[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE DENSITIES AND COMPRESSIBILITIES OF SEVERAL ORGANIC LIQUIDS AND SOLUTIONS, AND THE POLYMERIZATION OF WATER

BY THEODORE WILLIAM RICHARDS AND HARRIS MARSHALL CHADWELL

RECEIVED MAY 21, 1925 PUBLISHED SEPTEMBER 5, 1925

This investigation is part of a comprehensive research which had as its object an attempt to estimate the effect of changing internal pressure on the volumes and compressibilities of liquids, and especially to obtain further light on the extent of polymerization of water. The present paper deals with only a small part of the investigation, but it is now published separately because the data may possibly be useful to others, and because they throw light on factors, important but usually ignored, which affect the volume changes suffered by liquids.

The chief influences at work in determining the volume changes of mixed liquids seem to be the three following.

1. **The Cohesive Affinities Concerned.**—That the relation of the mutual affinity or attraction manifested by the liquids for one another to the cohesive affinities of the pure liquids should affect the volume is no new idea; it has been considered by Galitzine, D. Berthelot, S. Young and many others.[1] The situation is analogous to that of the volume changes suffered by solids and liquids on chemical combination, considered especially by Traube (incompletely) and by one of the present authors. Few will be inclined now to deny that internal pressures due to chemical and cohesive affinity tend to diminish volume and compressibility.

2. **The Effect of Polymerization of One or Both Liquids.**—When two liquids are mixed, any polymerization present must be diminished in extent. Therefore, any volume changes due to diminution in the proportion of polymerized matter will be added to that due to pressure or the interaction of the two different molecular species. This idea also is not new; the probability that water is partly polymerized was first definitely indicated by Whiting over 40 years ago, restated by Röntgen in 1891 and developed

---

[1] (a) Galitzine, *Wied. Ann.*, **41**, 770 (1890). (b) Berthelot, *Compt. rend.*, **126**, 1703 (1898). (c) Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 4 (1901). (d) Young, "Stoichiometry," Longmans and Co., London, **1908**, p. 255. (e) Biron, *J. Russ. Phys.-Chem. Soc.*, **41**, 569 (1909); **42**, 135, 188 (1910); **43**, 663 (1911); **44**, 65, 1264 (1912); **45**, 1985, 2002 (1913); through *J. Chem. Soc.*, **98** (ii), 393 (1910), etc. Biron was particularly interested in "isofluid" liquids, and took some account of compressibilities.

For many cases, see (f) Landolt-Börnstein-Roth-Scheel "Tabellen," 5th ed., **1923**, vol. 1, pp. 443–76 (1923). A complete bibliography of pertinent papers would far exceed the available space here. Many more references will be found in the thesis presented by H. M. Chadwell for the degree of Doctor of Philosophy, at Harvard University, 1924.

quantitatively by Sutherland nine years later.[2] Many investigators have presented evidence that a polymerized substance is gradually depolymerized on dilution.[3] Obviously the formation of a complex molecule of solute and solvent (a solvate) might cause a similar effect.

3. The Effect of the Several Compressibilities of the Cohering Substances.—This effect has been considered in detail in G. P. Baxter's study of the density of aqueous solutions of electrolytes.[4] Nevertheless, it seems not to have been considered by most other commentators upon cohesion—in particular, those dealing with the mixing of non-polar liquids. Perhaps Biron[1e] (whose contributions, written in Russian, have never been fully translated) is the only investigator of such systems who has really taken compressibility into account, and he lacked adequate data. Cohen and Schut's admirable book gives no discussion of this effect of compressibility.[5] Yet obviously when two liquids with a given cohesive affinity for one another are mixed (or better, mutually dissolved) the contraction observed should be greater, the greater their compressibilities. A similar effect is observed in manifestations of chemical affinity.[6] The effect of the several compressibilities of the mutually dissolved substances will be seen to be probably at least as great as that of either of the other affecting circumstances, and may account for otherwise inexplicable discrepancies of volume change which appear on comparing the data for different pairs of substances. Compressibility is, indeed, a fairly trustworthy guide as to the relative magnitude of internal pressures.

Most of the many previous investigations[1] on density of solutions have had a practical end in view. Various temperatures and methods have been employed. For the present purpose new series of determinations were made under constant conditions with substances chosen appropriately.

The necessary data were divided into two series. In the first series, solutions of four different substances, urethan, ether, ethyl alcohol and methyl acetate, in a single solvent, water, were compared. In the second series, solutions of a single substance, urethan (generally supposed to be

---

[2] (a) Harold Whiting, "A New Theory of Cohesion," W. H. Wheeler, Cambridge, Mass., **1884**, p. 71. Several references to Röntgen, Sutherland and others are given by (b) Richards and Palitzsch, THIS JOURNAL, **41**, 64–65 (1919). Especially the "General Discussion," (c) *Trans. Faraday Soc.*, **6**, 71 (1910), is illuminating, although the participants (Sutherland among them) were evidently unaware of Whiting's priority. For an interpretation, see (d) Richards, *Proc. Am. Acad. Arts Sci.*, **39**, 594 (1904); (e) *Z. physik. Chem.*, **49**, 28 (1904).

[3] Bruni and Amadori, *Trans. Faraday Soc.*, **5**, 290 (1909). See also Oddo and Scandola, *Gazz. chim. ital.*, **40**, ii, 172 (1910).

[4] Baxter, THIS JOURNAL, **33**, 922 (1911). Baxter and Wallace, *ibid.*, **38**, 70 (1916). These cases are especially complicated by hydration and electrolytic dissociation.

[5] Cohen and Schut, "Piezochemie," Akademische Verlagsgesellschaft Leipzig, **1919**.

[6] Ref. 2 d, p. 586, etc.

but slightly associated in solution), in four different solvents, water, alcohol, ethyl ether and benzene, were compared.

For a complete demonstration of the causes of volume change, a far more complete and exhaustive series of determinations is needful. Nevertheless, the new data serve as a further confirmation of the principles stated above, and make possible a rough calculation of the relative quantities of two possible isomers existing in pure water.

The inferences drawn from considerations concerning density were amplified by less complete series of determinations of the compressibilities of some of these solutions. The most striking outcome of this part of the work was that several equimolal dilute solutions of different substances were shown to possess approximately the same diminished compressibility.

Purification of Materials

Water.—Thrice distilled water (free from oil, organic matter, ammonia and carbon dioxide) was used.

