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EARLY RESEARCH IN PHYSICAL CHEMISTRY IN INDIA

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Abstract

Early research in Physical Chemistry was initiated by SS Bhatnagar (in magneto-chemistry, emulsion and industrial research) and JC Ghosh (Electrochemistry Fischer-Tropsch process and catalytic gas reactions). They also took part in building many institutions (CSIR, IISc and IIT-s). This was followed by research in polymer chemistry (SR Palit), bio-physical (S Basu), and quantum chemistry and simulations (S Basu and Anessur Rahman). In this article, we will briefly describe the contributions of the Indian physical chemists in research and institution building.

Key words: Biophysical chemistry, Electro-chemistry, Industrial research, Magneto-chemistry, Molecular magnetism, Polymer, Quantum chemistry, Spectroscopy, Surfactants.

1. INTRODUCTION

Research in physical chemistry began in India around 1920 by two young men, SS Bhatnagar (1894-1955) and JC Ghosh (1894-1959), both in their early twenties. At that time there was hardly any institutional support, both financial and infra-structural. It required tremendous innovation in thinking and executing the research problem. Fortunately, the prevailing freedom movement provided enough impetus to overcome lack of material support. About the research condition in India in 1920-s, S. Chandrasekhar (famous astrophysicist and Nobel laureate) once said, "Between 1920 and 1925 we had suddenly 5 or 6 internationally well-known men. It was a part of the national movement to assert oneself. India was a subject country, but in the sciences we could show the West in their own realm that we are equal to them."

This nationalistic sprit fired up SS Bhatnagar and JC Ghosh. They did not stop just at setting up laboratories, publishing good papers and training good students. They actively participated in the building of Modern India with India's first Prime Minister, J. L. Nehru. In this article, we will describe the contributions of Bhatnagar, Ghosh and subsequent physical chemists in creating a tradition of research in physical chemistry in India.

2. CONTRIBUTIONS OF SS BHATNAGAR

The first among them, SS Bhatnagar (1894-1955) obtained his M. Sc. degree from Punjab University in 1919. He proceeded to England to work with Professor FG Donnan at the University College of London where he received the D. Sc. degree in 1921. On his return to India, Bhatnagar joined the Benaras Hindu University (BHU) in 1921 and worked there till 1924. BHU was founded in 1916 by the great visionary, educationist and nationalistic leader Madan Mohan Malaviya (1861-1946). Pandit Malaviya was vice-chancellor of BHU from 1919-1939 and made BHU the largest residential university in India (perhaps in Asia also). The 4-year tenure at BHU, in close contact with Malaviya, hugely inspired Bhatanagar. Bhatnagar

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was also an accomplished poet and wrote the *Kulgeet* (University anthem) for BHU.

In 1924, Bhatnagar shifted to the Punjab University (then at Lahore which is now in Pakistan) and remained there for the next 16 years. During this period, Bhatnagar made pioneering contribution in magneto-chemistry. The subject was in its infancy. He began with building equipment. With his student Mathur, he developed the Bhatnagar-Mathur interference balance for accurate determination of diamagnetic susceptibilities. He got a patent for this instrument and transferred the design to Adam Hilger and Company in London which was an internationally reputed manufacturer of scientific instruments. He applied magneto-chemistry to a variety of problems ranging from structure determination (using Pascal's additivity rule) to colloids, photochemical decompositions and allotropy. As an example of his ingenious research style, one may recall his work on the nature of the black film formed on heating a copper strip in air. From magnetic measurements, he showed that it is CuO (paramagnetic) and not Cu_2O (diamagnetic). He also studied effect of magnetic field on optical rotation. He authored a text book- *Physical Principles and Applications of Magneto-Chemistry*.

SS Bhatnagar (1894-1955)

Bhatnagar's other major area of interest is emulsions, which he picked up at Donnan's laboratory in London. He studied many emulsions involving organic, inorganic and biological substances (lecithin and albumin). He showed that formation of emulsion is related to wetting (adsorption of liquids on solid surfaces) and on surface potential.

