

PART I  
GENERAL PRINCIPLES OF  
PHYSICAL CHEMISTRY



CHAPTER I  
EXPERIMENTAL FOUNDATIONS OF THE  
KINETIC-MOLECULAR THEORY

It is one of the aims of physical chemistry to predict quantitatively, from the ascertainable properties of individual chemical species, the material and energetic behaviour of systems containing several species. To do so requires experimental information from calorimetric, spectroscopic and electrostatic sources, and a mastery of the chemical aspects of kinetic, quantal and thermodynamic theory. The task demands, not only an acquaintance with many different branches of science, but a due sense of perspective. The ultimate result, however, more than compensates for the effort, and enables the physical chemist to describe the phenomena under his purview with a precision as great as is possible in any of the other exact sciences, with most of which it makes direct contact.

Let us consider, for example, some of the physicochemical facts available in the description of hydrogen iodide, a typical diatomic molecule. In the crystalline state, which it naturally assumes at low temperatures, each molecule finds itself separated by  $4.370 \times 10^{-8}$  cm. from twelve equidistant neighbours in a cubic lattice. Its energy in this state, though low, can never sink below  $5.005 \times 10^{-15}$  erg, and manifests itself as an oscillation which, combining with similar motions of the other molecules, sets the whole crystal vibrating at various frequencies, the fastest of which is  $1.529 \times 10^{12}$  times per sec. When the crystal is heated, the molecular energy increases rather slowly, at a known rate, until at  $222.31^\circ$  it melts, and each molecule acquires an energy of  $4.720 \times 10^{-14}$  erg during the change of state. A further rise of  $15.44^\circ$  in the temperature brings the system to the boiling-point, when the molecule, absorbing a further  $3.261 \times 10^{-13}$  erg, detaches itself from its liquid neighbours, and passes into the comparative freedom of the vaporous state, where the average force of attraction between two molecules is as low as  $7.0 \times 10^{-12}$  dyne. It is only when the molecule has reached the vapour phase that it begins to reveal some of the secrets of its internal

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structure. The atoms of hydrogen and iodine, though slightly approaching and receding from each other  $6.924 \times 10^{13}$  times per sec., retain a constant average separation of  $1.617 \times 10^{-8}$  cm. Of the fifty-four electrons which, with the two atomic nuclei, constitute the molecule, two are in an exceptional state, vibrating with opposite spins about their mean positions at a frequency of  $2.566 \times 10^{15}$  reciprocal seconds, and causing the molecule to behave as if the nuclei had equal and opposite charges, their magnitude being one-twentieth of the electronic charge. Apparently unconcerned with these violent internal agitations of nuclei and electrons, the molecule moves about at an average velocity of  $1.984 \times 10^4$  cm./sec., encountering in that time about  $9.11 \times 10^8$  other molecules. Most of these intermolecular collisions leave the molecules unchanged, but there is a small probability—amounting to one in  $7 \times 10^{40}$ —that a collision between two molecules of hydrogen iodide under these conditions brings about their destruction, and the formation of molecular hydrogen and iodine. The chance that this event shall occur, though extremely small, is of the utmost significance, for if it were zero, hydrogen iodide would always remain hydrogen iodide, and chemistry would cease to exist. As things are, a slow reaction sets in and persists until one molecule out of every twenty-six initially present has been chemically converted. Nor is this its only possible fate; given an energy of  $2.127 \times 10^{-11}$  erg, the hydrogen iodide molecule dissociates into atoms.

Detailed accounts of how such results have been obtained form the bulk of the present text, which may appropriately begin with a description of some of the fundamental facts upon which the theories of chemistry are based.

