

Sadhan Basu – A Physical Chemist Extraordinaire

A Glimpse into his Research Work

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(left) Ramprasad Misra did his doctoral studies (integrated PhD) in S P Bhattacharyya's research group at IACS and is presently in the University of Pittsburgh. His research interests are in physical organic chemistry and molecular spectroscopy.

(right) S P Bhattacharyya, Fellow of the Indian Academy of Sciences, retired as Senior Professor of physical chemistry, IACS, Kolkata in March 2012 and is presently at IIT Bombay as Raja Ramanna Fellow (DAE). His main research interest is in the area of quantum chemistry.

Sadhan Basu was an inspiring teacher and scientist and among the best that our university system has produced. He carried out important and thoughtful research work in the fields of polymers, spectroscopy and quantum chemistry that bear the signature of a highly creative mind. And all these he did with so little resources at his disposal. No wonder that his memory still inspires awe and respect among many of his immensely successful students and colleagues.

Sadhan Basu (1922–1992) was a physical chemist in the true sense of the term. Possessed with a fever of creative thinking, he pursued research with rare zeal in practically all areas of physical chemistry – polymers, kinetics, spectroscopy and theoretical chemistry. He attracted the best students and his group in the University College of Science and Technology in Kolkata (then Calcutta) became very famous. He was a dedicated teacher and enjoyed teaching. He was indeed an illustration of how teaching and research could wonderfully complement each other in a university set up. After a brief stint in the Lac Research Institute, Ranchi, Basu started his research career in Physical Chemistry in India in the year 1948 when he joined the Indian Association for the Cultivation of Science (IACS), Kolkata – the cradle of Indian science, established in 1876. A few years later, he moved to take up a teaching position in the University of Calcutta (C.U.). Much later, he became the Director of IACS, a job he did not perhaps relish. He went back to C.U. as Palit Professor, after a brief stint in IACS as the Director. He never went for big budget projects and shunned publicity. The research he carried

Keywords

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out, however, had the unmistakable stamp of brilliance that dazzled all and inspired many. In what follows, we shall focus on Basu's work in the early years of his career in India which began with a foray into the realm of physical chemistry of polymers (1950).

Polymerization Kinetics

The prevailing ideas at that time were based on kinetic data on bulk polymerization and it was assumed that the degree of polymerization was equal to the kinetic chain length. That is, the stabilization of the growing polymer molecule and destruction of its activity for growth took place simultaneously.

Kinetic data on polymerization in solution that were then just coming in, however indicated that the rate of polymerization in solution was virtually the same as that in the bulk while the degree of polymerization predicted from solution data was invariably lower than its bulk polymerization counterpart. Moreover the plots of $\log P$ against $\log A$ (where P and A are the degree of polymerization and monomer concentration, respectively) were not linear as would have been expected. The best linear fit produced straight lines with slopes less than one (< 1). One was therefore forced to conclude that the growth of the polymer chain in solution was being terminated by a process that did not stop polymerization. P J Flory¹ (1937) hypothesized that the growing polymer molecule could transfer the activity for growth to a solvent molecule, a monomer molecule or another polymer molecule. Initial work by Suers *et al* (1937), Schultz (1938–39), Mayo (1943) on polymerization of styrene in solution led to evaluation of chain transfer efficiency of a few solvents.

Basu *et al* (1950) in two landmark papers [1–2] critically examined Flory's hypothesis through a large number of carefully planned experiments on both uncatalyzed and catalyzed chain transfer polymerization kinetics of

¹ See *Resonance*, Vol.8, No.6, 2003.

Basu pioneered the study of kinetics of catalyzed and uncatalyzed chain transfer polymerization.



methyl methacrylate in more than 25 solvents. The highlights of the study were (*Box 1*):

1. Evaluation of chain transfer efficiency of a large number of solvents and relating the efficiency to structural features of the molecules.

Box 1.

