

Chapter 1. Interactions between atoms and molecules, bonds

The properties of the atoms and molecules and the interactions between them determine the characteristic properties of any matter. This chapter deals with the forces between atoms and molecules and the „so-called” primary and secondary bonds.

What determines the type of the primary bond?

Ionic, covalent and metallic bonds are the **primary bonds**. The electronegativity of the atoms is the main determinant of bond formation. The definition of **electronegativity (EN)** is:

$$EN = I + |A|,$$

where I is the **ionization energy** (the amount of energy that is necessary to remove the most loosely bound electron from an atom), A is the **electron affinity** (the amount of energy released when an electron is added to an atom – this energy is negative, according to the agreement, so to calculate the affinity we must take the absolute value). The usual unit is the eV (electronvolt), or we can use aJ (attojoule), or J/mol.

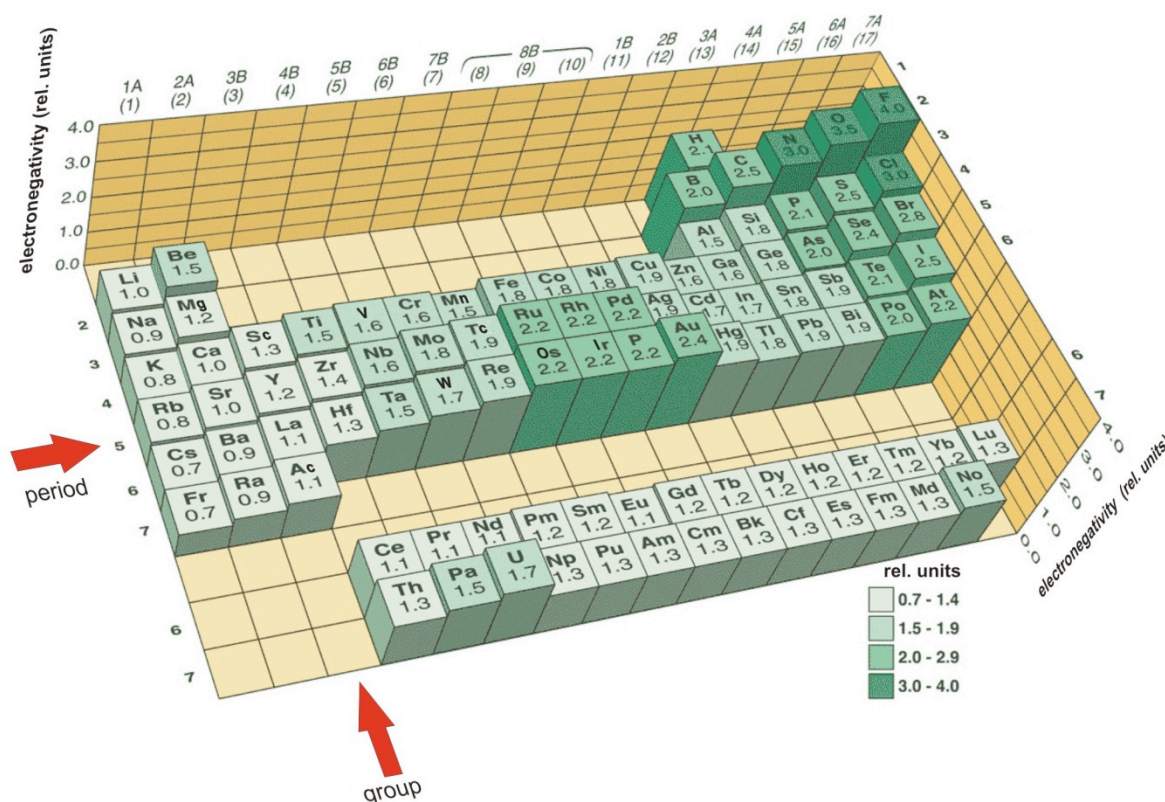


Fig. 1.1 Electronegativity of the elements (according to Pauling). (www.ptable.com site is very informative, where besides the electronegativity you can find other characteristics of the elements)

There are different electronegativity scales in the literature. One of them is the most widely used Pauling's scale. In Fig. 1.1 the height of the columns on each element represents the value of its electronegativity. The electronegativity increases from left to right in each period, as the electron shell becomes more filled and so the atoms approach the noble gas configuration. As we move down

in each group of the periodic table, more and more electrons build up the electron shells of the atoms. Therefore, the radius of the atoms will increase and the valence electrons will be further away from the nucleus. This will cause the electronegativity to decrease from top to bottom in each group. We can summarize all these in a simple rule that says, from the bottom left (Francium) to the top right corner (Fluorine) of the periodic table the electronegativity increases. (We do not mention the electronegativity of noble gases due to their low practical importance.)

What is the role of electronegativity in determining the type of chemical bonds? If the electronegativity values of two atoms are very different, the atom with the higher electronegativity will accept an electron from the one with the lower value. The electron acceptor will become negatively while the electron donor will become positively charged. Finally, the electrostatic attraction between the positive and negative charges will form an **ionic bond** between the atoms (Fig. 1.2).

