V25.0109: College Chemistry I: Honors

Notes for Lecture 8

I. CONNECTION BETWEEN MICROSCOPIC MOTION AND MACROSCOPIC OBSERVABLES

All macroscopic observable properties of a substance arise from the microscopic detailed motions of its individual constituent atoms. There is a subdiscipline of physical science, whose goal is to provide the connection between the microscopic details of a system and macroscopic, measurable observables that is called *statistical mechanics*. We will explore just a little of this rich and actively developing area of research.

From the fundamental laws of physics, we know that all microscopic motion arises from the forces that particles exert on each other. In bulk matter, following the detailed motion of a single atom in an experiment is virtually impossible. However, using modern, state-of-the-art computers, it is possible to follow the motion of each individual atom in a system theoretically, and from this motion *calculate* macroscopic observables. These can then be compared with experimental measurements.

Let us first discuss what we need in order to specify a macroscopically large system consisting of N atoms in a container of volume V, as illustrated below:

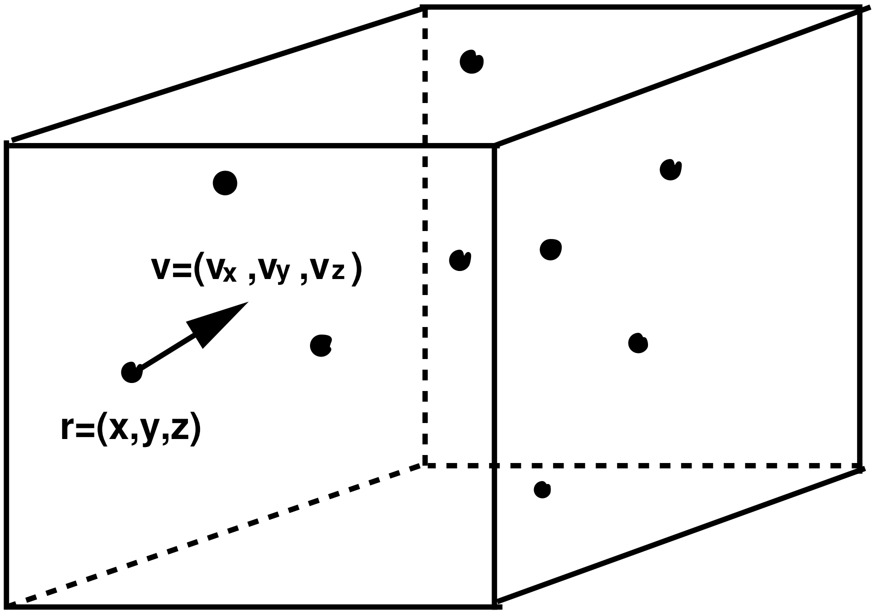

FIG. 1.

The particles in the box are constantly in motion, hence the position of each particle, as specified by its three coordinates (x, y, z) in space will be different at each instant in time. A *microscopic* state of this system is specified by giving the (x, y, z) coordinates of each particle in the system at every instant in time. Thus, for each particle, we must specify the coordinates as *functions of time*, $(x(t), y(t), z(t))$.

In addition, in order to complete the specification of the microscopic state, we need to give the direction of motion of each particle and how fast it is going there. That is, we must specify, for each particle, the three components of the particle's velocity $(v_x(t), v_y(t), v_z(t))$, which are also functions of time due to the never-ceasing motion.

If we know these six functions of time for each particle in the system, then we know everything about the system and can determine all of its properties. But how can we determine the position and velocity of each particle in the system at each instant in time?

Since all microscopic motion arises from the forces that particles exert on each other, and forces are determined by the fact that atomic nuclear carry charge and that they are surrounded by clouds of electrons that essentially move with the nuclei, Newton's second law of motion determines the position and velocity of each particle at each instant in time. To see this, consider that the *total* force on each particle is the sum of the individual forces that all other particles exert on a given particle. Thus, for each particle

$$\sum \mathbf{F} = m\mathbf{a}$$

where $\mathbf{a}$ is the acceleration of the particle. There will be such an equation for every particle in the system. This full set of Newton's second law equations are called the *equations of motion* of the system. Recall that the acceleration is the change in velocity with respect to time:

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \left(\frac{dv_x}{dt}, \frac{dv_y}{dt}, \frac{dv_z}{dt}\right)$$

and that velocity is the change in position with respect to time:

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \left(\frac{dx}{dt}, \frac{dy}{dt}, \frac{dz}{dt}\right)$$

Thus, Newton's equation takes the form:

$$m\frac{d^2\mathbf{r}}{dt} = \mathbf{F}$$

for each particle in the system. This constitutes a set of *differential equations*, which, when solved, yield the potision $\mathbf{r}(t)$ and velocity $\mathbf{v}(t)$ at each instant in time.

