the papers of Hirschfelder and collaborators on the subject.[26]

H_3.—The only use of H_3 energies was to determine the crossing points with the H_3^+ contour (Fig. 6). In view of the extreme difficulty in calculations involving three electrons and three centers, an empirical method was used. The London formula

$$E = q_1 + q_2 + q_3 \pm \frac{1}{\sqrt{2}}\sqrt{(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2}$$

was assumed to give the energies of the two H_3 surfaces of interest. This formula only takes into account interaction of pairs of atoms in the complex. The values of q (coulombic energy) and α (exchange energy) for a pair were obtained from the two lowest potential curves of H_2. It was assumed that

$$E(^1\Sigma_g) = q + \alpha$$
$$E(^3\Sigma_u) = q - \alpha$$

Energies obtained in this way agreed satisfactorily with those calculated by Hirschfelder, *et al.*,[26] by more complicated means.

Clearly much reliance cannot be placed on the quantitative features of Fig. 6. It can be pointed out, however, that due to the nature of the surfaces, the crossings must be approximately correct. The H_3^+ surface is near a minimum at the crossing point, while the H_3 surfaces are rising very steeply. Thus the interatomic distances indicated in Fig. 6 probably give the crossing points with rather good accuracy. The precise energy values, on the other hand, are much less well known.

(26) J. O. Hirschfelder, H. Eyring and N. Rosen, *J. Chem. Phys.* **4**, 130 (1936); J. O. Hirschfelder, H. Diamond and H. Eyring, *ibid.* **5**, 695 (1937); D. Stevenson and J. O. Hirschfelder, *ibid.*, **5**, 933 (1937); J. O. Hirschfelder, *ibid.*, **6**, 795 (1938).

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Summary

1. For purposes of this study, capture of an electron by a molecule or ion is treated as a non-adiabatic chemical process.

2. Necessary potential energy curves are given for application of this method to hydrogen systems. A contour surface is calculated for the isosceles H_3^+ system (plus an electron) and the intersections of that surface with the isosceles $H_2(^3\Sigma)$ + H and $H_2(^1\Sigma)$ + H surfaces have been calculated to a required degree of approximation.

3. It is shown that probability of non-radiative capture of an electron by a positive ion exceeds that of radiative capture by a factor of 10^6.

4. Capture of an electron by normal H_2^+ leads with maximum probability to one normal and one excited H atom.

5. Capture of an electron by normal H_3^+ considerably favors transition to the $H_2(^1\Sigma)$ + H state rather than to the $H_2(^3\Sigma)$ + H state because of a sensible activation energy difference between the two processes. No comparison is made with the probability of transition to the system H_2^* + H, although it is shown that transitions of this class are important for complicated-molecule systems. The transition to $H_2(^1\Sigma)$ + H leads to immediate dissociation into three H atoms.

6. Capture of an electron by an isolated complicated-molecule ion appears to lead in most cases to immediate dissociation into two particles, one of which is excited. Dissociation into radicals is favored over dissociation into molecules. In the liquid state the ultimate molecule mechanism increases in relative importance.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

An Experimental Technique for Micro-conductometric Analysis of Moving Boundary Systems

BY HARRY SVENSSON[1]

Introduction

In the electrophoretic analysis of a protein mixture by the Tiselius method[2,3] each peak in a pattern, except that due to the δ or ϵ effect, corresponds to a boundary in which the concentration of one of the proteins falls to zero with increasing height in the channel. Moreover, the area under this peak is taken as proportional to the concentration of the protein that thus "disappears" in the boundary. At each of the moving boundaries the theory[4,5] of ionic migration requires, however, the superposition, upon the concentration gradient of the disappearing ion, of gradients of all other ion species that are present. These superimposed gradients, which are comparatively small under the conditions of standard electrophoresis, not only introduce an error into the analysis but are also largely responsible for the conductivity changes at the

(1) Present address: Institutes of Physical Chemistry and Biochemistry, University of Uppsala, Uppsala, Sweden.