Urethan.—The first sample (from a trustworthy source) was crystallized thrice from water and centrifuged; m. p., 47.94° (corr.). A second sample was crystallized twice from water and once from alcohol; m. p., 47.99°.[7] Both had been dried over sodium hydroxide, but may have contained a little included solvent. The density of supercooled liquid urethan[8] at 20° was taken as 1.083.

Alcohol.—Commercial "pure absolute" alcohol was refluxed four times for periods of four hours each with calcium oxide formed by the dehydration of calcium hydroxide. It was then distilled from a Richards-Barry distilling flask,[9] previously swept out with dry air, the middle fraction being collected. Its density (d_4^{20}) was 0.78922 as compared with 0.7893 to 0.7894, found by others.[10] All dry liquids were kept in glass bottles under bell jars, over concd. sulfuric acid.

Ethyl Ether.—For Sample I, one of the purest commercial preparations of ether was dried with successive samples of fresh metallic sodium wire for about 30 hours until fresh sodium wire was not visibly attacked. After distillation (while protected from damp air) its middle fraction (boiling over 0.1°) had a density[11] of 0.71368. A second sample (Ether II), prepared by drying with phosphorus pentoxide according to the method of Wade and Finnemore,[12] had a density of 0.71375.

Benzene.—"Analyzed" benzene, reported to be free from thiophene, was shaken thrice with concd. sulfuric acid. After the first treatment the acid remained colorless. The hydrocarbon was then shaken with porous calcium oxide and was crystallized fractionally thrice (with centrifuging). The product, after treatment with sodium,

---

[7] Others have found melting points as follows: Richards and Palitzsch, 48.0–48.2°; Block, 48.5°; Bridgman, 47.9°; Tammann, 48.14°. See (a) Richards and Palitzsch, THIS JOURNAL, **41**, 61 (1919).

[8] Ref. 7a, p. 67.

[9] Richards and Barry, THIS JOURNAL, **36**, 1787 (1914).

[10] Ref. 1f, pp. 366, 448.

[11] Others have found the following values: Oudemans, 0.7138; Lorenz, 0.7157; Landolt, 0.7166; Jahn, 0.7141 [for the preceding see Ref. 1f, 4th ed., **1912**, p. 1024]; Squibb, 0.71348 [*Chem. News*, **51**, 66, 76 (1885)]; Keyes and Felsing, 0.7135 [THIS JOURNAL, **41**, 589 (1919)]; see also Ref. 1f, p. 366.

[12] Wade and Finnemore, *J. Chem. Soc.*, **95**, 1842 (1909).

was fractionally distilled. The middle fraction (boiling over 0.2°) had a density[13] of 0.87843.

Methyl Acetate.—The best commercial methyl acetate obtainable was treated thrice successively with phosphorus pentoxide, as recommended by Young and Thomas.[14] On distillation, nearly all came over within 0.1°. The density[15] of the middle fraction at 20° was 0.93347. Afterwards this preparation was found to contain a trace of acetone, in amount sufficient to affect the density by about 0.00005.

It was necessary for the determination of compressibility to free the liquids (purified as described above) from dissolved gases, in order to prevent large bubbles of air from forming in the piezometer. Water was sufficiently freed from air by continued boiling followed by cooling without agitation; also, by slow freezing, pouring off the supernatant liquid, and melting the ice in a vacuum. Methyl acetate and ether were partially freed from gas by boiling at about 10° under reduced pressure.

Ether gave trouble also through the well-known formation of a film of black precipitate on the surface of mercury, due presumably to "peroxide." This impurity was eliminated by shaking the ether with sodium amalgam in an atmosphere of nitrogen. Since the presence of air partly nullifies the purification, the ether was subsequently distilled in an atmosphere of nitrogen, kept in a bottle under nitrogen, and used within a few days after purification.

A possible error in the determination of compressibility of aqueous solutions of methyl acetate might arise through the hydrolysis of the ester during the application of pressure. If hydrolysis is accompanied by loss of volume, pressure should accelerate the process.[16] In this case the effect was found to be negligible. A concentrated solution of methyl acetate, kept under 500 atmospheres' pressure at 18° for 24 hours, remained wholly neutral to phenolphthalein slightly reddened with a trace of alkali.

Preparation of Solutions

Various solutions of known concentration by weight were prepared in glass-stoppered, 75cc. Erlenmeyer weighing flasks. In order to diminish loss by volatilization the more volatile material was added last, and the ground-glass top of the flask was kept dry.

Density Determinations

Ostwald pycnometers (provided with fine capillaries, and caps to prevent evaporation) were used. Volumes were exactly adjusted at 20.000° (±0.002°) in an adequate thermostat. After external drying, the capped pycnometers were allowed to come to the temperature of the balance, and weighed against a sealed counterpoise by standardized weights.[17] The advantage of using a sealed counterpoise in this way is that the vacuum correction is made once for all in the weight of the empty pycnometer.[18] Not even the brass weights used in measurement need be corrected to the

---

[13] Richards, Stull, Mathews and Speyers [THIS JOURNAL, **34**, 971 (1912)] found 0.8788. Ref. 1 f, p. 368 gives 0.87865. The value quoted on p. 240 of the 4th edition of this work is unquestionably erroneous.

[14] Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).

[15] Ref. 1 f, p. 370, gives 0.9338.

[16] The only discussion of the effect of pressure on similar reactions appears to be that of Cohen and Schut on the inversion of sugar, Ref. 5, p. 411.

[17] Richards, THIS JOURNAL, **22**, 144 (1900).

[18] Cooke and Richards, *Proc. Am. Acad. Arts Sci.*, **23**, 162 (1887).

vacuum standard (unless a weighing is made under very abnormal atmospheric conditions) since the apparatus is standardized by water under similar conditions.[19] The following details giving the determination of the volume of the pycnometers and of the density of a single solution will serve to show not only the simplicity of the counterpoise method, but also the degree of accuracy sought and attained.

The tares of three pycnometers filled with dry air (751.9 mm. (corr.) and 12.0°) were, respectively, 3.0074, 3.0592 and 2.4435 more than the counterpoise. These tares would have been 2.9960, 3.0488 and 2.4330, respectively, if the pycnometers had been evacuated. Filled with water, the latter gave tares of 12.2933, 11.5194 and 10.9834; the values to be used for the three volumes were thus found to be 9.3138, 8.4856 and 8.5656, respectively. These measurements were repeated until the last figure was certain—usually at least thrice. Occasionally breakage and repair necessitated new standardization. Typical data for a single solution are given in Table I.

