

## OBITUARY NOTICE.

HERBERT FREUNDLICH.

1880—1941.

THE death of Professor Herbert Freundlich at Minneapolis, Minnesota, on March 30th, 1941, after an illness (coronary thrombosis) lasting less than a day, deprived the world of science of its most distinguished investigator and expounder of colloid and interfacial phenomena, and a great host of friends in many lands of a man who had won their respect, esteem, and sincere affection.

Herbert Max Finlay Freundlich was born on January 28th, 1880, at Berlin-Charlottenburg, the eldest son of Friedrich Philipp Ernst Freundlich, manufacturer, and Ellen (Nellie), née Finlayson, the daughter of William Finlayson, of Scotland. His father was half-Jewish (his mother being a Jewess), but he was a member of the Christian Protestant Church when he married Miss Finlayson, and all their children were baptised and confirmed in the Protestant Church.

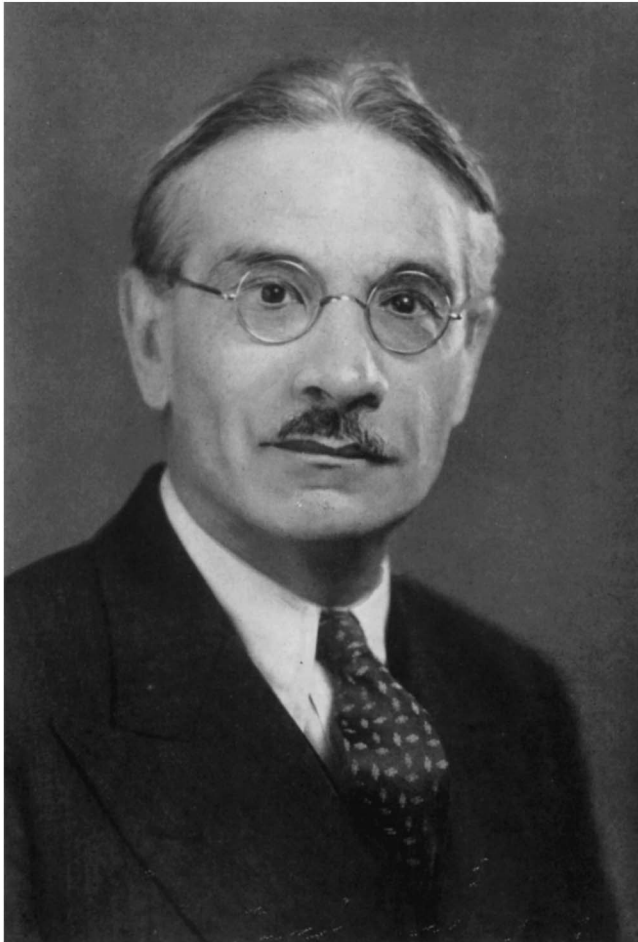
Soon after Herbert's birth, his father, who had been appointed director of an iron foundry at Biebrich-Wiesbaden, bought a house at Biebrich-on-the-Rhine and settled there with his family. So it was in the sunny, light-hearted, and artistic atmosphere of the beautiful Rhineland that Herbert and his brothers and sisters spent a happy childhood and youth.

From his earliest years Herbert Freundlich had a passion for music and musical composition, and for animal study (especially entomology). His brothers and sisters had few dull moments, for under Herbert's energetic leadership something new was always turning up. When they were not singing his songs they were tracking caterpillars under his enthusiastic guidance, or hunting for leaves to feed them with.

After a period of preliminary studies (1886—1892) at the preparatory school and the *Realprogymnasium* at Biebrich, Herbert Freundlich entered the classical side of the "humanistic" Gymnasium (higher secondary school) at Wiesbaden in 1892, successfully completing his studies there with the "certificate of maturity" in 1898. During this period he devoted himself particularly to the study of Greek and German, Greek literature remaining an inspiration which influenced his whole life. Science, however, was to claim the chief allegiance and the lifelong service of this young lover of music and fine literature, and in October, 1898, he entered the University of Munich, where he spent two semesters (one academic year) in preliminary science studies. Deciding on chemistry as his main subject of study and research and attracted, no doubt, by the fame of Wilhelm Ostwald and the rich summer tide of the "new" science of physical chemistry, he moved on to the University of Leipzig. Here he continued his scientific training, studying especially physical chemistry in Ostwald's new physico-chemical Institute in the Linné Strasse, and after four years obtained the Doctorate in February, 1903, with a Dissertation on the "Precipitation (Coagulation) of Colloid Solutions by Electrolytes." It is related that Freundlich was attracted to the study of colloid phenomena by his deep interest in biology, having the intuitive feeling that the investigation of this special branch of physico-chemical science might prove one of the best available approaches to a better understanding of the complex structure and activity of "living" protoplasm. However that may be, it is certainly true to say that throughout Freundlich's life he never lost sight of the intimate relations between colloid and biological science, and took delight on various occasions in drawing the attention of biologists to the current (and relevant) advances in the investigation of colloid systems. In his last years at the University of Minnesota (1938—41) he was devoting special attention to the linking of experimental research in colloid and biological science, as anyone may see who reads his last two (posthumously) printed papers, entitled "Colloid Chemistry of Development and Growth" (1940) and "Some Mechanical Properties of Sols and Gels and their Relation to Protoplasmic Structure" (1942). Although written with the author's customary scientific caution and critical moderation, the reader of these papers cannot fail to observe how well the intuition of the young investigator of 1901—1903 was borne out by the results achieved in colloid research nearly forty years later—results due in large measure to the work of himself and his collaborators. Thixotropic sols and gels, structural viscosity, reversible coagulates, geloids, tactoids, tactosols, intrinsic and morphic double refraction in streaming solutions containing oriented anisotropic and anisometric molecules and micelles—these were indeed phenomena of high importance for him who would try to unravel any part of the nature of protoplasmic structure; and Freundlich was able to point out how the newly discovered and very curious phenomena exhibited by aqueous solutions of the tobacco mosaic virus could be easily interpreted in terms of modern discoveries in colloid science. To the present writer it is a very solacing thought that before his death Freundlich was able to realise this partial though very striking consummation of his early hopes and intuitions.

