

FROM EDITORIAL DESK

Why are we proud to be Kineticists?

R.Sanjeev¹, V.Jagannadham^{*2} ¹Department of Chemistry, Mizan-Tepi University, Tepi Campus, (ETHIOPIA) ²Department of Chemistry, Osmania University, Hyderabad-500 007, (INDIA) E-mail: jagannadham1950@yahoo.com

In the recent past for the last four to five years, when we used to attend some departmental conferences, some scientific meetings and PhD viva-voce examinations, in the lunch break or in the tea break timings some teachers so called modern day chemists whom we knew very well and who do the research in solid state chemistry and drug discovery used to talk to us ill of chemical kinetics. They look down the subject of chemical kinetics. But as we understood, like mathematics which is the mother of science, we can proudly say that chemical kinetics is the mother of chemical science. This is well understood by the following diagram by any average chemist or chemistry teacher or by a freshmen college student.



From the diagram it is very clear that the subject of chemical kinetics can not simply keep quite without peeping and interacting through almost all branches of chemistry including pharmacology. Some of the lightning facts give the support to this contention by virtue of being awarded "Nobel Prizes" to several Scientists working in Reaction Dynamics or Chemical Kinetics. The events of Nobel Laureates who were awarded Nobel Prizes for their work in "Reaction Dynamics/Chemical Kinetics" with their names, photographs and their discoveries are being summarized chronologically in the following, at first starting with a small introduction.

The processes grouped together by Berzelius were:

- The transformation of starch into dextrin and sugar by acids (Kirchhoff, 1811).
- The same transformation by malt extract (Kirchhoff, 1814).
- The decomposition of hydrogen peroxide into water and gaseous oxygen in the presence of platinum, manganese dioxide, etc. (Thénard, 1818).
- The action of finely divided platinum on inflammable gas mixtures (Davy, 1817; and Döbereiner, 1823).
- The formation of ether by the action of sulphuric acid (Mitscherlich, 1834).

The factor which Berzelius regarded as being common to all these processes was that the substances which interact to form the product do not do so on their own or spontaneously but only after the addition of a certain substance which is not itself consumed.

Mitscherlich had termed the process which he studied is a chemical *action by contact*; Berzelius introduced the name *catalysis* instead, with the active but unconsumed substance being termed the catalytic substance or *catalyst*, and the cause underlying the phenomena *catalytic force*.

The development of a rational view of the nature of catalysis was thus absolutely dependent on the creation of the concept of the *rate of a chemical reaction*. The concept was formulated (after an inadequate attempt by Berthollet) by the German amateur scientist Wilhelmy and by a remarkable chance (or is it the intrinsic logic of historical evolution?) the first paper to submit a proper concept of the rate of a chemical reaction also constitutes the first quantitative study of a process proceeding under catalytic action.

The reaction in question was the *inversion of cane sugar*. The name originates from a prior study by Biot and Persoz who used the polarimeter to study the reaction.

The solution of cane sugar which rotates the plane polarized light to the right but which rotates it to the left on the addition of a dilute acid. It was found chemically that cane sugar absorbs the elements of water and changes into a mixture of two different sugars, one being weakly dextrorotatory and the other strongly laevorotatory, hence the resultant is a rotation to the left. At the same time these workers observed that the process is not completed instantaneously but requires a period of time varying with the nature and concentration of the added acid. Biot who, as a physicist, was more readily inclined than all the chemists of his day (Wilhelmy too was a physicist) to regard the observed phenomenon as a systematic transient process, also pointed out the importance of a more thorough investigation of these phenomena. However, only Wilhelmy was sufficiently interested to undertake not only the necessary experiments, but in particular also the fundamental task of formulating the concepts.

Wilhelmy's work (1850) in chemical kinetics concerned the acid-catalyzed conversion of a sucrose solution into a 1:1 mixture of fructose and glucose, a reaction that he followed with a polarimeter. He wrote a differential equation to describe the reaction, integrated it, and used it to interpret his experimental results. Wilhelmy found that the reaction's rate was proportional to the concentrations of sucrose and of acid present. The ratio of the amount of substance (cane sugar in this case) converted in a given time to the time required for the process he conceived and defined as a new concept, the *rate of chemical reaction*, recognizing its appropriate mathematical definition at once to be the differential quotient of the amount of substance with respect to time.

