Introduction

Chemistry – the science of matter and the changes it can undergo.

Physical Chemistry – concerned with the physical principles that underlie chemistry.

Seeks to account for the properties of matter in terms of fundamental concepts: atoms, electrons, and energy.

Provides the basic framework for all other branches of chemistry – inorganic chemistry, organic chemistry, biochemistry, geochemistry, chemical engineering.

Provides the basis of modern methods of analysis, the determination of structure, and the elucidation of the manner how chemical reactions occur.

Draws on two of the great foundations of modern physical science: *thermodynamics* and *quantum mechanics*.

The states of matter

A **gas** is a fluid form of matter that fills the container it occupies.

A **liquid** is a fluid form of matter that possesses a well-defined surface and (in a gravitational filed) fills the lower part of the container it occupies.

A **solid** retains its shape independent of the shape of the container it occupies.

Role of the physical chemistry – to establish the link between the properties of bulk matter and the behavior of the particles – atoms, ions, and molecules – of which it is composed.

Model – a simplified description of each physical state. The state's properties can be understood in terms of this model. The properties of the three states suggest that they are composed of particles with different freedom of movement.

A gas – widely separated particles in continuous rapid, disordered motion. A particle travels several (often many) diameters before colliding with another particle. The particles are so far apart (for most of the time) that they interact to each other only very weakly.

A liquid – particles are in contact but are able to move past each other in a restricted manner. They are in a continuous state of motion, but travel only a fraction of a diameter before bumping into a neighbor. The overriding image – motion, but with molecules jostling one another.

A solid – particles are in contact and unable to move past one another. The particles oscillate around an average location but they are essentially trapped in their initial positions and typically lie in ordered arrays.

The essential difference between the three states of matter – the freedom of the particle to move past one another.

If the average separation is large – hardly any limitation on their motion – the substance is gas.

If the particles interact so strongly with one another that they are locked together rigidly – the substance is solid.

If the particles have an intermediate mobility – the substance is liquid.

Melting of a solid and vaporization of a liquid can be understood in terms of the progressive increase in the liberty of the particles as a sample is heated and the particles become able to move more freely.

Physical state

Physical state – a specific condition of a sample of matter in terms of its physical form (gas, liquid, or solid) and the *volume*, *pressure*, *temperature*, and *amount of substance* present.

$\boldsymbol{V}$ $\boldsymbol{p}$ $\boldsymbol{T}$ $\boldsymbol{n}$

Example: 1 kg of hydrogen gas in a container of volume of 10 L at a specified pressure and temperature.

Two samples of a given substance are in the same physical state if they are the same state of matter (gas, liquid, or solid) and if they have the same mass, volume, pressure, and temperature.

The **mass**, *m*, of a sample is a measure of the quantity of matter it contains. The SI unit of mass is the **kilogram** (kg).

1 kg = 1000 g = 2.205 Lb   1 Lb = 453.6 g = 0.4536 kg

The **volume**, *V*, of a sample is the amount of space it occupies. The units: cubic meters, m^3; liters, L; milliliters, mL).

1 L = 0.2641 gallons = 1.057 quarts = 33.81 ounces

$1\ m^3 = 10^3\ L = 10^6\ mL$

Pressure

Pressure = force / area $p = F / A$

Pressure can arise in ways other than from the gravitational pull of the Earth on the object. The impact of gas molecules on a surface gives rise to a force and hence to a pressure.

The SI unit of pressure – **pascal**, Pa $1\ Pa = 1\ N\ m^{-2} = 1\ kg\ m^{-1}\ s^{-2}$

Atmospheric pressure at sea level – about 10^5 Pa

Pressure units and conversion factors

bar	1 bar = 10^5 Pa
atmosphere	1 atm = 101.325 kPa = 1.01325 bar
torr	760 Torr = 1 atm 1 Torr = 133.32 Pa

One of the most important units of pressure in physical chemistry is the **bar**. Normal atmospheric pressure is close to 1 bar.

Example: Calculating pressure

Suppose some person weighed 65 kg. Calculate the pressure he exerted on the ground when wearing (a) boots with soles of total area 250 cm^2 in contact with the ground, (b) ice skates, of total area 2.0 cm^2.

