Wilhelm Ostwald, the Father of Physical Chemistry

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[1] See *Resonance,* Vol.17, No.1, 2012.

[2] See *Resonance,* Vol.5, No.5, 2000.

[3] See *Resonance,* Vol.15, No.1, 2010.

Wilhelm Ostwald was among the pioneers of chemistry in the early 20th century who was largely responsible for establishing physical chemistry as an acknowledged branch of chemistry. In the early part of his research career, he investigated the chemical affinities of various acids and bases. Subsequently, he broadened his horizons and performed path-breaking work in the field of chemical catalysis. An outcome of this work was the famous Ostwald process which continues to be a mainstay of the modern chemical industry. For his work on catalysis, chemical equilibrium relationships and rates of reactions, he was awarded the Nobel Prize in the year 1909. In addition to these colossal pieces of work, he performed very interesting research on the sidelines in various fields. This includes identifying the growth phenomenon of sol particles which is popularly called Ostwald ripening, development of a viscometer, a theory of colours and even philosophy. *Zeitschrift für Physikalische Chemie*, the first ever physical chemistry journal was founded by Ostwald in 1887. Also, he wrote several textbooks of chemistry which mirrored his extraordinary teaching capabilities. Quite aptly, for his immense contributions, he is called the Father of Physical Chemistry. This article will discuss the work of this great scientist.

The 19th century saw the end of alchemist theories in chemistry and the beginning of modern chemistry. The contributions of Lavoisier[1], Mendeleev[2] and Dalton[3] saw chemistry flourishing as a science. One of the most

prominent findings of this century was the accidental synthesis of urea from inorganic substances by Freidrich Wöhler in 1828. This was indeed sensational because never before was an organic compound synthesized from inorganic substances. This event resulted in a spate of research in chemical synthesis and by the end of the century scientists could synthesize hundreds of compounds which included the lifesaving drug 'aspirin'. However, this led to an increasing focus on the synthesis and description of chemical compounds and not on the laws governing the reactions themselves. Many questions on reaction rates, direction and equilibrium were left unanswered.

"Modern chemistry is in need of reform", quipped a twenty-three year old Ostwald during his masters examination at the University of Dorpat [1]. This statement would have been received with hostility, but it certainly showed a sense of urgency in Ostwald to change the way chemistry was being taught and practiced at that time. Ostwald noticed that physics had grown into a quantitative and rational science because it started answering the 'hows' and 'whys' of the field while chemistry was still addressing the 'whats'. A marriage between chemistry and the techniques and thought processes of physics, he realized, was the need of the hour.

1. Early Work

In the early part of his research, during his student days at Dorpat, Ostwald was interested in studying chemical affinities of acids and bases. Chemical affinity is the tendency shown by dissimilar compounds to combine and form products. He came across the work of a Dutch scientist Julian Thomson who used thermochemistry to study solutions. Ostwald later said, "Like lightning, the thought occurred to me that instead of heat development, every other measured quantity which was sufficiently influenced by a chemical change could be used

Ostwald's initial research involved establishing chemical affinities of acids and bases which he did by monitoring volume changes in acid-base reactions.

The genius of Ostwald lied in recognizing that conductivity measurements can be used to measure chemical affinities. He gave the relation in the form of his famous *dilution law*.

for the study of solutions." He realized that by monitoring the changes in volumes of acid-base reactions, he could establish their chemical affinities [2].

The following concept is applied in the study of chemical affinities by observing volume changes. Consider two acids A and A^*; the aim is to find their chemical affinities for a base B. We begin with equimolar solutions of A, A^* and B. Upon adding 1 litre of A to 1 litre of B, a solution of AB is prepared. To 1 litre of this solution AB, if we add 1 litre of the acid A^*, the resulting volume will differ from 2 litres by v^*. This v^* will reflect the amount of A displaced from AB by A^*. Using this volume, the relative chemical affinities of A and A^* for B can be determined. Ostwald called this new method of studying solutions as 'volume chemistry'. Using this method, he was able to collect a large amount of data which helped him to assign independent chemical affinities for acids and bases irrespective of the particular nature of the chemical reaction [3]. He published an account of this work titled 'Volume Chemical Studies' in *Poggendorff's Annalen* in the year 1876. This work also served as his Master's thesis.

