lowering Tube P. If it is necessary to stir a viscous liquid a metronome is useless because, making contact only momentarily, the stirrer would not have time to start moving. Suppose for instance that for a definite current it requires 10 seconds for the magnet to draw the stirrer up the proper distance and 20 seconds for the stirrer to drop back again due to its own weight. The natural period of the stirrer is then 30 seconds and the control is first of all regulated by means of Tap 2 leading to the suction pump to give this period, *i. e.*, go through a complete cycle every half minute. Then Rod P is adjusted so that S is below level *c* about a third of the distance between levels *e* and *g*. Then the current will be on one-third of the time, *i. e.*, 10 seconds, and off two-thirds of the time, *i. e.*, 20 seconds. Another advantage is to be found in the fact that where large currents, say 10 amperes under a voltage of 110 or more volts, are used no relay is required. At the moment of break there is a small spark between the mercury left in cup S and the column of mercury moving downwards. But this spark occurs in the water which, as was mentioned above covers the mercury in O, and the only effect is that in time a minute amount of mercury becomes colloidal; this colloidal mercury is reabsorbed and does not accumulate. An apparatus as described above was in continuous use for several months without requiring any readjustment or addition of fresh mercury.

MONTREAL, CANADA.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

COMPRESSIBILITY OF AQUEOUS SOLUTIONS, ESPECIALLY OF URETHANE, AND THE POLYMERIZATION OF WATER.[1]

BY THEODORE W. RICHARDS AND SVEN PALITZSCH.

Received October 29, 1918.

In previous papers from this laboratory[2] a marked relation between compressibility and surface tension, as far as certain pure liquids are concerned, has been pointed out. This relation may be expressed approximately by the empirical equation $\beta.\gamma^{4/3} = k$, where β represents the compressibility and γ the surface tension. In mixtures of two liquids, however, the conditions are less simple and the relation between surface

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[1] The measurements in the present and a following paper were carried out at the Wolcott Gibbs Memorial Laboratory during the winter of 1915–16, when S. Palitzsch was at work at Harvard University as Fellow of the American Scandinavian Foundation, having leave from Carlsberg Laboratorium, Köbenhavn; they may be considered as the beginning of a research to be carried out in the future on the volume condition in solution of organic substances, especially those of biochemical significance. Responsibility for the theoretical part of the paper must be borne entirely by the senior author, because the present difficulty of communication has rendered the complete interchange of views impracticable.

[2] THIS JOURNAL, 30, 11 (1908); *Z. physik. Chem.*, 61, 451 (1908).

tension and compressibility more obscure, especially if water is one of the two. On account of the very complicated internal condition of these mixtures, their behavior could not reasonably be expressed in any formula as simple as that holding true for unmixed substances.[1] Nevertheless they offer a problem of considerable interest.

As early as 1886 Röntgen and Schneider[2] measured and compared the two properties of many aqueous solutions of inorganic salts, which showed without exception a higher surface tension and a lower compressibility than pure water.[3] They found a significant dependence without being able to express it by any equation. In the case of cane sugar, which in aqueous solution decreases the compressibility,[4] measurements of surface tension showed values sometimes greater, sometimes less than pure water.[5] The very few measurements published about colloidal solutions indicate that both their surface tension and their compressibility decrease at the same time. (Compare the following paper.)

Aqueous solutions of two solid organic acids, namely, mono- and trichloroacetic acid, were found by Drucker[6] to have a much smaller surface tension than water, normally decreasing with the concentration, whereas the compressibility at first decreases and then increases with rising concentration. In this latter respect these solutions resemble several mixtures of liquids: ethyl alcohol and water; acetic acid and water; and dichloroacetic acid and water. Whether or not this peculiarity corresponds to irregularities of the other properties of the involved substances was not investigated. Definite conclusions are not easily drawn from this collection of apparently conflicting data.

