One and a Half Century of Diffusion: Fick, Einstein, before and beyond

Jean Philibert

Former Professor of Materials Science
 UNIVERSITE PARIS-SUD
e-mail : jean.philibert@lpces.u-psud.fr

1. INTRODUCTION

Migrations of atoms or molecules are the mechanism of kinetic processes in materials for their synthesis and processing as well as for their structural evolutions. Very often stress has been put on thermodynamics aspects, but only later on kinetic ones. The former are only stating necessary conditions for a given process to take place. However they are not 'sufficient', because the rate of a process cannot be predicted from thermodynamic data.

It seems rather surprising that scholars of the Enlightenment Century apparently didn't question the mechanisms of many technical processes, which are, as we know, controlled by diffusion processes : carbon diffusion in cementation process in order to produce steel from the iron, already described by the Roman scholar Pliny, and more generally by analogy other "cementation" processes (copper alloys for instance), the colours of stained glasses or earthenwares and Chinas (have a look at the diffusion of Copper (green colour) in the glaze of some earthenware artefacts).

2. THOMAS GRAHAM

The first systematic study was due to a Scottish Chemist, Thomas Graham. He was born in Glasgow in 1805 and considered as the "leading chemist of his generation". Let us just mention that Graham was the inventor of dialysis, that he defined as a method of separation by diffusion through a membrane (1854). His research work on diffusion in gases was performed from 1828 to 1833 and he presented his results to the Royal Society of Edinburgh in 1831. These were later published in the Philosophical Magazine in 1833 [1]. Let us quote the first lines of his first paper [2]:

"Fruitful as the miscibility of the gases has been in interesting speculations, the experimental information we possess on the subject amounts to little more than the well established fact, that gases of different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lighter uppermost, *but they spontaneously diffuse, mutually and equally, through each other*, and so remain in the intimate state of mixture for any length of time."

Graham did not only perform the first *quantitative* experiment of diffusion, but moreover the first reliable measurement allowing the determination of a coefficient of diffusion. The notion of coefficient of diffusion was not yet established at this time, not until 26 years later thanks to Fick. But time flowed until 1867, when Maxwell calculated the

coefficients of diffusion in gases from the numerical results of Graham! His coefficient of diffusion of CO_2 in air is accurate at ± 5%. Isn't it extraordinary ? An experimental set-up identical to Graham's was later used by J. Loschmidt in 1863 for his classical measurements on diffusion in a handful of gas couples.

Later on, Graham performed a series of diffusion experiments in liquids and noticed that diffusion in liquids is by three orders of magnitude smaller than in gases and that the diffusion rate slowed down during time. He also studied the uptake of Hydrogen by Palladium.

3. ADOLF FICK

We now arrive at this year 1855 which we are now celebrating, when Adolf Fick, only 26 years old, proposed the quantitative laws of diffusion. At that time, Fick was an anatomy demonstrator in Zürich. It is quite interesting to note that these basic equations are not due to a Chemist or a Physicist, but to a Physiologist! But Fick was a man with a large scientific culture, not only in medicine, but also in mathematics and physics. In 1856, he published a monograph entitled "Medical Physics", the first book of this kind, where he discussed biophysical problems, such as the mixing of air in the lungs, the work of the heart, the heat economy of the human body, the mechanics of muscular contraction, the hydrodynamics of the blood circulation, etc…Fick's name remains well known in the history of cardiology.

Let us come back to our main purpose by quoting the first lines of Fick's paper published in the Philosophical Magazine, (a paper translated from the original one in Poggendorff's Annalen) [3] : " A few years ago, Graham published an extensive investigation on the diffusion of salts in water, in which he more especially compared the diffusibility of different salts. It appears to me a matter of regret, however, that in such an exceedingly valuable and extensive investigation, *the development of a fundamental law*, for the operation of diffusion in a single element of space, was neglected, and *I have therefore endeavoured to supply this omission*."