TABLE I

THE DENSITY OF SOLUTION A OF URETHAN IN BENZENE

5.989%

	I	II	III
Weight of pycnometer + solution, g.	11.2649	10.5818	10.0372
Weight of pycnometer empty, g.	2.9960	3.0488	2.4330
Weight of solution, g.	8.2689	7.5330	7.6042
Density of solution in vacuum	0.88781	0.88774	0.88776
Mean value of density		0.88777	

When the first three determinations were more deviant than these, the process was repeated until the probable error of the total mean was sufficiently small.

TABLE II

DENSITIES OF PURE SOLVENTS AND SOLUTIONS

Experimental results at 20.00°, corrected to vacuum

Pure solvents	D.	Methyl acetate in water		Ethyl ether II in water	
		%	D.	%	D.
Water	[0.99823]	6.544	1.00055	0.558	0.99703
Ethyl alcohol	.78922	9.257	1.00139	1.169	.99573
Ethyl ether I	.71368	13.084	1.00244	1.758	.99452
Ethyl ether II	.71375	19.449	1.00318	2.149	.99372
Benzene	.87843			2.909	.99220
Methyl acetate	.93347			3.283	.99155
				3.840	.99078
				4.163	.98989
				4.494	.98899
				4.754	.98880

---

[19] In this case the weights are not the true weights in vacuum; nevertheless, the *ratio* of the weights of solution and of water thus found is the true vacuum ratio.

TABLE II (*Concluded*)

Urethan in ether I		Urethan in alcohol		Urethan in benzene	
%	D.	%	D.	%	D.
6.277	0.73268	5.160	0.80128	2.995	0.88307
9.817	.74387	10.983	.81529	5.989	.88777
19.617	.77425	19.902	.83704	10.390	.89488
29.321	.80612	21.070	.84001	11.214	.89624
37.353	.83364	29.343	.86117		
		38.409	.88521		
		47.472	.91059		
		55.558	.93466		
		59.221	.94495		

The results appear in Table II. Each reported value of density is the mean of from three to eight determinations.

TABLE III

DENSITIES OF SOLUTIONS (FROM SMOOTH CURVES) AT 20° IN VACUUM, SYSTEMATICALLY TABULATED

Solute per 100 g. of solution G.	Ether in water	Ethyl alcohol in water[a]	Methyl acetate in water	Urethan in water[b]	Urethan in ether	Urethan in alcohol	Urethan in benzene
0	0.9982	0.9982	0.9982	0.9982	0.7137	0.7892	0.8784
1	.9961	.9963	.9986	.9995	.7167	.7915	.8800
2	.9940	.9945	.9990	1.0008	.7197	.7938	.8815
3	.9921	.9927	.9993	1.0021	.7227	.7962	.8831
4	.9902	.9910	.9996	1.0034	.7258	.7986	.8846
5	.9884	.9893	1.0000	1.0046	.7289	.8010	.8862
10		.9819	1.0016	1.0110	.7442	.8130	.8942
20		.9687	1.0032	1.0230	.7754	.8375	
30		.9538		1.0335	.8083	.8628	
40		.9352		1.0430	.8430	.8895	
50		.9139		1.0517		.9177	
60		.8911				.9470	
100	.7137	.7893	0.9334				

[a] The average mean of many determinations by others (Ref. 10).
[b] From the data of Richards and Palitzsch, Ref. 2 b, p. 63.

Possibly none of these liquids (except water) has ever been prepared in a state of purity so great as to make the fourth place of decimals entirely certain. Such purity cannot, at least, be claimed for the present preparations. When the exact specific gravities of the pure liquids are known, however, each of the densities of solutions herewith given can easily be corrected *pro rata* accordingly, since the simple rule of mixing must apply with sufficient accuracy to the very small amount of impurity present.

Interpretation of Results for Densities

As a first step toward the elucidation of the factors determining these densities, values for the contraction which takes place during formation of one liter of each of the various solutions were computed; these are given in Table IV and are depicted in the accompanying diagrams, Figs. 1 and 2. The concentrations are expressed in terms of moles per liter, since the depolymerizing effect of a solute may be dependent upon its molal concentration.

TABLE IV

CONTRACTION ON SOLUTION

Solute %	Concentration, moles per liter	Contraction Cc. per liter
URETHAN IN WATER		
5	0.564	2.45
10	1.135	4.57
20	2.298	8.43
30	3.482	10.94
40	4.685	12.01
50	5.905	12.17
URETHAN IN ETHER		
5	0.409	3.86
10	.835	7.15
20	1.741	12.34
30	2.722	16.61
40	3.786	19.94
URETHAN IN ALCOHOL		
5	0.449	1.17
10	.913	2.18
20	1.881	3.57
30	2.907	4.20
40	3.995	4.66
50	5.153	4.94
60	6.381	4.43

Solute %	Concentration, moles per liter	Contraction Cc. per liter
ETHER IN WATER		
1	0.134	1.87
3	.402	5.77
5	.667	9.81
ETHYL ALCOHOL IN WATER		
5	1.072	4.21
10	2.128	9.72
20	4.198	21.84
30	6.200	31.43
40	8.106	36.13
50	9.901	36.78
METHYL ACETATE IN WATER		
1	0.135	1.09
3	.405	3.18
5	.675	5.26
10	1.352	10.34
20	2.709	18.64
URETHAN IN BENZENE		
1	0.099	— 0.08
3	.297	— .36
5	.497	— .67
10	.894	— 1.28

Fig. 1 records the comparison of contractions of solutions of four solutes in a single solvent, water. The widely different behavior manifested by the different substances is striking. Three of the solutes involved are usually considered as but little associated, namely, ether, methyl acetate and urethan. They are, therefore, suitable for preliminary comparison. The average compressibilities (between 100 and 300 megabars) of these three substances in the liquid condition at 20° are, respectively, 132, 88 and about 46 (each $\times\ 10^{-6}$). Evidently, the contractions (15, 8 and 4.2 cc.) which take place on forming a solution containing one mole of solute per liter are roughly proportional to these compressibilities.

One might infer that the compressibility of the solute is the only factor in the volume change, but this inference would be superficial. It is not the compressibility of the solute alone which must be considered, but rather its relation to that of the solvent. Now the compressibility of liquid urethan is not far from that of water, although probably somewhat greater. If no other circumstance entered into the situation, liquid urethan ought to be nearly "isofluid" with water, involving no volume change on mixing. There is thus reason to believe that the rather large volume change which actually occurs when urethan is dissolved in water is primarily due not to further compression of urethan or water in the act of solution, but rather to some other circumstance, presumably the depolymerization of some of the water, which would cause a diminution in volume, since there can be little question that the more complex molecule of water is more bulky than a less complex molecule. This conclusion gives a clue which will be followed later as to the extent of polymerization of water. It does not, however, invalidate the conclusion that compressibility, as indicated by the behavior of the solutions of ether, methyl acetate and urethan, is probably an essential factor in the volume change, the latter being greater, the greater the compressibility of the solute. The same solvent is common to all.

