

EXPERIMENTAL METHODS IN GAS REACTIONS

**Harry Melville
and
B. G. Gowenlock**

SECOND EDITION

Experimental Methods in Gas Reactions

by

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Preface

PROGRESS in the field of chemical kinetics has been considerable in the twenty-five years that have passed since the publication of *Experimental Methods in Gas Reactions*. The original book gave a virtually complete coverage of the literature on experimental techniques for gas reactions. The frequency with which it has been cited as a source book of techniques, together with its unavailability, indicated that a new edition could fill a real need for the experimentalist. It has been obvious to us both that much of the original is still relevant, and that there is much new material to be incorporated into a book of this kind.

In this new edition we have endeavoured not to dispense with any material from the original edition which might be of use to the research worker. It is possible that, in setting ourselves this aim, we have erred on the side of leniency. In particular, we have retained details of many of the older methods of gas analysis. This has been done not because we are unaware of the usefulness of gas chromatography, but because it seemed to us that these methods, which are rapidly becoming unfamiliar to the younger generation of experimentalists, might suggest analytical techniques in fields where gas chromatography is difficult to employ and alternative approaches to problems of rate determination.

The publication rate in gas kinetics is now many times greater than in 1938, and this has made the compilation of the new edition difficult, since inclusion of detailed descriptions of every new or modified relevant technique would have materially increased the size of the volume. The plan has therefore been to keep the book reasonable in size by eliminating matter that is now irrelevant and bringing in much material, together with a greatly extended system of references to help the reader locate the relevant papers.

The purpose of the book remains. It is to help the new experimenter (and also the more experienced) not only by directing how he can set about new experimental techniques but also by stimulating him to adopt, modify and develop the methods described in the book and thereby contribute his quota to the sum total of knowledge in this field. The techniques described have a much wider application than simply to gas reactions. Almost every research laboratory makes use of vacuum systems and the manipulative devices first developed for gas kinetic

studies. The hope is therefore that this revised edition will have a wider field of usefulness than the original edition.

The authors welcome information on new techniques and on further developments of those which we have included. It is our pleasant duty to acknowledge the help and assistance of colleagues in the United Kingdom, Europe and North America, who answered our queries, gave us the benefit of their experience and pointed out details of some techniques and of literature references of which we were unaware. Our thanks are also due to the staff of Macmillan and Company for their courteous co-operation and assistance.

H. W. M.
B. G. G.

December 1963

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I

Kinetic Theory of Gases

THE principal formulae, laws and data are summarised: for details of the derivations standard texts¹⁻⁷ should be consulted.

Molecular dimensions

Table 1.1 lists values for some molecular diameters as determined by a variety of methods.

TABLE 1.1
Molecular diameters in Å

Molecule	I	II	III	IV	V	VI
Helium	2.18	2.64	2.14	1.48		
Neon	2.59			1.84		
Argon	3.64	2.87	2.33	2.96		
Krypton	4.16	3.14	2.54	3.34		
Xenon	4.92	3.42	2.78	4.00		
Hydrogen	2.74	2.76	2.24	1.86	2.72	2.45, 2.93, 2.98
Nitrogen	3.75	3.15	2.55	2.40	3.39	0.44
Oxygen	3.61	2.91	2.36	2.34		
Chlorine	5.55	3.31	2.68	3.29		
Bromine	6.16			3.72	10.0	
Iodine	6.92				6.33	
Carbon monoxide	3.77	4.55	3.69		5.29	2.02
Carbon dioxide	4.59	3.23	2.62			
Nitric oxide	3.69					4.97
Water	4.32	2.89	2.34	2.26		1.00
Ammonia	4.42					1.72, 1.74
Hydrogen chloride	4.50	3.18	2.58	2.74		
Hydrogen bromide				3.03		
Mercury		2.37	1.92			
Methane	4.16				0.33	0.24, 0.29
Acetylene						4.80
Ethylene	4.96				6.63	5.10, 6.93
Ethane	5.30				0.41	0.33, 0.65, 0.77

Key: I Viscosity data⁸
 II Volume correction in van der Waals' equation¹
 III Volume correction in Wohl's equation¹
 IV Molecular refraction¹
 V Physical quenching of Na (²P)⁹
 VI Chemical quenching of Hg (³P₁)⁹

Number of molecules

One mole of gas contains 6.0227×10^{23} molecules. This number is denoted by N and is usually referred to as Avogadro's number, or in the German literature as Loschmidt's number.

