

CHM 3400 – Fundamentals of Physical Chemistry

Chapter 1 - Handout

1. Physical constants

The table below lists several constants and conversion factors of use in doing calculations. Additional constants will be given when we get to the quantum mechanical material in the class.

1 L = 1 dm ³ = 1000 cm ³ = 1000 mL (exact)	R = 0.082057 L·atm/mol·K
1 m ³ = 1000 L (exact)	R = 8.3145 J/mol·K
1 atm = 1.01325 bar = 1.01325 x 10 ⁵ Pa = 760 torr (exact)	k = 1.3806 x 10 ⁻²³ J/K
1 bar = 10 ⁵ Pa = 10 ⁵ Nt/m ² (exact)	N _A = 6.0221 x 10 ²³ molecule/mol
1 Nt = 1 kg·m/s ² (exact)	F = 96485. C/mol
1 J = 1 kg·m ² /s ² = (1 volt)(1 Coulomb) (exact)	1 L·atm = 101.325 J (exact)

2. State functions and equations of state

Consider a system at equilibrium. Under most circumstances, we can describe the properties of the system in terms of large scale (macroscopic) variables. For example, for a sample of gas we can give the pressure (p), volume (V), temperature (T), and amount of gas (in moles, n). For a mixture of pure substances additional information, such as the mole fraction (X_i) of each substance, can also be given.

Two systems that can be described by the same set of variables are considered the same in terms of their physical and chemical properties. For this reason, these variables are called state variables.

Experimentally, it is usually found that the values of the state variables are not all independent. For example, a sample of nitrogen gas (N₂) with the same value for p, V, and T will always contain the same number of moles of nitrogen. Because of that, we can conclude that there is a mathematical relationship, called an equation of state, that gives a relationship between the state variables of a system. The ideal gas law, discussed in the next section, is a simple example of an equation of state.

A great deal of work has been done to find equations of state for real substances. While it is impossible to find an exact equation of state for a system (except as a limiting case or for a model system) it is possible to find equations of state that give a good description of a system for some conditions. In fact, it is possible to find equations of state that agree with the observed behavior of a system to within the experimental error involved in measuring the state variables.

3. The ideal gas law

The most common equation of state used for a gas is the ideal gas law

$$pV = nRT \quad (1.3.1)$$

The variables in the ideal gas law can be divided into two types – extensive variables (n, V, whose value depends on the size of the system), and intensive variables (p, T, whose values are independent of the size of the system).

It is sometimes convenient to rewrite the ideal gas law entirely in terms of intensive variables. If we define the molar volume of a gas, V_m, as

$$V_m = V/n \quad (1.3.2)$$

then the ideal gas law can be rewritten as

$$pV_m = RT \quad (1.3.3)$$

By rewriting the ideal gas law so that it is entirely in terms of intensive variables we lose information about properties related to the size of the system. However, it allows us to better focus on the fundamental behavior of an ideal gas.

Common units for the variables in the ideal gas law are as follows:

Amount of substance

This is almost always given in terms of moles (n), the MKS unit for amount of substance.

Temperature

This requires the use of an absolute temperature scale. The only common scale is Kelvin, which is related to the Centigrade scale by the relationship

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15 \quad (1.3.4)$$

Kelvin is the MKS unit for temperature.

Volume

The MKS unit for volume is a derived unit, m^3 , the volume occupied by a cube whose sides have a length of 1 meter. Since this is a large volume for laboratory work, a smaller unit, the liter, is defined as the volume occupied by a cube whose sides have a length of 10 cm. Therefore

$$1 \text{ m}^3 = 1000 \text{ L (exact)} \quad (1.3.5)$$

For smaller volumes we can use the mL (a metric unit, with $1000 \text{ mL} = 1 \text{ L}$), or the cubic cm (cm^3 , with $1 \text{ cm}^3 = 1 \text{ mL}$).

Pressure

Since pressure is force per unit volume, the MKS unit for pressure is Nt/m^2 , a derived unit. This is given the name Pascal ($1 \text{ Pa} = 1 \text{ Nt/m}^2$). This is a relatively small pressure, and so it is convenient to define an additional pressure unit that corresponds to the approximate pressure of air at sea level. This is called the bar. By definition

$$1 \text{ bar} = 10^5 \text{ Nt/m}^2 = 10^5 \text{ Pa (exact)} \quad (1.3.6)$$

Two older units for pressure are commonly used, the atmosphere (atm), now defined as

$$1 \text{ atm} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ Nt/m}^2 \text{ (exact)} \quad (1.3.7)$$

and torr (mm Hg), defined as

$$1 \text{ atm} = 760 \text{ torr (exact)} \quad (1.3.8)$$

Note that for an ideal gas Dalton's law of partial pressures will apply

$$p_i = X_i p \quad (1.3.9)$$

where p_i is the partial pressure of gas i, n and p are the total moles of gas and total pressure of gas, and $X_i = n_i/n$ is the mole fraction of the i^{th} gas.

