

# THE PHYSICS AND CHEMISTRY OF GASES

by  
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## ABSTRACT

It is possible from simple gas behavioral theories to develop more complex relationships which allow prediction of transport phenomena such as diffusivity and viscosity of gas mixtures. Such physical data can be used in engineering calculations for both bulk gas movement and gaseous chemical species movement. Both of these are important in the solution of mines ventilation systems.

There are specific limits of flammability of some common mines gases.

## NOMENCLATURE

### SYMBOLS

P	Pressure
V	Volume
T	Temperature
T <sub>c</sub>	Critical Temperature
n	Number of moles
R	Universal gas constant
N	Number of molecules
m, M	Molecular weight
$\bar{v}$	Mean molecular velocity
E <sub>k</sub>	Total kinetic energy/mole of gas
d	Molecular diameter
k	Boltzmann constant
$\lambda$	Mean free path of a molecule
$n_v, n_t, n_t$	Molecular distribution or number density

g	Gravitational acceleration
h	Height
$\phi(r)$	Intermolecular potential energy
n	Intermolecular distance
$\epsilon$	Maximum energy of attraction
D <sub>12</sub>	Coefficient of Diffusion

## DEFINITIONS, LAWS, THEORIES, ETC.

Appropriate material is available from handbooks, etc such as the Chemical Rubber Publishing Co., (1970) and Barrow (1980) used in the preparation of this paper.

A qualitative definition of a gas is that state of matter which exhibits no fixed volume for a given mass.

The basic experimental laws of gas behaviour are:

1. Boyle's Law  
 $PV = \text{constant} \quad (1)$
2. Charle's Law  
 $V/T = \text{constant} \quad (2)$
3. Avogandro's Hypothesis

This states that at constant temperature and pressure, volumes of different gases contain the same number of molecules. The above laws were based on observed or empirical behaviour. If the above laws are combined, then the result is the ideal gas law or the Equation of State. This equation takes the following form:

$$PV = nRT \quad (3)$$

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The Kinetic Theory of Gases is an attempt to explain gas laws and properties in terms of Molecular motion. This is done by breaking down the gas to follow the physics of movement of an individual molecule.

Assumptions made in this theory are:-

1. Gases consist of molecules in constant motion.
2. In a given volume, the number of molecules is large and the volume occupied by the molecules themselves is negligible.
3. Molecules are hard small spheres which exert no forces upon each other except at the instant of collision.
4. All molecular collisions are perfectly elastic.

The result is:-

$$PV = \frac{Nm\bar{v}^2}{3}$$

on rearranging

$$= \frac{2}{3} N(\frac{1}{2}m\bar{v}^2)$$

$$= \frac{2}{3} Ek \quad (4)$$

where Ek is the total kinetic energy per unit mole of gas. If the equation of state (3) is equated to equation (4) it is found that the kinetic energy of a gas is a function of temperature only:-

$$Ek = 3/2 RT \quad (5)$$

From this molecular result, the experimental results of Boyle, Charles and Avogadro are proven.

Taking equation (5) a step further, at constant temperature, for one molecule of gas the velocity of the molecule is dependent on the molecular weight:-

$$\frac{1}{2} m_1 \bar{v}_1^2 = \frac{1}{2} m_2 \bar{v}_2^2$$

$$\text{or } \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}} \quad (6)$$

This is known as Graham's Law of Diffusion. It would therefore be expected that smaller molecules would diffuse more quickly as they move at higher velocities.

Table 1 lists some physical properties of typical coal seam gas.

TABLE 1  
Properties of Some Mine Gases

Gas	$\bar{v}$ m/s	l um	Collision frequency s <sup>-1</sup>
Air	44.7		
O <sub>2</sub>	42.5	9.05	4430 x 10 <sup>6</sup>
CO <sub>2</sub>	36.2	5.56	6120 x 10 <sup>6</sup>
CH <sub>4</sub>	60.0		
CO	45.4	8.45	5100 x 10 <sup>6</sup>
H <sub>2</sub> S			
N <sub>2</sub>	45.4	8.50	5070 x 10 <sup>6</sup>
H <sub>2</sub>	169.6	16.0	10060 x 10 <sup>6</sup>

If molecules were to move at the velocities shown in Table 1 then gas diffusivity would be a very quick process. The reason for this not being so is that molecules have a mean free path. This defines the distance travelled between two successive collisions. It is assumed here that

1. Molecules are hard impenetrable spheres of diameter  $\sigma$ .
2. All molecules are moving with the same velocity  $\bar{v}$

The mean free path is given by:-

$$l = \frac{kT}{\sqrt{2}\pi\sigma^2 p} \quad (8)$$

Thus by increasing  $P$  or  $\sigma$ , the mean free path will decrease and hence reduces the average velocity through the increased probability of collision. Table 1 shows that the mean free path is very small and the collision frequency is very high. Hence the more slower process of diffusion can be foreseen.

Because of these random collisions one can look at the probability of a molecule having a certain velocity and hence kinetic energy. Statistical mechanics permits the definition of the velocity distribution at a given temperature for all molecules using the Maxwell-Boltzmann Distribution shown in equation (9)

$$n_i = n_t \exp(-E_i/kT) \quad (9)$$

Expressions for the most probable, the average and the root mean square velocity can be mathematically obtained from the Maxwell-Boltzmann Distribution (Fig. 1).

