

Graham's Laws of Diffusion and Effusion

Although Graham's Law is discussed in almost every introductory chemistry textbook, an amazing amount of misunderstanding and misinformation on the subject exists. It is our contention that the discussion of Graham's Law in virtually every current textbook is either incomplete or incorrect. Incomplete because there are two distinct laws enunciated by Thomas Graham—a law of diffusion and a law of effusion. Incorrect because the explanations offered for the diffusion law are invariably incorrect. It is a rather surprising fact that the two laws give apparently identical final answers, although their basic molecular mechanisms are quite different.

The purpose of the present paper is threefold: (1) to straighten out the historical record; (2) to offer simple but essentially correct theoretical explanations of both laws; (3) to present experiments on the diffusion law which are suitable for lecture demonstrations or laboratory exercises.

The effusion law is seldom misconstrued, but the diffusion law has been consistently misunderstood. Indeed, the diffusion law was rediscovered experimentally in 1953 (1), and has since been the subject of considerable activity among those who study the diffusion of gases in porous media (2-15). Its current name is "equal pressure counterdiffusion" or "isobaric diffusion." It is nothing but Graham's law of diffusion (*not* effusion), first discovered in 1831.

The effusion law is rather difficult to demonstrate experimentally, but easy to explain theoretically. In contrast, the diffusion law is easy to demonstrate experimentally, but rather difficult to explain theoretically. The fact that both laws yield superficially identical results has no doubt contributed to the confusion. From a theoretical point of view, the effusion law and the diffusion law are manifestations of rather different aspects of gas behavior, and can be effective pedagogic tools in any discussion of kinetic-molecular theory. From an experimental point of view, some very simple but effective experiments on the diffusion law are possible, as are some experiments quoted in textbooks as illustrations of Graham's diffusion law, but which in fact have nothing to do with it. These erroneous experiments can nevertheless be valuable as the basis for a discussion of gaseous diffusion in the conventional modern sense of the word.

Historical

Graham's paper on diffusion was read before the Royal Society of Edinburgh in December 1831, and

later published in three sections in the 1833 Philosophical Magazine (16). In modern terminology the law of diffusion he gave may be stated as follows: when two gases interdiffuse at uniform pressure, their fluxes are in the inverse ratio of the square roots of their molecular weights. Graham's diffusion experiments were apparently inspired by some observations published by Doeberleiner in 1823, in which he noticed the escape of hydrogen from a jar with a slight crack in it, so that the water of the pneumatic trough rose into the jar. Graham repeated Doeberleiner's experiment, with variations, and finally settled on an elegantly simple instrument which he called a "diffusion-tube."

The diffusion-tube consisted of a length of calibrated glass tube, plugged at one end with porous plaster about $\frac{1}{5}$ in. thick. The open end of the tube was immersed in a vessel of water or mercury. The gas to be investigated was added to the tube (by displacement of water or mercury) and its volume noted. As the gas diffused out through the porous plug and the air diffused in, the liquid level tended to rise or fall in the tube, depending on whether the gas was lighter or heavier than air, respectively. Graham noted that such a change in liquid level would produce a pressure difference across the plug and make the interpretation of the results difficult; he therefore kept the pressure uniform by flowing water or mercury into or out of the outer vessel so as to keep the outer liquid level the same as that inside the tube. After some time all the gas had diffused out and been replaced by the air which had diffused in. The volume of diffused gas would be just the same as the initial volume of gas added to the tube, since all of the gas would have diffused out. The volume of diffused air would be equal to this volume plus or minus the volume change during the diffusion. The ratio of these two volumes would then be the ratio, not of the instantaneous fluxes, but of their time integrals. In modern notation this would be expressed as

$$\frac{V_{\text{gas}}}{V_{\text{gas}} + \Delta V} = \frac{\int_0^{\infty} J_{\text{gas}} dt}{\int_0^{\infty} J_{\text{air}} dt} = \frac{J_{\text{gas}}}{J_{\text{air}}} \quad (1)$$

the last step following from the assumption that the ratio of the fluxes is a constant even if the individual fluxes vary with time.

