The results obtained may be summarized as follows (compounds of undetermined composition being omitted):

Salt formula.	Acid compounds isolated.
K_2SO_4	(*a*) $K_2SO_4.3H_2SO_4$; m. p., 91.5°.
	(*b*) $K_2SO_4.H_2SO_4$; m. p., 218.6°; existent in three modifications, with transition points at 182° and 202°.
$(NH_4)_2SO_4$	(*a*) $(NH_4)_2SO_4.3H_2SO_4$; m. p. 48.0°.
	(*b*) $(NH_4)_2SO_4.H_2SO_4$; m. p. 146.9°.
Na_2SO_4	(*a*) $2Na_2SO_4.9H_2SO_4$; unstable at m. p. (60°, by extrapolation), transition points to the two modifications of (*b*) occurring at 57° and 58°.
	(*b*) $Na_2SO_4.2H_2SO_4$; existent in two modifications both unstable at their m. p., transition to (*c*) occurring at 95° and 109°.
	(*c*) $Na_2SO_4.H_2SO_4$; m. p., 186°.
Li_2SO_4	(*a*) $Li_2SO_4.7H_2SO_4$; m. p., 13.6°.
	(*b*) $Li_2SO_4.2H_2SO_4$; unstable at m. p., transition to (*c*) occurring at 50°.
	(*c*) $Li_2SO_4.H_2SO_4$; unstable at m. p. (170.5°, by extrapolation).

The bearing of the results here obtained upon the general problem of the factors affecting compound formation in solutions has been briefly pointed out, but full discussion is reserved for a later article, in which the compound formation, solubility and ionization relationships of a more complete series of metal sulfates in sulfuric acid will be considered.

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COLLOIDAL ADSORPTION.

BY ARTHUR MUTSCHELLER.

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From the work of Stokes, Einstein, von Smoluchowski, The. Svedberg, and others, we have a clear notion of the properties of the unstable colloids when suspended in a fluid; for in their case all the conditions upon which Stokes' law is based seem to be realized. On the other hand, the properties of the gelatinizing and swelling colloids are so much at variance with the requirements for the validity of Stokes' law, that it seems clearly impossible to consider the metallic and the gelatinous colloids in one class, and separate efforts to establish a securely based view-point from which the mechanism of the action of the latter might be considered, does not seem to have hitherto been made.

To make generalizations and general deductions safely, requires a set of accurately determined experimental facts obtained under uniform standard conditions and sufficiently complete so that by coördinating the variations in properties a complete set of descriptive data on the system are secured showing the changes in the properties of the substance under investigation when certain changes in the surrounding conditions are forced upon it.

In view of the fact that such uniform experimental data on the gelatinous or swelling colloids are not directly available nor found in the literature, the investigations herein recorded were carried out with the same typical colloid, with an electrolyte added in varying concentrations, and under uniform experimental conditions. An attempt was made to study all such physical or physico-chemical properties of a typical colloid as are capable of investigation by modern methods and as seem to have a bearing in defining the properties of the colloid.

The distinctions, heretofore made, between suspensoids, and emulsoids, between irreversible and reversible colloids, between unstable and stable colloids, between anhydrophils and hydrophils, etc., are undoubtedly all based upon differences in the properties of the 2 classes of colloids, which it becomes interesting to investigate. When considered together with the general properties of colloids, these differences between the 2 classes of colloids would form an important item in a set of data from which it should be possible to derive general principles applying to both classes or if that is not possible, to describe models of colloidal particles which exhibit the properties of both classes.

When a colloid is precipitated the properties which characterize it as a colloid generally vanish. It appears, therefore, that a study of the properties of colloids would have to be directed toward investigating the factors of stability or, on the other hand, of the conditions under which a colloid is coagulated or precipitated. Since the factors upon which the stability of a colloid system depends are quite numerous, and coagulation or precipitation can be initiated by any one of a great number of factors, it appears that the study of the factors of stability of colloidal systems should cover the most important properties which characterize colloids.

Nearly all of the aforesaid factors seem to be connected with or dependent upon changes in the concentrations of electrolyte which is generally present. Thus, the addition of gradually increasing quantities of electrolyte to a colloidal solution is known to produce many changes such as adsorption of ions and salts; changes in the migration velocity of the particles in the electrostatic field, surface tension, viscosity or internal friction, swelling and shrinking, etc.

As far as possible, the writer's experimental work covers the changes above outlined and, therefore, the topics given below. Unless otherwise stated, the experiments of all sections were performed with identical series of solutions, at the same temperature, and as far as possible, under identical experimental conditions.

The topics of the investigation were (1) the migration velocities of the ions as influenced by the presence of a reversible colloid; (2) the concentration of the anions and cations as influenced by the presence of a reversible colloid; (3) the migration velocity of the colloid as influenced by increasing concentrations of electrolyte; (4) the surface tension of emulsoid solutions as influenced by increasing concentrations of electrolyte; (5) the viscosity or internal friction of emulsoid solutions as influenced by increasing concentrations of electrolyte; (6) the swelling of gelatin as influenced by increasing concentrations of electrolyte.

EXPERIMENTAL PART.

Preparation and Composition of the Solutions.

In view of the variety of determinations and observations planned, all with the same series of mixtures, it became necessary to select a colloid and a salt both adapted to the carrying out of such determinations and observations. To avoid complications and to obtain the results as simply as possible, it seemed desirable to select a salt ionizing into equivalent ions, the concentrations of which could be determined by electromotive-force measurements.

In previous experimental work it was found that gelatin, which is a typical representative of the emulsoids, is suitable for the experiments planned, and also that zinc sulfate is satisfactory as an electrolyte, both the sulfate and the zinc-ion concentrations being determinable independently by electromotive force measurements by means of electrodes, one (first kind) for the zinc ion and one (second kind) for the sulfate ion. The experiments were, therefore, made with 1% solutions of gelatin containing increasing concentrations of zinc sulfate as indicated in Col. 2 of the tables.