Kinetics of Chain Transfer Polymerization in Solution, Catalyzed or Uncatalyzed

1. A generalized derivation given by Basu *et al* [1] proceeds as follows:

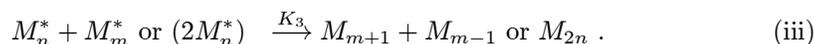
Let A , B and M_1^* be the monomer, catalyst and the activated molecule, respectively. The bimolecular initiation reaction, then reads



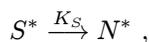
The propagation step consists of successive addition of the monomer (A) to M_1^* .



The deactivation/stabilization then involves



The growing molecule could transfer its activity to a monomer (A) or solvent molecules leading to



where S stands for solvent molecules and N^* the active radical formed by the interaction between an active solvent molecule and the monomer.

The number average degree of polymerization (\bar{P}) is simply the ratio of the velocity of chain propagation and velocity of chain termination; so,

$$\bar{P} = \frac{K_1[A][C^*]}{K_3[C^*]^2 + K_{tr}[A][C^*] + K_{tr'}[C^*][S]} , \quad (\text{vi})$$

Box 1. Continued...



Box 1. Continued...

where $[C^*]$ denotes the overall concentration of the active free radical. When the rate at which active centres are produced becomes equal to the rate of their destruction, we have

$$K_1[A][B] = K_3[C^*]^2 \quad (\text{vii})$$

whence,

$$[C^*] = \left\{ \frac{K_1}{K_3} [A][B] \right\}^{\frac{1}{2}} \quad (\text{viii})$$

Using $[C^*]$ given by equation A8 in equation A6, we have

$$\frac{1}{\bar{P}} = \frac{\{K_1 K_3 [B]\}^{\frac{1}{2}}}{(K_2 + K_{tr}) [A]^{\frac{1}{2}}} + \left(\frac{K_{tr}}{K_2 + K_{tr}} \right) \quad (\text{ix})$$

$$= \frac{\lambda [S]}{[A]}, \quad (\text{x})$$

where $\lambda = \frac{K_{tr'}}{[K_2 + K_{tr}]}$ is called the chain transfer constant[#].

Since, $K_{tr} \ll K_2$, one writes $\lambda = \frac{K_{tr'}}{K_2}$

2. In bulk polymerization $[S]$ and $K_{tr'}$ are equal to zero, whereby

$$\frac{1}{\bar{P}_0} = \frac{\{K_1 K_3 [B]\}^{\frac{1}{2}}}{(K_2 + K_{tr}) [A]^{\frac{1}{2}}} + \left(\frac{K_{tr}}{K_2 + K_{tr}} \right) \quad (\text{xi})$$

3. For uncatalyzed bulk polymerization $B = A$ so that for this case we have

$$\frac{1}{\bar{P}_0} = \frac{\{K_1 K_3\}^{\frac{1}{2}}}{(K_2 + K_{tr})} + \left(\frac{K_{tr}}{K_2 + K_{tr}} \right) \quad (\text{xii})$$

The corresponding equation for uncatalyzed polymerization in solution then reduces to

$$\frac{1}{\bar{P}} = \left\{ \frac{K_{tr'}}{K_2 + K_{tr}} \right\} \frac{[S]}{[A]} + \frac{1}{\bar{P}_0} \quad \text{or,} \quad \frac{1}{\bar{P}} = \frac{\lambda \times [S]}{[A]} + \frac{1}{\bar{P}_0} \quad (\text{xiii})$$

4. The crucial question regarding the bimolecularity/unimolecularity of the initiation step was answered by examining the features of plots of $\frac{1}{\bar{P}}$ against $\sqrt{\frac{[B]}{[A]}}$ and the experimental data obtained by Basu *et al* (II) showed that the plots of $\frac{1}{\bar{P}}$ against $\sqrt{\frac{[B]}{[A]}}$ were linear with slope independent of $[A]$, which confirmed bimolecular initiation. The features of plots of $\frac{1}{\bar{P}}$ against $\frac{\sqrt{[B]}}{[A]}$ rejected the idea of unimolecular initiation.