(2) Tiselius, *Nova Acta Reg. Soc. Sci. Upsal.*, IV, 7, No. 4 (1930).

(3) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(4) Svensson, *Arkiv. för Kemi, Mineralogi och Geologi*, **17A**, No. 14 (1943); **22A**, No. 10 (1946).

(5) Dole, THIS JOURNAL, **67**, 1119 (1945).

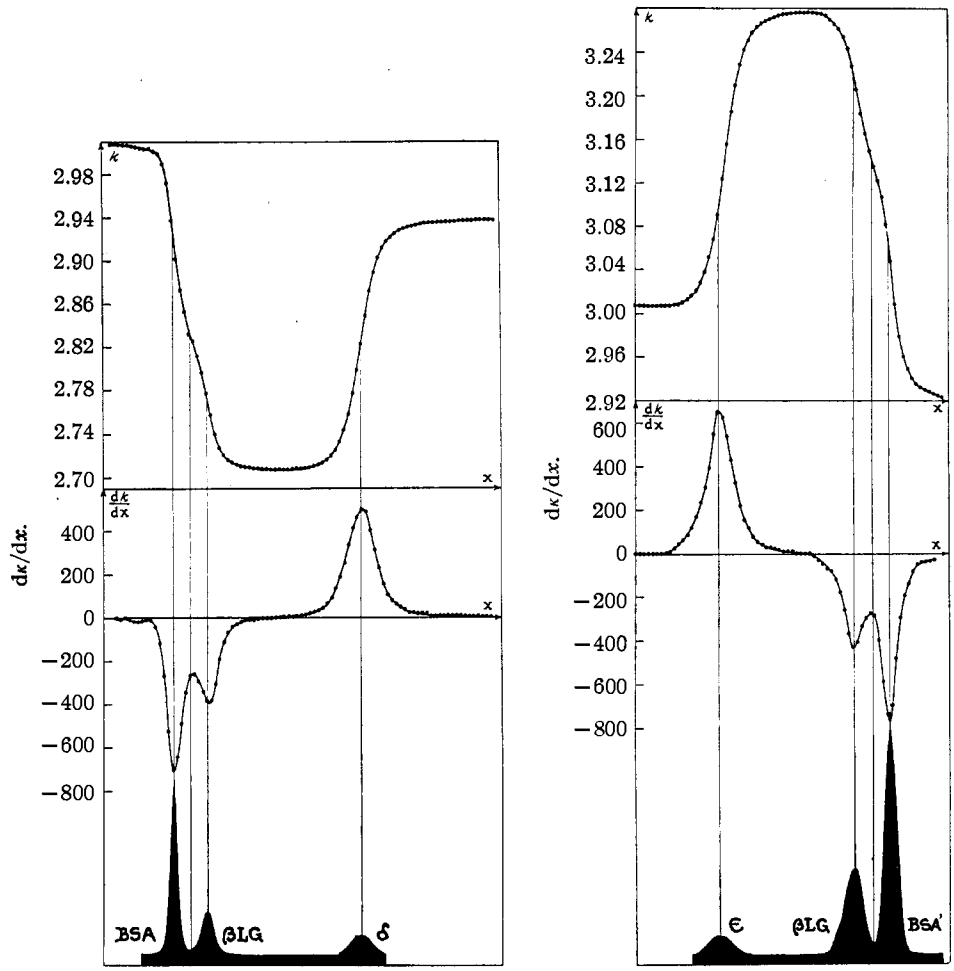

Fig. 1.—Comparison of conductometric and electrophoretic analyses of a mixture of bovine serum albumin and β-lactoglobulin in a 0.1 *N* sodium diethylbarbiturate buffer at *p*H 8.6 and a total protein concentration of 2.67%.

boundaries such as those shown by the upper curves of Fig. 1.

