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HISTORICAL NOTE

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Einstein and the osmotic theory

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One hundred years ago a young scientist called Albert Einstein published several papers [1–5] which brought forth a paradigmatic change in Physics. The United Nations declared the year 2005 as the Year of Physics celebrating the "annus mirabilis" of Einstein. This was certainly justified since these studies provided an explanation and theoretical background for the photoelectric effect and the quantization of energy [1], (because of the intense debate over the theory of relativity it was the only achievement which was mentioned in the reasons of Einstein's Nobel prize 1921 awarded in 1922 [6]), for the Brownian motion [3, 7], and the special theory of relativity [2, 4] (the first form of the famous $E=mc^2$ equation appeared in [4]). Soon it became clear that all of these discoveries are important also for chemists, especially the theory of Brownian motion which proved the existence of atoms, and gave a new tool for the determination of atomic dimensions and the Avogadro constant. In fact, it was the very purpose of Einstein's study since at that time the atomic theory was still questioned by leading scientists such as Wilhelm Ostwald and Ernst Mach. Actually, Einstein did not have too much information about the previous literature on the Brownian motion, although it was mentioned in [3] that the thermal motion, he intended to describe, might be equivalent to the Brownian movement. In the beginning of his second paper devoted to this problem [5] Einstein remarked that after the publication of his first paper Siedentopf (Jena) informed him that several physicists, including Gouy (Lyon), based on direct observations had come to the conclusion that the so-called Brownian motion is caused by irregular thermal movements of the molecules of liquids. Einstein used the molecular theory of heat developed by Herapath, Waterston, Clausius, Maxwell, Boltzmann, Gibbs and other scientists, and this statistical approach became very fruitful especially regarding the kinetic theory of gases. In Ref. [3] after a remarkable treatment he derived a fundamental relationship between the average distance x that a particle travels in time t if the diffusion coefficient of this suspended particle is D, i.e.

$$x=\sqrt{2Dt} \tag{1}$$

It is a measurable quantity, i.e. the prediction of the theory can be proven. Besides Refs. [3] and [5] Einstein published two more papers, a little surprisingly, in Zeitschrift für Elektrochemie [7, 8]. (If we define an electrochemist as a scientist whose work is published in electrochemical journals then Einstein could be enrolled to our community.) This unusual choice by Einstein was because Svedberg's paper appeared in this journal [9], and he wanted to make evaluation of the results of measurements easier. Svedberg wanted to measure the velocity of Brownian particles, and Einstein pointed out the basic flaws of this approach [7]. Ref. [8] was intended directly for use by chemists since R. Lorenz told Einstein that the elementary theory of Brownian motion could be very useful for the chemists.

Dozens of papers and books about Einstein's works had appeared solely in this year with detailed analysis of their content, the circumstances of their creation and their impact on science during the past 100 years (see e.g. [10, 11]). It is striking that neither Einstein in the course of the next 45–50 years (see e.g. Ref. [12] nor the legion or researchers noticed a capital mistake regarding the theory of osmotic pressure which was considered by Einstein as the driving force of diffusion and the Brownian movement of molecules.

The title of Sect. 1. of Ref. [3], i.e. "About the osmotic pressure attributed to the suspended particles", already gives rise to some ground of suspicion regarding the complete misunderstanding of the nature of osmotic pressure. Sect. 1 of Ref. [8] entitled "Diffusion and osmotic pressure" describes an experiment which makes the problem even more evident. According to Einstein

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the dissolved molecules or the large particles of a suspension (even the pollen grains whose motion had been observed by R. Brown in 1827) exert real pressure on the wall of the vessel, and on the semipermeable membrane dividing the vessel into two parts and serves as a piston. After more than 40 years Einstein still insisted on his original model since in Ref. [12] the following argumentation can be found: "The simplest deduction was based on the following conception. If the molecular–kinetic theory is in principle correct, the suspension of visible particles possesses an osmotic pressure which obeys the gas laws similarly to that of the dissolved molecules."

For anybody who has some idea about the thermodynamics of solutions and the origin of osmotic pressure it is evident that the dissolved molecules do not exert any such pressure (there is no such thing as the pressure of a solution), and osmotic pressure is a pressure that must be applied to the solution to bring it into a certain equilibrium condition. It is analogous to the freezing point of a solution, which has no relation to the actual temperature of the solution, but is the temperature to which it must be brought to reach a certain equilibrium state. Osmotic pressure is nevertheless sometimes defined as the pressure exerted on a membrane, permeable only to the solvent, separating the solution from the pure solvent (usually water). This definition, unless carefully explained, is incorrect. However, the definition that was used also by Einstein, i.e. it is a pressure exerted by the solute molecules on a membrane permeable only to the solvent, is certainly incorrect [13]. The fact regarding the pressure on the membrane is that the flow of the solvent through the membrane from the pure solvent phase to the solution is negligibly small, and may be in either direction. If the solution (and not the solvent as Einstein described in Ref. [8]) is subjected to a certain external pressure, the flow of solvent through the membrane will be equal in both directions. The excess pressure on the solution over the pressure of the solvent, which can establish an osmotic equilibrium, is by definition the osmotic pressure.

Nevertheless, Einstein cannot be held responsible as he learnt the false interpretation from eminent physical chemists such as van't Hoff, Ostwald, Arrhenius and Nernst.

