

CHEM2100J Chemistry Autumn2024

Chapter 05 Gases



Dr. Milias Liu

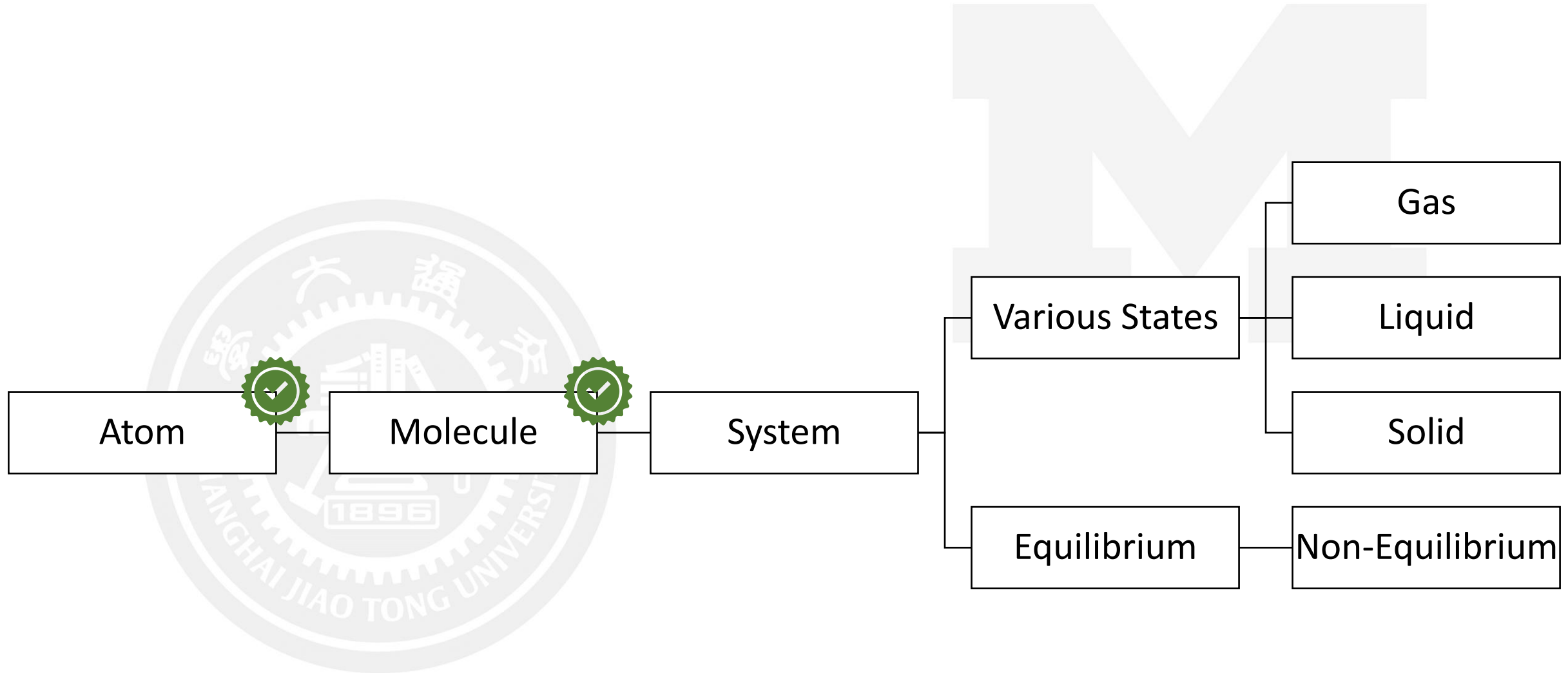
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The Journey So Far



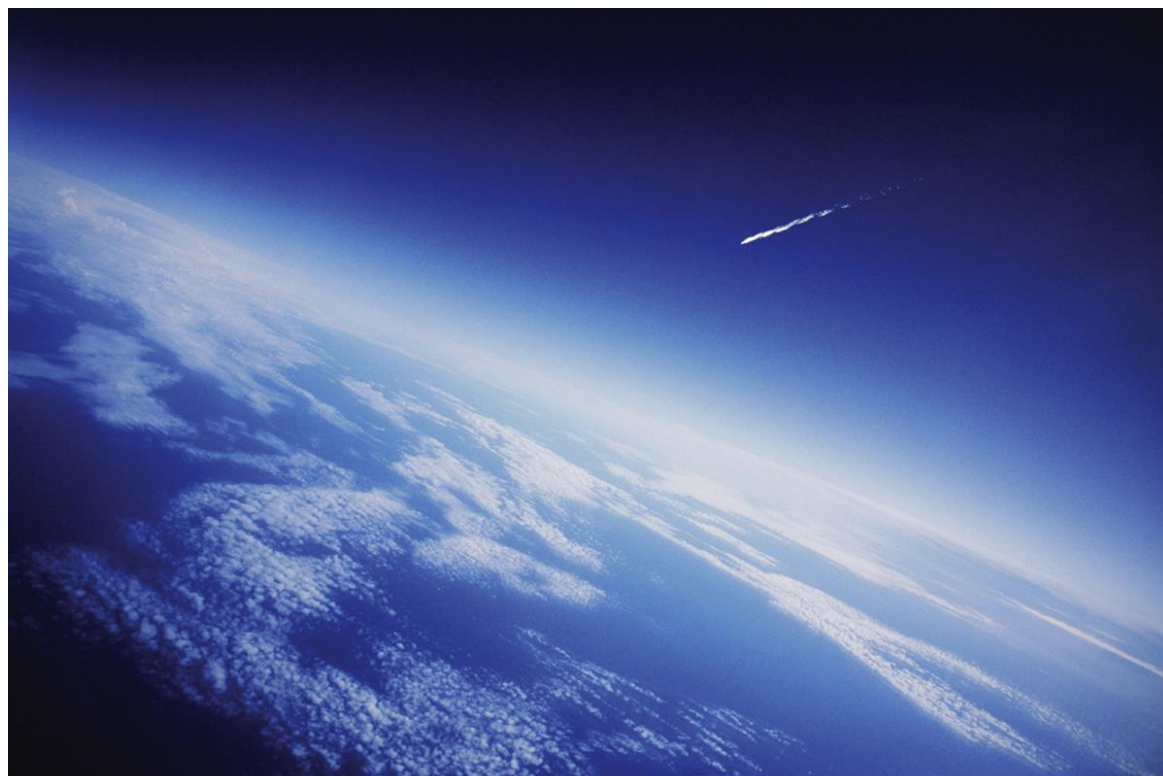


Figure 3A.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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A thin layer of gas is held by gravity to the Earth's surface.

Half of its mass lies within 5.5 km above our heads.

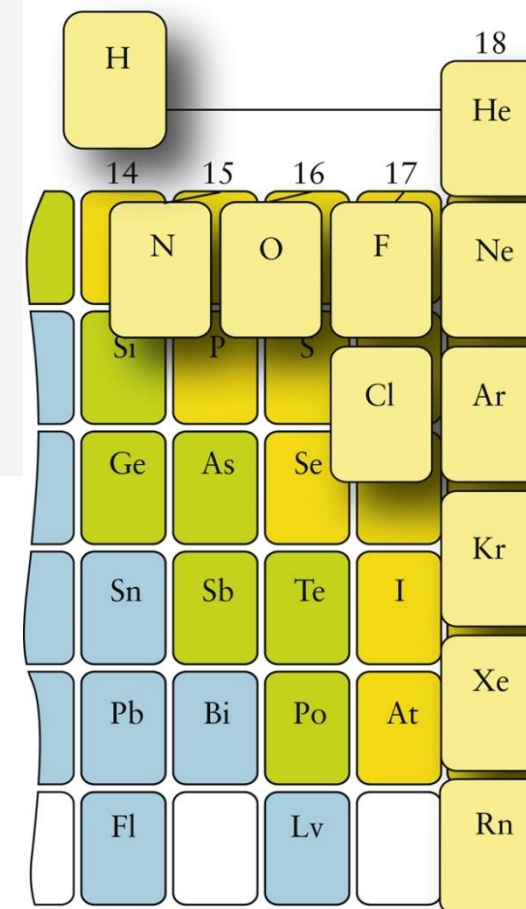
Viewing Earth as a basketball, the atmosphere is only 1 mm thick. This layer shields us from harmful radiation and supplies us with oxygen, nitrogen, carbon dioxide, and water.

The Nature of Gases

Eleven elements are gases under normal conditions.

Low molar mass compounds such as carbon dioxide, hydrogen chloride are also gases.

A remarkable characteristic of gases is that many of their physical properties are very similar, particularly at low pressures, regardless of the identity of the gas.