On the assumption of ideal gas laws (no interaction between molecules and negligible volume of the molecules), one mole of gas is contained in $22,414 \text{ cm}^3$ at 0°C and 760 mm Hg pressure. This quantity is the mole-volume. Thus at 0°C one cubic centimetre of gas contains 2.687×10^{19} molecules at 760 mm Hg pressure and 3.536×10^{16} molecules at 1 mm Hg. At the temperature $T^\circ\text{K}$ and the pressure p mm the number of molecules per cm^3 is $9.652 \times 10^{18} p/T$.

The molecular velocity

From elementary theory the speed of the molecules can be deduced in the following way. Consider a mole of gas confined in a cubical box of volume v and assume that each molecule has the same velocity u and that one-third of the total is moving parallel to each one of the three edges of the cube. One molecule will traverse the box in one second $u/\sqrt[3]{v}$ times and hit each wall $u/2\sqrt[3]{v}$ times. Since $N/3$ molecules travel in each direction and at each impact the change of molecular momentum is $2Mu/N$, the total change of momentum is (M = molecular weight)

$$\frac{2Mu}{N} u \frac{N}{3} \frac{u}{2\sqrt[3]{v}} = \frac{Mu^2}{3\sqrt[3]{v}} \quad (1)$$

and is equal to the force f exerted on any one of the walls. The area of the wall being $v^{\frac{2}{3}}$, the pressure,

$$p = f/v^{\frac{2}{3}} = \frac{Mu^2}{3v} \quad (2)$$

or since

$$pv = RT \quad (R = \text{gas content}) \quad (3)$$

$$\frac{Mu^2}{3} = RT \quad (4)$$

and

$$u = \sqrt{3RT/M} \quad (5)$$

This formula is valid also in the exact theory if we take into consideration the velocity and direction distribution of the molecules. In that case u denotes the root mean square velocity, being defined as

$$N \cdot u^2 = u_1^2 + u_2^2 + u_3^2 + \dots u_N^2 \quad (6)$$

$u_1, u_2, \dots u_N$ denoting the velocities of each molecule. With $R = 8.31436 \times 10^7$ erg/deg mol we have

$$u = 1.5793 \times 10^4 \sqrt{T/M} \text{ cm/sec}^{-1} \quad (7)$$

This velocity is sometimes referred to as the effective velocity. From formula (5) we find, introducing the density $\rho = M/v$, $u = \sqrt{3p/\rho}$, p being expressed in dyn/cm². Besides this velocity we shall have to deal with the average velocity and the most probable velocity.

Distribution of the velocities

The deduction of the law governing the distribution of the molecular velocities is due to Maxwell.

If N_0 molecules are present in a cm³ the number of molecules with the velocity between c and $c + dc$ is

$$dN_c = N_0 \frac{4}{\sqrt{\pi}} \left(\frac{M}{2RT} \right)^{\frac{3}{2}} e^{-\frac{c^2 M}{2RT}} c^2 dc \quad (8)$$

The most probable velocity is given by $\frac{d^2 N_c}{dc^2} = 0$ and is

$$\alpha = \sqrt{2RT/M} = 1.2895 \times 10^4 \sqrt{T/M} \text{ cm/sec}^{-1} \quad (9)$$

The average velocity is

$$\bar{c} = \int_0^\infty \frac{cdN_c}{N_0} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2RT}{M}} = \sqrt{\frac{8RT}{\pi M}} = 1.4551 \times 10^4 \sqrt{T/M} \text{ cm/sec}^{-1} \quad (10)$$

It will be recognised that the most probable velocity < average velocity < root mean square velocity u .