Standard solutions of zinc sulfate were prepared from the chemically pure salt and distilled water; they were standardized by precipitating the zinc and weighing it as zinc ammonium phosphate. The gelatin solutions were prepared from a good quality of gelatin previously dialyzed and again desiccated. For each day's work, fresh solutions were prepared containing 2 g. in every 100 cc. of distilled water. The mixtures were slowly heated while stirring when the gelatin went rapidly into solution, and heating was continued until boiling just *began*. After cooling and while the gelatin solution was still fluid the mixtures were finally prepared by adding an equal volume of the properly diluted standard zinc sulfate solution to make the gelatin content of the mixtures uniformly 1% and then allowing them to stand at 25° for *one hour*. This uniform method of preparing the mixtures was found necessary, for otherwise varying results were obtained.

A series of solutions of concentrations as indicated in the tables and prepared as stated above was employed for all experiments reported in this paper, unless otherwise stated. The working temperature was uniformly maintained near 25°. The reaction vessels were placed into a carefully regulated thermostat until this temperature was attained, and the measurements were then made and repeated until found constant. Thus all experimental work was performed under identical conditions, such as the preparation of the solutions, the regulation of the temperature, the lapse of time, etc., unless the contrary is indicated. The experimental data reported are the result of several measurements, and, as a rule, the average of at least 2 measurements made at different times is given in the tables.

The Migration Velocities of the Ions as Influenced by the Presence of a Reversible Colloid.

In a previous publication experiments were described which show that the migration velocities of the silver and the nitrate or the copper and the sulfate ions are changed considerably when certain quantities of an emulsoid are added to their solutions.[1] Thus the silver and the nitrate ions of a pure silver nitrate solution migrate with relative migration velocities of 0.562 for the nitrate ion and 0.438 for the silver ion. These relative migration velocities are generally determined by estimating the changes in the concentrations at the 2 electrodes when a certain quantity of the metal is electrically deposited on the cathode. Thus it is found that while one equivalent of silver is deposited on the cathode there have arrived by migration only 0.438 equivalent; hence there is a decrease in the concentration of silver ions at the cathode. It is then also found that at the anode there have only arrived 0.562 equivalent of nitrate ions, so that there is also a decrease in the concentrations of silver nitrate. Moreover, the deposit on the cathode is not smooth but rather crystalline, forming the so-called silver trees. The height of these silver trees probably indicates the thickness of the layer of fluid near the cathode in which impoverishment of the silver content has developed.

Marked changes in the migration velocities of these ions are observed, however, if to their solutions addition of certain quantities of gelatin is made. Thus a small quantity of gelatin added to a normal solution of silver nitrate causes a decrease in the migration velocity of the nitrate ions and a proportional increase in the velocity of the silver ions. At the same time, the tendency to form silver trees and a loose deposit on the cathode is decreased, the deposit being quite smooth, well adherent to the cathode, and less crystalline. Furthermore, a small amount of organic material having the appearance of coagulated gelatin had gathered around the anode.

Quite different results are observed when larger additions of gelatin are made to a normal silver nitrate solution. The deposit on the cathode is then smooth and well adhering and a layer of gelatin is found to have gathered around the cathode; the deposit on the cathode consists in this

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[1] Mutscheller, *Met. Chem. Eng.*, **13**, 353–7 (1915).

case of a mixture of silver and gelatin. The migration velocity of the silver ions is found to be either unit or more, according to whether the organic deposit on the cathode was weighed with the silver or whether it was removed and the silver only had been weighed. The migration velocity of the nitrate ions, however, is found to be zero.

Under ordinary conditions gelatin without the addition of electrolyte, migrates to the negative electrode, hence carries a positive charge. When a small quantity of it is added to a normal silver nitrate solution, then there is adsorption of negative ions until the charge of the gelatin particles is reversed, at which time they migrate to the anode instead of as before to the cathode.[1] If the quantity of gelatin added is larger, the negative ions in the solution which are being adsorbed are not sufficient to reverse the charge of the gelatin particles and they still continue to migrate to the cathode. There is, naturally, a point when the gelatin particles are just neutralized and they do not migrate either to the cathode or to the anode.[2]

Experiments to determine the migration velocities of the zinc and the sulfate ions in the series of solutions of zinc sulfate of increasing concentrations containing 1% of gelatin were carried out for the purpose of finding at what concentration the negative sulfate ions are just sufficient to neutralize the positive charge of the gelatin particles of a 1% solution. The apparatus employed for this work is the same as that formerly employed. The entire cathode compartment was emptied into a weighing

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[1] That there is a reversal in the direction of migration of the anions when gelatin is present in the solution has already been observed by A. Carpentier (*Compt. rend.*, **136**, 1652 (1903)). He found that when the solution is of a chromate or dichromate placed upon a film of 10% gelatin, the reddish-yellow chromate ion migrates with great velocity, not to the anode but to the cathode. While Carpentier does not give an explanation, this observation is evidently in agreement with the theory of adsorption as expounded in this paper.

[2] Paul Richter (*Z. physik. Chem.*, 80, 449, (1912)) determined the influence of certain colloids upon the migration velocities of several electrolytes and found only slight decreases when increasing additions of colloid were made. He analyzed the anode fluid and in all cases he neglected the presence of the colloid or he assumed that no changes in the concentration of the colloid could occur. But, as will be shown, when a small quantity of colloid is added its charge is reversed and made negative so that the colloid migrates to the anode. When larger additions of colloid are made, however, more and more of the colloid migrates toward the cathode for its charge then becomes more and more positive. Thus, when larger additions of colloid are made, the anode fluid will have a lower specific gravity after the electrolysis than before, so that at the rate at which the additions are increased, the anode fluid loses progressively in specific gravity. This gives the impression that the anode fluid is of smaller volume than it actually is, and the chlorine ion concentration is found to be higher with the result that the differences before and after the electrolysis appear larger and the migration velocities also larger than they are. This error in the case of a 0.05 N solution of monovalent ions is much larger than it would be in the case of a molar solution of polyvalent ions.

flask and its exact weight was determined. From this weight, that of the zinc sulfate as found later by analysis, was subtracted. From the remaining weight and the specific gravity of the solution the exact volume of the cathode fluid was calculated. Finally, from the data obtained by analysis (*i. e.*, precipitating and weighing the zinc as zinc ammonium phosphate) the relative migration velocities of the sulfate and the zinc ions were calculated. These results are reported in Table I.