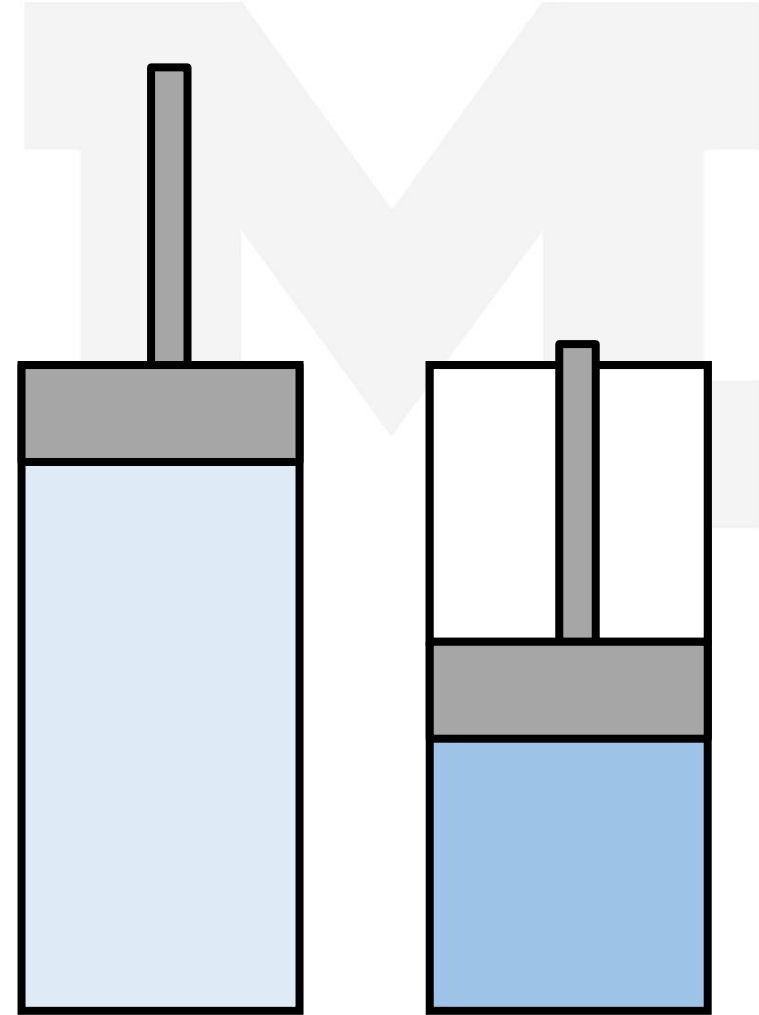
	H				18	He
	14	15	16	17		
	N	O	F			Ne
	Si	P	S	Cl		Ar
	Ge	As	Se			Kr
	Sn	Sb	Te	I		Xe
	Pb	Bi	Po	At		
	Fl		Lv			Rn

Figure 3A.2
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Observing Gases: Compressibility



The observation that gases are more compressible than solids and liquids suggests that there is a lot of space between the molecules of gases.

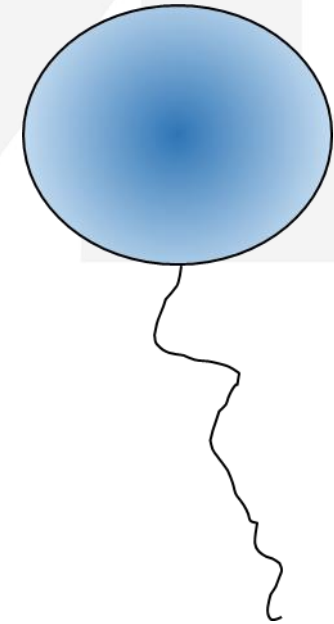


Observing Gases: Motion

Releasing air from an inflated balloon, we know the gas expands rapidly to fill the space available to it.

Also, because balloons are spherical, we can infer that the motion of the molecules is chaotic, not favouring any single direction.

Our first primitive picture of a gas could be that gases are a collection of widely spaced molecules in ceaseless rapid chaotic motion.



The First Thing about Gas: Pressure

$$\text{pressure} = \frac{\text{force}}{\text{area}} \text{ or } p = \frac{F}{A}$$

The SI unit of pressure is Pascal (Pa):

$$1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2} = 1 \frac{\text{kg}}{\text{m} \cdot \text{s}^2}$$

Colliding gases exert a pressure on the sides of the container walls.

The more vigorous the motion, the stronger the force and hence the higher the pressure.

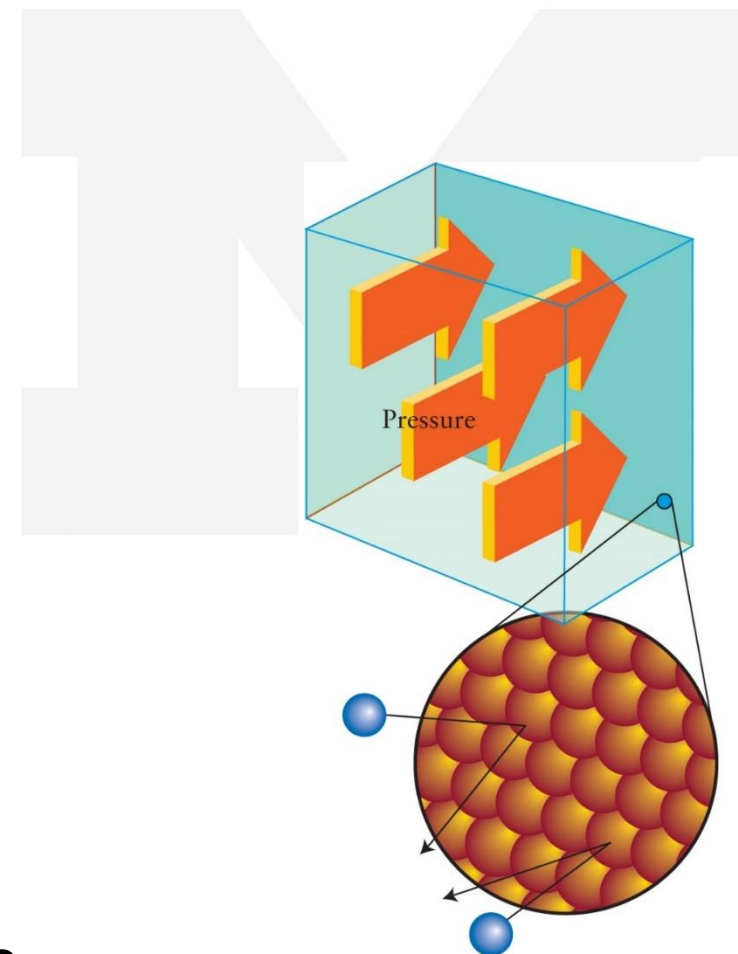


Figure 3A.3
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Measuring Pressure

A glass tube, sealed at one end, was filled with liquid mercury. The column was inverted into a pool of mercury. The mercury stopped falling when the weight of the falling mercury was matched by atmospheric pressure weight pushing against the pool of mercury.

$$p = d \cdot h \cdot g$$

d : density ($13\,534\text{ kg}\cdot\text{m}^{-3}$)

h : height

g : gravitational constant ($9.81\text{ m}\cdot\text{s}^{-2}$)

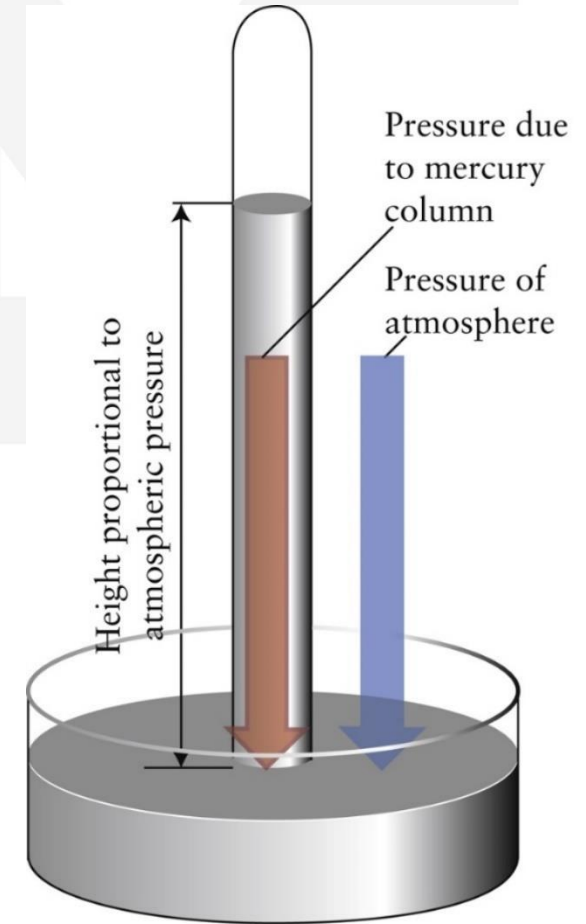


Figure 3A.4
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Alternative Units of Pressure




Although the SI unit of pressure is the pascal (Pa), there are several other units in common use.