Thinking about Graham results, Fick perceived the deep analogy between diffusion and conduction of heat or electricity. In other words, he had the premonitory intuition that diffusion could be described according to the same mathematical formalism as Fourier's law for heat conduction, (Fourier in 1822 [3b]), or Ohm's law for electricity. Going along this analogy, he posited that the flux of matter is proportional to the gradient of its concentration denoted by y with a proportionality factor k, which he called "a constant dependent upon the nature of the substances". Following always Fourier approach, by combining with the conservation of matter, he ends up with the basic equation (Fick's *original* notation [1]) :

$$\frac{\partial y}{\partial t} = -k \frac{\partial^2 y}{\partial t^2}$$

i.e. a partial derivative equation of the second degree.

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[1] The minus sign appears in both papers (German and English [3]).

Fick met a lot of difficulties to verify the validity of his equation. The second derivative of a concentration versus distance is not an easy quantity to measure with the required accuracy. However he was successful in performing a series of experiments under a stationary regime : in these conditions, he could check his equations since the mathematical solution, i.e. composition versus distance, is a linear one. He measured the diffusion of salt in water, within tubes of different lengths connecting two large reservoirs respectively of salt and pure water. In such a case, as Fick clearly explains, "the amount of salt was determined, which diffused out of the terminal section of the tube, in measured spaces of time, and which therefore also, in the same time, passed through any section of the cylindrical tube". Moreover, he pointed out that " as might be expected from Graham's experiments, the value of k increases with increase of temperature". And he added " probably this dependence upon temperature *is not a simple one*".

At this time, diffusion measurements by Graham and Fick were confined to fluids, because such measurements were possible at temperatures around room temperature. Apparently diffusion in solids was not a subject of concern to scientists, because such a process was not credible, as, for instance, acknowledged by a famous *savant* as Gay-Lussac. This belief was founded on a common opinion among chemists, according to the well known adage :"*corpora non agunt nisi soluta*". According to common sense, if diffusion in fluids appears as a quite "natural" process, in solids on the contrary it could seem exceptional, if not impossible… However solid state diffusion was active in many technical processes which should have been well known from scientists of this time. Not only technical processes, but also some experiments could have been seen as a signature of diffusion. Perhaps Robert Boyle (1627-1691) was, according to ref [4] the author of the first experimental demonstration of solid state diffusion. He observed the penetration of a "solid and heavy body" (probably Zinc) in a farthing (a small copper coin), so that this side took a golden colour, while the other side kept its original one. Boyle was a wise experimentalist: he explained in his Essay: "To convince the scrupulous, that the pigment really did sink… and did not merely colour the superficies, … By filing off a wide gap from the edge of the coin towards, it plainly appeared that the golden colour had penetrated a pretty way beneath the surface of the farthing (quotation from ref [4]). Boyle successfully synthesized Brass by the means of interdiffusion !

4. W.C. ROBERTS-AUSTEN

In the second part of the nineteenth century, metallurgical studies on steels opened the way to the study of diffusion in metals. But quantitative measurements were not performed before the very last years of the nineteenth century, thanks to William Chandler Roberts-Austen, a well known British metallurgist celebrated for his study of the equilibrium diagram Fe-C (one of the main steel component has been named 'austenite'). The excellent micrographs, due to his French friend Floris Osmond, of specimens of carburised iron, clearly showed the penetration of Carbon inside the bulk of Iron. Other experiments were quite demonstrative, for instance "diffusion welding" between two pieces of two metals pressed against each other (W. Spring, 1894) [4].