In interpreting results concerning single components, one of us has shown in several publications that the compressibility of a pure substance is probably in part contingent upon the internal pressure—the external pressure required to compress the substance to a given extent being greater the more the molecules are previously compressed by molecular pressure. The more complicated the system, the less likely would this general rule be to hold true. On the other hand, Tammann[7] has denied

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[1] A. Ritzel, *Z. physik. Chem.*, **60**, 319 (1907).

[2] W. C. Röntgen and J. Schneider, *Wied. Ann. Phys. Chem.*, **29**, 165 (1886).

[3] Max Schumann observed, it is true, a compressibility greater than that of water dealing with very dilute aqueous solutions of potassium, calcium, ammonium, and strontium chlorides (*Ibid.*, **31**, 14 (1887), but Röntgen and Schneider (*Ibid.*, **31**, 1000 (1887)) thoroughly repeating his experiments, could not verify his conclusion.

[4] G. de Metz, *Ibid.*, **41**, 663 (1890).

[5] G. Quincke, *Ibid.*, **35**, 582 (1888), Grunmach, *Ibid.*, [4] **3**, 660 (1900); F. Plato, *Wissenschaftl. Abh. d. Kaiserl. Normal-Eichungskommission*, 2 Heft, 123, 1900 (quoted from G. Wiegner, *Kolloid-Z.*, **8**, 127 (1911); J. Traube, *Ber.*, **42**, 86 (1909).

[6] K. Drucker, *Z. physik. Chem.*, **52**, 641 (1905).

[7] G. Tammann, "Ueber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907, p. 178, Leipzig.

the existence of any relation between the surface tension of solutions and the internal pressure ("Binnendruck" computed from thermal expansion), and W. C. McC. Lewis[1] has found that in aqueous solutions the surface tension and the internal pressure change in the same direction, except with volatile and colloidal solutions. The importance of a decision between the apparently conflicting opinions is emphasized by the fact that a theory based on the relationship between internal pressure and surface tension recently was employed by Traube[2] to explain many different physiological-chemical and physico-chemical effects.

Seeking to obtain more light on these questions, we thought it worth while to study several properties of aqueous solutions of a highly soluble substance, neither dissociated nor associated in aqueous solutions, in order to obtain results as easy to interpret as possible.[3]

The substance employed (urethane, or ethyl carbaminate, NH_2-CO-O-C_2H_5, molecular weight 89.1) was beautifully crystallized, and its solution gave no turbidity with added silver nitrate.[4] The melting point was 48.0 to 48.2°, compared with 48.5°, H. Block;[5] 47.9°, Bridgman;[6] and 48.14°, Tammann.[7] When dissolved it was nearly neutral; tested with litmus paper and phosphate mixtures[8] as liquids of comparison the hydrogen-ion concentration was found to be about 10^{-6}. On account of the volatility of the substance the nitrogen content could not be determined by Kjeldahl's method, nor a possible water content by drying in a vacuum desiccator. This substance dissolves very freely with increase of the total volume, and its solutions possess considerably less surface tension than water. Hence it presents an unusually interesting case, different from most others which have been investigated.

The compressibility of urethane was the chief property to be studied. In order to obtain as much light as possible, rough estimations were made also of density, surface tension, and viscosity.

All the determinations of *compressibility* were carried out under precisely the same conditions and in the same way as usual at the Wolcott Gibbs Memorial Laboratory,[9] of course with the improvements gained in recent years.

The glass piezometer used was precisely like that pictured in the article just mentioned.[10] The pressure was measured 15 minutes after applying

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[1] W. C. McC. Lewis, *Z. physik. Chem.*, **74**, 640 (1910).

[2] J. Traube, *Arch. ges. Physicol. (Pflüger's)*, **132**, 511 (1910); **140**, 109 (1911).

[3] Meldrum and Turner, *J. Chem. Soc.*, **97**, 1805 (1910).

[4] Dumas, *Ann.*, **10**, 284 (1834).

[5] Block, *Z. physik. Chem.*, **78**, 397 (1912).

[6] Bridgman, *Proc. Amer. Acad.*, **51**, 120 (1915).

[7] Tammann, "Kristallisieren und Schmelzen," **1903**, p. 239, Leipzig.