During the next eight years, *i.e.*, in the period 1903—1911, Freundlich was an Assistant in the Leipzig physico-chemical Institute, holding this position in both the Sections for analytical and physical chemistry; whilst in the period 1904—1906, when Ostwald was having trouble with his opponents in the philosophical Faculty and was travelling abroad a good deal on lecture tours, he carried out the editorial work for the *Zeitschrift für physikalische Chemie*. In October, 1906, he obtained the *venia legendi*, *i.e.*, the status of a Privatdozent or University Lecturer (in both physical and inorganic chemistry) on the basis of a special Thesis (Habilitationsschrift) dealing with "Adsorption in Solutions."

He married in September, 1908, Marie Mann, the daughter of the apothecary Wilhelm Mann at Mainz.



*Photographic Laboratory, U. of Minn.*

HERBERT FREUNDLICH.

*[To face p. 646.*

She has been described as a lovely fair-haired Rheinländerin, and there is no doubt that Freundlich was deeply attached to her. She bore him two sons and two daughters, but died in 1917 at the birth of her fourth child. This and the death of his second son, from infantile paralysis, were heavy blows from which he never completely recovered.

Although he had relinquished the thought of adopting music as a profession, Freundlich continued the active study and practice of music during his school and university years, becoming a skilled pianist and composing songs, trios, and quartets. An oratorio composed by him was sung at Biebrich-Wiesbaden. Even in later years when he had almost entirely given up piano practice, he could still play Beethoven sonatas, though not from memory (London, 1935).

In 1911 he received a call to the Technische Hochschule at Braunschweig as Associate Professor of Physical Chemistry and Inorganic Technology. He accepted the invitation and went to Braunschweig in the autumn of that year.

During the period 1911—1916 a stream of important researches in colloid science issued from the Braunschweig Laboratory. Here we may note, in passing, the work on electric endosmose with Elissaffoff (1912), on swelling-pressure with Posnjak (1912), and the important work on optical phenomena in certain colloid solutions, *i.e.*, stream double refraction, dichroism, and "Schlierenbildung," with the physicist Professor H. Diesselhorst (1915—1916).\*

This period of active and fruitful research was interrupted by the war of 1914—18. Owing to general physical weakness Freundlich had not been required to undergo the usual period of military training and had been transferred in 1913 to the *Landsturm*. So he was not called up for active military service in 1914. Being well acquainted with the phenomena of adsorption, he had made, in the autumn of 1915, certain proposals concerning the best use of charcoal in anti-gas respirators. The result was that Professor Haber asked him to come to the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry at Berlin-Dahlem to assist in the working out of the best methods of protection against war gases. So Freundlich joined Haber in February, 1916, and did important work in connection with the production, filling, and testing of the materials used in the canisters of the anti-gas outfits. For this good war service he was decorated with a number of military crosses, including the "iron cross with white and black ribbon."

In January, 1919, Freundlich resigned the Braunschweig Professorship, having been invited to become chief of the Division of Colloid Chemistry and Applied Physical Chemistry in Haber's Institute and also an Associate Director of the Institute.

A new career of active research in his chosen field and in one of the most famous centres of research in physical chemistry was now opened to him, and of these great opportunities Freundlich made the fullest use. The work on colloid optics was continued and developed with a number of collaborators, amongst whom the chief was H. Zocher. The theory of the electrokinetic "zeta" potential as distinct from the thermodynamic "epsilon" potential was developed and elaborated ("potential" here means difference of electrical potential) in a number of important papers. The mechanical and rheological properties, such as viscosity and elasticity, of colloid systems were intensively investigated with a number of collaborators. This led to the great series of researches on the phenomenon of thixotropy, rediscovered by Szegvari and Miss Schalek in 1923, and the contrasted phenomenon of dilatancy, discovered many years previously by Osborne Reynolds in England. Special attention was paid to the remarkable optical phenomena due to the presence of non-spherical, *i.e.*, rod-like or plate-like, particles in colloid sols, and Freundlich was able to show how the investigation of such phenomena could lead to valuable conclusions concerning the shape of the particles. As mentioned previously, Freundlich's chief collaborator in this series of researches was H. Zocher, who acted as collaborator also in the beautiful work on the passivity of iron mirrors. Reference must also be made to the discovery of "mechanical" coagulation, and especially to the important researches (with K. Sollner) on the effects produced on gels (especially thixotropic gels) and biological systems by supersonic vibrations. During these years (1919—33) Freundlich created in the Dahlem Laboratory one of the world's chief centres of research in colloid science. In 1923 he was made honorary Professor of Chemistry in the University of Berlin, and the same honour was conferred on him by the Berlin Technische Hochschule in 1930. The University of Minnesota and the Colloid Committee of the National Research Council of the United States invited him in 1925 to be the distinguished guest scholar at the second National Colloid Symposium, held in Minneapolis. Freundlich accepted the invitation and remained in residence at the University during the ensuing summer term, giving a series of lectures on colloid chemistry and captivating his American colleagues and students by his modest and charming personality. On the invitation of the Chemical Society, he delivered the second Liversidge Lecture (London, 1930), the title being "Surface Forces and Chemical Equilibrium."