[#] λ was determined from the slopes of plots of $\frac{1}{\bar{P}}$ against $\frac{[S]}{[A]}$ at constant $\frac{[B]}{[A]}$.

Box 1. Continued...



Box 1. Continued...

The monomolecular initiation leads to

$$\frac{1}{\bar{P}} = K \frac{\sqrt{[B]}}{[A]} + \lambda \frac{[S]}{[A]} + \frac{K_{tr}}{K_2}$$

and predicts that the plots of $\frac{1}{\bar{P}}$ against $\frac{\sqrt{[B]}}{[A]}$ should be linear at all monomer concentrations while the plot of $\frac{1}{\bar{P}}$ against $\sqrt{\frac{[B]}{[M]}}$ would reveal changing slope with change in monomer concentration which was not the case experimentally.

2. Demonstration that the kinetic model of chain transfer was equally applicable to catalyzed and uncatalyzed polymerization in solution.
3. The initiation step was unambiguously identified to be bimolecular.

Basu continued his research in polymer chemistry for a while. His ability to innovate was striking. End-group titration was then a popular and useful method for the determination of molecular weights of polymers. Basu [3] noted that because of the insolubility of certain nylons² in common organic solvents, it was not possible to apply the end-group titration technique to all nylons. Taking cue from S R Palits's observation that weak bases could be conveniently titrated in organic solvent, with a solution of perchloric acid in glycolic mixtures, he went on to dissolve nylon in phenol containing a small amount of glycol and titrated it electrochemically with dilute perchloric acid (0.01 N – 0.1 N) in 1:1 glycol–isopropyl alcohol mixture. Assuming that there was one free primary amino group at the end of each polymer chain, and noting the locations of the inflexion points in the observed pH versus volume of acid-added plots, the molecular weight could be correctly estimated.

Swelling–Deswelling of Polymers

The ingenuity of Sadhan Basu and his ability to design simple experiments to demonstrate the working of

² Nylons are condensation copolymers formed by dicarboxylic acids and diamines, the most common variant being nylon 6-6 obtained from hexane dioic acid and hexane 1,6 diamine.



a physicochemical principle is amply illustrated by his design of the mechanochemical Carnot engine. Basu argued that a water-insoluble polymer containing many ionizable (dissociable) groups ($-\text{COOH}$, say) distributed along the chain would expand when placed in water because the ionization (dissociation) would create similarly charged groups (COO^- , for example) distributed along the polymer chain. When 'dissolved' in water and completely neutralized by adding alkali (NaOH), many COO^- groups would be created which would mutually repel each other rather strongly and overcome the normally encountered Coutschouc type (rubber-like, entropic) of contractile force in neutral polymers. To minimize the repulsive energy, the chain would uncoil further and elongate. If the surrounding water is replaced by a strong salt solution (MX , say), some of the M^+ ions would leave the solution and go back into the chain ($\text{COO}^- + \text{M}^+ \rightarrow \text{COOM}$), reducing the charge density and repulsive energy. The polymer would then coil back and contract. If all the electrolytes are removed by repeated washing, the original length would be restored.

Basu made a film [4] of partially hydrolyzed (33%) methyl methacrylate polymer of a given average degree of polymerization and demonstrated the reversible expansion and contraction that the film underwent as the salt concentration of the water surrounding it is changed. He then went a step further and used the phenomenon to set up a working mechanochemical Carnot engine. It would be worthwhile to outline the experiment here.

A thin film ($2\text{cm} \times 1\text{cm} \times 0.1\text{cm}$) was made of the sodium salt of partially hydrolyzed MMA polymer, dipped in water, and the lower end was kept fixed to a heavy weight resting at the bottom of the container of water (*Figure 1*). The upper end of the film was attached to one arm of a balance made of a light and thin

Basu designed and demonstrated a mechanochemical Carnot engine.



