

CHAPTER ONE

The Properties of Gases

1.1. INTRODUCTION

In general, matter can be exists in one of the three states such as solid, liquid or a gas. A solid may be defined as a body possessing definite volume and shape at a given temperature and pressure. Solids are orderly arranged arrays of atoms, molecules or ions having definite geometry depending up on the arrangements of these atoms, molecules or ions. Solids are relatively rigid. The constituents are held together by strong attractive forces. A liquid on the other hand has a definite volume but no definite shape. Molecules consist a liquid are held by molecular forces which are not as strong as solids. Gases are important but usually unseen portion of the world around us. Gases have neither a shape nor a volume and the molecular forces of attraction are very much weaker.

Important Characteristics of Gases

- Gases are highly compressible: An external force compresses the gas sample and decreases its volume, removing the external force allows the gas volume to increase.
- Gases are highly thermally expandable: When a gas sample is heated, its volume increases, A gas fills any container it occupies. This is a result of the second law of thermodynamics i.e. gas expanding to fill a container is a spontaneous process due to the accompanying increase in entropy. And when it is cooled its volume decreases.
- Gases have low viscosity: Gases flow much easier than liquids.
- Most gases have low densities: Gas densities are on the order of grams per liter whereas liquids and solids are grams per cubic cm, 1000 times greater.
- Gases are infinitely miscible: Gases mix in any proportion such as in air, a mixture of many gases

1.2. Gas Law Variables

A state variable is a precisely measurable physical property which characterizes the state of a system. It must be inherently single-valued to characterize a state. Some texts just use the term "thermodynamic variable" instead of the description "state variable". An ideal gas is characterized by four *state variables*: These commonly accepted gas law variables are: *temperature, Pressure, Volume and number of moles*.

1. Volume

All gases must be enclosed in a container that, if there are no openings or sealed with no leaks. The three-dimensional space enclosed by the container walls is called volume. Volume (V) in chemistry is usually measured in liters (L) or milliliters (mL). A liter is also called a cubic decimeter (dm^3) or cubic centimeters (cc or cm^3).

☞ 1 cm^3 (cubic centimeter) = 1 mL (milliliter) and 1 dm^3 (cubic decimeter) = 1 L (liter) = 1000 mL

2. Temperature

All gases have a temperature, usually measured in degrees Celsius ($^{\circ}\text{C}$). When the generalized variable of temperature is discussed, T is the symbol. There is another temperature scale which is very important in gas behavior is called the Kelvin scale ($\text{K} = \text{Celsius} + 273.15\text{K}$). All gas law problems will be done with kelvin temperatures. Standard temperature is defined as zero degrees Celsius or 273 K. The kelvin temperature of a gas is directly proportional to its kinetic energy. If you double the kelvin temperature, you will double the kinetic energy. The other scale used to measure temperature is Fahrenheit scale ($^{\circ}\text{F}$). Its conversion equations are given as;

$$\left. \begin{array}{l} 1.8^{\circ}\text{C} + 32 = ^{\circ}\text{F} \quad \text{from Celsius to Fahrenheit} \\ (^{\circ}\text{F} - 32)5/9 = ^{\circ}\text{C} \quad \text{from Fahrenheit to Celsius} \end{array} \right\} \text{----- (1.1)}$$

3. Pressure

Gas pressure is created by the molecules of gas hitting the walls of the container. This concept is very important in helping you to understand gas behavior. Keep it solidly in mind. This idea of gas molecules hitting the wall will be used often when the generalized variable of pressure is discussed. Pressure is the force per unit area and P is its symbol.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \text{----- (1.2)}$$

Conversion factors for different units of pressure to Atmospheres

Atmosphere	1 atm = 1 atm
mm of Hg (torr)	1 atm = 760 torr
Newton per square meter (Pascal)	1 atm = 101325 Pa
kilopascal	1 atm = 101.325 kPa
Bar	1 atm = 1.01325 bar

Standard Temperature and Pressure (STP)

STP is used widely as a standard reference point for expression of the properties and processes of gases. The standard temperature is the freezing point of water (0°C) and the standard pressure is one atm and the standard volume for 1 mole of an ideal gas at STP is 22.4 liters

4. Amount of Gas

The amount of gas present is measured in moles (mol) or in grams (g or gm). Typically, if grams are used, you will need to convert to moles at some point. The generalized variable of amount is moles (n). A mole of any material will contain Avogadro's number of atoms. One mole of an ideal gas will occupy a volume of 22.4 liters at STP.

$$\text{Avogadro's number, } N_A = 6.0221367 \times 10^{23}/\text{mol}$$

1.3. The Equation of State

A sample of a substance is defined by its physical properties. Two samples of a substance that have the same physical properties are in the same state. For example, the state of a pure gas is specified by giving its volume, V , amount of substance (number of moles), n , pressure, p , and temperature, T . However, it has been established experimentally that it is sufficient to specify only three of these variables then the fourth variable is fixed. It is an experimental fact that each substance is described by an **equation of state**, an equation that interrelate these four variables. The general form of an equation of state is

$$p = f(n, V, T) \quad \text{-----} \quad (1.3)$$

This equation tells us that, if we know the values of T , V , and n for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $PV = nRT$, where R is a gas constant.

