Lecture 4

Effusion and diffusion

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2-9 Effusion and diffusion التدفق والانتشار

The English chemist Thomas Graham, professor at the University of Glasgow and the University of London (1805-1869), discovered in 1846, after conducting several experiments on measuring the speed of gas flow (Effusion), that the speed of effusion is inversely proportional to the square root of the density of the gas. The process of effusion means the process of escaping gases from the container that contains them through a very small hole. Figure 2-7 shows the difference between the phenomena of effusion and diffusion.

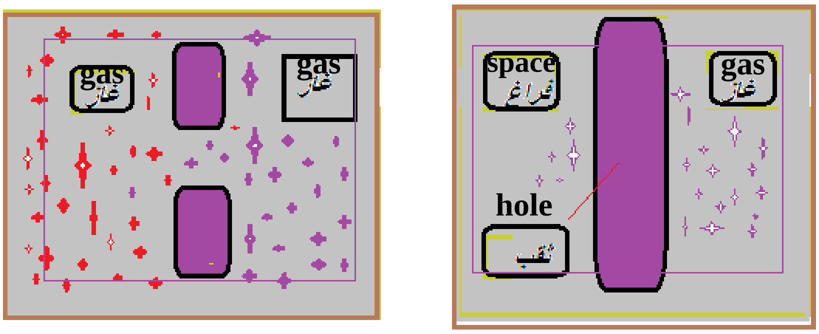

Figure 2-7: The difference between diffusion and effusion.

It is known that the density of a gas is proportional to the molecular weight of the gas, so Graham's law of effusion can take the following form: (The gas effusion rate is inversely proportional to the square root of the molecular weight of the gas)

The mathematical expression of Graham's law of effusion according to equation 2-40 is as follows:

$$\frac{1}{m} \propto Rate \qquad 2-40$$

Argon gas (Ar) effusion faster than krypton gas (Kr), so the ratio of the effusion speeds of the two gases will be as follows:

$$\frac{Rate_{Ar}}{Rate_{kr}} = \sqrt{\frac{m_{kr}}{m_{Ar}}} \qquad 2-41$$

Accordingly, Graham's effusion law can be used to calculate the molecular weight of an unknown gas when measuring its effusion and comparing it with the effusion speed of another known gas, such as Helium, as follows:

$$\frac{Rate_x}{Rate_{He}} = \sqrt{\frac{m_{He}}{m_x}} \qquad 2-42$$

The phenomenon very close to gas effusion is the diffusion of gases, as the diffusion phenomenon represents the movement of gas particles through another gas, and comparing the diffusion speeds of gases shows that it can be described quantitatively by Graham's law according to the following equation:

$$\frac{1}{\sqrt{m}} =\propto \ Rate\ of\ diffusion \qquad 2-43$$

What is mentioned in Equation 2-43 about the phenomenon of diffusion can be applied when comparing the diffusion of two gases.

2-10 Collision theory

We mentioned at the beginning of this lecture that there are other names for the kinetic theory of gases, including the collision theory. This theory assumes that gas molecules are solid circular balls and that there is no interference between them (no repulsive or attractive forces). There are two types of collisions:

1- Collision that occurs between similar gas molecules (belonging to the same gas)

2- Collision that occurs between different gas molecules ((belonging to different gases)

A collision may occur between a moving molecule and a fixed one or between two moving molecules. The collision diameter is known as a special property of the molecule, which is the distance between the centers of the two colliding molecules and the closest proximity between them (see Figure 2-8).