A dark and tragic shadow was soon to fall on this scene of high and successful endeavour. In the spring of 1933, soon after the rise of the National Socialist Party to power in Germany, Haber and Freundlich were ordered to dismiss all their associates who were not of "pure Aryan race." Rather than do this, they resigned their positions. As is well known, Haber, on the invitation of Sir William Pope, went to Cambridge University in the Autumn of 1933, whilst Freundlich, on the invitation of the writer of this Memoir, came to University College, London, as Honorary Research Associate. Funds were provided for a period of five years by the generosity and wise foresight of the Directors of Imperial Chemical Industries. It may be interesting to mention here that William Rintoul, of Imperial Chemical Industries, and the writer met Freundlich in Germany

\* The work with Posnjak and Elissaffoff (or some part of it) may have been carried out at Leipzig.

in May, 1933, and conveyed the invitation personally. Freundlich said he would like to bring with him his principal research assistant and collaborator, Dr. Karl Sollner, and this suggestion was readily accepted.

So it came about that in the same College where Thomas Graham had worked Herbert Freundlich came as an honoured and welcome guest to continue his researches. The work on the effects of supersonic vibrations was actively developed with the expert assistance of Dr. Sollner, whilst the researches on thixotropy were extended in many directions and led, for example, to the discovery (with Dr. F. Julius Burger) of the remarkable phenomenon of "rheopexy." It was found, namely, that the time required for the sol  $\rightarrow$  gel transformation of a thixotropic system could be enormously reduced by a gentle rolling or tapping motion of the containing test-tube. It was suggested that this remarkable "rheoplectic" effect might be due to an "orthokinetic" acceleration of the formation of the reversible coagulates (geloids), assisted perhaps by orientation due to the presence of highly anisometric particles.

The work on the behaviour of systems containing relatively coarse particles was further extended during the London period, as examples of which may be quoted the interesting papers on quicksand as a thixotropic system, the plasticity of powdered Solnhofen slate and the thixotropic behaviour of its suspensions (with F. Julius Burger), and the sedimentation volume, dilatancy, thixotropic and plastic properties of concentrated suspensions (with A. D. Jones). Reference may also be made to the investigation of the isoelectric point and swelling-pressure of isinglass (with P. S. Gordon), and the thixotropic behaviour of silica gels (with D. W. Gillings).

Although free from any regular courses of lectures, Freundlich gave a number of inspiring special lectures on colloid science to postgraduate workers in the laboratory, and was invited by various outside scientific and technical societies to give discourses on special topics. Everywhere his wide knowledge and learning, his lively and imaginative perception of the possibilities of explanation, application, and further research, and his lucid and cautiously critical exposition of scientific results were highly appreciated by his audiences, and were of the greatest value for the progress of colloid science in Great Britain.

In 1936 the University of Utrecht conferred on him the honorary degree of Doctor of Philosophy. An invitation to be the distinguished guest scholar at the fourteenth National Colloid Symposium, held at the University of Minnesota, came in 1937, and again Freundlich remained (as in 1925) at the University for a series of lectures in the following summer session.

These two successful visits to the United States were very fortunate, since efforts by his English friends to secure a permanent University position for Freundlich in London were, alas, unsuccessful. However, by this time he had many active friends and admirers in the University of Minnesota. The result was that in January, 1938, he was called to that University as Distinguished Service Professor of Colloid Chemistry in the graduate school, without College or Departmental assignment. During the short period that he held this unique position he was very successful in initiating and guiding the researches of advanced students from a variety of fields, such as physiological chemistry, biochemistry, and physical chemistry. How much his services as teacher, investigator, and wise counsellor were appreciated can be seen from the excellent obituary memoir by Professor Ross Aiken Gortner and Dr. Karl Sollner, published in the *American Journal Science* (vol. 93, pp. 414—416, 1941).

Freundlich was elected a Foreign Member of the Royal Society in 1939, and an Honorary Fellow of the Chemical Society in February, 1938.

In 1923 he married Hella Gellert, who came with him to London in 1933 and accompanied him to America in 1938. Of his two daughters by his first marriage, Kate now lives at Rochester, Minnesota, and Marie married a Dutchman and lives in Holland. His son, Herbert, a radio research physicist, resides at Cambridge, England. Two sisters of Freundlich live in Great Britain. One, Mrs. Elizabeth F. Wardale, has lived most of her life at St. Andrews. Another sister came with Freundlich to England in 1933 and now resides in this country. His brother, the famous astronomer E. Finlay-Freundlich, who was the first astronomer to give important and practical support to Einstein and his theories, is now Professor of Astronomy at the University of St. Andrews.

The results of the scientific researches of Freundlich and his collaborators are contained in more than 200 published papers. When in 1901 he began his first work on the coagulation of "hydrophobic" colloid sols by electrolytes, the results obtained by Linder and Picton, Schulze, and Hardy were known, especially the Schulze-Hardy rules concerning the opposite sign of the electric charge and the valency of the effective ions. Freundlich's work helped greatly in establishing and extending these results, and showed, for example, that the strikingly increased effectiveness of bi- and ter-valent metal ions in coagulating negatively charged sols could not be explained by increasing degrees of hydrolysis of the corresponding salts. It was also shown that many organic ions had a much greater coagulating effect than would be expected from their valency, a result which was also true in many cases for the hydrogen and hydroxyl ions.

His investigations on adsorption in solutions, for example, the adsorption of non-electrolytes and weak electrolytes by charcoal in aqueous and non-aqueous solutions, greatly advanced the knowledge of what was then a somewhat mysterious phenomenon. Although the work of Ostwald and others had established the existence of well-defined reversible equilibria in such cases, Freundlich's work showed the insufficiency of the earlier crude ideas relating to the formation of chemical compounds or solid solutions as explanations of such adsorption phenomena. In this his famous "adsorption-isotherm" played a notable part, and although this equation was of a purely empirical character, was not new, and did not explain the saturation effect, in Freundlich's hands it was of great value in correlating a great mass of experimental material, in giving precision to the

reversible equilibria, and in explaining the relatively great effect in the case of small concentrations of the adsorbed substance.