[8] *Compt. rend. trav. lab. Carlsberg*, **8**, 42 (1909).

[9] THIS JOURNAL, **34**, 974 (1912).

[10] *Loc. cit.*, p. 975.

it, the temperature was 20.00°, and compressibilities were calculated as average values for the pressure range from 100 to 300 megabars, as usual[1] with the aid of the equation

$$\beta_{100-300} = \frac{(w - w_1)D}{13.562 \cdot W \cdot 200} + 3.96 \cdot 10^{-6}$$

where β = average compressibility between 100 and 300 megabars.
W = weight of solution used.
D = density of solution at 20°.
w = weight of mercury corresponding to the change of volume caused by the pressure within the range 100 to 300 megabars.
w_1 = the like weight when the whole jacket is filled with mercury. For the piezometer used this weight amounts to 0.1269.
13.562 = density of mercury at 20° under a pressure of 300 megabars.
$3.96 \cdot 10^{-6}$ = the average compressibility of mercury between 100 and 300 megabars.

The difference between the compressibilities of the glass of the piezometer and the mercury was found to be $1.48 \cdot 10^{-6}$ and consequently the compressibility of the glass $3.96 \cdot 10^{-6} - 1.48 \cdot 10^{-6} = 2.48 \cdot 10^{-6}$.

Concentrations in the tables are given as g. urethane per 100 g. water (Table I and Fig. 1), as g.-mol. urethane in 1000 cc. solution (Table II), and as g. urethan in 100 g. solution (Tables I and II). The concentrations, expressed in the last terms, are plotted as abscissas in Fig. 1, where the data for the different proportions are plotted as ordinates.

The solution volume of the dissolved salt is computed from the difference of the volume of the solution and of the water and calculated for one g. urethane. This quantity will be discussed more fully later; the name is due to Bousfield and Lowry.

Surface tension was measured only roughly, because the object was not to obtain exact values, but merely to ascertain how the tension varies with the concentration. Traube's stalagmometer was employed;[2] the number of drops was 52.8, when the apparatus used was filled with water. In Table II are given the number of drops with the several solutions, and the surface tension in dynes/cm., computed from the ratio between the drop number of the water and of the solution, multiplied by the surface tension of water,[3] 72.6 dynes/cm., by the density of the solutions, and finally divided by 0.9982. In these terms the surface tension is plotted as ordinates in Fig. 2.

Viscosity was measured by an Ostwald's viscosimeter of glass. The amount of liquid used in the apparatus was 25 cc. and the time of flow of

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[1] *Loc. cit.*, p. 980.

[2] The much more exact apparatus of J. L. R. Morgan for determining drop weights was not needed in this approximate determination.

[3] Richards and Coombs, THIS JOURNAL, **37**, 1674 (1915).

pure water was 331.5 seconds. A thermostat kept the temperature constant at 20.00° to within 0.02°. In Table II are recorded the times of flow in seconds as well as these values divided by the time of flow of pure water, and, furthermore, this rate multiplied by the ratio of density of the solution to that of water of the same temperature. In Fig. 1 the viscosities, expressed in the last term, are shown graphically.

TABLE I.

Compressibility of Urethane Solutions at 20.0° under a Pressure of 100 to 300 Megabars.

	Concentration.					
	G./100 g. water.	G./100 g. soln.	Density *D*.	Weight of solution used. *W*.	*w*.	Compressibility × 10^6
Water......	0.00	0.00	0.99823	..	..	43.25
A..........	2.28	2.22	1.00105	29.410	3.1970	42.49
B..........	20.88	17.27	1.01945	29.628	2.9024	39.17
C..........	37.22	27.12	1.03050	28.206	2.7236	38.93
D..........	61.63	38.13	1.04125	29.695	2.8618	39.32
E..........	89.63	47.25	1.04950	29.397	2.8653	40.00
F..........	127.35	56.01	1.05620	29.500	2.9221	40.86

TABLE II.

Solution Volume and Surface Tension of Urethane Solutions.