In Fig. 1 the shaded areas are the patterns of the ascending (left) and descending (right) boundaries that were obtained on electrophoresis of a mixture of bovine serum albumin, BSA, and β-lactoglobulin, β-LG. The outline of the shaded area is a plot of the refractive index gradient, dn/dx, in the channel as ordinate against the height, x, as abscissa. Plotted on the same abscissa in Fig. 1 are the conductivities, κ (upper curve) of the solutions at different heights in the channel and also the conductivity gradients, $d\kappa/dx$ (lower curve). The positions of the extrema in the gradient curves of both refractive index and conductivity are seen to be almost identical. As will be shown in a later report conductance data such as those of Fig. 1 may be used to make a partial correction for the errors in the electrophoretic analysis that are due to the superimposed gradients. The purpose of the present communication is to describe the experimental procedure for obtaining conductance curves such as those of Fig. 1.

Experimental

In principle the method consists in obtaining the boundary pattern in the usual manner in a Tiselius cell, after which the solutions in each channel are forced, at a uniform rate and with a minimum of mixing, through a microconductivity cell during which time resistance readings are taken at intervals. In contrast with the procedure followed by Lagercrantz[6] this permits the use of a conductivity cell having a favorable and well-defined constant.

An "exploded" view of the moving boundary and conductivity cell assembly is shown diagrammatically in Fig. 2. In this figure A, D and E are the conventional top, center and bottom sections of the Tiselius cell except that a capillary tube, F, is sealed to the bottom section. Although not shown in the figure this tube is connected to the syringe of the compensator and provides for the introduction of protein solution in forcing the boundary system through a conductivity cell. As is indicated at G, the "cut-off" plate, B, and the "take-off" plate, C, have slots cut in them to match the rectangular cross-section of the moving boundary channel. In the assembled cell movement of the cut-off plate either to the left or right isolates the channel contents from those of the top section and the electrode vessels connected thereto. The plate, C, remains in position throughout an experiment and is sufficiently thick to take the ground glass tips, *t*, of the conductivity cells, H. When in position the ends of these

(6) Lagercrantz, *Arkiv. för Kemi, Mineralogi och Geologi*, **19A**, no. 7, 1-21 (1944).

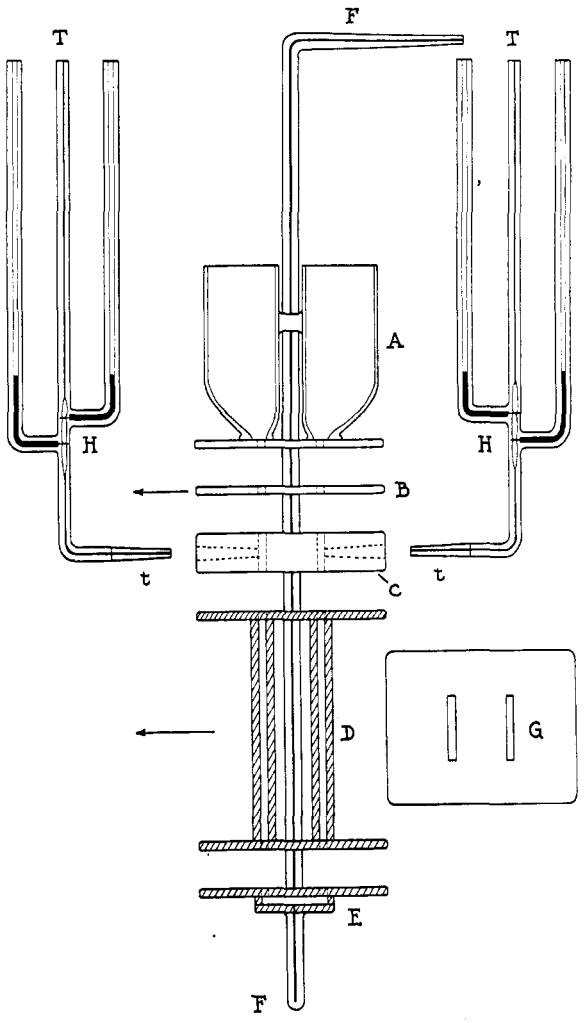

Fig. 2.—The Tiselius electrophoresis U-tube with additional parts for conductivity analysis.

tips are flush with the channel wall and thus provide a connection between this channel and a cell, H, that avoids pockets in which stagnant solution can collect.