### *The Atomic Nature of Matter*

The familiar facts which lie at the root of the atomic theory of matter may be restated in the following convenient, if somewhat artificial, description. Consider a box in the form of a cube of length 28.194 cm., which is kept at the temperature of melting ice ( $0^\circ\text{C.} = 273.1^\circ\text{K.}$ ). Let the box be successively filled at atmospheric pressure (1 atm. = the weight of a column of mercury 76 cm. in height and 1 cm.<sup>2</sup> in cross-section =  $76 \times 13.596 \times 981 = 1.014 \times 10^6$  dynes/cm.<sup>2</sup>) with various pure gases which are subsequently removed and analysed. The weight of any pure gas thus defined is its gram-molecular weight. The specified quantity of hydrogen chloride is found to weigh 36.4648 g. Chemical analysis attributes a weight of 1.00778 g. to combined hydrogen and 35.4570 g. to combined chlorine. If the box were filled with pure hydrogen and pure chlorine, the weights would be  $2 \times (1.00778)$  and  $2 \times (35.4570)$  g. respectively. A box full of chloroform vapour under the same conditions (referred to as normal temperature and pressure) would

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give on analysis 1.00778 g. of hydrogen,  $3 \times (35.4570)$  g. of chlorine and 12.009 g. of carbon. All hydrogen-containing compounds filling the container under the stipulated conditions are found to contain 1.00778 g. of combined hydrogen or an integral multiple of this amount. Similarly, the minimum weight of combined carbon in a gram-molecular weight of any of its gaseous compounds is 12.009 g. These facts make it clear that when the elements of matter react with one another they do so in fixed amounts which are characteristic of the elements, or in integral multiples of these fixed amounts. The situation is most readily comprehended if we assume, with Dalton, that elements consist of reacting units (atoms) such that one atom of any element can only react with 1, 2, 3, ... atoms of another element. This supposition enables us to determine directly the relative combining weights, or equivalent weights, of the elements, and the actual numbers of atoms in the molecules ( $\text{HCl}$ ,  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{CHCl}_3$ ). The minimum experimental value of the equivalent weight is termed the atomic weight. By weighing known volumes of argon gas under known conditions of temperature and pressure, the following values (Table 1) have been obtained by different observers:

TABLE 1

*Chemical Values for the Atomic Weights of Certain Elements*

Element	Atomic wt. g.	Investigator
Argon	39.91	Ramsay and Travers <sup>1</sup>
	39.88	Watson <sup>2</sup>
	39.9	Fischer and Fröbose <sup>3</sup>
	39.945	Schultze <sup>4</sup>
	39.91	Leduc <sup>5</sup>
Bromine	79.920	Moles <sup>6</sup>
	79.914	Reimann <sup>7</sup>
	79.922	Murray <sup>8</sup>
	79.920	Guy <sup>9</sup>
Silver	107.857	Baxter and Tilley <sup>10</sup>
	107.871	Richards and Willard <sup>11</sup>
	107.880	Stachler and Meyer <sup>12</sup>

<sup>1</sup> *Proc. Roy. Soc. A*, **64**, 183 (1899).

<sup>2</sup> *J. Chem. Soc.* **97**, 833 (1910).

<sup>3</sup> *Ber. dtsh. chem. Ges.* **44**, 92 (1911).

<sup>4</sup> *Ann. Physik*, **48**, 269 (1915).

<sup>5</sup> *Ann. Physique*, **9**, 5 (1918).

<sup>6</sup> *J. Chim. phys.* **14**, 389 (1916).

<sup>7</sup> *J. Chim. phys.* **15**, 293 (1917).

<sup>8</sup> *J. Chim. phys.* **15**, 334 (1917).

<sup>9</sup> *J. Chim. phys.* **17**, 171 (1919).

<sup>10</sup> *J. Amer. Chem. Soc.* **31**, 201 (1909).

<sup>11</sup> *J. Amer. Chem. Soc.* **32**, 48 (1910).

<sup>12</sup> *Z. anorg. Chem.* **71**, 368 (1911).

Argon does not react with any chemical atom, so that the only method available for determining its molecular weight is that outlined above. For reasons which will be clear later on, the actual weighing of the gas must be

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made at densities rather lower than that corresponding to a pressure of 1 atm. The atomic weights of bromine and silver have been determined by a variety of methods. In the cases cited in Table 1—which is merely representative of a much richer crop of results—the bromine was obtained from hydrogen bromide (HBr) and the silver from silver nitrate ( $\text{AgNO}_3$ ).