Gases are conventionally classified in to two types, as **Ideal gases (perfect gases)** and **Real gases**. Real gas behavior is actually complex. For now, let's look at ideal Gases, since their behavior is simpler. By understanding ideal gas behavior, real gas behavior becomes more tangible.

1.4. Ideal Gases and Ideal gas laws

An ideal gas is defined as one in which all collisions between atoms or molecules are perfectly elastic i.e. no attractive or repulsive forces are involved during collisions. and in which there are no intermolecular attractive forces, since these inter particle forces are lacking the kinetic energy of the gas molecules remains constant. One can visualize it as a collection of perfectly hard spheres which collide but which do not interact with each other. In such a gas, all the *internal energy* is in the form of kinetic energy and any change in internal energy is accompanied by a change in *temperature*. An ideal gas is considered to be a "point mass". A point mass is a particle so small, its mass is very nearly zero. This means an ideal gas particle has virtually no volume.

1.4.1. Ideal Gas Laws

⇒ Boyle's Law

In 1662, Robert Boyle notices the law that gives the relationship between pressure and volume if temperature and amount are held constant. Boyle's Law states that "*the volume of a gas is **inversely proportional to the pressure at constant temperature***". If the volume of a container is increased, the pressure will decrease. If the volume of a container is decreased, the pressure will increase, why?

Suppose the volume is increased. This means gas molecules have farther to go and they will impact the container walls less often per unit time. This means the gas pressure will be less because there are less molecule impacts per unit time. If the volume is decreased, the gas molecules have a shorter distance to go, thus striking the walls more often per unit time. This results in pressure being increased because there are more molecule impacts per unit time.

The mathematical form of Boyle's Law is: $PV = k$

Suppose P_1 and V_1 are a pressure-volume pair of data at the start of an experiment. In other words, some container of gas is created, the volume and pressure of that container is measured. Keep in mind that the **amount of gas** and the *temperature does not change*. When you multiply P and V together, you get a number that is called **k**. We don't care what is the exact value? Now, if the volume is changed to a new value called V_2 then the pressure will spontaneously change to P_2 . It will do so because the PV product must always equal **k**, we can conclude that

$$P_1V_1 = P_2V_2 \text{ ----- (1.4)}$$

Example 1.1: 2.00 L of a gas is at 740.0 mmHg pressure. What is its volume at standard pressure?

$$(740.0 \text{ mmHg}) (2.00 \text{ L}) = (760.0 \text{ mmHg}) (x)$$

$$x = 1.947 \text{ L}$$

Example 1.2: 5.00 L of a gas is at 1.08 atm. What pressure is obtained when the volume is 10.0 L?

$$(1.08 \text{ atm}) (5.00 \text{ L}) = (x) (10.0 \text{ L})$$

$$x = 0.54 \text{ atm}$$

⇒ **CHARLES' LAW**

In 1787, Jacques Charles offers the law that gives the relationship between volume and temperature if pressure and amount are held constant. This law states that “the volume of a gas is **directly** proportional to the temperature **in Kelvin**”.

If the volume of a container is increased, the temperature will increase. If the volume of a container is decreased, the temperature will decrease. Why? Suppose the temperature is increased. This means gas molecules will move faster and they will impact the container walls more often. This means the gas pressure inside the container will increase but only for an instant. Think of a short span of time. The greater pressure on the inside of the container walls will push them outward, thus increasing the volume. When this happens, the gas molecules will now have farther to go, thereby lowering the number of impacts and dropping the pressure back to its constant value.