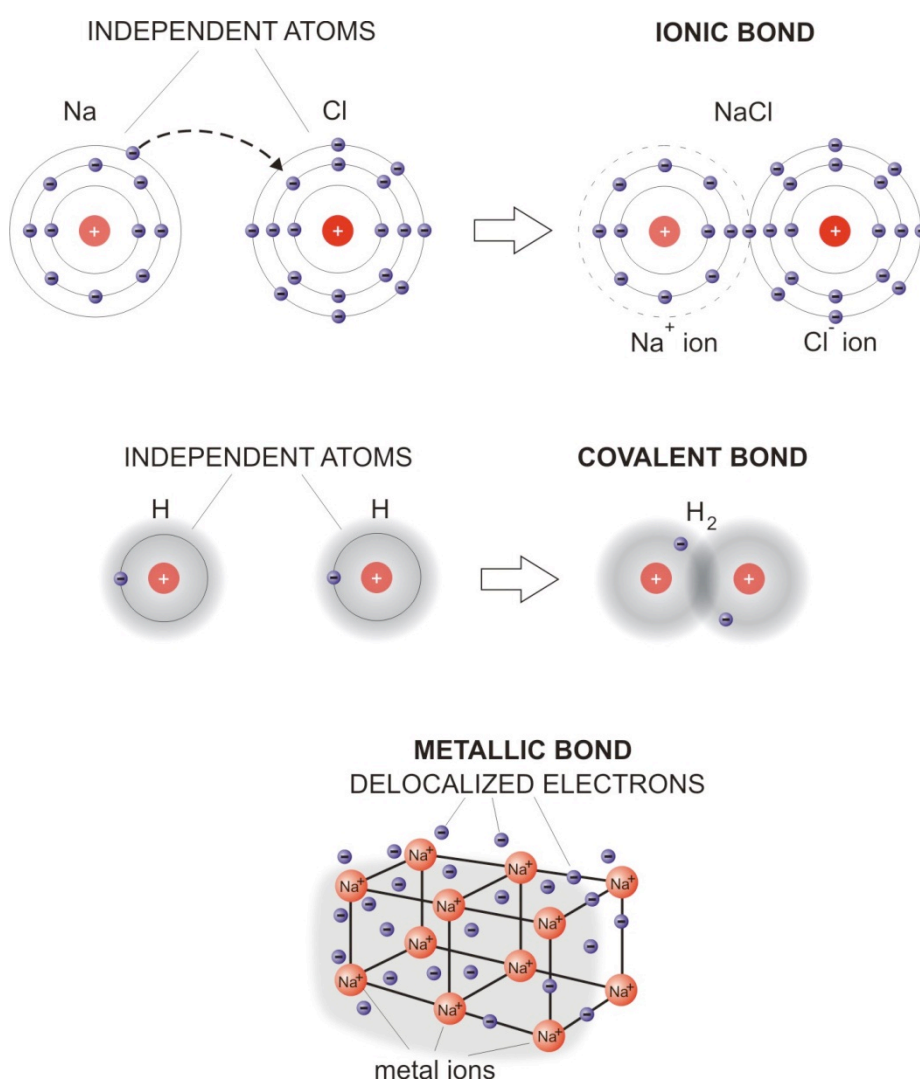


Fig. 1.2 Formation of the strong (primary) bonds

If the electronegativities of two atoms are equal or the difference between them is small, some of the valence electrons will be shared between the two atoms. The common electron orbital of the shared electrons –that produces a certain attraction between the atoms – result in the formation of the covalent or the metallic bonds. In these cases, the atoms are sharing some of their valence

electrons. Whether the bond is covalent or metallic will be decided by the average electronegativity of the binding partners. If the average value of electronegativities is large the sharing of electrons will localize only for a few atoms, forming the **covalent bond**. If the average value of electronegativity of the binding partners is low, then the electron sharing will be extended up to billions of atoms. In this case, a delocalized electron cloud will spread out in the whole macroscopic body, forming a **metallic bond**. (Practically the metal crystal is one gigantic molecule.)

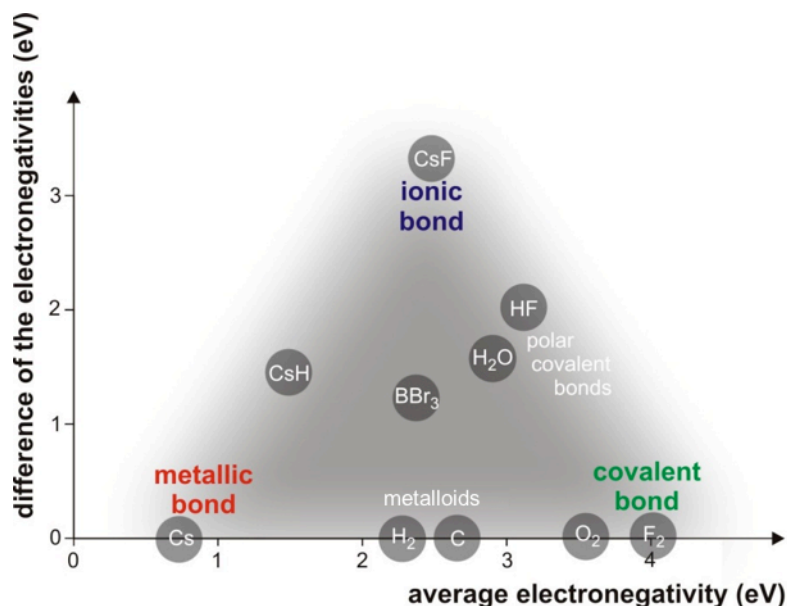


Fig. 1.3 Examples of the primary bonds (In the vertices of the triangle the examples show compounds with purely one bond type, other examples are compounds with multiple bond types.)

Based on of the previous discussion we can place the different bonds into a coordinate system (Fig. 1.3) where the average of the electronegativities is on the horizontal axis and their difference is on the vertical axis. The different types of chemical bonds will form a triangular area on the chart. The top vertex of the triangle together with its vicinity represents the ionic bond (large difference in electronegativities, e.g. CsF). The lower left vertex and its vicinity represents the metallic bond (small difference in electronegativities and low average values of electronegativity, e.g. Cs). The lower right vertex corresponds to the covalent bond (e.g. F₂). Most compounds contain more than one type of chemical bonds as shown by the figure.

Why do chemical bonds form at all?

Naturally, chemical bonds will not be formed between atoms of any kind. The requirement for bond formation is that the total energy of the binding partners at close range must be lower than their total energy when separated far apart. Figure 1.4 shows the total energy of two atoms as a function of the distance between them. Starting to approach the two atoms from far distance, the energy decreases as they get closer to each other. After a certain energy minimum as the distance decreases further the energy will increase rapidly. The equilibrium distance is where the energy of the system has its minimum. Increasing the distance between them starting from the equilibrium, they will tend to return to the equilibrium distance by attracting each other. Moving them closer than the equilibrium distance, they will tend to return to the equilibrium distance by repelling each other. The

solid line representing the total energy on the figure is the sum of the two dashed ones representing the attractive and repulsing forces.

The origin of the attractive forces can be either the electrostatic interaction between two ions of opposite charge or shared electron orbitals (bonding orbitals). The origin of the repulsive forces may be due to the electrostatic repulsive forces arising between the positively charged atomic nuclei when they are too close to each other. On the other hand, non-bonding orbitals produced by the electrons due to Pauli's principle may also cause the repulsion. The equilibrium distance (r_0) is called the **binding distance** that has a typical range of around 0.1 nm. The depth of the energy minimum (E_0) is the **binding energy** with a **typical energy of 100-1000 kJ/mol**. Generally, the binding energy of a covalent bond is larger than that of the metallic or ionic bonds.