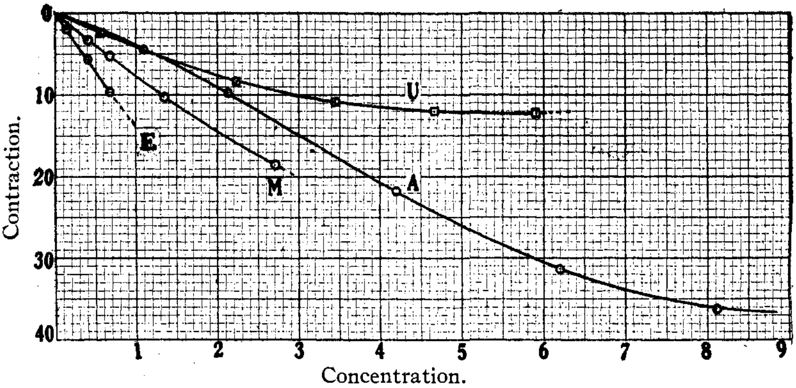

Fig. 1.—Contractions caused by solution of four substances in water. Contractions in cc. plotted as ordinates; concentrations (moles per liter) as abscissas. Curve U indicates contraction caused by urethan, Curve A by alcohol, Curve M by methyl acetate, Curve E by ether.

The relative positions of the curves cannot be due to the effect of the several affinities because, judging from the extent of solubility, ether has the least and urethan the greatest affinity of the three substances for water. This latter inference might also be drawn from the heats of solution of similar substances in various solvents, determined by Speyers.[20]

The case of alcohol in Fig. 1 is in another category. Alcohol is generally believed to be considerably associated;[3] but probably the polymer of alcohol is (in contradistinction to that of water) somewhat *less* bulky than the unassociated molecule. The fairly constant coefficient of expansion is among the properties indicating this latter inference. Ethyl alcohol has very

---

[20] Speyers, This Journal, **18**, 146 (1896).

nearly the same compressibility as methyl acetate, but the contraction which takes place when ethyl alcohol is dissolved in water must be diminished by the dissociation (and consequent expansion) of part of the associated alcohol. The curves support this hypothesis, and the difference between those for methyl acetate and alcohol might perhaps serve as a rough guide to the extent of association existing in alcohol. The double inflection in the alcohol curve is probably due to the same cause. The case of alcohol is further complicated, however, by the probable formation of a solvate.

Tammann has suggested that the introduction of a dissolved substance has the same effect upon a solvent as compressing the pure liquid under external pressure.[21] In many cases this generalization holds, but clearly it does not hold in the case above (alcohol) where the polymer has a smaller volume than the single molecule, for in this case external pressure will increase concentration of the polymer and decrease that of the single molecule, whereas the dissolving of some other substance in this polymerized solvent will have the opposite effect. Tammann's analogy appeared to hold only because in the case chiefly studied (water) the two effects agree in direction.

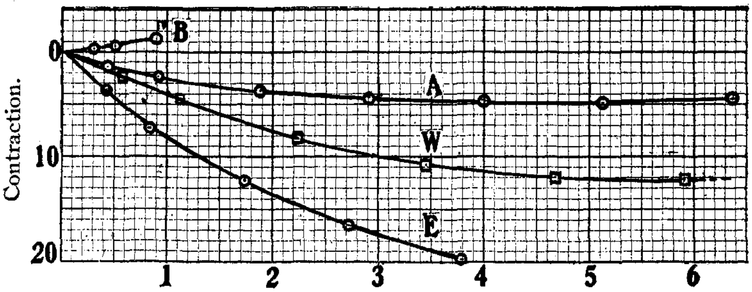

Fig. 2.—Contractions caused by dissolving urethan in four solvents. Coördinates as in Fig. 1.

Curve B indicates expansion caused by solution in benzene, Curve A indicates contraction in alcohol, Curve W contraction in water, Curve E contraction in ether.

Turning now to Fig. 2, which depicts the effect of various solvents with a single solute, we find evidence of the same tendencies. Again ether, the most compressible of all these solvents, gives by far the greatest change in volume. In the case of benzene the smaller compressibility (77×10^{-6}) and small affinity (shown by the slight solubility and great negative heat of solution)[20] are presumably the reason why this substance gives a slight *increase* rather than a decrease in volume. Alcohol and water behave as would be expected, taking account of their association; the volume change

[21] Tammann, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," Leopold Voss Hamburg and Leipzig, **1907**, p. 179.

in the case of water is over twice as great as in the case of alcohol, although the compressibilities show the opposite relation. When urethan is dissolved in water, the dissociation of a part of the more complex molecules of water may be assumed to cause considerable contraction, and this contraction is to be added to that (if any) due to the mutual compression of the two substances. On the other hand, in the case of alcohol the dissociation (by causing expansion) would tend to decrease the volume change. Hence, the transposition of the two curves is only to be expected. The effect of change of polymerization may then be inferred (with regard to this particular pair) to exceed that due to the different compressibilities.

These qualitative considerations are inevitably incomplete, especially in view of the fact that the compressibilities of all substances diminish (to various extents) with increasing pressure. Nevertheless, they are not without significance. A qualitative survey must always precede a quantitative one in such inductive cases.

Fortunately, the aspect of the question which was primarily in view, namely, the effect of dissolved substances on the polymerization of water, is more susceptible to approximate quantitative treatment than most of the other specific problems discussed above.

When two liquids having approximately the same compressibility and not very different cohesive affinities are mixed, very little heat is evolved and very little change of volume occurs.[1] In more than two-thirds of the cases cited by Sidney Young, contraction is accompanied with rise of temperature (or expansion with fall of temperature). Only in the case of one pair of liquids, bromobenzene and chlorobenzene, was the pair found to be strictly "isofluid," that is, to suffer no change of volume or internal energy when mixed. If a solute could be found which should have essentially the same average internal pressure in its union with itself and the two forms of water, as these have with themselves, and identical compressibility, no change of volume due to the solute would occur on solution. Any change in volume actually observed could then be referred wholly to the depolymerization of the water. Probably no such solute exists; nevertheless it appears, as already suggested, that supercooled liquid urethan ($NH_2COOC_2H_5$) may be a fairly close approximation to such a substance. Let us assume, then (for the sake of argument), that the contractions in volume which occur when urethan is dissolved in water to various concentrations (depicted as Curve U in Fig. 1 and as Curve W in Fig. 2) indicate approximately the volume change due to the depolymerization of water alone.