In chemical kinetics it is often necessary to know the number of molecules, the velocity of which exceeds a certain value c . This number is

$$N_1 = \int_c^\infty dN_c = N_0 \frac{4}{\sqrt{\pi}} \left(\frac{M}{2RT} \right)^{\frac{3}{2}} \int_c^\infty e^{-\frac{c^2 M}{2RT}} c^2 dc \quad (11)$$

and introducing

$$c / \sqrt{\frac{2RT}{M}} = \frac{c}{\alpha} = x \quad (12)$$

we can define an expression in terms of the Gaussian distribution function and the error integral

$$\frac{N_1}{N_0} = 1 + \frac{2}{\sqrt{\pi}} \left(\frac{c}{\alpha} \right) e^{-c^2/\alpha^2} - \text{Erf} \left(\frac{c}{\alpha} \right) \quad (13)$$

or
$$\frac{N_1}{N_0} = 1 - \frac{1}{2} \text{Erf}' \left(\frac{c}{\alpha} \right) - \text{Erf} \left(\frac{c}{\alpha} \right) \quad (14)$$

When (c/α) exceeds unity, and on integration by parts, equation (15) is obtained

$$1 - \text{Erf}(x) = \frac{e^{-x^2}}{x\sqrt{\pi}} \left(1 - \frac{1}{2x^2} \right) + \frac{3}{2\sqrt{\pi}} \int_x^\infty \frac{e^{-x^2}}{x^4} dx \quad (15)$$

When $x > 5$ this is represented to within 1 per cent by

$$1 - \text{Erf}(x) = \frac{e^{-x^2}}{x\sqrt{\pi}} \quad (16)$$

and thus in the range $x_0 \geq 5$ we can express equation (14) in the form

$$\frac{N_1}{N_0} = \frac{2}{\sqrt{\pi}} e^{-x_0^2} \left(x_0 + \frac{1}{2x_0} \right) \quad (17)$$

The error function

$$\text{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$$

and tables of the error functions and its derivatives are available.^{10,11} For $x_0 = 3, 4$, use may be made of the following expansion with sufficient accuracy

$$\frac{N_1}{N_0} = \frac{2}{\sqrt{\pi}} e^{-x_0^2} \left\{ x_0 + \frac{1}{2x_0} - \frac{1}{4x_0^3} + \frac{3}{8x_0^5} - \dots \right\} \quad (18)$$

A simplified expression is obtained by considering the translational motion of the molecules in two dimensions instead of in three. Then putting

$$Mc^2/2 = E$$

$$\frac{dN_c}{N_0} = \frac{1}{RT} e^{-E/RT} dE \quad (19)$$

This formula is for all practical purposes sufficiently accurate and gives instead of (18)

$$\frac{N_1}{N_0} = \int_{c_0}^\infty \frac{dN_c}{N_0} = \int_{E_0}^\infty \frac{1}{RT} e^{-E/RT} dE = e^{-E_0/RT} \quad (20)$$

The numerical values of the average velocities of different molecular species are readily calculated from equation (10), or from $\bar{c} = 2.514/\sqrt{M}$ km/sec at 25° C.

Collisions

Collisions between molecules (or atoms)

The number of collisions per unit volume and per unit time is denoted by Z and termed the collision number. Let us consider two different molecules A and B , then the total number of collisions of one molecule A with those of type B per second (Z_{AB}) is given by

$$Z_{AB} = (8\pi kT/\mu)^{\frac{1}{2}} \sigma_{AB}^2 n_B \quad (21)$$

where σ_{AB} the collision diameter equals one-half the sum of the respective molecular diameters, μ is the reduced mass, m_A and m_B are the masses of molecules A and B respectively

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

and n_A and n_B are the number of molecules A and B per cm.³ Z_{AB} is about 10^{10} collisions per molecule second at STP. The total number of bimolecular collisions $Z(AB)$ between unlike molecules of type A and B per cubic centimetre per second is given by

$$Z(AB) = n_A \cdot Z_{AB} \quad (22)$$

$$\text{or} \quad Z(AB) = (8\pi kT/\mu)^{\frac{1}{2}} \sigma_{AB}^2 n_A n_B \quad (23)$$