Interest of Roberts-Austen for diffusion is not a surprise, as he began as an assistant of Thomas Graham and later on succeeded him as Master of the Mint in London. When he was 'chemist and essayer" in this institution, he had at his disposal good analytical tools, useful to investigate systems based on precious metals. The limitations were essentially the range of temperatures he could manage, but he was lucky since the Pt/RhPt thermocouple was just invented at that time by the French physico-chemist Henri LeChatelier. Roberts–Austen measured the diffusivity of precious metals (Au, Pt, Rh) in liquid Lead, of Au and Ag in liquid Tin, and Au in liquid Bismuth.[5]. The specimens were cut in thin sections which were analysed by weight measurements (with a balance of maximum load 0.5 g and a sensitivity of 2 μg). His values of the coefficients of diffusion are comparable to modern ones. Finally he made a tentative of solid interdiffusion, gold into lead. On the basis of 6 or 7 sections of the lead substrate, he analysed the diffusion profiles after heat treatments at 4 different temperatures, and applying Fick's law he calculated the diffusion coefficients. His results are quite comparable to modern tracer measurements, with a right value of the activation energy, if the lower temperature coefficient is discarded. Roberts-Austen was specially lucky in choosing for his investigations the system Au/Pb, since it is now known that gold is a "fast" diffuser in lead - an imperative condition for measurements with the space resolution he could manage in his experiments.
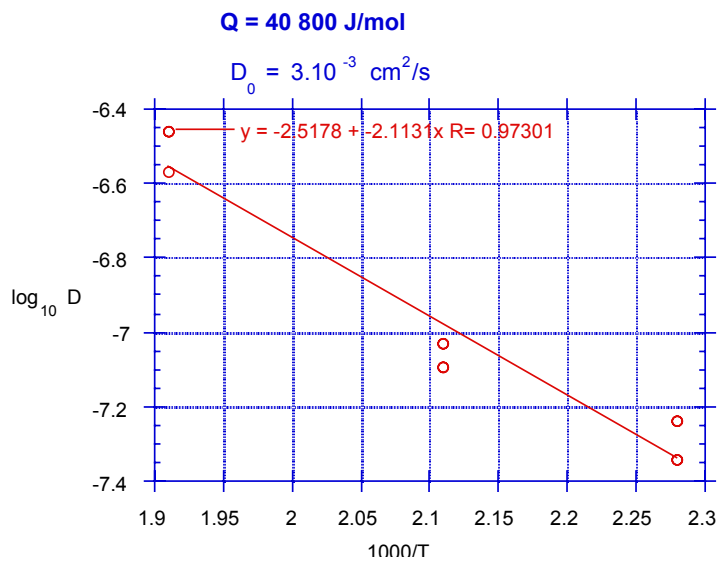
$Q = 40\ 800$ J/mol

$D_0 = 3.10^{-3}$ cm^2/s

Fig1 – Roberts-Austin data Au/Pb [5]

The Arrhenius graph (figure 1) is not Roberts-Austen's, it is mine! Apparently he didn't discuss the temperature dependence of the coefficient of diffusion in his "Bakerian Lecture" on the Diffusion in Metals published in 1896. The Arrhenius graph, so familiar to everybody with its pervasive use – and abuses – is based on Arrhenius equation, that Svante Arrhenius (1859-1927) proposed in his 1889 paper [6],— in the course of his investigations on the reaction rate of cane sugar (i.e. saccharose) inversion by means of

polarised light rotation — to describe quantitatively experimental results on a collection of the temperature dependence of chemical reaction rates. This proposal was completed by a theoretical assumption on the "active " state of the concerned substances). It came as a surprise to me, as I found that the $\exp(-Q/T)$ variation with temperature of the coefficient of diffusion was only invoked 30 years later (1922-1923) by Saul Dushman and Irving Langmuir [7] and independently by H. Braune (1924) [8] and that Langmuir considered this T-dependence as an empirical relation, without mentioning Arrhenius name!

Let me conclude this paragraph with a quotation from Roberts-Austen: "The evidence gathered by the metallurgist of active atomic movement in fluid and solid metals may sustain the hope of the physiologist that he will ultimately be able to measure the atomic movements upon which vitality and thought depend". This audacious sentence should take us back to Adolf Fick, a physiologist! Is life and consciousness purely a matter of chemistry? I leave my reader to choose his own opinion!

5. ALBERT EINSTEIN

There are two ways to begin with, in order to teach basic diffusion: either a phenomenological approach starting with Fick's laws and their mathematical solutions, or a physical and atomistic one, by considering the "random walk" of the diffusing particles. Random walk of particles in suspension in a fluid was discovered by a Scottish botanist, Robert Brown (1773-1858), who was observing with his microscope the "swarming" motion of small particles in the fluid extracted from living pollen grains[2]. He noticed that this motion was quite general in fresh pollen grains, as well as in dried ones. Brown's experiments with organic and inorganic substances, reduced to a fine powder and suspended in water, revealed such motion to be a general property of matter in this state. He published these results in a paper "A brief Account of Microscopic Observations" in 1828 [9]. The name "Brownian motion" has been coined in honour of Brown to name the random walk of microscopic particles in suspension in a fluid. This was probably one of the origins of Maxwell's kinetic theory of gases. It is pleasant to describe it in popular books (e.g. Gamow renown books [10]) as the wanderings of a "drunk sailor" (fig.2) !