Charles' Law is a direct mathematical relationship of the form: $\frac{V}{T} = k$

So we know that: $\frac{V_1}{T_1} = k$, and we know $\frac{V_2}{T_2} = k$. Since $k = k$, we can conclude that

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{----- (1.5)}$$

Example 1.3: A gas is collected and found to fill 2.85 L at 25.0°C. What will be its volume at standard temperature?

$$\frac{2.85 \text{ L}}{298 \text{ K}} = \frac{x}{273 \text{ K}}, \quad x = 2.61 \text{ L}$$

Example 1.4: 4.40 L of a gas is collected at 50.0°C. What will be its volume upon cooling to 25.0°C?

$$\frac{4.40 \text{ L}}{323 \text{ K}} = \frac{x}{298 \text{ K}}, \quad x = 4.06 \text{ L}$$

⇒ **GAY-LUSSAC'S LAW**

In the early 1800's, Joseph Louis Gay-Lussac gives the relationship between pressure and temperature when volume and amount are held constant. This law states that “the pressure of a gas is **directly** proportional to the temperature **in Kelvin**”. If the temperature of a container is increased, the pressure increases. If the temperature of a container is decreased, the pressure decreases. Suppose the temperature is increased. This means gas molecules will move faster and they will impact the container walls more often. This means the gas pressure inside the container will increase, since the container has rigid walls (volume stays constant). The mathematical form of Gay-Lussac's Law is:

$$\frac{P}{T} = k$$

We know this: $\frac{P_1}{T_1} = k$ And we know that $\frac{P_2}{T_2} = k$ Since $k = k$, we can conclude that .

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{OR} \quad P_1 T_2 = P_2 T_1 \quad \text{-----} (1.6)$$

Example 1.5: 10.0 L of a gas is found to exert 97.0 kPa at 25.0°C. What would be the required temperature (in Celsius) to change the pressure to standard pressure?

$$\frac{97\text{kPa}}{298\text{K}} = \frac{101.325\text{kPa}}{x}, \quad x = 311.28\text{K}$$

Example 1.6: 5.00 L of a gas is collected at 22.0°C and 745.0 mmHg. When the temperature is changed to standard, what is the new pressure?

$$\frac{745\text{mmHg}}{295\text{K}} = \frac{x}{273\text{K}}, \quad x = 689.44\text{mmHg}$$

⇒ **AVOGADRO'S LAW**

Amedeo Avogadro discovered the relationship between volume and amount when pressure and temperature are held constant. In the previous laws, the **amount** of gas was always constant. However, the amount of a gas (n) is **directly** proportional to the volume of the gas, meaning that as the amount of gas increases, so does the volume. Why? Suppose the amount is increased. This means there are more gas molecules and this will increase the number of impacts on the container walls. This means the gas pressure inside the container will increase (for an instant), becoming greater than the pressure on the outside of the walls. This causes the walls to move outward. Since there is more wall space the impacts will lessen and the pressure will return to its original value.

The mathematical form of Avogadro's Law is: $\frac{V}{n} = k$

We know this: $\frac{V_1}{n_1} = k$ And we know that $\frac{V_2}{n_2} = k$, since $k = k$, we can conclude that

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \text{ ----- (1.7), this equation is called Avogadro's Law.}$$

Example 1.7: 5.00 L of a gas is known to contain 0.965 mol. If the amount of gas is increased to 1.80 mol, what new volume will result (at a constant temperature and pressure)?

$$(5.00 \text{ L}) (1.80 \text{ mol}) = (x) (0.965 \text{ mol}), \quad x = 9.32 \text{ L}$$

⇒ **Combined Gas Law**

To derive the Combined Gas Law, do the following:

Step 1: Write Boyle's Law: $P_1 V_1 = P_2 V_2$

Step 2: Multiply by Charles Law: $P_1 V_1^2 / T_1 = P_2 V_2^2 / T_2$

Step 3: Multiply by Gay-Lussac's Law: $P_1^2 V_1^2 / T_1^2 = P_2^2 V_2^2 / T_2^2$

Step 4: Take the square root to get the combined gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ ----- (1.8)}$$

Example 1.8: 2.00 L of a gas is collected at 25.0°C and 745.0 mmHg. What is the volume at STP? Insert the values in their proper places in the combined gas law equation and solve for V_2 .

$$\frac{745 \text{ mmHg} \times 2.00 \text{ L}}{298 \text{ K}} = \frac{760 \text{ mmHg} \times V_2}{273 \text{ K}}, \quad V_2 = 1.796 \text{ L}$$

⇒ **Ideal Gas Law: $PV = nRT = NKT$**

The Ideal Gas Law was first written in 1834 by Emil Clapeyron. This is just one way to "derive" the Ideal Gas Law: For a static sample of gas, we can write each of the following three gas laws as follows: $V \propto 1/P$, $V \propto T$ and $V \propto n$. Then $V \propto nT/p$. the proportionality constant is universal gas constant R