Freundlich was led to see in adsorption an exemplification of Gibbs' thermodynamic equation relating the excess "surface" amount (per unit interface) of a dissolved solute with the rate of decrease of the surface tension between two fluid phases with increase in bulk concentration of the "adsorbed" solute. Although a surface concentration of this type was shown later by other investigators to be in certain cases in approximate agreement with Gibbs' equation (in its approximate form), it was not possible for Freundlich to deal in this manner with adsorption phenomena where the adsorbent was a solid substance. As is now well known, the work of Haber and especially that of Langmuir has established in such cases a satisfactory theory on the basis of reversible kinetic equilibria and "residual" chemical valencies at the surface of the solid adsorbent.

Freundlich obtained valuable and fruitful results when he applied the concept of adsorption to the explanation of the coagulating effects of ions. The greater effect of organic ions (in comparison with their valency) could now be correlated with a greater "specific" adsorption of such ions. The "taking up" or co-precipitation of the effective ions by the coagulated flocks (a phenomenon already observed and stressed by Picton and Linder) was found to agree with the adsorption formula. Of great importance was Freundlich's explanation of the extraordinarily great and hitherto unexplainable influence of the valency of the effective ions. It was found that the adsorption curves for ions of different valency, for example, those of the "light" metals, were approximately coincident when the concentrations and the adsorbed amounts were reckoned in mols. Since, for coagulation, *equivalent* amounts of ions must be adsorbed (equal amounts of electricity for neutralisation of the electric charges of the colloid particles), the shape of the adsorption curves showed that the necessary concentrations of ions of different valency must lie as widely apart as experiment had shown to be the case.

The marked parallelism between the influence of electrolytes on coagulation and on electrokinetic phenomena (electric endosmose, cataphoresis) led Freundlich to undertake investigations of the latter. Although the physical theory of the "electrical double layer" had been established by Helmholtz, little was known about the effect of electrolytes thereon, and clear ideas were lacking concerning the relationship (or even identity) of the Helmholtzian (electrical) "potential jump" with the "thermodynamic" potential jump introduced by Nernst in his theory of galvanic cells. Freundlich came to the conclusion that the two types of potential difference were essentially different, the electrokinetic one, the "zeta potential", lying entirely in the liquid phase and being strongly influenced by adsorbed ions. In an experimental investigation with Rona he was able to establish this view by simultaneous measurements of the electrokinetic zeta potential and the thermodynamic "epsilon potential" (so-called Nernst potential) at the same interface. Freundlich's work in this field may indeed be regarded as one of his most important contributions to the science of colloid and interfacial phenomena.

In connection with the subject of adsorption, a brief reference may be made to several interesting investigations, for example, the effect of adsorption on the velocity of crystallisation (a subject also investigated by Marc and Ritzel); the effect of adsorption on certain chemical reactions and their kinetics (the effect of charcoal in accelerating the oxidation of phenylthiourea, of colloidal sulphur in accelerating the transformation of maleic into fumaric acid, and the effect of adsorption on charcoal in *reversing* the normal change of bromoethylamine into dimethylene-imino-bromohydrate); and the velocity of decrease of adsorption in the change of mercuric sulphide from the amorphous to a more crystalline form, and its analogy with the velocity of coagulation.

The work of Zsigmondy had demonstrated the influence of various hydrophilic colloids, such as albumen, gelatin, gum, etc., in protecting hydrophobic sols from coagulation by electrolytes in concentrations otherwise effective. Freundlich made the remarkable discovery that a number of these "protective" colloids when present in very small concentration could produce the opposite effect, that is to say, they could actually promote the coagulating effect of the electrolytes. This phenomenon he termed "sensitisation." It is probable that both the protecting and the sensitising action are related to adsorption and to the isoelectric points of the hydrophilic colloids.

It is well known that gels under suitable conditions can take up a liquid dispersion medium and swell, and that such a swelling can often produce very considerable pressures. This phenomenon had been investigated by Reinke in the case of discs cut from the leaves of *Laminaria*, but it was left to Freundlich to find that well-defined thermodynamically reversible equilibria occur in such cases. His careful quantitative work with Posnjak on the "swelling-pressure" of rubber in organic liquids and of gelatin in water showed that this pressure increased with a high power of the concentration of the gel, and could be thermodynamically related to the vapour pressure of the gel in the same manner as the osmotic pressure of a solution to its vapour pressure. Katz, who soon afterwards carried out an extensive investigation of the vapour pressure and heat of swelling of gels, was able to make considerable use of the relations established by Freundlich.

The chance observation that an "aged" sol of vanadium pentoxide on stirring showed curious effects—optical "streakiness" (Schlieren), "twinkling," and a marked dichroism and birefringence—led Freundlich to a famous series of researches and the creation of a practically new branch of "colloid optics." He was able to show that an enforced optical anisotropy, in the form of double refraction and dichroism, could be produced by laminar streaming in sols containing rod-like or plate-like particles. The streaming or laminar flow had the effect of producing a more or less parallel orientation of the elongated highly "anisometric" particles, the degree of orientation depending mainly on the range and intensity of their Brownian motion. Thus a

tube, with a rectangular cross section, full of a non-turbulent streaming liquid containing very small uniaxial crystals with their long axes parallel to the lines of flow will behave like a plate cut from a uniaxial crystal parallel to its optical axis. This type of stream double refraction, where it is due to the special crystalline structure of the particles, *i.e.*, to their intrinsic double refraction, was called by Freundlich "intrinsic stream double refraction." But there exists another equally important type of case where the colloid units are not themselves doubly refracting, being either amorphous or belonging to the regular crystal system. In this case double refraction can occur if the anisometric particles undergo sufficient parallel orientation and possess a refractive index different from that of the dispersion medium. In the special case of rod-shaped particles the double refraction can then be calculated according to an equation given by O. Wiener. Freundlich termed this second type of case "morphic stream double refraction." There may exist also morphic dichroism, and cases exist where both intrinsic and morphic optical anisotropy occur.