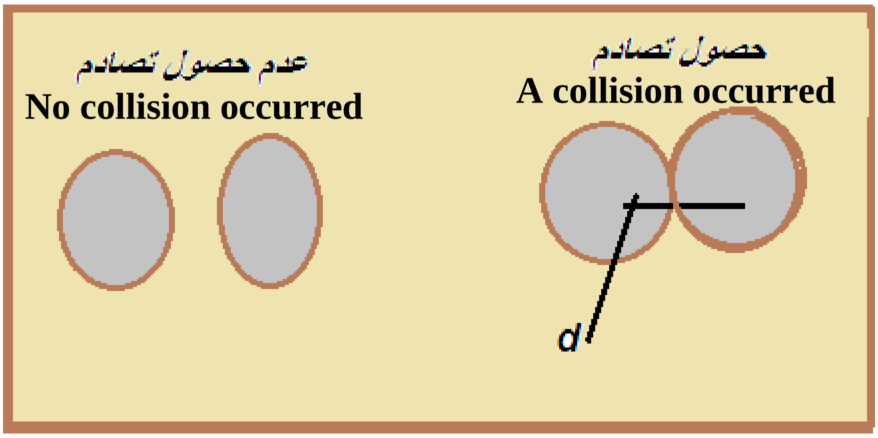

Figure 2-8: Collision Diameter.

If we assume that a gas molecule of mass m and diameter d moves through a cylinder of diameter d (radius r) containing a large number of gas molecules at break, then each collision will cause a gas molecule to be ejected (see Figure 2-9).

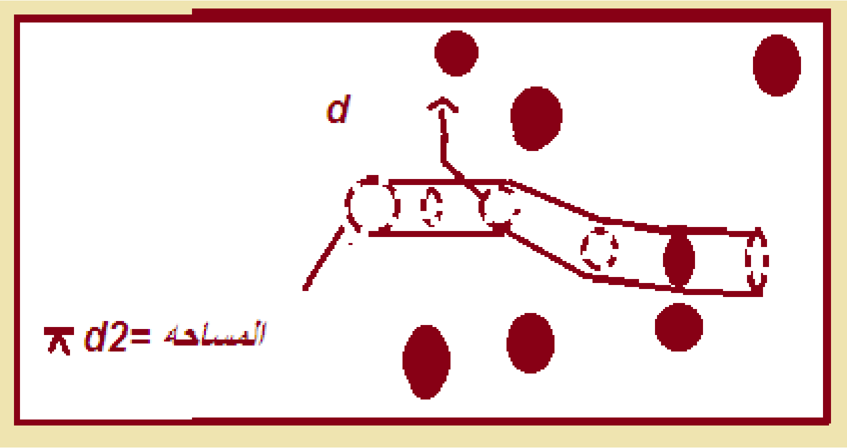

Figure 2-9: Collision inside a hypothetical tube.

If the time of movement of the molecule inside is equal to Δt, then the collision frequency is equal to the number of collisions per unit time. The number of molecules inside is equal to the volume of the tube multiplied by the density of the molecules inside the tube. The value of the collision frequency that occurs between similar gas molecules can be found from the following equation.

$$Z_{11} = (2)^{1/2}\,\pi\,\sigma^{2} C^{-} n \qquad 2\text{-}44$$

While its value when there is a collision between molecules of two different gases according to the equation:

$$Z_{12} = 1/(2)^{1/2}\,\pi\,\sigma^{2} C^{-} n^{2} \qquad 2\text{-}45$$

It is clear from equations 2-44 and 2-45 that the collision frequency increases with increasing temperature while the volume remains constant, because any increase in temperature leads to an increase in the speed of the molecules. Increasing the pressure also leads to an increase in the collision frequency, although the speed of the molecules remains constant, because the density of the molecules increases. The value of Z for a nitrogen molecule at 25 °C and a pressure of 1 atmosphere is equal to $7 \times 10^{9}\ S^{-1}$, which means that a molecule of this gas collides 7 billion times every second.

Figure 2-10 shows the effective collision cross section, represented by the symbol σ, which represents the effective collision area and is also called the collision cross section.

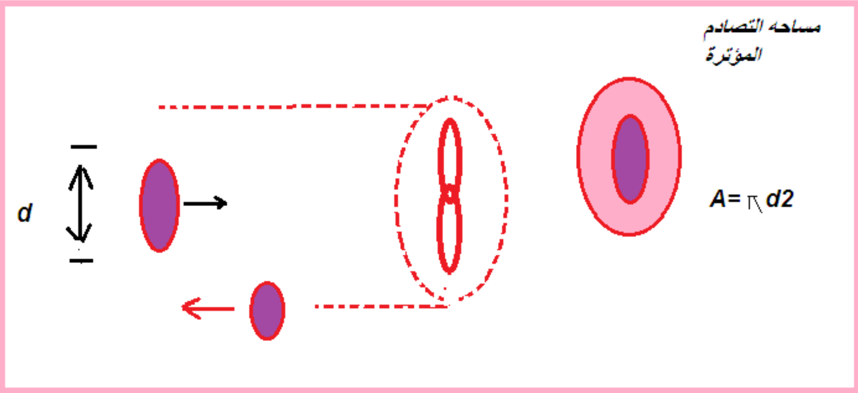

Figure 2-10: Cross section of collision.