$V = nRT / P$ Thus the *Ideal gas law become*

$$PV = nRT = NKT \text{ ----- (1.9)}$$

Where n is number of moles, R is universal gas constant = $8.3145 \text{ J/mol}\cdot\text{K}$ = $0.08206 \text{ L atm / mol}\cdot\text{K}$ = $1.987 \text{ cal / mol}\cdot\text{K}$, N is number of molecules, k is Boltzmann constant = $1.38066 \times 10^{-23} \text{ J/K}$ = $8.617385 \times 10^{-5} \text{ eV/K}$ ($k = R/N_A$) and N_A is Avogadro's number = $6.0221 \times 10^{23} / \text{mol}$

Example 1.9: A sample of dry gas weighing 2.1025 grams is found to occupy 2.850 L at 22.0°C and 740.0 mmHg. How many moles of the gas are present? And what is the molar mass of the gas?

$$\frac{740 \text{ mmHg}}{760 \text{ mmHg / atm}} = 0.9737 \text{ atm},$$

$(0.9737 \text{ atm})(2.850 \text{ L}) = (n)(0.08206 \text{ L atm / mol K})(295.0 \text{ K})$. then $n = 0.1146 \text{ mol}$

$$\text{Mwt} = \frac{2.1025 \text{ gm}}{0.1146 \text{ mol}} = 18.34 \text{ gm / mol}$$

1.5. Mixtures of gases:

We are often concerned with mixtures of gases such as the properties of the atmosphere in meteorology, the composition of exhaled air in medicine, or the mixtures of hydrogen and nitrogen used in the industrial synthesis of ammonia. We need to be able to assess the contribution that each component of a gaseous mixture makes to the total pressure.

In the early 19th C, John Dalton carried out a series of experiments that led him to formulate what has become known as Dalton's law: The pressure exerted by a mixture of perfect gases is the sum of the pressures that each gas would exert if it were alone in the container at the same temperature:

$$P = P_A + P_B + \dots \quad \text{-----} \quad (1.10)$$

In this expression, p_J is the pressure that the gas J would exert if it were alone in the container at the same temperature. Dalton's law is strictly valid only for mixtures of perfect gases (or for real gases at such low pressures that they are behaving perfectly), but it can be treated as valid under most conditions we encounter.

For any type of gas (real or perfect) in a mixture, the partial pressure, p_J , of the gas J is defined as

$$P_J = \chi_J P \quad \text{-----} \quad (1.11)$$

Where χ_J is the mole fraction of the gas J in the mixture. The mole fraction of J is the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture. In a mixture that consists of n_A A molecules, n_B B molecules, and so on (where the n_J are amounts in moles), the mole fraction of J (where $J = A, B, \dots$) is

$$x_J = \frac{n_J}{n} \quad \begin{array}{l} \text{amount of J molecules in the mixture} \\ \text{total amount of molecules in the mixture} \end{array} \quad \text{----- (1.12)}$$

where $n = n_A + n_B + \dots$. Mole fractions are unitless because the unit mole in numerator and denominator cancels. For a binary mixture, one that consists of two species, this general expression becomes

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B} \quad x_A + x_B = 1 \quad \text{----- (1.13)}$$

When only A is present, $x_A = 1$ and $x_B = 0$. When only B is present, $x_B = 1$ and $x_A = 0$. When both are present in the same amounts, $x_A = 1/2$ and $x_B = 1/2$.

Problem 1.1.:

Calculate the mole fractions of N_2 , O_2 , and Ar in dry air at sea level, given that 100.0 g of air consists of 75.5 g of N_2 , 23.2 g of O_2 , and 1.3 g of Ar. Hint: Begin by converting each mass to an amount in moles.

[Answer: 0.780, 0.210, 0.009]

- For a mixture of perfect gases, we can identify the partial pressure of J with the contribution that J makes to the total pressure. Thus, if we introduce $p = nRT/V$ into partial pressure equation, we get

$$p_J = x_J p = x_J \times \frac{nRT}{V} = \frac{n_J}{n} \times \frac{nRT}{V} = n_J \times \frac{RT}{V} \quad \text{----- (1.14)}$$

Definition
 $p = nRT/V$

The value of $n_J RT/V$ is the pressure that an amount n_J of J would exert in the otherwise empty container. That is, the partial pressure of J provided all the gases in the mixture behave perfectly. For that definition partial pressure equation applies to all gases, and the sum of these partial pressures is the total pressure (because the sum of all the mole fractions is 1); however, each partial pressure is no longer the pressure that the gas would exert when alone in the container.