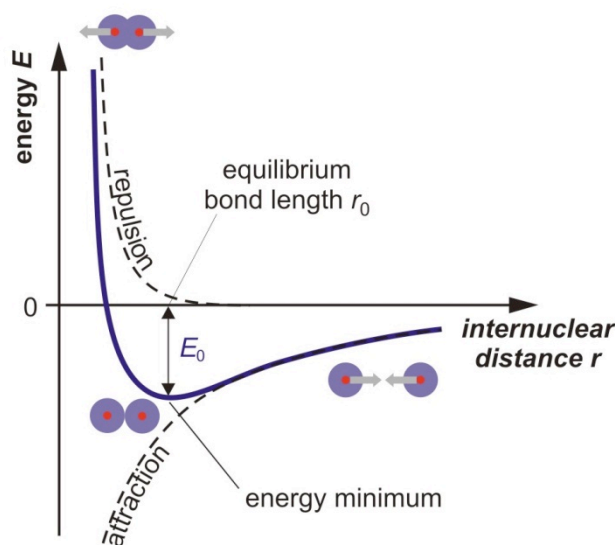


Fig. 1.4 Formation a chemical bond between two atoms (or molecules)

An interesting and important property of the energy curve is that around its minimum it approximately resembles the shape of a parabolic energy curve of a spring. The parabolic energy curve of a spring is the consequence of the linear force law (Hooke's law). As a result, we expect a similar spring like behavior in the case of atomic bonds around the equilibrium distance. This will be important later when we will discuss the deformation of materials. For example, we will deal with the forces between atoms when they are pulled apart in case of elongating an object.

Finally, we must mention the directional properties of the primary bonds. While the covalent and ionic bonds provide strong attraction forces only in specific directions, in case of metallic bond we see no directional preference due to the homogenous distribution of the delocalized electron cloud.

Secondary bonds

Atoms and molecules can attract each other even in the cases when they do not have electric charge or they do not share any binding electrons, but have a permanent or temporary electric dipole moment. The electric interaction between the properly situated dipoles gives the base of the

secondary bonds such as the **van der Waals** or **hydrogen bonds**. The forces between dipoles are much weaker compared to the previously discussed primary bonds, their energy range is approximately 0.2-50 kJ/mol. The H-bond is strongest while the van der Waals bond is the weakest among the secondary bonds. (However, sufficiently large number of these bonds can produce very strong cohesion between particles or bodies.)

1-1. table Bond energy of some materials

bond strength	bond type	material	binding energy (kJ/mol)
<i>weak (secondary)</i>	<i>van der Waals</i>	neon (Ne)	0.26
		argon (Ar)	7.7
	<i>H-bond</i>	water (H ₂ O)	23
<i>strong (primary)</i>	<i>metallic</i>	mercury (Hg)	68
		aluminum (Al)	324
		tungsten (W)	849
	<i>ionic</i>	NaCl	640
		MgO	1000
	<i>covalent</i>	silicon (Si)	450
		carbon (C, diamond)	713

Types of the van der Waals interactions are orientation, induction and dispersion interactions. **Orientation** interaction is formed when two permanent dipoles align in the proper direction. In case of the **induction interaction** a permanent dipole induces dipole moment with proper direction in a neutral molecule. The **dispersion** interaction is the weakest of the three. In this case, the participating atoms or molecules do not have a permanent dipole but due to the fluctuations of the electron clouds temporary dipoles will be formed. These temporary dipoles can induce a properly orientated dipole in the neighboring atom or molecule (Fig. 1.5)

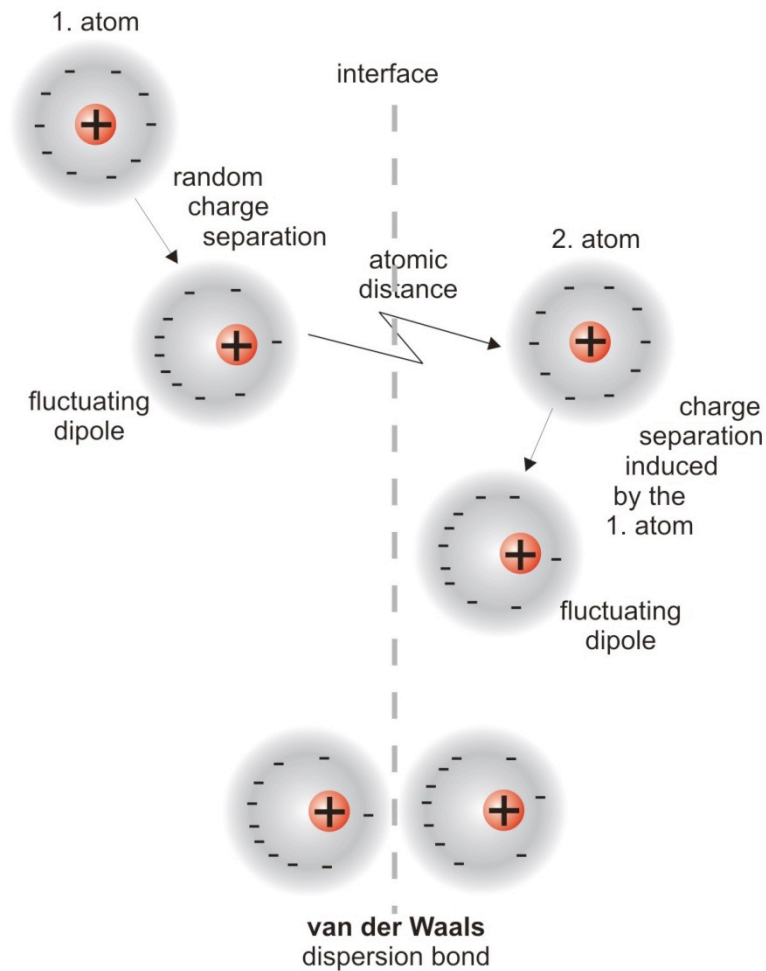


Fig. 1.5 Formation of the dispersion van der Waals bond

Secondary interactions are important in determining the phase (gaseous, liquid or solid) of materials on the macroscopic level. The level of particle movement in any material (that is related to the temperature) will have a strong influence on the formation of these interactions. This will be discussed in the following chapter.

In sum, the properties of various materials are determined by the properties of their particles – atoms, ions, molecules – and the characteristics of the bonds formed between them – types, number and orientation of bonds, binding energy, the shape of the energy curve etc.