For the present purpose it is immaterial whether this depolymerization is from $(H_2O)_2$ to H_2O (according to Whiting) or from $(H_2O)_3$ to $(H_2O)_2$ (according to Sutherland). The more complex molecular condition will be designated as "polyhydrol" and the less complex condition as "hydrol," leaving in abeyance for the present the question as to the precise molecular magnitude of each.

To compute the quantity of polyhydrol present, the unknown change of volume caused by its depolymerization to hydrol is needed. Since polyhydrol is generally conceded to be more bulky than the less complex form, one may assume (with Whiting and Sutherland) provisionally that the former is similar to ordinary ice. These two assumptions, namely, that the volume change on solution of urethan represents the partial dissociation of polyhydrol to hydrol and that the specific volume of the former is that of ice, give a tentative (and necessarily rather hypothetical) means of determining the percentage of polyhydrol present, as follows.

One g. of ice on melting contracts 0.0906 cc., but the water which is formed is supposed still to contain much polyhydrol. Hence, the complete change from polyhydrol to the simpler molecule must represent a larger change of volume than 0.0906 cc. per g.

Some of the polyhydrol present in water at 0° is generally supposed to be depolymerized on being heated to 20°. The change in the polymerization of water over this range of temperature may be roughly approximated by the following method, which was probably used by Whiting (although he gives no details). One liter of water heated from 0° to 20° expands only 1.8 cc., whereas a normal substance with a boiling point of 100° should expand about 20 cc. (For example, the coefficient of expansion of propyl alcohol is 0.00109; of toluene, 0.0011; of sulfur dichloride, S_2Cl_2, 0.00097; and of allyl iodide, 0.00109.) The coefficient of expansion of water itself at 100° is about 0.0008, although some of the polymer must still remain. A conservative estimate would then place the coefficient of expansion of "hydrol" at 0.0009. If this is true, a liter of water at 20° actually occupies about 16 cc. less than it would have occupied if no polyhydrol existed in water at 0°.

But how much polyhydrol exists in water at 20°? If from the curve U, in Fig. 1, the changes in volume caused by dissolving different amounts of urethan in 1000 g. of water are computed, a nearly linear curve is obtained (Fig. 3), which indicates by extrapolation that an infinite amount of urethan dissolved in a liter of water would cause a contraction probably of between 40 and 44 cc. This contraction may be supposed to correspond to the complete depolymerization of the polyhydrol in 1000 g. of water at 20°. Then (from the preceding paragraph) the same process at 0° would cause a contraction of about $16 + 42 = 58$ cc.

Thus the complete change of pure polyhydrol (ice) would appear to involve a loss of volume of (roughly) 149 cc. per kg. $(90.6 + 58)$ or 0.15 cc. per g. Hence the percentage by weight of polyhydrol present in water at 0° is reckoned to be $100 \times 58/149 = 39\%$, and the percentage of polymer present in water at 20° is reckoned to be $100 \times 42/149 = 28\%$.

The numerical outcome agrees well with those of Whiting and of Sutherland[22] (who found 37.5% at 0°), but gives much smaller values than those of van Laar.[23]

From these values and the curve U in Fig. 1, one may infer (tentatively as before) that one mole of urethan (and perhaps of other unassociated or undissociated substances) in a liter of solution may lower the amount of polyhydrol present at 20° by 27 cc. (one-half mole if polyhydrol is H_6O_3), or about 10% of the amount of polyhydrol present. All these estimates may be somewhat too great, since a small part of the contraction due to the solution of urethan may be due to true compression.

Conversely, if the estimates of Whiting and of Sutherland as to the extent of the polymerization of water are true, the result shows that urethan in solution may give a fairly good estimate of the amount of polyhydrol present at each concentration.

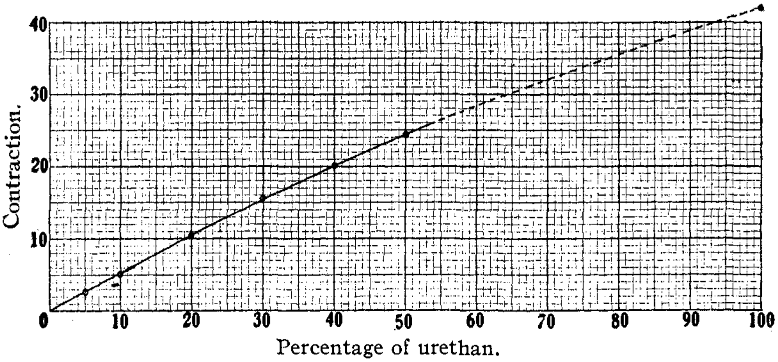

Fig. 3.—Contractions caused by dissolving urethan in one liter of water. Contractions in cc. plotted as ordinates; percentages of urethan in solution as abscissas.

If there are three different isomers (trihydrol, dihydrol and monohydrol) simultaneously present in water,[24] the above rough estimates would require numerical modifications, which cannot be applied with the present knowledge, but the underlying idea would not be affected. All of the data considered here, however, are adequately explained by two forms of water. The most questionable of the several assumptions required is that water and urethan are (apart from the effect of association) approximately "isofluid." No pretense is made that the result is conclusive; but at least the

---

[22] Sutherland's calculation was more complicated, and was qualified by various precise and thoughtfully conceived numerical considerations, which seem, however, to be beyond the limit of accuracy of such a necessarily rough calculation as the present one. *Phil. Mag.*, [5] **50**, 460 (1900); [6] **12**, 1 (1906).

[23] van Laar, *Z. physik. Chem.*, **31**, 1 (1899). Criticized by Doroschewsky and Roschdestvensky, *J. Russ. Phys.-Chem. Soc.*, **42**, 442 (1910); through *C. A.*, **5**, 410 (1911).

[24] Ref. 2 b, p. 65. Especially Bousfield and Lowry, *Trans. Faraday Soc.*, **6**, 85 (1910).

method is a new one, and apparently not more hypothetical than others which have been proposed.

Taking all these results into account it becomes probable that the contractions which occur when two liquids are mutually dissolved, and therefore the resulting density of the solution, are dependent upon the mutual cohesive affinities, the changes in molecular state, and the compressibilities of the substances concerned. The evidence is not exact enough to exclude other possible causes of volume change, but the argument seems to show that the three mentioned are adequate to account for at least the greater part of the effects observed.