In connection with Freundlich's work on this subject in the field of anisotropic and anisometric particles in colloid sols, it will be remembered that Clerk Maxwell in 1868 investigated the production of "artificial" double refraction by shearing motion in Canada balsam, and that subsequently Kundt (1881), Umlauf (1892), Almy (1897), De Metz (1888—1903) and Hill (1899—1901) published interesting researches on this subject, using a great variety of liquids and producing rotational shear (velocity-gradient) by the relative rotational motion of two concentric cylinders. Almy obtained very curious results in the case of gelatin solutions. The formal mathematical theory based on the strains produced by the shearing stresses and the time of relaxation was dealt with by Maxwell and subsequently by Natanson (1901—1904). The great merit of the work of Freundlich and his collaborators (Diesselhorst, Zocher, Dannenberg) was to demonstrate in the case of certain sols the relation between the "stream" optical anisotropy and the shape (and sometimes the intrinsic optical anisotropy) of the colloid particles in the sols. This work certainly constitutes another of the major contributions of Freundlich to colloid science.

Beginning with a paper published with Seifriz in 1923 on the elasticity of sols and gels, and another with Miss Schalek (in the same year) on the viscosity and elasticity of colloid solutions, Freundlich became deeply interested in the "mechanical," or, as one might now say, the "rheological" properties of colloid systems. The investigations of various cases of anomalous or "structural" viscosity, where the Newtonian viscosity coefficient is no longer constant but decreases with increase of the rate of shear (velocity-gradient), and its time relations (recovery after a period of rest following the motion), prepared him for a famous series of researches on thixotropy, dilatancy, and plasticity. The phenomenon of thixotropy (a name coined for it by Freundlich) is strikingly shown by a concentrated ferric oxide sol to which a certain amount of electrolyte has been added. The sol sets to a gel or stiff paste which cannot be poured out of the test tube. On vigorous shaking, however, the gel becomes a fairly mobile liquid which can be easily poured, but after a period of rest reverts to the gel state. This reversible isothermal sol  $\rightleftharpoons$  gel transformation is a striking (and perhaps rather extreme) example of the general phenomenon of thixotropy. A good account of work on this subject as it stood in 1935 may be found in Freundlich's little monograph on Thixotropy (No. 267 of the *Actualités Scientifiques et Industrielles*, published by Hermann, Paris). The following quotation taken from his last published paper (1942) gives a good summarised account of his latest views.

"It has been found that there may exist a number of intermediate stages between the normal liquid state and the state of a crystalline solid. These are frequently observed in colloidal systems, particularly if they contain a sufficiently high amount of disperse phase. Consequently, concentrated colloidal solutions may differ essentially in their mechanical properties (viscosity, elasticity, etc.) from normal, so-called Newtonian liquids. These differences may be manifold. Two limiting cases are of outstanding importance; the first is that of thixotropy. Whereas the viscosity of a Newtonian liquid is not changed by mechanical means, such as flowing or stirring, a thixotropic system becomes less viscous while flowing or when being stirred. This phenomenon is particularly obvious if we have a thixotropic gel: it is liquefied by shaking and sets again to a gel when at rest. We thus have an isothermal, reversible, sol-gel transformation.

"We are dealing with a thixotropic change, too, if the viscosity of a concentrated sol can be reduced by shaking or stirring and if it increases again when at rest. The viscosity of such a sol differs in other respects from that of a Newtonian liquid. It is anomalous, *i.e.*, it does not obey Poiseuille's law for laminar flow; the amount of liquid passing through a capillary in a given time depends on the applied pressure in a different way. Speaking more specifically, the viscous resistance is not directly proportional to the velocity gradient of the laminar flow, as in Newtonian liquids. The characteristic behaviour of anomalously viscous, thixotropic sols and likewise of thixotropic gels is correlated with the existence of a yield value. This can be demonstrated in a graphic way by using a viscometer, in which a ball is pulled through the viscous system in question by a weight which can be increased at will; for different weights the speed of the moving ball is compared. In a Newtonian liquid the speed is proportional to the weight applied. In a thixotropic sol or gel we have a yield value. The weight must exceed a certain minimum to cause the ball to move; only with higher weights does its speed change in a way similar to that observed in a normal liquid. . . .

"Systems showing anomalous viscosity also exhibit a characteristic behaviour with respect to their electrical conductivity. The electrical conductivity of an aqueous solution is markedly influenced by its Newtonian viscosity; as a rule, it is, in a first approximation, inversely proportional to the viscosity. For instance, the electrical conductivity of an aqueous salt solution having a fairly high viscosity, owing to the

presence of a suitable concentration of glycerol, is lower than that of a solution of the same salt concentration in pure water. The anomalous viscosity of a thixotropic sol or gel, on the other hand, leaves the electrical conductivity practically unchanged. The electrical conductivity of a salt solution remains the same, although it may contain so much gelatin that its apparent viscosity is about equal to that of the solution containing glycerol. It is well known that even gels of gelatin (containing electrolytes) or of soaps do not differ in their electrical conductivity from the sols from which they were produced. Presumably the movement of the ions is not influenced by the structure of thixotropic sols and gels, which is very coarse compared to the small size of the ions.

“ Finally, not only gels but also sols of this type (gelatin, soaps, etc.) show elastic properties. Small solid particles suspended in such a sol may be moved by an external force but return to their original position when the force stops acting, a phenomenon not observed in Newtonian liquids. This elasticity in sols is not found so regularly as the other characteristic properties just mentioned. The presence of distinctly rod-shaped colloidal particles is perhaps more decisive in causing elastic effects than it is with the other properties characteristic of this kind of anomalous viscosity.

“ Thixotropic behaviour is not exceptional; it is very common, provided that suitable concentrations of the colloid are chosen. Examples are: thixotropic, aqueous gels of many oxides (aluminium, iron, scandium, vanadium, titanium, thorium, etc.), of colloidal bentonite, of myosin, and tobacco mosaic virus, of dibenzoylcystine and of barium malonate in a medium of water and alcohol. Aqueous solutions of gelatin have been found to show thixotropy, both as concentrated solutions and as gels.