	Concentration.			Surface tension.	
	G./100 g. soln.	Molecular.	Solution volume.	Drop number.	Dynes/cm.
Water..........	0.00	0.00	0.000	52.8	72.6
A..............	2.22	0.25	0.877	65.2	59.0
B..............	17.27	1.98	0.881	87.5	44.7
C..............	27.12	3.14	0.886	96.3	41.1
D..............	38.13	4.46	0.893	101.5	39.4
E..............	47.25	5.57	0.898	103.1	39.1
F..............	56.01	6.66	0.904	105.8	38.6

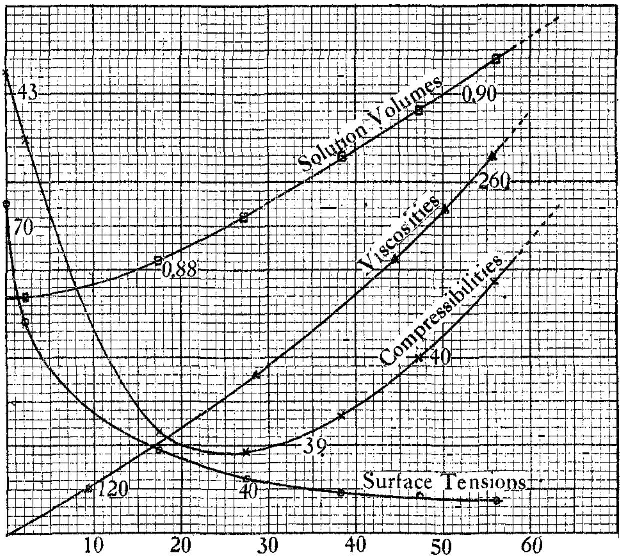
TABLE III.

Viscosity of Urethane Solutions.

Concentration.					
G./100 g. water.	G./100 g. soln.	Density, *d*.	Time of flow seconds: *t*.	$t/t_0.100$.	$t/t_0.d/d_0.100$.
0	0	0.9982	331.5	100.0	100.0
10.03	9.12	1.0096	395.0	119.2	120.6
20.03	16.69	1.0188	454.0	137.0	139.8
40.10	28.62	1.0320	554.5	167.3	173.0
80.21	44.51	1.0470	711.0	214.5	225.0
100.28	50.07	1.0517	777.5	234.5	247.1
125.49	55.65	1.0559	851.5	256.9	271.6

The 4 properties, named in the downward order of appearance on the left of the diagram—compressibility, surface tension, solution volume, and viscosity—are plotted on appropriate scales in the figure.

These 4 curves at first sight appear to have very little relation to one another; but a reasonable interpretation of them is nevertheless quite possible. This interpretation depends upon the remarkable properties of pure water, which obviously enter essentially into every one of the curves (especially on the left-hand branches of them, where water is in excess), and is entirely in accord with the modern view that water is not pure hydrol, but contains also varying amounts of di-hydrol and tri-hydrol according to circumstances.



Compressibilities, Surface Tensions, Viscosities and Solution-Volumes of Urethane Solutions.

Fig. 1.—The abscissas common to all these curves are given at the base of the diagram. The ordinates are easily identified from the tables with the help of the guide numbers placed immediately adjacent to the respective curves. The compressibilities are multiplied by 1,000,000. All of the curves are included in one diagram in order to save space as well as to render comparison convenient.

In view of the fact that most text-books on physical chemistry pass over the polymerization of water with but brief reference, a brief résumé may be apropose. In a work published in 1884 Harold Whiting states very clearly that water on melting must contain "dissolved particles of ice."[1] He points out that in freezing water there may be somewhere between 25% and 38% of dissolved ice, and in boiling water somewhere between 17% and 28%; and that the true expansion of water (apart from the contraction caused by the melting of dissolved ice), instead of being only 4%, is probably from 8 to 10% between 0 and 100°. The notion

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[1] Harold Whiting, "A New Theory of Cohesion Applied to the Thermodynamics of Liquids and Solids," pp. 70–71, Harvard University, Cambridge, Mass., published by W. H. Wheeler. This interesting monograph, which contains much food for thought, seems not to have received the attention which it deserves.