What kind of motion might we expect?

1. Internal motion within a molecule – bonds can fluctuate around their equilibrium bond lengths, angles between bonds can fluctuate around their equilibrium values, long chain molecules and proteins can fold or bend and unfold due to hinge-type torsional motion, etc.

2. Translations/rotations – molecules can translate in space, diffusing through the system. As they do so, they can tumble or rotate.

3. If two molecules approach each each other closely, they exert large forces on each other and will undergo a strong collision. This can either cause the molecules simply to bounce off each other, leaving them intact, or it can cause them to undergo a chemical transformation and change their molecular identities, e.g. a chemical reaction of the type:

$$\mathrm{N_2 + O_2 \longrightarrow 2NO}$$

All of this seemingly complex motion is contained within the equations of motion and is, therefore, in principle predictable. All that is required by Newton's law of motion is that the position and velocity of each particle at one particular instant in time be completely specified. From this information the fate of the system infinitely far into the future and infinitely far into the past can be calculated. The 18th century French mathematician once noted that if the position and velocity of every particle in the universe could be specified at some instant in time, then, according to Newton's law of motion, the origin and ultimate fate of the universe, itself, could be predicted.

Of course, doing anything of the sort is impossible. Even to specify with finite precision the position and velocities of a system of 10^{12} particle, only a tiny fraction of a mole, would require the thousands of gigabytes of computer memory. However, infinite precision would be needed. The reason for this is that the nature of the intermolecular forces is complicated enough that the dynamics of large systems is chaotic, which means that any error made in the specification of initial conditions will grow exponentially in time and lead to a trajectory that deviates from the true one. Moreover, even if we *could* determine the Newtonian dynamics of a system with infinite precision, we now know that Newtonian dynamics is only an approximation to the true dynamics of a system which is correctly described by quantum mechanics.

The good news is that we do not need to know all of the precise microscopic details of a system. The reason is that many microscopic configurations will give have the same macroscopic observable properties, e.g. there is an infinite number of possible configurations that would correspond to a given temperature or a given pressure. Thus, we only need to understand the microscopic details at a relatively crude level, obtained by averaging over *all* of the microscopic configurations that give rise to the same macroscopic observable properties. This process of averaging washes out many of the minute details of the microscopic motion.

II. PHYSICAL STATES OF MATTER

Macroscopic observable quantities of a system depend on its physical state. The common physical states of matter are:

1. Gas
2. Liquid
3. Solid

There is also a “fourth state of matter” called a plasma, which occurs when all of the electrons are stripped from their nuclei, leaving a “soup” of charged particles. We will only be concerned with the three common states, beginning with a study of gases.

III. THE GASEOUS STATE: BACKGROUND

A *gas* is defined to be a state of matter, in which the number of particles (atoms or molecules) N in a volume V is small enough compared to the volume that the forces between particles play a small to negligible role.

An *ideal gas* is defined to be a system in which there are no intermolecular/interatomic forces. Such a system can only exist as a gas. Any real system will approach ideal gas behavior in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

The fact that intermolecular forces are not important in the gas phase means that the laws governing the behavior of gases will be universal in the sense that they will pertain to all gaseous systems independent of the types of particles that compose them.

In addition to the volume V, there are two other observable quantities that are useful in the physical description of a gas. These are the pressure P and temperature T. Quantities such as N, P, V and T are examples of *thermodynamic* variables. How these are related to each other and other thermodynamic variables comprises the subject of *thermodynamics*, which we will study in later chapters. How these variables can be calculated from a microscopic description of the system is the subject of an area of science called *statistical mechanics*, which is a rich and actively growing area of research.

A. Pressure

The pressure of a gas is defined to be the force exerted by the gas on the walls of its container. It is often assumed that pressure is *isotropic*, i.e., it is the same in all three spatial directions.