“ Coarse suspensions containing particles with a diameter of  $1\ \mu$  and more may also be thixotropic. They behave as a liquid while being shaken and settle to a solid paste when shaking stops. This behaviour is again found very frequently with aqueous suspensions of clays, slates (Solnhofen slate), and many powdered minerals (mica, iron oxide, jet, etc.); with finely powdered mercaptobenzothiazole in many organic liquids (light petroleum, carbon tetrachloride, chloroform, benzene, toluene, etc.); and in suspensions of many pigments in oils. Bentonite is a particularly good example of a substance forming thixotropic systems both in colloidal and in coarse suspensions. The mechanical properties of coarse suspensions are important because they enable us to understand better the mechanism of these phenomena. Hence I shall have to refer to them frequently, although protoplasm is certainly a truly colloidal system containing very much smaller particles.

“ The other limiting case is that of dilatancy. So far, it has been investigated only in coarse suspensions. Although observed and named by Osborne Reynolds in 1885, it has only recently been recognised as a remarkable counterpart to thixotropy. Osborne Reynolds used the term when describing the behaviour of moist quartz sand: It whitens and appears to be dry when the foot falls on it and becomes wet again when the foot is raised. An aqueous suspension of finely ground quartz powder (particle size 1 to  $5\ \mu$ ) at a concentration of about 44% of the solid is strongly dilatant. A glass rod can easily be moved through the mass at low speed, but an enormous resistance is set up if the speed is increased above a certain limit. . . . The suspension behaves like a Newtonian liquid at low speeds but, from a certain higher speed, the behaviour is like that of a solid. Suspensions of intact starch grains in water are strongly dilatant too.

“ There is every reason to believe that colloidal solutions may also be dilatant. A colloidal solution of silicic acid of a suitable concentration and  $p_H$  is found to be extremely viscous but Newtonian in its behaviour; it becomes hard and brittle, breaking up to a white, dry powder when crushed with a stout glass rod. Left to itself, the powdered mass returns again to its original viscous liquid state. A technical product, Nuodex Calcium-S (a colloidal solution of about 10% calcium naphthenate in a petroleum distillate), shows a similar behaviour.

“ The behaviour of coarse particles of suspensions under the microscope gives us a clue concerning that property of the particles which makes a suspension dilatant or thixotropic. The particles of a dilatant suspension are quite independent of each other; there is not the least indication of coagulation. If they are settled on the slide, they are all separated from each other; if dislodged and driven into the liquid by a slight knock, they remain separated in Brownian movement until they have settled again. On the other hand, the particles of a thixotropic suspension are always found to be coagulated to a certain degree, sticking together and forming clusters. If brought into suspension in the liquid, they may be temporarily separated from each other, but they always unite again to clusters.

“ This distinctive behaviour allows us to understand many results obtained with thixotropic or dilatant systems. For instance, in order to make a concentrated iron oxide sol thixotropic a small amount of a coagulating electrolyte like sodium chloride must be added, an amount much smaller than that needed for actual coagulation. In agreement with the positive zeta-potential of the iron oxide particles and with the Schulze-Hardy rule, the anions are especially effective. Smaller concentrations of multivalent anions are necessary to obtain the same state of thixotropy, which is characterised by the same time of re-solidification to a gel after the original gel has been liquefied to a sol by shaking. The thixotropic state, therefore, is often considered to be a primary stage of coagulation.

“ The following experiments done by W. Heller prove this concept more quantitatively. If an iron oxide sol, which is just too dilute in iron oxide to give a thixotropic gel on adding a certain amount of electrolyte, is centrifuged after the electrolyte has been added, a more concentrated, gelatinous sediment is accumulated at the bottom of the vessel. This sediment is not formed on using the same centrifugal force, if no electrolyte has been added. The sediment can be reversibly redispersed in the liquid by shaking. If the sediment is separated

from the less concentrated liquid on top, it is found to be a normal, *i.e.*, reversible, thixotropic gel. From the way the rate of sedimentation is correlated with the concentration of the added electrolyte, it can be concluded that reversible coagulates are formed. These are very rich in water and contain a number of colloidal iron oxide particles. This number increases greatly with increasing concentration of the added electrolyte. Such reversible coagulates, "geloids," are also formed in the original dilute sol on adding electrolyte, but their concentration is not high enough to let them coalesce to a coherent structure and turn the whole sol to a gel. If, however, the geloids are concentrated by centrifuging, they coalesce to a thixotropic gel. By investigating the change of so-called conservative light absorption during the process of thixotropic gelation, *i.e.*, the light absorption caused exclusively by the scattering of light (due to the presence of the colloidal particles), it can be shown that the reversible coagulation causing thixotropy is always accompanied by a certain degree of irreversible coagulation, which increases strongly with increasing electrolyte concentration. This irreversible coagulation is the chief factor in the regular coagulation occurring at higher concentrations of electrolyte.

"How many colloidal particles are contained in a geloid and how their number depends on the nature of the colloid is not known. These differences may be marked, as can be concluded from the fact that the minimum concentrations of colloid, when a thixotropic gel is formed, vary distinctly: for an iron oxide sol (of the Graham type), this concentration is about 5 g. per litre, for a vanadium pentoxide sol, it is only about 0.1 g. per litre.

"Thixotropy may be sensitive to very small changes in the concentration of substances contained in the sol. Thus iron oxide sols are particularly sensitive to hydrogen and hydroxyl ions; the time of solidification is strongly increased by an increase in hydrogen ions, decreased by an increase in hydroxyl ions, *i.e.*, an increase in hydrogen ions has a liquefying effect and vice versa. A  $p_H$  change from 3.9 to 3.1 caused the time of solidification to rise from 82 seconds to 150 minutes. By dipping a silver plate into an iron oxide gel for 18 hours, the  $p_H$  changed from 3.4 to 3.8, producing a decrease in the time of solidification from 33 minutes to 72 seconds. It was further found that amino-acids had a liquefying action upon these gels, independent of the change they caused in  $p_H$ , *i.e.*, they increased the time of solidification, although they increased the  $p_H$ .