Table 2-2 shows the collision cross section for some molecules.

σ/nm^2	Molecule
0.93	Chlorine
0.88	Benzene
0.52	Carbon dioxide
0.46	Methane
0.43	Nitrogen
0.40	Oxygen
0.36	Argon
0.27	Hydrogen
0.21	Helium

2-11 The mean free path متوسط المسار الحر

The mean free path is defined as the average distance traveled by a molecule between collisions and is symbolized by the symbol λ.

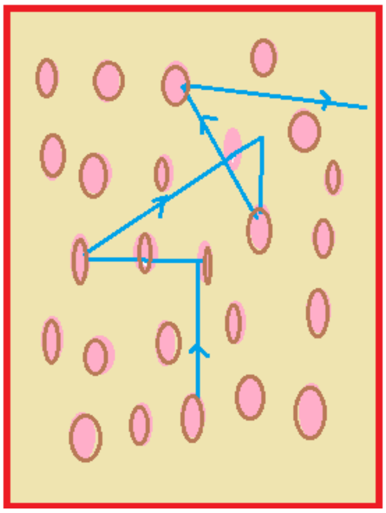

Figure 2-11: Mean free path.

If the number of collisions of a molecule is equal to Z, then it will take a time equal to 1/Z from its first collision until its last collision, and the distance it has traveled will be equal to (1/Z x C). Accordingly, the mean free path of the molecule will be equal to

$$\lambda = \frac{C}{Z} \qquad 2-47$$

$$\lambda 11 \;\; = 1/\,(2)^{1/2} \pi\, \sigma^2 n$$

$$\lambda \quad = (2)^{1/}2/\pi\, \sigma^2 n^2$$

Doubling the pressure reduces the mean free path by half. The mean free path of a nitrogen gas molecule at a pressure of 1 atmosphere is 70 nanometers. That is, it is about a thousand times larger than the diameter of the molecule.

The distance a molecule travels between collisions is calculated by the number of molecules in a given volume of gas, not by the speed at which the molecules move. Comparing the mean free path value to the diameter of the molecule, where:

$$\lambda \gg d$$

It shows that the distances between gas molecules are very large.

2-12 Real Gas

Ideal gases have been defined as those gases to which the general gas equation (PV=nRT) applies for all pressures and temperatures. In reality, there is no ideal gas, as the components of gases show clear deviations from the ideal properties. Gases such as hydrogen, nitrogen, and carbon dioxide do not apply to the ideal gas equation, so they are considered non-ideal or so-called real gases.

Real gases follow the ideal gas laws precisely. At low pressures and high temperatures (not very high, but moderate), real gases follow approximately the Boyle, Charles, Gay-Lussac, and Avogadro laws, given the equation of state for one mole of gas. However, when the pressure increases and the temperature decreases, the deviation from the ideal behavior becomes obvious.

Figure 2-12 shows the deviation of nitrogen and hydrogen gases at 0 ^{O}C and carbon dioxide at 40 ^{O}C from ideal behavior, noting that the value of the pressure multiplied by volume at one atmosphere pressure is equal to one in each case. The dotted line in Figure 2-12 represents the gas's compliance with the ideal gas laws. It shows that real gases exhibit significant deviations from ideal behavior, especially at high pressures.