Electronegativity (EN): the sum of the absolute value of the ionization (I) energy and the absolute value of electron affinity (A), $EN = I + |A|$. Its usual unit is the eV (electronvolt) but dimensionless relative scales are also used such as the the most frequent Pauling-scale.

Primary (strong) bond: they are the ionic, covalent and the metallic bonds.

Ionic bond: the bond formed between atoms having very different electronegativity. During the electron transfer between the binding partners, one binding partner is losing an electron while the other is gaining one.

Covalent bond: the bond formed between atoms of high electronegativity. In this case atoms share a few electrons with each other.

Metallic bond: the bond formed between atoms of low electronegativity. All atoms in the material share some of the electrons and these electrons can move freely in the metal.

Binding energy: the energy that is necessary to move two atoms infinitely far apart. The energy range of strong bonds is between 100 and 1000 kJ/mol, for weak bonds it is 0.2-50 kJ/mol.

Secondary (weak) bonds: van der Waals and the H-bonds.

Van der Waals bond: the bond formed between atoms or molecules with permanent or temporary dipole moment. Types: orientation, induction, dispersion.

H-bond: the bond formed through a H atom between two atoms of high electronegativity.

Problems to solve: 1.3, 1.4, 1.6, 1.7

Chapter 2. States of matter

What determines the phase of a material?

Most of the materials under usual circumstances are in one of three phases: **solid**, **fluid** and **gaseous**. The actual state is defined by the circumstances, mainly by the temperature and the strength of bonds between the atoms (or molecules) (Fig. 2.1).

Let's use neon (Ne) as an example! Due to its noble gas electron configuration neither sharing of electron orbitals nor electron transfer, but only very weak dispersion interactions will be formed between the Ne atoms. Thus, the movement of Ne atoms must be reduced greatly in order to keep them bound by these weak interactions. In other words: at room temperature the neon is gaseous and only at very low temperatures, at about 77 K (-196 °C) will become fluid and at about 63 K (-210 °C) will freeze to solid.

Water molecules can form much stronger H-bonds, thus already at 373 K (100 °C) it will become fluid and at 273 K (0 °C) it solidifies.

The metallic bonds between aluminum atoms have a binding energy that is one order of magnitude stronger than H-bonds. As a result, this strong binding can keep the Al atoms in a crystal lattice against the atomic movements even at room temperature. In order to break these interaction, these movements have to be enhanced greatly by heating. The Al crystal has to be heated to 933 °K (660 °C) to melt and to 2792 °K (2519 °C) to boil.

Another example is diamond, which has even stronger covalent bond between the carbon atoms. The melting point of diamond is 3823 °K (3550 °C) and its boiling point is 4300 °K (4027 °C). (All the temperatures in the examples above are given for normal atmospheric pressure.) The so-called phase diagrams can tell us which phase is stable at given circumstances (e.g. temperature, pressure)

We deal with them in chapter 6.

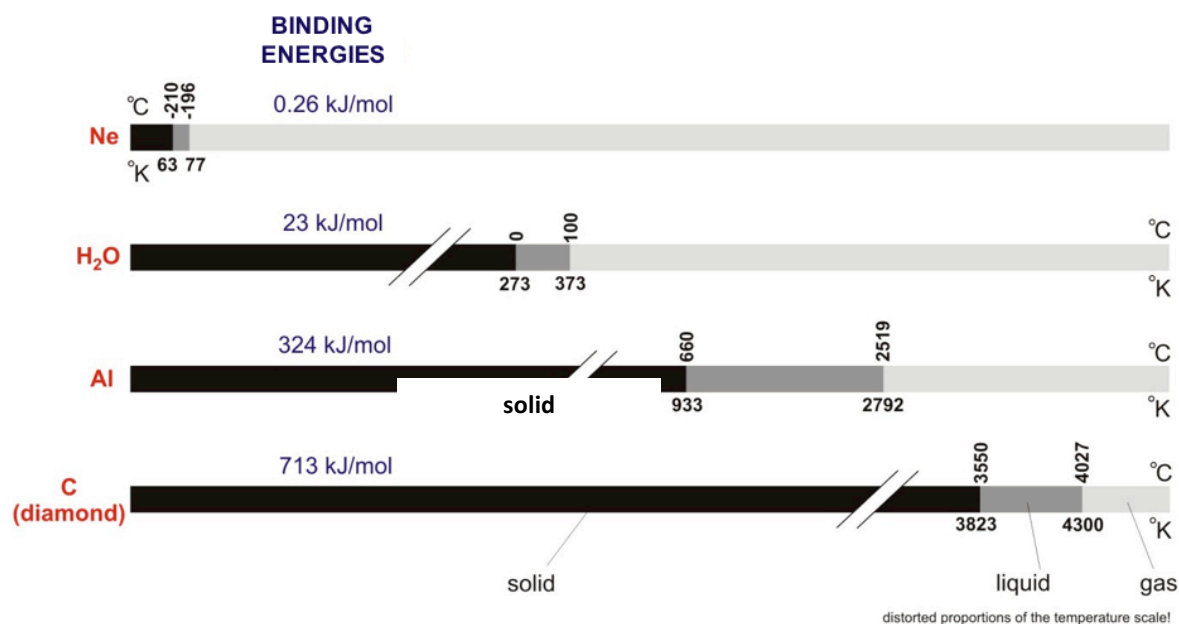


Fig. 2.1 Melting- and boiling point of a few materials having different binding energy

What are the characteristics of each phase? (Fig. 2.2)

A **gas** has no definite volume and stable shape and will fill up the space available to it. None of its properties have directionality they are **isotropic**. These properties derive from the lack of any internally ordered structure.

Liquids have definite volume but have no stable shape, they flow. Having their own volume is the consequence of the bond formation between the atoms or molecules that keeps them in close distance to each other. These bonds will provide a certain structural order inside the fluid, however due to the movement of particles these bonds will continuously break and reform, thus the whole structure will become dynamic. The dimension of the ordered domains is very small, it spans from a few bonds up to a maximum of hundreds of bonds. This feature is called **short-range order**. The ordered domains can easily move along each other, thus fluids will not develop a defined shape and there will be no shear forces in them at equilibrium. Since the orientation of every order domain is random, there will be no directional preference in the structure, thus fluids are also **isotropic**.

Solids are classified into two different groups: **crystals** and **amorphous solid** bodies.