"It is important also from a biological point of view, that not only electrolytes, but also suitable organic non-electrolytes, are able to produce thixotropy. Alcohol added to a suitable iron oxide sol makes it thixotropic. We are probably dealing with a coagulation due to "dehydration." These iron oxide sols may be considered to be sufficiently hydrophilic to allow one to expect such effects of dehydration as are discussed by Kruyt and Bungenberg de Jong in their theory of the stability of hydrophilic sols and of coacervation. If the alcohol is removed from the thixotropic gel by exposing it to sulphuric acid in a desiccator, the gel is liquefied to a sol.

"All these results show that substances causing a certain degree of coagulation lead to the formation of thixotropic systems. Inversely, a strong peptising agent, making the particles independent of each other, can transform a thixotropic system (having the proper particle size) into a dilatant one. A technical dispersing agent, "Hornkem," a sulphonated product of vegetable origin, applied in a suitably high concentration in aqueous solution, acts upon zinc oxide particles in such a way that it produces a strongly dilatant suspension, parallel with a maximum degree of dispersion. In pure water, the same zinc oxide produces a very stiff paste without any indication of dilatancy. In this case it can even be observed that thixotropy requires a medium degree of coagulation: in pure water the degree of clustering is too great to allow a thixotropic behaviour of the suspension; if, however, the right amount of a dilute solution of Hornkem is added, the paste becomes thixotropic, whereas at higher concentrations of Hornkem a state of high dispersion and dilatancy is reached.

"It fits in well with these results that a dilatant paste can be transformed into a thixotropic one by causing a certain degree of coagulation of the particles. Hydrophilic colloids at low concentrations favour the coagulation of hydrophobic particles, the phenomenon of sensitisation; whereas at high concentration they protect the hydrophobic system. In this way lecithin at low concentrations may coagulate aqueous quartz suspensions to a certain degree; this is proved by the marked increase in the rate of sedimentation of the clustered particles after lecithin has been added. Only in this range of sensitisation by the lecithin are these quartz suspensions found to be thixotropic, whereas they are dilatant in pure water.

The following facts cannot, presumably, be applied to biological phenomena, but they deserve to be mentioned briefly, nevertheless. The thixotropic or dilatant state depends strongly on the dispersion medium. Whereas suspensions of quartz or of intact starch grains are dilatant in water, they are thixotropic in organic liquids such as benzene, carbon tetrachloride, etc. It is possible to pass gradually from one state to the other by using two miscible liquids.

"In these organic liquids, too, a small amount of a second substance may cause a marked change in behaviour. A paste made from a very fine iron powder and carbon tetrachloride is pronouncedly plastic, a behaviour which is practically always correlated with a marked thixotropy. On adding a small amount of oleic acid, the paste is liquefied to a strongly dilatant suspension. The adsorption of the oleic acid on the surface of the particles produces a state of independence, and hence dilatancy.

"Suspensions of finely powdered solids in organic liquids, such as mixtures of oils, have been used for a very long time as paints. It is therefore no wonder that painters have been acquainted with the manifold, anomalous mechanical properties of suspensions, though without having defined such limiting cases as thixotropy and dilatancy. But it can hardly be doubted that many pastes of paints, described as stiff and plastic and as having a marked yield value, are thixotropic (in our terminology) if the concentration of the solid is suitably chosen, whereas if they were dispersed to a mobile liquid by the right dispersing agent, they would show dilatancy,



again at a suitable concentration of the solid. Green, at a time when the phenomenon of thixotropy was hardly known, published striking photomicrographs of plastic pastes of zinc oxide formed by suspensions in kerosene, which showed the zinc oxide particles to be coagulated. When poppy seed oil was added as a dispersing agent, the same particles were independent and dispersed. They are good examples of the state of the particles in a thixotropic and in a dilatant system.

“Our knowledge of the forces acting between the particles and causing these phenomena is not yet sufficiently advanced to allow me to state concisely the processes involved. Only a few points may be mentioned. The gels in thixotropic sols and gels are closely related to the tactoids, *i.e.*, double refracting groups of oriented particles formed spontaneously in concentrated sols containing non-spherical particles, and to the coacervates as defined by Bungenberg de Jong, *i.e.*, liquid coagulates of hydrophilic sols containing one or more kinds of colloidal particles. In gels, tactoids, and coacervates, the colloidal particles are very far apart, up to many  $\mu$ . It is, therefore, improbable that the attraction between the particles is due to van der Waals forces, which act over smaller distances; an attraction due to electric forces is more probable. The possibility has been considered that both attractive and repulsive forces between the particles may be of electric origin. But this concept is perhaps not easily reconciled with the fact that the forces between the particles may be markedly specific. Vanadium pentoxide, as well as benzopurpurin sols, form tactoids which carry a negative electric charge. In a mixed sol of the two, under proper conditions, both kinds of tactoids may be formed side by side, containing only vanadium pentoxide and benzopurpurin particles respectively. These two kinds of tactoids can be distinguished, because those of vanadium pentoxide are positively, those of the dye negatively, double refracting. The very specific behaviour of some ions when producing autocomplex coacervates must also be mentioned in this connection.

“The non-spherical shape of the colloidal particles strongly favours thixotropy. But the opinion, which has been occasionally expressed, that non-spherical shape is an indispensable factor for thixotropy is not correct. Thixotropic systems are known whose particles hardly deviate from the spherical shape, *e.g.*, pastes of intact starch grains in organic liquids. . . .”

There can be no doubt that Freundlich's researches on the viscosity and elasticity of colloid systems and the phenomena of thixotropy must be regarded as another of his major contributions to the advance of colloid science and also to that of the modern subject of rheology.