For collisions between like molecules in a single gas, the collision number $Z(AA)$ is given by

$$Z(AA) = (4\pi kT/m_A)^{\frac{1}{2}} \sigma_{AA}^2 n_A^2 \quad (24)$$

substituting the known numerical values in equations (21), (23) and (24), we obtain

$$Z_{AB} = 4.571 \times 10^4 \cdot T^{\frac{1}{2}} \left(\frac{M_A + M_B}{M_A M_B} \right)^{\frac{1}{2}} \sigma_{AB}^2 n_B$$

$$Z(AB) = 4.571 \times 10^4 T^{\frac{1}{2}} \left(\frac{M_A + M_B}{M_A M_B} \right)^{\frac{1}{2}} \sigma_{AB}^2 n_A n_B$$

$$\text{and} \quad Z(AA) = 3.232 \times 10^4 \cdot (T/M_A)^{\frac{1}{2}} \sigma_{AA}^2 n_A^2$$

At STP $Z(AA)$ is equal to $3.852 \times 10^{44} \sigma_{AA}^2 / M^{\frac{1}{2}}$ collisions per cm³ sec. The mean time between collisions is the reciprocal of Z_{AB} , and the

mean free path (mean distance travelled between successive collisions) is given by equations (25) and (26), for like and unlike molecules respectively.

$$\lambda = \frac{1}{2^{\frac{1}{2}} \pi \sigma_{AA}^2 n_A} \quad (25)$$

$$\lambda = \frac{1}{\pi \sigma_{AB}^2 n_B} \quad (26)$$

These formulae are valid at high temperatures when there is no attraction between the molecules. At lower temperatures the mean free path is somewhat dependent on the temperature owing to an attraction between the molecules. According to Sutherland,¹²

$$\lambda = \lambda_{\infty} \frac{T}{C + T} \quad (27)$$

where λ_{∞} is the mean free path at very high temperatures and C a constant. The values of C are listed in Tables 1.2 and 1.3.

The mean free path λ is also calculated from the relation

$$\lambda = 2.331 \times 10^{-20} \left(\frac{T}{P \sigma^2} \right) \text{ cm} \quad (28)$$

at STP this equals $8.39 \times 10^{-21} / \sigma^2$ cm. P is the pressure in millimetres of mercury.

Collisions with a surface. To obtain the elementary derivation of the number \dot{n} of molecules striking a unit area per second we will again assume that the molecules are all moving with the same velocity uniformly divided in three dimensions. An area of, say, 1 cm^2 will be hit within a second by $\frac{1}{6}$ of all those molecules which are contained in the cylinder, of base 1 cm^2 and length \bar{c} . The factor $\frac{1}{6}$ enters, since only $\frac{1}{6}$ of the molecules move in a direction perpendicular to and towards the area. Thus

$$\dot{n} = \frac{1}{6} N \bar{c} = \frac{1}{6} N \sqrt{\frac{8RT}{\pi M}} \quad (29)$$

If we allow for the distribution of the velocities and directions

$$\dot{n} = \frac{1}{4} N \bar{c} = N \sqrt{\frac{RT}{2\pi M}} = 3.637 \times 10^3 N \sqrt{T/M} \quad (30)$$

The number of molecules per cc at a pressure of p mm Hg and temperature $T^\circ \text{ K}$ is

$$N = 9.652 \times 10^{18} p/T$$

and therefore

$$\dot{n} = 3.511 \times 10^{22} p / \sqrt{MT} \text{ mol/sec cm}^2 \quad (31)$$

In hydrogen ($M = 2$) at $p = 1$ mm Hg and $T = 298^\circ$ K.

$$\dot{n} = 1.438 \times 10^{21} \text{ mol/sec cm}^2.$$

Triple collisions. The collision between three particles is called a triple collision. The three particles can collide simultaneously, or the third particle can collide with two others which are already in the state of (double) collision. This latter case is considered in calculating the number of triple collisions.^{13,14,15}