Crystals have definite volume and shape, that is usually a three-dimensional geometric shape (e.g. the cubic salt crystal). In solids, due to their strong chemical bonds, a highly ordered and directional structure, the so-called crystal lattice is formed. The order in the lattice can spread up to meter-long distances, thus it is called **long-range order**. Because of this order and directionality most crystals are **anisotropic**, meaning that their various properties depend on the direction.

The amorphous solids materials may be viewed as frozen fluids, because their inner structure is similar to that of fluids (e.g. glass). However, the movement of particles are much slower in them, thus the dynamic properties of the structure and the fluidity of an amorphous material can only be observed on a long time scale (e.g. tar). Since their inner structure resembles that of fluids, amorphous solids are **isotropic**.

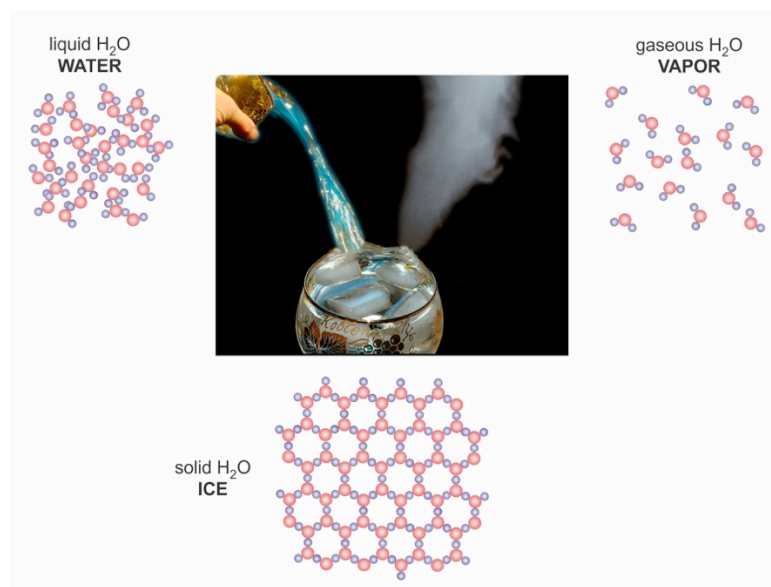


Fig. 2.2 The internal structure of different phases of water

Simple quantities used to characterize materials

Amount of substance (usual symbol in physics: ν) measures the size of an ensemble of elementary entities in a body, its unit is mole (unit symbol: mol). One mole of substance contains $6,02 \cdot 10^{23}$ elementary entities. This is the so-called **Avogadro constant**: $N_A = 6,02 \cdot 10^{23} \text{ 1/mol}$. The number of entities (i.e. atom, molecules) found in a body is given by:

$$N = \nu \cdot N_A .$$

The usual symbol for the **mass** of a body is m (unit: kg) and for the **molar mass** is M (unit: kg/mol). In the case of homogenous material it is true that:

$$m = \nu \cdot M .$$

The extension of the body in space is characterized by the **volume** V (m^3). The **density** ρ (rho) characterizes the „compactness“ of the body and it is defined as mass per unit the volume:

$$\rho = \frac{m}{V} .$$

The unit of density is: kg/m^3 .

Table 2-1. Density of a few materials(ρ) at 20°C

material	ρ (g/cm ³)
water	0.9
dentine	1.9
enamel	2.2
PMMA Poly(methyl methacrylate)	≈ 1.2
silicon	≈ 1.4
ceramics	1.6-3.9
porcelain	2.2-2.4
glass	2.2-2.7
gypsum	2.31-2.76
Ni-Cr alloys	≈ 8
Co-Cr alloys	8-9
Pd-Ag alloys	10-12
amalgam	≈ 12
gold alloys	12-17
gold	19.3

Instead of the density we can use its reciprocal the **specific volume** (v):

$$v = \frac{V}{m}.$$

This quantity characterizes how much space is required by a unit mass. Unit is m³/kg.

The **temperature** of a body is given in (Celsius) degrees (°C) or in Kelvin (°K) that is the official SI unit. The conversion between them is:

$$T(\text{K}) = t(^{\circ}\text{C}) + 273 .$$

The symbol for the **pressure** of a gas or a liquid is p and its unit is Pascal ($\text{Pa} = \text{N/m}^2$). This is also the unit of (mechanical) stress arising in solids due to deformation.

Gas: material without inner structure, definite volume and stable shape.

Liquid: material having a short-range and dynamic order, definite volume but having no stable shape (fluidity).

Crystal (solids): Material characterized by long-range order having stable shape and definite volume.

Amorphous solid body: Material characterized by short-range order and definite volume, but having no stable shape (fluid in the long term).

Density (ρ): $\rho = \frac{m}{V}$ where m is the mass and V is the volume of the body (kg/m^3)

Specific volume (v): $v = \frac{V}{m}$ where V is the volume and m is the mass of the body (m^3/kg)

Problems to solve: 1.1, 1.2, 1.8, 1.9, 1.10, 1.11.

Chapter 3. Gaseous state

Although gases have lower significance in dental science, this chapter will deal with their properties because explaining the molecular interpretation of temperature and the Boltzmann-distribution is the easiest with gases.

What are the characteristic of gases?

A substance is in gaseous state if the movement of its particles is stronger than the attractive forces between them, thus the particles in a gas are individually separated. In case of neon, the only interaction between the atoms are the weak van der Waals bonds with a binding energy is 0.26 kJ/mol. Therefore, already at a low temperature of 77 K the movement of atoms will break these weak bonds. In case of water, the H-bonds formed between the molecules are much stronger with a binding energy of 23 kJ/mol. Therefore, water must be heated to 373 K to reach the gas phase, where these bonds are broken and the molecules are separated. Finally, aluminum having metallic bonds between atoms will become gas above 2792 K and diamond with its covalent bonds will be in gas phase above 4300 K.

As we can see, in a gas there are practically no bonds between the particles, so they are constantly moving independently of the other particles present. The gas particles will completely fill any container in which they are placed by their **random movements**. That is why a gas does not have a defined volume or shape. The physical properties in a gas are the same in every direction, there is no directional preference, thus a gas is **isotropic**.

So far, all the examples we based on the assumption that temperature is a measure of particle movement. The higher the temperature is, the stronger the movement of particles will be.

What is the temperature?

Everyone can feel what temperature means when drinking from a still hot coffee or going into cold water on a hot day. What could be the molecular explanation of it? How can we feel the temperature of a gas if it is such a simple system without internal structure or bonds but only the movement of its particles? Therefore, it must be the movement of particles that we feel as temperature. In order to understand the connection between molecular motion and temperature or pressure, we have to use a simplified model called the ideal gas. (Ideal gas: Theoretical gas composed of many randomly moving point particles whose only interactions are perfectly elastic collisions.)