The original reason for choosing a box of this size ( $28 \cdot 194^3 = 22,412$  c.c.) was to give hydrogen an atomic weight of unity, which would be a convenient arbitrary standard. The convention failed in this respect, since the atomic weight of hydrogen turned out to be 1.00778, but the conventional standard is nevertheless retained. The atomic weight of oxygen on this scale is 16.0000 g., hence this value is taken as the standard to which the weights of other atoms are related. The atomic weights of the elements are given in Table 2.

The ratio of the equivalent weight of an atom to its atomic weight is called the valency. Atoms, therefore, can possess only integral valencies. Experiment reveals the maximum valency of any atom to be 7.

Adoption of the atomic theory to explain the laws of combining weights outlined above implies that equal volumes of all pure gases at the same temperature and pressure contain an equal number of molecules (Avogadro's law). The number of molecules which occupy 22,412 c.c. under normal conditions is termed the Avogadro number. It was first evaluated by Loschmidt.

#### *The Corpuscular Nature of Electricity*

The passage of electricity through conducting solutions (termed electrolytic conduction) differs from its passage through metals (termed electronic conduction) in that matter is transported and transformed in the former case. For example, a flow of electricity through an aqueous solution of hydrogen chloride causes the liberation of gaseous hydrogen at one electrode and of chlorine (not necessarily in the gaseous state) at the other. On the other hand, an indefinite amount of electricity may pass through a copper wire without effecting substantial change. In electrolysis, therefore, there occurs a radical interaction between electricity and matter which is absent in electronic conduction. Faraday's laws, which rank among the most accurate generalisations of science, state that 96,540 coulombs (= 1 faraday) of electricity are necessary to liberate 1.00778 g. of hydrogen, 35.457 g. of chlorine from a solution of hydrogen chloride, or, in short, 1 g.-equiv. of any element from conducting solutions of its compounds. For example, the complete electrolysis of a solution containing 1 g.-mol. of barium chloride ( $\text{BaCl}_2$ ) or of aluminium chloride ( $\text{AlCl}_3$ ) requires double and treble this amount respectively. Hence atoms of hydrogen, barium and

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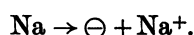
TABLE 2  
*Atomic Weights and Atomic Numbers of the Elements\**

	Sym- bol	At. no.	At. wt.		Sym- bol	At. no.	At. wt.
Aluminium	Al	13	26.97	Neodymium	Nd	60	144.27
Antimony	Sb	51	121.76	Neon	Ne	10	20.183
Argon	A	18	39.944	Nickel	Ni	28	58.69
Arsenic	As	33	74.91	Niobium	Nb	41	92.91
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	191.5
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Caesium	Cs	55	132.91	Potassium	K	19	39.096
Calcium	Ca	20	40.08	Praseodymium	Pr	59	140.92
Carbon	C	6	12.01	Protoactinium	Pa	91	231
Cerium	Ce	58	140.13	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Copper	Cu	29	63.57	Rubidium	Rb	37	85.48
Dysprosium	Dy	66	162.46	Ruthenium	Ru	44	101.7
Erbium	Er	68	167.64	Samarium	Sm	62	150.43
Europium	Eu	63	152.0	Scandium	Sc	21	45.10
Fluorine	F	9	19.00	Selenium	Se	34	78.96
Gadolinium	Gd	64	156.9	Silicon	Si	14	28.06
Gallium	Ga	31	69.72	Silver	Ag	47	107.880
Germanium	Ge	32	72.60	Sodium	Na	11	22.997
Gold	Au	79	197.2	Strontium	Sr	38	87.63
Hafnium	Hf	72	178.6	Sulphur	S	16	32.06
Helium	He	2	4.002	Tantalum	Ta	73	180.88
Holmium	Ho	67	163.5	Tellurium	Te	52	127.61
Hydrogen	H	1	1.0078	Terbium	Tb	65	159.2
Indium	In	49	114.76	Thallium	Tl	81	204.39
Iodine	I	53	126.92	Thorium	Th	90	232.12
Iridium	Ir	77	193.1	Thulium	Tm	69	169.4
Iron	Fe	26	55.84	Tin	Sn	50	118.70
Krypton	Kr	36	83.7	Titanium	Ti	22	47.90
Lanthanum	La	57	138.92	Tungsten	W	74	184.0
Lead	Pb	82	207.21	Uranium	U	92	238.07
Lithium	Li	3	6.940	Vanadium	V	23	50.95
Lutecium	Lu	71	175.0	Xenon	Xe	54	131.3
Magnesium	Mg	12	24.32	Ytterbium	Yb	70	173.04
Manganese	Mn	25	54.93	Yttrium	Y	39	88.92
Mercury	Hg	80	200.61	Zinc	Zn	30	65.38
Molybdenum	Mo	42	96.0	Zirconium	Zr	40	91.22