Problem 1.2.: The partial pressure of molecular oxygen in air plays an important role in the aeration of water, to enable aquatic life to thrive, and in the absorption of oxygen by blood in our lungs. Calculate the partial pressures of a sample of gas consisting of 2.50 g of oxygen and 6.43 g of carbon dioxide with a total pressure of 88 kPa. [Answer: 31 kPa, 57 kPa]

1.6. Kinetic Molecular Theory of Gases

The **Kinetic Molecular Theory of Gases** is the model used to explain the behavior of gases in nature. This theory presents physical properties of gases in terms of the motion of individual molecules.

1. Average Kinetic Energy \propto Kelvin Temperature
2. Gas molecules are points separated by a great distance
3. Particle volume is negligible compared to gas volume
4. Gas molecules are in rapid random motion
5. Gas collisions are perfectly elastic
6. Gas molecules experience no attraction or repulsion

1.7. REAL GASES

Real gases do not obey the perfect (ideal) gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid. The ideal gas model is an approximate model of gases that is often used to simplify calculations on real gases. An ideal gas has the following properties:

- a. There are no intermolecular forces between the gas particles.
- b. The volume occupied by the particles is negligible compared to the volume of the container they occupy.
- c. The only interactions between the particles and with the container walls are perfectly elastic collisions.

⇒ Note that an elastic collision is one in which the total kinetic energy is conserved (i.e. no energy is transferred from translation into rotation or vibration, and no chemical reaction occurs).

What is the term Real Gas?

Scientists describe a real gas as any gas that significantly disobeys any part of the Kinetic Molecular Theory. As long as a gas has sufficiently high kinetic energy and has the particles spaced far enough apart, then that gas will usually behave like the Ideal Gas. There are two sections of Kinetic Molecular Theory that will always cause problems for chemists.

The ideas that the particles are volumeless and that they do not interact with each other are common potential sources of error. *Under what circumstances will the concept of the Ideal Gas and Kinetic Molecular Theory disagree most significantly?*

- a. Very large volume gas molecules will deviate significantly from Ideal behavior. Since the Ideal Gas is able to move anywhere in the container, if the particles are of large volume, then they will be restricted from parts of the container that are occupied by the other gas particles.
- b. Gas particles that exhibit nonpolar qualities are going to be more ideal. Any gas that is highly polar, such as water, will experience significant attractions for the other particles in the system this will create problems with the concept of Ideal gases not interacting with each other. The Noble Gases, with their nonpolar character, will be the closest to Ideal in behavior.

Van der Waals Equation

A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 to take into account molecular size and molecular interaction forces. It is usually referred to as *the van der Waals equation of state*. As one would imagine, this equation becomes complex and difficult to work with. In addition, it establishes two more variables.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \text{ ----- (1.29)}$$

These variables are **a** that represent the finite interactions of the gas particles and **b** that represent the finite volumes of the gas particles.

In the van der Waals equation, the term $n^2 a/V^2$ reflects the fact that the attractive forces between molecules are not zero. The measured pressure is thus less than it should be because the attractive forces act to reduce it. The term nb reflects the fact that the volume of the molecules of a real gas is not zero, and so the volume in which the molecules may move is less than the total measured volume. A table of the van der Waals coefficients for several common gases is given below.

Table 1.3. Van der Waals Coefficients of Selected Gases

Gas	Ideal	He	Ar	O ₂	N ₂	CO ₂	CH ₄	H ₂	NH ₃
a (atm.L ² mol ⁻²)	0.00	0.034	1.345	1.360	1.390	3.592	2.253	0.244	4.170
b (lit mol ⁻¹)	0.00	0.0237	0.0322	0.0318	0.0391	0.0427	0.0428	0.0266	0.0371

Example 1.10: Calculate the pressure in atmospheres exerted by 2.0 moles of chlorobenzene vapours confined to 10.0 liter vessel at 298 K assuming that **a)** the gas is an ideal gas **b)** the gas is real gas ($a=25.43 \text{ atm lit.}^2 \text{ mol}^{-2}$ and $b=0.1453 \text{ lit. mol}^{-1}$).

$$\text{a) } PV = nRT \quad P = \frac{nRT}{V} = \frac{2.0 \text{ mol} \times 0.0821 \text{ lit. atm. mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{10.0 \text{ lit.}} = 4.8931 \text{ atm}$$

$$\text{b) } \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT, \quad P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$P = \frac{2.0 \text{ mol} \times 0.0821 \text{ lit. atm. mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{(10 \text{ lit.} - 2.0 \text{ mol} \times 0.1453 \text{ lit. mol}^{-1})} - \frac{(2.0 \text{ mol})^2 \times 25.43 \text{ atm lit}^2 \text{ mol}^{-2}}{(10 \text{ lit})^2} = 4.0224 \text{ atm}$$