Pressure is the force exerted on a unit surface, which is generated as the gas particles collide with the wall of the container. During every collision, each particle will exert a tiny force on the wall. The sum of these tiny forces on the container's wall will become the macroscopically measurable pressure. When the particles move faster, then more collisions will happen during the same time interval, thus the total sum of the forces will become greater and pressure will increase. Other macroscopic observations show that in case of an ideal gas the pressure (p) is proportional with the temperature (T) if the volume (V) and the number of gas particles (N) are constant:

$$pV = NkT, \text{ thus } p \sim T.$$

This is the ideal gas law. The law suggests that not only pressure but also temperature is related with the movement of particles (detailed explanation is found in the yellow text box):

$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}kT. \quad [3.1]$$

In the equation m_0 is the mass of a particle, v is the velocity of a particle, k is Boltzmann-constant and T is absolute temperature (the line above v^2 is a symbol of averaging). The left side of the equation represents the average kinetic energy of particles which is directly proportional to the absolute temperature of the gas.

The right side of equation 3.1 contains the number 3, which represents that the particles move in 3 dimensions in space, in other words the particles have three degrees of freedom. That means that the available energy for each degree of freedom is $\frac{1}{2}kT$. In case of a gas that is composed of polyatomic molecules, other movements can appear (rotation, vibration) which will increase the number of degrees of freedom. This model can be translated to the liquid and solid state as well and as a general consequence we can state, that **the temperature is a parameter proportional to the average kinetic energy available for each degree of freedom**. The value of kT (unit: J) is called **thermal energy**. For one mole of substance the value RT (unit: J/mol) is used; $RT = N_A kT$, ($R = N_A k$).

The particles in a gas move with different velocities, that is why the left side of equation 3.1 contains the average velocities. The so-called **Maxwell-Boltzmann distribution** (Fig. 3.2) shows us which velocities are found in what ratio in a gas at a given temperature.

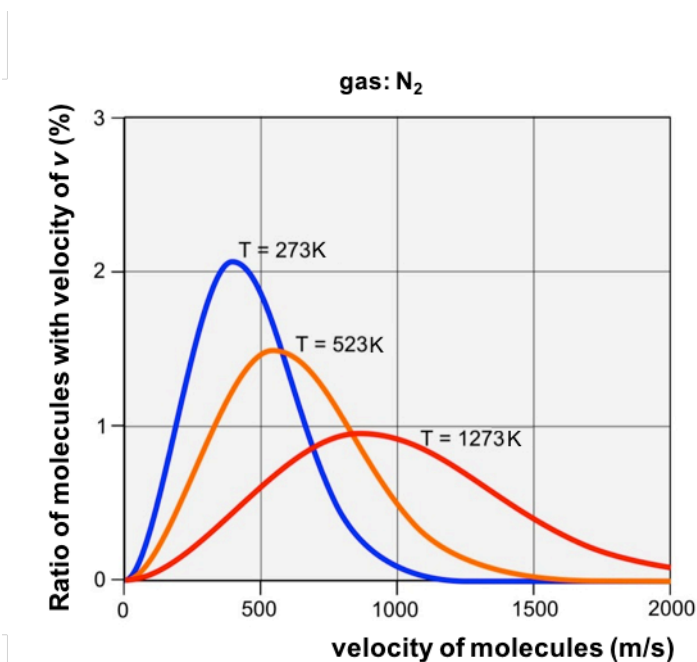


Figure 3.2 Velocity distribution of molecules in nitrogen gas at various temperatures (Maxwell–Boltzmann distribution)

Kinetic theory of temperature

Figure 3.1 shows a container with volume V that is filled with an ideal gas. In the container a number of N particles with a mass of m_0 are moving randomly, each with the same velocity of v . The gas has a pressure p and temperature T . Particle density in the container is given by $n = N/V$.

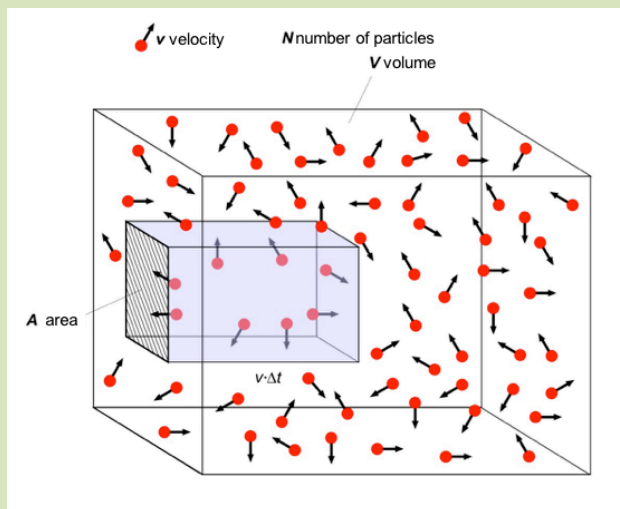


Figure 3.1 Kinetic theory of temperature in case of an ideal gas

Let us calculate how many particles will collide with the surface area of A of the wall during the time interval of Δt . Only those particles can collide that are not further from the wall than a distance of $v \cdot \Delta t$. The shaded volume inside the container is given by $A \cdot v \cdot \Delta t$, the number of particles inside it, supposing homogenous distribution, is $n \cdot A \cdot v \cdot \Delta t$. Not all of these particles will collide with the wall, only those that move towards it. Simply we can assume that $1/6$ th of the particles will collide because they can move in 6 directions (left-right, up-down, back-forth). Finally, the number of particles that collide with the area A during Δt time: $\frac{1}{6} n A v \Delta t$.

