-CHAPTER II-

THERMODYNAMIC PROPERTIES OF PURE SUBSTANCES

I-IDEAL GAS

1-introduction

We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities.

Heated gases expand, which can make a hot air balloon rise figure or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

2-empirical gas low: Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an ideal gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the ideal gas law—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

2-1-Pressure and Temperature: Amontons's or Gay-Lussac's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter and the pressure increases.

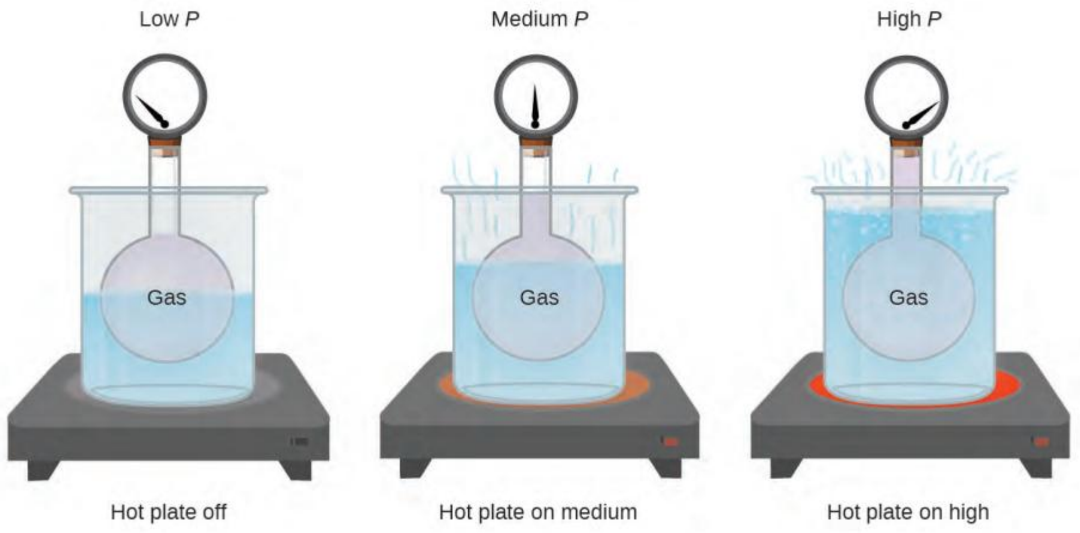


Figure show us the effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the P-T relationship for gases is known as either Amontons's law or **Gay-Lussac's law**. Under either name, it states that the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant. Mathematically, this can be written:

If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that P_1 T_1 = k and P_2 T_2 = k, which reduces to

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This equation is useful for pressure-temperature calculations for a confined gas at constant volume.

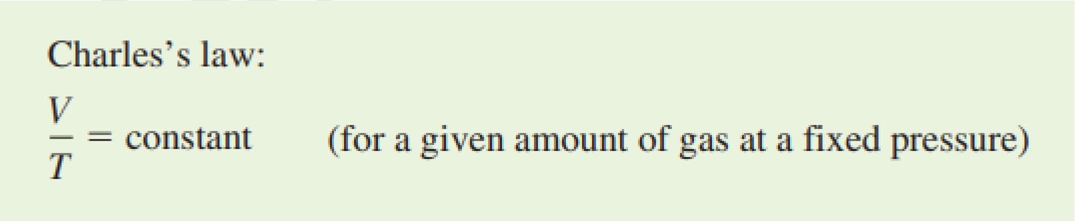
2-2-Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. Charles's law states that the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant.

Mathematically, this can be written as:

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

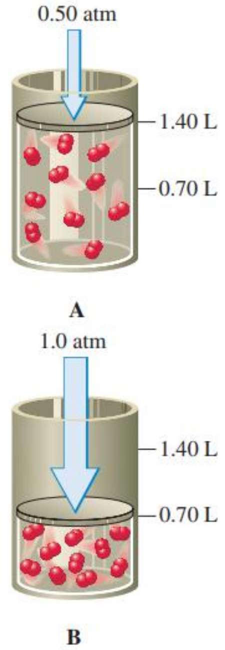


Charles's law:

$$\frac{V}{T} = \text{constant} \qquad \text{(for a given amount of gas at a fixed pressure)}$$