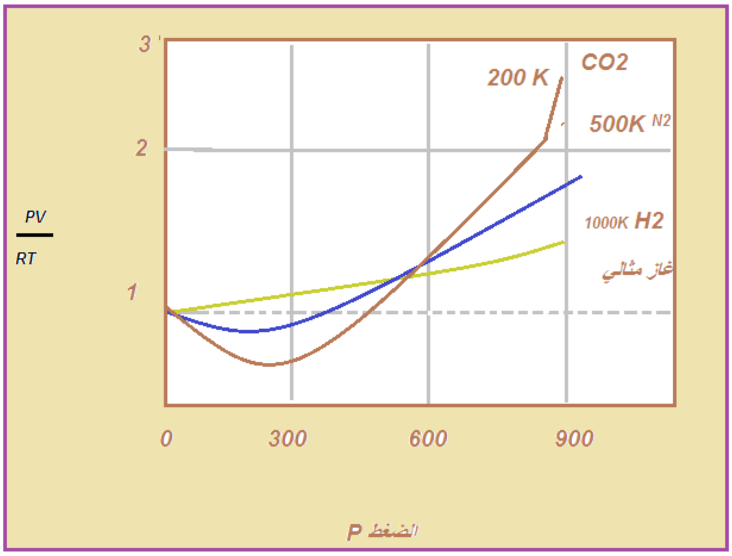

Figure 2-12: Deviation of real gases from ideal behavior.

The deviation from the behavior increases with decreasing temperature and increasing pressure.

When the pressure is at or below one atmosphere and the temperature does not approach the liquefaction temperature of the gas, the deviations from the ideal gas laws are only a few percent. Under these conditions, the equation of state and related equations can be used approximately to make some calculations in this regard, and (PV=RT) is relied upon for results in this regard at lower pressures and higher temperatures. We will discuss some factors that we will see have significant deviations in real gases.

1- **Compressibility factor معامل الانضغاطية**

The compressibility coefficient is defined according to the following equation:

$$Z=PV/\ nRT \qquad 2\text{-}49$$

This factor is equal to 1 in ideal gases, and the deviation from this number is the measure of deviation from ideal behavior.

Deviation from ideal properties is determined by temperature and pressure. Figure 2-13 shows the relationship between compressibility and atmospheric pressure for a group of gases. It is noted that there is a deviation from the value (1) of the compressibility coefficient, and that this deviation is in two directions, as the upper lines represent the deviation from the value given by the ideal gas, while the lower lines represent the negative deviation from that.

Positive diffraction means that the repulsive force between the molecules is dominant, while negative diffraction means that there is attraction between the gas molecules.

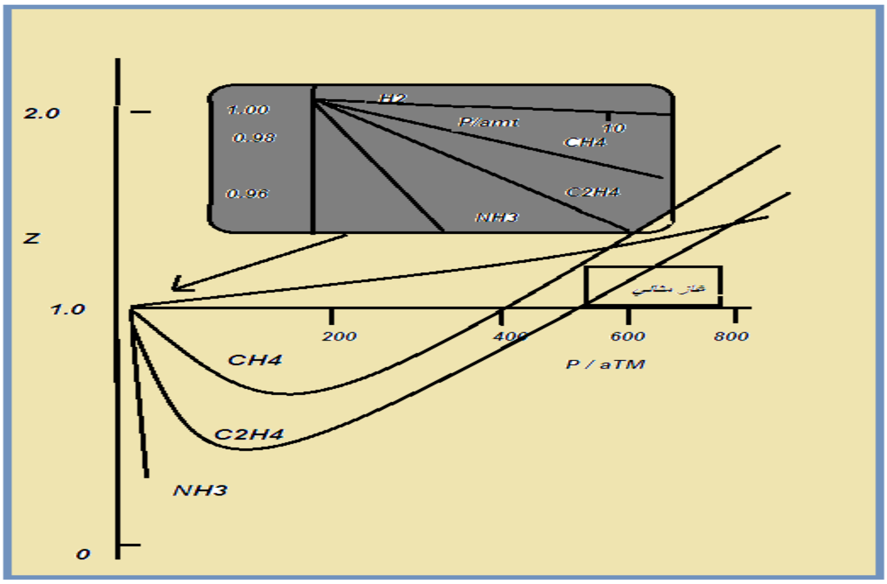

Figure 2-13: The relationship of the compressibility coefficient to the pressure for a group of gases at 0°C.