Around this time, Ostwald came across the work of another great scientist of his times, Arrhenius. As a part of his dissertation, Arrhenius had described a method to determine the conductivity of very dilute solutions. His work showed that electrolytes dissociate into their respective ions in solutions. While the solutions are neutral as a whole, the ions present in it make the solutions conduct electricity. Arrhenius pointed out that the electrolyte need not be completely dissociated at all concentrations; instead it will only be partially dissociated to yield ions which will be in equilibrium with the unionized electrolyte. From the laws of equilibrium, we can anticipate that the degree of dissociation will depend on the concentration and it becomes larger as the concentration becomes lower. Therefore, the largest amount of

conductivity will be seen for a solution at infinite dilution.

The degree of dissociation 'α' of the electrolyte can be measured from conductivity measurements. Higher the degree of dissociation, greater will be the conductivity. In terms of molar conductivity, α can be expressed as

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} , \tag{1}$$

where Λ_m^0 is the molar conductivity at infinite dilution. The genius of Ostwald lay in recognizing that measurement of conductivity can be used to measure chemical affinities (yet another method to obtain them). Chemical affinity of an acid should depend on the number of H^+ ions present in the solution which can interact with a base. Therefore, it is easy to see that chemical affinity is closely related to the equilibrium constant. The contribution of Ostwald was to give an expression for the equilibrium constant in terms of the extent of dissociation of the acid. For an acid at equilibrium $HA \rightleftharpoons H^+ + A^-$, the equilibrium constant 'K_a' is given as,

$$K_a = \frac{\alpha^2 c}{1 - \alpha} , \tag{2}$$

where c is the concentration of the acid. Using (1) and (2), Ostwald arrived at his famous *dilution law*,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a (\Lambda_m^0)^2} . \tag{3}$$

On plotting $1/\Lambda_m$ against $c\Lambda_m$ (*Figure* 1), the intercept will give the conductivity at infinite dilution (Λ_m^0) and the equilibrium constant can be calculated from the slope.

Electrolytes are of two types, strong and weak [4]. Strong electrolytes show a high degree of dissociation at all concentrations while the weak electrolytes are barely dissociated at high concentrations and their degree of dissociation starts to grow rapidly as they approach infinite

Figure 1. Ostwald dilution law [5].
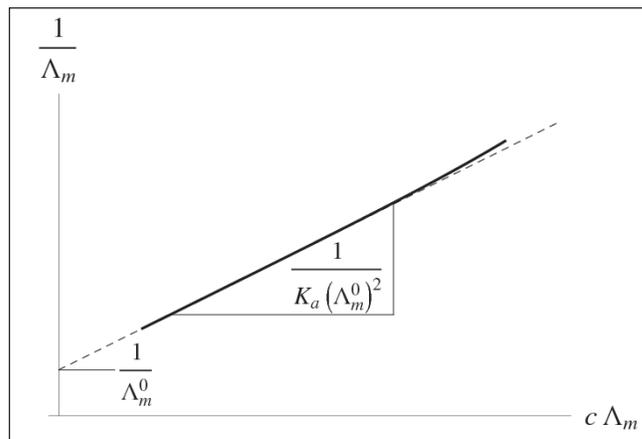
dilution. *Figure* 2 shows a plot of molar conductivity vs. concentration for a strong electrolyte (KCl) and for a weak electrolyte (CH_3COOH). Ostwald's dilution law holds good only for weak electrolytes. For weak electrolytes, the degree of dissociation is governed by (2). Hence, the decrease in α with increase in concentration is because of partial dissociation. The theory of Arrhenius was based on the assumption that the solution with ions behaves like an ideal solution with neutral particles; in other words, the interionic attraction is neglected. Such an assumption is reasonable for weak electrolytes which are hardly dissociated at high concentrations.

However, this assumption will not work for strong electrolytes which show a large degree of dissociation at