When using mmHg and the aforementioned mmHg barometer, a conversion into Pa is not strictly necessary.

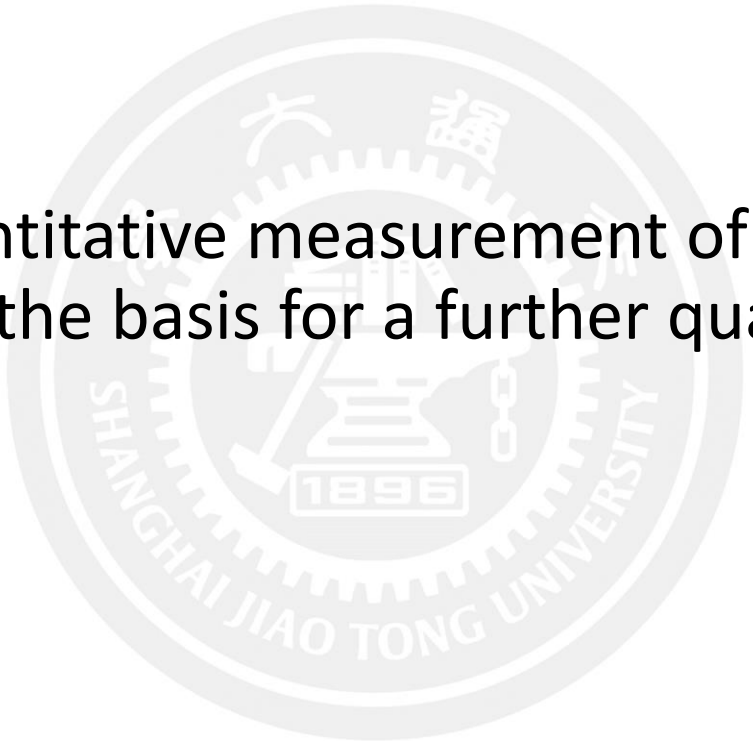
It is quite common and safe to use mmHg and Torr interchangeable.

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

$$\begin{aligned} 760 \text{ mmHg} &= 760.000123 \text{ Torr} \\ &\approx 760 \text{ Torr} \\ &= 1 \text{ atm} \\ &= 14.7 \text{ lbf}\cdot\text{in}^{-2} \text{ (PSI)} \\ &= 1.01325 \times 10^5 \text{ Pa} \\ &= 1.01325 \text{ bar} \end{aligned}$$

A large, light gray, stylized letter 'M' that serves as a background element on the right side of the slide.

Quantitative measurement of pressure, temperature, volume, mass, *etc.* are the basis for a further quantitative understanding of gas behaviour.

A large, light gray, circular logo of Shanghai Jiao Tong University, featuring a gear, a book, and the year '1896'.

Gas Law properties
include **pressure**,
volume, **temperature**,
and **moles**.

The first reliable measurements of gases were made by the Anglo-Irish scientist Robert Boyle in 1662.

- He examined the effect of pressure on volume.

150 years later, a new pastime, hot-air ballooning, motivated two French scientists, Jacques Charles and Joseph-Louis Gay-Lussac, to formulate additional gas laws.

- Charles and Gay-Lussac measured how the temperature of a gas affects its pressure, volume, and density.

The Italian scientist Amedeo Avogadro made a further contributions.

- He established the relation between the volume and the amount of molecules.
- He was then about to help establish the belief in the reality of atoms.

The Gas Laws



What are the
relationships between
 p , V , n , and T ?

$$pV \propto nT$$

p and V

If $p \uparrow$ then $V \downarrow$ **inverse**

p and n

If $n \uparrow$ then $p \uparrow$ **direct**

p and T

If $T \uparrow$ then $p \uparrow$ **direct**

T and V

If $T \uparrow$ then $V \uparrow$ **direct**

Boyle's Pressure Experiment

Boyle took a J-shaped tube, with the short end sealed, and poured mercury into the tube.

The more mercury he added, the more the trapped air was compressed.

He concluded that at constant temperature the volume decreases as the pressure increases:

$$\downarrow V \quad \uparrow p$$

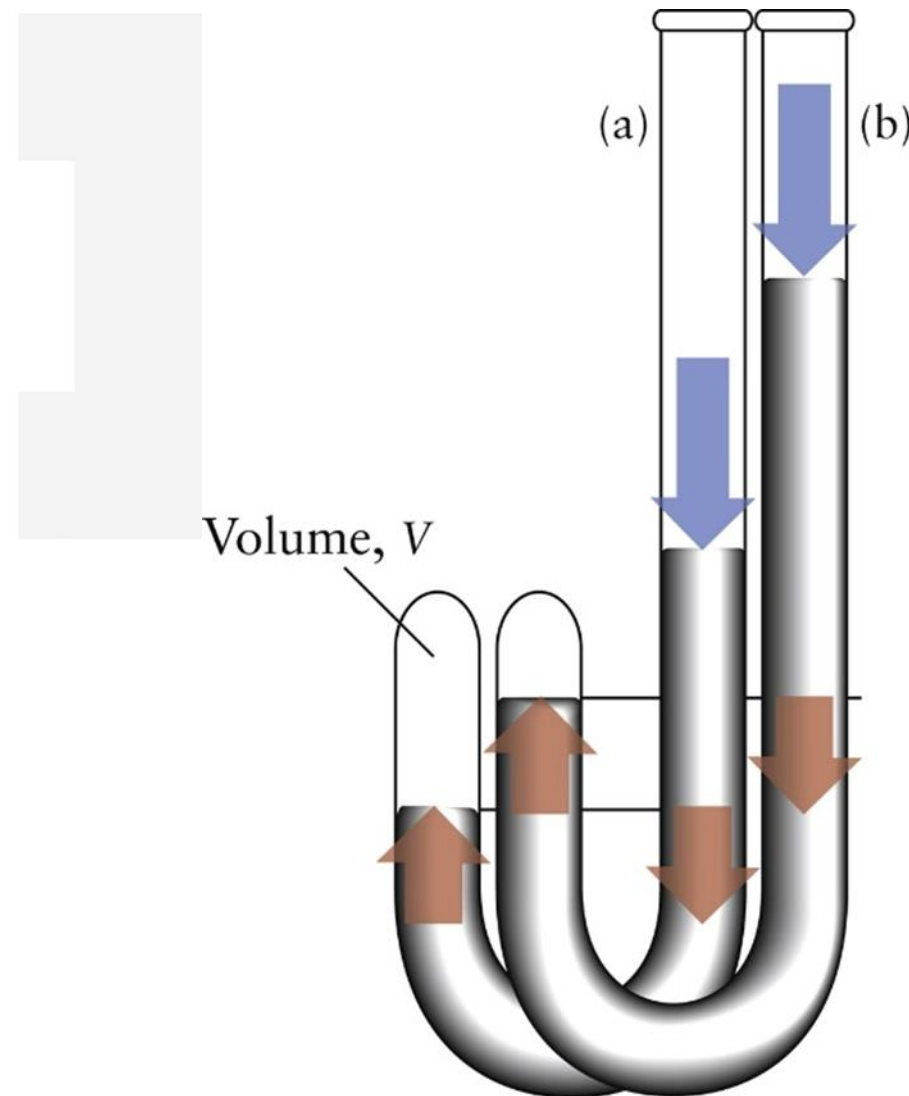
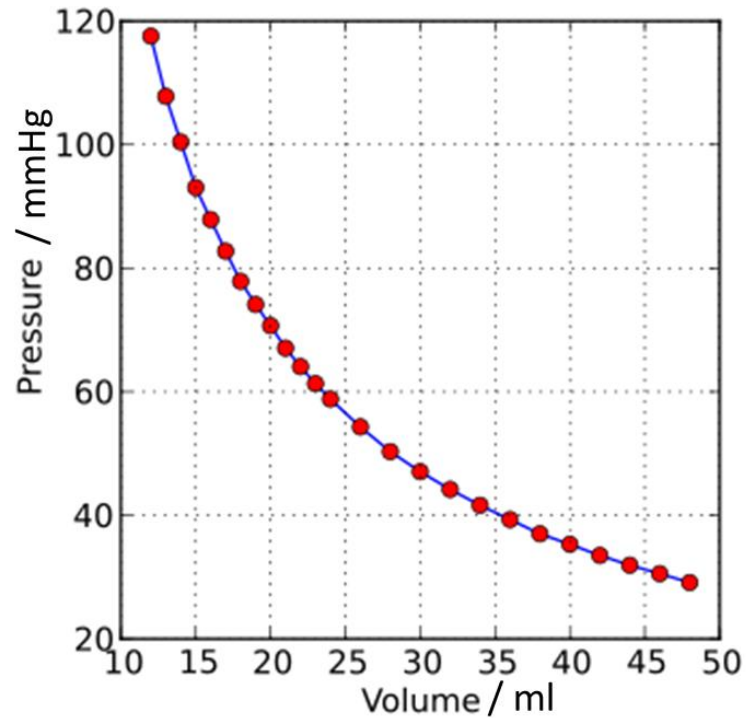


Figure 3B.1

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$pV = \text{constant}$



Boyle's data give a straight line for a plot of p against $1/V$ at a constant temperature.