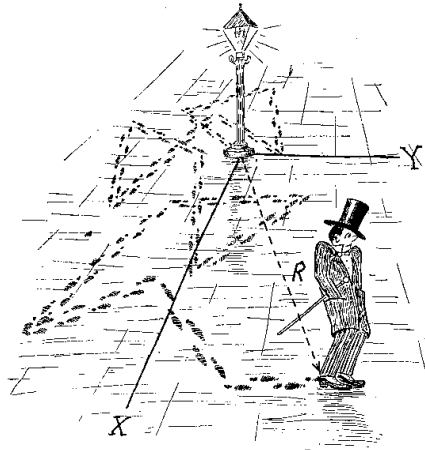[2] Brown was interested in the fecundation process of plants.

Figure 2 Random walk according to Gamow [10])

The mathematical form of Brownian motion was only derived almost a century later (in 1905) by Albert Einstein [11]. He was the first to understand, contrarily to many scientists of his time, that the basic quantity was not the average velocity of the particles, but their mean square displacement in a given time $<R^2(t)>$. Trajectories are such (see fig.3) that velocity is meaningsless. The mean displacement $<R(t)>$ of a large number of particles is nil in the case of a truly random walk, so it is the mean square which is the meaningful quantity. Einstein was then able to derive the fundamental relation between a macroscopic quantity, i.e. the coefficient of diffusion, and a microscopic one, the mean square displacement :

$$D = <R^2>/6t.$$

This first paper was followed a few months later by a more theoretical one, where Einstein studied not only the translational movement of suspended particles, but also the rotational one of spherical particles. Later on (1908) Einstein published "a simple theory of this phenomenon" (Brownian motion), which "would be welcomed by … chemists" ! In this paper, Einstein proposed thank to "simplified assumptions" a straightforward derivation of his equation, the one which was later given in most elementary text-books[3].

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[3] The five Einstein papers on Brownian movement have been published in an English translation with several notes and comments in a book [11].
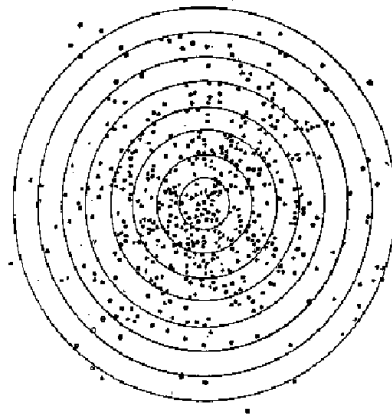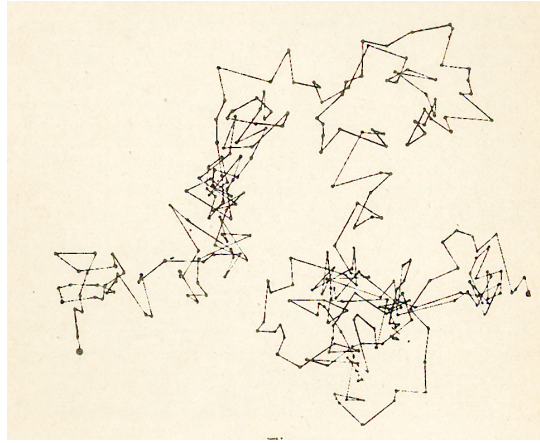
Fig 3. Brownian motion, after Jean Perrin [12]: An example of a trajectory (above) and statistical distribution of displacements (below, the circles correpond to fractions and multiples of the square root of the mean square displacement $<X^2>$)

