should protect in the same way ; but there are no convincing experiments to this effect.

Marrow transfusion experiments do, however, show that the marrow can take up cells from the blood stream rapidly and in large numbers. In such cases there is, furthermore, rapid regeneration of thymus and lymph glands. In all these instances the transfused cells function presumably as homografts, and if so it would follow that transfused marrow cells can colonize lymphoid tissues. In fact, if a small amount of marrow is shielded during severe irradiation, recovery of the animal and regeneration of its lymphoid tissues will usually follow.

Cellular Migration Streams in the Normal Animal

The trend of work in recent years has been to suggest that, through the blood, lymphocytes may stream in either direction between the lymphoid complex and the bone marrow, and also between different parts of the lymphoid complex. The thymus may exert some chemical influence on the other members of the lymphoid complex, or it may send continuous cellular reinforcements to them. The blood appears to be the great pathway for all these cellular migrations from one tissue to another.

ELECTRICAL DOUBLE LAYER IN COLLOID SCIENCE

NEARLY one hundred physical chemists, from academic and industrial laboratories, attended a one-day informal discussion sponsored by the Colloid and Biophysics Committee of the Faraday Society and held on September 16 in the Chemistry Department of the Royal College of Science, London, at the invitation of Prof. R. M. Barrer and his staff.

The practical significance of electrokinetic effects was reflected in the wide range of materials which had been studied by different speakers—for example, polyelectrolytes in solution, dispersions of inorganic oxides or synthetic resins, oil-in-water emulsions stabilized by monolayers of detergents or macromolecules, organic salts in non-aqueous solvents (relevant to the paint and petroleum industries), a concentrated inorganic sol, and membranes of ion-exchange resins (similar to those now coming into use for electrodialytic de-salting of brackish water).

Four of the electrokinetic effects were discussed, namely, electrophoresis, streaming currents, electro-viscosity and electro-osmosis ; but it is recognized that these are equivalent experimental means of studying the mechanical properties of the electrical double layers which are to be found at almost all interfaces, and which are largely responsible for such widely different practical effects as, for example, the stability of soap emulsions, stickiness of clay soils, and the dangerous electrostatic charges sometimes encountered when petroleum products are pumped through metal pipes. The discussion, however, was concerned with fundamental problems of the origin and structure of double layers and the quantitative theory of their effects. These are by no means new problems ; but as the chairman, Sir Eric Rideal, reminded the meeting, electrokinetic effects are among the easiest to detect and the most difficult to interpret.

Prof. J. Th. G. Overbeek and Dr. B. van Geelen (Utrecht) reported a comprehensive study of electrophoresis and electrical transport in solutions of polymethacrylic acid partially neutralized by sodium hydroxide and containing between 10^{-4} and 10^{-1} M sodium chloride. The mobility of the chloride ions is little affected by the presence of the poly-ions (from which, of course, they are repelled), but the mobility of the sodium counter-ions is low, particularly when the polymethacrylate ions are highly charged and the ionic strength is low ; indeed, the majority of the counter-ions are then carried along

with the poly-ions. The mobility of the poly-ions increases, as to be expected, with increasing charge, though less than linearly. Quantitative treatment of such effects in terms of current theories[1] of poly-electrolytes is only partially successful. Rather drastic refinements will have to be introduced into the theories. It was pointed out that in electrophoresis of polyelectrolytes the polymer coil is more nearly 'free-draining' than in sedimentation or diffusion because of the migration of the counter-ions through the coil.

Dr. P. J. Anderson (Atomic Energy Research Establishment, Harwell) surveyed recent studies[2] of dispersions of several inorganic oxides (for example, the dioxides of titanium, zirconium and thorium) in dilute inorganic electrolytes. The electrophoretic velocities of the particles were translated into ζ-potentials and electrokinetic charge densities (σ) by use of the standard Gouy–Chapman theory and its modern refinements for electrophoresis (Henry, Overbeek). The values of σ, regarded as due to adsorption of ions from solution on to an inert surface, provide an adsorption isotherm which is generally of the Langmuir form, and the constant of the isotherm is a measure of the adsorbability of the ions. The usual effects of ion valence are found with the oxides, provided allowance is made for specific (chemical) effects of lattice ions, and the order of adsorbability in a series of ions of given valence can often be correlated with their polarizabilities, etc. An outstanding problem is why saturation of adsorption, calculated from the isotherms, would correspond to only about 1 ion per 1000 A.^{2} of surface, or 1 per cent of the surface available. If the adsorption model is a valid interpretation of electrokinetic data for such surfaces, the results suggest that adsorption occurs only on special sites—perhaps point defects or dislocations.

