little extent therefore be attributed to the fact that the volume of reaction mixture is reduced by the presence of the neutral salt. This in in agree-ment with the conclusions arrived at by McBain and Coleman,[12] who have shown in a number of cases that if the catalytic effect of the un-dissociated acid formed in the presence of neutral salts be taken into ac-count the velocities of inversion are within 4% of the predicted rates.

Summary.

The addition of an inert substance, to keep the concentration of water and cane sugar constant while varying the concentration of the acid, has no appreciable effect in producing a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity of cane sugar.

The increase in velocity of cane sugar hydrolysis produced by a strong acid in the presence of a neutral salt of that acid, over the velocity pro-duced by that acid alone, can to very little extent be attributed to the fact that the volume of the reaction is reduced by the presence of the salt.

On the assumption that both the undissociated and dissociated forms of an acid are catalytically active in cane sugar inversion, the values of K_i for the hydrogen ion from hydrochloric, hydrobromic and nitric acids have the same value $(K_i = 0.234)$; the corresponding value for sulfuric acid is considerably lower $(K_i = 0.144)$.

VANCOUVER, B. C.

THE VISCOSITY OF GELATIN SOLS.

BY ROBERT H. BOGUE.[1]

Introduction.

A mathematical expression for the viscosity of two-phase systems was developed by A. Einstein[2] in 1906 and generalized by E. Hatschek[3] in 1910–1913. According to the latter investigator, the viscosity of all two-phase systems may fall in one of two possible conditions. So long as the particles of dispersed phase occupy so small a proportion of the total volume of the system that they do not touch each other, the increase of vis-cosity should be a linear function of the concentration only and indepen-dent of the size of the particles. In the derivation of his formula, the particles of dispersed phase are assumed to be spherical, undeformable, and

[12] McBain and Coleman, *J. Chem. Soc.*, [II] 105, 1523 (1914).

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[2] A. Einstein, *Ann. Physik.*, 19, 289 (1906).

[3] E. Hatschek, *Kolloid, Z.*, 7, 301 (1910); 8, 34 (1911); *Trans. Faraday Soc.*, 9, 80 (1913).

of smooth surface. These conditions are probably seldom attained, but a reasonable conformity to his formula has been found in the case of gamboge and mastic by Bancelin,[4] and in the case of starch by Harrison.[5]

Hatschek writes the equation,

$$\eta' = \eta \left(1 + 4.5 f \right) \tag{1}$$

when η' is the viscosity of the system, η the viscosity coefficient of the liquid or continuous phase, and f the ratio of the volume of the dispersed phase to the total volume of the system. The constant 4.5 has been given several different values, however, by different observers. Einstein first gave it a value of unity, and later changed it to 2.5. Bancelin found it to be 2.9.

Just as soon, however, as the ratio of the volume of the dispersed phase to the total volume of the system becomes so great that the particles touch each other, then the viscosity-concentration curve no longer remains linear, but becomes curvilinear. (The volume of the dispersed phase, as here used, includes the sum of the volume of the dispersed particles *per se* and the volume of the liquid or dispersion medium which has become associated with the dispersed particles in a solvated or hydrated condition.) The volume of the dispersed phase at the moment when the above condition is attained will be 74.04% of the total volume, according to Hatschek's calculations, and as the concentration becomes greater, the previously spherical particles will, in the case of an emulsion and an emulsoid at least, become dodecahedral; and if the system is now subjected to shear it will quickly assume a position in which such shear will take place entirely in the continuous phase. Under these new conditions, the viscosity is expressed by

$$\eta = (\sqrt[3]{A} \ / \ \sqrt[3]{A-1}) \tag{2}$$

in which η is the coefficient of viscosity of the system, and A is the ratio of the total volume of the system to the volume of the dispersed phase. As we are unable directly to measure the volume of the dispersed phase of an emulsoid, we may obtain the value of A by a rearrangement of Equation 2; thus,

$$A = (\eta / (\eta - 1))^3, \tag{3}$$

and if the amount of dispersed substance is expressed in percentage, *e. g.*, total volume divided by dispersed weight, then this value, which Hatschek calls A' should bear a constant ratio to A which is total volume divided by the dispersed volume, or $A' / A = K$.

[4] Bancelin, *Kolloid Z.*, 9, 154 (1911).
[5] Harrison, *J. Soc. Dyers Colorists*, 27, 84 (1911).