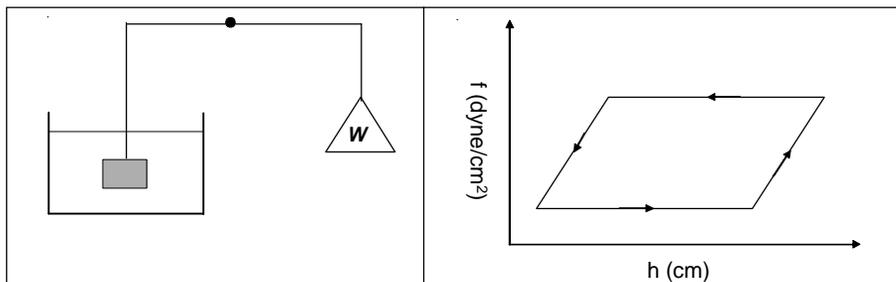


Figure 1 (left).

Figure 2 (right).

glass rod, while the other arm carried a light aluminium pan on which necessary weights could be placed. The film was set fully stretched and the arm of the balance was horizontal, to start with.

1. Increasing amount of weights (0–2 gm in steps of 0.5 gm) were placed on the pan, and the stretching measured.
2. Keeping the weight fixed, strong NaCl solution was added (till 0.026% strength was reached). The contraction was measured at each salt concentration.
3. Keeping the NaCl concentration fixed, the weights were removed from the pan in steps, and the further contraction underwent by the film was noted.
4. Water was added to the container, till the salt concentration reduced to $< 0.006\%$. The expansion of the film was noted.

The cycle of expansion and contraction is shown in *Figure 2*. The area under the curve yielded the work done (5268 ergs). This simple but beautiful transcription of the reversible expansion–contraction at molecular level onto a macroscopic scale underscores the kind of innovative mind that Basu had.

Coiling–Uncoiling of Protein

The coiling–uncoiling of proteins in response to changes in surroundings and its possible relation to the activity

The mechano-chemical Carnot engine uses reversible expansion–contraction at the molecular level to do macroscopic work.



protein stirred his imagination. Basu and Nandi [5] showed that the extent of deactivation of an enzyme due to the unfolding of a protein chain of the enzyme molecule could be measured iodometrically by titrating the $-SH$ groups exposed by the unfolding process. They went on to hypothesize further that the extent of enzyme activity at different pH of the medium could depend, at least to some degree on the extent of coiling/uncoiling of the enzyme. They found that pepsin, for example, had the lowest I_2 absorption at $pH = 2$ suggesting that it is possibly maximally coiled at $pH = 2$. Indeed, the enzyme was maximally active at this pH. A similar conclusion was reached by examining the extent of I_2 absorption by trypsin at different pH and observing the correlation between its activity and the pH.

The viscous response of a neutral polymer and a poly electrolyte can be strikingly different!

Anomalous Viscosity of Sodium Thymonucleate Solutions

Basu noted that the viscosity of an aqueous solution of sodium thymonucleate displayed a rather odd behavior [6]. Unlike neutral polymers, the reduced specific viscosity of a solution of sodium thymonucleate increased with dilution (*Figure 3a*). Basu suggested [6] that the root of the observed pattern of changes in the viscosity of the thymonucleate lay in the progressive uncoiling of the chain with dilution. The chain contained many dissociable groups. The dilution caused increasing dissociation and created many similarly charged groups along the chain. To minimize energy the chain progressively unfolded, causing the observed increase in viscosity. That

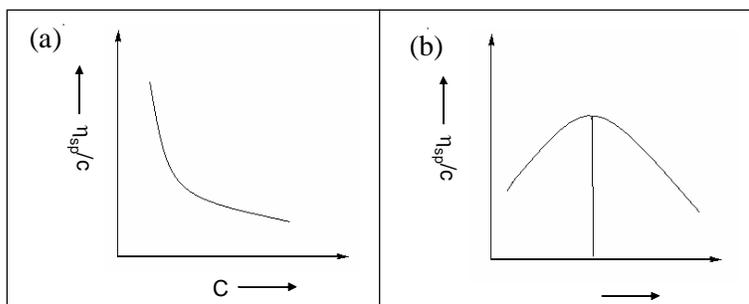


Figure 3.