The force exerted by this person:

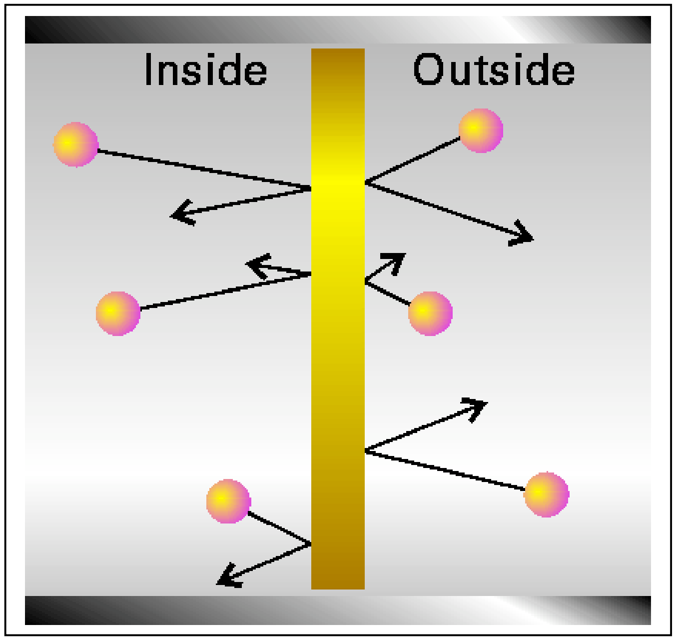
$F = mg = 65 \text{ kg} \times 9.81 \text{ m s}^{-1} = 640 \text{ N}$

(a) $p = 640 \text{ N} / 2.50\times10^{-2} \text{ m}^2 = 2.6\times10^4 \text{ Pa} = 26 \text{ kPa}$

(b) $p = 640 \text{ N} / 2.00\times10^{-4} \text{ m}^2 = 3.2\times10^6 \text{ Pa} = 3.2 \text{ MPa}$

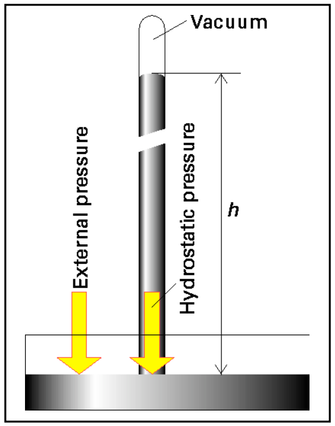
If an object is immersed in the gas, it experiences a pressure over its entire surface because molecules collide with it from all directions. The atmosphere exerts a pressure on all the objects in it. We are essentially battered by molecules of gas in the atmosphere and experience this battering as the atmospheric pressure. The pressure is greatest at sea level because the density of air, and hence the number of colliding molecules is greatest there.

The atmospheric pressure – 1 kg of lead (or any other material) on to a surface of area 1 cm^2. 1000 m below the sea level – the pressure is 100 times greater than at the surface.



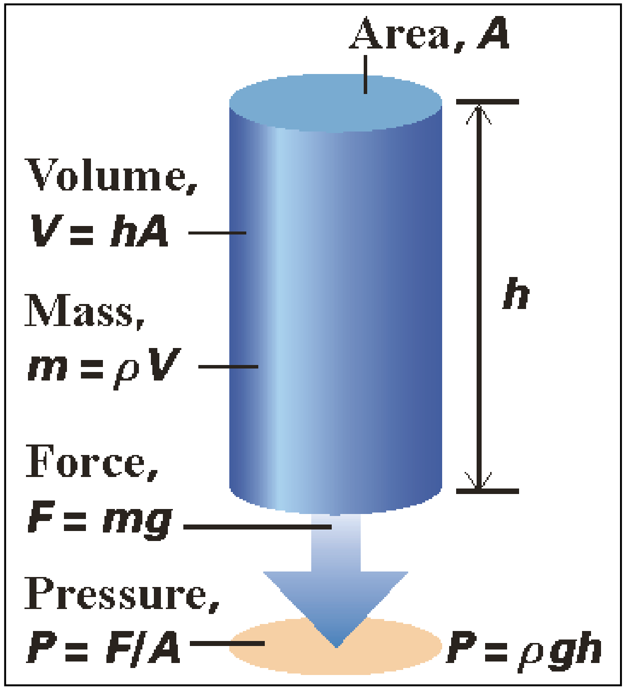
When a gas is confined to a cylinder fitted with a movable piston, the position of the piston adjusts until the pressure of the gas inside the cylinder is equal to that exerted by the atmosphere. When the pressure on either side of the piston are the same – the two regions on either side are in **mechanical equilibrium**. The pressure of the confined gas arises from the impact of the particles: they batter the inside surface of the piston and counter the battering of the molecules on the outside of the piston. Provided the piston is weightless, the gas is in mechanical equilibrium with the atmosphere.