Wilhelmy then demonstrated that on the simplest assumption that the amount of sugar converted under the given conditions in each element of time is proportional to the amount remaining unchanged, there is a large measure of agreement between the observed changes in rotation and those calculated on the basis of this assumption, and thus he discovered the general law for the time dependence of the chemical processes. It

has subsequently proved to be the fundamental law of chemical kinetics.

Ostwald found that methyl acetate proved even more suitable owing to its greater solubility and faster reaction rate, and so one of his first studies in chemical dynamics, in 1883, dealt right away with a catalytic process, i.e. the catalytic saponification of this particular ester under the action of various acids.

The Nobel Prize was awarded 15 times, to a total of 24 recipients, for work involving various aspects of chemical dynamics beginning with Jacobus van't Hoff in 1901, out of a total of 161 recipients in Chemistry which is 18% of the total Nobel Prizes went to the people working on Chemical Dynamics or Chemical Kinetics.

Had the award of Nobel Prizes started a century before, about a dozen scientists like Berzelius, Mitscherlich, Kirchhoff, Thénard, Davy, Döbereiner, Berthollet, Biot, Persoz and Wilhelmy more would have been awarded Nobel Prizes in Chemical Kinetics.



J.H.van't Hoff 1901

The first Nobel Prize went to a Physical Chemist in1901, who is none other than VAN'T HOFF for his work on Chemical Dynamics in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic

van't Hoff

pressure in solutions. He discovered how to express the state of chemical equilibrium in reactions and the electromotive force which a reaction can produce; he explained how the transition occurs between the various modifications of the elements. van't Hoff's investigations showed that the law, which has been named after the Italian Avogadro, according to which the number of gas molecules in a given volume is the same for all gases at the same pressure and temperature, embraces not only substances in the gaseous phase but also those in solution, provided that their pressure, known as osmotic pressure, is taken into account in the same way as the gas pressure in the case of gases. He proved that gas pressure and osmotic pressure are identical, and thereby that the molecules themselves in the gaseous phase and in solutions are also identical. As a result of this the concept of the molecule in chemistry was found to be definite and universally valid to a degree hitherto undreamed-of.

Svante Arrhenius 1902



This, the second of Nobel Laureates in chemical dynamics, features the work of Svante Arrhenius, who won the Nobel Prize in 1902 for his electrolytic theory of dissociation. Although it was not mentioned specifically in his Nobel presentation, the well-known

Arrhenius

Arrhenius equation relating reaction rate constants to activation energies and temperature is fundamental to all subsequent studies of reaction energetics and catalysis, and no modern discussion of chemical dynamics could begin without it. Arrhenius is best remembered today by teachers and students of chemistry because the definition of acids and bases and also the equation $k = A e^{-Ea/RT}$ relating reaction rate constants to temperature through the activation energy that are both named for him.



Wilhelm Ostwald 1909

The third Nobel Laureates in chemical dynamics, features the work of Wilhelm Ostwald, who won the Nobel Prize in 1909 for his work on catalysis, equilibriums, and reaction rates. Ostwald's name remains associated with the catalytic process used

Ostwald



George de Hevesy 1943

to manufacture nitric acid from ammonia.

The fourth Nobel Prize for research related directly to chemical dynamics was awarded to George de Hevesy in 1943 "for his work on the use of isotopes as tracers in the study of chemical processes".

Hevesy



Hinshelwood

N m ir

Semenov

Nobel Prize in chemical dynamics during the 20th century. Cyril Hinshelwood

This is the fifth

Hinshelwood and

Semenov 1956

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and Nikolay Semenov received the Nobel Prize in 1956 "for their researches into the mechanism of chemical reactions," in particular, chain reactions.







Porter

Eigen

Eigen, Norrish, and Porter 1967

The 1967 Nobel Prize for research in chemical dynamics awarded to receive the Nobel Prize in 1967 "for studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short impulses of energy," i.e., temperature jump, pressure jump, and flash photolysis.



Fukui

Fukui

Fukui and Hoffmann 1981 The 1981 Nobel

Prize was awarded to Kenichi Fukui and Ronald Hoffmann "for their theories,

developed indepen-

dently, concerning the course of chemical reactions." Those theories, which have come to be known as "frontier orbital theory" and the "Woodward-Hoffmann rules" respectively, remain important tools for predicting the course of organic reactions and they are frequently taught in courses in mechanistic organic chemistry.