The electrodes of each of the similar conductivity cells, H, consist of a platinum wire sealed through the wall of a short length of 2 mm. i.d. capillary tubing with the end anchored in the opposite wall. The filling tubes, T-t, are 0.5 mm. i.d. capillaries. Each cell has an effective volume of about 0.04 ml. and a constant of about 40 cm.$^{-1}$. In spite of the small electrode area sharp minima were obtained on the bridge described by Shedlovsky[7] without an excessively heavy deposit of platinum black on the electrodes.

In an experiment the cell is filled and the initial boundaries are formed in the usual manner, the additional precaution being taken that the conductivity cells are filled with buffer solution and closed at their upper ends with the aid of rubber tubes and pinch clamps. Moreover, after shifting the initial boundaries from behind the horizontal plates of the cell the compensator syringe of 20-ml. capacity is then filled with the protein solution and connected to the tube, F.

After passage of a sufficient quantity of electricity to give the desired separation of the boundaries the current is interrupted, schlieren scanning photographs taken, the cut-off plate shifted to isolate the channel, the pinch clamp of the right-hand conductivity cell, say, removed and the motor that drives the compensator syringe started. Since the temperature fluctuations of the electrophoresis thermostat were found to be too great for precise conductance measurements it was also necessary at this stage to introduce crushed ice into the bath. As the solutions from the channel flowed through the conductivity cell the resistance was followed continuously and its values at 1 minute intervals recorded.

The transport of solution was such as to give a complete record of one side of the channel in ninety minutes. After a constant value of the resistance, corresponding to the original protein solution, is reached in one conductivity cell the compensation is stopped, that cell is closed, the second cell opened, the compensation resumed and the same procedure followed with the contents of the other side of the channel. In most of the experiments the conductances of the original protein and buffer solutions were the same as those measured independently in a conventional cell but in a few cases discrepancies of as much as a few tenths of a per cent. occurred. This may be due to the fact that the cement used in the Tiselius cell appears to have a slight conductivity and it is thus difficult to avoid a high resistance leak to ground when the cell is connected to the conductivity cell.

Results and Discussion

In addition to the experiment represented by Fig. 1 others of a similar nature have been performed in which the ratio of the two proteins was held constant but the total concentration was varied from 0.3 to 3%. Qualitatively the results are similar to those of Fig. 1, the magnitude of the conductivity changes at the boundaries increasing regularly with increasing protein concentration, and this figure may thus be taken as typical.

As predicted by the theory[4,5] and observed experimentally by Longsworth and MacInnes[8] and Lagercrantz,[6] on passing downward through the system the conductivity decreases at a moving boundary and increases at a concentration or "stationary" one. The changes at each boundary appear more distinctly, however, if the conductivity curve is differentiated. The curves of $d\kappa/dx$ shown in Fig. 1 and below in Fig. 3 are simply a plot of the tabular differences in κ for each two-minute interval. The derivative curves are, therefore, objective and are not influenced by smoothing of the primary conductance data.

As the moving boundary theory predicts,[4,5] both the refractive index and the conductance are complicated functions of the equivalent concentrations and mobilities of all of the components of the system. The refractive index depends largely on the protein concentrations and to a minor degree on the buffer salt concentrations. The conductivity is determined chiefly by the salts and only slightly by the proteins. There is thus no reason why the two gradient curves should be identical. There is a similarity, however, in that both functions change at each boundary and their derivatives have extrema at these positions. In the figures the enlargement of the optical patterns has been selected to give coincidence, as

(7) Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

(8) Longsworth and MacInnes, *ibid.*, **62**, 705 (1940).

shown by the light vertical lines, between the two extreme peaks and the corresponding ones in the conductivity derivative. The coincidence between the intermediate maxima and minima which then results indicates that the conductivity record is a fairly correct representation of this property of the moving boundary system.