Since a very compressible substance such as ether causes great contraction, one may reasonably conclude that such a substance is in a more compressed condition in solution than in the pure state and therefore, after being dissolved, is much less compressible than in the pure state.

The Determination of Compressibilities

The method used for the determination of compressibilities was that already used in many investigations in this Laboratory. It has been described so fully that further detailed description is unnecessary.[25] In brief, a glass piezometer containing mercury was first subjected to successively increasing pressures after the addition of successive small quantities of mercury, the exact volume being determined by a sharp platinum point fixed in the capillary tube. Most of the mercury was then displaced by the liquid to be investigated and the operation was repeated. The data thus obtained permit the algebraic calculation of the difference between the compressibilities of mercury and the other liquid. The piezometer had a volume of about 16 cc. and resembled that pictured in earlier papers,[26] except that the upper part of the wide tube was drawn down to a diameter of 5 mm.[27] This change made possible a more perfectly fitting glass stopper and improved the accuracy of the process. The piston area of the absolute gage was very carefully measured, the weights employed were standardized, and every other precaution indicated in earlier research necessary for the obtaining of exact results was adopted. If, in spite of precaution very small bubbles of air formed in an organic liquid in the piezometer, they were removed by brief application of high pressure, when they dissolved and did not reappear. In a dissolved state their effect on the compressibility was negligible.

[25] See, for example, Richards and Shipley, THIS JOURNAL, **38**, 989 (1916). This paper contains reference to earlier work.

[26] See, for example, Richards and Stull, THIS JOURNAL, **26**, 399 (1904); also Richards and Jones, *ibid.*, **31**, 162 (1909).

[27] Richards, "Die Bestimmung der Kompressibilität flüssiger und fester Substanzen II," in "Handbuch der Arbeitsmethoden in der anorganischen Chemie," by A. Stähler, Veit and Comp., Leipzig, **1913**, vol. 3, p. 250 (Fig. 99d).

The results are given in Table V. The pressure unit used is the megabar (megadyne per sq. cm. = 0.987 atmosphere). The apparatus was tested by determining the compressibility of water, which was found to agree exactly with previous determinations under the same conditions. The equation necessary for calculating the results is, $\beta_{100-300} = \frac{(W - 0.0670)\,D}{13.562 \times 200 \times W} + 3.96 \times 10^{-6}$.

TABLE V

RESULTS OF COMPRESSIBILITY DETERMINATIONS

Average compressibility over the range 100 to 300 mgbr. $t^{\circ} = 19.81^{\circ}$

	Solute %	W	D	w	$\beta_{100-300}$
Water	0	13.050	0.9982	1.460	43.25
Alcohol	0	....	....	...	88.7
Methyl acetate	0	11.617	.9335	2.920	88.48
Ether	0	9.386	.7137	4.633	132.0
Ether	0	9.252	.7137	4.569	132.0
ETHER IN WATER					
	1.993	13.425	0.9942	1.470	42.26
	2.067	12.521	0.9941	1.371	42.12
	3.982	12.704	0.9903	1.383	41.78
	5.319	13.042	0.9878	1.407	41.38
METHYL ACETATE IN WATER					
	5.43	11.928	1.0002	1.284	41.58
	10.16	13.270	1.0016	1.374	40.34
	13.86	13.069	1.0023	1.346	40.12
	14.84	13.208	1.0025	1.364	40.27
	17.46	13.369	1.0028	1.386	40.44
	17.80	13.365	1.0028	1.377	40.20
	20.86	13.215	1.0031	1.378	40.64
	20.98	13.363	1.0031	1.409	41.11

Interpretation of Compressibilities

Evidently, in spite of the great compressibility of both methyl acetate and ether, the solution of small amounts of these volatile substances in water diminishes the compressibility of the liquid. This diminution is parallel to that observed by Palitzsch in a former research with one of us;[8] but in the present case it is all the more striking because of the great compressibility of the two solutes. Such a phenomenon can probably be caused only by two circumstances; first, the depolymerization of the water, and second, the affinity between solute and solvent, which would cause a corresponding effect in compressibility.

In the effort to trace inductively the relative preponderance of these effects, the changes of compressibility with concentration (computed as moles per liter) in different solutions were compared as follows, and plotted in Fig. 4. On the assumption that this depolymerization would be equal in equimolal solutions of these three substances, a further advance may be made in the interpretation of the curves. Table VI presents the data recalculated in this form, including those previously found by Palitzsch.[8]

TABLE VI

DECREASE OF COMPRESSIBILITY IN RELATION TO MOLAL CONCENTRATION

G. of solute per 100 g. of solution	Moles per liter of solution	β_{Solution}	$\beta_{H_2O} - \beta_{\text{Solution}}$
	ETHER		
1.99	0.2670	42.28	0.97
2.07	.2777	42.15	1.10
3.98	.5319	41.81	1.44
5.32	.7092	41.41	1.84
	METHYL ACETATE		
5.43	0.7331	41.58	1.67
8.75	1.181	40.91	2.34
10.16	1.374	40.34	2.91
13.86	1.876	40.12	3.13
14.84	2.009	40.27	2.98
17.46	2.358	40.44	2.81
17.80	2.410	40.20	3.05
20.86	2.825	40.64	2.61
20.98	2.841	41.11	2.14
	URETHAN		
5.0	0.563	41.65	1.60
10.0	1.14	40.34	2.91
20.0	2.30	39.00	4.25
30.00	3.48	39.00	4.25
40.00	4.69	39.42	3.83
50.00	5.95	40.23	3.02

That these three dilute solutions, when equimolal, have approximately the same compressibility is evident on comparing the 5.32% solution of ether with the 5.43% solution of methyl acetate and the 6% solution of urethan. These contain about the same fraction of a mole per liter, and they give values of β, respectively, 1.84, 1.67 and 1.90 (each multiplied by 10^{-6}) less than the β of water. Fig. 4 illustrates the relation. It would appear, therefore, that a 0.5 M aqueous solution of a compressible solute at 20° has usually a compressibility 1.4×10^{-6} less than that of water over the range 100–300 megabars. If water has a compressibility of 43.25×10^{-6}, a 0.5 M solution of any undissociated or unassociated substance should have a compressibility not far from 41.9×10^{-6}, and a molal solution not far from 40.7. The conclusion is verified by other results, in so far as they may be reduced to this temperature and pressure range. Even in electrolytes, if one assumes that each ion acts as a molecule, about the same effect seems to be produced. Unfortunately, however, but few compressibilities of other solutions have been determined systematically.[28] Of the few available, the temperatures were varied, the pressure ranges were often very small, and the methods were not always satisfactory. Few of the earlier investigations yield smooth curves for the concentration-compressibility relation. Nevertheless, in every case it appears that the compressibility of any dilute aqueous solution is much less than that of water.