Example 1.11: 2.0 moles of ammonia at 300 K occupy the volume of $5 \times 10^{-3} \text{ m}^3$. Calculate the pressure using Van der waals equation.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad \text{which gives } P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2} = 9.328 \text{ atm}$$

1.8. The compression factor

The deviations of a real gas from ideal gas behavior may be quantified by a parameter called the compression factor, denoted by symbol Z. At a given P and T, attractive and repulsive intermolecular forces between gas particles mean that the molar volume is likely to be smaller or larger than for an ideal gas under the same conditions. The compression factor is simply the ratio of the molar volume V_m of the gas to the molar volume of an ideal gas at the same pressure and temperature.

$$Z = \frac{V_m}{V_m^o} \quad \text{----- (1.14)}$$

The value of Z provides information on the dominant types of intermolecular forces acting in a gas. For $Z=1$, No intermolecular forces, the gas acts ideally. $Z < 1$, Attractive forces dominate, gas occupies a smaller volume than an ideal gas. $Z > 1$, Repulsive forces dominate, gas occupies a larger volume than an ideal gas

1.9. Critical constants

At lower temperatures, gas molecules occupy a smaller volume and move more slowly than they do at higher temperatures. Attractive forces among molecules or atoms become more important at lower temperatures. Ultimately, they become so strong that the gas liquefies. Thus, a useful physical picture of the liquid state is that liquefaction is the limiting behavior of an extremely non-ideal gas and it results from large interparticle attractive forces.

As the temperature of a real gas is lowered, its deviation from Boyle's law behavior becomes more pronounced until the p - V curve has become so distorted that it goes through a horizontal inflection point. The temperature at which this occurs is called the critical temperature, T_c .

The locus of p - V points at the same temperature is called an isotherm. The pressure, volume, and temperature at the inflection of the critical isotherm define a point called the critical point, which is unique to each real gas. The coordinates of the critical point (the critical constants) are the **critical pressure p_c , critical volume V_c , and critical temperature T_c** . The vapour pressure at the critical temperature is called the critical pressure, p_c , and the critical temperature and critical pressure together identify the critical point of the substance.

Below the critical temperature, the system may be in the liquid or gaseous state, or it may exist as equilibrium between liquid and vapor. The term "vapor" means gas, but it is usually applied to a gas in equilibrium with its liquid form. When a liquid is in equilibrium with its vapor, heat can be applied with no change in temperature but with conversion of some or all of the liquid to its vapor. When spheroids of vapor rise from the bottom of a heated liquid to the top, we say that the liquid boils. It is sometimes said that "no gas can be liquefied above the critical point." This is true, but it is a little misleading because there is no distinction between liquid and gas above the critical isotherm. Above the critical isotherm, the system is a supercritical fluid. The liquid-vapour phase boundary terminates at the critical point. The phase boundary at which solid-liquid-vapour co-exist together is triple point.

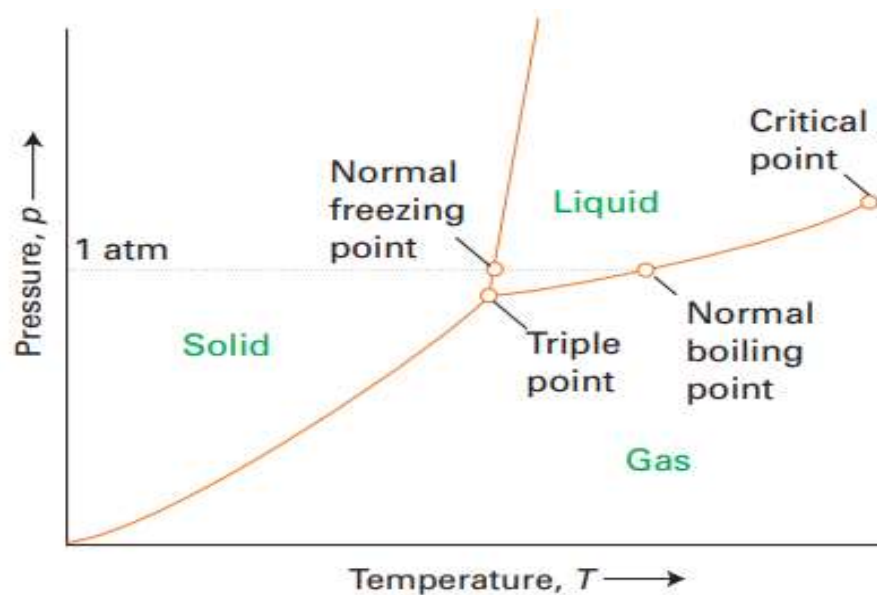


Figure 1.1. The significant points of a phase diagram.