Also apparent in Fig. 1 is the greater overlapping of the peaks in the conductivity gradient curve than in the optical pattern. In the absence of a coupling between salt and protein diffusion one would expect the salts to diffuse more rapidly than the proteins and the conductivity derivative curve would thus be more blurred than that of the refractive index. Two more effects tend to increase this difference. Firstly, the conductivity analysis extends over a much longer period of time than the schlieren photography and thus there is a period of diffusion between the optical and conductivity records. Secondly, the transport of liquid from the channel to the conductivity cell involves a certain degree of mixing. It is not possible to say at the present time how much of the blurring is attributable to these three effects separately.

Another difference between the two gradient curves is seen in the relative magnitudes of the stationary, *i.e.*, δ and ϵ, boundaries. In the optical patterns the δ and ϵ peaks are unequal in size and contribute relatively little to the total pattern area. In the conductivity derivative diagrams the stationary boundaries are of essentially the same size in both limbs of the channel and their areas are comparable in magnitude to the total area of the moving boundaries.

As can be seen in Fig. 1, the relative proportions of the areas under the albumin and globulin peaks are different in the refractive index and conductivity derivatives. The faster component appears to be present in a greater proportion in the optical diagram than it does in the conductometric one. Knowing that an optical pattern always gives too high a proportion of the faster component, one may ask whether the conductometric analysis gives more correct results. This is not the case, however. An apparent composition derived from conductivity increments across the boundaries is also in error, and the conductivity data underlying Fig. 1 and similar experiments indicate that these errors go in the other direction. This is also to be expected from the moving boundary theory.

In order to study the usefulness of the method for more complicated systems, an experiment with normal human serum was performed with the results shown in Fig. 3. The characteristics already mentioned in connection with the two-protein system can also be observed here but the similarity between the two types of derivative curves is less pronounced. It is noteworthy that the sharp peak known as the β-anomaly in the descending limb does not appear in the conductivity curve. This is consistent with the view that the material responsible for this peak is of high molecular weight.

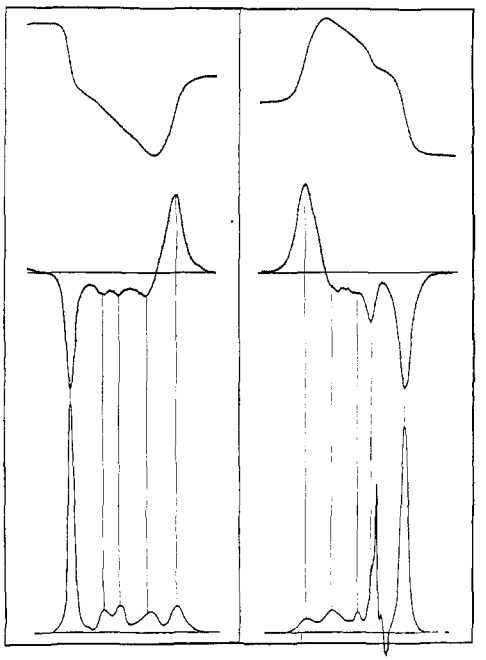

Fig. 3.—Comparison of conductometric and electrophoretic analyses of a normal human serum.

Since the conductivities of all of the solutions in the system are known it is also possible to compute, as was done by Lagercrantz, the correct mobility of the ion species that disappears in each of the moving boundaries. Moreover, the conductance data provide an additional set of equations for the system which, when combined with the boundary displacement and pattern area relations, should make possible a more precise electrophoretic analysis than in previous work. The evaluation of the available experimental material will be given in a forthcoming article.

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Summary

A method for making a complete record of the conductivity throughout moving boundary systems has been developed. It is based on the use of microconductivity cells outside the electrophoresis apparatus and on a careful transport of the boundary system from the apparatus into these cells. On differentiation of the conductivity diagrams, patterns are obtained which are very similar to the optical patterns but also show certain characteristic differences, which have been pointed out and briefly discussed.