The table shows results taken from Graham's 1833 paper, together with the results obtained by us as described later. The agreement with the square-root law is remarkable. The values reported to only two significant figures were obtained with mercury instead of water, so that it was more difficult to keep the pressure uniform; the value for CO₂ was obtained with satu-

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Ratios of Diffusion Fluxes at Uniform Pressure

Gas	Graham	$J_{\text{gas}}/J_{\text{air}}$	$(M_{\text{air}}/M_{\text{gas}})^{1/2}$
	Present work		
H ₂	3.83		3.791
He		2.66 ± 0.01	2.690
CH ₄	1.344	1.33 ± 0.01	1.3437
C ₂ H ₄	1.0191		1.0162
CO	1.0149		1.0169
N ₂	1.0143	1.02 ± 0.01	1.0168
O ₂	0.9487	0.960 ± 0.005	0.9514
H ₂ S	0.95		0.9219
Ar		0.855 ± 0.011	0.8516
N ₂ O	0.82		0.8112
CO ₂	0.812		0.8113
SO ₂	0.68		0.6724

rated brine, in which CO₂ is not as soluble as in water. It should be emphasized that in all these experiments the mean free path of the gas molecules is smaller than the holes in the porous plug, so that many molecular collisions occur. In other words, the molecules do *not* behave independently.

To skip ahead a few years, the next important work on the interdiffusion of gases was carried out by Loschmidt (17), who dispensed with the porous diaphragm and used a closed vessel in the form of a long tube with a valve in the middle. Each half of the tube was filled with a different gas, the middle valve was opened for a measured period of time, and then the partially mixed gases analyzed. This general method is still in use. It is obvious, from the fact that the pressure does not continuously increase in one half of the tube during the diffusion, that the fluxes of the two gases must be equal and opposite. It is not so obvious that a small pressure gradient must develop to keep the two diffusion fluxes equal, and that the Loschmidt diffusion experiment is therefore fundamentally different from the Graham one. As a matter of fact, the pressure gradient is almost immeasurably small, except in capillary tubes, and it is only in comparatively recent times that it has been detected by direct experimental measurement (18–20). Its consequences, however, are large. In any event, Loschmidt and subsequent workers assumed that Graham's law of diffusion was applicable to experiments of the Loschmidt type; a consequence of this assumption is that the diffusion coefficients of gases 2 and 3 into a reference gas 1 should vary inversely as the square roots of the molecular weights of 2 and 3,

$$\frac{J_2}{J_3} = \frac{D_{12}}{D_{13}} \approx \left(\frac{M_3}{M_2}\right)^{1/2} \quad (2)$$

This is actually only a crude approximation for most systems, although it is correct in the limiting case that the reference gas 1 has molecules which are infinitely large and heavy compared to the molecules of 2 and 3. The result was that Graham's law of diffusion came to be regarded as only a rough approximation instead of the highly accurate result shown in the table (21).

To return to the chronological order, Graham's paper on the *effusion* of gases into a vacuum through an aperture in a thin plate was published in 1846 (22), thirteen years after the publication of his diffusion paper. The law of effusion sounds much like the law of diffusion: the effusive fluxes of two gases at the same pressure are in the inverse ratio of the square roots of their molecular weights. But the basic mechanisms of diffusion and effusion must be different, as shown by the fact that the effusion law holds only for small holes in *thin*

plates. If the plate is replaced by a capillary tube, the discharge of the gas no longer follows such a simple relation to the molecular weight; this phenomenon was also studied by Graham in his 1846 paper, and named *transpiration*. In modern terminology it would be called viscous flow.

Graham was perfectly clear that diffusion, effusion, and transpiration were three different processes, and stated so in the most explicit terms in a much later paper on the passage of gases under pressure through porous plates (23):

... but it is important to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature.

Graham's insight seems all the more remarkable when we recall that most of his work was done before the mathematical basis of the modern kinetic theory of gases was formulated by Clausius, Maxwell, Boltzmann, and others. It is a pity that he has been so badly served in modern times that his original law of diffusion had to be rediscovered experimentally 120 years later.

Theoretical

We discuss the effusion law first, because it is conceptually the simpler, and discuss the diffusion law second, even though it was discovered thirteen years earlier. We finally discuss the theory of diffusion coefficients, as measured in Loschmidt's experiments.