This has been tested by Hatschek using the data of Botazzi and d'Errico[6] upon glycogen sol, and of Chick and Martin[7] upon sodium caseinogenate sol. Hatschek finds the value of K to be nearly constant at about 2.1 between the concentrations of 30 and 45 in the glycogen sol, and at about 9.5 between the concentrations of 6.04 and 9.39 in the case of the casein sol.

As expressions of the type developed by Hatschek are fundamental and must inevitably lead to a better understanding of the complex conditions obtaining in colloid sols, it becomes desirable that experimental data be accumulated which will tend either to confirm the hypotheses upon which the formulas are based, or to indicate points which will require mathematical revision. With this end in view, the following experiments have been conducted upon gelatin sols.

Experimental.

A high grade of gelatin was used in concentrations varying by small increments from 0.01 to 30.00%. In order that comprehensive data might be obtained the viscosity of gelatin in five different conditions was studied. In Series 1 the gelatin was dissolved in distilled water giving a solution whose hydrogen-ion value in 1% concentration was 1.5×10^{-6}, so that the solute was essentially calcium gelatinate. In Series 2, an iso-electric gelatin was obtained by screening gelatin powder, taking that portion which passed a 40-mesh screen but was retained by one of 60 mesh, soaking it for an hour in hydrochloric acid of 0.0078 N concentration, filtering, and washing several times with distilled water. A 1% solution had a hydrogen-ion concentration of 2×10^{-5}, the value of gelatin at its iso-electric point. Series 3 was treated in a similar way to the preceding, except that the acid used was of 0.031 N concentration. It had previously been found that such treatment resulted in the maximum of swelling and of viscosity, while at the iso-electric point these properties possessed their minimum values. Series 4 and 5 were treated similarly to Series 2 and 3 respectively, except that the acids in which they were allowed to soak were not removed, but the gelatin was dissolved and diluted to the desired concentration in the presence of the large excess of acid.

The temperature selected for all determinations was fixed at 35° in order that no complications due to an equilibrium between what Smith[8] calls sol form A and gel form B should arise. At 35° the gelatin is, according to Smith, entirely in the condition of the sol form A. The tempera-ture was maintained constant by the immersion of all samples and appa-

[6] Botazzi and d'Errico, *Pfluger's Arch.*, 115, 359 (1906).

[7] Chick and Martin, *Kolloid Z.*, 11, 102 (1912).

[8] C. R. Smith, THIS JOURNAL, 41, 135 (1919); *J. Ind. Eng. Chem.*, 12, 878 (1920).

ratus in a thermostat, the average fluctuation of which was $\pm 0.05°$ at $35°$.

All viscosity measurements, with three exceptions, were made by the use of an Ostwald capillary viscosimeter, employing 3 cc. for each determination. Duplicate runs were made in each case, and the average used in the calculations. The variation between duplicate measurements was rarely more than 0.2 to 0.3 second, even in the more viscid concentrations. The viscosity of Expts. 23, 24 and 25 of Series 1 was measured by the use of a MacMichael viscosimeter.

The data obtained are given, in part, in the following tables. The first column of Table I shows the percentage concentration, C, of the gelatin sol; in Col. 2 is given the coefficient of viscosity, water being taken as unity; in Col. 3 the values calculated for A by Equation 3; in Col. 4 the value for A', e. g., 100 divided by dispersed weight in percentage; and in Col. 5 the ratio of A'/A. The remaining two columns will be discussed later.

TABLE I.

SERIES 1.

NORMAL GELATIN, 1.5×10^{-6}.

