Lecture 25 - Thermal expansion, Ideal gas, Kinetics

Temperature

Zeroth law of thermodynamics. It is possible to build a thermometer. If $T_A = T_B$ and $T_B = T_C$, then $T_A = T_C$.

The zeroth law also implies that if two bodies are in thermal equilibrium, then their temperatures are the same.

We need to know about three temperature units, Kelvin(K), Celcius or Centrigrade(^0C) and Fahrenheit(^0F). The relations are as follows,

$$T(Celcius) = T(Kelvin) - 273.15; \quad T(Fahrenheit) = \frac{9}{5}T(Celcius) + 32 \tag{1}$$

The value $-273.15^0C = 0K = -459.67^0F$ is the "absolute zero" of temperature, where nothing moves at least according to classical physics. Quantum motion still occurs. The cosmic microwave background is at a temperature of $2.73K$, so that the space which we live in is not at absolute zero.

Thermal expansion

Most materials expand when heated and the change in length, ΔL, area ΔA and volume ΔV are related to the change in temperature, ΔT through,

$$\frac{\Delta L}{L_0} = \alpha \Delta T, \quad \frac{\Delta A}{A_0} = \gamma \Delta T, \quad \frac{\Delta V}{V_0} = \beta \Delta T, \tag{2}$$

where L_0, A_0 and V_0 are the original length, area and volume of the sample, while α, γ and β are material properties called the coefficient of linear expansion, coefficient of area expansion and coefficient of volume expansion respectively. All of them have units of inverse temperature.

The mole and molecular weight

Since materials contain a lot of atoms or molecules, we define a unit of particle number which is large, this is the mole. This is the mole and it is defined by,

$$1mole = N_A \ particles, \quad where \ N_A = 6.023 * 10^{23} \tag{3}$$

N_A is Avogadro's number after an Italian chemist. The mole is a base unit of physics and is defined to be the number of atoms in $12g$ of carbon-12 atoms.

This definition means that the molar mass of carbon-12 is $12g$. The molar mass of any other substance is the mass of one molecule of the substance times N_A.

The mass of one atom of carbon-12 is also used to define the atomic mass unit

$$1u = (mass\ of\ Carbon - 12\ atom)/12 = 1.66 * 10^{-24} g \tag{4}$$

which is almost the same as the mass of one proton or one neutron. Note that this definition is in grams, so when you do calculations in SI units it is necessary to convert to kg. When you see a periodic table, the atomic mass given there is in atomic mass units, however the value given is an average over the naturally occuring isotopes of the element. For example the value given for carbon is 12.111 due to the fact that in addition to the dominant C-12 isotope, there is a small natural abundance of C-13. Note that the terminology used in the chemistry and chemical engineering texts if often different so that $1u = 1dalton = 1Da = 1amu$. Similarly, the molecular weight (it really should be molecular mass!) of a molecule is the weight measured in atomic mass units (or equivalently daltons), so that the molecular weight of carbon-12 is 12 daltons = 12u = 12amu. The molecular weight of water is 18.015 and the molecular weight of sucrose is approximately 342. To a first approximation, the molecular weight of a molecule is the total sum of the number of neutrons and protons in the nuclei of the atoms making up the molecule. However this approximation is rather poor for large molecules. Large molecules like polymers have molecular weights measured in the thousands, for example the protein lysosyme (egg white) has a molecular weight of $14.4kDA$ where kDa is 1000 daltons, which means that the total number of neutrons and protons in the whole molecule is about 14000.

Ideal gases

Ideal gases obey the ideal gas law,

$$PV = nRT = \frac{N}{N_A} RT = N k_B T \tag{5}$$

This is called the equation of state and relates the pressure P, volume V, number of moles n and temperature T through the ideal gas constant, $R = 8.31 J/molK$. Alternatively we can use N the number of molecules in the gas and the Boltzmann constant $k_B = 1.38 * 10^{-23} J/K$.

Kinetic theory of gases

The ideal gas law describes the behavior of macroscopic quantities such as pressure, volume and temperature which are thermodynamic quantities. We would also like to know what the behavior of individual atoms or molecules in the gas is like. The motion of these atoms is chaotic so the trajectory of each atom is crazy, however we can measure average properties and relate them to the pressure temperature etc. First we consider the pressure. Pressure is caused by atoms or molecules bouncing off the walls of the container. Consider the force in the x-direction imparted to a wall of the container when an atom with x-component of velocity v_x strikes it.

$$F_x = \frac{\Delta p_x}{\Delta t} \tag{6}$$

where $\Delta p_x = 2mv_x$. The time between collisions of this atom and a wall is $\Delta t = 2d/v_x$, so we find that the average force which each atom imparts to the wall is,

$$\overline{F}_x = \frac{m\overline{v_x^2}}{d} \tag{7}$$

The area of the wall is d^2, so we find that

$$P_1 = \frac{\overline{F}_x}{d^2} = \frac{m\overline{v_x^2}}{d^3} \tag{8}$$

Rather than using the x-component of the velocity, it is better to consider the speed, which is given by,

$$v^2 = v_x^2 + v_y^2 + v_z^2 \tag{9}$$

In ideal gases the motion in the x, y, and z-directions are on average the same, so we find that $v_x^2 = v^2/3$. Using this subsitution, we find that the pressure is given by,

$$P = NP_1 = N\frac{2m\overline{v^2}}{3d^3} = N\frac{m\overline{v^2}}{3V} \tag{10}$$

where we used $V = d^3$. This equation may be written as,

$$PV = N\frac{m\overline{v^2}}{3} \tag{11}$$

By comparing this we can find the average speed of atoms or molecules in the gas,

$$k_B T = \frac{m\overline{v^2}}{3} \tag{12}$$

Solving for v, we find that,

$$v_{rms} = (\frac{3k_B T}{m})^{1/2} \tag{13}$$

We may also write,

$$U = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}Nk_B T \tag{14}$$

where U is the internal energy of the ideal gas. This is the formula for a monoatomic ideal gas. For diatomic and polyatomic gases, the internal energy is $k_B T/2$ per degree of freedom. In real gases the internal energy has contributions due to interactions with the other particles of the gas.

Units

The units used in thermodynamics are quite confusing, primarily because there are so many different ones. For example pressure is measured in the following units: $bar, millibar(mbar), atmosphere(atmos), Pascals(Pa), N/m^2$, $mmHg, mmH_20, torr, mtorr, ...$ The SI unit for pressure is the Pascal, $1Pa = 1N/m^2$ and in exams you will be given the conversions to the other units if needed. For CAPA problems you can find the unit conversions online or in the textbook. The SI unit for volume is m^3, though you will often see the volume given in liters or cubic centimeters (cc). The SI unit for temperature is the Kelvin (K), so you will need to convert to Kelvin in most calculations involving temperature. The SI unit for density ρ is kg/m^3, though in most applications it is given as g/cc, so a conversion is again necessary. The SI unit of energy is the Joule, but in chemistry the heat is usually given in calories $1cal = 4.182J$. Note that the food calorie is actually $1kcal = 1000cal = 4182J$, so that an average food consumption of $2000 food\ calories$ per day is actually $8,364,000J$ per day. Finally the number of particles, ie atoms or molecules is measured either as a number N or as the number of moles $n = N/N_A$. This only changes the constant, so we use R when using n and k_B when using N.