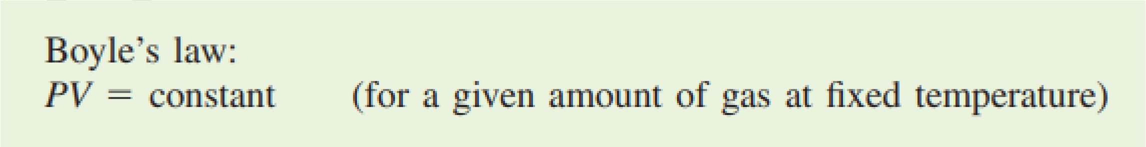
2-3-Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in the figure



Unlike the P-T and V-T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P_1V_1 = P_2V_2$$


Boyle's law:
PV = constant (for a given amount of gas at fixed temperature)

2-4-The Pressure of a Mixture of Gases: Dalton's Law

Each individual gas in a mixture exerts the same pressure that it would exert if it present alone in the container(figure).

The pressure exerted by each individual gas in a mixture is called its **partial pressure**.

This observation is summarized by Dalton's law of partial pressures: The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases:

$$P_{Total} = P_A + P_B + P_C + \ldots = \Sigma_i P_i$$

The partial pressure of gas A is related to the total pressure of the gas mixture via its mole fraction (X):

$$P_A = X_A \times P_{Total} \qquad \text{where} \qquad X_A = \frac{n_A}{n_{Total}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

3-The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's or Gay Lussac's law: P T = constant at constant V and n
- Charles's law: V T = constant at constant P and n
- Avogadro's law: V n = constant at constant P and T

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

Ideal gas law:

$$PV = nRT$$

where P is the pressure of a gas,

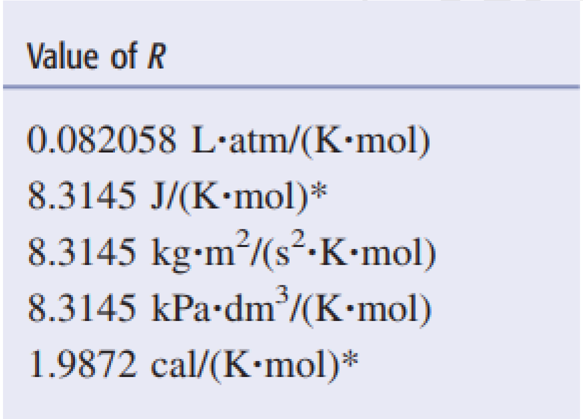
V is its volume,

n is the number of moles of the gas,

T is its temperature on the kelvin scale

R is a constant called the ideal gas constant or the universal gas constant.

The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being



Value of R
0.082058 L·atm/(K·mol)
8.3145 J/(K·mol)*
8.3145 kg·m^2/(s^2·K·mol)
8.3145 kPa·dm^3/(K·mol)
1.9872 cal/(K·mol)*

4-The Density of a Gas

One mole of any gas behaving ideally occupies the same volume at a given temperature and pressure, so differences in gas density depend on differences in molar mass

We can rearrange the ideal gas law to calculate the density of a gas from its molar mass. Recall that the number of moles (n) is the mass (m) divided by the molar mass. Substituting for n in the ideal gas law gives

$$PV = \frac{m}{\mathcal{M}}RT \qquad \frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT}$$

Rearranging to isolate m/V gives:

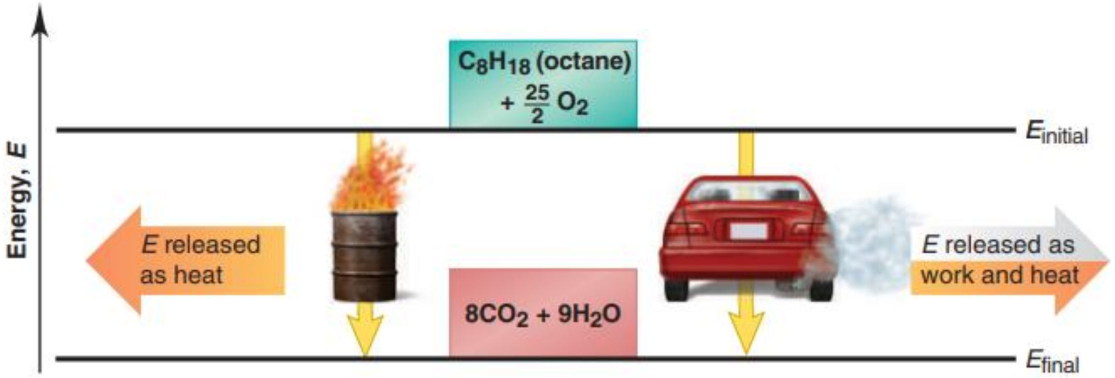
6-Heat and Work: Two Forms of Energy Transfer

Energy transferred from system to surroundings or vice versa appears in two forms:

1. **Heat.** Heat or thermal energy **(**symbolized by **Q)**: is the energy transferred as a result of a difference in temperature between the system and the surroundings.