Dr. D. A. Haydon (Imperial College of Science and Technology, London) discussed the results of a critical investigation of the interface between petroleum ether and solutions of sodium dodecyl sulphate and dodecyl trimethylammonium bromide in water, with and without excess sodium chloride. The surface charge densities (σ) of adsorbed detergent were determined from measurements of interfacial tension by application of the Gibbs equation (in its appropriate forms). From these results a surface potential (ψ_r) was calculated, assuming a Gouy-type diffuse double layer of counter-ions, but with allow-

ance for the size of the ions. Stern adsorption, on the available independent evidence, was considered unlikely in this system. The ψ_r-potentials so obtained were in reasonable agreement with phase-boundary potentials determined directly by a vibrating-plate electrometer, though the latter were slightly lower with substrate concentrations above $0 \cdot 01\ M$, suggesting that a small proportion of the counter-ions penetrates between the detergent ions. A striking difference, however, was found between the ψ_r-potentials and the ζ-potentials determined by microphoresis ; ζ was always less than ψ_r, often less than $\frac{1}{2}\psi_r$. Furthermore, changes of ζ and ψ_r did not necessarily follow one another in sign ; in the presence of excess sodium chloride ζ passed through a maximum with increasing concentration of anionic detergent, whereas ψ_r showed no maximum, nor was a maximum exhibited by the cationic detergent. These results seem to point to the conclusion that only a fraction of the diffuse double layer is sheared off in electrokinetics, the 'plane of shear' depending on ψ_r and on charge density, which perhaps cause some modification of the properties of water in the vicinity of the fixed monolayer. In discussion, Prof. Overbeek mentioned calculations which suggest that water might be immobilized in that part of the double layer where the field strength is greater than about 500,000 V. cm.$^{-1}$.

These ideas were supported by Dr. J. A. Kitchener and Dr. J. H. Schenkel (Imperial College of Science and Technology, London), who had made electrophoretic measurements in the course of studying the stability of a model suspension consisting of 10-μ spheres of surface-sulphonated polydivinyl benzene resin. The surface charge density of ionizing —SO$_3$H groups, determined by ion-exchange, was of the order of 10^5 e.s.u. cm.$^{-2}$, but σ calculated from the mobilities was only around 2×10^3 and, surprisingly, increased with addition of indifferent electrolyte. Since adsorption of co-ions on this highly ionogenic surface seems most unlikely, the results suggest a variable plane of shear in electrophoresis, an idea which was supported by the observation that ζ was reduced by addition of a non-ionic polymer. However, the system is complicated by the polyelectrolyte character of the surfaces, and Dr. D. C. Henry (Manchester) mentioned that in recent measurements of the surface conductivity of a similar material he had obtained much higher values than any previously reported for this quantity and suggested that a correction for the influence of surface conductivity might remove some of the anomalies.

Dr. H. W. Douglas (Liverpool) reported an investigation of the electrophoresis of a synthetic polycarboxylic acid having a hydrocarbon–ester backbone and an equivalent weight of about 250. This polyelectrolyte was studied in free solution in a Tiselius apparatus and also adsorbed on oil droplets (by the microscopic method). The mobility increased with pH from 2 to 6 and remained constant from 6 to 9 ; it decreased with increase of ionic strength. It was remarkable that the mobilities of the poly-ions were very similar to those of the coated droplets. (Prof. Overbeek confirmed this also for polymethacrylic acid.) The surface charge density at high pH was estimated to be around 50,000 e.s.u. cm.$^{-2}$, which was five to ten times that found by electrophoresis. Again a strong retention of counter-ions near the poly-ion is indicated. Furthermore, σ calculated from electrophoresis was found to increase with

increasing concentration of sodium chloride at, for example, pH 9.