4. Derivation of the ideal gas law

By making a few simplifying assumptions about the behavior of a gas, the ideal gas law may be derived. The assumptions needed for this derivation are as follows:

1. The volume occupied by gas molecules is small
2. The forces of interaction between gas molecules, which are expected to be attractive forces, are small

Based on these assumptions, we can immediately conclude that all gases obey the ideal gas law in the limit $V_m \rightarrow \infty$, (equivalent to the limit $p \rightarrow 0$). This is because for a fixed number of molecules at a constant temperature both the volume physically occupied by gas molecules and the forces of attraction between molecules become small as the volume of the system increases.

We can now proceed as follows. Consider a molecule inside of a cubic container whose sides have length ℓ . We can calculate the average pressure exerted by this molecule against one wall of the container by recalling that p (per molecule) = F/A , where F is the force exerted by the gas molecule and $A = \ell^2$ is the area of the wall. But

$$F = ma = m \frac{dv_x}{dt} = \frac{dp_x}{dt} \cong \frac{\Delta p_x}{\Delta t} \quad (1.4.1)$$

where $p_x = mv_x$ is the component of the momentum of the gas molecule in the x direction. This equation says that for a sufficiently long period of time (or a large number of collisions per unit time) $dp_x/dt \cong \Delta p_x/\Delta t$.

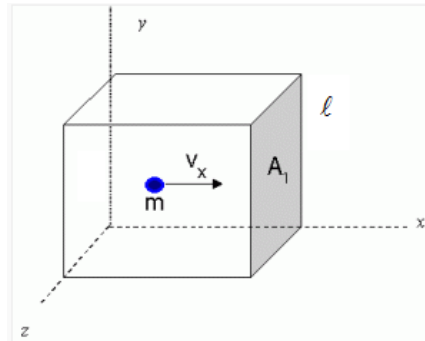


Figure 1. A molecule inside of a cubic box. m = mass of particle, v_x = x -component of velocity.

Collisions with the walls of the container are elastic, and so the change in momentum (Δp_x) when the gas molecule collides with the wall is

$$\Delta p_x = 2 mv_x \quad (1.4.2)$$

The time between collisions (Δt) is the time between successive collisions of the molecule with the shaded wall. Since the molecule has to travel from the shaded wall to the opposite wall and back again, it must travel a distance $d = 2\ell$. Therefore

$$\Delta t = \frac{d}{v_x} = \frac{2\ell}{v_x} \quad (1.4.3)$$

Combining all of the above, we get

$$p(\text{per molecule}) = \frac{F}{A} = \frac{1}{\ell^2} \frac{\Delta p_x}{\Delta t} = \frac{1}{\ell^2} \frac{2m v_x}{2\ell/v_x} = \frac{m v_x^2}{V} \quad (1.4.4)$$

where $V = \ell^3$ is the volume of the container.

Now if there are N molecules in the container, the total pressure is

$$p = N p(\text{per molecule}) = N \frac{m \langle v_x^2 \rangle}{V} \quad (1.4.5)$$

where we have replaced v_x^2 , the square of the speed of one molecule in the x -direction, with $\langle v_x^2 \rangle$, the average square of the speed of a molecule in the x -direction. There is nothing special about motion in the x -direction, and so we may say

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \quad (1.4.6)$$

But

$$\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v^2 \rangle \quad (1.4.7)$$

where $\langle v^2 \rangle$ is the average square of the speed of a gas molecule in the container. By combining eq 1.4.6 and 1.4.7 we get

$$\langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3} \quad (1.4.8)$$

Substituting eq 1.4.8 into eq 1.4.5 gives

$$p = \frac{N m \langle v^2 \rangle}{3V} \quad (1.4.9)$$

Finally, since $n = N/N_A$, and $M = m N$, (where N_A is Avogadro's number and M is the molecular mass of the gas), we can rewrite eq 1.4.9 to get as a final result

$$p = \frac{nM \langle v^2 \rangle}{3V} \quad (1.4.10)$$

If we set eq 1.4.10 equal to the ideal gas law ($p = nRT/V$) we can solve for $\langle v^2 \rangle$

$$\langle v^2 \rangle = \frac{3RT}{M} \quad \langle v^2 \rangle^{1/2} = v_{\text{rms}} = (3RT/M)^{1/2} \quad (1.4.11)$$

where v_{rms} is the root mean square average speed for a gas molecule. For N_2 at $T = 300$ K, $v_{\text{rms}} \cong 500$ m/s.