that water contains a dissolved polymer is usually ascribed to Röntgen,[1] although his work followed 8 years after Whiting's. Röntgen's paper elaborated the idea and Sutherland[2] after another 8 years discussed it still further, with the addition of some assumptions of less validity. His quantitative conclusions were nevertheless strikingly similar to Whiting's. Ten years later the Faraday Society conducted a highly interesting symposium on the subject of the constitution of water,[3] at which papers were read by Walden, Guye, Bousfield and Lowry, Sutherland and Nernst. At the end of the discussion, the chairman, Professor James Walker, spoke as follows:

"Often in a discussion of this nature we have great diversity of opinion, but here there seems to be little divergence, although the experimental material which has been worked with is so exceedingly diverse in the different cases. I should think, as a result of this discussion, one will soon find even in the text-books that while ice is trihydrol, and steam monohydrol, liquid water is mostly dihydrol with some trihydrol in it near the freezing point, and a little monohydrol near the boiling point."

The more recent highly interesting work of Bridgman at high pressures[4] entirely supports the conclusion that the abnormality of water is due to polymerization, and the shift of the minimum volume toward lower temperatures with increasing pressure is entirely in accord with the rational assumption that pressure diminishes the proportion of "dissolved ice." At 2500 atmospheres, indeed, so little of the polymer appears to remain that the liquid behaves in a normal way, like other liquids, possessing no minimum of volume (maximum of density) with increasing temperature. The similar effect on coefficient of expansion of dissolving other substances in water (for example in sea-water) is well known. One other circumstance in Bridgman's results is at first puzzling; namely, that the well-known minimum of compressibility at 50° is not thus shifted toward lower temperatures, but with increasing pressure is wiped out where it stands at 50°. As Bridgman says, this fact is not consistent with the assumptions of Röntgen and Sutherland. On the other hand, it seems to us entirely consistent with that of Bousfield and Lowry, which assumes that above 50° monohydrol (possessing like trihydrol a greater bulk than dihydrol) becomes important in concentration. One can hardly doubt that pressure in every instance tends to diminish the quantity of the more bulky form of substance, since this is the verdict of the theorem of Le Chatelier.

The conclusion reached at the meeting of the Faraday Society offers the basis of the explanation of the 4 curves presented in the present paper.

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[1] Röntgen, *Ann.* (*Wiedemann's*), [5] **45**, 91 (1892).

[2] W. Sutherland, *Phil. Mag.*, [5] **1**, 464 (1900).

[3] *Trans. Faraday Soc.*, **6**, 71–123 (1910).

[4] *Proc. Am. Acad.*, **47**, 538 (1912).

Of the 4 curves given, that representing compressibility was the main object of the present work and is the most interesting, since it possesses a well-marked minimum; hence this will be considered first. As regards the left-hand branch of this curve: the remarkable decrease in compressibility with increasing concentration of urethane may be ascribed rather to the change in the water than to any direct effect of the comparatively small quantity of urethane added, especially as the latter must have a compressibility in the liquid state not very far different from that of water. From a single case such a conclusion might be hazardous, but so far as we know all aqueous solutions show thus a marked diminution in compressibility in dilute solutions with increasing concentration, even when the dissolved substance is more compressible than pure water. A striking example is the well-known behavior of the alcohol and water mixture, in spite of the fact that alcohol has nearly twice the compressibility of water, the addition of alcohol to water diminishes the compressibility of the solution until (at 20°) 20% of alcohol has been added.[1] Nearly all, if not quite all, among other liquids than water show a much more nearly additive relationship in solutions. One can hardly escape the conclusion that the first and most striking effect of dissolving anything in water is to dissociate part of the trihydrol present, thus diminishing the compressibility. This diminution is entirely parallel to the diminution of compressibility of water with rising temperature above 0°, a phenomenon which disappears at high pressures because the pressures must have already largely dissociated the trihydrol ("dissolved ice") present, and which disappears at higher temperatures because increase of temperature has the same effect.