The force exerted on the wall by a colliding particle can be calculated from the change in the particle velocity. Since the collision is elastic, the magnitude of the velocity will remain the same, but its direction will change to an opposite (from v to $-v$). Thus, the change in velocity is:

$$\Delta v = v - (-v) = 2v$$

The change in the momentum of the particle during the collision is $m_0 \cdot 2v$ and the force of a single particle collision is given by the change in momentum during Δt time:

$$F = \frac{m_0 2v}{\Delta t}.$$

The total force exerted on area A is the product of a single collision's force and particle number:

$$\frac{1}{6} n A v \Delta t \cdot \frac{m_0 2v}{\Delta t} = \frac{1}{3} n A m_0 v^2.$$

Pressure is the total force over the area of A :

$$p = \frac{1}{3} n m_0 v^2.$$

From the gas law:

$$p = \frac{N}{V} k T = n k T.$$

Combining the two gives:

$$\frac{1}{3} n m_0 v^2 = n k T$$

$$\frac{1}{2} m_0 v^2 = \frac{3}{2} k T.$$

If we calculate the velocity of N_2 molecules in nitrogen gas at 0°C by using formula [3.1], assuming that the velocities of all molecules are the same, we will get a result of 493 m/s. This gives a good approximation to the average velocity of the 0°C Maxwell-Boltzmann distribution, which is a little faster velocity than the maximum point of the curve (because of the skewed right nature of the distribution). The velocity distribution curve will shift to the right and get wider as we increase the temperature (see Fig. 3.2). An important observation is that about half of the particles have larger velocities and thus larger kinetic energy than the average. The velocities can be 2-3 times greater than the average and thus, the kinetic energies can be 4-9 times greater than the average. In case we compare the binding energies between particles with the average kinetic energy available at a given temperature, it is important to remember that a significant amount of the particles have larger energies than the average.

An example

Calculate the velocity of N_2 molecules in nitrogen gas at 0°C , assuming that all molecules have the same velocity. Molar mass of nitrogen is (considering that the gas particles are N_2 molecules) is 28 g/mol, that is 0,028 kg/mol. Mass of a single N_2 molecule is given by dividing the molar mass by Avogadro's constant. Using equation [3.1]:

$$v = \sqrt{\frac{3kT}{m_0}} = \sqrt{\frac{3 \cdot 1,38 \cdot 10^{-23} \cdot 273}{0,028/6,02 \cdot 10^{23}}} = 493 \frac{\text{m}}{\text{s}}.$$

What is the distribution of molecules in the atmosphere? (Fig. 3.3)

We would like to find out the distribution of molecules in the atmosphere that is how the density and pressure of air is changing as we move to higher altitudes. We know that they are decreasing with the altitude, but according to what function?

The distribution of molecules in the atmosphere is determined by two effects of opposite direction: gravity and the movement of particles. Without particle movement, gravity would pull all molecules to the ground and they would form a thin layer at the surface. Without gravity, the distribution of moving particles would be homogenous in the available space. The result of these two opposing effects is the exponential distribution of the molecules shown in Fig. 3.3. Starting to move upwards from an altitude of $h = 0$ the p_0 pressure first decreases quickly, then the decrease slows down as we get higher up. (Where the value of the function is greater, the change in the value will be greater too and vice versa.) The equation describing this distribution is

$$p = p_0 e^{\frac{m_0 g h}{kT}}, \quad [3.2]$$

where m_0 is the mass of the particle, g is the gravitational constant, h is the altitude, k is the Boltzmann constant and T is the absolute temperature. (The formula is only valid for thermal equilibrium meaning that the temperature is equal everywhere in the atmosphere.)

The exponent in equation [3.2] is the ratio of two energies of the opposing effects. The numerator is the potential energy (mgh) that depends on the magnitude of gravity and the nominator is the thermal energy (kT) that determines the magnitude of particle movement. The ratio of these two energies will

determine how quickly the curve is decreasing. At a given temperature the heavier molecule's curve decreases faster than the lighter one's, because the absolute value of this ratio will be greater.

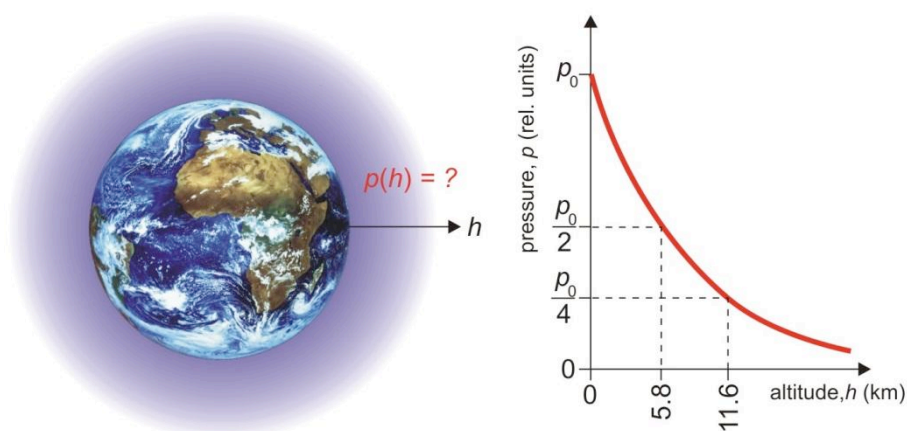


Figure 3.3 The change in atmospheric pressure as a function of altitude

Equation [3.2] is the **barometric formula**, which is a general manifestation of the so-called Boltzmann-distribution.

The Boltzmann-distribution

The Boltzmann distribution describes the distribution of the particles between energy levels in a force field in case of thermal equilibrium.

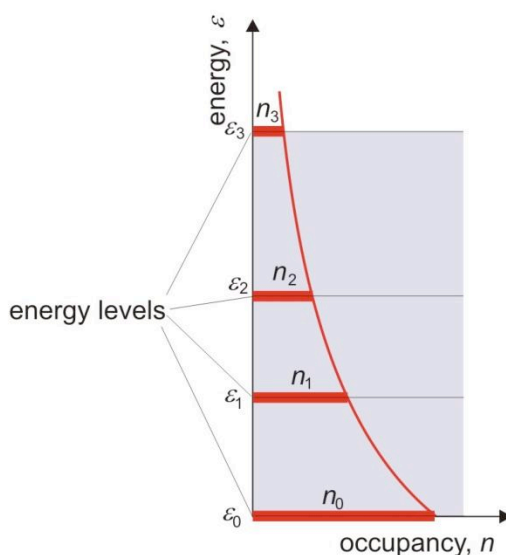


Figure 3.5 An example for possible energy levels of particles and their occupancy in a force field (Boltzmann distribution)