The validity of the effusion law depends on the condition that the molecules make no collisions with each other after entering the orifice. Under these conditions the flux J (molecules or moles cm⁻² sec⁻¹) through the orifice and into a vacuum is proportional to the molecular (or molar) density n and to the mean molecular speed v , and the constant of proportionality depends only on the properties of the orifice,

$$J = \alpha nv \quad (3)$$

where α is a constant. For example, $\alpha = A/4$ for an infinitesimally thin orifice of area A . Two different gases at the same pressure and temperature will therefore effuse from the same orifice in the ratio, as measured in two separate experiments,

$$\frac{J_1}{J_2} = \frac{v_1}{v_2} \quad (4)$$

The well-known equality of mean molecular kinetic energies requires that v vary inversely as the square root of the molecular mass, from which the effusion law follows immediately.

The foregoing explanation is often applied also to the diffusion law, but is clearly inapplicable because of the fundamental assumption of no molecular collisions. The best simple physical explanation of the diffusion law is based on a calculation of the momentum transferred to the walls of the porous septum by the diffusing gases, as suggested by Hoogschagen (1, 2) following the ideas of Kramers and Kistemaker (18). The basic idea is that there is no force on the porous septum if there is no pressure gradient in the gas. Since the only way the gas can exert force on the septum is by impacts of molecules, there must be no net momentum transferred to the septum by the diffusing molecules according to Newton's second law of motion. In other words, the momentum transferred by one of the diffusing gases

must be exactly balanced by an equal and opposite momentum transferred by the other gas. We can calculate the average momentum transferred per unit time as approximately equal to the average momentum per molecular impact multiplied by the average number of impacts per unit time on an elementary section of the septum material. The average momentum transferred per collision will be proportional to the average net momentum per molecule, mV , where V is the mean diffusion velocity. It must be emphasized that V is an entirely different quantity from the mean speed v . In the first place, $V = 0$ in a nondiffusing gas because as many molecules come from one direction as from another; in the second place, V is usually of the order of 1 cm/sec or less, whereas v is of the order of 10^4 cm/sec. By definition, V is related to the flux by $nV = J$. The average number of impacts per unit time will be proportional to nv , so that the momentum transferred is proportional to $(mV)(nv)$. Zero pressure gradient requires that this quantity be the same for each diffusing gas,

$$(m_1 V_1)(n_1 v_1) = (m_2 V_2)(n_2 v_2) \quad (5)$$

This can be rearranged to

$$\frac{n_1 V_1}{n_2 V_2} = \frac{m_2 v_2}{m_1 v_1} \quad (6)$$

and since the flux is, by definition, equal to nV , we obtain for the diffusion law

$$\frac{J_1}{J_2} = \frac{m_2 v_2}{m_1 v_1} = \left(\frac{m_2}{m_1} \right)^{1/2} \quad (7)$$

The similarity and contrast between the effusion law, eqn. (4), and the diffusion law, eqn. (7), are remarkable. Both yield the same final result, $J_1/J_2 = (m_2/m_1)^{1/2}$, but the effusion law does so because J is directly proportional to v , whereas the diffusion law does so because J is inversely proportional to mv . The accuracies and ranges of validity of the two laws are also quite different. The effusion law is exact provided that the mean free path of the molecules is much larger than the dimensions of the aperture. The diffusion law is, from the foregoing derivation, only approximate, but its range of validity does not depend on any relation between the mean free path and the internal geometry of the porous medium. The approximation arises from calculating the average of a product as the product of two averages; it can be shown from the rigorous Chapman-Enskog kinetic theory of gases that this approximation is very accurate in the present case (11, 24), but this is not obvious from the derivation as given. Thus the diffusion law applies to any porous medium (including capillaries) over the whole pressure range from the free-molecule region to the hydrodynamic region, whereas the effusion law applies only in the free-molecule region.

Neither of the foregoing explanations can be applied to the Loschmidt experiment, in which the experimental arrangement automatically requires that $J_1 = J_2$. The usual mean-free-path treatment of such diffusion experiments starts much like the foregoing effusion calculation, but then inserts an extra flow term to force $J_1 = J_2$ (25). The physical cause of this flow term is the small pressure gradient that develops during the experiment. From this it is found that the diffusion coefficient D_{12} , which is defined by the equation

$$J_1 = -D_{12} \frac{dn_1}{dz} \quad (8)$$

is given by

$$D_{12} = (\text{constant}) \left(\frac{1}{m_1} + \frac{1}{m_2} \right)^{1/2} \frac{T^{1/2}}{S_{12}} \quad (9)$$

where S_{12} is a cross section describing the collision between molecules of gases 1 and 2. The mass and temperature factors occur as they do because D_{12} is proportional to an average relative speed,

$$v_{\text{rel}} = (v_1^2 + v_2^2)^{1/2} \propto T^{1/2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right)^{1/2} \quad (10)$$