2- Critical point الدرجة الحرجة

Gases can liquefy when the pressure increases and the temperature does not decrease. The diagram shown in Figure 2-14 shows the liquefaction of a gas at a constant temperature, where the volume of the gas decreases as the pressure increases until all or part of the gas turns into a liquid.

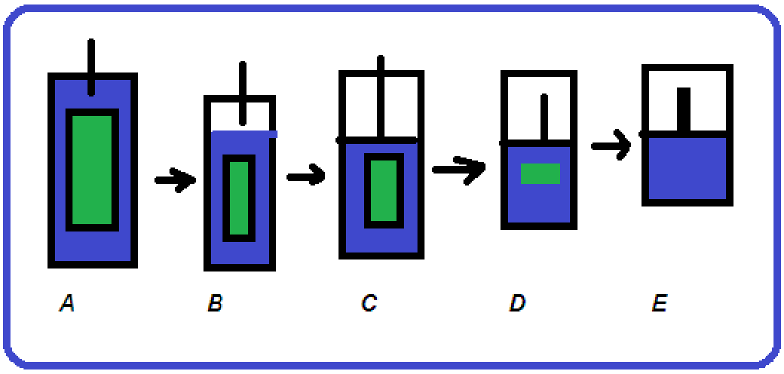

Figure 2-14: Liquefaction of a gas at a constant temperature.

Figure 2-15 shows the relationship between the pressure and volume of a gas at constant temperature and is called the thermodynamic diagram for the liquefaction of gases.

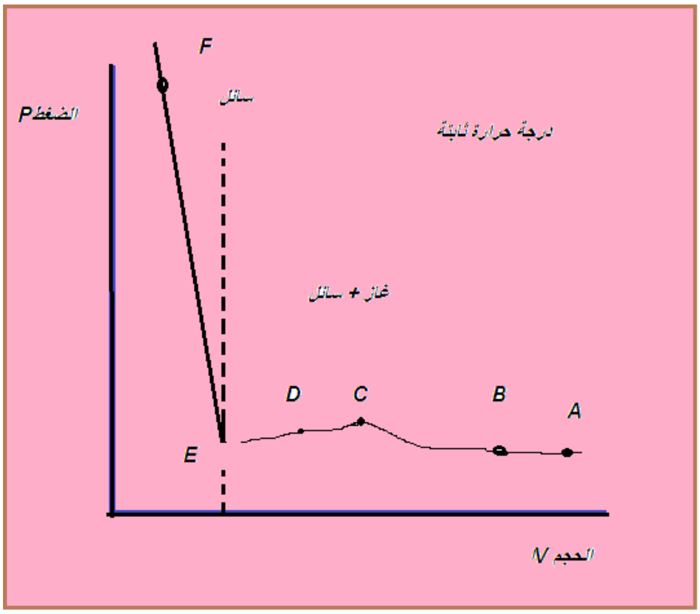

Figure 2-15: Thermal isotherm diagram for gas liquefaction.

It is also possible. Gases liquefy when the pressure increases and the temperature decreases. Some gases, such as carbon dioxide, can be liquefied at room temperature when the pressure increases, but when the temperature reaches 304.16 Kelvin, the gas cannot be liquefied, no matter how much pressure is applied to it. This temperature is called the critical temperature. The critical temperature is defined as the temperature above which the vapor cannot be converted into a liquid, no matter how much pressure is applied to that gas (sometimes it can be converted into a solid when sufficient pressure is applied, but it does not convert into a liquid). Figure 2-16 shows a test tube containing water at different temperatures. It is clear from the figure that in the tube whose temperature is 374°C, which is higher than the critical temperature, there is no liquid water, but only water vapor.