TABLE I.—CHANGES IN THE RELATIVE MIGRATION VELOCITY OF THE ZINC ION IN SOLUTIONS OF VARIOUS CONCENTRATIONS BY 1% GELATIN.

Zinc anode, platinum cathode; volts 12, from storage battery; time, 2 to 3 hours.

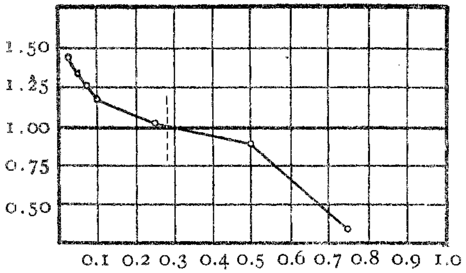
Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Deposit on cathode.	Zn^{++} migrated to cathode.[c]	Relative migration velocity of Zn^{++} calculated.	Form of the deposit.	Gelatin.
4....	0.025	0.0142	0.0118[b]	0.0169	1.438	Dark color; impure	Thick layer dep. on cathode
5....	0.05	0.0234	0.0136[b]	0.0180	1.323	Gray with tendency to peel off	Layer of gel. dep. on cathode
6....	0.075	0.0326	0.0381[b]	0.0483	1.269	Slightly gray	Film of gel. dep. on cathode
7....	0.10	0.0397	0.0624[b]	0.0734	1.177	Well adherent; slightly dull	Small amt. of gel. gathered at cathode
8....	0.25	0.0803	0.0297	0.0302	1.016	Brilliant, pure, adherent	No accumulation of gelatin
9....	0.50	0.141	0.0585	0.0517	0.884	Pure, tendency to form striae	Small quan. of gel. gathered around anode
10....	0.75	0.185	0.0421	0.0143	0.340	Pure, forming striae and bubbles	Layer of gel. gath. around anode
11....	1.00	0.229	0.0560	0.362	0.154	Very poor, forming craters and striae	Gel. precipitated upon add. of *N* $ZnSO_4$ sol.

[a] Calculated from the conductivity measurements of Jones and West, *Am. Chem. J.*, 34, 357 (1905).

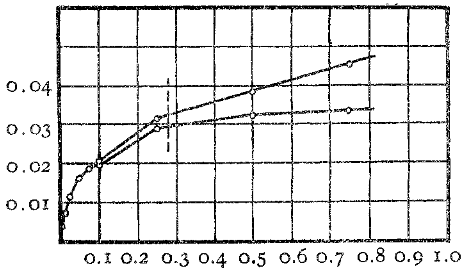
[b] Deposit of zinc and organic material.

[c] Zinc deposited minus the loss of zinc in the cathode compartment.

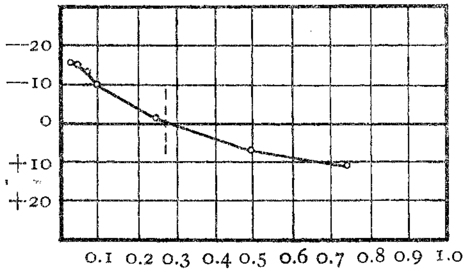
The results which are plotted in Fig. 1 Curve 2, show that concentrations higher than 0.28 molar zinc sulfate furnish, probably through progressive ionization, more sulfate ions than the colloid added is capable of adsorbing. The migration velocities of the zinc ion in the solutions containing zinc sulfate in higher concentration than 0.28 molar are, as the experimental data show, less than unity and the deposit is less smooth and less adherent as the concentration of the zinc sulfate in the solutions increases. At the point where the addition of zinc sulfate just amounts to 0.28 molar the migration velocity of the zinc ions is unity and the



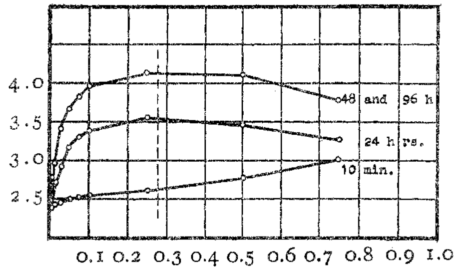
Curve 2 showing changes in the relative migration velocity of the Zn^{++} ion.



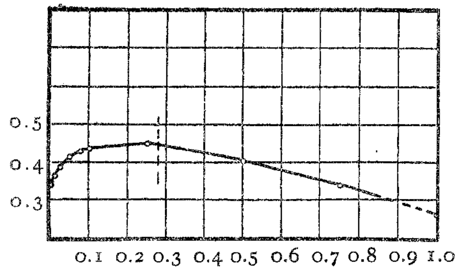
Curve 2a showing the $SO_4^=$ and the $Zn^{++} + SO_4^=$ adsorbed.



Curve 4 showing the changes of the migration velocity of the gelatin particles.



Curve 5 showing the viscosity of the solutions after various intervals of time



Curve 6 showing the extent of swelling of gelatin in the various dilutions of $ZnSO_4$.

Fig. 1.—Molar concentration of $ZnSO_4$ added

velocity of the sulfate ion is zero. At lower than 0.28 molar concentrations of zinc sulfate the migration velocities of the zinc ion are apparently higher than unit velocity since the deposit of organic material was weighed along with the zinc deposited on the cathode. The deposition of gelatin on the cathode probably takes place due to the fact that gelatin when negatively charged adsorbs positive ions as shown in the next section, and may thus be deposited on the cathode.

The results of this series bring into evidence again the fact that the particles of gelatin adsorb negatively charged ions, rendering them electrically neutral, so that at proper proportions the current which is transported across the electrolyte is then carried by the positive ions. This is indicated by the fact that the positive ions actually migrate with increased velocity for the concentration of positive ions around the cathode is found to remain constant when just the proper quantity of gelatin sufficient to adsorb the free negative ions is present. The results of this series show that the negative ions of a 0.28 molar zinc sulfate solution are approximately neutralized by 1% of gelatin with the result that the zinc ions migrate with unit velocity and they deposit as a smooth and noncrystalline layer on the cathode.