These considerations, together with the fact that ether has comparatively little affinity for water, dismiss at once the effect of the different affinities as the chief cause of the remarkable diminution of compressibility in dilute solutions of non-polar substances. The cause is more probably common to all aqueous solutions alike. The only plausible cause of this common effect seems to be the depolymerization of water.

With more concentrated aqueous solutions the curves diverge widely, showing in many cases a marked minimum. This minimum naturally occurs at a lower concentration, the greater the compressibility of the solute (with methyl acetate at about 2 *M* and with urethan at about 2.7 *M* solution). When the compressibility of the solute is much below 30×10^{-6} the minimum must disappear, and the curve must unceasingly descend from left to right. This is the case, of course, with solutions of the comparatively incompressible inorganic salts. The branches of the curves ascending to the right of the minima, where present, are evidently due to the great compressibilities of

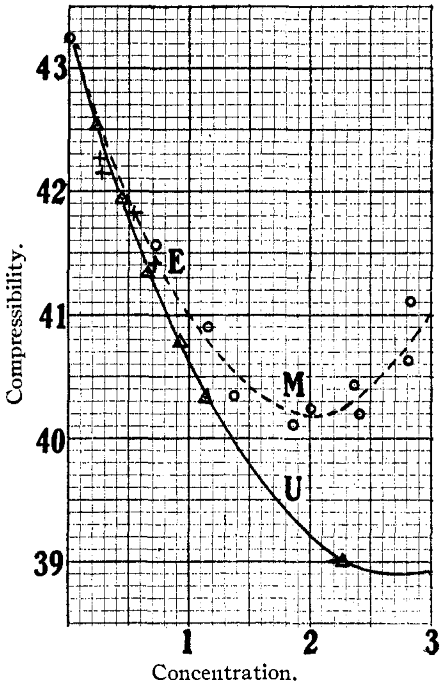

Fig. 4.—Change of compressibility of aqueous solutions. Compressibility plotted as ordinates; molal concentration per liter; as abscissas.

Curve M (circles) represents compressibilities of aqueous solutions of methyl acetate. Curve E (crosses) represents compressibilities of aqueous solutions of ether. Curve U (triangles) represents compressibilities of aqueous solutions of urethan.

---

[28] See Ref. 5, pp. 113–139. A brief bibliography is given on p. 139. The chief investigators were Braun, 1887; Drecker, 1888; Drucker, 1905; Gilbault, 1897; Grassi, 1851; Pohl, 1906; Röntgen and Schneider, 1886–1888; Schmidt, 1905; Schumann, 1887; Tait, 1895. Pagliani, *Gazz. chim. ital.*, **50**, ii, 186 (1920). Compare Ritzel, *Z. physik. Chem.*, **60**, 319 (1907); and Carnozzi, *Nuovo Cim.*, [5] **9**, 166 (1905).

the solutes, not to their organic nature.[29] This same tendency doubtless affects to a slight extent even the dilute solutions.

On the other hand, with organic solvents investigated by Drecker, Ritzel and Carnazzi, no such striking minimum is noticeable, although the compressibility-concentration curves are not perfectly linear. Solutions of acetic acid in other organic liquids, as investigated by Ritzel, tend on the contrary to show maxima, rather than minima. This is consistent with the assumption that acetic acid is polymerized in the liquid form, the polymer occupying less volume than the monomolecular substance.

The inference that the compressibility of a solution consists of a number of added effects, depending upon the polymerization, the internal pressures and the compressibilities involved, leads to the conclusion that there is not yet any means of predicting with exactness the compressibility of a concentrated solution. The present evidence shows, however, that a close approximation may be had to the compressibility of a dilute solution, because in a dilute aqueous solution the chief effect may be ascribed to the degree of the polymerization of the water, which seems to be affected approximately (at least in the three cases considered) to an equal extent by an equal number of moles of any solute. This is the most important quantitative outcome of the work. Superposed upon the chief effect of depolymerization one finds evidence of the subsidiary effect of the compressibility of the solute in its dissolved condition—which effect, in dilute solution, is small and cannot at present be predicted with certainty. It is doubtless influenced by the affinity pressures concerned.

Thus, the great decrease of compressibility of dilute aqueous solutions may be ascribed chiefly to two causes; first, to the fact that the amount of water present in unit volume is diminished (in these cases nearly 10% per mole) and second, to the probability that the percentage of polyhydrol present in this water has been reduced (according to the inferences drawn from density) by about 10% more. If about 0.3 of the total compressibility is due to the act of depolymerization, the total change of compressibility should then be about $0.06 \times 43 \times 10^{-6} = 2.6 \times 10^{-6}$ per mole, which is that actually observed. This confirmation is welcome.

The molecular weights of the solutes are not sufficiently different to make certain that the depolymerization is always proportional to molal concentration and not to the volume or surface of the dissolved molecule, but the former relation seems to be more probable. The same limitation applies to conclusions concerning density.

As already stated, these inferences are independent of any assumption as regards the molecular weights of the two forms of water. Much is to be said in favor of Sutherland's[30] conclusion that "polyhydrol" is really trihy-

---

[29] Compare Ref. 5, p. 127, for a different interpretation.

[30] Sutherland, *Trans. Faraday Soc.*, **6**, 105 (1910).

drol, and that the less polymerized molecule which constitutes the bulk of liquid water (called "hydrol" above) is really dihydrol. Some facts (but not any of those discussed in the present paper) seem to indicate that there may be also a small amount of further dissociation into monohydrol.[8] Unfortunately, the X-ray analysis of ice, which might throw light upon the subject, is inconclusive. As Wyckoff says[31] ". . . nothing definite can be considered as known about its atomic arrangement." If any monohydrol can exist in liquid water, the present method of extrapolation in Fig. 3 is perhaps a more satisfactory method of obtaining the maximum contraction than the solution of a little water in a very large quantity of any "isofluid" solvent could be, because the latter operation might cause an appreciable quantity of the dihydrol to dissociate into monohydrol, with additional change of volume.