The specific viscosity of a solution of sodium thymonucleate passes through a maximum as one increases the concentration of the solution.

meant the thymonucleate behaved like a polyelectrolyte and not like a neutral polymer. He then suggested a strikingly simple experiment that would validate his assumption. It was known that the viscosity of the sodium thymonucleate diminished remarkably in 1% NaCl solution. Basu argued that if the NaCl concentration was $\ll 1\%$, there would be a critical concentration of thymonucleate below which Na^+ ions would be drawn back into the thymonucleate chain thereby forcing it to be fully undissociated and behave like a neutral polymer. Above the critical concentration of thymonucleate (and assuming the same concentration of sodium chloride as before), some of the electrolyte groups in thymonucleate would dissociate forcing it to behave like a polyelectrolyte. The specific viscosity of the solution plotted against the thymonucleate concentration would pass through a maximum (*Figure 3b*). At the maximum, Na^+ ions contributed by the thymonucleate and sodium chloride would be approximately the same. Basu measured the viscosity of sodium thymonucleate in the presence of different (but low) concentrations of NaCl and demonstrated the validity of the proposed mechanism.

Charge Transfer Spectroscopy

Donor-acceptor (charge transfer) interactions are ubiquitous in chemistry. Ever since Mulliken proposed a theoretical model for exploring the characteristic absorption spectrum of $\text{I}_2 + \text{benzene}$ system based on the formation of intermolecular charge transfer (CT) complexes, a lot of research has been carried out on the CT phenomenon. To the best of our knowledge, the research group of S Basu was the first in India who systematically investigated many facets of charge transfer process and the properties of CT complexes. Chowdhury and Basu [7](1960) observed that the spectral data pertaining to a mixture of iodine and polynuclear aromatic hydrocarbon dissolved in CCl_4 pointed to the formation of 2:1 molecular (CT) complexes of contact type with rel-



atively much higher values of equilibrium constant than the corresponding 1:1 complexes and that they were independent of the nature of the aromatic hydrocarbon. Later, Majumdar and Basu [8] (1960) proposed a mechanism mediated by CT interaction for explaining the quenching of fluorescence of a number of polynuclear hydrocarbons by aromatic solvents, particularly methylated benzenes. They found the quenching efficiency to be in the order benzene < toluene < xylene < mesitylene which is also the order in which the ionization energy of the solvent molecules diminishes. The emission intensity was found to increase in the order benzene > toluene > xylene > mesitylene, i.e., the order in which the donor strength of the solvent increases. The authors argued that these observations indicated that the quenching of fluorescence was mediated by CT interactions. The authors, in fact, went a step ahead. They noted that the absorption spectra in different solvents were not affected appreciably so that the question of molecular complex formation in the ground state did not arise. It was therefore argued that the CT interaction with solvents took place when the fluorophore was in the excited state. Moreover, the fluorescence intensity was not affected at all in n-heptane solution even when methylated benzenes were added. The authors concluded that the interaction that took place could be of 'contact-type', not all of which were effective for degrading the energy. Only specific contacts in which the donor (D) and acceptor (A) were properly oriented, succeeded in degrading energy. Majumdar and Basu then proposed a kinetic scheme (Box 2) which led to the prediction that $\log K_2$ at a constant temperature would vary linearly with the ionization energy of the solvents if K_2 was primarily determined by the CT interaction energy. Good linear plots were indeed obtained, validating the proposed mechanism.

Mulliken's theory of CT interaction [9] introduced the

The idea of CT interaction in the excited state takes shape.

The quenching of fluorescence in solutions of polynuclear hydrocarbons in aromatic solvents was concluded to be due to charge transfer interactions.