Figure 2. Molar conductivity vs. concentration for electrolytes. Molar conductivity of CH_3COOH, which is a weak electrolyte, is shown as solid line and that of KCl, which is a strong electrolyte, is shown as dashed line [5].
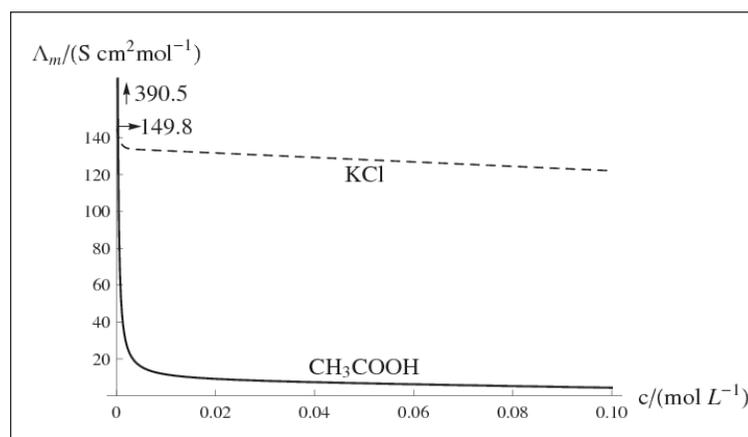
all concentrations where interionic forces cannot be neglected. The explanation for a decrease in conductivity with increase in concentration is given by the Debye–Hückel–Onsager theory. According to this theory, there are two factors that affect conductivity: (i) Each ion will be surrounded by an atmosphere of oppositely charged ions whose charge, on an average, will be equal to that of the central ion. These charges will be symmetrically distributed around the central ion in the absence of a field. In the presence of a field, the central ion will move towards one electrode and the charged atmosphere will move towards the other. This will retard the movement of the ion and thereby reduce conductivity. (ii) Also, the ions are always solvated. So, when an ion moves, it has to move against the current of solvent molecules which are carried by oppositely charged ions. This phenomenon, popularly called electrophoresis, also leads to reduced conductivity. Both the factors become more prominent with increasing concentration which explains the reduction of conductivity with concentration for strong electrolytes.

Ostwald's theory found more support with the findings of yet another great scientist, van't Hoff [4], who also was working on solutions at that time [6]. He was studying osmotic pressure of solutions and observed that dilute solutions behaved similar to ideal gases. They obeyed an equation, $PV = iRT$, where P is the osmotic pressure, V is the volume which contains one mole of the solute, R is the universal gas constant, T is the temperature and i is an empirically introduced factor that depended on the nature of the solute. van't Hoff observed that if the solution conducted electricity, i was greater than unity and if they did not conduct electricity, i was equal to unity. From the theory of electrolytes by Arrhenius, it is immediately obvious that i is equal to unity for non-electrolytes and i is greater than unity for electrolytes. Ostwald, Arrhenius and van't Hoff, called the 'Ionists',

Ostwald, Arrhenius and van't Hoff were called the 'Ionists' for their seminal contribution in describing dissociation of electrolytes in solutions.

[4] See *Resonance,* Vol.12, No.5, 2007.

Ostwald researched on both homogeneous and heterogeneous catalysis. He was the inventor of the industrially important method to produce nitric acid, which is now popularly called Ostwald process.

had performed very instructive individual pieces of work. But, Ostwald can be credited with unifying the three and giving a complete picture about solutions.

2. Work on Catalysis

Ostwald had the greatest passion for his work on catalysis for which he was awarded the Nobel Prize in 1909 [7]. During his Nobel Prize acceptance speech, he mentioned, "In my innermost being, I used to, and still do consider this part of my work the one in which the personal quality of my method of work definitely has shown up and which I therefore have more at heart than all the others." The phenomenon of catalysis was observed long before Ostwald, and it was the Swedish chemist Berzelius who formulated the concept and coined the name. A few early examples of catalysis were the transformation of starch into dextrin and sugar by acids, action of finely divided platinum particles on inflammable gas mixtures, and the decomposition of H_2O_2 into water and gaseous oxygen in the presence of platinum and MnO_2. Berzelius identified a commonality among these scattered pieces of work. He realized that in all these reactions, the substances which combined to form products did not do it spontaneously but only after the addition of a certain substance which itself did not get consumed in the reaction. He named this as the *catalyst*.

Though Berzelius identified the phenomenon, he was unable to give a theory for catalysis because the concept of 'rate of a reaction' was not established at that time. It was the German scientist Wilhelmy who proposed that the ratio of the amount of product formed in a given time to the time required for the process can be defined as the *rate of the reaction*. Being a physicist with a sound mathematical foundation, he at once realized that this is the differential of the amount of substance formed with respect to time (rate $= \frac{d[\text{Product}]}{dt}$). Such a definition for

the rate of a reaction made it a measurable quantity and all the factors affecting the rate also became measurable, including catalytic activity. Wilhelmy was investigating the inversion of cane sugar (i.e., a conversion of dextrorotatory cane sugar to a laevorotatory isomer) in the presence of acids. Though he observed the influence of acid in the reaction rates, he mentioned nothing about catalysis in the publication of his work.

Ostwald had to keep himself updated with the literature of organic chemistry due to his teaching commitments. In some experiments, where he monitored the extent of ester hydrolysis under the action of various mineral acids, he saw that the rate of the reaction was affected by the concentration of the acid used. This was his very first attempt to study the dynamics of chemical reactions. Soon after, he studied the inversion of cane sugar in the presence of acids in the same light. By this time, Ostwald was already a champion of acid–base chemistry. He could immediately see that those acids with a high chemical affinity also proved to be better catalysts. Also, he was the first to establish enzymes as biocatalysts.