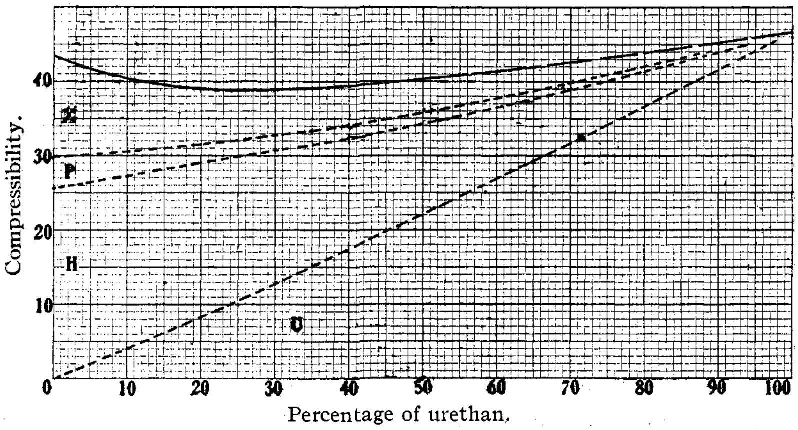

Fig. 5.—Representation of factors determining compressibilities of aqueous solutions of urethan. Hypothetical compressibilities plotted as ordinates; percentages of urethan as abscissas.

Curve X indicates the part played by molecular change, Curve P the part by compressibility of polyhydrol, Curve H the part by compressibility of "hydrol," Curve U the part by compressibility of urethan.

A graphic indication of the respective parts taken by the different constituents in the compressibility of an aqueous solution of a non-polar substance may be of interest. Fig. 5 is an attempt to represent the situation very roughly. The upper curve indicates the actual compressibilities (as ordinates) of solutions of urethan (with pure water on the left and pure liquid urethan on the right), the extrapolated portion being indicated by a broken line. The part of any ordinate falling within any one of the four fields (defined by the broken lines beneath) is intended to show the fraction

---

[31] Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, **1924**, p. 266.

of the total compressibility due to that particular cause. The field labeled U represents the part played by urethan; that labeled H, the part played by "hydrol;" the field P, the part played by the compression of unchanged polyhydrol;[32] and the field X, that portion of the compressibility which corresponds to the act of depolymerization. This last is not true compressibility, but rather a volume change due to enforced molecular dissociation; it might be called "*pseudo-compressibility*." The diagram is, of course, extremely crude, but it serves to make clear the most important influences which determine the compressibilities of such solutions. Probably none of the lines dividing the fields is quite straight. Moreover, since the volume attained by cohering molecules must be due to the balancing of opposing pressures, the volume assigned to any given molecule is inevitably somewhat arbitrary. The outcome is essentially consistent with the conclusions of Baxter,[4] and of Richards and Palitzsch.[8] The field X is in reality probably somewhat larger than the diagram indicates.

We hope in the near future, by means of a far more comprehensive systematic study of the properties of other similar solutions, to determine to what extent the assumptions and inferences discussed above may need modification. Although tentative, they nevertheless seem to be in accord with common sense and, furthermore, appear to present a clear, even if inexact, picture of the causes determining the volumes and compressibilities of solutions of non-polar substances.

We are indebted to the Carnegie Institution of Washington and to an anonymous benefactor of this Laboratory for generous financial support in this investigation.

Summary

This paper gives results for the densities of the following solutions: urethan, ether, alcohol and methyl acetate in water from zero concentration to saturation; and urethan in alcohol, ether and benzene. It gives also compressibilities of solutions of methyl acetate and ether in water as well as of pure methyl acetate and ether.

A convenient method (hitherto not employed for this purpose) for determining densities of liquids in vacuum was used.

The volume changes which occur on forming these solutions are shown to be explicable by reference to three causes, of which the first two have been considered before by others: (1) the mutual affinity or attraction manifested by the liquids for one another in relation to the cohesive affinities of the pure liquids; (2) the effect of depolymerization of one or both liquids and to solvation; (3) the effect of the several compressibilities of the cohering substances. The last of these three causes has not (for non-polar solutions) been sufficiently considered in the past.

---

[32] The compressibility of ice is very small compared with that of water. Richards and Speyers, THIS JOURNAL, **36**, 491 (1914).

This analysis of the situation makes it possible to define more clearly the role played by polymerization in the volume change. A rough estimate of the extent of polymerization of pure water and of water containing dissolved urethan is attempted.

The effect of a dissolved substance on the compressibility of the solution is shown to be dependent upon the same causes which determine density. A dilute solution, even of ether, is much less compressible than pure water. Half molal solutions of three different substances in water are shown each to possess a compressibility about 3% less than that of pure water. This quantity is inevitably affected somewhat by the specific compressibility of the solute and by the internal pressures concerned.

Further investigation is planned.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CRYOGENIC RESEARCH LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

A CRYOSTAT FOR PRECISION MEASUREMENTS AT TEMPERATURES EXTENDING TO —180°[1]

BY J. E. WALTERS AND A. G. LOOMIS

RECEIVED JUNE 11, 1925 PUBLISHED SEPTEMBER 5, 1925

Introduction

For precision measurements at low temperatures it is essential that the temperature be maintained constant to ±0.01° for considerable periods of time, since the temperature scale has now been established within this limit. In this paper we describe a cryostat that maintains any desired temperature within the range 0° to —180° constant to ±0.01° for several hours at a time, with the added features of simplicity, economy and safety.

Types of Cryostats

Among the cryostats that have been described in the literature are those of Onnes,[2] Timmermans,[3] Henning,[4] Maass,[5] Stock,[6] Henning and Stock,[7] von Siemens,[8] Cardoso,[9] Keyes[10] and Jackson.[11] All of these may be divided into five general classes: (1) boiling liquids, (2) addition of liquid air to the cryostat bath by hand, (3) regulation of the flow

---

[1] Published by permission of the Director of the Bureau of Mines.

[2] Onnes, *Leiden Communications*, Nos. 83, 94, 123 a.

[3] Timmermans, *Proc. Roy. Soc. Dublin*, **13**, 310 (1912).

[4] Henning, *Z. Instrumentenkunde*, **33**, 33 (1913).

[5] Maass and Wright, THIS JOURNAL, **43**, 1098 (1921).

[6] Stock, *Ber.*, **53**, 751 (1920).

[7] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[8] von Siemens, *Ann. Physik*, [4] **42**, 871 (1913).

[9] Cardoso, *Arch. Sci. Phys. Nat.*, **13**, 317 (1915).

[10] Keyes, Townshend and Young, *J. Math. Phys., Mass. Inst. Techn.*, **1**, No. 4, 213. Also Taylor and Smith, THIS JOURNAL, **44**, 2450 (1922).

[11] Jackson, *J. Sci. Instruments*, **2**, No. 5, 158 (1925).