The Concentration of the Free Anions and Cations as Influenced by the Presence of a Reversible Colloid.

The results of the foregoing series of experiments indicate that a union takes place between the colloidal particles and the negatively charged ions when a neutral salt is added to the solution of the colloid. The storage of electrolyte in finely divided substances is an old and a well-known phenomenon generally called adsorption. The relation of the adsorbed to the unadsorbed quantities of electrolyte, in the case of a number of suspensoids has been investigated by H. Freundlich and many others. Freundlich[1] found that the ratio of distribution of the electrolyte between the colloid and the solvent is well represented within certain limits, by the equation

$$x/m = Bc^{1/q}$$

where x/m is the quantity of electrolyte adsorbed by m grams of the colloid, c is the concentration of electrolyte remaining in solution, and B and $1/q$ are constants. Since taking the logarithms of both sides of this equation gives an equation for a straight line, plotting the logarithms of the experimental data must give a straight line, if they satisfy the adsorption equation.[2] Freundlich,[3] however, found that the logarithmic plot of the points corresponding to larger additions of electrolyte bends somewhat and tends to run parallel with the log-c axis. The curve of

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[1] "Kapillarchemie," 1909, p. 143ff.

[2] Freundlich, *Z. physik. Chem.*, 57, 391 (1907).

[3] "Kapillarchemie," p. 94.

this plot, therefore, is only a straight line when smaller additions of electrolyte are made to the colloid.

In order to test the ratio of adsorption of ions by the emulsoid chosen for this investigation a series of determinations of the concentrations of the free zinc and sulfate ions was made, first in a series of pure solutions of zinc sulfate of increasing strengths, and then in a similar series of solutions containing in addition 1% of gelatin. Differences found in the results evidently indicate the formation of a neutral combination consisting of colloidal particles and ions, and the numerical values of these differences represent the adsorbed quantity of ions. These values and those of the ionic concentrations found in the solutions can then be suitably plotted to determine whether they represent an adsorption equilibrium.

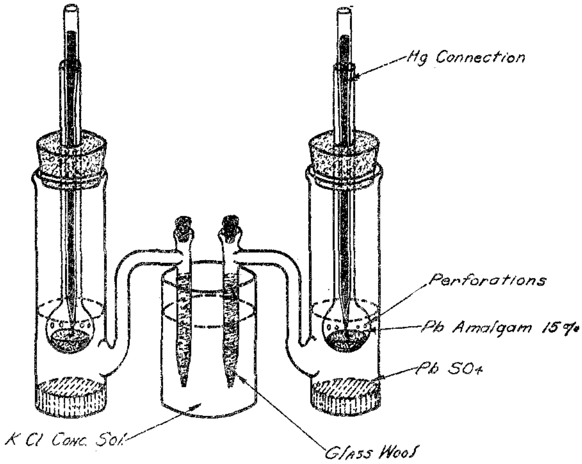

Fig. 2.

The apparatus employed for determining the concentration of the zinc ion and the sulfate ion in solutions of zinc sulfate consists of a potentiometer as a balancing instrument, an electrometer as a zero instrument, a standard cadmium element as a standard of electromotive force and an accumulator as a constant electromotive force. All determinations were made at 25°, the temperature of the cells being controlled in a carefully regulated thermostat. The type of cell representing the combination is

$$\mathrm{Zn} \left| \frac{\mathrm{ZnSO_4}}{C_1} - \text{conc. KCl} - \frac{\mathrm{ZnSO_4}}{C_2} \right| \mathrm{Zn}$$

where C_1 and C_2 are the concentrations of $\mathrm{Zn^{++}}$, respectively, in the 2 solutions.

A concentrated solution of potassium chloride served as a connecting fluid between the 2 electrode halves.

The electromotive force of this cell is given by the formula

$$E = \frac{0.0000198T}{2} \times \log \frac{C_1}{C_2}.$$

The concentration of C_2, the concentration sought was calculated from

$$\log C_2 = \log C_1 - \log \psi$$

where

$$\log \psi = \frac{E}{0.0000198T/2}.$$

The concentrations of the sulfate ion was determined with the aid of a cell represented by

$$\text{Pb} \left| \frac{\text{PbSO}_4}{\text{ZnSO}_4/C_1} - \text{conc. KCl} - \frac{\text{PbSO}_4}{\text{ZnSO}_4/C_2} \right| \text{Pb}$$

Metallic lead as an electrode was employed in the form of a 15% amalgam. The electrode vessels illustrated in Fig. 2 were found to be most satisfactory, especially for operation with solutions containing colloidal matter.

The electromotive force of this cell is given by

$$E = \frac{0.0000198T}{2} \times \log \frac{C_2}{C_1}$$

and is calculated from

$$\log C_2 = \log C_1 + \log \psi$$

where log ψ is again equal to

$$\frac{E}{0.0000198T/2}.$$

Thus Fig. 3 is a direct plot of the experimental results recorded in Table II and Fig. 4 (*a*) is the logarithmic plot of the ratio of distribution of the sulfate ion between gelatin and the solvent; Fig. 4 (*b*) is the logarithmic plot of the sum of the concentrations of the sulfate and the zinc ions and is clearly a straight line.