Box 2	
Process	Rate
$A + h\nu \rightarrow A^*$	1
$A^* \rightarrow A + h\nu'$	k_1
$A^* + S \rightarrow A + S$	k_2 (S is the solvent)
$(\frac{1}{F} - 1) = \frac{k_2}{k_1}$, where F is the fluorescence yield.	

famous a , b , and a^* , b^* parameters that reflected the degree to which CT takes place in the ground state (a , b) or in the excited state (a^* , b^*). How could one estimate these quantities from experimental data on CT complexes Basu investigated this question in the context of CT interaction between tetrahalobenzoquinones and aromatic hydrocarbons like anthracene, pyrene, stilbene, etc. [10–12]. To put the work in a proper perspective we will briefly review Mulliken's theory. The ground and excited state wave functions of the donor-acceptor complex were written as superposition of the no-bond wavefunction ($DA \equiv \psi_0$) and a completely charge transferred or dative bond wave function ($D \rightarrow A$ or $D^+A^- \equiv \psi_1$). Thus, one could write

$$\psi_g = a\psi_0 + b\psi_1,$$

$$\psi_e = a^*\psi_1 - b^*\psi_0.$$

The normalization requirements on ψ_g and ψ_e led to

$$a^2 + b^2 + 2abs = 1,$$

$$(a^*)^2 + (b^*)^2 + 2a^*b^*s = 1,$$

where $s = \int \psi_g \psi_e d\tau$ is the overlap integral. Their mutual orthogonality requires

$$a^*(b + as) = b^*(a + bs).$$

Let the dipole moment of the fully charge transferred species be μ_1 ($= e \cdot r$, where r is the separation between the D and the A at equilibrium). If the component



donor/acceptor is non-polar or weakly polar, it is possible to write, for the dipole moments of the complex in the ground and excited states,

$$\begin{aligned}\mu_g &= (b^2 + abs)\mu_1, \\ \mu_e &= [(a^*)^2 + a^*b^*s]\mu_1.\end{aligned}$$

Basu used solvent-shift of the position of the CT band maxima in non-polar solvents to estimate μ_g and μ_e and therefrom went on to predict the values of a , b , and a^* , b^* . Arguing that a large change in the dipole moment occurred due to the CT interaction which meant that dipolar interaction would dominate over dispersive interactions, Basu [13] found that the solvent-shifted CT absorption frequency, ν_{sol} could be related to the corresponding absorption frequencies in the isolated gas phase (ν_{gas}), by

$$h(\nu_{\text{gas}} - \nu_{\text{sol}}) = \frac{1}{a^3} \left(\frac{2n_0^2 + 1}{n_0^2 + 2} \right)^2 \left\{ 2\mu_g(\mu_g - \mu_e) \cdot \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \cdot \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) + (\mu_g^2 - \mu_e^2) \cdot \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right) \right\}$$

with n_0 being the long wavelength refractive index and ε the static dielectric constant of the solvent; ν_{sol} was measured in several non-polar solvents and μ_g , μ_e and ν_{gas} were estimated which finally led to the calculation of a , b , and a^* , b^* values.

Crystal Spectroscopy

The spectra of CT complexes are broad and structureless. The transition metal complexes in solution are also characterized by broad bands. Could the broad bands reveal underlying finer structures if the spectrum could be recorded in thin transparent crystalline state where the averaging effect of the surrounding solvent molecules be absent? Basu explored this idea systematically [14]. His objective was to understand the nature

Basu used solvent-shift of the CT band to estimate dipole moments in the ground and excited states.