Tolman¹⁴ defines a ternary collision as occurring when the rigid spheres approach to within an arbitrary distance of each other. Then, using the previous symbolism,

$$Z(ABC) = 8\sqrt{2} \cdot \pi^3 \sigma_{AB}^2 \sigma_{BC}^2 \delta \sqrt{kT} \left(\frac{1}{\sqrt{\mu_{AB}}} + \frac{1}{\sqrt{\mu_{BC}}} \right) n_A n_B n_C \quad (32)$$

where δ is of the order of 1 \AA .¹⁶

Alternatively, the frequency of ternary collisions may be derived from the collisions of the molecular pair AB with all the C molecules. On this basis, Moelwyn-Hughes¹⁷ gives the collision frequency

$$Z(ABC) = n_A n_B n_C 4\pi(r_A + r_B + r_C)^2(r_A + r_B)^3 \left[\frac{kT}{\pi} \left(\frac{1}{m_C} + \frac{1}{m_A + m_B} \right) \right]^{\frac{1}{2}} \quad (33)$$

where r is the appropriate molecular radius.

When A and B are the same this expression reduces to

$$Z(AAC) = n_A^2 n_C 4\pi(2r_A + r_C)^2(2r_A)^3 \left[\frac{kT}{\pi} \left(\frac{2}{m_A} + \frac{1}{m_C} \right) \right]^{\frac{1}{2}} \quad (34)$$

Obviously this collision frequency is a very sensitive function of the molecular radius r_A . The expressions for ternary collisions are valid to within the order of magnitude, due to the uncertainty involved in defining the collision.¹⁸

At 0°C and 760 mm Hg the ratio of the triple collisions to double collisions is given by

$$\frac{Z_3}{Z_2} = 2.5 \times 10^{25} \tau \cdot \frac{1}{\sqrt{M}} \left(\frac{\sigma + \sigma_2}{2} \right)^2 \quad (35)$$

The exact values for the life time τ and the effective diameter of the double complexes σ_2 are not known exactly, but σ_2 will be of the same order of magnitude as σ and $\tau = \frac{\sigma}{c} \simeq 10^{-12} \text{ sec}^{-1}$. With these values

$$\frac{Z_3}{Z_2} \simeq 10^{-3} - 10^{-4}$$

Another approximation^{13,19} for the relative number of the triple collisions is the ratio of the molecular diameter, σ , to the mean free path, λ .

$$\frac{Z_3}{Z_2} \simeq \frac{\sigma}{\lambda} \quad (36)$$

Viscosity

Consider two horizontal and parallel plates at a distance x , one of which (the upper) is moved with the velocity W . Then the force acting on 1 cm² of the stationary plate is

$$F = \eta \frac{\partial W}{\partial x} \quad (37)$$

where $\partial W/\partial x$ is the velocity gradient between the two plates and η is the coefficient of viscosity of the gas. Since the force is equal to the momentum transferred in unit time, we obtain the following kinetic expression for the coefficient of viscosity. In any arbitrary plane between the two plates the molecules arrive from layers situated at a distance of λ above and below this plane. The difference in the additional velocities (due to streaming) of the molecules in these two layers is $2\lambda \frac{\partial W}{\partial x}$, and the number of molecules passing per second through 1 cm² of the arbitrary plane $\frac{1}{6} N\bar{c}$ (N = number of molecules per cc). Thus we have

$$F = 2\lambda \frac{\partial W}{\partial x} \cdot \frac{1}{6} N\bar{c}m \quad (38)$$

or comparing this with (37)

$$\eta = \frac{1}{3} \lambda N\bar{c}m = \frac{1}{3} \lambda N\bar{c}M/N \quad (39)$$

or since

$$\lambda = \frac{1}{N\pi\sigma^2\sqrt{\pi}}$$

$$\eta = \frac{1}{3\sqrt{2}} \cdot \frac{\bar{c}M}{\pi\sigma^2N} \quad (40)$$

More rigorous calculations employing certain correction factors lead to the following expression (41), for the coefficient of viscosity of a gas at medium pressures.

$$\eta = \left(\frac{mkT}{\pi}\right)^{\frac{1}{2}} \cdot \frac{1}{\pi\sigma^2} \quad (41)$$