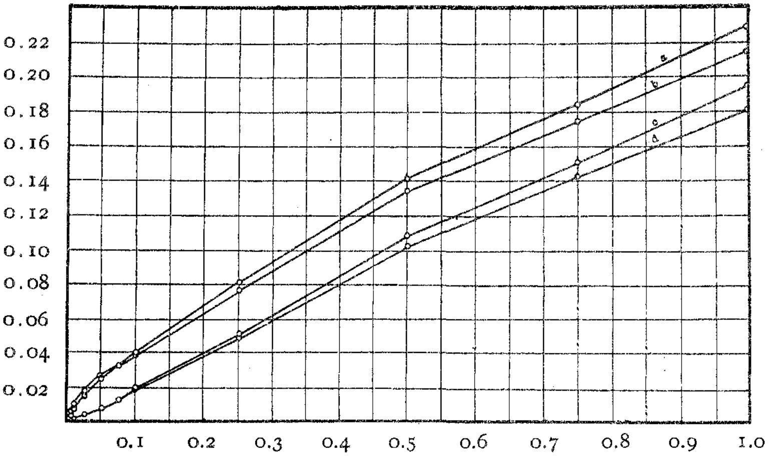

Fig. 3.—Showing (*a*) the concentrations of the $SO_4^=$ and of the Zn^{++} in the pure solutions; (*b*) the concentrations of the Zn^{++} when 1% of gelatin is added; (*c*) the concentrations of the $SO_4^=$ when 1% of gelatin is added; (*d*) the loss of $Zn^{++} + SO_4^=$ when 1% of gelatin is added.

TABLE II.—CHANGES IN THE CONCENTRATION OF THE SULFATE AND ZINC IONS PRODUCED BY THE ADDITION OF 1% GELATIN.

			Found by e. m. f. measurement.						
			No additions. Concentrations.		1% gelatin solutions.		Adsorbed by gelatin.		
Solu. No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Zn^{++}.	$SO_4^{=}$.	Zn^{++}.[b]	$SO_4^{=}$.	Zn^{++}.	$SO_4^{=}$.	$Zn^{++} + SO_4^{=}$[c]
2....	0.005	0.0035	0.003	0.0035	0.0045	0.0002	—0.00094	0.0042	0.0042
3....	0.01	0.0063	0.0062	0.0063	0.00872	0.0007	—0.00238	0.00701	0.00701
4....	0.025	0.0142	0.0136	0.014	0.0180	0.0031	—0.0038	0.0111	0.0111
5....	0.05	0.0234	0.0247	0.034	0.0248	0.0077	—0.0014	0.0159	0.0159
6....	0.075	0.0326	0.033	0.0326	0.0324	0.0134	+0.0002	0.0192	0.0194
7....	0.10	0.0397	0.0394	0.0395	0.0385	0.0199	+0.0010	0.0196	0.0206
8....	0.25	0.0803	0.0813	0.0803	0.0775	0.0517	+0.0028	0.0286	0.0314
9....	0.50	0.141	0.141	0.141	0.135	0.109	+0.0060	0.032	0.038
10....	0.75	0.185	0.184	0.188	0.176	0.155	+0.0120	0.033	0.045
11....	1.00	0.229	0.219	0.229	.....	....	....	.....	.....

[a] Calculated from the conductivity measurements of Jones and West, *Am. Chem. J.*, **34**, 357 (1905).

[b] With regard to the dissociation of zinc sulfate, it must be considered to exist in accordance with the equilibrium

$$\frac{(Zn^{++})(SO_4^{=})}{(ZnSO_4)} = K.$$

If the colloidal particles remove $SO_4^{=}$ from the solution, there will be a rearrangement of the equilibrium so that if x moles per liter of $SO_4^{=}$ are removed,

$$\frac{(Zn^{++} + x)\ SO_4^{=} - x)}{(ZnSO_4 - x)} = K.$$

There is, therefore, an increase of zinc ions due to the further ionization of zinc sulfate initiated by the removal of sulfate ions. Thus we find such an increase of zinc ions as recorded in Table I below 0.1 molar dilutions. From there on, however, there is then a decrease of zinc ions which shows that from that point on, the colloid has also adsorbed some zinc ions. Assuming that y moles were adsorbed, then there is again a rearrangement of the equilibrium so that

$$\frac{(Zn^{++} + x - y)\ (SO_4^{=} - x + y)}{(ZnSO_4 - x + y)} = K.$$

The amount of Zn^{++} and $SO_4^{=}$ actually adsorbed is, therefore, in all probability considerably larger than that found by difference from the remaining concentrations. That is, the removal of zinc ions and sulfate ions is followed by further ionization of zinc sulfate through which loss in these ions is made to appear smaller. The actual extent of this difference cannot be accurately determined, the difference would appear in the constants of the adsorption equation, which, however, at the present has no definite meaning. The result might be a slight difference in the slope and the intersection of the logarithmic curve with the log x/m axis but the differences, in all probability, are only slight.

[c] These increases in the case of the zinc ion in the solution are not added as negatively adsorbed for they are probably due to the readjustment of the equilibrium of the zinc and sulfate ions when the latter are withdrawn from the solution by the colloid.

The results brought into evidence by this series of determinations are two-fold. First, it is shown that the sulfate ion (not the zinc ion) maintains a typical adsorption equilibrium between the solvent and the gelatin present in the solution in the sense of H. Freundlich's criteria; second, it is shown that the logarithmic plot of the ratios of distribution of the sulfate and the zinc ion taken as their sums and plotted against the concentrations of $^1/_2$ the sums of the concentrations of the sulfate and the zinc ions in the solutions is better represented by the adsorption equation used by Freundlich, than the ratio of the sulfate-ion concentrations alone without including the zinc (positive) ion also. (Fig. 1. Curve 2*a*.)

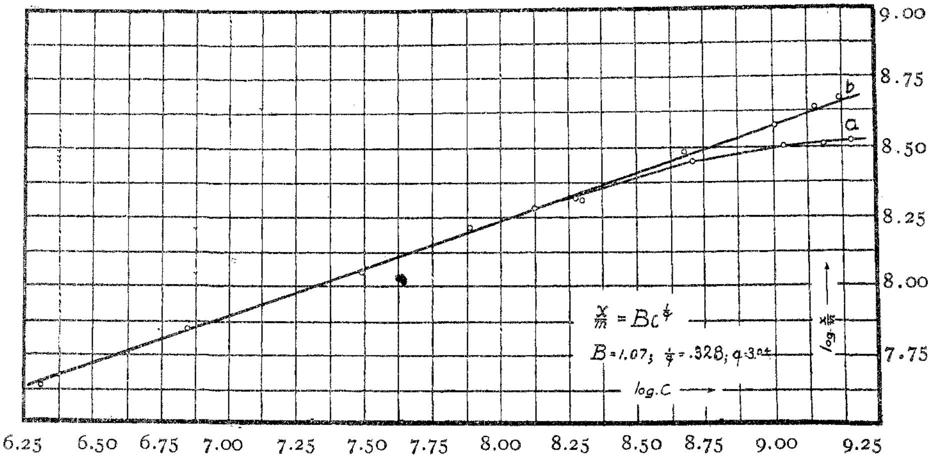

Fig. 4.—Logarithmic plot of (*a*) the $SO_4^{=}$ and of (*b*) the $Zn^{++} + SO_4^{=}$ as distributed between the colloid and the solvent.