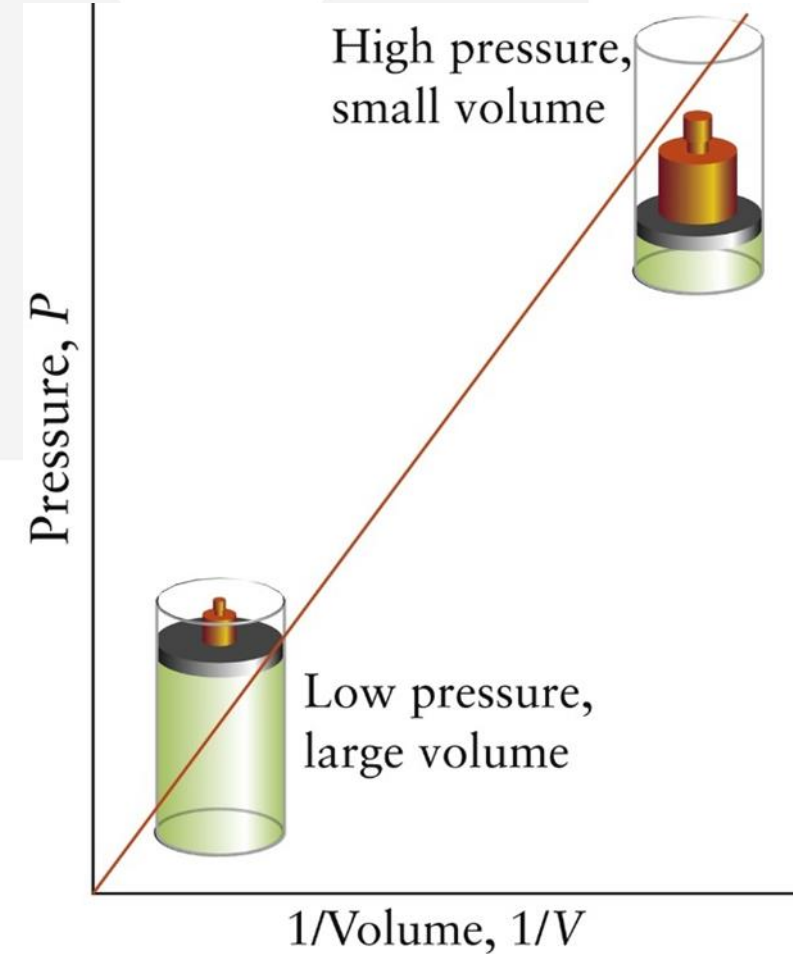


Figure 3B.3
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Charles' Law

Charles and Gay-Lussac, found that the **volume** of a gas **increases** as its **temperature** is **increased** or $\uparrow V \uparrow T$.

A straight-line graph shows a direct relationship when volume is plotted against the temperature.

$$\frac{V}{T} = \text{const.}$$

(T on absolute scale)

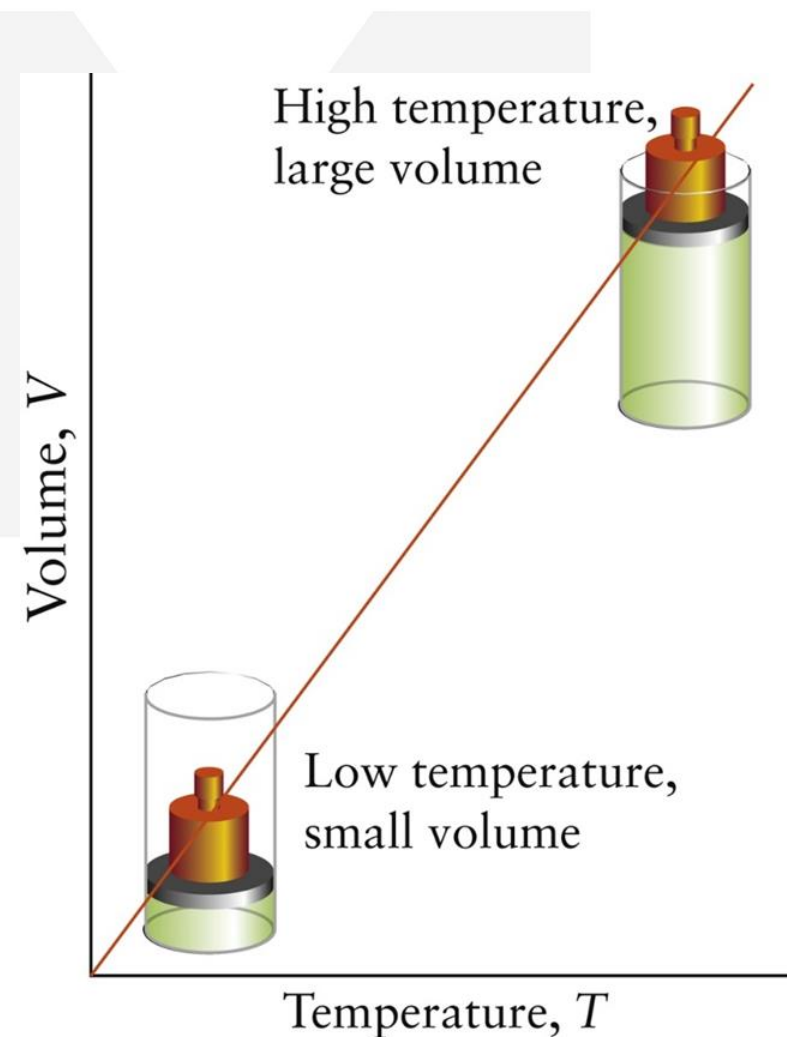


Figure 3B.4
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Charles' Law



Plotting V against T and extrapolating backward, it is found that all gases reach **zero volume** at $-273.15\text{ }^{\circ}\text{C}$.

This point cannot be reached in practice, because **no real gas has zero volume**.

Because a volume cannot be negative, -273.15°C must be the **lowest possible temperature**.

This corresponds to **zero** on the **Kelvin scale**.

$$0\text{ K} = -273.15\text{ }^{\circ}\text{C}$$

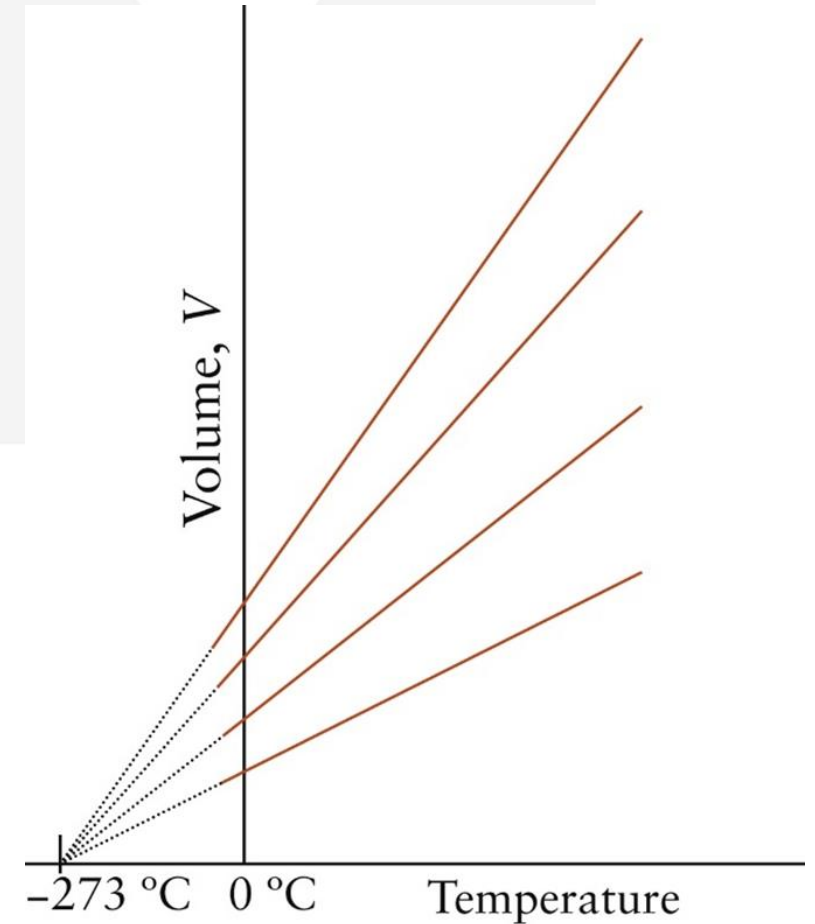


Figure 3B.5

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Avogadro's Principle



All gases occupy the same volume under the same conditions of temperature and pressures.