A paper by Prof. A. J. Rutgers (with Drs. M. de Smet and W. Rigole, of the University of Ghent) on streaming currents with non-aqueous solutions provided a glimpse of a different aspect of electrokinetics[3]. Prof. Rutgers described new results for solutions of tetra-iso-pentile ammonium-picrate in benzene (0–1,000 μmole/l.) streaming through long capillaries of various widths, wide capillaries of various lengths, a cylindrical slit or a system of closely fitting glass rings. Under some conditions, turbulence occurred with a consequent non-linear increase of the streaming current with increase of pressure. The currents were very small (10^{-13}– 10^{-11} amp.) and special precautions were taken to collect them without loss. High ζ-values (for example, -280 mV.) were obtained with dilute solutions provided the capillaries were wide enough to exceed the thickness of the double layer, and long enough to exceed the value $V\tau$, where τ is the time of relaxation of the solution and V the mean velocity. A quantitative treatment of the effect of length and width of the tube has been developed, with allowance for the current carried by conduction and convection and by the glass itself. As predicted from the equations, a potential of several volts can be detected with dilute solutions flowing through a glass capillary.

Dr. R. H. Ottewill (Cambridge) reported work on the electro-viscous effect which he had carried out with Prof. Overbeek at Utrecht[4]. The effect is the apparent enhancement of viscosity observed in colloidal solutions or suspensions owing to the presence of electrical double layers around the particles. (With solutions of polyelectrolytes another factor, the expansion of the macromolecules, is sometimes also included under the term 'electroviscous effect'.) The system studied was a concentrated sol of silver iodide. The volume concentration and total electrolyte concentration were varied, and the apparent viscosity determined in a capillary viscometer at mean shear rates ranging from 200 to 2,000 sec.$^{-1}$. At high concentrations of electrolyte the viscosity was practically Newtonian and could be accounted for by purely hydrodynamic interaction between the suspended particles. In dilute solutions of electrolyte a strong electroviscous contribution enhanced the viscosity. Furthermore, the viscosity decreased with increasing rate of shear. The effects can be understood in terms of interaction between the diffuse double layers of neighbouring particles : at high rates of flow the counter-ion cloud becomes elongated and therefore interacts less with that of particles in adjoining flow lines.

The final two papers were concerned with a very different system, namely, membranes of ion-exchange resin. Electro-osmosis in such resins was first proved by the observation that their electrical conductivity is significantly higher than can be accounted for by the intrinsic mobility of the mobile ions ('internal counter-ions'), as determined by measurements of self-diffusion. It is clearly demonstrated by the fact that the passage of an electrical current through the material transports water in the direction of movement of the counter-ions. The system differs from the capillaries and porous plugs of classical electro-osmosis in that the solid wall is here replaced by a cross-linked polymer network and the inter-chain distance is not much greater than the mean distance

of spread of the counter-ions from the chains. Despite superficial differences, therefore, this system has certain similarities to the polyelectrolytes considered in earlier papers in the discussion.

Drs. D. Mackay and P. Meares (Aberdeen) reported systematic studies[5] of electrical conductivity and electro-osmotic water transport through a highly swollen membrane of a phenolsulphonic acid resin in sodium form and in equilibrium with sodium chloride solutions of $0.01-1 M$ sodium chloride at 15°, 25° and 35° C., and also with mixed sodium and hydrogen forms of resins at two concentrations of electrolyte. These results were interpreted in conjunction with those previously obtained for the self-diffusion of sodium and chloride ions through the same resins. It appears that the conductivity of the sodium form of the resin in contact with very dilute solutions is simply equal to the sum of the ionic mobilities and electro-osmotic velocity ; but at higher concentrations the conductivity is lower than that calculated in this way. It was suggested that this might be due to decreasing electro-osmotic velocity and particularly to its effect on the mobility of co-ions, which apparently have a different migration mechanism from the counter-ions. The velocity of electro-osmotic streaming of solution through the membrane was found to be proportional to the potential gradient.