There is another kind of pressure that is directional, however, and that is the pressure exerted on the Earth's surface by the weight of the atmosphere (due to the pull of gravity). This amounts to a pressure of approximately 15 lb/in^2 and is referred to as *atmospheric pressure.*

A device for determining atmospheric pressure, called a *barometer* was first developed by Torricelli (1608-1647). A dish containing liquid mercury is subject to the effects of atmospheric pressure. If an evacuated tube with one end closed is placed with its open end over the liquid in the dish, the weight of the atmosphere causes an amount of mercury to rise into the tube. The height that the mercury reaches in the tube is a measure of atmospheric pressure.

Recall that the weight of an object on the Earth's surface is determined directly from its mass m and from the acceleration, g due to gravity:

$$\text{weight} = mg$$

The weight is also the force that the object exerts on the Earth's surface. The value of g is 9.8 m/s^2 or 980 cm/s^2. Thus, if m is the mass of mercury in the dish, then the force exerted by the column of mercury in the tube on the surface of mercury in the dish is just its weight mg. Thus, the measure of atmospheric pressure will be the force (due to the weight of mercury in the column) divided by the cross-section area, A, of the tube:

$$P = \frac{F}{A} = \frac{mg}{A}$$

In an actual experiment of this sort, the mercury is observed to rise to a height $h = 76$ cm. The volume of mercury in the tube is $V = Ah$. Then, since $A = V/h$,

$$P = \frac{mgh}{V} = \rho gh$$

Using $\rho = 13.5951\ \text{g/cm}^3$ for mercury,

$$P = (1.35951 \times 10^4 \text{kg/m}^3)(9.8\text{m/s}^2(0.76\text{m} = 1.01325 \times 10^5 \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

The unit $\text{kg/(m·s}^2)$ is defined to be a Pascal (Pa), which is the SI unit for pressure. Another common pressure unit is the atmosphere (atm), related to Pa by

$$1\text{atm} = 1.01325 \times 10^5 \text{Pa}$$

In the late 17th century, an important discovery was made by R. Boyle, while he was investigating the relation between pressure and volume using a J-tube. He found that the product of the pressure of a sample of trapped air in the J-tube and the volume the air occupied was a constant at fixed temperature and amount of air:

$$PV = C$$

where C is a constant having units of energy. The numerical value of C will actually vary depending on the temperature and number of moles of gas used in the experiment, however, when these are fixed, the value of C is fixed. The value of C can be determined by recognizing that

$$P = C\frac{1}{V}$$

Therefore, if we plot P vs. $1/V$, the result will be a line with slope C:

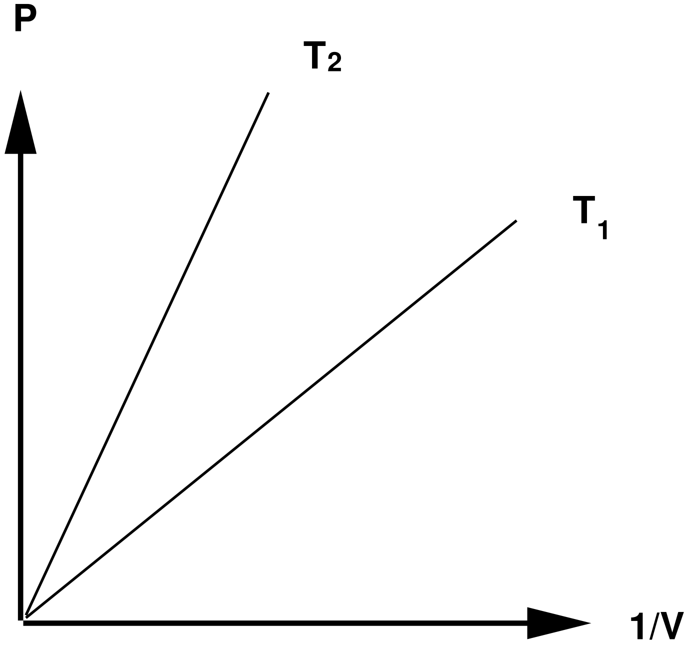

FIG. 2.