The molar volume of all gases is close to $22 \text{ L}\cdot\text{mol}^{-1}$ at 0°C and 1 bar.

Ideal gas	22.41
Argon	22.09
Carbon dioxide	22.26
Nitrogen	22.40
Oxygen	22.40
Hydrogen	22.43

Figure 3B.7

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Standard Ambient Temperature and Pressure (SATP)

SATP means exactly 25 °C (298.15 K) and exactly 1 atm.

The molar volume of an ideal gas is 24.46 L·mol⁻¹.

$$T = 298.15 \text{ K}$$

$$p = 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$V_{ideal \text{ gas}} = 24.46 \frac{\text{L}}{\text{mol}}$$

Standard Temperature and Pressure (STP)

STP means 0 °C (273.15 K) and 1 bar (both exactly).

The molar volume of an ideal gas is 22.71 L·mol⁻¹.

$$T = 273.15 \text{ K}$$

$$p = 1 \text{ bar} = 1.00000 \times 10^5 \text{ Pa}$$

$$V_{ideal \text{ gas}} = 22.71 \frac{\text{L}}{\text{mol}}$$

The three properties of a gas can all be combined into a single expression relating pressure (p), volume (V), temperature (T), and amount (n) of a gas:

$$pV = \text{const.} \times nT$$

When the constant of proportionality for the laws is written as R , this expression becomes the ideal gas law:

$$pV = nRT$$

R: The Ideal Gas Constant



$$pV = nRT$$

The constant R is *independent of the identity of the gas*; we say that it is a “**universal constant**”.

The value of the gas constant can be found by measuring p , V , n , and T .

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

Ideal gas: *no molecule volume, no intermolecular forces*

The ideal gas law is an example of a *limiting law*, a law that is strictly *valid only under certain conditions*.

It is reasonably reliable at **normal pressures**, and so we can use it to describe the behaviour of most gases under **normal conditions**.

Combined Gas Law



We note that, if the initial conditions of a gas are:

$$p_1V_1 = n_1RT_1$$

Then a change in conditions leads to:

$$p_2V_2 = n_2RT_2$$

Because R is a constant, we can equate the two equations:

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2}$$

This expression is called the **combined gas law**. However, it is a direct consequence of the ideal gas law and is not a new law.

Molar Concentration



The molar concentration, molarity (M), of any substance is the amount of molecules (n in moles) divided by the volume (V):

$$\text{molarity, } M = \frac{\text{amount of solute}}{\text{volume of solution}} = \frac{n}{V}$$

It follows from the ideal gas law that ($n = \frac{pV}{RT}$):

$$M = \frac{n}{V} = \frac{pV}{RTV} = \frac{p}{RT}$$

The density, d , of a gas, like that of any substance, is the mass divided by its volume, $d = \frac{m}{V}$. Because the densities of gases are so low, they are usually expressed in grams per liter ($\text{g}\cdot\text{L}^{-1}$).

Since mass is amount times molar mass, $m = nM$, and $n = \frac{pV}{RT}$, it follows that:

$$d = \frac{m}{V} = \frac{nM}{V} = \frac{pVM}{RTV} = \frac{pM}{RT}$$

Stoichiometry of Reacting Gases



We might need to know

- the volume of carbon dioxide produced when a fuel burns, or
- the volume of oxygen needed to react with a given mass of hemoglobin in the red cells of our blood.

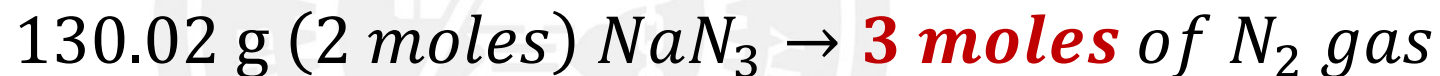
We answer these questions by using the **mole-to-mole** calculations we learned in *Fundamentals*, together with the **conversion of moles into volume**.

An Example of a Gas Reaction

Sodium azide, NaN_3 , forms large volume of nitrogen gas; a reaction triggered electrically in air bags.



$$M_{\text{NaN}_3} = 65.01 \frac{\text{g}}{\text{mol}}$$



$$V = \frac{nRT}{p} = \frac{3 \text{ mol} \cdot 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} \cdot 298.15 \text{ K}}{101325 \frac{\text{N}}{\text{m}^2}} = 0.073 \text{ m}^3 = 73 \text{ L}$$



Figure 3C.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Benelux Press BV/Science Source.

Mixtures of Gases



The atmosphere of air is a mixture of nitrogen, oxygen, argon, carbon dioxide, and many other gases.

A mixture of gases behaves like a **single** pure gas.

Dalton concluded that the total pressure is the sum of the individual pressures of each gas.

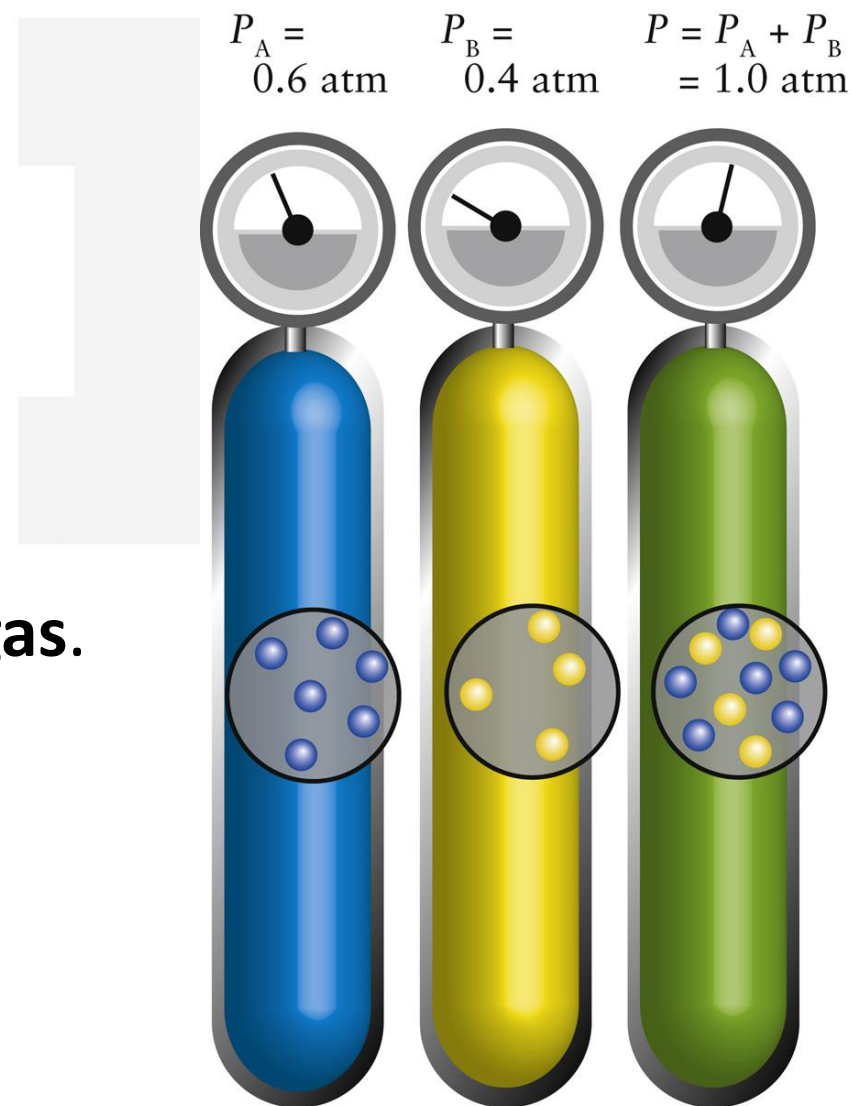


Figure 3C.1

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Dalton's Law of Partial Pressures



The easiest way to express the relation between the *total pressure* of a mixture and the *partial pressures of its components* is to introduce the mole fraction, χ .