$C.$	$\eta/\eta_w.$	$A.$	$A'.$	$K.$	$V_m.$	$k_s.$
0.05	1.023	....	....	....	....	....
0.10	1.045	....	....	....	....	....
0.20	1.073	....	....	....	....	....
0.40	1.124	....	....	....	....	....
0.60	1.211	....	....	....	....	....
0.80	1.328	....	....	....	....	....
1.00	1.404	42.2	100.0	2.37	....	....
1.50	1.522	24.9	66.66	2.68	....	....
2.00	1.818	11.0	50.00	4.54	....	....
2.50	2.100	7.00	40.00	5.72	....	....
3.00	2.400	5.08	33.33	6.55	....	....
3.50	2.740	3.94	28.58	7.25	....	....
4.00	3.078	3.27	25.00	7.64	....	....
4.50	3.475	2.78	22.12	7.95	64.2	8.46
5.00	4.125	2.32	20.00	8.62	56.8	8.97
6.00	5.970	1.74	16.66	9.57	42.6	9.57
7.00	7.430	1.56	14.28	9.16	35.8	9.36
8.00	9.550	1.40	12.50	8.92	28.6	9.36
9.00	11.82	1.31	11.11	8.48	23.6	9.11
10.00	15.62	1.23	10.00	8.13	18.7	8.97
11.00	19.40	1.18	9.09	7.71	15.1	8.73
12.00	23.45	1.15	8.33	7.24	13.1	8.38
15.00	29.00	1.12	6.66	5.95	10.8	7.23
20.00	63.00	1.08	5.00	4.63	7.4	6.17
30.00	800.00	1.013	3.33	3.28	1.6	5.60

In Table II are shown the values obtained for K and for k_s for the five series.

<div align="center">TABLE II.</div>

<div align="center">COMPARISON OF VALUES OF K AND k_s FOR THE FIVE SERIES.</div>

Concentration.	Normal gelatin. $C_{\mathrm{H}}+=1.5\times10^{-6}$		Iso-electric gelatin. $C_{\mathrm{H}}+=2\times10^{-5}$		Gelatin chloride. $C_{\mathrm{H}}+=3.1\times10^{-4}$		Made up in 0.0078N HCl.		Made up in 0.031N HCl.	
	K.	k_s.	K.	k_s.	K.	k_s.	K.	k_s.	K.	k_s.
2.00	....	....	....	....	10.10	10.34	....	....	....	....
2.50	....	....	....	....	10.52	10.64	....	....	....	....
3.00	....	....	....	....	10.96	10.96	....	....	....	....
3.50	....	....	....	....	10.85	10.96	....	....	7.88	8.70
4.00	....	....	7.18	7.98	10.72	10.94	8.06	8.79	8.20	8.92
4.50	7.95	8.46	7.88	8.55	10.57	10.89	8.38	9.00	8.70	9.29
5.00	8.62	8.97	8.41	8.93	10.47	10.91	8.78	9.26	8.74	9.23
6.00	9.57	9.57	8.76	9.03	10.27	10.96	8.86	9.12	8.86	9.12
7.00	9.16	9.36	8.92	8.92	9.64	10.51	8.92	8.92	8.92	8.92
8.00	8.92	9.36	8.56	8.75	9.32	10.44	8.75	8.99	8.68	8.90
9.00	8.48	9.11	8.18	8.55	8.82	10.14	8.42	8.87	8.42	8.87
10.00	8.13	8.97	7.88	8.46	8.40	9.94	8.66	9.63	8.00	8.63
11.00	7.71	8.73	7.57	8.37	7.97	9.72				
12.00	7.24	8.38	7.18	8.12	7.56	9.52				

In Figs. 1 and 2 the coefficient of viscosity, η/η_w, is plotted on the ordinate axis against the percentage of gelatin concentration on the abscissa
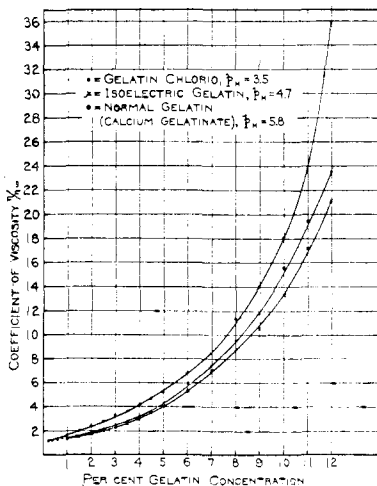

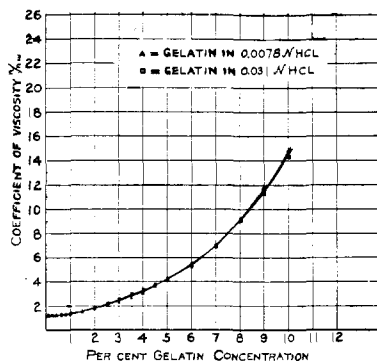Fig. 1.—Relation of viscosity to concentration in gelatin solutions.

Fig. 2—Relation of viscosity to concentration in gelatin solutions.

for the five series. In Fig. 3 the values of K are plotted against gelatin concentration.