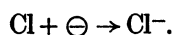
\* This table (from *J. Chem. Soc.* p. 1909 (1937)) has been compiled by Baxter, Hönigschmid and Lebeau for the International Union of Chemistry.

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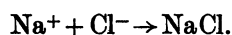
aluminium, which react with 1, 2 and 3 atoms of chlorine respectively, react also with 1, 2 and 3 units of electricity. As Johnstone Stoney first pointed out, electricity must therefore have a unitary structure, the maximum value of the unit being that which is sufficient to react with one univalent atom. The particle carrying a unit of negative electricity is called the electron (p. 28). All atoms, as is now quite well known (Chapter V, p. 236), contain electrons, identical in nature but differing in number and in the strength of attachment to the remainder of the atom. An atom of sodium, for example, can be fairly readily induced to part with one electron, yielding also a positively charged sodium atom (i.e. a sodium ion):



An atom of chlorine needs no encouragement to take up an electron, forming a negatively charged chlorine atom (i.e. a chlorine ion):



We see, then, that there are at least two distinct ways in which a neutral molecule of sodium chloride may be formed, according as the reacting units are atoms or ions:



The former of these occurs at fairly high temperatures on the walls of a vessel containing dilute chlorine gas and sodium vapour. The latter is the chemical reaction taking place when brine evaporates.

### *The Ideal Gas Laws*

At constant temperature, the volume of a given mass of gas varies inversely as the pressure (Boyle's law). At constant pressure, its volume is directly proportional to the absolute temperature (Charles's law). The two laws may be combined in the form  $PV/T = \text{constant}$ . The value of the constant depends clearly on the amount of gas considered. By Avogadro's law, we know that equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules, so that, if we express the constant as a function of the number ( $n$ ) of gram-molecules involved, we have

$$PV = nRT, \tag{1}$$

where  $R$  is a universal constant. The product (pressure)  $\times$  (volume) has the dimensions of energy, as may easily be verified by expressing both in terms of the fundamental units of mass, length and time. In the same way it may be shown that the products (surface tension)  $\times$  (area), which is a measure of superficial energy (p. 38), and (force)  $\times$  (distance), which is a measure of

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potential energy, have the same dimensions.\* Since  $n$  is a number,  $R$  has the dimensions of energy per degree of temperature, per gram-molecule of pure substance.

Sufficient data have already been given to allow an evaluation of  $R$ . For 1 g.-mol.,  $R = PV/T$ , and we have simply to insert any values for  $P$ ,  $V$  and  $T$  for any system containing 1 g.-mol. It will be most convenient to refer to the box described above, and the conditions prescribed for it. Since  $P = 1$  atm. and  $V = 22.412$  l. when  $T = 273.1^\circ$ ,  $R = 0.0821$  l.-atm./degree. In centimetre-gram-second (c.g.s.) units,  $P = 1.014 \times 10^6$  dynes/cm.<sup>2</sup>, and  $V = 22,412$  c.c., therefore

$$R = 8.318 \times 10^7 \text{ erg/degree.}$$

Finally, since Joule's mechanical equivalent of heat is  $4.184 \times 10^7$  erg/cal., we have  $R = 1.988$  cal./degree. Repeating the calculation which includes all the significant figures, we find the internationally accepted value of

$$R = 1.9869 \text{ cal./degree.}$$

Although most gases obey the laws  $PV = nRT$  to a first approximation, no material system obeys them absolutely—with the possible exception of photon gas, which consists of light quanta only. The extent of the deviations between actual behaviour and that defined by the equation depends upon the gas examined as well as on its condition. Generally, the most marked deviations are found in systems of complicated molecules, such as the vapours of organic liquids, at low temperatures and high pressures. Systems of simple molecules, such as the noble gases, at high temperatures and low pressures conform very well, the agreement becoming closer with increasing temperatures and dilutions. The ideal gas laws consequently represent a state of affairs to which real but simple gases approximate when highly rarefied.