The Velocity of Motion of Colloidal Particles as Influenced by the Presence of Increasing Concentrations of Electrolyte.

That many colloidal particles migrate when subjected to the force of an electrostatic field and that this motion is the result of the action of the field on the electrical charges carried by the particles, is a fact known for many years and which has been the subject of lively investigation. The work of Wiedemann and Perrin[1] brought out the fact that if 2 different mutually insoluble substances, especially when present in different phases, come in contact, that there is generally a difference of electrical potential at or near the surface of contact.

Although the mechanism of the action of a field on a charged particle and the factors upon which the motion imparted to the particle by the field depends are rather clearly understood, there are still quite a number of theories under consideration regarding the origin of the charge of the particles. The chemical theories seem to fail utterly to account for the original charge of the particle and to explain the existence of a charge when

[1] *J. chim. phys.*, 2, 607 (1904).

electrolyte is present in the solution. The theory of Helmholtz and Lamb, however, has in recent time received very good support from the work recently performed on the structure of solids to which reference is made later in another article.

When testing the electrical properties of suspensoids it is, as a rule, possible to obtain definite and well agreeing results, but with emulsoids there seem changes of a more complicated nature to be going on around the electrodes so that the same interpretations do generally not apply. But this series of experiments was carried out for the sole purpose of finding the point at which the charge of the gelatin particles is neutralized by the added electrolytes.

For the determinations the same tube as that used for the determinations of the changes of migration velocities of the ions was employed. The distance between the electrodes is 12.4 cm.; the voltage of the current applied to the electrodes is 44.6 volts, so that there existed a potential drop across the electrodes of 3.6 volts per centimeter. The time of running was generally about 30 minutes. The estimation of the gelatin that migrated was carried out by determining the changes in the gelatin content at the 2 electrodes. From determinations of the total nitrogen content of a given volume of the well mixed content of the cathode vessels the velocity of the gelatin particles that migrated was calculated for an existing drop of one volt per centimeter in one second of time.

TABLE III.—CHANGES OF MIGRATION VELOCITY OF GELATIN PARTICLES WITH INCREASING ADDITIONS OF ELECTROLYTE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Velocity of motion cm./sec. pot. drop volt/cm.
3	0.01	0.0063	-16×10^{-5}
4	0.025	0.0142	-15×10^{-5}
5	0.05	0.0234	-13×10^{-5}
6	0.075	0.0326	-10×10^{-5}
7	0.10	0.0397	-3×10^{-5}
8	0.25	0.0803	7×10^{-5}
9	0.50	0.141	11×10^{-5}

[a] *Loc. cit.*

The numerical data of Table III, which are plotted to Fig. 1, Curve 4, bring out the fact that the colloidal particles are deprived of all their charge when 0.28 molar zinc sulfate is present in the solution. This point, therefore, represents the isoelectric conditions of the colloidal gelatin particles as indicated by the fact that, at that point, they are unsusceptible to the force of an electrostatic field.

The Surface Tension of a Solution of an Emulsoid as Influenced by Increasing Concentrations of Electrolyte.

It has been observed experimentally that the surface tension of water is decreased by a class of colloids which includes gelatin, albumin, dextrin, agar-agar, gum arabic, soaps, rosins, etc., as against being increased by metallic colloids. The results of H. Freundlich and W. Neumann[1] show that some of these substances, when dispersed in water, decrease the surface tension, but when dispersed in alcohol they cause a rise in the surface tension. These differences in the effects upon the surface tension of the pure solvent, can, therefore, be considered as constituting a property characteristic of emulsoids.[2]

The surface tension of a gelatin solution, as G. Buglia[3] and W. Frei[4] show is further decreased by the addition of H^+ (positive ions) and is increased (*i. e.*, the difference between the surface tension of the gelatin solution and the pure solvent is made smaller) by the addition of OH^- (negative ions). As is shown by W. Frei, the order in which the anions increase the surface tension of gelatin solutions and in which the cations decrease it, is in the order of the Hofmeister series. Furthermore, as is characteristic of the Hofmeister series, the order is reversed when the reaction of the solution is changed by the addition of either an acid or an alkali.

It seems indicated to mention that these and the observations described in the following are in agreement with W. Gibbs' well-known theorem; for, as reported by W. Frei,[5] the anions cause a decrease in the difference between the surface tension of the pure solvent and that of the gelatin solutions, as the result of which the anions are adsorbed by the gelatin particles.

The surface tension of the solutions described in the introduction was measured by the capillary-rise method.[6] A capillary of uniform cross section was employed; a thread of mercury in this capillary 10 cm. long weighs 0.1053 g. As a criterion of cleanness, it was observed that the capillary rise and fall should not differ by more than one mm. The data recorded in Table IV are calculated with the aid of the formula, $n = {}^1/_2\, rhsg$, where r is the radius of the capillary calculated from the weight of the thread of mercury, h the height of ascent in cm., s the specific gravity, and g the constant of gravity equal to 980.6.

The results show a decrease in the surface tension of water caused by the solution of 1% of gelatin. But, within the limits of experimental error attainable by the capillary rise method, it is not possible to find any change in the surface tension of the solutions due to the addition of increasing quantities of zinc sulfate to the gelatin solution. This, at first, might be contrary to the expectations, but since the effectiveness of the

[1] Freundlich and Neumann, *Kolloid Z.*, **3**, 80 (1908).

