Meetings

Faraday Society Discussion: Proton Transfer Processes

Proton transfers are widespread in reactions occurring in solution, and are frequently very fast processes with half-times down to 10^{-11} second. The recent development of techniques capable of following these very fast reactions has enhanced progress in this field. The latest advances in the field of proton transfer processes were discussed at a meeting of the Faraday Society held at the University of Newcastle-upon-Tyne, England, 12–14 April 1965. About 20 European and American researchers delivered lectures attended by over 200 chemists.

M. Eigen (Max-Planck Institut, Göttingen, Germany) has performed extensive research on the application of relaxation measurements to the study of acid-base systems involving proton transfers. Under the chairmanship of the president of the Society, F. S. Dainton (Leeds University), Eigen gave the general introduction to the meeting. In relaxation measurements, physical methods are used to perturb the position of a chemical reaction a small distance away from equilibrium. Thus the dissociation of weak acids can be induced by high fields or temperature jumps by means of large currents. Data are obtained by examining the solution spectrophotometrically or by some physical parameter such as electrical conductivity. Eigen has applied these methods to the examination of a large number of chemical systems, and has made a critical examination of the Brönsted catalysis law. This law relates the catalytic coefficient k of an acid or base to its dissociation constant K by the relationship $k = GK^{\alpha}$, where α is a constant between 0 and 1 for the reaction of a particular acid with a series of bases. Eigen finds that the value of α varies between 0 and 1. He noted the reaction of an acid HA with a series of bases. With strong bases the rate will probably be diffusion-controlled, and hence the rate is independent of the basicity of the base. Thus the Brönsted coefficient α has a value of 0. If on the other hand the acid HA transfers a proton to species which are much stronger acids, then the back-reaction becomes diffusion-controlled and the forward reaction will have a coefficient of 1. It is only in the intermediate range where the proton transfer occurs between species of not too dissimilar acidities that the coefficient can have intermediate values. It is over this range that traditional methods of measurement are useful. The Brönsted law is thus a special case of a more general overall picture which the new methods of observation have brought into view by increasing the accessible range of measurement.

Eigen also mentioned how a solvent molecule can participate in the transfer of a proton between two entities. This action was affirmed by E. Grunwald (Brandeis University) in a paper dealing with the use of proton magnetic resonance spectroscopy. He showed that in aqueous solutions containing methylamine and methylammonium ions the two species exchange a proton through one water molecule. Other systems also follow the same pattern. The use of nuclear magnetic resonance spectroscopy to illustrate the exchange of hydrogen between various sites was also demonstrated by D. Brouwer (Koninklijke/Shell Laboratory, Amsterdam). He reported on intramolecular hydride transfers between carbon atoms in carbonium ions. H. Strehlow (Max-Planck Institut) also found the technique useful in his study of the acid-catalyzed hydration of acetaldehyde.

No conference on proton transfers would be complete without the presence of R. P. Bell (Oxford University). He attempted to derive information about the detailed structure of transition states from hydrogen isotope effects. Factors of interest are the shape of the energy surface of the transition state, its nuclear configuration, and the position of the proton within. Kinetic investigations of a single process give only general information about the transition state, such as its enthalpy or entropy of formation, and do not readily yield structural information. Isotopic substitution, that is, replacement of the proton being transferred by deuterium or tritium, will not affect the shape of the energy surface. However, such substitution will modify the energy levels in a way depending on the shape of the energy surface, yielding useful information about its dimensions. Bell's experimental observations compared the rate of abstraction of a proton k_H or deuteron k_D from a given organic species by a series of bases of increasing strength. Contrary to simple theory, the ratio of k_H to k_D was found to be not constant for the various bases; the ratio showed a wide variation, thus indicating that isotopic substitution affected not only the initial state but also the transition state. The results were discussed in terms of vibrations of the transition state, and led to the conclusion that there may be real vibrations of the transition state. Such vibrations may involve movement of the transferred proton, the presence of which leads to large variations in the magnitude of the isotope effect. Bell also mentioned quantum-mechanical tunneling by which reaction can occur through, rather than over, the energy barrier. He concluded on the hopeful note that the study of isotope effects should prove a most useful means of revealing the detailed structure of transition states.

The form of the proton in aqueous solution also stimulated comment. It is generally agreed that the proton in solution is hydrated; however, the extent of hydration is open to question. Two favored possibilities are H_3O^+ and $H_9O_4^+$ where the proton is solvated by one or four molecules of water, respectively. In acidic solutions containing water and deuterium oxide, the deuterium isotope is not randomly distributed between hydrogen ions and water molecules. The isotope does, however, show a preference for water molecules. V. Gold (King's College, London) showed that this isotopic fractionation involved three sites only; he argued in favor of an H_3O^+ entity. Measurements of kinetic effects and effects of the isotope products in the hydration (catalyzed by hydrogen ion) of isobutene in media containing various isotopes are well explained by a direct proton transfer from H_3O^+ to the olefin. The evidence does not, however, preclude indirect proton transfer from H_3O^+ by a water molecule to

the olefin, that is, effective transfer from an $H_9O_4^+$ species.