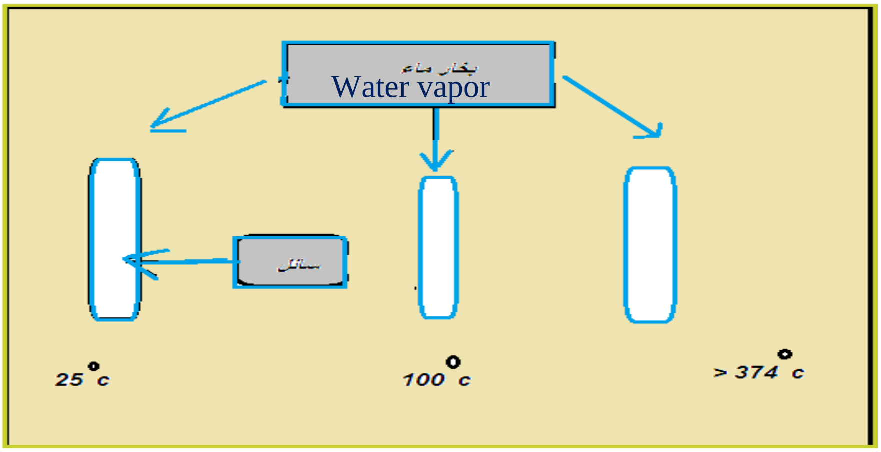

Figure 2-16: Examples of water at different temperatures.

Table 2-5: shows the critical temperature of some materials.

The material	The critical temperature (°C)
NH_3	132
O_2	-119
CO_2	31.2
H_2O	374

Critical Pressure represents the vapor pressure of a substance at the critical temperature. Table 2-6 shows the critical pressure of some of the substances defined at the critical temperature.

The material	Critical Pressure (atm)
NH_3	111.5
O_2	49.7
CO_2	73.0
H_2O	217.7

In the figures that express the thermodynamic relationships of a particular substance, the term critical point is used. The critical point is defined as the point at which the substance is at the critical temperature and pressure. Critical molar volume is not equal to the volume of one mole of the substance at the critical temperature and critical pressure.

Figure 2-17 shows the thermal isotropy (constant temperature) of a real gas model. Note that the critical point is an inflection point. Therefore, the equation for the change in pressure to volume at constant temperature is as follows:

$$(\partial p/\partial v)_T = 0 \qquad 2-50$$

$$(\partial p^2/\partial v^2)_T = 0 \qquad 2-51$$

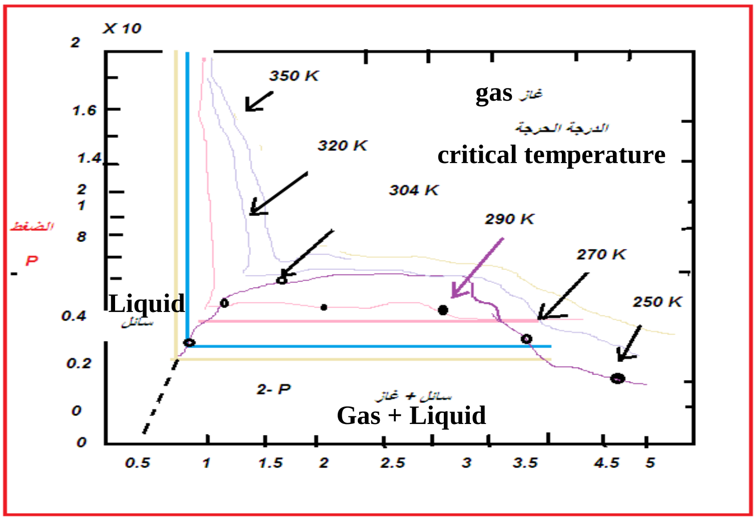

Figure 2-17: Thermal isoform of a real gas model (CO_2).

2-13 Deviation from the general law gases and the effect of attractive and repulsive forces

The ideal gas laws are derived from the kinetic theory based on two important points:

The first is ignoring the size of the molecules compared to the total volume. The second is that the molecules do not attract each other, and because both points cannot be applied to real gases, they show a deviation from the ideal behavior.

If gas molecules do not attract each other, then gas liquefaction becomes impossible, but in fact any gas can be transformed into a liquid using low temperatures and high pressures. One of the essential properties of a liquid is adhesion, which is due to the attraction between molecules. The phenomenon of molecular attraction is as clear in gases as it is in liquids.