In a series of clever experiments, Jean Perrin and his students could verify this relation, whose beautiful description can be found in his book "Les Atomes" [12], published in 1913, a book whose reading can still be recommended. Perrin's experiments just require a microscope, and a suspension in a liquid of small particles (tenths of microns in diameter). You merely have to observe the motion of a given particle and to point its position at regular time intervals. Jean Perrin describes enthusiastically "le prodigieux enchevêtrement de la trajectoire réelle" (fig.3), "the prodigious entanglement of the real trajectory. If we could plot the particle positions at time intervals hundred times smaller, every linear segment of the trajectory would take a polygonal shape as complicated as the whole trajectory, and so forth… We can see how in such a case the notion of a

tangent to a trajectory vanishes". What a premonitory description of a fractal line, fifty years before Benoit Mandelbrot's works [13]!

Jean Perrin checked that the particle displacements did exactly follow random laws. In two dimensions, the plane of the observations under the microscope, the values of $r(t)$ are distributed according to a Gaussian law. With a well defined standard deviation around the square root of $<R^2(t)>$ (fig. 4). According to J. Perrin again, "the randomness of the particle motion is definitely established".

In the same series of experiments, easy to reproduce with a simple experimental set-up, Jean Perrin succeeded in a quite remarkable result : the measurement of Avogadro's number according to another relation given in Einstein's first paper. Combining Einstein's relation with Stokes' law for the viscous liquid medium, he ends up with the X component of the displacement:

$$<X^2>/t = (RT/N)(1/3\pi\eta\rho)$$

where R is the (Joule) gas constant, N Avogadro's number, η the medium viscosity and ρ the particle diameter. The results with N of the order of a few units times 10^{23} is quite remarkable as it is an *absolute* determination, thanks to so simple an experimental tool – so far from our modern and sophisticated investigation machines! These simple experiments bore the definite proof of the existence of atoms against ambient scepticism. Let us quote Einstein:

"The agreement of these considerations with experience together with Planck's determination of the true molecular size from the law of radiation (for high temperatures) convinced the sceptics, who were quite numerous at that time (Ostwald, Mach) of the reality of atoms. The antipathy of these scholars towards atomic theory can indubitably be traced back to their positivistic philosophical attitude. This is an interesting example of the fact that even scholars of audacious spirit and fine instinct can be obstructed in the interpretation of facts by philosophical prejudices." [18].

6. … AND LATER ON…

With these strong bases, Fick's and Einstein's equations, the way was open to new experiments in order to determine diffusion coefficients in solids. But there were still the need for better experimental techniques. I would just select two of them, for the sake of limiting the length of this paper : radioactive tracers for self- (and hetero-) diffusion, and electron microprobe for interdiffsuion.

A critical stage in diffusion measurements was the work of another scientist, who deserves to be better known, György von Hevesy, a Hungarian born and a European personage (1885-1966) who worked in several famous places with scientists such as Ernest Rutherford, Henry Moseley or Niels Bohr. He was probably the first one to understand the usefulness of radioactive tracers as a tool in physics and chemistry. In 1912, when he was working in Vienna at the Radium Institute, he used radioactive Lead

as a "radioindicator" – "radiotracer" in modern language— (^{210}Pb, also called radium D, ^{212}Pb or Thorium B) in several studies, including Pb self-diffusion. Later on, in Vienna, Budapest or Copenhagen, he was using these radiotracers to study diffusion in salts, in liquid and solid Lead, and even in vegetables. After the discoveries in 1934 of artificial radioactivity by Irene and Frederic Joliot-Curie and neutron activation by E. Fermi, he prepared several artificial radioelements to study the assimilation of Phosphorus by plants or the metabolism of this element in rats. These studies are a little away from our field, but because of this large range of applications the Nobel Prize in Chemistry was awarded to Hevesy in 1943. An account of these studies was the object of a book "Radioactive Indicators" he published in 1946 [14][4]. Radiotracers were largely used after World War in many various ways developed by a lot of scientists in several countries, because this technique allowed very accurate measurements of diffusion coefficients in most of solids. Their importance is even underlined by their absence or rarity (and high price!) in a few important cases: Aluminium, Silicon and Oxygen, to cite the more important ones. There was no good remedy to this lack until the mass spectroscopy analysis of stable isotopes (specially Oxygen thanks to ^{18}O).

