COAGULATION OF COLLOIDS

By PROF. ERIC K. RIDEAL, M.B.E., F.R.S.

IN his presidential address delivered to the Chemistry Section of the Indian Science Congress last January, Prof. S. S. Joshi, of the Benares Hindu University, discussed *inter alia* various aspects of the kinetics of colloid systems.

In dealing with molecular reactions in solution, three methods of attack have yielded interesting and important results; one based upon gas kinetic concepts, the second on the Einstein diffusion equations and, finally, the transition state method of approach. In reactions between colloid particles or macromolecules, the second method of approach is generally employed and we are indebted to Smoluchowski for formulating the general principles.

The rates of coagulation are arbitrarily divided into rapid and slow rates respectively, the latter being derived from the former by the introduction of a factor ξ giving the fraction of collisions which are 'successful'. Since the rate of coagulation falls as particle charge rises, the potential barrier due to the diffuse layer of ions around the particles (the zeta potential ζ) can be regarded in the light of a potential barrier to be overcome for successful collision; we would thus anticipate that an equation of the type

$$\log \xi = \frac{K\zeta}{RT} + C$$

should connect the collision factor ξ with the zeta potential ζ . This is true for certain cases. We have found it to hold for quartz covered with gliadin, but in many cases the rate of coagulation is independent of ζ over a considerable range. Wiegner, Tuorila and Müller have shown that Smoluchowski's equations can be applied with considerable success to the problem of coagulation of uncharged particles, and extended the work to anisodimensional particles and more particularly to polydisperse systems. In the latter case it was shown that if the system were in motion the larger particles would 'strain out' the smaller ones. We might anticipate that the walls of the containing vessel would serve as collectors to neutral colloid particles undergoing auto-coagulation if the suspension was kept agitated. Prof. Joshi cites many cases of the effect of the containing vessel on the coagulation rates of sols, and makes the important observation that it is not necessary that the wall should have a zeta potential opposite in sign to that of the colloid.

Prof. Joshi rightly directs attention to the fact that the kinetics of coagulation do not obey the simple theory. The work of Levine in Great Britain and of the Amsterdam school of investigators has shown that for charged particles a position of minimum potential energy can be found in which the particles are a finite distance apart. We might thus expect to find doublets present in solution, which would require a definite energy of activation before they underwent true coagulation or coalescence; here the coagulation-rate would be pseudo-unimolecular. Another difficulty, which was first emphasized by Haber, is that the particles on coalescence undergo the phenomenon of 'ageing', resulting in a change of size and consequently a change in the diffusion coefficient on which the kinetics of coagulation are dependent. This ageing process, which can be followed in many cases by means of X-rays or by the rate of liberation of absorbed emanation or dyes, is virtually

a process of recrystallization and proceeds most rapidly in heteropolar systems such as colloidal sodium chloride, and much more slowly in colloids such as the hydrous oxides or sulphides.

The most satisfactory method of determining the rate of coagulation of a colloidal solution is by direct observation with the aid of an ultra-microscope. This method is eminently suitable for colloidal systems in which the refractive index of the disperse phase is markedly different from that of the dispersion medium; but where the light scattering is poor, as is the case for the proteins or hydrous oxides, many observational errors are apt to creep in. Many observers have consequently employed more indirect methods, especially the viscosity. The Benares school has made much use of refractivity measurements for this purpose.

The utilization of viscosity measurements for following the rate of coagulation may be seriously called in question. To a first approximation the viscosity of a sol, if the electroviscous effect be eliminated by the addition of an electrolyte, should, in accordance with Einstein's equation, be independent of the dispersity of the disperse phase, and only depend on its total volume. Prof. Joshi states that the viscosities of a number of dilute emulsions likewise obey the Einstein equation. This can scarcely be the case if the disperse phase has a measurable viscosity *per se*. Prof. G. I. Taylor, some years ago, evaluated the viscosity of a dilute emulsion in terms of the volume fractions and specific viscosities of the two phases, but so far as I am aware, this equation has not been subjected to any detailed experimental verification. Changes in viscosity do, however, occur in coagulation of colloidal systems, partly because the specific volume of the disperse phase changes due to dehydration, partly because a shape factor begins to emerge as the particles grow and, in some cases at least, as investigations on solutions of polymers have revealed, the larger particles may be deformable under shear and thus raise the viscosity.

It is evident that many factors enter into the problem of the kinetics of coagulation and their determination, and we are indebted to Prof. Joshi and his school at Benares for much painstaking and detailed work in this difficult experimental field. It is satisfactory to note that real progress is being made in that the factors operative are being isolated and identified.

ANGLO-PORTUGUESE SCIENTIFIC RELATIONS

By SIR GEORGE THOMSON, F.R.S.

IN view of the renewed intimacy which recent events have infused into the centuries-old association of Portugal and Great Britain, and of the prospect of increased co-operation between the two countries, there is a special significance in the publication of a study in Portuguese by Prof. H. Amorim Ferreira on Anglo-Portuguese scientific relations*. The history of science is often treated as if it were a matter of a few great names, and one is apt not to realize the importance of the part played by those whose fame was greater in their life-time than in after ages. In particular, problems of the

* *Relações científicas entre Portugal e a Grã-Bretanha*. Por H. Amorim Ferreira. Pp. viii+76. (Lisbon: Academia das Ciências de Lisboa, 1943.)

transmission of ideas are often a matter of exploring the movements of the less well-known workers. This is a difficult and laborious task, but essential for an understanding of the spread of scientific knowledge and the birth of ideas by the cross-fertilization of two strains of thought. Prof. Ferreira has made a most successful and detailed essay on these lines, and one may hope that this book will inspire others to similar tasks.