Atmospheric pressure (varies with altitude and weather) is measured with a barometer.



A mercury barometer – an inverted tube of mercury that is sealed at its upper end and stands with its lower end in a bath of mercury. The mercury falls until the pressure it exerts at its base is equal to the atmospheric pressure. By measuring the height of the mercury column we can calculate the atmospheric pressure, provided we can find a relation between height and pressure.

Hydrostatic pressure

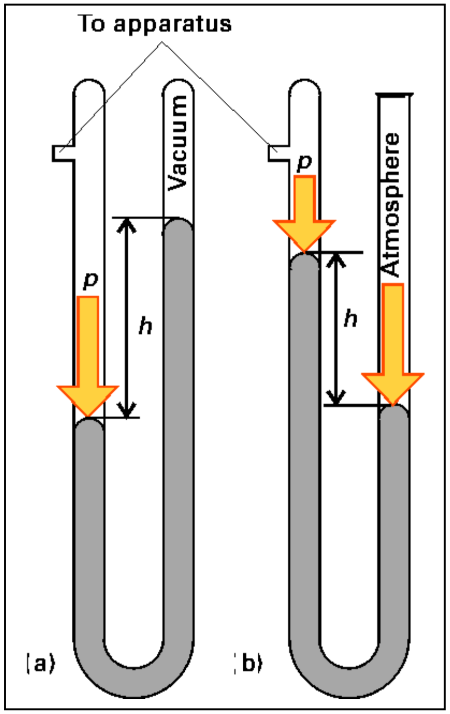


The volume of a cylinder of liquid of height h and cross-sectional area A is hA. The mass, m, of this cylinder of liquid is the volume multiplied by the mass density, ρ,

$$m = \rho \times hA$$

The downward force exerted by this mass is mg, where g is the acceleration of free fall, a measure of the Earth gravitational pull on an object ($g = 9.81$ m s^{-2} at sea level). The force exerted by the column is $\rho \times hA \times g$. The pressure at the base is ρhAg divided by A:

$$\boldsymbol{p = \rho hg}$$



We can measure the pressure of a gas inside a container by using a pressure gauge – the simplest type is a **manometer** – a U-tube containing a liquid. One limb can be connected to the container and the other either sealed (a) or open to the atmosphere (b). The difference in heights of the liquid in the two arms of the open-tube manometer is proportional to the difference in pressure between the gas in the container and the external atmosphere.

(a) The height difference, h, of the two columns in the sealed-tube manometer is directly proportional to the pressure of the sample.

(b) The difference in heights of the columns in the open-tube manometer is proportional to the difference in pressure between the sample and the atmosphere.

Temperature

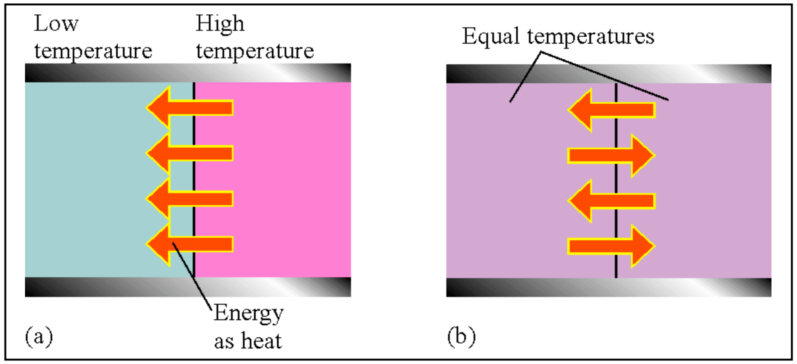
Temperature, *T*, is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall. If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B. Energy flows from high temperature to lower temperature.