[2] Wo. Ostwald, "Kolloidchemie," **1912**, p. 227.

[3] Buglia, *Biochem. Z.*, **11**, 311 (1908).

[4] Frei, *Diss.*, Zürich, **1907**.

[5] *Loc. cit.*

[6] Ostwald-Luther, "Physico-chemische Messungen," **1904**, p. 234.

ions varies in the order of the Hofmeister series, and since the zinc ions and the sulfate ions as decreasing and increasing the surface tension of the gelatin solution might be nearly equivalent, it is probable that the changes which might actually exist are too small as to be discernible by this method.[1]

TABLE IV.—SHOWING THE SURFACE TENSION OF 1% GELATIN SOLUTIONS WITH INCREASING CONCENTRATIONS OF ZINC SULFATE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Sp. gr.	Capillary ascent, cm.	Surface tension.
Water.	......	......	1.000	9.60	741×10^{-5}
1% Gel.	......	......	0.9936	8.20	629×10^{-5}
2............	0.005	0.0035	0.9946	8.30	631×10^{-5}
3............	0.01	0.0063	0.9950	8.20	629×10^{-5}
4............	0.025	0.0142	0.9966	8.20	630×10^{-5}
5............	0.05	0.0234	1.0021	8.15	630×10^{-5}
6............	0.075	0.0326	1.0058	8.15	632×10^{-5}
7............	0.10	0.0397	1.0103	8.10	631×10^{-5}
8............	0.25	0.0803	1.0304	7.85	629×10^{-5}
9............	0.50	0.141	1.0723	7.60	629×10^{-5}
10............	0.75	0.185	1.1042	6.30	630×10^{-5}
11............	1.00	0.229	coagulated	....	......

[a] *Loc. cit.*

The conclusions from this series of determinations are that the addition of increasing quantities of zinc sulfate to 1% gelatin solutions is not accompanied by any great changes in the surface tensions of the original pure gelatin solution.

The Viscosity or Internal Friction of a Solution of an Emulsoid as Influenced by Increasing Concentrations of Electrolyte.

Viscosity measurements of colloidal solutions were hitherto used mostly for the purpose of comparing different qualities and different sols, yet they seem also to indicate changes in such physical properties which are the result of changes in the internal structure of the dispersed component of the system. The Faraday Society, in 1913, called a meeting for the discussion of the theme "The Viscosity of Colloids."[2] A large part of the discussions at this meeting were on 2 formulas which should represent the viscosity of suspensoids and emulsoids, respectively. These formulas, the Einstein-Hatschek formula for a suspension of rigid spheres in any liquid in terms of the viscosity of the pure liquid, and a second formula deduced by Hatschek for the variation in the viscosity of the emulsoids, differ in that in the latter, there is taken into consideration the fact that in emulsoids the dispersed phase consists of a deformable aggregate formed by the dispersed substance in association with a large and varying proportion of the dispersion medium. This formula, which has received

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[1] *Biochem. Z.*, 11, 311 (1908), and *Diss.*, Zürich, 1907.

[2] *Trans. Faraday Soc.*, 9, 34 (1913).

a considerable amount of experimental verification expresses that, if the viscosity of the system increased, the ratio of the total volume to the volume of the dispersed phase becomes larger; hence an increase in the association of the dispersed phase with the dispersion medium, generally called swelling, is indicated by an increase in the viscosity.

The influence of electrolyte addition to gelatin solutions were studied and demonstrated in a set of curves by P. von. Schroeder.[1] His curves show that the sulfates in general cause an increase in the viscosity, but that the chlorides and nitrates of the alkali metals decrease the viscosity of a gelatin solution. The addition of sulfates, however, were carried only to 0.5 *N* concentration and the viscosity determinations were made one hour after the mixing of the solutions.

In the series of solution upon which the experiments herein reported are made, the concentration of the salt added was increased to normal concentration. Also the determinations of the viscosities were made after different intervals of time and these differences in the procedure gave interesting results that were not brought out by Schroeder.

For the determination of the viscosity of the series of gelatin solutions with increasing additions of zinc sulfate a viscosimeter as described by Ostwald[2] was employed. The temperature of the bath in the thermostat was, as in all other cases, very near 25°. The time of outflow and the relative viscosity, taking the viscosity of pure water at 25° as unity, are given in Table V. These results are also plotted in Fig. 1, Curve 5, which shows that the viscosity and consequently the degree of hydration are decreased when the additions of zinc sulfate approach the point where precipitation begins, *i. e.*, at concentrations higher than 0.5 *N*. The plot of the data obtained, after different lengths of time of standing of the solutions after mixing, brings out the fact that the shape of the curve changes consid-

TABLE V.—CHANGES OF VISCOSITY OF 1% GELATIN SOLUTIONS WITH INCREASING CONCENTRATIONS OF ZINC SULFATE.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Shortly after mixing.	Standing 24 hours.	Standing 48 hours.	Standing 96 hours.
1% Gel.	.....	......	2.38	2.44	2.52	2.46
2	0.005	0.0035	2.39	....	2.80	2.78
3	0.01	0.0063	2.41	2.70	3.07	2.95
4	0.025	0.0142	2.43	2.90	3.50	3.40
5	0.05	0.0234	2.48	3.16	3.77	3.68
6	0.075	0.0326	2.50	3.30	3.86	3.80
7	0.10	0.0397	2.53	3.37	4.00	3.95
8	0.25	0.0803	2.60	3.55	4.20	4.12
9	0.50	0.141	2.75	3.45	4.10	4.10
10	0.75	0.185	3.00	3.25	3.77	3.68

[a] *Loc. cit.*

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[1] *Z. physik. Chem.*, **45**, 75 (1903).

[2] "Phys. Chem. Mess.," p. 232, 3rd Ed.

erably with the time. Thus from an upward bent curve obtained immediately after the mixing of the solutions, this curve changes to a downward-bending curve upon standing for 24 and 48 hours. There is also a considerable increase in the viscosity of the various solutions except in those which have the larger additions of the zinc sulfate. The results obtained 96 hours after the mixing of the solutions are practically identical with the 48-hours results.