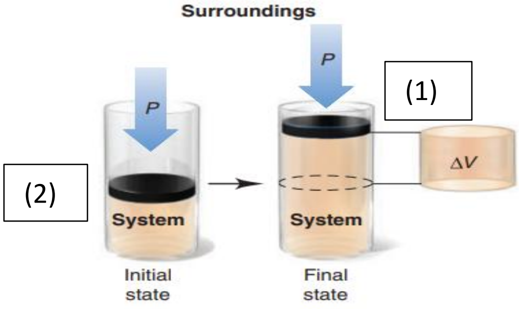
For example, energy in the form of heat is transferred from hot soup (system) to the bowl, air, and table (surroundings) because they are at a lower temperature.

2. **Work**. All other forms of energy transfer involve some type of work **(w):** the energy transferred when an object is moved by a force. When you (system) kick a football, energy is transferred as work because the force of the kick moves the ball and air around it (surroundings). When you pump up a ball, energy is transferred as work because the added air (system) exerts a force on the inner wall of the ball (surroundings) and moves it outward.



Two different paths for the energy change of a system. Even though **q** and **w** for the two paths are different, DE is the same

let's consider a system represented by a perfect gas enclosed in a cylinder by means of a mobile piston



let's subject this system to an infinitesimal change that takes the piston from position 1 to position 2, resulting in a change dV in volume at P_{ext} , the work required is given by:

$$\partial W = -P_{ext}\, dV$$

for a finite displacement, the total work is equal to the sum of the elementary work, i.e.

$$W = \int_{V\,int}^{V\,fin} -P_{ext}\, dV$$

Remark

the inequality between the external pressure and the internal pressure determines the speed of the transformation and its type:

- if the external pressure is greater than the internal pressure, the process is compression
- if the external pressure is lower than the internal pressure, the process is expansion

6-1-The work of an irreversible process

the work of an irreversible process is given by the following formula:

$$W = \int_{V\,int}^{V\,fin} -P_{ext}\, dV$$

6-2-The work of a reversible process

a transformation is reversible if it takes place through a succession of equilibrium states that allow the previous state to be reverted to at any moment, then it takes a long time to achieve

The work is reversible if the external pressure P_{ext} is equal to the pressure P of the system represented by the perfect gas:

$$P_{ext} = P = \frac{nRT}{V}$$

The expression for reversible work is therefore:

$$W = -\int_{V\,int}^{V\,fin} P_{ext}\, dV = -\int_{V\,int}^{V\,fin} \frac{nRT}{V}\, dV$$

Example

a) For isobaric transformation (P = cste)

$$W_{12} = -\int_1^2 PdV = -P\int_1^2 dV = -P\,(V_2 - V_1)$$

b) For isothermal transformation (T = cste)

$W_{12} = -\int_1^2 PdV$;

P constant ; ideal gas **:** $PV = nRT$

$$\Longrightarrow \quad P = \frac{nRT}{V}$$

$$W_{12} = -\int_1^2 nRT\frac{dV}{V} = -nRT\int_1^2 \frac{dV}{V} = -\,nRT\ln\frac{V_2}{V_1}$$

$$\Longrightarrow \quad W_{12} = nRT\ln\frac{V_1}{V_2}$$

We have : $P_1V1 = nRT_1$

$P_2V_2 = nRT_2$

$$\Longrightarrow \quad \frac{P_1}{P_2} = \frac{V_2}{V_1} \qquad \text{so} \qquad W_{12} = nRT\ln\frac{P_2}{P_1}$$

c) For isochoric transformation (V = cste)

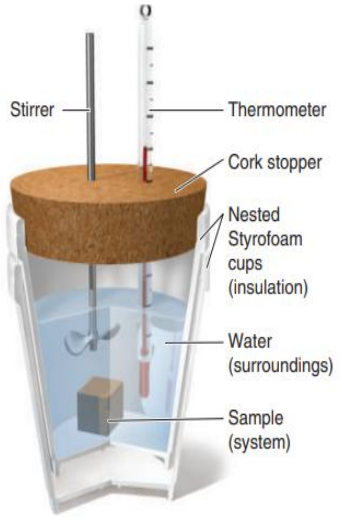
$dV = 0$ so $W_{12} = -\int_1^2 PdV = 0$