Discussion.

The data presented above reveal several points of interest, the most important being the failure to obtain a real constant for the ratio of A'/A. In each of the five series studied the value of this ratio rises to a maximum

with increasing concentration, and then as regularly, but more slowly, drops. Within a range of several per cent. the value of K varies but little, but the fact that, although the variation is small, it is nevertheless perfectly regular (except in special cases as noted below) can be interpreted in no other way than that a real constant is not obtained under the conditions of the experiment, and the variation may not be regarded as an experimental error.

In this connection it must be pointed out that in the calculations of Hatschek upon work reported by Botazzi and d'Errico on glycogen sols, and by Chick and Martin upon casein sols, the same regular rise to a maximum, in the value of K, followed by a similar regular drop, is observed. Hatschek makes no mention of this fact, however, and apparently regards the values attained as *constant* in the customary

Fig. 3.—Variation in K with concentration of gelatin.

sense of the term. In Series 1 it will be observed that on carrying the concentration of the gelatin up to 30% the value of K had dropped from a maximum of 9.57 to 3.28. In experiments upon cellulose nitrate dissolved in 30% camphor-alcohol Sherrick[9] found similar results; e. g., at a concentration of 2.54% his value for K was 34.64, and on increasing the concentration above that value the value of K also dropped as follows.

Concentration g. per 100 cc.	Absolute viscosity of sol.	Absolute viscosity of solvent.	A.	A'.	A'/A.	Percentage volume of sol. occupied by solvated disperse phase.
2.54	23.03	0.96	1.1364	39.37	34.64	88.00
4.00	205.21	0.96	1.0142	25.00	24.65	98.6
7.50	565.65	0.96	1.0050	13.33	13.27	99.5
10.00	960.95	0.96	1.0030	10.00	9.97	99.7
12.00	1372.30	0.96	1.0020	8.33	8.31	99.8
15.00	3201.00	0.96	1.0010	6.666	6.66	99.9

The value of K may be analyzed as follows.

$$\frac{A'}{A} = \frac{\text{total volume}}{\text{dispersed weight}} \times \frac{\text{dispersed volume}}{\text{total volume}} = \frac{\text{dispersed volume}}{\text{dispersed weight}}$$

In other words K represents the volume occupied by unit weight of the dispersed phase. At low concentrations the structure upon which the formula is based is not present and accordingly the above statement

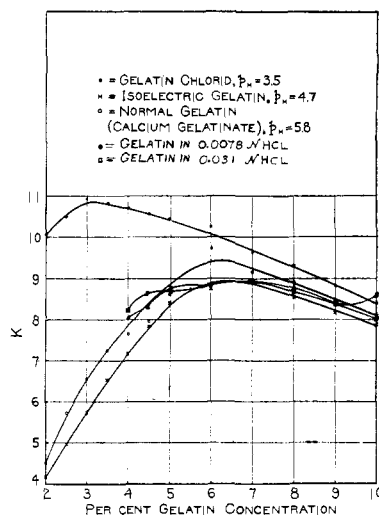[9] J. L. Sherrick (Mellon Institute); personal communication.

may be applied only to more concentrated sols, but as soon as the necessary concentration is reached, it would be expected that the formula would accurately represent the result until such an amount of dispersed phase was present that there no longer was sufficient water, or other dispersing medium, present to allow the solvate action to proceed to its maximum. As soon as that concentration was reached the volume occupied by unit weight of dispersed phase (K) would thereafter decrease with increasing concentration. But an examination of the data shows that the total volume of dispersed phase ($K \times C$) has in no case except in the last experiment listed in Series 1 reached a value approaching the total volume of the system. Indeed, in the present experiment the maximum value of K is reached when the total volume of dispersed phase is only 32.8% of the total volume of the system in the case of the gelatin chloride, and 57.4 and 62.4% respectively in the other series. In the cases of the glycogen and casein sols previously mentioned the maximum value of K is obtained when the volumes of dispersed phase are 77.4 and 68.6% respectively of the volumes of the systems. In every case cited the value of K drops regularly from this point. Only in the experiments of Sherrick may this drop be explained as due to an actual insufficiency of dispersing medium for in his determinations the volume of dispersed phase is already 88.00% at the lowest concentration which he employed, and very quickly rises above 99%.