Ratios of diffusion coefficients are thus given not by eqn. (2) but by

$$\frac{J_2}{J_3} = \frac{D_{12}}{D_{13}} = \left(\frac{M_3}{M_2} \right)^{1/2} \left[\left(\frac{M_1 + M_2}{M_1 + M_3} \right)^{1/2} \frac{S_{13}}{S_{12}} \right] \quad (11)$$

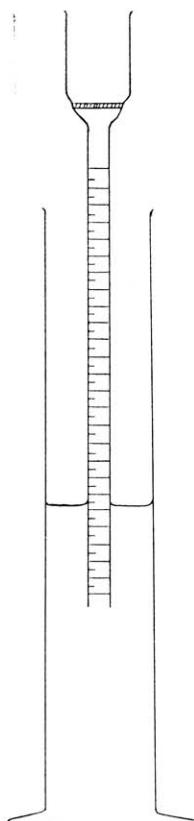
where the M 's are molecular weights. Only in rare cases is the quantity in brackets equal to unity.

In short, the molecular mechanisms are quite different for effusion, equal pressure diffusion (Graham), and equal flux diffusion (Loschmidt).

Demonstration Experiments

A diffusion-tube for student use is easily constructed from a small funnel with a sintered glass frit of ultrafine porosity, to the bottom of which is sealed a length of calibrated glass tubing (see figure). The present experiments were performed with a Büchner funnel having a 3-cm diameter frit with a nominal maximum pore size of 0.9–1.4 micron, to which was sealed a piece of tubing of about 25 cc capacity salvaged from a broken buret, as shown in the figure. The diffusion-tube could be filled with water by pumping from the top of the funnel with a water aspirator so as to draw water in from the bottom. The water level in the tube was noted, gas was quickly introduced by bubbling it in from the bottom, and the new water level noted. The water levels were equalized on the inside and outside of the tube, and kept equal while diffusion occurred by running water into, or siphoning it out of, the outer vessel. Diffusion was complete for the heavier gases in $1/2$ to 1 hour. The flux ratio was then easily calculated from eqn. (1).

In the first experiments the gas-to-air volume ratios were consistently below the theoretical values by at least 1%. The error was attributed to the fact that the gas inside the diffusion-tube was saturated with water vapor, but the air outside the tube was not. A piece of dampened tissue or filter paper placed in the upper part of the funnel saturated the outer air with water vapor and removed this small systematic error. In this way consistent results repro-



Diffusion-tube constructed from a fritted-glass Büchner funnel and a piece of buret tubing.

ducible to 1–2% could be easily obtained, as shown in the table. The agreement with the square-root law is within the reproducibility of the experiments, even though the pore size is about ten times the mean free path. The uncertainties shown in the table are the average absolute deviations for a series of about six separate runs.

Such light gases as hydrogen and helium diffused through the porous frit too fast to allow accurate initial volumes to be obtained. After the runs with the heavier gases were finished, about $\frac{2}{3}$ of the surface area of the porous frit was painted over with nail polish; this reduced the diffusion rate sufficiently to obtain consistent results with helium, which are given in the table.

An experiment quoted in many textbooks as an illustration of Graham's law of diffusion is the diffusion of NH_3 and HCl gases towards each other from opposite ends of a tube filled with air. A ring of NH_4Cl smoke forms where they meet, and the distances from the ring to the ends of the tube are supposed to be in the same ratio as the square roots of the molecular weights of HCl and NH_3 , which is 1.47. In actual fact this experiment illustrates Loschmidt's experiments, not Graham's, and the ratio of the distances should be the same as the ratio of the diffusion coefficients of NH_3 -air and of HCl -air, as given by eqn. (11). These diffusion coefficients are not known from independent experiments, but their ratio can easily be calculated from the known intermolecular forces (26), which are characterized by a range or size parameter σ and another parameter ϵ equal to the maximum energy of attraction between two molecules. The ratio of cross sections in eqn. (11) is then given by