From Figure 2 it can be seen how with increased temperature, the mean velocity increases. This agrees with the fact that the kinetic energy of the gas increases with temperature.

The Maxwell-Boltzmann equation can be used to establish the effect of gravitation on the number density of a binary mixture of gases (Fig. 2). If the kinetic energy term is replaced with a gravitational term, equation 9 becomes:-

$$n_i = n_t \exp(-mgh/kT) \quad (10)$$

Using an example of a 3 m column of  $\text{CO}_2/\text{N}_2$ , the exponent term in equation (10) becomes  $-1.2 \times 10^{-14}$ . This means that given a column of a binary mixture of gas, the two gases

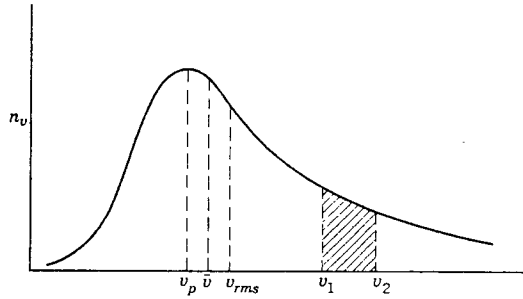


Fig. 1. Number of molecules related to molecular velocity

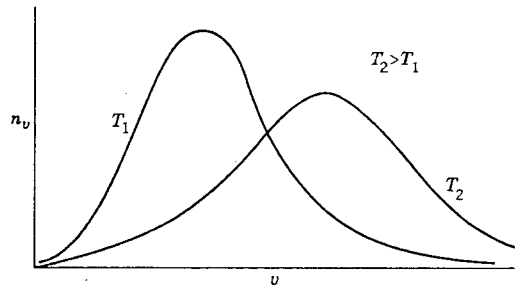


Fig. 2. Effect of temperature - distribution on molecular velocity

will not stratify according to density or molecular weight. Therefore height will not change molecular distribution.

Up until now all theories have been based on ideal behaviour of the physical motion of gas molecules. However deviation from ideal gas behaviour occurs because attractive/repulsive forces exist between molecules and molecular volume is finite, especially at high pressure. Figure 3 shows that deviation is small at low pressures. In terms of the equation of state these deviations are not that significant, however knowledge of these forces is needed to permit the calculation of transport coefficients such as viscosity and diffusion.

Attempts to account for the non-ideality

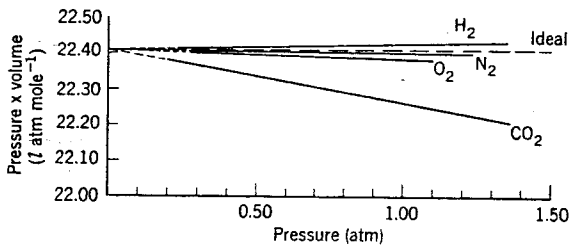


Fig. 3. Deviation from ideal gas behaviour relative to pressure

of gases are numerous. Some examples of expressions to modify the equation of state are:

$$1. \quad PV = RT + BP + CP^2 + \dots \quad (11)$$

where B, C, ... are called virial coefficients and are functions of the nature and temperature of the gas.

$$2. \quad P(V-nb) = nRT$$

$$\text{or}$$

$$\left(P + \frac{an^2}{V^2}\right) (V-nb) = nRT \quad (12)$$

where a and b are characteristics of the gas. The equations were put forward by Van der Waals.

Forces that exist between molecules include:

1. Electrostatic. This includes dipole moments and consists of typical +ve/-ve interactions between polar molecules.
2. Induction. Which is the effect of a polar molecule on a non-polar molecule because of their relative positive and negativeness.
3. Dispersion forces are instantaneous dipoles as a result of collisions between molecules. These are most prominent between non-polar molecules. A popular model to

explain dispersive forces between non-polar molecules was put forward by Lennard-Jones and Devonshire (1937):

$$\phi(r) = 4 \epsilon \left( \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right) \quad (13)$$

This model relates the intermolecular potential energy to the maximum energy of attraction, repulsive and dispersive interactions. If equation 13 is represented graphically (Figure 4) then it can be seen that for values of  $\sigma/r > 1$ , the two molecules repel one another and conversely values of  $\sigma/r < 1$ , molecules attract one another.

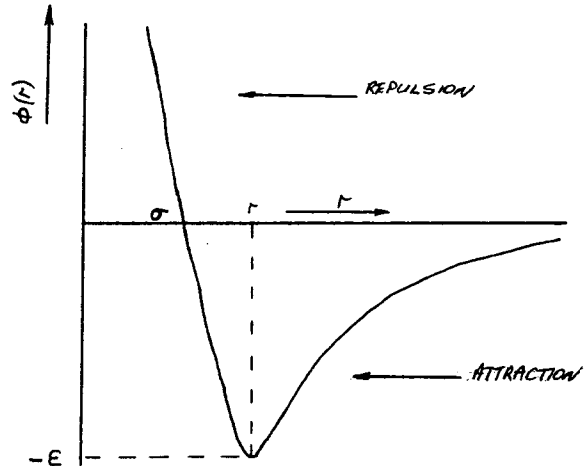


Fig. 4. Determination of positive and negative dispersive forces

Values of  $\epsilon$  and  $\sigma$  are tabulated or can be estimated from critical temperature and pressure data.