UPPSALA, SWEDEN RECEIVED OCTOBER 28, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Sulfides. II. Preparation of Polyhexamethylene Sulfide in Emulsion[1]

BY C. S. MARVEL AND PAUL H. ALDRICH[2]

The present work on polyhexamethylene sulfide was undertaken to see if means could be found to produce polymers of higher molecular weight than those obtained in the earlier work in this Laboratory.[1] The first changes made in the techniques developed earlier were the use of highly purified cyclohexane as a solvent, use of larger samples to reduce chance of error in exact balance of reacting groups, and elimination of air and oxygen from the reaction flasks. These changes gave slightly higher molecular weight products as judged by intrinsic viscosity than had been regularly obtained before, but no major improvements were noted. It was found, however, that solutions of polymers of an intrinsic viscosity of 0.29 in benzene followed by precipitation with methanol to give fractionation of the polymer gave as much as 50% of the original polymer with an intrinsic viscosity of about 0.5. Such polymers melted very sharply, would cold-draw to give highly oriented fibers, and could be oxidized to higher melting polysulfones.

A more satisfactory method of polymerization was found in the use of the emulsion techniques. The potassium salt of a completely hydrogenated rosin acid[3] as an emulsifier with potassium persulfate as a catalyst gave rapid polymerizations with hexamethylene dimercaptan and biallyl to give good yields of polyhexamethylene sulfides with intrinsic viscosities of 0.34 to 0.44. All products prepared by this method would cold-draw if the intrinsic viscosity was above 0.36. In one run MP-189-EF[4] was used as emulsifier and some sodium hydroxide was added to increase the *p*H. Under these conditions the polyhexamethylene sulfide obtained had a low intrinsic viscosity and had a high sulfur content which indicates that oxidation of –SH group to –S–S– group has occurred with resulting loss of balance between reacting groups.

Since alkaline conditions favor oxidation of mercaptans to disulfides, further work on the polymerization in emulsion was carried out in MP-189-EF emulsions on the acid side. Runs were made using potassium persulfate as a catalyst and copper sulfate and sodium metabisulfite as activators as recommended by Bacon and Morgan for the reduction activation polymerization of acrylonitrile.[5] These polymerizations started rapidly and developed fast. The yield of polymer was high in a very short time, but the intrinsic viscosity of such polymer was always low. However, when the polymerization was allowed to proceed at 30° from one to four days, a few polymers with an intrinsic viscosity of 0.94 to 1.44 were obtained. However, the normal polymer prepared in this manner had an intrinsic viscosity of 0.45 to 0.65. The exact factors responsible for the formation of the high polymers in a few runs have not yet been determined.

The polymers with an intrinsic viscosity of 0.35 or more would yield fibers from a melt and the fibers could be cold-drawn. However, such fibers were very weak unless drawn from a polymer with an intrinsic viscosity of 0.45 or more. Figures 1 and 2 show the X-ray pattern of an unstretched and stretched fiber, respectively, prepared from polyhexamethylene sulfide, having an intrinsic viscosity of 1.44.[6] This high molecular weight polyalkylene sulfide had the same general structure as did the usual polymer made in solution by ultraviolet light activation as shown by a comparison of the infrared patterns of polymer made by each process (Fig. 3).[7]

Some experiments were carried out on the oxidation of polyhexamethylene sulfide in an attempt to prepare polyhexamethylene sulfone. Three oxidizing agents, perbenzoic acid, aqueous

(1) For the first communication on this subject see Marvel and Chambers, THIS JOURNAL, **70**, 993 (1948).

(2) Monsanto Fellow in Chemistry 1948–1949.

(3) We are indebted to Dr. John Hays of Hercules Powder Company for this material.

(4) MP-189-EF is an electrolyte-free emulsifier which consists essentially of mixed alkane sulfonic acids. We are indebted to Dr. Stanley Detrich of Jackson Laboratory, E. I. du Pont de Nemours and Company, for this material.

(5) Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); Morgan, *ibid.*, **42**, 169 (1946).

(6) We are indebted to Mr. R. S. Sprague and Professor G. L. Clark for these X-ray photographs.

(7) We are indebted to Miss E. M. Peterson for the infrared data reported here.