Let us give the energy of any lower energy state as ε_0 and the energy of any higher energy state as ε_i . (Fig. 3.5). The energy difference is calculated as $\Delta\varepsilon = \varepsilon_i - \varepsilon_0$. The number of particles found in these states are n_0 and n_i . According to Boltzmann-distribution:

$$n_i = n_0 e^{\frac{\Delta\varepsilon}{kT}}, \quad [3.3a]$$

where k is the Boltzmann constant and T is the temperature of the system in thermal equilibrium. It is true for the exponential called the **Boltzmann-factor** that

$$0 < e^{\frac{\Delta\varepsilon}{kT}} \leq 1,$$

since the exponent has a negative sign, the same is true for the occupancy of the states:

$$0 < \frac{n_i}{n_0} \leq 1, \text{ thus } n_i \leq n_0.$$

The higher energy state (n_i) is always less occupied than the lower energy state (n_0) in thermal equilibrium. (The occupancy will become equal only if $\Delta\varepsilon = 0$.) If going up the energy axis on Fig. 3.5, the occupancy of each level decreases exponentially. *(You will learn about the inversed distribution of occupancies ($n_i > n_0$), the so-called population inversion, in case of lasers. Remember there that the operating laser material is not in thermal equilibrium).* In sum, **the ratio of occupancies of the energy levels** is given by the Boltzmann-factor. The Boltzmann factor contains **two energies: the $\Delta\varepsilon$ is the energy difference describing the strength of the force field and the thermal energy kT describing the strength of particle movement.**

Equation [3.3a] is used in case of single particles. It is more practical to use molar energies instead: $\Delta E = N_A \cdot \Delta\varepsilon$ (J/mol) and $RT = N_A \cdot k \cdot T$ (J/mol), where N_A is Avogadro's constant and R is the universal gas constant. The Boltzmann distribution for molar energies is

$$n_i = n_0 e^{\frac{\Delta E}{RT}}. \quad [3.3b]$$

Although Boltzmann distribution is not valid for any kinds particle in any kind force field but it can be used in many cases as a good approximation of the particle distribution. Some examples:

- Distribution of the molecules in Earth's gravitational force field (barometric formula). In this case $\Delta\varepsilon$ is the difference in potential energy.
- The distribution of the thermal defects in crystals (number of the vacancies, particle distribution between free and bound states in the crystal lattice). In this case $\Delta\varepsilon$ is the energy needed to produce a lattice defect.
- The saturation vapor pressure, that means the distribution of particles between bound (liquid phase) and free states (gaseous phase). In this case $\Delta\varepsilon$ is the work needed to leave the bound state.
- Number of broken H-bond in biological macromolecules. In this case $\Delta\varepsilon$ is the binding energy.
- Thermal electron emission of metals, that means the distribution of electrons between a bound state (in the metal) and a free state (in vacuum). In this case $\Delta\varepsilon$ is the work function of electrons. (i.e. the heated cathode of an X-ray tube)

- The equilibrium rate of chemical reactions, that means the distribution of molecules the initial and final states. In this case $\Delta\varepsilon$ is the energy difference between these states.

Exponential function

This is the first time to use the exponential in this subject, so here is a short mathematical introduction. This is a frequent function in all sciences. Let us start with the two most commonly used forms of the exponential function: $y = e^x$ and $y = e^{-x}$. The number e is the Euler's number, $e = 2,7182\dots$ (The value of the exponential can be other number too, for example 2 or any other positive number, see Fig 3.4 left)

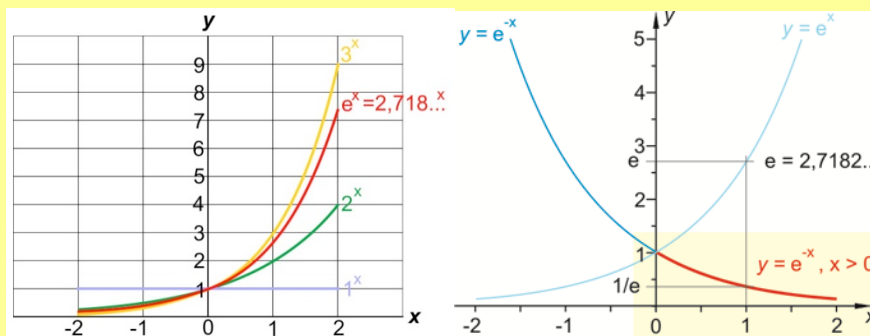


Figure 3.4 Exponential functions

The two functions are the mirror images of each other so we will only characterize the $y = e^x$ function. This function has a y-intercept at 1 and on the left side asymptotically tends to 0, while it rises more and more steeply to infinity on the right. This means that **the value of the function at any point equals its slope at that point**. (More precisely: the function and its derivative are equal.) The larger the value of the function, the faster the function will change. Therefore, it is so frequent in natural sciences. Many of the physical, chemical and biological phenomena are such that the rate of change is proportional to the initial value. The smaller the initial value, the smaller the change and the larger the initial value, the larger the change will be. Cell division, population growth, chemical reactions, radioactive decay, radiation attenuation, particle distribution in the atmosphere etc. are such kind of phenomena under certain conditions.

The exponential function has another interesting property: if we increase the x variable constantly by a number, the y variable will be multiplied by a constant number. Therefore, a doubling a half-life, half-value thickness etc. can be used to characterize the function.

In most of the cases we do not need the negative range of the x -axis because negative variables are irrelevant (e.g. time of the measurement cannot be negative). Therefore, practically only the right side is plotted of these functions. For example, only the red part in Fig. 3.4 right (also in Fig. 3.3 only the positive range is plotted for the barometric formula).

Two additional parameters are used to modify the basic function. Parameter a is the y-intercept and parameter b is the rate of the gradient: $y = ae^{bx}$.

Gas: material without inner structure, volume and shape.

Temperature: a parameter proportional to the average kinetic energy available for each degree of freedom. An ideal gas has three degrees of freedom, thus $\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}kT$, where m_0 is the mass, v is the velocity of a particle, k is Boltzmann-constant and T is absolute temperature.

Thermal energy: for a single particle it is kT (unit J), for a mole of particles it is RT (unit J/mol).

Maxwell–Boltzmann-distribution: distribution of the velocities of gas particles at a given temperature

Barometric formula: an exponential function describing the distribution of particle density in the atmosphere as a function of altitude

Boltzmann distribution: describes the distribution of the particles between energy levels in a force field in case of thermal equilibrium. $n_i = n_0 e^{\frac{\Delta\varepsilon}{kT}} = n_0 e^{\frac{\Delta E}{RT}}$, where $\Delta\varepsilon$ is the energy difference between states for a single particle, or ΔE for one mol, n_0 and n_i gives the number of particles at a given state, k is the Boltzmann constant and T is the absolute temperature.

Problems to solve: 1.13, 1.14, 1.16, 1.17, 1.19, 1.20