It is, therefore, pertinent to raise the question: Why does the volume occupied by unit weight of dispersed phase decrease with increasing concentration after attaining a definite maximum? (We are admitting the validity of Hatschek's postulations by which he formulated his equations, and therefore assume the value A'/A to express correctly the volume per unit weight of dispersed phase.) Two possible causes may bring about this decrease in volume; the increasing surface tension of the dispersion medium, or an actual reversal of phase. From a consideration of the laws of surface tension it becomes evident that as the number of particles of dispersed phase (the concentration) increases, the film of liquid separating them must become ever thinner and thinner in order to maintain its continuity. As this process continues the free surface of the dispersion medium becomes ever greater, and this may take place only at an expenditure of energy, e. g., it is opposed by the surface tension of the liquid, and the greater the surface under stress, the greater will be the force opposing further increase in free surface. We may regard this force as entering into competition for the liquid against the solvate potential of the dispersed particles. An equilibrium must therefore be attained between these two forces at any given concentration.

Surface tension (of dispersion medium) $\rightleftharpoons$ Solvation potential (of dispersed phase).

An excess of liquid will increase the solvation potential of the dis-

persed phase and an excess of dispersed particles will increase the surface energy of the dispersion medium.

The extent to which the surface tension may influence the solvation, and consequently the volume occupied by unit weight of dispersed phase, is shown to be a function of the percentage volume of the dispersion medium and if we may regard that volume of dispersion medium at which the dispersed phase reaches its maximum volume per unit weight as the point of neutrality in the above equation, the two forces there being equal, then the increasing effect of the surface tension is found to follow very nearly the empirical expression,

$$\sqrt[3]{V^\circ_m} - \sqrt[3]{V_m} = s, \tag{4}$$

where V°_m is the volume of dispersion medium when A'/A is at its maximum, V_m is the volume of the dispersion medium at any other concentration, and s is the decrease in volume per unit weight of dispersed phase at the concentration V_m. Then

$$K \pm s = k_s, \tag{5}$$

where k_s is a constant corrected for surface tension. s is added at concentrations of dispersed phase greater than that at V°_m, and subtracted at the lower concentrations. In Table I, Col. 6 shows the value of V_m and Col. 7 the value of k_s. The values of K and k_s for the five series are shown in Table II. In Fig. 4 k_s is plotted against gelatin concentration.

In the case of the gelatin dissolved in $0.0078\ N$ and in $0.031\ N$ hydrochloric acid the uniform variations and consistency of direction which characterize the curves for the gelatin chloride, the iso-electric gelatin, and the calcium gelatinate, are not obtained. This is true for both the K and the k_s concentration curves. The reason for this difference in behavior of these two gelatins is not obvious, but it undoubtedly is connected with the presence of the free acid in the solution, and the variation, by the alteration in gelatin concentration, of the hydrogen-ion concentration of the system. Further study will be made of these special cases.

Fig. 4.—Variation in k_s with concentration of gelatin.

If the process of stretching out the thin film of dispersion medium by increasing concentration is continued beyond a certain point, this film
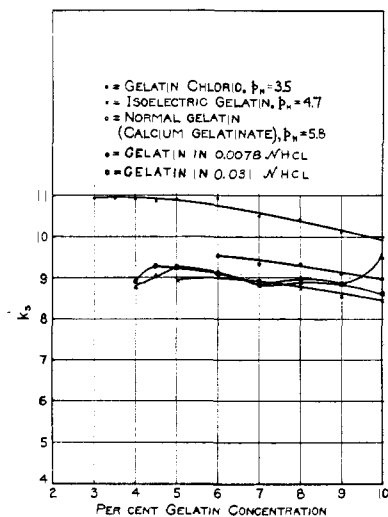
must break and cease to be continuous.   When this happens there will probably follow a reversal of phase. The previously dispersed phase will become continuous, and the former dispersion medium will become dispersed. When this happens the formula of Hatschek would no longer hold good, as the system has suffered an abrupt change not accounted for in his equations. This fact might also explain the failure of Hatschek's K to remain constant, but it would scarcely be expected that a reversal of phase would occur at the low concentrations where the value of K begins to decline in gelatin sols.