The change in temperature is known as the Joule and Thomson effect, which causes a decrease in the speed and hence the kinetic energy of the molecules. This happens because energy must be lost to overcome the forces of molecular attraction when the gas expands during its passage through the porous plug. Figure 2-18 shows that the repulsive forces are zero when the compressibility coefficient is equal to 1 (the ideal gas case as explained earlier). The increase in the compressibility coefficient value with increasing pressure to more than 1 for some hydrogen gas behavior. On the contrary, there are other gases such as methane gas where the compressibility coefficient is less than 1 when the pressure increases up to 150 atmospheres. This means that its molecules are attracted to each other. We note that nitrogen gas has both properties but at different pressures, as nitrogen molecules are attracted to each other as the pressure increases up to 140 atmospheres. Then they begin to repel each other after they intersect with the ideal gas line at a pressure of 140 atmospheres.

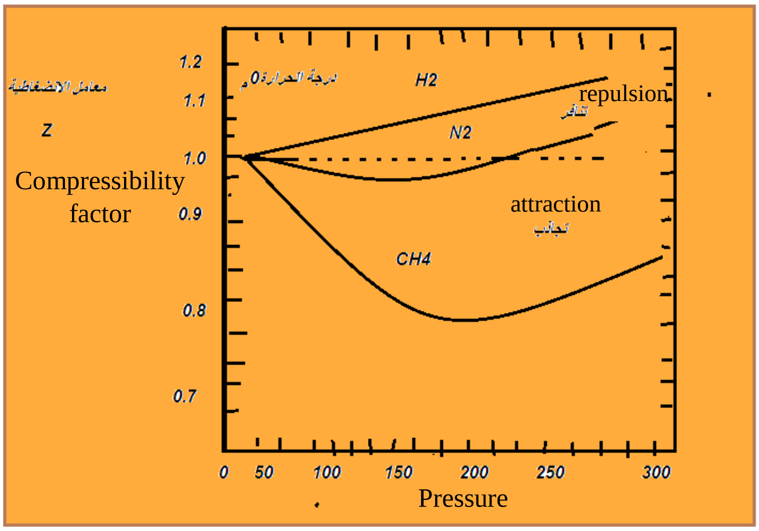

Figure 2-18: Effect of compressibility coefficient on attractive and repulsive forces.

The forces between molecules (or atoms) are usually represented in terms of the potential energy diagram (Figure 2-19), which represents a graph of the joint potential energy of two gas molecules as a function of the distance between them.

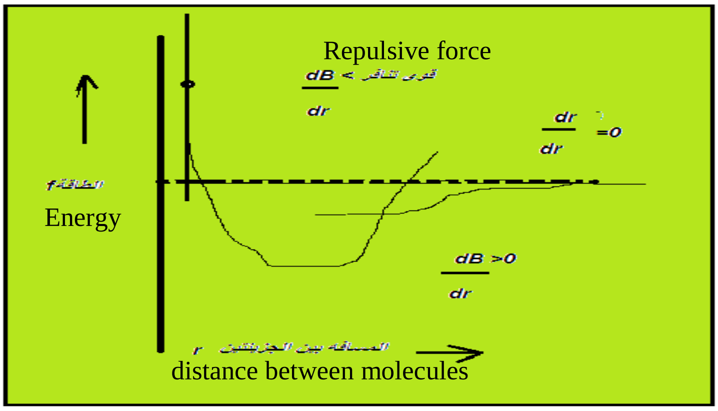

Figure 2-19 Potential energy diagram for two gas molecules.

The upper curve in Figure 2-19 represents the repulsion curve. In order for the two molecules to attract each other, work must be done to counteract the repulsive force. Therefore, the potential energy of the system increases at a certain distance. The curve rises sharply, indicating a rapid increase in the repulsive energy. The effect of attraction on the potential energy is shown by the dotted curve. Because the force of attraction increases, the potential energy increases—but negatively—the closer the two molecules are to each other.

The shape of the curves shows that the increase in attractive forces is less rapid as the molecules approach each other than as the repulsive forces increase. The final joint potential energy of the molecules is shown by the undotted curve in Figure 2-19 and represents the sum of the repulsive and attractive forces. The quantitative details of this curve vary from one molecule to another, but the general shape of the curve is generally the same. When the distance between the two molecules reaches such that the potential energy becomes equal to zero, the repulsive and attractive forces are balanced. This distance is then called the collision diameter.