Basu was ambidextrous, equally adept in theory and experiments.

of $d-d$ transition and get an idea about the symmetry of the molecular field. Copper biguanides, like the bis-biguanide dibromide dihydrate formed transparent crystals. The solution spectrum consisted of a single broad band, which resolved into three bands in the crystal spectrum with light polarized along the long axis, of the crystal (485 nm, 540–550 nm and 600 nm). When light was polarized perpendicular to the long axis the 600 nm band went missing. A comparison with predictions of ligand field theory suggested that the long axis of the crystal coincided with the z -axis of the molecular field. The work provided the nucleus for further exploration of the crystal spectrum of transition metal and rare earth complexes at room and low temperatures. Basu was ambidextrous, equally adept in theory and experiments. His interest in theory took a firm shape while he was still in IACS.

Quantum Chemistry

Phthalocyanine (*Figure 4*) and its derivatives are important molecules in the dye industry. The molecule was just made visible under field emission microscope in 1952 and its work function and ionization energy were determined. It was a big molecule and an intrinsic semiconductor in the solid state. The band structure of the electronic energy levels was available. Basu [15] took

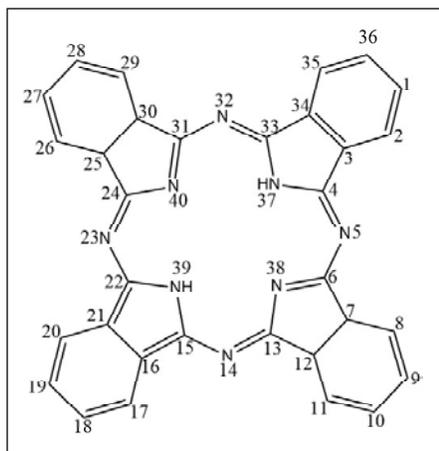


Figure 4.

upon himself the task of calculating the electronic structure of the molecule using π -MO theory. The permanent charge distribution in the molecule was obtained and its chemical reactivity sought to be correlated with the computed π -electron densities. In fact, the paper, so to say, marked the birth of quantum chemical research in India.

Basu was probably the first to do a quantum chemical calculation in India.

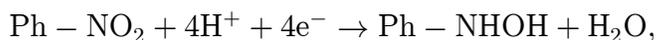
Even at the simplest level of π -MO theory (Hückel), the molecule was too big and complex to be handled in 1954. Basu introduced certain simplifying features, namely the Coulomb integral of all the atoms were equal ($\alpha_C = \alpha_N$) and so also were the resonance integral ($\beta_{CC} = \beta_{CN}$). Under these approximations the point symmetry of the molecule was D_{4h} and Basu used group theory to reduce the (40×40) secular equation to equations of lower dimensionalities corresponding to the different irreducible representations of the D_{4h} group. The approximation was introduced consciously. Thus, Basu wrote, “Nitrogen is more electronegative than carbon and will certainly have a higher value for the Coulomb integral. However, it is most convenient to begin by assuming that all the α values are equal and correct the resulting values later on”. We mention this because the approximations made were later criticized as an ‘error’. In fact in the same paper, Basu tried to obtain corrections to the energy levels perturbatively by treating the difference between the α_N and α_C as perturbation. The neglect of overlap also sought to be corrected.

The calculation predicted that atoms numbered 37, 38, 39, 40 have the highest π -electron densities, even though the higher electronegativity of nitrogen compared to carbon was not introduced in the theoretical description. Basu observed, “This suggests two things. First, the greater stability of phthalocyanine is largely due to the presence of nitrogen at points in the skeleton, where purely for geometrical reason, the π -electrons tend to congregate”. He noted further that the π -electron den-



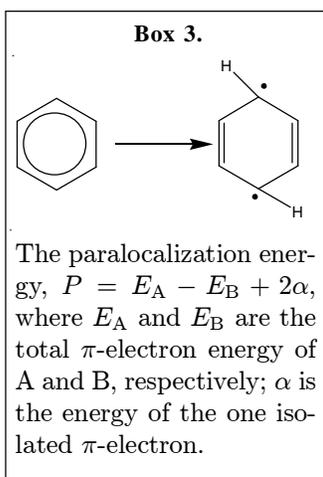
sity is the lowest at positions numbered 5, 14, 23 and 32 (*Figure 4*) and therefore “introduction of nitrogen atoms at these positions will tend to draw electrons away from other parts of the molecule. Consequently it is expected that although in porphine neglect of nitrogen electronegativity is permissible, for phthalocyanine this is a rather drastic approximation”. It appears to us that Basu was probably trying to assess how much of the π -electron density on different atoms in phthalocyanine is dictated by topology alone and how much of it is determined by the energetics. He also predicted the electronic spectrum of phthalocyanine in the same paper, noting at the same time, that neglect of configuration mixing makes the predicted spectrum rather approximate in nature.