These facts plainly indicate that during that time of standing there was going on a readjustment of the equilibrium of hydration or swelling of the gelatin particles in the solutions. This fact is also made more probable by the increasing clarification of the solutions upon standing in the center region of the series. These differences in clearness and turbidity of the solutions were hardly visible immediately after the mixing of the solutions but were most distinct after about 48 hours standing.

The results revealed by viscosity determinations show that there is a maximum of hydration or swelling of the gelatin particles in the region of the series corresponding to the addition of about 0.28 molar zinc sulfate to 1% gelatin solution.

The Swelling of Gelatin as Influenced by Increasing Concentrations of Electrolyte.

Closely following the viscosity measurements should be cited experiments which show how much dry pieces of gelatin swell when submerged in solutions of zinc sulfate in concentrations as used throughout this investigation. If viscosity measurements indicate the extent of swelling of the gelatin particles in the solutions, in other words, if the assumptions upon which the 2 viscosity formulas are based are correct, then we should expect the experiments on swelling to give results that are similar to those obtained by viscosity measurements.

The relative amounts of water adsorbed by dry pieces of gelatin when placed for identical lengths of time[1] into zinc sulfate solutions were determined by cutting from one sheet of gelatin equal pieces and making their weights as nearly equal as possible; these sheets were placed into the previously prepared solutions, which were kept in the thermostat until their temperature was 25°. After remaining in these solutions for exactly 10 minutes the pieces of gelatin were removed, blotted between hard pieces of filter paper and weighed. The increases in weight obtained are recorded in Table VI and the results are plotted in Fig. I, Curve 6, as usual against the concentrations of the solutions into which the gelatin foils were placed.

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[1] The correct length of time to produce the full amount of swelling was determined by experiment, so that the results given are not proportional to swelling velocities but to the maximum extent of swelling in the solutions.

TABLE VI.—WEIGHT OF WATER ADSORBED BY PIECES OF DRY GELATIN PLACED INTO SOLUTIONS OF ZINC SULFATE OF INCREASING CONCENTRATIONS.

Solution No.	$ZnSO_4$ added molar.	Conc. of free ions.[a]	Increase in weight. G.
Water	.....	......	0.346
2	0.005	0.0035	0.350
3	0.01	po.0063	0.362
4	0.025	0.0142	0.388
5	0.05	0.0234	0.411
6	0.075	0.0326	0.425
7	0.10	0.0397	0.438
8	0.25	0.0803	0.443
9	0.50	0.141	0.400
10	0.75	0.185	0.331
11	1.00	0.229	0.254

[a] *Loc. cit.*

The curve obtained is strikingly similar to the curve obtained by viscosity measurements. The last point corresponding to molar concentration of zinc sulfate shows that there was less water adsorbed from this solution than from the pure solvent without the addition of zinc sulfate. From this fact it can be inferred that the precipitation of gelatin from its solution by strong solutions of salts, especially of polyvalent salts, is due to dehydration of the gelatin particles, osmotic withdrawal of solvent from the gelatin particles beyond the point to which they normally hydrate in the pure solvent.

Summary of Conclusions from the Experimental Work.

The arrangement of the curves on page 2148 shows the results of the various experimental series and the various changes taking place when increasing concentrations of electrolyte are added to uniform solutions of gelatin. Considering the sign of the electrical charge of the colloidal particles, these curves can be divided into 3 vertical columns. A vertical line at concentration 0.28 of the electrolyte added indicates the condition when the colloidal particles are neutral and possess no charge. To the left of this line, when smaller concentrations of electrolyte were added, the colloidal particles are positively charged; to the right of the line, when larger than 0.28 concentration are added, the colloidal particles are negatively charged.

A—In the zone corresponding to small additions of electrolyte.

(1) The migration velocity of the anions is zero and the velocity of the cations is unity, so that in electrolysis the cations alone seem to carry the current across the electrolyte.

(2) The anions alone are adsorbed, and only near the point where the colloid is neutral, are a small quantity of cations adsorbed by the colloid.

(3) The colloidal particles migrate to the negative pole, which indicates that they are positively charged.

(4) The viscosity or internal friction increases as the charge of the particles approaches the zero point.

(5) The rate of swelling of gelatin increases as the concentration of electrolyte approaches 0.28 molar.

B—In the zone when the concentration of electrolyte added is 0.28 molar.

(1) The migration velocity of the anions is zero and that of the cations is exactly unity. The electrolytic deposit on the cathode is smooth and pure.

(2) The anions and the cations are being adsorbed by the colloid in proportion to their mobilities; as the anions generally migrate faster than the cations there is adsorption of a larger quantity of anions than cations.

(3) The velocity of motion of the colloidal particles in the electrostatic field is zero.

(4) The viscosity of internal friction is a maximum.

(5) The rate of swelling of gelatin is a maximum.

C—In the zone when larger additions of electrolyte are made.

(1) The migration velocity of the anions is increased as the electrolyte additions are increased and the velocity of the cations is decreased in the same proportion.

(2) The adsorption of positive and negative ions continues until the particles assume a negative charge when the cations are then being adsorbed in larger proportions.

(3) The particles migrate to the anode hence are negatively charged.

(4) The viscosity of the solutions gradually decreases as the charge of the particles increases.

(5) The rate of swelling of gelatin decreases as the concentration of the electrolyte added increases. At molar concentration of zinc sulfate gelatin is precipitated.

WAPPLER ELECTRIC CO.
LONG ISLAND CITY, N. Y.

THE SALT ERROR OF CRESOL RED.[1]

BY ROGER C. WELLS.

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In the course of a study of the water of Chesapeake Bay now being made by the U. S. Geological Survey in coöperation with the U. S. Bureau of Fisheries, it was desired to determine the hydrogen ion concentration of the water taken directly from the bay at various points, and for this purpose it was decided to use the colorimetric method involving comparison with standard tubes. As the salinity of the water of the bay is considerably lower than that of sea water it appeared necessary to make new determinations of the salt error of the indicator, cresol red, for the

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[1] Published by permission of the Director, United States Geological Survey.