It is useful to distinguish between two types of boundary:

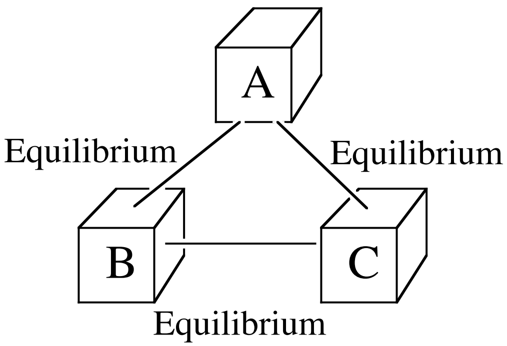
diathermic – if a change of state is observed when two objects at different temperatures are brought into contact;

adiabatic – no change occurs even though the two objects have different temperatures. A metal container has diathermic walls.

The temperature is a property that indicates whether two objects would be in **thermal equilibrium** if they were in contact through a diathermic boundary. Thermal equilibrium is established if no change of state occurs when two objects A and B are in contact through a diathermic boundary.



Zeroth Law of thermodynamics



If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A

The Zeroth Law justifies the concept of temperature and the use of **thermometer**, a device for measuring the temperature.

Celsius scale: the freezing point of water at 1 atm corresponds to 0ºC and the boiling point at 1 atm corresponds to 100ºC.

θ / ºC = (θ / ºF – 32) × 5/9

Absolute temperature (**Kelvin scale**), also called a **perfect gas temperature scale** or **thermodynamic temperature scale**:

T / K = θ / ºC + 273.15

Water at 1 atm freezes at 273 K; a warm day (25ºC) corresponds to 298 K.

Amount of substance

Mass – a measure of the quantity of matter in a sample regardless of its chemical identity.

In chemistry, where we focus on the behavior of atoms, it is usually more useful to know the quantity of each specific kind of atom, molecule, or ion in a sample rather than the mass itself. Since even 10 g of water consists of about 10^{23} H_2O molecules, it is appropriate to define a new unit that can be used to express such large numbers simply. Chemists have introduced the **mole** unit (mol).

1 mol of specified particles is equal to the number of atoms in exactly 12 g of carbon-12.

That number is found by dividing that mass by the mass of one atom of carbon-12 determined by using a mass spectrometer.

The result is 6.022×10^{23}.

To avoid ambiguity, one should always specify the identity of the particles when using the unit mole.

The mole – the unit used when reporting the value of the physical property called the **amount of substance**, n, in a sample.

n = 1 mol H_2 or $n(H_2) = 1$ – the amount of hydrogen molecules in a sample is 1 mol.

The term ‘amount of substance’ is commonly referred to ‘the number of moles’ in a sample. The term **chemical amount** is also often used.

The **Avogadro constant** (N_A) – the number of particles (of any kind) per mole of substance:

$$N_A = 6.0221367 \times 10^{23} \text{ mol}^{-1}$$

Number of particles = chemical amount (in moles) × number of particles per mole

$$N = n \times N_A$$

The **molar mass**, M – the mass per mole of substance – the mass of a sample of the substance divided by the chemical amount of atoms, molecules, or formula units it contains.

Molar mass of an element – the mass per mole of its atoms.

Molar mass of a compound – the molar mass of its molecules.

Molar mass of an ionic compound – the mass per mole of its formula units.

The molar mass of water is the mass per mole of H_2O molecules, with the isotopic abundances of hydrogen and oxygen those of typical samples of the elements, and is 18.02 g mol^{-1}.

The unit **Dalton** – 1 g mol^{-1} – used in biophysical applications.

1 kDa = 1 kg mol^{-1}

Molar mass of an element – determined by mass-spectrometric measurement of the mass of its atoms and then multiplication of the mass of one atom by the Avogadro constant. Care has to be taken of the isotopic composition of an element – a suitably weighted mean of the masses of different isotopes. The values are tabulated in the periodic table.

Molar mass of a compound – known composition – a sum of the molar masses of its constituent atoms.

Unknown composition – determined experimentally by using mass spectrometry in a similar way as for atoms, but allowing for the fragmentation of molecules in the course of the measurement.

Molar mass – used to convert from the mass, m, of a sample (which we can measure) to the amount of substance, n (which, in chemistry, we often need to know):

Mass of sample (g) = chemical amount (mol) $\times$ mass per mole (g mol^{-1})

$$m = n \times M$$