CHAPTER TWO

2. Units and Mathematics

The value of a physical quantity can be expressed as the product of a numerical value and a unit. The International System of units (SI) was adopted by the 11th General Conference on Weights and Measures (CGPM) in 1960. The SI units are currently divided into base units and derived units, which together form what is called the coherent system of SI units. The SI also includes the prefixes to form decimal multiples and submultiples of SI units.

2.1. Basic SI units

There are seven quantities which have base units for every other SI unit in existence.

Table 2.1: Base quantities and their symbols

Base quantity		SI unit	
Name	Symbol	Name	Symbol
Length	l	Meter	m
Mass	m	Kilogram	kg
Temperature	T	Kelvin	K
Time	t	Second	s
Current	I	Ampere	A
Amount of Substance	n	Mole	mol
Luminous intensity	I_v	Candela	cd

2.2. Derived Units

Many properties cannot be described directly with one of the seven SI base units. For example, chemists often need to measure volume (the amount of space that something occupies), and volume is not on the list of SI base units. Rather than create a new definition for volume, we derive its units from the base unit for length, the meter. Volume can be defined as length cubed, so cubic meters, m³, can be used as a volume unit. Various other units are derived in similar ways. There are numerous derived units that are complementary to the base units. They may have special names (e.g. hertz, Pascal, joule, watt, etc.). There are also dimensionless derived units. The SI derived units are expressed as products of powers of the base units, analogous to the corresponding relations between physical quantities but with numerical factors equal to unity. Derived quantities are regarded as having dimensions derived algebraically from the seven base quantities by multiplication and division.

Table 2.2: Examples of SI derived units

Derived quantity		SI derived unit	
Name	Symbol	Name	Symbol
Area	A	Square meter	m^2
Volume	V	Cubic meter	m^3
Density	ρ	Kilogram per cubic meter	kg m^{-3}
Concentration	C	Mol per cubic meter	mol m^{-3}
Entropy	S	Joule per Kelvin	J K^{-1}
Permittivity of vacuum	ϵ_0	Farad per meter	F m^{-1}
Surface tension	γ	Newton per meter	N m^{-1}

Table 2.3: Examples of SI derived units have special names and symbols

Derived quantity		SI derived unit		
Name	Symbol	Name	Symbol	Expression in base units
Frequency	ν, f	Hertz	Hz	s^{-1}
Force	F	Newton	N	kg m s^{-2}
Pressure	P	Pascal	$\text{Pa} = \text{N m}^{-2}$	$\text{kg m}^{-1} \text{s}^{-2}$
Energy	E	Joule	$\text{J} = \text{N m}$	$\text{kg m}^2 \text{s}^{-2}$
Electromotive	E	Volt	V	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$
Electric charge	Q	Coulomb	C	A s
Electric resistance	R	Ohm	$\Omega = \text{V A}^{-1}$	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-2}$
Capacitance	C	Farad	$\text{F} = \text{C V}^{-1}$	$\text{kg}^{-1} \text{m}^{-2} \text{s}^4 \text{A}^2$
Plane angle	$\alpha, \beta, \theta...$	Radians	$\text{Rad} = \text{m/m}$	Dimensionless

2.3. Exponents and Logarithms

Exponential and logarithmic functions occur frequently in mathematical models for economics, finance, and other social sciences as well as in the natural sciences. First we review some of the basic rules and notation for exponentials and logarithms. For a positive number a ; and a positive integer n , we have

$$a^n = a \times a \times a \times a \times a \dots \times a \quad \text{where the } a \text{ on the right side of the equation appears } n$$

times. Similarly for n a positive integer

$$a^{1/n} = b \quad \text{then } a = b \times b \times b \times b \times b \dots \times b \quad \text{where the } b \text{ appears } n \text{ times on}$$

the right side of the equation.