$$\frac{S_{13}}{S_{12}} = \frac{\sigma_{13}^2 \Omega^{(1,1)} * (kT/\epsilon_{13})}{\sigma_{12}^2 \Omega^{(1,1)} * (kT/\epsilon_{12})} \quad (12)$$

where $\Omega^{(1,1)}$ is a tabulated function of the dimensionless variable kT/ϵ , k being Boltzmann's constant. Mason and Monchick (26) report $\sigma = 3.384 \text{ \AA}$ and $\epsilon/k = 186^\circ \text{ K}$ for air- NH_3 , and $\sigma = 3.488 \text{ \AA}$ and $\epsilon/k = 178^\circ \text{ K}$ for air- HCl . From eqn. (11) we thus obtain

$$\frac{D_{\text{air-NH}_3}}{D_{\text{air-HCl}}} = (1.47)[(0.84)(1.04)] = 1.28 \quad (13)$$

This diffusion coefficient ratio of 1.28 is significantly different from 1.47. Anyone who tries this experiment soon discovers that the results do not conform to Graham's law; most textbooks are remarkably vague, or actually misleading, regarding the numbers involved. One notable exception is the text by Keenan and Wood (27), who quote actual experimental data and give a distance ratio of $42 \text{ cm}/33 \text{ cm} = 1.27$, in very good agreement with the calculated diffusion coefficient ratio.

We performed the smoke-ring experiment using a piece of 22 mm glass tubing 120 cm long, to which a meter stick was taped. Two partially hollowed corks were filled with cotton, one dipped in 12N HCl and the other in 6N NH_4OH , and plugged into the ends of the tube at the same instant. Approximately 20 minutes later a smoke ring of NH_4Cl formed. The distance ratio, obtained from seven runs, was 1.27 ± 0.02 . If the tube is allowed to stand undisturbed for a time, a beautiful series of Liesegang rings forms (28), which is interesting for a demonstration except that the Liesegang ring pattern is not reproducible from run to run. Tube diameter is an important factor in this experiment.

Convection occurred in a larger tube of 38 mm diameter, and in a smaller tube of 16 mm diameter the results seemed to depend erratically on the condition of the glass surface (our experiments were carried out in the summer, when humidity was high). Moisture is known to affect the NH_4Cl formation (29).

Professor L. C. Krisher has informed us that he performed this smoke-ring experiment as a lecture demonstration at Columbia University in 1961–63, and obtained a ratio of 1.27 ± 0.04 . Thus three completely independent sets of experiments are in good agreement with each other and with the diffusion coefficient ratio. It is of some interest that the shift from the ratio 1.47 to 1.27 is caused almost entirely by the extra mass factors of eqns. (10) and (11); the ratio of the cross sections is only 1.04, and is in fact in the opposite direction.

Discussion

It is remarkable that Graham's work on gaseous diffusion has been so long misunderstood. Even a fairly recent republication (30) of his experimental results did not seem to help, although the agreement with the square-root law clearly showed that it was no rough approximation that was in question, but a very precise result. Moreover, most of the textbook explanations of diffusion show a deep lack of comprehension of the rudiments of kinetic theory, in their assumption that a macroscopic diffusion flux is proportional to a molecular speed.

The correct kinetic theory explanations of Graham's diffusion, Loschmidt's diffusion, and even of Graham's transpiration (viscous flow) are not especially difficult. There seems to be no reason why they could not be discussed properly in even a beginning course. These phenomena represent quite assorted aspects of molecular behavior, and can be used to give a clear experimental basis to many of the fundamental ideas involved in the kinetic-molecular picture of matter, without the necessity of involving so much of the elaborate apparatus of modern physics in what amounts to little more than an appeal to authority.

As a final remark, we note that the Loschmidt diffusion coefficient *can* be obtained from Graham's experiment if the rate of change of the volume is observed, and not just the initial and final volumes. The correct diffusion equation when a net flow occurs is not eqn. (8), but is

$$J_1 = -D_{12} \frac{dn_1}{dz} + \frac{n_1}{n} J \quad (14)$$

where J is the net total flux (i.e., the algebraic sum of J_1 and J_2). Dr. R. B. Evans III at the Oak Ridge National Laboratory has used our diffusion-tube in such experiments and obtained good results. This experiment cannot be recommended for freshmen, unfortunately, because the differential equation describing the volume change with time is somewhat difficult to handle, and requires more mathematical background.

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