Is not a similar cause the reason for the generalization of Tammann, at least as regards aqueous solutions? namely, "Das Volumen einer Lösung verhält sich Temperaturänderungen gegenüber, wie das Volumen des einen höheren Druck unterworfenen Lösungsmittels."[2] The dissolved substance must be supposed to have the same effect as pressure; it partially dissociated the associated molecules, and the resulting material must therefore act similarly in the two cases.

These considerations entirely explain the behavior of the left-hand branch of the compressibility curve. The behavior of the right-hand branch may be supposed simply to be due to the possession of a somewhat greater compressibility on the part of the urethane than is possessed by dihydrol, and although the curve does not extend so far because of the saturation of the solution, one has a right to conclude that the compressibility of liquid urethane at 20° (supposing that it could exist in the

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[1] Pagliano, *Nuovo cimento,* [3] **27,** 209 (1890). See also Landolt-Börnstein-Roth, 1912, p. 62.

[2] Quoted by Lewis: *Z. Phys. Chem.,* **74,** 629 (1910).

liquid state at this temperature) would be not far from that of pure water under low external pressures.

The upward departure from a straight line, visible at the right-hand end of the curve, may reasonably be ascribed to the increasing presence of monohydrol, since we know that when water is dissolved in other substances very appreciable amounts of it may be present as H_2O.[1]

It will be noted that the other cases in which water enters, alluded to earlier in this paper, are all consistent with this interpretation.[2] The compressibility curve, then, offers no difficulties.

The "solution volume" curve exhibits no unexpected peculiarities if the interpretation of Bousfield and Lowry is accepted. From the table it appears that in a dilute solution the solution volume of urethane is 0.877, and that this increases, at first slowly and then rapidly, until in a 50% solution it attains the value 0.904. Both of these numbers are smaller than the specific volume of liquid supercooled urethane at that temperature.

The specific volume of solid urethane, computed by interpolation from H. Block's values, is, at 20° 0.8704, and the hypothetical specific volume of the supercooled liquid at 20° (by extrapolation from Block's values from 46° to 57°) is not less than 0.923. It appears, then, that although solid urethane expands on being dissolved, this expansion must be due primarily to the act of melting (*i. e.*, to the breaking up of the crystal structure), not to the act of solution. As a working hypothesis, the larger value will be taken for the substance in solution, since this is more probably more like the liquid than like the solid. Evidently when the liquid is thus mixed or dissolved to a dilute solution in much water, it must be supposed to cause a great contraction in the water, like that produced when, for example, alcohol is dissolved in water; and from the curve it is clear that this contraction per unit of urethane is greatest at first, gradually decreasing as the concentration of solution increases. In the space from 30 to 50% the curve is almost linear, but for higher concentrations it begins again to turn upward. May this not be due here also to the increasing appearance of the more bulky monohydrol as the concentration of the water diminishes? In brief, the performance of the solution volume curve is precisely what one would expect if water contained an appreciable amount of trihydrol in dilute solutions and an appreciable amount of hydrol (monohydrol) in concentrated solutions, with dihydrol present throughout.

Turning now to the surface-tension curve, we note that at first the falling off is very marked, and that later in solutions containing 40% or more of urethane from which, supposedly, the trihydrol has been elimi-

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[1] G. Bruni and M. Amadori, *Trans. Faraday Soc.*, 5, 290 (1909).

[2] De Metz, Drucker, Tammann, Lewis, *Loc. cit.*

nated, the surface tension decreases far less rapidly but more regularly. Here again the two markedly different branches of the curve must be ascribed to the changing constitution of the solvent. The part of the curve between 40% and 50% (representing a solution influenced as little as may be by changing association, if we may judge from the other curves) manifests the general principle applicable to pure substances concerning the relation between compressibility and surface tension. Here the surface tension decreases about 1.25% where the compressibility increases about 2% between these limits, a relationship which is remarkably in accord with the equation found for pure liquids, $\beta\gamma^{4/3} = K$. Thus this relationship seems to hold in some solutions as well as with pure substances, when abnormal side-reactions have been eliminated.