5. Kinetic theory

We showed in the last section how we can find an expression for v_{rms} , the rms average speed of a molecule. However, some molecules will be moving faster than v_{rms} and some will be moving more slowly. Using the Boltzmann distribution law, an expression for the fraction of molecules in a gas with speed between v and $v + dv$ (written as $F(v) dv$) can be derived. The result of the derivation gives

$$F(v) dv = 4\pi (M/2\pi RT)^{3/2} v^2 \exp(-Mv^2/2RT) dv \quad (1.5.1)$$

the Maxwell-Boltzmann distribution. A sketch of the Maxwell-Boltzmann distribution for N_2 at two different temperatures is given below. Note the following:

$$1) \int_0^\infty F(v) dv = 1 \quad (1.5.2)$$

This simply means that the fraction of molecules with a speed between 0 and ∞ is 1, as expected. This condition is called a normalization condition, and is responsible for the collection of constants that appear in eq 1.5.1

2) The peak of the Maxwell-Boltzmann distribution shifts to larger values for v , and the height of the peak decreases, as temperature increases.

3) For two gases at the same temperature, the peak in the Maxwell-Boltzmann distribution will have a higher value for speed for the gas that has the lower molecular mass.

4) Finally, the fraction of molecules with speeds between two values a and b is given by the expression

$$F(a < v < b) = \int_a^b F(v) dv \quad (1.5.3)$$

which represents the area under the curve in Fig 2 between a and b . The value for this integral is found numerically, since an exact value for the integral does not exist.

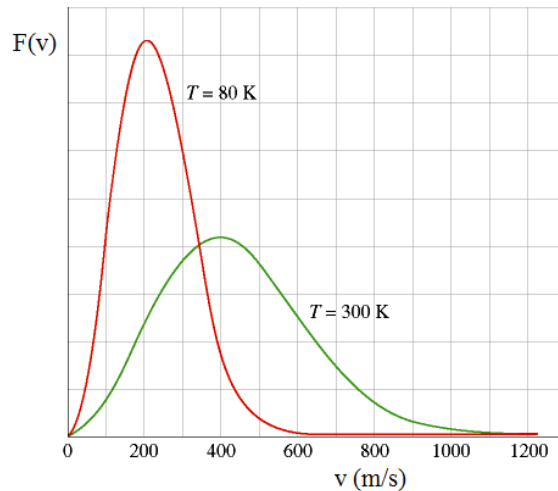


Figure 2. Distribution of speeds for N_2 at two different temperatures.

If we relax the condition that molecules in a gas have zero volume, we can derive other interesting properties for the molecules. In particular, we can derive expressions for z (the collision frequency, or average number of collisions made by a molecule per unit time) and λ (the mean free path, or average distance a molecule travels between collisions). λ , z , and v_{ave} (the average speed of a molecule) are related by the expression

$$\lambda = \frac{v_{ave}}{z} \quad (1.5.4)$$

The values for λ and z are given in terms of σ , the collision cross-section of a molecule. Note that $\sigma = \pi d^2$, where d is the average diameter of the molecule. A simple derivation gives the following expressions for λ and z .

$$\lambda = \frac{kT}{2^{1/2} \sigma p} \quad z = \frac{2\sigma p}{kT} (8RT/\pi M)^{1/2} \quad (1.5.5)$$

Values for λ and z have several interesting applications. In particular, the value for z is one of the factors determining the rate of a bimolecular gas phase reaction.

6. Compressibility factor and non-ideal gas laws

A typical gas at or near room pressure and temperature will obey the ideal gas law to a precision of $\sim 0.1\%$. For more precise work, or for gases at lower temperatures and/or higher pressures, more significant non-ideal gas behavior will be observed.

One way to characterize non-ideal gas behavior is in terms of Z (the compressibility factor), defined as

$$Z = \frac{pV}{nRT} = \frac{pV_m}{RT} \quad (1.6.1)$$

where, as before, $V_m = V/n$ is the molar volume of the gas. For an ideal gas, $Z = 1$ for any value for pressure (since $pV = nRT$). For a real gas, the value for Z will be a function of pressure, and will depend on both the gas and the temperature of the gas. Figure 3 gives the compressibility factor for nitrogen (N_2) at several different temperatures. Note the following:

1) At any temperature, $Z = 1$ in the limit $p \rightarrow 0$. This is expected, as we previously stated that all gases obey the ideal gas law in the limit of low pressure.