Inspired by the prevailing nationalistic spirit, Bhatnagar along with others, took big strides to make the country self-reliant through science and technology. He closely interacted with the industry. In those days, the petroleum companies faced a major problem of clogging of drilling machines because of formation of mud during drilling of oil by saline water. He solved this problem by a clever application of Indian gum which prevents flocculation. For this technology, M/s Steel Brothers, paid Punjab University Rs. 150,000 for petroleum research for 5 years. With this grant Bhatnagar developed new technologies for deodorization of waxes, increasing flame height of kerosene, and utilization of waste in vegetable oil industries. The company was so pleased that they extended the support from 5 to 10 years.

In 1939, the Congress Party formed the National Planning Committee under the chairmanship of Pandit Nehru. Nehru and other leaders approached the British Government to form Board of Science & Industrial Research (BSIR). BSIR was created in 1940 and Bhatnagar became its first secretary. In 1942, BSIR was named CSIR and he was the first DG of CSIR. He was elected FRS in chemistry from India in 1943. Later he became the first chairman of UGC. Between 1942 to 1947, he, along with Pandit Jawaharlal Nehru, planned major research institutes after Independence. As a result of this 5-6 CSIR institutes were started within a year after independence. During the foundation ceremony of Central Food & Technology Research Insitute (CFTRI) at Mysore, CV Raman has applauded creation of CSIR laboratories as "Nehru-Bhatnagar Effect." Because of the monumental contribution of Bhatnagar after his demise, Nehru instituted the SS Bhtanagar award as the highest scientific award for Indian scientists below 45 years of age. The first Bhatnagar award was given to KS Krishnan in 1958. Krishnan was well above 45 years.

3. Contributions of JC Ghosh

JC Ghosh (1894-1959) stood first in M.Sc. in Chemistry at the Presidency College, Calcutta in 1915. His batch mates included SN Bose and MN Saha (in Physics) and JN Mukherjee (in chemistry). In 1914, Sir Asutosh Mukherjee (1864-1924) created University College of Science (Science College) of Calcutta University with the donation received from two lawyers Sir TN Palit and RB Ghosh. Asutosh invited PC Ray and CV Raman to be the Palit Professor in Chemistry and Physics. Ghosh joined the Science College newly created as a lecturer in chemistry.

JC Ghosh (1894-1959)

In a series of papers published between 1918-1920 in the *Journal of Chemical Society*, Ghosh developed the theory of strong electrolytes. He proposed the so called "lattice model" that in a solution an ion is surrounded by ions of opposite charge and are held by strong Coulombic force. At a distance from the central ion the attractive force decreases and they are rather free. Using this model, he explained a large volume of experimental results reported by Walden. Ghosh's works made big impact on contemporary physical chemistry. His work was immediately quoted in famous text books by Nernst (*Theoretische Chemie*, 1921) and G. N. Lewis (*Thermodynamics*, 1923). GN Lewis wrote,

> "to decide whether we shall say that a certain fraction of such an electrolyte is dissociated obeying Coulomb's Law or say with Ghosh that a certain fraction of the ions are free or outside the sphere of mutual attraction".

15 years later Deby and Huckel extended Ghosh' model to propose the concept of ionic atmosphere and then went on to develop the Debye-Huckel theory.

Ghosh, later shifted to photochemistry and worked on photosensitization, photocatalysis, photosynthesis and also Raman spectroscopy. He observed an interesting effect of circularly polarized light on photochemistry of colloids. In the later part of his life, he moved to industrial chemistry e.g. liquid fuel from coal (Fischer-Tropsch process), chemical equilibrium in isoprene formation and catalytic gas reactions and wrote a book (*Some Catalytic Gas Reactions of Industrial Importance*). In 1921, Ghosh joined the newly created Dacca University as the first Head of the Department of Chemistry. He remained at Dacca till 1938.

In 1933, CV Raman joined Indian Institute of Science (IISc) at Bangalore as its first Indian Director. In the same year, Hitler came to power in Germany and the famous Jewish scientists started leaving Germany. Raman invited several of them including Max Born and Schrodinger to be a faculty of IISc. Max Born actually came to Bangalore and stayed for a few months. Unfortunately, because of big internal politics Born could not be offered a position. Eventually, Raman had to resign in 1936. For the next 12 years Raman remained in IISc as a "wounded tiger."

In 1939, JC Ghosh joined as Director of IISc and remained there for 9 years from 1939 to 1948. Initially, Raman was opposed to JC Ghosh. But gradually Ghosh built a good relation with Raman. During this period Homi Bhabha was appointed as a faculty at IISc and IISc developed into an internationally reputed institute. Ghosh was largely responsible of the favorable transition of IISc.