*The Laws of Ideal Solutions*

The osmotic pressure of a solution may be regarded as the pressure exerted on the walls of the containing vessel by the solute only. If the vessel containing a solution is furnished with a membrane which is permeable to the solvent but not to the solute, and is then immersed in the pure solvent, the latter exerts, at equilibrium, an equal pressure on both sides of the membrane. The resultant pressure exerted on the membrane, which can be measured directly, is therefore the osmotic pressure. Experiment shows that dilute solutions of non-electrolytes exert an osmotic pressure equal in magnitude to the gas pressure which the solute—or any other compound—

\* Let the units of mass, length and time be denoted by  $M$ ,  $L$  and  $t$ . The units of derived quantities are then: volume ( $L^3$ ), velocity ( $Lt^{-1}$ ), acceleration ( $Lt^{-2}$ ), force ( $MLt^{-2}$ ), momentum ( $MLt^{-1}$ ), energy ( $ML^2t^{-2}$ ), pressure ( $ML^{-1}t^{-2}$ ), surface tension ( $Mt^{-2}$ ).

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would exert if it existed as a gas at the same temperature and molecular concentration. Table 3 contains Pfeffer's experimental values for the osmotic pressure of a solution containing 0.02906 g.-mol. of sucrose per litre

TABLE 3

*The Osmotic Pressure of Solutions of Sucrose in Water*

$t^{\circ}\text{C.}$	Pressure (atm.)	
	Observed by Pfeffer	Calculated by van't Hoff
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

of solution (which equals 1 g. of sugar per 100 c.c.). The third column shows the values calculated by van't Hoff using the equation  $PV = nRT$ , or  $P = RTC$ , where  $C$  is the concentration.\* Table 4 contains more recent and more accurate figures obtained in a non-aqueous solution, with a

TABLE 4

*The Osmotic Pressure of Solutions of Tetraphenylethylene in Benzene at 26.85° C.*

Concentration (weight, molar)	Osmotic pressure (mm.)	
	Observed	Calculated
0.01919	313.2	312.7
0.01502	242.9	244.8
0.01007	162.1	164.1
0.004057	66.7	66.1
0.000466	10.5	7.6

porous disk as a semipermeable membrane. The pressures given in the last column were calculated for the equation  $PV_0 = xRT$ , where  $V_0$  is the molar volume (i.e. volume of 1 g.-mol.) of solvent, and  $x$  is the molar fraction of solute. The absolute error in the last experiment is about the same as for the others, but the percentage error is higher.† The direct applicability to

\* van't Hoff's figures are reproduced as he gave them, although they are in need of a slight correction due to the expansion of the solution.

† Eichelberger, *J. Amer. Chem. Soc.* **53**, 2025 (1931).



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solutions of the laws of Boyle, Charles and Avogadro was first demonstrated by van't Hoff. It affords the clearest insight yet given into the nature of the dissolved state of matter. Moreover, since the molecules of most substances cannot be obtained in the gaseous state—at least at ordinary temperatures, or at concentrations sufficient to be of any practical use—the van't Hoff laws, in one form or another, are used almost exclusively in the determination of molecular weights.

*The Kinetic Theory of Gases*

The kinetic theory of gases, developed concurrently with the atomic theory of matter, offers an interpretation of the ideal gas laws. The postulates underlying the kinetic theory in one of its original forms are that the molecules constituting a gas are hard, elastic spheres endowed with incessant and temperature-dependent translatory motion, and occupying a volume which is negligible in comparison with the total volume of the gas. Since the molecules are perfectly resilient, the kinetic energy of an assembly of molecules at constant temperature remains constant in spite of repeated collisions amongst themselves and against the walls of their container. There exists neither repulsion nor attraction between the molecules, and the pressure exerted by the gas is ascribed completely to molecular bombardments on the walls. When the gas is at equilibrium, the molecular motions are quite random; and the exact mathematical theory (Chapter III) takes this into account. In the present chapter, however, we must be satisfied with considering how this simple picture of gaseous constitution explains the ideal gas laws.