The moles of each gas n_A, n_B expressed as a molar fraction of gases A and B are:

$$\chi_A = \frac{n_A}{n_A + n_B + \dots} \quad \text{and} \quad \chi_B = \frac{n_B}{n_A + n_B + \dots}$$

Note that: $\chi_A + \chi_B + \dots + \chi_N = 1$

Dalton's Law of Partial Pressures



In terms of total pressure and moles of all gases:

$$p_{total} = \frac{n_{total}RT}{V} = \frac{(n_A + n_B + \dots)RT}{V} \text{ and } p_A V = n_A RT$$

Combine and rearrange $\frac{RT}{V}$ to get:

$$\frac{p_{total}}{(n_A + n_B + \dots)} = \frac{p_A}{n_A}$$

Rearrange to get:

$$p_A = \frac{n_A p_{total}}{(n_A + n_B + \dots)}$$

Assigning $\chi_A = \frac{n_A}{n_A + n_B + \dots}$ to arrive at:

$$p_A = \chi_A p_{total}$$

(the same applies to each gas)

The Kinetic Model of Gases

From **kinetic molecular theory**, KMT:

1. A gas is in continuous random motion
2. Gas molecules are infinitesimally small
3. They move in straight lines until collision
4. Gas molecules do not influence one another except during collisions
5. The collisions are elastic (no kinetic energy converted)

The kinetic model of a gas allows us to derive the **quantitative** relation between pressure and the speeds of the molecules.

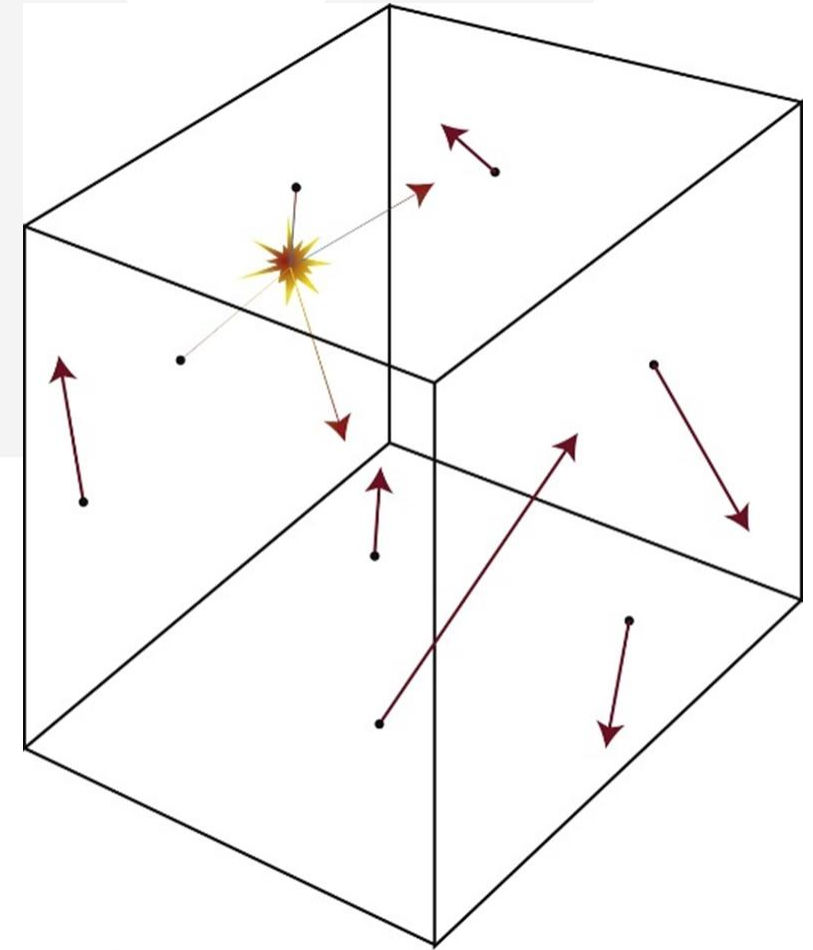


Figure 3D.3

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Quantitative Description



$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

rms: root mean square

$$T = \frac{M v_{rms}^2}{3R}$$

Temperature is proportional to the mean square speed of the molecules.

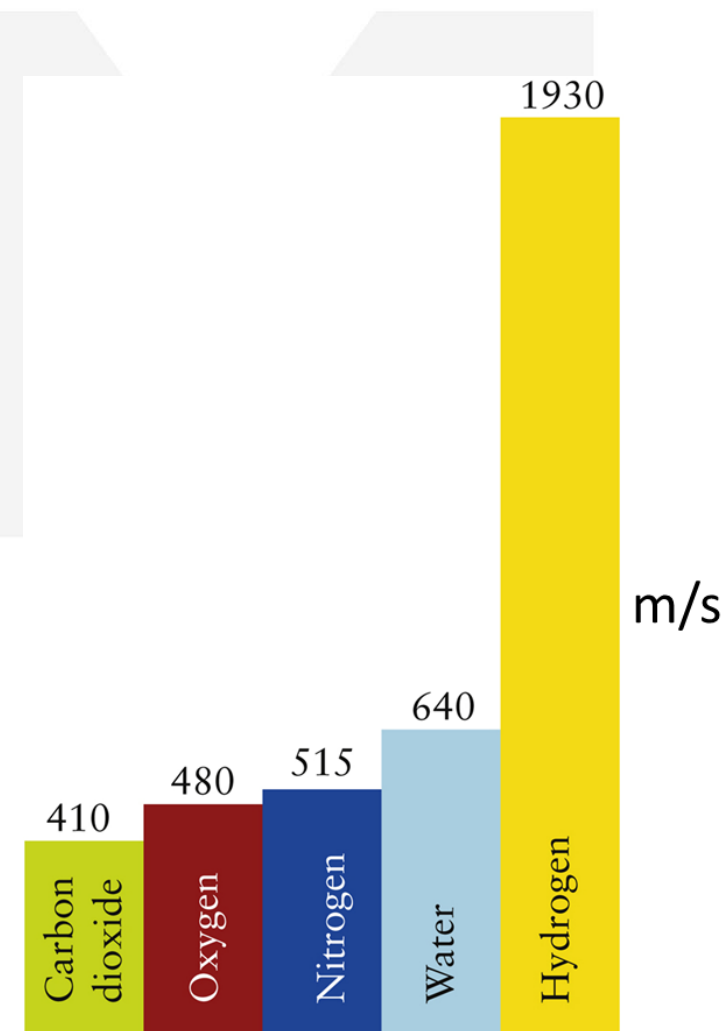
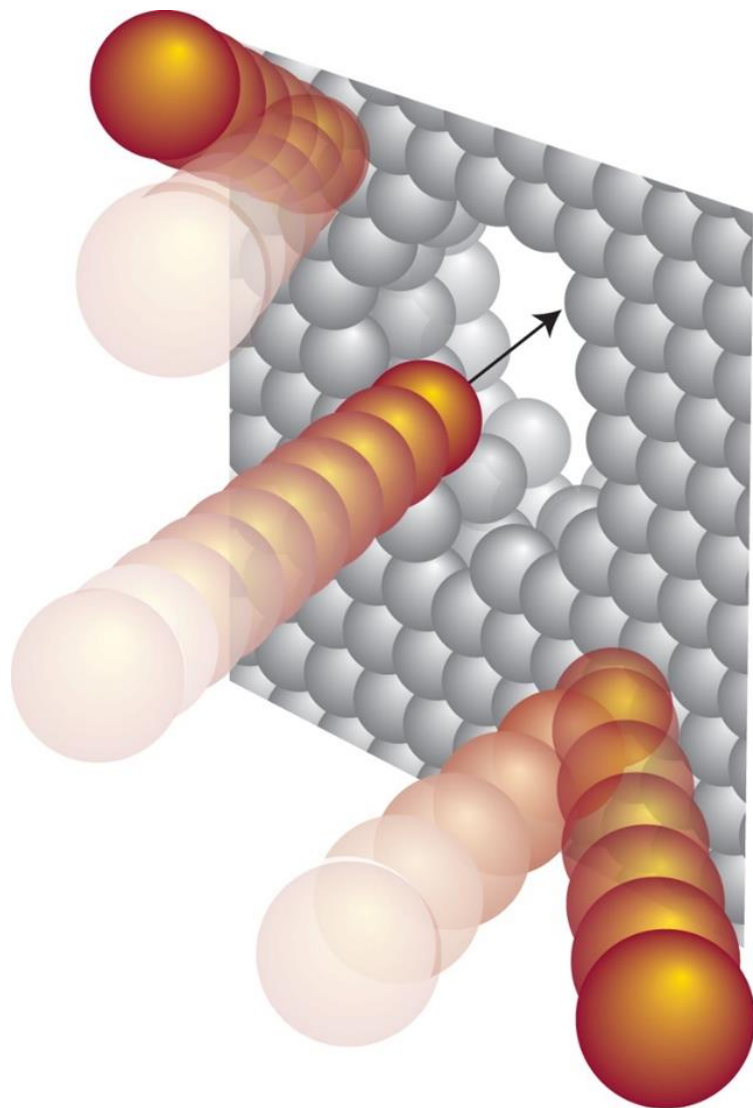


Figure 3D.5

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Is Kinetic Molecular Theory
consistent with observation?