Because of his success in transforming IISc Bangalore, JC Ghosh was invited by Nehru to be the first Director of the first Indian Institute of Technology (IIT) Kharagpur. From 1950 to 1954 JC Ghosh served as Director of IIT-

Kharagpur and nurtured it to reach great heights. Prof CNR Rao spent about a year with JC Ghosh as Ph.D. student during this period. Ghosh later served as Vice-Chancellor of Calcutta University and ultimately member of the Planning Commission. He was adored as an amicable and affectionate leader.

4. JN Mukherjee and Surface Science

JN Mukherjee, a class mate of JC Ghosh started his career as a lecturer at University College of Science, Calcutta University. Mukherjee, Ghosh and Bhatnagar worked together at Professor Donnan's laboratory. Mukherjee's major interest was in surfactant assemblies (micelles) and soil chemistry. He was the first Director General of the Imperial Council of Agricultural Research which was the precursor of Indian Council of Agricultural Research (ICAR). JN Mukherjee and his student BN Ghosh (younger brother of JC Ghosh) established a very active school of research in surfactant assemblies in India.

The three musketeers (Bhatnagar, Ghosh and Muherjee) at the insistence of Prof Donnan formed the Indian Chemical Society in 1924 with PC Ray as the President.

5. Magnetic Anisotropy and Molecular Magnetism: Krishnan and Guha

After these three pioneers, several physicists started research on various aspects of solid state physics which are now being pursued under chemistry. In 1930-s, KS Krishnan (1898-1961) developed the method of measurement of magnetic anisotropy of inorganic crystals. In 1939, Krishnan, wrote a paper entitled "Jahn-Teller theorem and arrangement of water molecules around paramagnetic ions in aqueous solution" (*Nature*, 1939).[2] In this paper, Krishnan examined the implications of Jahn-Teller theorem in anisotropy & birefringence. It may be mentioned that Jahn and Teller proposed a theory of splitting of energy levels of *d*-orbitals in inorganic crystal in two papers published in 1937 and 1938. Research in Jahn-Teller splitting became popular much later after the famous paper by Bleaney and Bowerson on EPR spectrum of Cu (II) complexes, published in 1952.

In 1951, from magnetic susceptibility measurements BC Guha, an associate of Krishnan, proposed that the two Cu (II) in copper acetate dimer, are anti-ferromagnetically coupled (*Proc. Roy. Soc*. 1951).[3] This has been hailed as the discovery of the first molecular magnet. About this Olivier Kahn wrote in his famous book (*Molecular Magnetism, VCH***)** that,

> "The magnetic interaction phenomenon within a molecule was discovered in 1951 by Guha [6.8] and then by Bleaney and Bowers [6.11], (for the compound) …known at that time as copper (II) acetate monohydrate. Guha found that the magnetic susceptibility exhibits a maximum as a function of temperature; Bleaney and Bowers observed that the EPR spectra resemble those of triplet states rather than doublets expected for non-interacting copper (II) ions. … The metal atoms are bridged by four acetato groups. The Cu…Cu separation is 2.4 Å."[3]

6. Polymer Science

After second world war, polymer science emerged as a new frontier of physical chemistry. SR Palit and Sadhan Basu started research in polymer science at the Lac Research Institute at Ranchi. Finding a good solvent for the polymers, was a major challenge in 1940-s. Palit pioneered the use of solvent mixtures (co-solvency) for shellac, soaps, and high molecular weight polymers. He popularized the use of solvent mixtures of glycol and other solvents as a medium for titration of weak bases or acids or their salts resulting in sharp end points. Palit's monograph on the subject 'Non-aqueous Titration' (1954) was translated into Russian. His works on co-solvency

was included in many text books on quantitative analysis of functional groups. Palit discovered a simple spectroscopic method for the estimation of the ionic end-groups of polymer by attaching an oppositely charged dye. Knowledge of the nature of the end groups, provides insight into the mechanisms of initiation, termination, and chain transfer in chain polymerization. Since the end groups constitute only a few ppm in a high molecular weight polymer, detection of end group was a major challenge. Palit's method is therefore, considered a major break-through. Before Palit, the polymer chemists used to prepare polymer with radio-labeled end groups which is a very expensive method.