Henry Taube 1983

The 1983 Nobel Prize was awarded to Henry Taube for his work on the mechanisms of electron transfer reactions, especially in metal complexes. Taube's work represents a watershed in the development of the mechanistic chemistry of inorganic

transition metal complexes. His studies of those reactions is a central feature in courses in mechanistic inorganic chemistry, and his description of inner-sphere and outer-sphere electron transfer mechanisms remain as the textbook examples.







Herschbach

Polanvi

Dudley Herschbach, Yuan Lee, and John Polanyi 1986

The 1986 Nobel Prize was awarded to Dudley Herschbach, Yuan Lee, and John Polanyi for their work extending chemical dynamics to the level of individual atoms and molecules, using molecular beam and infrared chemiluminescence experiments.



Rudolph A.Marcus 1992

The 1992 Nobel Prize in Chemistry was awarded to Rudolph A. Marcus for development of a theoretical treatment of electron transfer reactions in chemical systems. He undertook an experimental research program on both gas phase and solution

Marcus

reaction rates, wrote the 1952 RRKM papers, and wondered what to do next in theoretical research. He felt at the time that it was pointless to continue with RRKM since few experimental data were available. Some of their experiments were intended to produce more.

G.A.Olah 1994

George A. Olah gave the cations of carbon longer life.







The cations of the carbon compounds – carbocations - are common in the organic chemistry. They occur as extremely reactive and short-lived intermediates in chemical reactions. By giving them longer lives George A. Olah has made it possible to observe them directly.







Crutzen

Rowland

Molina

Paul Crutzen, Sherwood Rowland and Mario Molina 1995

The 1995 Nobel Prize was awarded to Paul Crutzen, Sherwood Rowland, and Mario Molina "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone". Collectively, their work established atmospheric chemistry as a major focus at the end of the twentieth century. The results have drawn attention to significant environmental issues-in particular, the threat posed to the ozone layer by chlorofluorocarbons.





Walter Kohn and John Pople 1998

The 1998 Nobel Prize was awarded to Walter Kohn "for his development of the density-functional theory" and to

John Pople "for his development of computational methods in quantum chemistry." They enabled improved energy calculations on molecules and other multi-atom systems. Chemists have taken advantage of those developments to perform calculations on systems during reactive encounters, thereby obtaining a better understanding of chemical dynamics and allowing for predictions regarding the course of chemical reactions based on the energies of various possible transition states.



Ahmed H.Zewail 1999

The 1999 Nobel Prize was awarded to Ahmed Zewail "for his studies of the transition states of chemical reactions using femto second spectroscopy." His pioneering investigation of fundamental chemical reactions using ultra-short flashes allowed

Zewail

chemists, for the first time, to monitor reactions on the time scale on which the atoms are actually moving as bonds are broken and formed. The fundamental limit of femto second resolution represents the culmination of a century of progress in chemical dynamics that began with the first Nobel Prize awarded to Jacobus van't Hoff in 1901.







Knowles

Sharpless

William S.Knowles, Ryoji Noyori and Barry Sharpless 2001

Prize for their development of catalytic asymmetric synthesis. The achievements of these three chemists are of great importance for academic research, for the development of new drugs and materials, and are being used in many industrial syntheses of pharmaceutical products and other biologically active substances. This is a description and background information about the scientists' award-winning discoveries.



Agre

Peter Agre and Roderick MacKinnon 2003

Through pioneering discoveries concerning the water and ion channels of cells. They have

opened our eyes to a fantastic family of molecular machines: channels, gates and valves all of which are needed for the cell to function. The liquid pressure in

plant and animal cells is maintained through osmosis. The osmotic pressure thus arising is the reason why cells are often swollen and stiff, in a flower stalk, for example.





Gerhard Ertl 2007

Has succeeded in providing a detailed description of how chemical reactions take place on surfaces and has in this way laid the foundation of modern surface chemistry. He is awarded the prize for showing how reliable results can be obtained in this

area of research.

TABLE		
Number awarded	Percentage	
24	15	
34	21	
15	9	
41	25	
29		
Reaction Kinetics	70	
and		
Reaction Dynamics		
	Number awarded 24 34 15 41 29 Reaction Kinetics and	

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From the table it is very clear that out of 41 Nobel Prizes in Physical Chemistry 29 went to the field of Reaction Dynamics/Chemical Kinetics which is 70% and it is 25% out of total Nobel Prizes. So what we mean to say whether one likes a particular subject or not but he can not ignore it. If our face is not beautiful, it doesn't mean that we should break the mirror.



So..... Yes we are proud to be kineticists!!!