CHAPTER 1 LECTURE NOTES

System, Surroundings, and States

Fig. 1.4

Note the three different types of systems based on the type of boundary between system and surroundings.

Intensive and Extensive Properties

<u>Intensive Properties:</u> Intrinsic to the substance, does not change with the amount of substance.
Examples: density, molecular mass, refractive index

<u>Extensive Properties:</u> Depend on the amount of substance.
Examples: mass, volume, energy

State Variables: The minimum number of properties that need to be specified (i.e., measured) in order to determine the state of the system.

Equilibrium: A system is in equilibrium with its surroundings when its state variables do not change with time.

Thermal Equilibrium: When two bodies are in contact and their temperature remain constant, they are in thermal equilibrium. *Two bodies in thermal equilibrium with a third are also in thermal equilibrium with each other.*

Temperature scales

Celsius & Farenheit: Both based on the freezing point and boiling point of water at 1 atm pressure.

Kelvin Scale: Based on ideal gas behavior extrapolated to absolute zero.

Triple point scale: Based on a single point: the triple point of water, which is *defined* to be *exactly* 273.16 K.

Pressure

Pressure is force per unit area. The most common units in the US for pressure of gases are the atmosphere (atm), or pounds per square inch (psi). Another common unit is "torr" or "mm Hg," which refers to the height of a mercury column supported by the pressure of the gas.

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg.}$$

The SI unit of pressure is the Pascal (Pa). 1 Pa = 1 N m^{-2}. A more useful unit when dealing with gases is the "bar."

$$1 \text{ bar} = 10^5 \text{ Pa.}$$

1 bar is close to, but not the same as 1 atm.

$$1 \text{ atm} = 1.01325 \text{ bar} = 101.325 \text{ kPa} = 101{,}325 \text{ Pa} = 760 \text{ torr.}$$

$$1 \text{ bar} = 100.000 \text{ kPa} = 100{,}000 \text{ Pa} = 750 \text{ torr.}$$

Ideal Gas Law

Pressure measuring devices:
A mercury barometer is commonly used to measure atmospheric pressure.
A mercury *manometer* is commonly used to measure pressure of gases in various containers. There are two types of manometers: closed end and open end. See Fig. 1.4 and note how they work.

See Example 1.1, Problems 1.7–1.9

Boyle's Law: PV = constant, at constant T. Lines connecting points on a PV diagram at a fixed temperature are called *isotherms*.

Charles (Gay Lussac's) Law: V/T = constant, at constant P.

Ideal Gas Law: Combination of Boyle's and Charle's Laws: PV/T = constant.

Ideal Gas Law(alternate statement): $PV = nRT$

R is the Universal Gas Constant. Its numerical value in various systems of units is given in Table 1.1, on p. 16.

Problems: 1.11 – 1.13

Molecular masses from Ideal Gas Law:

$$PV = nRT = \frac{m}{M}RT$$

$$P = \frac{n}{V}RT = (\frac{m}{V})\frac{RT}{M} = \rho\frac{RT}{M},$$ where ρ is the density of the gas.

Therefore, $$M = \rho\frac{RT}{P}.$$

Also see Problems 1.15 – 1.17

Important Results from Kinetic Theory

Pressure:

$$PV = \tfrac{1}{3}Nm\overline{u^2}. \tag{1.41}$$

The quantity $\overline{u^2}$ is called "mean-square velocity."

Kinetic Energy:

$$\varepsilon_k = \tfrac{1}{2}m\overline{u^2} = \tfrac{3}{2}k_BT$$ per molecule, where k_B is called the Boltzmann constant.

$$E_k = \tfrac{3}{2}RT,$$ per mole.

Therefore, $R = Lk_B$, where L is the Avogradro number.

Graham's Law of Effusion:

Rate of effusion is **inversely** proportional to the molecular mass.

Assumptions of Kinetic Theory:

- Gases consist of particles which are so small compared to the distances between them that the volume of the individual particles can be assumed to be zero.
- The particles are in constant motion, colliding with each other and the walls of the container in *perfectly elastic* collisions.
- Collisions with the walls give rise to the pressure exerted by the gas.
- The particles have no forces of attraction or repulsion with each other or the walls of the container.
- The average kinetic energy of a collection of gas particles is directly proportional to the Kelvin temperature.