2) Z becomes much larger than 1 for large values for pressure. That is because at high pressure the volume approached a constant value related to the space physically occupied by the molecules, instead of zero volume, as predicted by the ideal gas law.

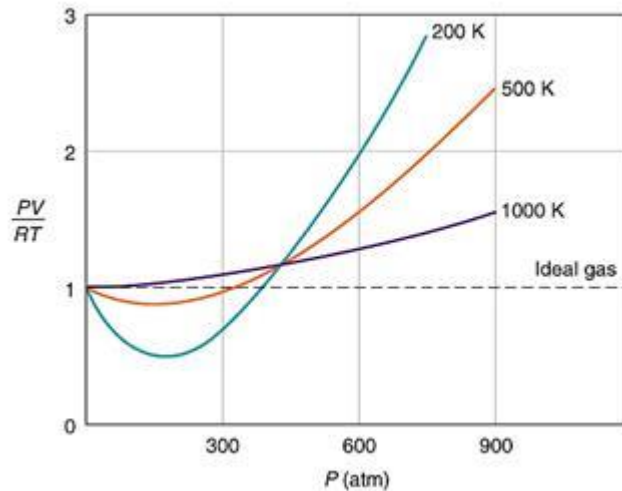


Figure 3. Compressibility factor for one mole of N_2 at several different temperatures. The dashed line represents Z for an ideal gas.

To come up with an improvement on the ideal gas law there are two approaches we can take.

Mathematical approach (virial equation)

A well behaved function $F(x)$ can be represented in terms of a power series expansion in powers of x

$$F(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \dots \quad (1.6.2)$$

where the values for the constants a_0, a_1, a_2, \dots are found either by fitting eq 1.6.2 to experimental data or by a Taylor series expansion (if the function $F(x)$ is a known function). Since the curves in Fig 3 are functions of pressure (and assuming they are well behaved functions) we may say

$$Z = pV_m/RT = 1 + B'p + C'p^2 + \dots \quad (1.6.3)$$

where the leading term on the right is 1 (so that $Z \rightarrow 1$ as $p \rightarrow 0$, as expected for all gases) and B', C', \dots are constants whose values depend on the gas and on temperature. Eq 1.6.3 is called a virial equation, and B', C', \dots are called virial coefficients. A second virial equation can be written in terms of powers of $1/V_m$.

$$Z = 1 + B/V_m + C/V_m^2 + \dots \quad (1.6.4)$$

The advantage of eq 1.6.4 over eq 1.6.3 is that it can be explicitly solved for the pressure of the gas

$$p = \frac{RT}{V_m} \{ 1 + B/V_m + C/V_m^2 + \dots \} \quad (1.6.5)$$

The constants B, C, \dots in eq 1.6.4 and 1.6.5 are also called virial coefficients, and also have values that depend on the gas and on temperature. The virial coefficients B', C', \dots are related to B, C, \dots but the constants are not equal to one another. Values for the virial coefficients are generally found by fitting eq 1.6.3 or 1.6.4 to experimental data.

In principle, the virial equation is an exact description of a real gas in the limit of keeping a large number of terms in the power series expansion. However, there are several problems with using the virial equation:

- 1) It is usually only possible to find values for a few of the virial coefficients from experimental data.
- 2) The values for the virial coefficients change with temperature, and so there will be different values at different temperatures. Thus values for the virial coefficients need to be found for every temperature of interest.
- 3) There is no simple physical interpretation for the values for the virial coefficients.
- 4) Because this is a purely mathematical approach for obtaining the equation of state for a real gas, there is no reason to expect the virial equation to quickly converge and become a good approximation for real gas behavior.

Chemical approach (van der Waals equation)

Instead of a purely mathematical approach, we can try to improve on the ideal gas law by correcting for the specific factors that lead to non-ideal behavior, namely that gases occupy volume and gas molecules are attracted to each other by weak forces of interaction.

We can proceed as follows. We start with the ideal gas law

$$pV = nRT \quad (1.6.6)$$

If we call b the volume physically occupied by one mole of gas molecules (related to the size of a gas molecule) we can correct the ideal gas law by excluding that volume, to get

$$p(V - nb) = nRT \quad (1.6.7)$$

or

$$p = \frac{nRT}{(V - nb)} \quad (1.6.8)$$

The attractive forces acting between gas molecules will slow the molecules down as they approach the walls of the container holding them. This will reduce the pressure. We can write this reduction in pressure in terms of a constant (the a coefficient) whose value is expected to increase as the intermolecular attractive forces increase. A simple argument shows that the reduction in pressure is proportional to (n/V) . Including this correction into eq 1.6.8 gives

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} = \frac{RT}{(V_m - b)} - \frac{a}{V_m} \quad (1.6.9)$$

This equation is called the van der Waals equation, and a and b are called the van der Waals coefficients.