Basu [16] continued his research in π -electron MO theory and sought to establish correlation between computed molecular parameters and relevant experimental quantities. In this context, we must mention his work on the para-localization energy (computed) (see *Box 3*) and polarographic half-wave reduction potential $E_{1/2}$ (experimental) of a series of polynuclear aromatic hydrocarbons. He extended the concept of para-localization energy to what he termed ‘group localization energy’. Taking the case of aromatic nitro compounds which then were almost surely known to undergo reduction by addition of four electron and four protons,



Basu [17] predicted that the reduction potential of such compounds at dropping mercury cathode would be proportional to the π -electron energy difference between the parent nitro compound and the transition state in which four electrons are localized on the nitro groups. He estimated the energy difference, $\Delta E(\pi)$ within the framework of the simplest π -electron theory and showed that $\Delta E(\pi)$ was indeed proportional to $E_{1/2}$.

One problem that Basu was fascinated by concerned the



Box 4. Biographical Information

Born to parents Jyotish Chandra Basu and Sarajubala on January 02, 1922 in the city of Kolkata, Sadhan Basu did his BSc (1942) and MSc (1944) from Calcutta University. He obtained his DSc degree from the same university in the year 1948. He joined the Lac Research Institute in Ranchi as Physical Chemist (1945-1948) and then moved to the Indian Association for the Cultivation of Science as Research officer (1948-51). He was Sr. Fulbright Fellow, Indiana University, Bloomington (1951-53), visiting professor of the same university during 1961-1962. He joined the Department of Chemistry, University College of Science and Technology, Kolkata, as Reader in the year 1954 and became the Palit Professor, a Chair he held till his retirement in 1985. He was visiting Professor in the Quantum Chemistry group of Uppsala University, Sweden (1962-1963).

Sadhan Basu was fellow, INSA, IAS (Bangalore), Indian Chemical Society, Royal Society of Chemistry (London), Societic de Chemie Physique (France). Recipient of Shanti Swarup Bhatnagar Prize in Chemistry (1965). He was appointed UGC National Lecturer (1972-73). He won the C V Raman Birth Centenary Commemoration Medal in 1988. His sad demise came in 1992 after a brief illness. He is survived by his wife Rama Basu, a theoretical chemist of repute and a son and a daughter.

free-electron theory of π -conjugated molecules. It was usually mapped into 'particles in a box' problem and the box dimensions adjusted. As the length of the box increases the lowest energy transition is predicted to become zero. In practice, in many conjugated systems, like the carotenoids, cyanines, etc., the transition energy tends to converge to a low but limiting frequency. In two well-researched articles [18,19], Basu explored different mechanisms that would explain the observed convergence. In one of the articles he analyzed if something like the collective oscillations of Tomonaga's electron gas model would explain the appearance of the convergence limit. In the other, he explored the idea of possible pairing interactions between electrons being responsible for creating the convergence of the HOMO-LUMO gap. These articles reveal how well aware he was of contemporary developments in theoretical physics and how eager he was to explore those ideas to resolve the problems of theoretical chemistry.

We have been able to cover only a minuscule portion of the research work of Sadhan Basu. We are sure, however, that the little we have written, is enough to illustrate the extraordinary brilliance of the man – with so

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little, he could do so much. For the inquisitive reader, a brief biographical sketch of Sadhan Basu is provided in the *Box 4*.

Suggested Reading

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