In **effusion**, molecules escape
through a small hole in a barrier into
a region of low pressure.

Figure 3D.2

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The nineteenth-century Scottish chemist Thomas Graham carried out experiments on the rates of gas effusion.

At constant temperature, the rate of effusion is inversely proportional to the square root of its molar mass:

$$rate_{eff} = \frac{1}{\sqrt{M}}$$

This is now known as Graham's law of effusion.

Since the average speed of molecules determines the rate they approach the hole, we conclude:

$$\bar{v} \propto \frac{1}{\sqrt{M}}$$

Grahams' Law with Two Gases



Rewriting Graham's law for two gases A and B with molar masses M_A and M_B , we would obtain:

$$\frac{rate_{eff,A}}{rate_{eff,B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

Since time is inversely proportional to rate:

$$\frac{t_{eff,A}}{t_{eff,B}} = \frac{\sqrt{M_A}}{\sqrt{M_B}}$$

The Maxwell Distribution of Speeds



The root mean square speed equation $\left(v_{rms} = \sqrt{\frac{3RT}{M}} \right)$ is like cars in traffic: individual molecules have speeds that vary over a wide range.

The formula for calculating the fraction of gas molecules having a given speed, v , at any instant was derived by the Scottish scientist James Clerk Maxwell.

$$\frac{dN}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}} dv$$

$\frac{dN}{N}$ is the fraction of molecules with speeds between v and $v+dv$, M is the molar mass, and R is the gas constant.

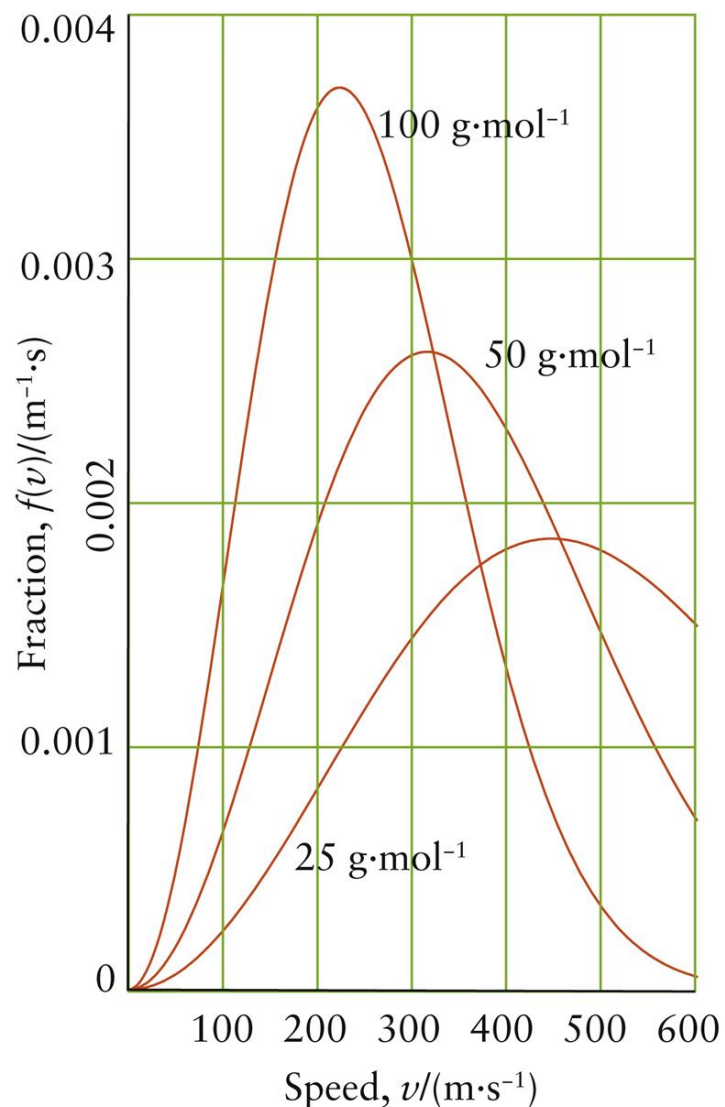
The Maxwell Distribution of Speeds



$$\Delta N = N \cdot 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

- The exponential factor (which falls rapidly toward zero as v increases) means that very few molecules have very high speeds.
- The factor v^2 that multiplies the exponential factor goes to zero as v goes to zero, so it means that very few molecules have very low speeds.
- The factor $4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}}$ simply ensures that the total probability of a molecule having a speed between zero and infinity is 1.

Velocities for different M ($T=\text{const.}$)



Maxwell distribution for the range of molecular speeds of three gases.

All distributions are at the same temperature of 300 K.

The greater the molar mass, the lower the speed.

Figure 3D.6
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Velocities for different T ($M=\text{const.}$)



In the Maxwell distribution, the curves correspond to the speeds of a single substance ($M = 50 \text{ g}\cdot\text{mol}^{-1}$) at different temperatures.

The higher the temperature, the higher the average speed and the broader the spread of speeds.