After working on homogenous catalysis, Ostwald moved on to probe heterogenous catalysis. He invented an industrial process for producing nitric acid from ammonia which is famously known as the *Ostwald process*. It is intimately connected to Haber's process which provides the raw material, ammonia. The reaction proceeds in three steps. In the first step, ammonia reacts with oxygen in the presence of a platinum-rhodium wire gauze at 900 °C to form nitric oxide. This is an exothermic process and the heat produced in the reaction maintains a high temperature necessary for this step.

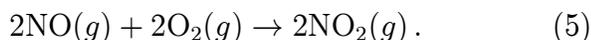$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \ . \qquad (4)$$

In the second step, NO reacts with oxygen at room tem-

The variety of topics on which Ostwald researched, was a hallmark of his greatness.

Some of the diverse topics that Ostwald researched on were the study of growth of sol particles, developing a visco-meter and a theory of colours.

perature to form NO_2.

$$2NO(g) + 2O_2(g) \rightarrow 2NO_2(g). \qquad (5)$$

In the third step NO_2 is made to react with water to produce nitric acid.

$$3NO(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g). \qquad (6)$$

The NO that is produced in this step can be recycled through the reaction. This process was patented by Ostwald in the year 1902 and it proved very useful for the Germans during the first World War in the production of explosives.

Ostwald did not support the idea of Berzelius that there exists a catalytic force. He defined catalyst as any substance that alters the rate of the reaction without being consumed in the reaction. His interesting contribution is to recast catalysis in terms of thermodynamics. He proposed that the total energy change in the reaction must be the same with or without the catalyst. In other words, a catalyst will not alter an equilibrium constant, and hence it alters the rate constants of the forward and backward reactions in the same proportion. Thus began his active involvement in 'energism' where he sought to understand all processes in terms of transfers and transformation of energy.

3. Other Interesting Contributions by Ostwald

The variety of topics on which Ostwald researched was a hallmark of his greatness. In this section, various interesting pieces of work done on the sidelines will be discussed.

3.1 *Ostwald Ripening*

In 1897, Ostwald performed a study on the nucleation of crystals in solutions. What he observed was that the dissolved particles aggregate into small particles in the

beginning. As time progresses, the small particles redeposit onto larger particles and grow in size. The small particles nucleate very easily and their formation is kinetically controlled. However, due to their large surface to volume ratio, they are not thermodynamically favourable. In order to reduce their surface to volume ratio, and thereby reduce their free energy, the small particles deposit onto large particles with time. At infinite time, we can predict that the solution will be completely devoid of small particles and there will be only one large spherical particle with minimum surface to volume ratio. In other words, the large particles grow at the expense of small particles and the small particles act as 'nutrients' for their growth. This phenomenon is now referred to as Ostwald ripening. A simple example is the re-crystallization of water in ice-creams which makes it lose its texture and become crunchy.

Ostwald ripening is a spontaneous process and therefore, has to be taken into account with care in various situations. Hydrogen storage using palladium nanoclusters poses one such situation. Hydrogen fuel is increasing being seen as the solution to the present day energy crisis. Palladium in bulk is known to have high hydrogen uptake property because of which it is widely used in catalytic hydrogenation. However, bulk material does not show high *rates* of hydrogen uptake and release and hence, cannot be used as a hydrogen storage material. Nanoparticles, on the other hand, have shown very promising hydrogen storage properties. Therefore, the palladium nanoclusters were investigated for hydrogen storage. The extent of Ostwald ripening for palladium nanoclusters is generally slow at room temperatures. However, in the presence of hydrogen, it was observed to be greatly accelerated. In other words, there is hydrogen-induced Ostwald ripening in palladium nanoclusters. The presence of interstitial hydrogen decreases the strength of host metal bonding and thereby

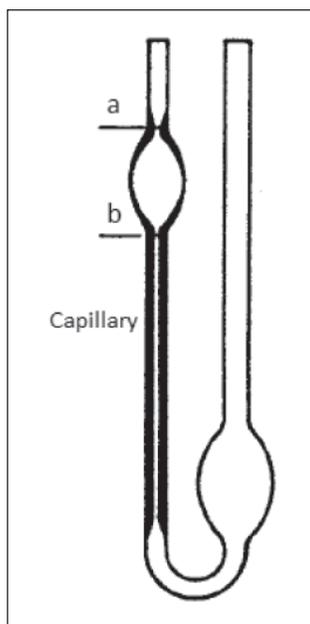Nanoparticles have shown very promising hydrogen storage properties.