II-Calorimetry

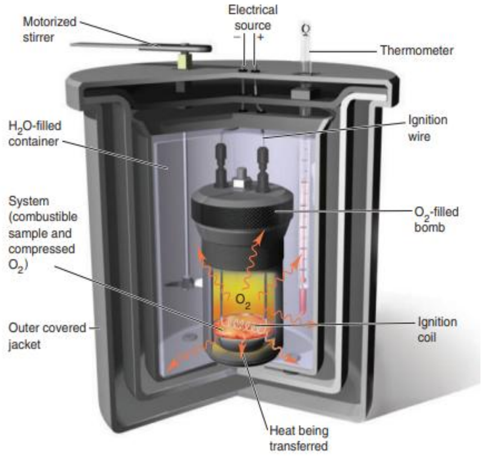
One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry.

Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter).

The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity).



Constant-Pressure Calorimeter



Constant-Volume Calorimeter

given that the calorimeter is an isolated system, this means that there is no exchange of matter and energy (work or heat) with the outside world, hence the calorimetry relation:

$$\boldsymbol{\Sigma Q_i = 0}$$

Q_i represents the different quantities of heat exchanged between the i substances

1- amount of heat:

if we bring a container of water close to a gas burner, the temperature will rise; this rise in temperature is due to the fact that the water has absorbed a certain amount of heat

or:

Q is the amount of heat absorbed by the substance of mass m when its temperature rises from T_1 to T_2, then:

$$\boldsymbol{Q = m\,c\,\Delta T = m\,c\,(T_2 - T_1)}$$

c: mass heat or specific heat is the quantity of heat (Q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin) of 1g substance exprimed in ($cal.g^{-1}.K^{-1}$)

The Equation says that when the object gets hotter, that is, when ΔT (T_{final} - $T_{initial}$) is positive, $q > 0$ (the object absorbs heat).

And when the object gets cooler, that is, when ΔT is negative, $q < 0$ (the object releases heat).

1-The heat capacity (C)

The heat capacity (C) of a sample of substance is the quantity of heat needed to raise the temperature of the sample of substance one degree Celsius (or one kelvin).

$$\mathbf{C = m.c}$$

C: heat capacity

c: specific heat capacity

M: substance mass

Remark

if the quantity of substance is expressed in moles the heat capacity (C) would be called the molar heat capacity and expressed in (J/mol.K) or (cal/mol.K)

the heat capacity (C) becomes: $\mathbf{C = n.c}$

3-calorimeter water value (μ)

this is the fictitious (assumed) **μ** mass of water which would have the same heat capacity as the calorimeter

$$\mu = \frac{C_{cal}}{c_{water}}$$

C_{cal} : heat capacity

C_{water} : specific heat capacity is 4.185 J/g.°C or 4185 $J.Kg^{-1}.K^{-1}$

4-expressing the amount of heat:

4-1-heating or cooling:

When heat is exchanged as a result of an increase in temperature (heating) or a decrease in temperature (cooling), the quantity of heat is given by the following formulae:

$$\mathbf{Q = C.\Delta T}$$

$$\mathbf{Q = m.c.\Delta T = n.c'.\Delta T}$$

C = heat capacity ($J.K^{-1}$ or $cal.K^{-1}$), m: mass (Kg)

c = specific heat capacity ($J.K^{-1}.Kg^{-1}$) or ($cal.K^{-1}.Kg^{-1}$),

c'= molar specific heat ($J.mol^{-1}.K^{-1}$)

$\Delta T = T_{final} - T_{initial}$ (K or °C)

- at constant pressure in a calorimeter:

$$Q_p = m.c_p.\Delta T = n.c'_p.\Delta T$$

c_p, c'_p: specific heat and molar specific heat capacity respectively at constant pressure

- at constant volume:

$$Q_v = m.c_v.\Delta T = n.c'_v.\Delta T$$

c_v, c'_v: specific heat and molar specific heat capacity respectively at constant volume

4-2- change of physical state:

when the heat exchange is due to a change of physical state, then the expression for the quantity of heat is:

$$Q = m.\ L$$

m: substance mass (Kg)

L : latent heat of the substance ($J.Kg^{-1}$) ($cal.g^{-1}$)

it is the heat absorbed or released that accompanies a change in the body's state in relation to the quantity of matter involved in this physical transformation, which takes place at a constant temperature.