The figure illustrates that different slopes will be obtained at different temperatures. At a temperature of T=0øC and 1 mol of gas, the value of C is

$$C = 22.424 \text{ L} \cdot \text{atm}$$

Finally, since $PV = C$, if we start with a gas sample at a pressure P_1 and volume V_1, and expand or compress the gas to a new volume V_2, the new pressure P_2 can be determined from

$$P_1V_1 = C \qquad P_2V_2 = C \qquad \Rightarrow\ P_1V_1 = P_2V_2$$

or

$$P_2 = \frac{P_1V_1}{V_2}$$

B. Temperature

In the next lecture, we will see that temperature is determined by the average amount of kinetic energy that particles in a gas sample have. Thus, the greater the kinetic energy, the more motion and the higher will be the temperature of the gas.

The French scientist Jacques Charles carried out experiments that showed temperature to be a linear function of volume V. If we let t denote the temperature on some arbitrary scale, then the general linear relation he wrote down is

$$t = C\left(\frac{V}{V_0} - 1\right)$$

where V_0 is a reference volume, such as the volume at the freezing point of water. Clearly, when $V = V_0$, $t = 0$. If V_0 *is* taken to be the freezing point of water, then we recognize $t = 0$ as corresponding to the familiar Celcius scale. The constant C is determined by measuring the volume at some other point of known temperature, such as the boiling point of water, i.e, where t =100^{o}C. Determination of C was carried out by Guy-Lussac, who obtained a value of $C \approx 267^o$C. Today, more precise experiments have shown that $C = 273.15^o$C, so that the linear relation of Charles becomes:

$$t = 273.15^o\text{C}\left(\frac{V}{V_0} - 1\right)$$

or

$$V = V_0\left(1 + \frac{t}{273^o\text{C}}\right)$$

The above relations are known as Charles' law.

Note that when $V = 0$, $t = -273.15^o$C, presumably the coldest anything can possibly be, since negative volumes are not allowed. Thus, it is useful to define a new scale, in terms of which $V = 0$ corresponds to zero-temperature. Letting T denote the temperature on this scale, we have a simple relation between T and t, namely:

$$T = t + 273.15^o\text{C}$$

the temperature T is known as the temperature on the *Kelvin* (K) scale. Using the Kelvin scale, we can write Charles' law as

$$V = \frac{V_0}{273.15^o\text{C}}\left(t + 273.15^o\text{C}\right) = \frac{V_0}{273.15^o\text{C}}T$$

or since $V_0/273.15^o$C is a constant, we have

$$\frac{V}{T} = c$$

where c is a constant that depends on the external pressure and number of moles of gas. Note that in order to use Charles' law in this form, the temperature *must* be in Kelvin.

As with Boyle's law, if we start with a gas sample at a temperature T_1 occupying a volume V_1 and the system is heated or cooled to a new temperature T_2 at constant temperature and number of moles of gas, the new volume of the gas is given by

$$\frac{V_1}{T_1} = c \qquad \frac{V_2}{T_2} = c \qquad \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or

$$V_2 = \frac{V_1}{T_1}T_2$$

IV. THE IDEAL GAS LAW

- From Boyle's law: $V \propto 1/P$ at fixed T and n.
- From Charle's law: $V \propto T$ at fixed P and n.
- Also $V \propto n$ at fixed P and T, since doubling the amount of gas at fixed P and T requires doubling the volume.

Combining these facts, we arrive at a statement that

$$V \propto \frac{nT}{P}$$

The constant of proportionality is known as the gas constant R, whose numerical value is

$$R = 0.08206\text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Inserting the gas constant R into the proportionality relation gives an equation known as the *ideal gas law*:

$$PV = nRT$$

The ideal gas law is exact for ideal gases and is a good approximation to real gases at very low pressures. If, instead of using the number of moles n to express the amount of gas, the actual number of particles N is used, then the ideal gas law becomes:

$$PV = \frac{N}{N_0} RT = N \frac{R}{N_0} T$$

where the fact that $n = N/N_0$ (N_0 is Avogadro's number) has been used. The new constant R/N_0 is known as Boltzmann's constant, denoted $k_{\rm B}$. Thus, the ideal gas law becomes:

$$PV = N k_{\rm B} T$$

V. MIXTURES OF IDEAL GASES

Consider a mixture of ideal gases consisting of particles of type A, type B and type C in a volume V. Define the *partial pressure* of each type as the pressure that each ideal gas type (A,B, or C) would have if it were alone in the container. If there $n_{\rm A}$ moles of type A, $n_{\rm B}$ moles of type B and $n_{\rm C}$ moles of type C, then the total number of moles, n, of gas overall will be

$$n = n_{\rm A} + n_{\rm B} + n_{\rm C}$$

Since the gases are ideal gases, if we denote the partial pressure of A by $P_{\rm A}$, the partial pressure of B by $P_{\rm B}$, etc. then by the ideal gas law, the partial pressures will be related to the number of moles of each gas by

$$P_{\rm A} = \frac{n_{\rm A} RT}{V} \qquad P_{\rm B} = \frac{n_{\rm B} RT}{V} \qquad P_{\rm C} = \frac{n_{\rm C} RT}{V}$$