Finally I would like to mention another important tool which appeared in 1950-51 as the French physicist Raimond Castaing (1921-1998) built the first Electron Microprobe [15], an instrument which, by a very fine beam of electrons, allowed a quantitative local (i.e. on a micron scale) chemical analysis by X-ray spectroscopy and showed its powerful applications with the diffusion profile through the multiphase couple Cu/Zn. A new way of investigating interdiffusion processes became rapidly available to a large number of laboratories thanks to the commercial production of the instrument. Later on other analytical tools were available to perform diffusion measurements [16], [17], but their development would deserve another lecture.

References

[1] Diffusion Processes, Thomas Graham Symposium, ed. J.N. Sherwood, A.V. Chadwick, W.M.Muir, F.L. Swinton, Gordon and Breach, London, , 1971, Vol.1, Pages VI-VII.

[2] From E.A. Mason, ibid, pages 3-27.

[3] A.Fick, Poggendorff's Annalen. (1855) 94, 59-86. and (in English) Phil.Mag. S.4, Vol.10, 30-39. (1855)

[3b] J. Fourier, *Théorie analytique de la Chaleur*, Firmin-Didot père et fils, Paris,1822. Fac simile, Ed. Jacques Gabay, Paris 1988.

[4] L.W. Barr, *Diffusion in Materials*, DIMAT 96, ed. H.Mehrer, Chr. Herzig, N.A. Stolwijk, H. Bracht, Scitec Publications Vol.1, 1-9. (1997).

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[4] Hevesy's works are not limited to radiotracer applications. He was the initiator of chemical analysis by X-ray fluorescence (the subject of a book published in 1932), and with Coster in 1923 he discovered the element hafnium.

[5] W.C. Roberts-Austen, Bakerian *Lecture on the Diffusion in Metals*, Philos. Trans. Royal Soc. London, A187 (1896).

Part I, Diffusion of molten Metals, pages 383-403

Part II, Diffusion of solid Metals, pages 404-415.

[6] S. Arrhenius,*Über die Reaktionsgeschwindigkeit bei des Inversion von Rohrzucker durch Säuren*, Zeitsch. Phys. Chem 4, 226-248. (1889).

[7]S. Dushman, I. Langmuir, Phys.Rev 20, 113 (1922).

and I. Langmuir, Phys.Rev. 22, 357-398 (1923).

[8] H. Braune, *Über Diffusion in Mischkristallen*, Zeitsch. Phys. Chem. (1924), 110, 147.

[9] R. Brown, *Phil. Mag.* 4, 161. (1828).

[10] G. Gamow, *One, Two, Three…Infinity*, The Viking Press, New-York.

[11] A. Einstein, *Investigations on the Theory of the Brownian Movement*, edited with notes by R. Fürth, Dover publications,(1956).

[12] Jean Perrin, *Les Atomes*, 1ère éd Paris (1913), 2de éd., Paris, Alcan (1936)

[13] B.Mandelbrot, *Fractal Geometry of Nature*, W. H. Freeman and Company, New York, pp.232 - ff. , (1982).

[14] G. de Hevesy, *Some Applications of Isotope Indicators*, (1946) Stockholm.

[15] R. Castaing, A. Guinier, Proc. *First Europ. Conf. Electron Microscopy*, Delft, M. Nijhof, La Haye, 1950, p. 60. (1949).

[16] G.E. Murch, H.K. Birnbaum, J.R. Cost, Eds. *Nontraditional Methods in Diffusion*, The Metallurgical Society of AIME, Warrendale (USA), 1984.

[17], J. Kärger, P. Heitjans, R. Haberlandt, Eds. *Diffusion in Condensed Matter*, , Vieweg, 1998, Second Ed, 2005.

[18] Albert Einstein: Philosopher-Scientist, Paul Arthur Schilpp, editor, Cited by E. Nelson, Dynamical Theories of Brownian Motion, Princeton University Press (1967), Second edition <www.math.princeton.edu/~nelson/books.html>