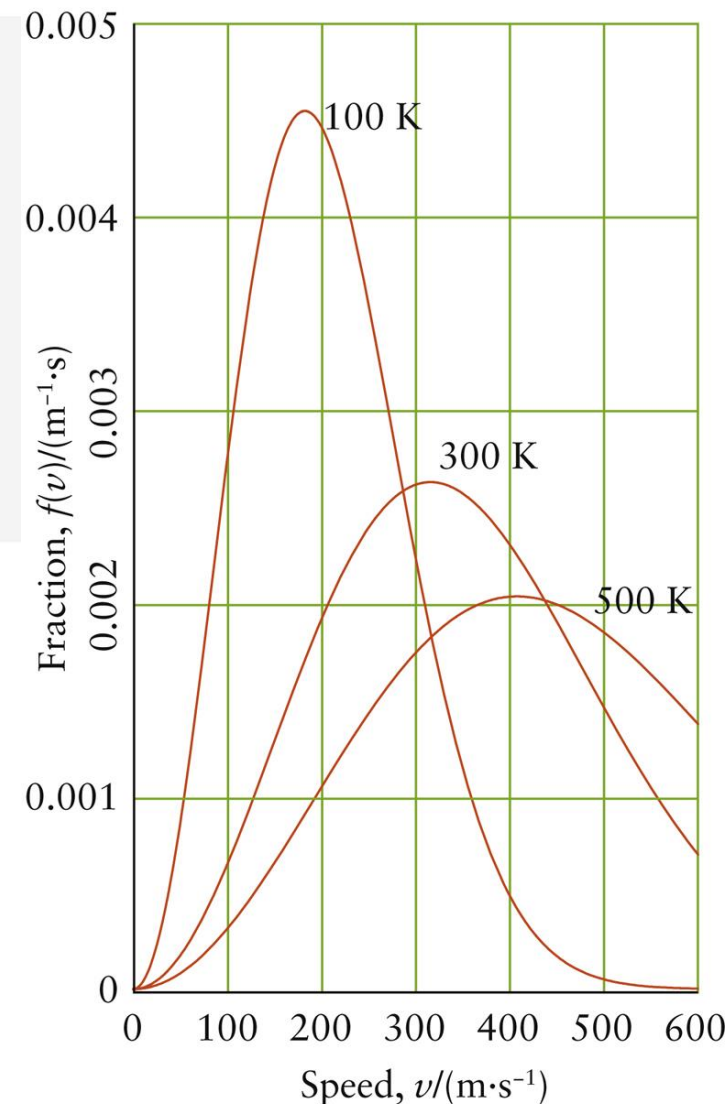


Figure 3D.7

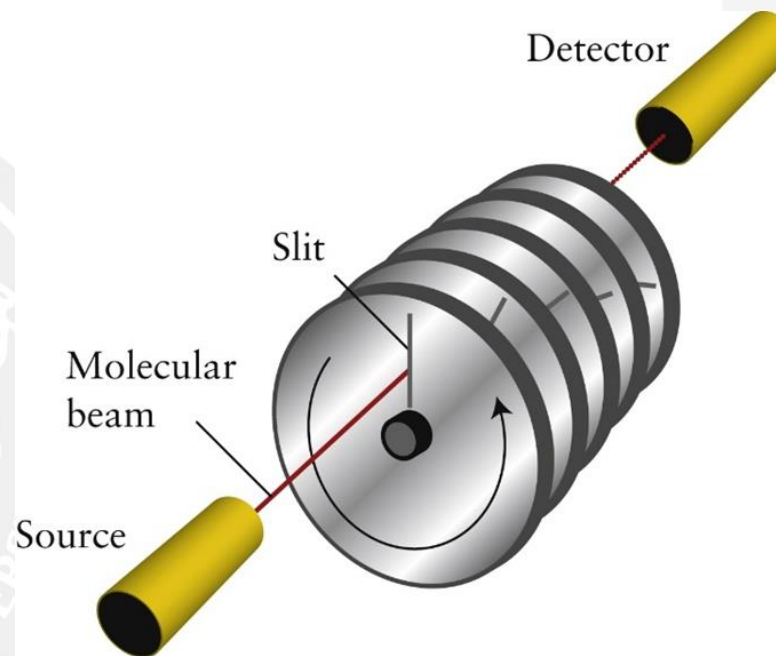
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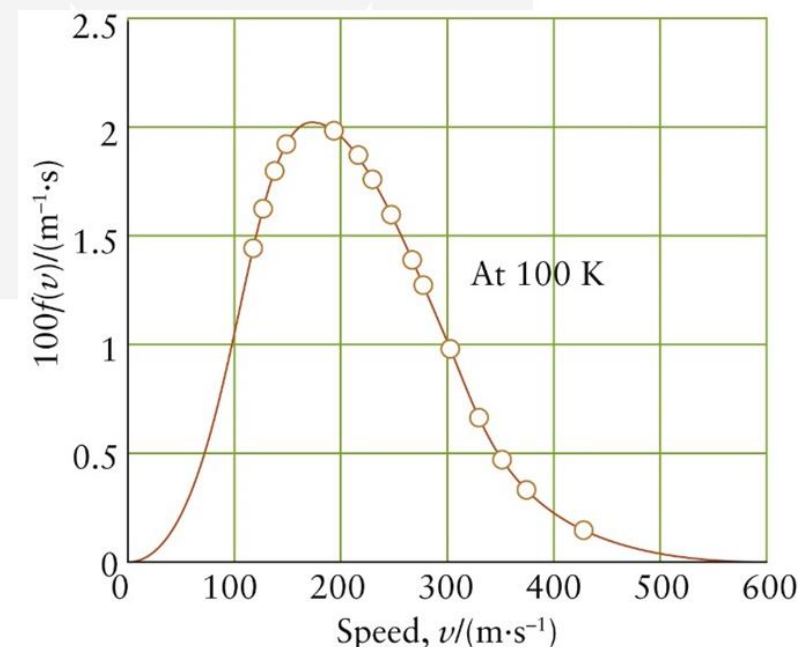
Experimental Determination of Speeds



The distribution of molecular speeds in a gas can be determined experimentally



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In industry and in many research laboratories, gases must be used under high pressures, when the ideal gas law is not followed closely.

The ideal gas law is a limiting law, valid only as $p \rightarrow 0$.

All actual gases, which are called **real gases**, have properties that **differ** from those predicted by the **ideal gas** law.

These differences are significant at high pressures and low temperatures.

All deviations from ideal behaviour can be explained by the intermolecular forces.

All molecules **attract** one another when they are a *few molecular diameters apart*.

They **repel** one another as soon as their *electron clouds come into contact*.

Gases can be condensed to liquids when cooled or compressed.

A measurement of the compression factor Z .

$$Z = \frac{V_{m,real}}{V_{m,ideal}}$$

Deviations from Ideality: Compressibility

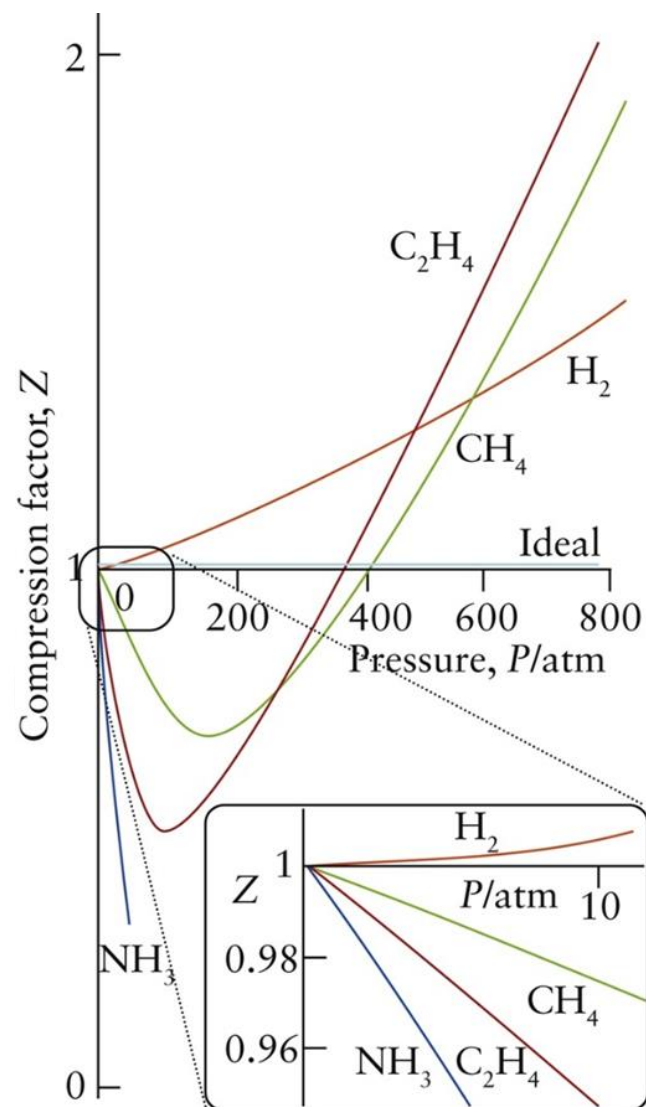


Figure 3E.1

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$$Z = \frac{V_{m,real}}{V_{m,ideal}}$$

At low pressures the **attractive forces** are dominant and $Z < 1$.

At high pressures, **repulsive forces** become dominant and $Z > 1$ for all gases.

Equations of State of Real Gases



A common procedure to describe the behaviour of real gases is to write the following expression:

$$pV = nRT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

This expression is called the virial equation. The coefficients B , C , ... are called the second virial coefficient, third virial coefficient, etc.

However, the virial coefficients are not always known for each gas at a given temperature.

Equations of State of Real Gases



So less accurate, but more common form is used, the temperature-independent **van der Waals** equation:

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

(values for a and b are found experimentally, or, for well known molecules, in tables)

Parameter “ a ” represents the attraction between molecules; the value is large for strongly attracting molecules.

Parameter “ b ” represents the role of repulsions; it can be thought of as representing the volume.

Van der Waals Parameters



Gas	$a / \text{bar}\cdot\text{L}^2\cdot\text{mol}^{-2}$	$b / \text{L}\cdot\text{mol}^{-1}$
Noble gases		
Helium	0.0346	2.38×10^{-2}
Neon	0.208	1.67×10^{-2}
Argon	1.355	3.20×10^{-2}
Krypton	5.193	1.06×10^{-2}
Xenon	4.192	5.16×10^{-2}
Halogens		
Fluorine	1.171	2.90×10^{-2}
Chlorine	6.343	5.42×10^{-2}
Bromine	9.75	5.91×10^{-2}
Nonpolar inorganic gases		
Hydrogen	0.2452	2.65×10^{-2}
Oxygen	1.382	3.19×10^{-2}
Carbon dioxide	3.658	4.29×10^{-2}

Gas	$a / \text{bar}\cdot\text{L}^2\cdot\text{mol}^{-2}$	$b / \text{L}\cdot\text{mol}^{-1}$
Polar inorganic gases and vapours		
Ammonia	4.225	3.71×10^{-2}
Water	5.537	3.05×10^{-2}
Carbon monoxide	1.472	3.95×10^{-2}
Hydrogen sulfide	4.544	4.34×10^{-2}
Nonpolar organic gases and vapours		
Methane	2.303	4.31×10^{-2}
Ethane	5.507	6.51×10^{-2}
Propane	9.39	9.05×10^{-2}
Benzene	18.57	11.93×10^{-2}