For example:

L_f: latent heat of fusion (melting)

L_v: latent heat of vaporisation

The different physical transformations

III-real gas behaviour

Thus far, the ideal gas law, **PV = nRT**, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws.

In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of PV = nRT can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, Vm) to the molar volume of an ideal gas at the same temperature and pressure.

This ratio is called **the compressibility factor (Z)** with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior.

Figure shows plots of Z over a large pressure range for several common gases:

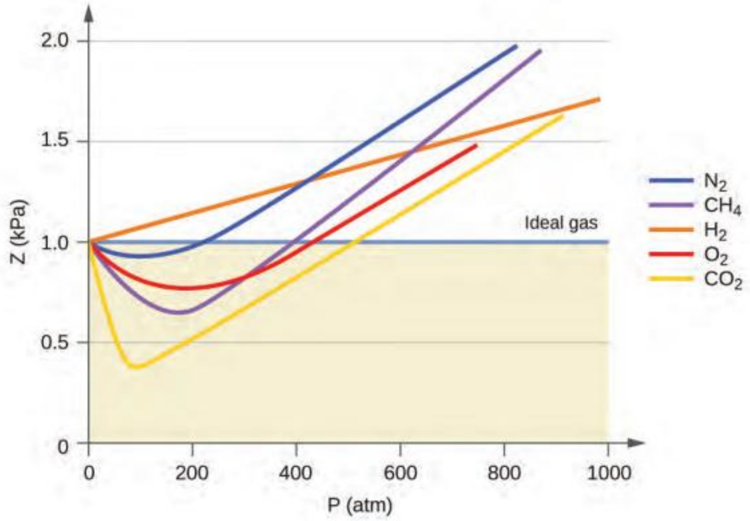
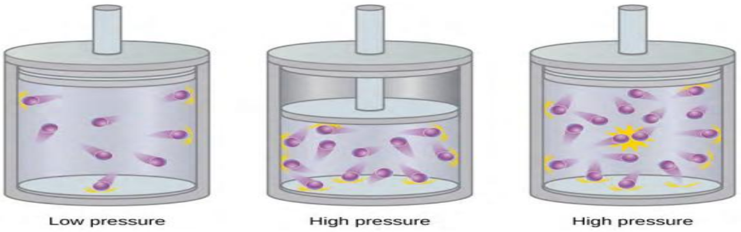


Figure: A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.



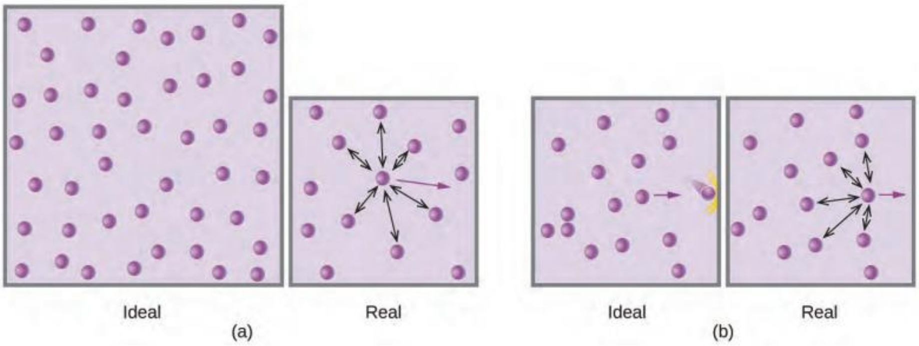
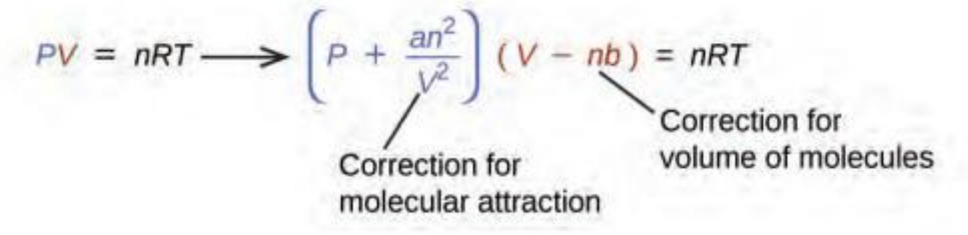