The story began about 20 years earlier when van't Hoff published a paper in the first volume of Zeitschrift für Physikalische Chemie [14], which was a journal launched by Ostwald and van't Hoff in 1887. Van't Hoff analysed the results of Pfeffer and found that for many systems the osmotic pressure (π) obeys the equation

$$\pi = cRT, \tag{2}$$

where R is the gas constant, T is the absolute temperature, and c is the concentration. Taking into account that $c = n/V$, where n is the molar amount of the solute and V is the volume, Eq. 2 is no doubt formally analogous to the equation for the ideal gas. However, van't Hoff's conclusion that the pressure is due to the impact of the dissolved molecules—which behave as molecules of the gases—on the semipermeable membrane was essentially wrong. Equation 1 is valid only in the case of dilute solutions where the mole fraction of the solvent (x_1) is much higher than that of the solute (x_2) which allows the following simplification:

$$ln\, x_1 = -x_2.$$

Arrhenius [15] and Ostwald enthusiastically supported van't Hoff's theory, especially because it provided a confirmation of the hypothesis of electrolytic dissociation (more solute molecules cause greater osmotic pressure which would be predicted without dissociation). Planck [16] cautiously remarked that the thermodynamic theory gives a perfect description, and the approach that appeared in van't Hoff's work was unnecessary.

An especially sharp criticism came from Lothar Meyer [17]. It is worth to cite him in some sentences: "The osmotic pressure is not the pressure of the dissolved material but that of the solvent... or in general the pressure of the substance for which the wall is permeable. It has always been considered in this way until Herr van't Hoff declared his diagonally opposite opinion." (L. Meyer was also a member of the Editorial Board of Z. Phys. Chem. together with scientists such as Berthelot, Le Chatelier, Mendelejew, V. Meyer, Ramsay or Raoult.) Bitter polemics had begun. Van't Hoff refused Meyer's critique [18]. Boltzmann [19], who had been striving for the recognition of the statistical–kinetic theory, joined van't Hoff, Arrhenius and Ostwald. Meyer was supported by van Laar, who published a correct thermodynamic derivation of the osmotic pressure [20–22]. However, the view of van't Hoff had triumphed over the opponents' fact, mostly because that group was much stronger and chemists prefer simple deductions and formulae. Furthermore, it was of immense assistance to electrochemistry when Nernst, while working under the guidance of Ostwald in Leipzig, derived his famous equation also by using van't Hoff's osmotic theory [23]. According to Nernst the reason for the dissolution of a metal or the deposition of metal ions is a pressure difference. Two types of pressures exist, i.e. the osmotic pressure (p) exerted by the dissolved molecules (ions) on the metal surface (which acts as a semipermeable membrane) and an opposite one, the "Lösungstension" of the metal (P), which drives the ions into the solution. An equilibrium will be established when $p = P$. It is understandable that Nernst used a hypothesis which was popular in those years; however, the problem was that Nernst insisted on it during the following decades substantially hindering the development of electrochemistry (we may think of, e.g., the incorrect explanations of the ideal polarised electrode, complex, second kind and redox electrodes, as well as the kinetics of electrode processes). His speech at the Nobel ceremony in 1921 [24] is characteristic in this respect: “So there arose in 1889 the osmotic theory of galvanic current generation, which has not been seriously challenged since it was put forward more than 30 years ago and has undergone no appreciable elaboration since its acceptance, surely a clear sign that it has so far satisfied scientific needs.” While it is true that in 1889 the electron was unknown, by 1921 the existence of the electron had been proven for 24 years and its properties had been thoroughly studied. Therefore, the elucidation of the ideal polarised or the redox electrodes would have not needed to create false explanations. New ideas gained ground after the death of Nernst (1943). Bockris, recalling the foundation of the International Society of Electrochemistry, described the situation in 1949 as follows: “The atmosphere and background of electrochemistry in this time was dominated by the dead hand of Nernst” [25].

We have evidence that Einstein acquired the idea from the followers of van’t Hoff and was inspired by Nernst’s work since he wrote: “It has been known for a long time that the driving force of the diffusion is the osmotic pressure. It is known that the study of the relationship between the ionic mobility, diffusion coefficient and electromotive force at galvanic cells based on different concentrations was founded by Nernst on this very fact.” [8].

It may seem strange that correct relationships can be derived on the basis of wrong models. Actually both Nernst and Einstein proved to be lucky as the nature of the driving force played no role in their deductions. However, the wrong explanation of the origin of osmotic pressure still appears in textbooks and papers, which causes many problems and misinterpretations. It is not unique in the history of science. The relationships derived on the basis of inadequate, but scientific models may meet the requirements which nothing else that the predictive power of theory. (It is the essential difference between science and pseudoscience.) However, the equations obtained can be used only under certain conditions. In the cases mentioned the van’t Hoff equation is valid only for dilute solutions, while Nernst equation can be applied solely under equilibrium conditions. Equation 1 has a more general validity; however, it would be a capital mistake that based on this fact, one would want to measure the osmotic pressure of the pollen particles floating on water.

The very nature of this controversy can easily be understood by recalling the history of ideas in the field of astronomy. The theory of the great Alexandrian astronomer, Ptolemy, has lived for 16 centuries and many phenomena concerning heavenly bodies could be predicted by using his conception in which the earth was a fixed body in the centre of the universe, with the sun and moon revolving round it.

The astronomical system of Copernicus—after a long and bitter struggle—overthrew this theory; however, in our understanding or at least in our (allegoric) speech Ptolemy’s ideas are still alive since we speak of sunrise and sunset.

This article has another message which is also of importance in our age when the scientific research advances at an accelerated rate. In this respect, I cite the warning of Lothar Meyer which was used in the debate regarding the nature of osmotic pressure [15]: “This fast and promising advancement is very pleasing, however, it is exactly the rate of this development that lay a duty upon us, i.e. to proceed in double carefulness so that we don’t insert loose building stones to the foundation pillars of the new building.”

The author thanks Prof. G. Horányi whose remarkable article on the osmotic pressure controversy, which appeared Kémiai Közlemények (1990) 71:73, turned his attention to this problem.

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