Other investigations into the structure of water have been on the basis of electrolytic conductance measurements. The proton has an abnormally high conductance, and the variation of conductance with temperature and pressure throws light on the mechanism of conduction. Two papers were presented on this topic by E. U. Franck (Baden Institute of Technology, Karlsruhe) and G. J. Hills (Southampton University). It was generally concluded that proton migration occurs principally by charge transfer to, and reorientation of, free water molecules. The rate is determined by the rotation of a water molecule in the field of the hydrated proton to a position in which it can form a hydrogen bridge to the hydrated proton.

I left this conference with the feeling that in this branch of chemistry many workers are successfully concerned with the application of new physical techniques to essentially old problems.

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Mathematical Sciences

Elementary particle physics, many-body problems, and mathematical topics of interest to physicists were the main topics discussed at the 3rd anniversary symposium of the Institute of Mathematical Sciences, Madras, India, 3–12 January 1965.

In the introductory lecture Victor Weisskopf (CERN, Geneva) presented a broad survey of the current situation in elementary particle physics; the most dominant trend in this field is toward the concept of symmetry. To demonstrate the value of a historical perspective, he traced how the concepts of rotational symmetry and symmetry under permutation of identical objects from the realm of atomic physics not only explain many of the properties of the atom but also explain the properties of nuclei when augmented by the concept of isotopic spin symmetry. In the case of elementary particles, we have, in addition, the hypercharge symmetry; the combination of this with isospin is the SU_3 symmetry. He mentioned the experiments at CERN in search of "quarks," the hypothetical building blocks of the observed strongly interacting elementary particles and the weak vector bosons. Other experiments have tested the hypothesis of a cosmic force; they were advanced to explain the small violation of conservation of parity in weak interactions. Weisskopf concluded with some speculations on the lepton spectra. His quotation from Newton's *Optics* at the beginning of the lecture was startlingly apt for what followed.

Ph. Meyer (Orsay, France) summarized his work on the conserved vector-current hypothesis in relation to broken symmetries. Assuming that the violation of SU_3 invariance can be described by a local Lagrangian, which transforms like the member of an SU_3 multiplet with isospin and strangeness equal to zero, he proved that the first-order correction to the vector-decay amplitude, in the limit of zero-momentum transfer, can be accounted for by using unrenormalized coupling constants, but with wave functions corresponding to the physical masses. The success of the application of SU_3 symmetry to weak interactions in the Cabibbo theory was discussed by Alladi Ramakrishnan (Matscience, Madras). T. K. Radha (Matscience, Madras) reviewed the various models which oppose conservation of parity. She also mentioned a calculation (which she has carried out with Meister) on the electric dipole moment of the nucleon; this calculation assumes the maximum possible violation of conservation of parity. Another topic related to weak interactions was dealt with in a talk on μ-capture from nuclei, by V. Devanathan (University of Madras). Virendra Singh (Tata Institute of Fundamental Research, Bombay) first discussed the multiplet assignments of various observed particles in the SU_6 scheme (in which the internal symmetry group for the hadrons is combined with the ordinary spin), and then derived various sum rules for the relations among the masses of the hadrons. The sums agreed closely with the observed masses.

The concept of an equivalent potential in quantum field theory and S-matrix theory, and the use of a nonlocal potential in calculations in elementary particle physics formed the subject matter of three talks. R. Blankenbecler (Princeton University) showed how to obtain upper and lower bounds for the phase shifts and the K-matrix elements in nonrelativistic problems. He then extended these ideas to the relativistic case where, starting from the Bethe-Salpeter equation and multiparticle states, a potential can be constructed in a nonperturbative fashion. Application of the method to the ρ-meson bootstrap problem does not lead to any self-consistent solution. L. A. P. Balazs (now visiting the Tata Institute of Fundamental Research, Bombay) discussed a generalization of the work by Charap and Fubini; the potential is constructed by requiring that it reproduce the relativistic amplitude at any energy. The energy is obtained by calculating the absorptive parts in the crossed-channel reactions for increasingly larger values of the momentum transfer by iterations with the strip approximation to the Mandelstam representation. Starting from a nonlocal potential corresponding to a repulsive interaction, A. N. Mitra (Delhi University, Delhi) explained how a detailed examination of the phase shifts, with the potential in a Schrödinger-type equation, can lead to an understanding of some of the pion resonances. K. Dietz (CERN) presented a model for peripheral interactions below 10 Gev in which the K-matrix elements for quasi-two-particle reactions are replaced by the corresponding Born terms. The remaining K-matrix elements for higher particle final states are assumed to have a statistical distribution with zero mean value.

J. Lukierski (University of Wroclaw, Poland) considered the renormalizability of theories of particles with spin greater than or equal to one (which, with a single exception, are traditionally considered to be unrenormalizable). Conditional projection operators can restrict the number of components of a tensor field, constructed for a given spin theory, to the maximal spin subspace only if the subsidiary components obey free-field equations. However, with the unconditional projection operator (in which the subsidiary components do not obey the free-field equations), one has to add a set of massless fields whose metric must be negative in order to obtain a covariant propagator. This also leads at the same time to less stringent renormalizability conditions. Illustrating this for the neutral vector meson fields, Lukierski showed how the usual requirement of current conservation need not be invoked to demonstrate the renormalizability of the theory. The possibility of renormalizing theories, previously considered unrenormalizable by use of Caianiello's