Having obtained (by means of a special grant from the Rockefeller Foundation) a Siemens piezo-electric quartz disc oscillator, Freundlich began about 1930—31 a series of investigations on the effects of supersonic (ultrasonic) vibrations, his chief collaborators in this field of work being K. Sollner, C. Bondy, and F. Julius Burger. It was shown that thixotropic gels, like those of iron oxide, are liquefied by ultrasonics of sufficiently high energy, and that a thixotropic decrease of the structural viscosity of concentrated colloid solutions can also be produced. Another striking effect is the dispersion of mixtures of liquids such as benzene and water, emulsions being formed. These “destructive” actions were shown to be due to the phenomenon of *cavitation*. The high-frequency waves produce periodic dilatations and compressions, and if the dilations be intense enough the liquid is caused to “tear,” cavities containing vapour being formed. When such cavities pass into the regions of high pressure they may suddenly collapse with almost explosive violence, leading to very high local concentrations of energy. This theory of cavitation was confirmed by the fact that in a vacuum or under sufficiently high external pressure the effects mentioned are not observed. No doubt in these cases the vapour-filled cavities either do not collapse or are not formed.

In emulsions and suspensions of suitable concentration, stationary ultrasonic waves were observed to produce periodic accumulations of the dispersed particles at the nodes or antinodes according as the particles are lighter or heavier than the surrounding liquid. Coagulation may occur where this accumulation takes place. Another interesting effect caused by very weak ultrasonic waves was observed; rod- or plate-like particles of a suspension are oriented with their long axes vertical to the direction of the energy-flow. It was an investigation (with K. Sollner) of the effects produced on biological systems by ultrasonic vibrations which attracted Freundlich to the special study of this field of research.

This account of his investigations in many parts of colloid science would be incomplete without at least a passing reference to his many published papers (1911—1933) on the chemistry and chemical kinetics of the transformation of halogen-substituted alkylamines into heterocyclic compounds (cyclic imines). Of interest in this connection was his demonstration (with Salomon) that adsorption on charcoal increases the “life” of  $\beta$ -chloro- $\beta$ -phenylethylamine, this “negative” catalytic action being probably or possibly due to an oriented adsorption of the molecules.

Freundlich was in no sense a mathematical physicist. He left the rigorous—or the attempted rigorous—treatment of the problems he investigated to others. His success as an investigator was due to his deep interest in phenomena as such, his excellent intuition and imagination, and his ability to correlate phenomena and perceive analogies between processes sometimes belonging to very different fields of science. Apart from the great effect of his researches in opening up and stimulating research in many different fields of colloid science, his famous book on *Kapillarchemie* has had a profound influence on the work of many investigators, both young and old. The latest German edition of this book in two volumes (Leipzig, 1930 and 1932) is a vast production which must have demanded immense industry on the part of the author. It is still an indispensable “reference book” for all active workers and all seekers in the lore of colloid and interfacial phenomena, though the author's

desire to make his book all-comprehensive has had the effect of making it rather cumbersome and perhaps in some respects not sufficiently selective and critical.

Freundlich's enthusiasm, wide knowledge and understanding of his subject, and his modest, cheerful, and kindly temperament made him a University teacher of the best type and a never-failing guide and friend of his many research students and collaborators. There was nothing of the drill sergeant or formal bureaucratic organiser about his methods. Both in Braunschweig and Berlin-Dahlem his work and influence in the conduct of the scientific *Colloquium* had a most valuable and inspiring influence on the young investigators who assembled weekly to discuss their own and others' researches. There is no better testimony to Freundlich's success in winning both the affection and the respect of his students and collaborators than the friendly nicknames bestowed on him. It is related that in Dahlem he was known as the "Gentle Shepherd," and in Minneapolis as "Uncle Herbert." When he came to us in London he never uttered a complaining word, although the small space in the laboratory that could be allotted to him must have been in sharp contrast to that in Dahlem. On the contrary, he exerted himself to be helpful in many ways, and although there must have been sorrow in his heart he kept a cheerful countenance to the world.

It is remarkable how many investigators owe the direction of their subsequent researches to the initial influence of their collaboration with Freundlich. He was always most unselfish in giving advice and help to those who sought it, and there must be many who never worked in his laboratory who owe much to him.

Freundlich was always moderate and critical in the statement of his results, and shunned speculative theories. Perhaps his only venture into this land of often unfulfilled promise was his paper on the "Occurrence of a mutation from the standpoint of probability," published in *Die Naturwissenschaften* in 1919.

Although devoted to research in pure science for its own sake, he was always anxious to show the value of applying the results to the explanation and improvement of industrial processes. Thus already in 1904 he published papers with F. Emslander on surface influences and phenomena in brewing, whilst in later years he did much technical work on rubber latex, and the rubber industry in general, and pointed out the bearing of thixotropy on the processes of the oil and paint industries. He was also interested in colloid phenomena in the industry of petroleum and in adsorption and interfacial actions in the processes of detergency and ore flotation. He well understood the meaning and importance of that great reversible equilibrium, Science  $\rightleftharpoons$  Industry.

Freundlich was a man of highly cultivated mind, tolerant spirit, and strongly artistic temperament. When such a man puts his faith in the power of experiment and reason to unravel some part at least of the mystery that surrounds and dwells within us, the cause of civilisation advances, even though it be but a little way, against the dark forces of blind unreason and savage prejudice that always seek to thwart it. We, his many friends in many lands, who live to mourn the passing of Herbert Freundlich, will keep his memory green.

In the writing of this memoir I have received most valuable assistance from Dr. Karl Sollner. Indeed, without that freely given help, the writing of it would have been well-nigh impossible. For many details concerning Freundlich's earlier life and career I have received great help from his sister, Mrs. Elizabeth Wardale, and his brother, Professor Erwin Finlay-Freundlich. I am also indebted to Dr. E. Heymann of Melbourne University for some valuable opinions. To all these friends I desire to express my most sincere thanks.

F. G. DONNAN.