The values for the van der Waals coefficients are related to the strength of intermolecular attraction (for the a coefficient) and the size of the molecules (for the b coefficient). The van der Waals coefficients are found by fitting eq 1.6.9 to experimental data.

The van der Waals equation has at least three advantages over the virial equation:

- 1) Because the van der Waals equation is derived by specifically correcting for the approximations used to find the ideal gas law, it is generally a better equation than a two or three term virial equation.
- 2) The van der Waals a and b coefficients are assumed to be temperature independent, and so are easier to work with than the virial coefficients, whose values depend on temperature.
- 3) Unlike the virial coefficients, it is easy to attach physical significance to the van der Waals coefficients.

One place where the van der Waals equation is useful is in describing real substances in the vicinity of the critical point. T_c , the critical temperature is the highest temperature where an isothermal reversible compression of a gas will result in a phase transition, a point in the compression where two distinct phases, a gas phase and a liquid phase, will be observed. (Note that at low temperatures it will be a gas phase and a solid phase that are observed). Above the critical temperature the change from a gas to a liquid occurs continuously, and there is never a point where two phases are observed in the system. This behavior can be seen in Fig 4. Note that in addition to a critical temperature, a pure substance will also have a critical pressure (p_c) and critical molar volume ($V_{m,c}$).

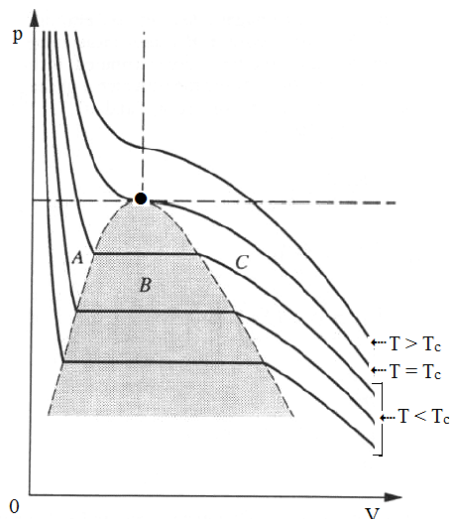


Figure 4. Pressure vs volume for one mole of a real gas for different values for T . The curves correspond to isotherms (curves where T is constant). Higher temperatures correspond to the higher curves in the figure. Region A = liquid present; region C = gas present; region B (shaded) both liquid and gas present. The dark dot (\bullet) on the critical isotherm is the critical point for the substance.

For the critical isotherm (the curve corresponding to $T = T_c$) the critical point (dark dot in the figure) is a saddle point. At that point we may say

$$dp/dV_m = 0 \qquad d^2p/dV_m^2 = 0 \qquad (1.6.10)$$

The condition $dp/dV_m = 0$ is a condition for a critical point, and $d^2p/dV_m^2 = 0$ is a condition for a saddle point.

If we assume our gas obeys the van der Waals equation, then we have three equations (the van der Waals equation and the equations obtained from $dp/dV_m = 0$ and $d^2p/dV_m^2 = 0$). Since we have three critical constants (p_c , $V_{m,c}$, and T_c) that is sufficient information to find the values for the critical constants. The results (obtained by taking the first and second derivative of p with respect to V_m , and then doing a bit of algebra) give the following expressions for the critical constants.

$$p_c = \frac{a}{27b^2} \qquad V_{m,c} = 3b \qquad T_c = \frac{8a}{27Rb^2} \qquad (1.6.11)$$

The values obtained from the van der Waals a and b coefficients for p_c and T_c are usually in good agreement with the experimental values. The calculated value for $V_{m,c}$ is typically 30-50% higher than the experimental value. This is because the b coefficient is based on the interaction of a pair of molecules, while at the critical point the molecules are all in close contact with one another.

While there are now better equations of state for describing the behavior of real substances around their critical point, the van der Waals equation is qualitatively correct, and is the simplest equation of state exhibiting critical behavior.

Note that there are dozens of other equations of state used to describe the behavior of real substances. Many of these are designed to provide a good description of real behavior over a limited set of conditions (for example, for pressures and temperatures near the critical point). The choice of which equation of state to use depends on the precision needed in the description of the real substance, the behavior being modeled, the available experimental data, and other factors.