Without question, the greatest contribution of Portugal to science was the long series of voyages of exploration brought about by the enthusiasm and drive of Prince Henry the Navigator, who was himself a most successful example of collaboration between the two countries, for his mother was an English princess. His work broke down the scientific lethargy of the Middle Ages by making it clear that the known, even on this earth, is only a fraction of the knowable, which after all is the first condition for a vigorous school of science. But, even leaving his work aside, the relations between the countries have been extensive and varied.

Early in the list in chronological order we meet a series of Portuguese physicians who went to England in the sixteenth and seventeenth centuries, taking with them the benefits of Moorish medical science. Some of them held positions of great importance at the court and elsewhere and their experiences were sometimes more exciting than pleasant. For example, Rodrigo Lopez, who came to England in 1559, had dealings with Leicester and Essex, became chief physician to the Queen, and helped to influence her to the expedition of 1589. The failure of this and the ill-will of Essex led to his being unjustly accused of an attempt to poison the Queen in the interests of Philip of Spain. He was imprisoned, tortured and finally executed, a cruel reward for excellent work among the poor in the wards of St. Bartholomew's Hospital.

Lopez was a Jew, as were many of the Portuguese in England at this time; and later, even well into the latter half of the eighteenth century, their position in Portugal was insecure. Religious and other persecution has played a great part in the spread of scientific knowledge at many periods of the world's history, and our age has had ample experience of this example of good coming from evil. The movement between England and Portugal was not all in one direction, for a number of English Jesuits, mostly mathematicians, went to Portugal in the seventeenth century and promoted the study of their subject in that country.

The Portuguese physicians introduced the use of Peruvian bark to England, and developed a preparation of it long known as "English Water". One of the greatest of them, Castro Sarmento (1691-1762), improved this and broke with the secrecy common at the time by publishing his method of preparing it. It is interesting to note that through him the observations of the Jesuit astronomers at Pekin were transmitted to the Royal Society, an early example of inter-continental scientific relations.

During the latter two thirds of the eighteenth century the relations between Portugal and the Royal Society were very close. A great many papers of Portuguese origin were published in the *Transactions*, and a surprisingly large number of Portuguese were elected fellows, some resident in England but others not. Among the former one of the most remarkable was Bento de Moura, a man of great mechanical genius who improved Savery's steam engine in a

way which earned the praise of John Smeaton. He afterwards returned to Portugal and entered the Government service, but fell foul of the then all-powerful Marquis de Pombal, and was imprisoned for five years in a fortress, where he died in 1766. Several of the correspondents of the Royal Society at this period were priests, among them Father da Serva, who helped to found the Academia Real das Ciências at Lisbon.

Towards the end of the eighteenth century, a number of students were sent from Portugal to England and Scotland to study medicine, a reversal of the tide in the previous century. Rather surprisingly, their director of studies at the Embassy was shocked at the expensive tastes of the Edinburgh students of the period.

In the nineteenth century a number of British scientific men did important work on the natural history of Portugal, and one, David Sharpe, is regarded there as the founder of Portuguese palaeontology. In one case at least they received magnificent recognition, Alfred Tait being made Baron de Soutelinho for his work on phylloxera.

The contacts between Britain and the Portuguese islands have for long been especially close, and besides visiting scientific men, a number of British residents in Madeira have made valuable contributions to the natural history of the island. In another field of activity it is interesting to read that the artificial harbour of Ponta Delgrada was designed by Sir John Rennie.

The present book, which is dedicated jointly to the Academia das Ciências and the Royal Society, belongs to a series of scientific and historical works sponsored by the Academy.

PATULIN

IN a recent article¹ we referred to the remarkable bacteriostatic properties of the fungal products which have been called 'penicillin' and 'helvolic acid'. Penicillin has recently been discussed at a meeting of the Royal Society of Medicine, which is reported in the *British Medical Journal*² and in the *Lancet*³. The *British Medical Journal* devotes an annotation to it entitled "Penicillin in Tunisia". Readers who wish to know the results of trials of penicillin in North Africa and the Middle East, and also the results of other clinical trials, should consult these two articles. Helvolic acid, isolated from *Aspergillus fumigatus*, var. *Helvolar*, is the subject of an annotation in the *Lancet*⁴. It is distinct from 'fumigacin', which was isolated from *Aspergillus fumigatus* by S. A. Waksman, E. S. Horning and E. L. Spencer⁵. To these must now be added 'patulin', isolated from *Penicillium patulum*. The chemical properties and use of this for the treatment of the common cold are described in the *Lancet*⁶.

In Part I of this article Prof. H. Raistrick explains that for some years he and his colleagues have been studying, at the London School of Hygiene and Tropical Medicine, the metabolic products of the lower fungi. A large number of these metabolic products have been isolated in a pure form, the chemical constitution of some of them has been determined and some of them have been synthesized. Prof. Raistrick and his co-workers have studied the anti-bacterial properties of some of these substances and give references in this article to their work. Patulin is one of these. Its chemical name is anhydro-