Another point which is well brought out in the present work, and is made manifest by a comparison of the several columns in Table II, and by the curves in Fig. 1, is the wide variation in the viscosity of gelatin in different states of hydrogen-ion concentration, and in the volume occupied by unit weight of gelatin in these different states.   As shown in Table II, the maximum volume per unit weight of gelatin chloride, at a hydrogen-ion concentration of 3.1×10^{-4} is 10.96, and is attained at a gelatin concentration of 3%, while in the case of iso-electric gelatin the maximum volume per unit weight is only 8.92 and is not reached until a concentration of 7% of gelatin is present.   The untreated gelatin, which is calcium gelatinate of a hydrogen-ion concentration of 1.5×10^{-6}, attains a maximum of 9.57 at a concentration of 6 %.   It is especially interesting that in the case of the gelatin which is treated with acid, and the excess of acid *not* removed, the maximum volume reached, and the concentration of gelatin at that point, are identical with those of the iso-electric gelatin.   In other words an excess of acid retards solvation in the sol state.   That viscosity and solvation run parallel is evidenced by the fact that the higher the viscosity, the higher also is the value of K.

Summary.

Experiments have been carried out upon gelatin sols to determine accurately the relation between viscosity and concentration. The data obtained have been applied to Hatschek's formula for the viscosity of emulsoids, and it is shown that the value A'/A, representing the volume occupied per unit weight of dispersed phase, is not a constant with varying concentration, but that this value rises regularly to a maximum, and thereafter regularly declines with increasing concentration. This behavior is noted also to exist in the cases of other colloids. A tentative explanation is presented based upon the effect which increasing concentrations of dispersed phase will have upon the surface tension of the dispersion medium.   Assuming the equilibrium,

surface tension $\rightleftharpoons$ solvation potential,

an empirical relation is developed which, with a fair degree of accuracy, defines the equilibrium.   At very high concentrations a reversal of phase

probably occurs, at which point no expressions yet developed adequately represent the relations involved.

A high degree of solvation is shown to be indicated by a high coefficient of viscosity, e. g., solvation and viscosity are parallel functions.

Iso-electric gelatin at a hydrogen-ion concentration of 2×10^{-5} is shown to have the lowest viscosity and the lowest degree of solvation, gelatin chloride at a hydrogen-ion concentration of 3.1×10^{-4} the highest, and calcium gelatinate at a hydrogen-ion concentration of 2.5×10^{-6} is intermediate.

If an excess of acid is allowed to remain in the gelatin solution, even though the acid be of very low concentration, the viscosity and degree of solvation will be retarded.[10]

PITTSBURGH, PA.

[10] In comment upon the above paper Dr. Emil Hatschek has written the author as follows.

"I think that my method of attack is correct in principle, but it involves several assumptions which go perhaps too far in the direction of simplifying the phenomena. One is obviously the assumption of spherical particles which, on crowding, become simple polyhedra. The gelatin molecule or aggregate is probably far from being of so simple a shape. If we had some information regarding it, the matter could probably be dealt with again, but, in the absence of such information it would be a fruitless mathematical exercise to investigate nonhomogeneous assemblages. That the formula applies, on the other hand, to deformable particles of a shape far different from the simple spherical, but still very symmetrical, is proved by the surprising closeness with which it fits red blood corpuscles. (E. Hatschek, *Kolloid Z.*, **27**, 163 (1920).)

"The second point is the inconstancy of the degree of hydration or, generally, solvation. I had noticed this, in trying to fit the formula to rubber, etc., sols, but have not published anything in that respect. The simplest explanation seems to me this: the formula assumes that the continuous phase is *pure dispersion medium*, and that all the colloid is in the disperse phase, associated with some dispersion medium. Now this is probably also an undue simplification of the conditions. It is probable that the dispersion medium also contains some of the colloid, and it seems to me at least possible that the proportion may change, *i. e.*, the ratio, colloid in disperse phase: colloid in continuous phase, may become smaller with increasing concentration.

"Both suggestions you make are very interesting. The interfacial tension between the two phases, being due only to the difference in concentration, can be very small only, but that would not prevent its defining an equilibrium. The suggestion that a reversal of phases may take place is ingenious, but one would like to have some further evidence to support it. It seems to me it would almost certainly entail a break in the viscosity-concentration curve, of which there is no indication. There is also the possibility that the hydration may really decrease at higher concentration, as it does with some true solutes. I think a clue to the distribution of water may perhaps be afforded by the solubility of gases, or liquids like ether, in gelatin sols—but the results published so far, particularly by A. Findlay, seem very difficult of interpretation."