At any rate the following notational rules hold even when the exponent is not a rational number

$$a^p \times a^q = a^{p+q}, \quad \frac{1}{a^p} = a^{-p}, \quad \frac{a^p}{a^q} = a^{p-q}, \quad a^0 = 1 \text{ and } 1^p = 1$$

The logarithm is the inverse of the exponential. Hence we must have some way to indicate the base used in the exponential when we write a logarithm. For example

$$2^3 = 8 \quad \text{will be expressed as} \quad \log_2 8 = 3$$

The mathematical statement $N = B^x$ serves as the basis for defining logarithms. The logarithm of a number (N) in base (B) is defined as (x).

$$\log_B N = x$$

Two bases (10 and e) are in common usage. The shorthand representations are:

$$\text{Base 10 logarithm is written as: } \log_{10} N = \log_{10} N = \log N$$

$$\text{And base e ("Natural" logarithms) } \log_e N = \log_e N = \ln N$$

Thus, the logarithm of a number is simply the power to which the base must be raised to give the number. There are a few basic rules for handling logarithms. Examples are given in base 10 but the rules are applicable to any base.

$$\text{Rule 1: } \log a^b = b \log a$$

$$\text{Rule 2 : } \log ab = \log a + \log b$$

$$\text{Rule 3: } \log \frac{a}{b} = \log a - \log b$$

$$\text{Rule 4: } \log 1 = 0$$

$$\text{Rule 5 : } \log \frac{1}{a} = -\log a$$

2.4. Differentials and Integrals

There are two common notations used to indicate derivatives. Consider the equation:

$$y = 2 + 3x - 4x^2$$

Some of you would say that; $y' = 3 - 8x$

$$\text{And others use the notation; } \frac{dy}{dx} = 3 - 8x$$

Most of the time, we will use the second method for denoting derivatives. The term dy is known as the differential of y and dx is the differential of x. The most common physical interpretation of a derivative is as the slope of a curve. If y is as a function of x (i.e., $y = f(x)$), then dy/dx is the slope of the curve obtained when y is plotted versus x.

Differential equations are mathematical equations which contain a derivative. Such equations play a very important role in physical chemistry. Differential equations are often the starting point in mathematical derivations that lead to better understanding of the physical properties of chemical systems. Most of the differential equations that we will encounter in physical chemistry will eventually be used to calculate a particular physical property. In order to make the calculation, the differential equation must first be integrated. Fundamental Differentiation formula

$$\frac{du^n}{dx} = nu^{n-1} \frac{du}{dx}, \quad \frac{de^u}{dx} = e^u \frac{du}{dx}, \quad \frac{d\ln x}{dx} = \frac{1}{x}, \quad \frac{d\sin x}{dx} = \cos x \quad \text{and} \quad \frac{d\cos x}{dx} = -\sin x$$

Special relation: Chain rule: $d[F(U(x))] = \frac{dF}{dU} \frac{dU}{dx}$

$$\text{Derivative of sum: } \frac{d}{dx}(u + v) = \frac{du}{dx} + \frac{dv}{dx}$$

$$\text{Derivative of a product: } \frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx}$$

If a function depends on two or more variables; $f(x, y)$, then the partial derivative expresses the dependence of f on one of the variables when all other variables are held constant. Mathematically the partial derivative of f with respect to x at constant y is represented by:

$$\left(\frac{\partial f}{\partial x}\right)_y$$

The differential of $z(x, y)$ is given by:

$$\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

The most common interpretation of the result of a definite integral is that the result of the integration represents a summation. For example, consider the definite integral:

$$\int_{10}^{50} f(x) dx = \text{Result}$$

Result, the numerical value of integral is the sum of an infinite number of rectangles with $F(x)$ high and dx wide. Height ($F(x)$) \times width (dx) is an area, the value of the integral given above can be interpreted as the area between $x = 10$ and $x = 50$ under the curve produced when $F(x)$ versus x is plotted. an integral is more complicated than the ones shown above, integral tables are often helpful. However, often

the integral you are trying to solve and the ones in the tables do not look the same and you may need to apply some manipulations to get them into the “standard” form.

Some basic indefinite integrals:

$$\int x^n dx = \frac{x^{n+1}}{n+1}, \int \frac{dx}{x} = \ln x, \int e^{ax} dx = \frac{1}{a} e^{ax}, \int \sin x dx = -\cos x \quad \text{and} \quad \int \cos x dx = \sin x$$

Some basic indefinite integrals

$$\int_0^{\infty} e^{-ax} dx = \frac{1}{a}, \int_0^{\infty} x^n e^{-ax} dx = \frac{1}{a^{n+1}} n! \quad \text{and} \quad \int_0^{\infty} x^n e^{-qx} dx = \frac{n!}{q^{n+1}}$$

Problem 2.1. find the derivatives of the following functions

a. $3x^2 - 6x + 1$

b. $\frac{x-1}{x+1}$

c. $\sin x \cos x$

Problem 2.2. compute the following integrals

a. $\int_0^1 (x^2 + 2x + 1) dx$

b. $\int e^{2x}$

c. $\int \frac{1}{x^{3/2}}$