Chapman and Cowling (1951) (and others including Enskog) obtained equations for transport coefficients from a numerical solution of the Boltzmann equation using the Lennard-Jones potential function for non-polar molecules. The Boltzmann equation relates the probability

of finding a molecule at a specified point with a certain momentum to the:

- (1) velocity of the molecule
- (2) position of the molecule
- (3) external forces acting on the molecule
- (4) time

The Chapman-Enskog assumptions were that:

- (1) The probability of more than two molecules colliding at an instant is remote and therefore only two body collisions need to be considered
- (2) All collisions are elastic and only transitional energy need be considered.
- (3) Intermolecular force field is symmetrical i.e., molecules are non-polar.

The result was a modified equation of state using virial equations to solve for an expression representing the coefficient of diffusion shown in equation (14)

$$D_{12} = 0.002628 \left\{ \frac{T^3(m_1+m_2)/2m_1m_2}{(\rho\sigma_{12}^2 \Omega_{12}^{(1,1)})} \right\}^{1/2} \quad (14)$$

where  $\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2)$

$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2}$

The values of  $\sigma$ ,  $\epsilon$ , as for the Lennard-Jones potential, are tabulated as is the collision integral  $\Omega_{12}^{(1,1)}$  which is a function of the reduced temperature ( $T/T_c$ ).

Thus an equation suitable for engineering purposes has been obtained. Using this equation to calculate the diffusivity of  $CO_2$  in air at 25°C and 1 atm. an answer of 0.15  $cm^2/sec$  is obtained which is in good agreement with the experimental value of 0.164  $cm^2/sec$ .

Expressions can likewise be derived for the thermal conductivity (equ. 15) and

viscosity (equ. 16) for binary, non-polar mixtures.

Thermal Conductivity =

$$1.989 \times 10^{-4} \times \left\{ \frac{T(m_1+m_2)/2m_1m_2}{(\sigma_{12}^2 \Omega_{12}^{(2,2)})} \right\}^{1/2} \quad (15)$$

Viscosity =

$$2.663 \times 10^{-3} \times \left\{ \frac{2m_1m_2T/(m_1+m_2)}{(\sigma_{12}^2 \Omega_{12}^{(2,2)})} \right\}^{1/2} \quad (16)$$

CHEMICAL PROPERTIES

The main concerns with mine gas are:

- (1) flammability
- (2) toxicity

The limits of flammability of a gas are those limits in which the gas will combine with a diluent gas such as air to form an explosive mixture. These limits change with the chemical composition of the diluent gas. Gases with high specific heats such as  $CO_2$  will reduce these limits most. Figure 5 shows the limits of flammability of methane in air diluted with various inert gases at 1 atm. pressure.

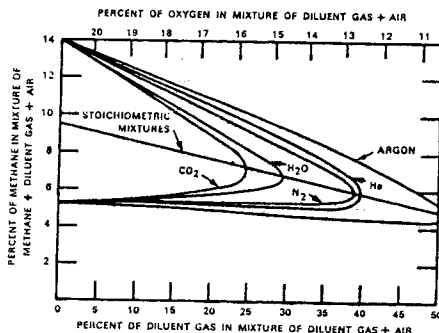


Fig. 5. Limits of flammability of  $CH_4$  - Air mixtures with various inert diluents

Table 2 shows a summary of some important characteristics of mines gas (Forster and Grove, 1954).

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TABLE 2  
SUMMARY OF SOME IMPORTANT CHARACTERISTICS OF MINES GAS

Gas and Chemical Formula	Weight kg/m <sup>3</sup> 21.20C 760mm Hg	Sp.gravity Air = 1	Limits of Flammable Range in Air % by Volume	Oxygen % Below which no mixture is flammable		Odour	Taste	Dangerous to Breathe
				N <sub>2</sub> Diluent of air	CO <sub>2</sub> Diluent of air			
Air	1.20	1.000	Non-explosive (supports combustion)			None	None	No
O <sub>2</sub>	1.33	1.1054	Non-explosive (supports combustion)			None	None	No, not at 1 atm. At higher pressures poisonous
CO <sub>2</sub>	1.84	1.5291	Non-explosive			None	Acid Taste in high concn.	Yes > 5%
CO	1.17	0.9672	12.5 to 74	5.6	5.9	None	None	Yes, even in very low concn.
CH <sub>4</sub>	0.67	0.5545	5 to 15	12.1	14.6	None	None	No
H <sub>2</sub> S	1.42	1.1906	4.3 to 45			Yes, rotten eggs	Yes	Yes, even in very low concn.
N <sub>2</sub>	1.17	0.9674	Non-explosive			None	None	No
H <sub>2</sub>	0.83	0.0695	4.0 to 75	5.0	5.9	None	None	No