Let there be  $n$  molecules, each of mass  $m$  grams and travelling with a velocity  $c$  cm./sec., enclosed in a cube of length  $l$  cm. In order to justify our use of the law of averages, we must add the proviso that  $n$  is a very large number. The velocity  $c$  of the molecules in space may be resolved into three component velocities,  $u$ ,  $v$  and  $w$ , referred to the three co-ordinate axes;  $c^2 = u^2 + v^2 + w^2$ . As  $n$  is very large, we may take as average values  $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}c^2$ . The motions may now be regarded as three independent motions, perpendicular to any two facing walls and parallel with the other four. Considering the to-and-fro motion along the  $x$ -axis only, the number of molecules striking one face of the cube in 1 sec. is  $n \cdot u/2l$ . The change of momentum due to each impact is  $2mu$ , hence the force  $f$ , or rate of change of momentum, is  $n \cdot u/2l \cdot 2mu = nm u^2/l$ ; and the pressure  $P = f/l^2 = nm u^2/V$ , or

$$PV = mnu^2. \quad (2)$$

But we have seen that, provided we take average values,  $\overline{u^2} = \frac{1}{3}c^2$ , hence

$$PV = \frac{1}{3}mnc^2. \quad (3)$$

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If we now let  $n$  stand for the number ( $N_0$ ) of molecules in 1 g.-mol., we have

$$PV = \frac{1}{3}Mc^2, \quad (4)$$

where  $M$  is the molecular weight ( $M = N_0m$ ). In order to coincide with the experimental law for 1 g.-mol. ( $PV = RT$ ), it follows that the molar energy is

$$E = \frac{1}{2}Mc^2 = \frac{3}{2}RT. \quad (5)$$

According to the kinetic theory, therefore, the energy of an ideal gas, which is entirely kinetic, is directly proportional to the absolute temperature. Since  $R$  is a universal constant, the energy of 1 g.-mol. of all ideal gases has the same value at a given temperature; in other words, we can insert any value for  $M$  which we choose into equation (5). If we compare two gases, the one containing  $n_1$  molecules and the other  $n_2$  molecules, in the same volume  $V$  at the same temperature and pressure, it follows from equations (3) and (5) that  $n_1 = n_2$ , which is Avogadro's law.

The value of  $c$  given by equation (5), namely,

$$c = \sqrt{\frac{3RT}{M}}, \quad (6)$$

is termed the root-mean-square velocity. It is the hypothetical velocity—differing a little from the most probable velocity—which all the molecules would possess if the total (kinetic) energy were distributed uniformly among them. For a given molecular species, the velocity is proportional to the square root of the temperature; for different gases at a fixed temperature, the velocities are inversely proportional to the square root of the molecular weights. The velocity, like the energy, is independent of the pressure. The relation  $c \propto \sqrt{1/M}$  was established experimentally by Graham. Different gases at a constant temperature were allowed to effuse through a porous plug (made of meerschaum, biscuit porcelain or perforated metal) into a Torricellian vacuum, and the times ( $t$ ) required to produce a fixed fall in the height of the mercury column were noted. Graham found, comparing nitrogen and ethylene  $t_{\text{C}_2\text{H}_4}/t_{\text{N}_2} = 987/986 = 1.001$ . Equation (6) would lead us to expect  $\frac{t_{\text{C}_2\text{H}_4}}{t_{\text{N}_2}} = \frac{c_{\text{N}_2}}{c_{\text{C}_2\text{H}_4}} = \sqrt{\frac{M_{\text{C}_2\text{H}_4}}{M_{\text{N}_2}}} = \sqrt{\frac{28.031}{28.016}} = 1.000$ . Graham\* was careful, however, not to conclude that the laws of effusion are obeyed with this degree of accuracy. In order to test any theory properly, it is always necessary to vary the parameters to as great an extent as experiment will allow. In the present instance, a fairer test is afforded by comparing the rates of effusion of two gases differing widely in molecular weights. Graham found hydrogen to diffuse 3.815 times faster than oxygen; equation (6) gives us a ratio of 3.985. The difference is greater than the margin of error

\* *Phil. Mag.* 2, 351 (1833).