There remains only the viscosity curve to be considered. Evidently urethane is, as one would expect, far more viscous even than trihydrol, so that even at first the addition of the dissolved substance causes an increase in viscosity, the added urethane more than compensating in this respect for the withdrawal of some of the trihydrol. That this assumption is not unreasonable is shown by the enormous increase in viscosity from 100 to nearly 250 in a 50% solution. The diminishing presence of trihydrol, therefore, manifests itself only in the departure from a straight line shown by the fact that dx/dc steadily increases. In the neighborhood of 40% again the curve seems to nearly linear. Hydration of the urethane may be the cause of the upward trend at the extreme right-hand end of this curve. But in any case viscosity is not very closely related to the other properties, since it must be considered to depend upon the size of molecules and their outward configuration more than on the internal pressures holding them together.

Thus all of the data recorded in this paper are reasonably explicable, if the most recent views concerning the constitution of liquid water are accepted; and being less easily explicable in any other way which has occurred to us, the data tend to support these views.

Summary.

The compressibilities of aqueous solutions of urethane were measured at 20.0° over a pressure range from 100 to 300 megabars. With rising concentration the compressibility decreases rapidly from $43.25\cdot 10^{-6}$, the compressibility of pure water, to $38.91\cdot 10^{-6}$, the compressibility of a solution having 34 g. urethane in 100 g. water. From this point the compressibility increases, at first slowly and then more rapidly; at the highest measured concentration, 127.35 g. urethane for 100 g. water, the compressibility is $40.86\cdot 10^{-6}$. The surface tension, the specific volume, and the viscosity were likewise measured; no minimum resembling that of compressibility was found by these latter measurements, and it is shown that none is to be expected. The bearing of the results on the theory of

Harold Whiting and others, ascribing polymerization to water, is emphasized.

It is a pleasure to express our thanks to the Carnegie Institution of Washington for the pecuniary support in this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

THE THERMAL DISSOCIATION OF SULFUR DIOXIDE.

BY J. B. FERGUSON.

Received November 13, 1918.

Carbon dioxide may be decomposed by heat to form carbon monoxide and oxygen, and the degree of this dissociation has been determined both by direct measurements and indirectly from considerations of the so-called water-gas reaction and the dissociation of water vapor. In an analogous fashion sulfur dioxide would be expected to dissociate into sulfur and oxygen, and theoretically the degree of this dissociation could be determined in a similar manner. However, in practice, Lewis, Randall and Bichowsky[1] even at 1500° were unable to study this reaction quantitatively because of the slight extent of the dissociation, and my own observations at temperatures ranging from 1000° to 1200° are confirmatory of their experiences with this reaction. The indirect methods would therefore appear to be the only ones available for this determination. In the present paper the mode of arriving at results by one indirect method and the results themselves are presented.

The equation for the dissociation of sulfur dioxide may be written $^1/_2 S_2 + O_2 \rightleftarrows SO_2$, if the temperature range considered is that in which the density of sulfur vapor corresponds to a formula S_2, and the recent work of Randall and Bichowsky[2] on the dissociation of hydrogen sulfide indicates that no great error is involved in the assumption of the formula S_2 for sulfur vapor at 1500°.

By a method similar to that employed in calculating the carbon dioxide dissociation from the water-gas equilibrium the sulfur dioxide dissociation may be calculated from equilibrium measurements of either the reduction of sulfur dioxide by hydrogen[2] or the reduction of sulfur dioxide by carbon monoxide.[3] The latter data were, however, obtained in a more direct manner than the former and will therefore be used. If the equilibrium constant for the reaction

$$CO + {}^1/_2SO_2 \rightleftarrows CO_2 + {}^1/_4S_2$$

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[1] G. N. Lewis, Merle Randall and F. Russell v. Bichowsky, THIS JOURNAL, 40, 356 (1918).

[2] Merle Randall and F. Russell v. Bichowsky, *Ibid.*, 40, 368 (1918).

[3] J. B. Ferguson, *Ibid.*, 40, 1626 (1918).