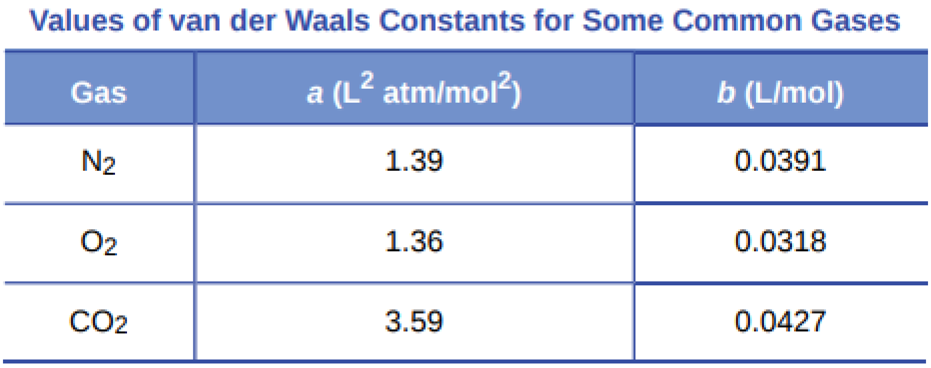
Figure: (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist **Johannes van der Waals** in 1879. The van der Waals equation improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.



Equation of Johannes van der Waals

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is $\mathbf{n^2a / V^2}$, and the "correction" to the volume is nb. Note that when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, PV = nRT. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table



Values of van der Waals Constants for Some Common Gases

Gas	*a* (L^2 atm/mol^2)	*b* (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427

At low pressures, the correction for intermolecular attraction, a, is more important than the one for molecular volume, b. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by PV = nRT over a small range of pressures.

III-liquid and solid properties:

1-properties of liquid: surface tension and viscosity:

You have seen that molecules tend to escape the liquid state and form a vapor. The vapor pressure is the equilibrium partial pressure of this vapor over the liquid; it increases with temperature. The boiling point is the temperature at which the vapor pressure equals the pressure applied to the liquid. Both vapor pressure and boiling point are important properties of a liquid.

a- Surface Tension:

Intermolecular forces have different effects on a molecule at the surface compared with one in the interior (Figure):

- An interior molecule is attracted by others on all sides.
- A surface molecule is attracted only by others below and to the sides, so it experiences a net attraction downward.

Therefore, to increase attractions and become more stable, a surface molecule tends to move into the interior. For this reason, a liquid surface has the fewest molecules and, thus, the smallest area possible. In effect, the surface behaves like a "taut skin" covering the interior.

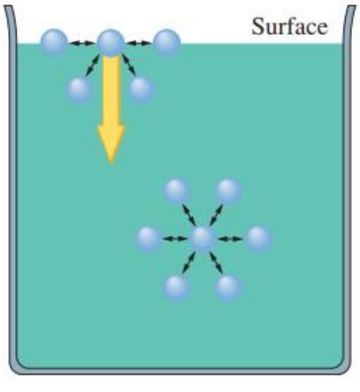
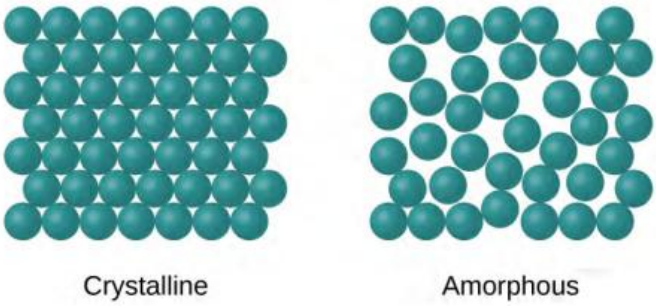


FIGURE: Explaining surface tension Note that a molecule at the surface experiences a net force toward the interior of the liquid, whereas a molecule in the interior experiences no net force

b- **Viscosity :** Viscosity is the resistance of a fluid to flow, and it results from intermolecular attractions that impede the movement of molecules around and past each other. Both gases and liquids flow, but liquid viscosities are much higher because the much shorter distances between their particles result in many more points for intermolecular forces to resist the flow of nearby molecules. Let's examine two factors—temperature and molecular shape—that influence viscosity:

2- properties of solid: When most liquids are cooled, they eventually freeze and form **crystalline solids**, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called **amorphous solids** or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged



The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous)

We can divide solids into two broad categories:

• Crystalline solids have well defined shapes because their particles—atoms, molecules, or ions—occur in an orderly arrangement. Examples are diamond and graphite

• Amorphous solids have poorly defined shapes because their particles lack an orderly arrangement throughout the sample. Examples are rubber and glass