The total pressure P will be related by the total number of moles n by

$$PV = nRT$$

Adding the three partial pressure together gives

$$P_{\rm A} + P_{\rm B} + P_{\rm C} = \frac{RT}{V} \left(n_{\rm A} + n_{\rm B} + n_{\rm C} \right) = \frac{nRT}{V} = P$$

Thus, we have a relation between the partial pressures and the total pressure, namely:

$$P_{\rm A} + P_{\rm B} + P_{\rm C} = P$$

or the total pressure is just the sum of the individual partial pressures. This is known as Dalton's law of partial pressures.

Furthermore, by dividing the partial pressures of each gas by the total pressure, we have

$$\frac{P_{\rm A}}{P} = \frac{\frac{n_{\rm A} RT}{V}}{\frac{nRT}{V}} = \frac{n_{\rm A}}{n}$$

or

$$P_{\rm A} = \frac{n_{\rm A}}{n} P$$

Thus, the partial pressure of A (or B or C) is a specific fraction of the total pressure P, namely, $n_{\rm A}/n$, the ratio of the number of moles of A to the total number of moles. This ratio is known as the *mole fraction* of A and is denoted $X_{\rm A}$. Thus, the partial pressure of A is the mole fraction of A times the total pressure:

$$P_{\rm A} = X_{\rm A} P$$

and the same holds for B and C.

VI. GAS PHASE STOICHIOMETRY

Doing stoichiometry calculations with reactants or products that are gaseous species is the same, in principle, as ordinary stoichiometry, except that the ideal gas law can be used to find the number of moles of a species. Obviously, this is an idealization, as ideal gas systems do not really exist in nature, however, as all gas systems approach ideal gas behavior at low enough density, the approximation can often be justified.

The following example illustrates how to perform stoichiometry calculations with gaseous species:

Example: A solid sample of Rb_2SO_3 having a mass of 6.24 g reacts with 1.38 L of gaseous HBr at $75°C$ and a pressure of 0.953 atm. The solid RbBr extracted from the reaction has a mass of 7.32 g. What is the percentage yield of the RbBr? Note that the additional products are H_2O and SO_2.

First, start by writing the balanced reaction:

$$\mathrm{Rb_2SO_3(s) + 2HBr(g) \longrightarrow 2RbBr(s) + SO_2 + H_2O}$$

Next compute the number of moles of each reactant. For Rb_2SO_3, we can use the mass given and the molar mass:

$$\text{moles of Rb}_2\text{SO}_3 = \frac{6.24\text{g}}{250.9946\text{g/mol}} = 0.0248 \text{ moles}$$

For the moles of HBr, we need to use the ideal gas law in the form $n = PV/RT$:

$$\text{moles of HBr} = \frac{PV}{RT} = \frac{(0.953 \text{ atm})(1.38 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(75 + 273.15)\ K} = 0.04603 \text{ moles}$$

Since 1 mole of Rb_2SO_3 yields 2 moles of RbBr, it follows that 0.02486 moles of Rb_2SO_3 yield 0.04972 moles of RbBr. On the other hand, 1 mole of HBr yields 1 mole of RbBr, so 0.04603 moles of HBr yield 0.04603 moles of RbBr. Hence, HBr is the limiting reagent, and only 0.04603 moles of RbBr are produced. Thus, according to the balanced reaction, the mass of RbBr produced should be

$$\text{mass of RbBr} = 0.04603 \text{ moles} \times 165.3718 \text{ g/mol} = 7.612 \text{ g}$$

This is the theoretical yield. The actual yield if 7.32 g, so the percentage yield is

$$\text{percentage yield} = \frac{7.32 \text{ g}}{7.612 \text{ g}} \times 100\% = 96.2\%$$