In contrast to this result, Drs. G. J. Hills, P. W. M. Jacobs and N. Lakshminarayanaiah (Imperial College of Science and Technology, London) reported that they had repeatedly observed that the volume of solution electro-osmotically transported per faraday increased with decreasing current density in the range below 20 m.amp. cm.$^{-2}$: the effect seemed to be well outside the experimental errors. However, at higher current densities the anomaly disappeared. Measurements on membranes of polymethacrylic acid and

phenolsulphonic acid in equilibrium with dilute aqueous solutions of the chlorides of lithium, sodium, potassium, rubidium and cæsium were reported. Water-transport was a little greater with lithium than with cæsium, but considerably greater in the phenolsulphonic acid membrane than in the polymethacrylic acid (for example, 28 moles of water per mole of sodium ion in the former, compared with 11 in the latter). Part of this water might be carried in a solvation sheath and the remainder by 'electro-convection', that is, by flow of the internal solution. However, attempts to separate the two by calculating a mean electro-convective velocity from a combination of electrical conductivity and self-diffusion coefficients, using the Nernst–Einstein equation, have not been encouraging. The difficulty probably arises from the non-uniform composition of the mobile medium inside the internal diffuse double layer. In this system, therefore, as in electrophoresis, a more precise model of the double layer seems to be called for if a quantitative treatment of the electrokinetic effects in terms of structure is to be achieved.

Dr. Hills emphasized in a discussion with Prof. Rutgers that he did not think that a classical electrokinetic approach to transport in ion-exchange membranes was appropriate.

J. A. KITCHENER
D. A. HAYDON

[1] Hermans, *J. Polymer Sci.*, **28**, 527 (1955). Overbeek and Stigter, *Rec. Trav. Chim.*, **75**, 543 (1956). Fujita, *ibid.*, **76**, 798 (1957). Longworth and Hermans, *J. Polymer Sci.*, **26**, 47 (1957). van Geelen, Ph.D. thesis (Utrecht, 1958).

[2] Anderson, *Proc. Second Int. Congr. Surface Activity*, 1957, **3**, 67 ; *Trans. Faraday Soc.*, **54**, 131, 562 (1958).

[3] cf. Rutgers *et al.*, *Trans. Faraday Soc.*, **48**, 635 (1952); **53**, 393 (1957).

[4] cf. Harmsen, van Schooten and Overbeek, *J. Colloid Sci.*, **8**, 64 (1953).

[5] cf. Meares, *J. Chim. Phys.*, **55**, 273 (1958).

THE YARD AND THE POUND (AVOIRDUPOIS) FOR SCIENCE AND TECHNOLOGY

THE directors of the following standards laboratories have discussed the existing differences between the values assigned to the yard and to the pound in different countries : Applied Physics Division, National Research Council, Ottawa, Canada ; Dominion Physical Laboratory, Lower Hutt, New Zealand ; National Bureau of Standards, Washington, United States ; National Physical Laboratory, Teddington, United Kingdom ; National Physical Research Laboratory, Pretoria, South Africa ; and National Standards Laboratory, Sydney, Australia. To secure identical values for each of these units in precise measurements for science and technology, it has been agreed to adopt an international yard and an international pound having the following definitions : the international yard equals 0·9144 metre ; the international pound equals 0·453 592 37 kgm.

It has also been agreed that, unless otherwise required, all non-metric calibrations carried out by the above laboratories for science and technology on and after July 1, 1959, will be made in terms of the international units as defined above or their multiples or submultiples.

The new international units conform with the recommendations of the Board of Trade Departmental Committee on Weights and Measures Legislation (the Hodgson Committee), but the Board of Trade points out that the units will have no statutory force and may not be used for trade purposes in the United Kingdom. The yard and pound units to be used in trade are the imperial units laid down in the Weights and Measures Act, 1878.

The values of the yard currently in use in the British Commonwealth and the United States of America are as follows, when expressed in terms of the metre : 1 imperial standard yard = 0·914 397 2 metre ; 1 Canadian yard = 0·9144 metre ; 1 yard as at present used by the National Physical Laboratory for science and technology, based on the 1922 value of the imperial standard yard = 0·914 398 41 metre ; 1 United States yard = 0·914 401 83 metre.

As the imperial standard yard is about 5 parts per million (0·0002 inch) less than the United States yard (which is defined in terms of the metre) and is shortening at the rate of more than one-millionth of an inch per annum, the consequent discrepancies in measurements of length are important in modern