The viscosity should therefore be independent of the concentration and vary as the square root of the temperature. In practice, the validity

of this formula is confined to a certain pressure region. Considerable discrepancies appear at high pressures when the dimensions of the molecules cannot be neglected compared with the mean free path, and at low pressures when the mean free path is comparable with the distance of the decisive dimensions of the apparatus used for the measurement of the viscosity. We shall deal with the behaviour of gases at low pressures in a separate section. Also the temperature variation, which is very different from that for liquids, where viscosity decreases as temperature increases, is not predicted accurately by formula (41). The power for the temperature variation is certainly greater than one-half, and for a variety of organic vapours it has been shown²⁰ that η varies linearly with T . It is to be expected²¹ that for non-polar gases η will vary linearly with temperature over the range $T/T_c = 0.4-0.9$. The Sutherland formula (27), which corrects for the variation of mean free path with temperature applies also to molecular diameters. Applying this to equation (41), the expression

$$\eta = \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \left(\frac{1}{\pi \sigma_{\infty}^2} \right) \left(1 + \frac{C}{T} \right) \quad (42)$$

is obtained, where σ_{∞} is the molecular diameter at infinitely high temperatures. This gives an expression for the ratio of the viscosity of a gas at two temperatures

$$\frac{\eta_1}{\eta_2} = \left(\frac{T_1}{T_2} \right)^{\frac{3}{2}} \left(\frac{T_2 + C}{T_1 + C} \right) \quad (43)$$

which gives a fair empirical fit for most gases over a range of about 100–200° C. Table 1.2 gives the viscosities of some gases and values for the Sutherland constant, C .

A further semi-empirical equation due to Keyes²² correlates the experimental data over a wider temperature range than the Sutherland equation. This relation is

$$\eta = \frac{a_0 T^{\frac{3}{2}}}{T + a 10^{-a_1/T}} \quad (44)$$

and details of the constants a_0 , a and a_1 are given in ref 23. Many other equations for the temperature variation of viscosity have been proposed, and a summary is given by Partington.²⁴ The Sutherland constant, C , is less than the critical temperature, T_c , for most examples and empirical relations such as $T_c/C = 1.12$ ²⁴ and $C/T_c = 0.98$ ²⁴ have been proposed. More detailed elaborations of the theoretical background of the viscosity of gases are given by Chapman and Cowling,⁵ and Hirschfelder, Curtiss and Bird.²⁵

TABLE 1.2
Viscosities of inorganic gases at various temperatures

Temp. (°C)	Partington ²⁴			Gray ²³			Moelwyn-Hughes ¹⁷			Dushman ⁴		
	0°	20°	50°	100°	20°	0°	0°	0°	0°	25°	25°	25°
Gas	C (°K)	$\eta \times 10^7$ poises			$\eta \times 10^7$ poises			$\eta \times 10^7$ poises			C (°K) $\eta \times 10^7$ poises	
Air	112	1708	1807	—	2171	1813	—	—	—	—	—	
Ammonia	503	916	982	1092	1278	974	377	944	472	1030	—	
Argon	142	2114	2217	—	2695	—	156	2104	133	2267	—	
Bromine	533	1464	1526	—	1921	—	—	1328	—	1528 ²⁴	—	
			(19°)		(94°)							
Carbon monoxide	101.2	1659	1763	1864	2083	1753	109	1665	—	—	—	
Carbon dioxide	254	1375	1493	—	1725	1463	357	1380	233	1503	—	
			(26.9°)		(76.9°)							
Carbon disulphide	499.5	886	—	—	1303	—	—	—	—	—	—	
					(114.3°)							
Chlorine	330	1227	1312	1470	1651	1330	325	1218	—	—	—	
				(55.1°)	(99.4°)							
Cyanogen	330	928	987	—	1271	—	—	—	—	—	—	
			(17°)									
Helium	80	1885	1941	—	2281	1953	79	1887	97.6	1966	—	
Hydrogen	84.4	835	876	937	1032	882	77	850	70.6	904	—	
Hydrogen bromide	357	1617	1819	—	2344	—	—	—	—	—	—	
			(18.7°)		(100.2°)							
Hydrogen chloride	362	1313	1434	1600	1832	—	357	1332	—	—	—	
			(21°)	(54°)	(99°)							
Hydrogen iodide	331	1726	1857	—	2310	—	—	—	—	—	—	
			(20.5°)		(96.6°)							