Real Gases

Real gases deviate from "ideal" behavior because they do not strictly conform to the assumptions listed above. The compression factor, *Z*, defined as

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT}, \qquad (1.98)$$

V_m is the molar volume, is useful to analyze the deviation from ideal behavior. For ideal gas, Z = 1 always. See Fig. 1.17 (p. 33).

Real gases have forces of attraction between molecules. Therefore, if the temperature is low enough, application of pressure will lead to the formation of molecular clusters. The clusters grow into liquid droplets. This is the principle of liquefaction of gases by application of pressure and cooling. If gases behaved ideally, they would *never* form liquids.

There is a special temperature, called **critical temperature**, T_c, beyond which gases cannot be liquefied by application of pressure. See Fig. 1.18. At T_c, there is a certain value of P and V at which the PV curve goes through an inflection. This is called the critical point. The pressure and volume at this point are called the critical pressure, P_c ,and critical volume, V_c , respectively. The Below T_c, there is a region where the gas and liquid are in equilibrium.

The van der Waals Equation:

- Corrects for two assumptions inherent in Ideal Gas Law:

  (a) attraction/repulsion between molecules, which affects the pressure term, and

  (b) the volume occupied by the molecules themselves, which affects the volume term.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \text{for } n \text{ moles, and}$$

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \qquad \text{for one mole.}$$

- The simplest two parameter gas equation in existence.
- The constants *a* and *b* have been experimentally determined for a large number of gases.
- Provides a natural explanation for "critical phenomena."
- Rearranges to give a closed form expression for pressure:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2},$$

  but yields a cubic equation for volume:

$$PV_m^3 - (nbP + nRT)V_m^2 + aV - ab = 0.$$

  A cubic equation has three roots, which explains the oscillatory behavior of the *P*-*V* curve predicted by van der Waals equation in the "critical" region. (See Fig. 1.21).

- Analysis of the behavior of the van der Waals equation in the critical region:

$$\left(\frac{\partial P}{\partial V}\right) = 0 \text{ and } \left(\frac{\partial^2 P}{\partial V^2}\right) = 0 \text{ at } V = V_c.$$

  These two equations and the equation for pressure above can be used to solve for the van der Waals constants a and b and yields an expression for R in terms of the critical variables P_c, V_c and T_c:

$$a = 3P_cV_c^2,\ b = \tfrac{1}{3}V_c,\ \text{and } R = \frac{8P_cV_c}{3T_c}. \qquad (1.109)$$

- Using these definitions in the van der Waals equation and simplifying, we get the "reduced equation of state:"

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r, \quad \text{where } P_r = \frac{P}{P_c}, \text{etc.,} \qquad (1.111)$$

  which is completely free from all parameters!

- This leads to the **law of corresponding states** which can be stated as "two gases are in corresponding states if they have the same values for their reduced variables."

The Virial Equation

- Equation for the compression factor:

  $$Z = \frac{PV_m}{RT} = 1 + B'(T)P + C'(T)P^2 + \ldots \tag{1.116}$$

  or

  $$Z = \frac{PV_m}{RT} = 1 + B'(T)\frac{RT}{V_m} + C'(T)\left(\frac{RT}{V_m}\right)^2 + \ldots$$ which can be written more simply as

  $$Z = \frac{PV_m}{RT} = 1 + B(T)\frac{1}{V_m} + C(T)\frac{1}{V_m^2} + \ldots \tag{1.117}$$

  It is a good approximation to substitute for $V_m = RT/P$ in the last equation so that it can be written in terms of pressure (as in the first equation). In other words, $B(T)/RT \approx B'(T)$.

  The constants B, B', C, C' etc., are called the second and third virial coefficients.

- Since terms corresponding to the second and higher powers are small, the temperature at which the second virial coefficient vanishes (which means $Z \simeq 1$) has a special importance: *at this temperature, the gas behaves almost ideally.* Therefore, this temperature is called the **Boyle temperature**.

- By following the steps in Problem 1.55, the van der Waals equation can be expressed as a Virial equation. From this expression, a relationship between the van der Waals constants a and b and the Boyle temperature can be derived.

Please see course web page for assigned problems (and answers) from Chapter 1.