Nylon, the first commercially successful synthetic thermoplastic polymer, was synthesized in 1935 by Wallace Carothers at Du Pont. Sadhan Basu showed that phenol is a good solvent for nylon and carried out end-group titration of nylon in phenol.[4]

In a series of papers published in the *Proceedings of Royal Society* in early 1950-s Basu and his co-workers elucidated the mechanism of chain transfer in polymerization and on the hypothesis made by Flory (Nobel Laureate) made in 1937. Basu's work was immediately cited in Flory's book which is considered to be the *bible* of polymers.

7. Bio-physical Chemistry

Avery (Nobel Laureate) discovered in 1944 that DNA is the main constituent of genetic materials. In 1950, Sadhan Basu first applied the concepts of polymer physics to DNA.[5] At that time, the subject of DNA was still in its infancy. The structure of DNA was still unknown. Rosalind Franklin determined the structure of sodium thymonucleate, two years after Basu's first paper (Franklin, *Nature* 1953). Basu's first paper on viscosity of DNA (sodium thymonucleate) appeared in *Nature* in 1951.[5a] His second paper on sedimentation and flexibility of DNA was published in *Science* (1952).[5b] In 1952, Basu published another paper in Nature on iodine absorption by an enzyme.[6]

8. Early Research in Quantum Chemistry

In the early 1950-s, Sadhan Basu started applying quantum mechanics to chemical problems. Using the simple free electron model he calculated activation energy of Diels Alder Reaction,[8a] energy levels of Tropolone,[7] phthalocyanine and so on.[8b] He calculated para-localization energy and related it to polarographic half wave potentials (*Nature*, 1957 and 1958).[8c] These works, in spite of rather drastic approximations, served as the building block of physical organic chemistry. Note, there was no computer available at that time. Basu used to diagonalize big matrices by hand. Basu was invited to be the founding editors of the *International Journal of Quantum Chemistry*. He wrote three reviews (on theory of solvent effect on molecular spectra, collective oscillation model in π-electron system and convergence limit in electronic spectra) in the *Advances in Quantum Chemistry*.

Aneesur Rahman (1927-1987)

Aneesur Rahman (1927-1987), born in Hyderabad, studied in Cambridge and Belgium. In 1953, Rahman returned to India as a lecturer at the Physics (1953-57) Department of Osmania University[10]. He, later, shifted to TIFR and worked there for four years as a Fellow (1957-60). Rahman initially worked on applications of quantum chemistry. In 1960, he joined Argonne National Laboratory in USA. 4 years later he carried out Molecular Dynamic (MD) simulation on the motion of 864 Ar atoms on a CDC 3600 computer

and published the seminal paper titled "Motion of atoms in liquid Argon" (*Phys. Rev.* A, 1964).[11] This paper gave birth to MD simulations. The codes developed by Rahman are used still today. In 1976, he carried the first computer simulation of a protein (BPTI). In 1982, he developed the micro-canonical ensemble approach to lattice gauge theory. He and his collaborators (Karplus, Klein, Parinello and Callaway) revolutionized computer simulations. Cancer cut short his life in 1987. In 2013, the Nobel Prize in Chemistry was awarded to Karplus, Levitt and Warshel for the development of large scale computer simulations, which essentially began with Rahman.

9. Spectroscopy

1n 1950-s Sadhan Basu initiated research in spectroscopy of inorganic complexes[9a-b] and on charge-transfer spectroscopy.[9c] His two students, M. Chowdhury and A. Chakravorty (co-authors of these papers) later played a major role in the development of physical chemistry and Inorganic Chemistry in India.

10. Conclusion and future Outlook

It is heartening to note that in spite of poor facilities, the early doyens of physical chemistry in India attracted global attention. The lack of facilities forced them to become highly original. They earned international respect because of their fresh and original approach and creativity. The more favorable conditions (in terms of facility and grant), at present, had a noticeable improvement in contributions from India, at least in terms of number of papers. India is currently (2011) ranked ninth in terms of total papers published per year in all subjects. In Chemistry, India is ranked 4th (after China, USA, and Japan). Recently, India overtook Germany, UK and France in terms of papers published in chemistry per year. About 100 Indian chemists are in the editorial board of international journals (ACS and RSC). This encourages us to nurture a hope that India will become a global leader in physical chemistry and in chemistry, as a whole.

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