molar volume of the gas, B the *second* virial coefficient, C the *third* virial coefficient, etc.

Attractive forces are needed to account for liquefaction of gases. When a compressed gas in a container is forced through a porous plug into another where it is less compressed (the Joule–Thomson Experiment), the gas cools. Why? In the compressed state the molecules are close to each other; there is great attraction. In the dilute state, the molecules are farther apart. Therefore, when the gas expands the attractive *van der Waals bonds* are broken. It takes energy to do that. The energy comes from the gas — the gas cools!