Figure 3. Ostwald viscometer.

increasing the probability of palladium atom detachment. Since the clusters are not very far apart, the free atoms have to do little travel to get attached to the neighbouring cluster [See cover]. The clusters grow in size through this process and the advantage of using nanoclusters will be lost. This has to be seriously considered in future applications of nanoparticle assemblies for hydrogen storage [8].

3.2 *Ostwald Viscometer*

Ostwald in his early years tried to use a variety of properties of solutions in order to determine their chemical affinity, and viscosity was one such property. He developed a simple apparatus to measure the viscosity of solutions. The apparatus (*Figure* 3) contains a U-tube, two bulbs and a capillary connecting the two. The time taken by an unknown solution to flow through two points a and b has to be noted and compared to a standard sample. The ratio of viscosity of the unknown, η, and that of the standard sample, η_0, is give by

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \times \frac{\rho}{\rho_0} , \qquad (7)$$

where ρ and ρ_0 are the densities of the unknown and the standard respectively, and t and t_0 are the time required by them to flow through the markings [9].

3.3 *Theory of Colours*

As a child, Ostwald showed great interest in music, painting and photography. He inherited his skill for painting from his father. Experience had shown him that some colour combinations are more pleasant or harmonious than the others. In his theory of colours, he aimed to sort them on the basis of their 'harmony' [10]. He devolped maps using which it was possible to arrive at those harmonious combinations. He compiled an atlas of 2500 colours called *Die Farbenfibel* (*The Colour Primer*). This theory of colours saw moderate success

and was applied in the textile industry for a while.

4. Publications and Final Years

Ostwald was a very gifted orator and a writer. He had a vast teaching experience which included a physical chemistry course at the University of Dorpat and years of teaching at the Dorpat High School. Using this experience, he embarked on writing his first book on general chemistry called *Lehrbuch der Allgemeine Chemie* (*Textbook of General Chemistry*). Due to his seminal work on acid–base chemistry and his popularity as a teacher, he was invited to be the physical chemistry chair at the University of Leipzig in 1887. The following decade was a golden period for Ostwald. In 1887, the *Lehrbuch* was published. He followed it up with several textbooks such as *Gründriâ der Allgemeinen Chemie* (*Outline of General Chemistry*) and *Hand-und Hilfsbuch Physikalisch-Chemischer Messungen* (*Handbook and Manual for Physicochemical Measurements*). Armed with the success of the *Lehrbuch*, he wanted to start a new journal for physical chemistry which was emerging as a new field then. The idea was received with skepticism and many of his colleagues did not see the need for such a journal. However, he managed to coax a publisher from Leipzig to start the first ever journal of physical chemistry titled, *Zeitschrift für Physikalische Chemie* (*Journal of Physical Chemistry*) in 1887, with van't Hoff as a co-editor. Ostwald edited the first 100 volumes by himself. He also established many societies, for example *Deutsche Electrochemische Gesellschaft* (German Electrochemical Society) in 1894. This was expanded in 1902 into the *Deutsche Bunsen-Gesellschaft für Angewandte Physikalische Chemie* (German Bunsen Society for Applied Physical Chemistry) [11].

The success at Leipzig was marred by differences of opinion he had with his colleagues at the university. This led to his stepping down from the Chair in just three years

> Ostwald wrote several textbooks, started a physical chemistry journal and various societies to popularize physical chemistry.

> Ostwald had the gift of expression that the others did not possess which made him the biggest proponent of physical chemistry.

after joining. He eventually retired from academics in 1906 at the age of 53. He was then absorbed in his theory of colours, energism and philosophy. He was philosophically a positivist and denied the existence of atoms. Only after Perrin's measurement of the Avagadro number and Einstein's theory of Brownian motion, Ostwald accepted the atomic theory. With a switch in research interest and retirement from chemistry, consideration for a Noble Prize became very difficult. However, his immense contributions could not be overlooked and he was awarded the most coveted prize in 1909.

Ostwald lived in the glorious era of physical chemistry with stellar contemporaries like van't Hoff, Arrhenius and Nernst who were no lesser in terms of intellect or quality of work. So, what set Ostwald apart? Why is he called the father of physical chemistry? It is widely said that Ostwald had the gift of expression that the others did not possess. He wrote and spoke in a way that made students understand chemistry. Therefore, he became the biggest proponent of physical chemistry while the others remained great scientists of Ostwald's era. As one of his foremost pupils, Bancroft said [10], "Ostwald was absolutely the right man in the right place. He did a great work that no other man could have done as well as he did." The rest of the scientific fraternity cannot agree more.

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Suggested Reading

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