the recalculated result may be considered as superseded by my later and more careful work. Because the probable errors of all of the other determinations are more than five times as great as those of Morley and myself, they would be excluded by the third principle proposed. The final value, if calculated from these two results, is **1.00775.**

It is interesting to notice the relation between the real errors of the various values (assuming this value as true) and the probable errors. *Only in those cases where we now know that there were serious constant errors, is the real error more than six times the probable error.*

Morley calculates a value corresponding to 1.00762 from his determinations of the densities of the gases and their combining volumes. This value has not been considered here, partly because the probable error of the density of hydrogen is about 3 in 100,000, instead of 2 for the chemical method, but chiefly because of the uncertainty of the ratio of the combining volumes.[1]

If a value is calculated by Professor Clarke's method, weighting each result in inverse proportion to its probable error, only Keiser's older value and my own original value would affect the value which I have selected by more than about one part in 100,000. Keiser's older value would, however, reduce it by about 40 parts and my own original value by about 4 parts in 100,000.

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THE RELATION BETWEEN COMPRESSIBILITY, SURFACE TENSION AND OTHER PROPERTIES OF MATERIAL.

(PRELIMINARY PAPER.)

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

Received October 30, 1907.

A recent paper by Albert Ritzel[2] upon gas solubility, compressibility and surface tension, seems to render important the brief publication of some work carried on by us during the winter of 1905–06. This work was presented to the Physico-chemical Club of Boston and Cambridge on May 2, 1906, under the title "The Relation of Compressibility to Other Physical Properties, with Particular Reference to Surface Tension," and was discussed there. On account of the subsequent absence of one of us in Germany the publication of this work has been delayed, the amount of material being so large that a careful study of the relations demanded more time than was then available.

The present notice seems desirable because Ritzel has touched upon one of the relations studied previously by us. He has used the method of determining compressibility which we have used, and shows that this

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[1] Morley: "Smithsonian Contribution to Knowledge," No. 980, p. 110 (1895).

[2] Z. physik. Chem., 60, 319 (1907).

property of substance is a significant one. His paper is interesting and valuable as far as it goes, and scarcely touches at all the immediate ground which we covered, but in order to save the time of any one else who might be thinking of continuing his work, it seems only fair that our results should likewise be put into print.

As Ritzel has referred in his paper to the suggestions of van der Waals and others concerning a possible relation between compressibility and surface tension, it is not necessary for us to repeat this discussion. The subject was studied by us from somewhat a different point of view, namely, from the point of view of the theory of compressible atoms.[1] The logic of our train of thought was this:

Premises.—(1) All bodies under high pressure have a smaller compressibility than the same bodies under low pressure. (2) The physical affinity which causes surface tension probably exerts pressure in its action.

Conclusion.—Therefore, the greater this physical affinity of surface tension, the less will probably be the compressibility under additional outside pressure, at any rate in substances of similiar composition. This probable relationship was suggested by Ostwald at a discussion concerning atomic compressibility in the same Physico-chemical Club in the autumn of 1905, and with his approval we immediately began the study of it. The subject fitted very suitably into the scheme upon which we had already begun work—a scheme which embraced many other physical properties of substance.

In this preliminary notice it is not necessary to describe in detail the methods which we used for determining the various quantities in question. It is enough to say that all the substances were redistilled fractionally until their purity was reasonably satisfactory, the substances of commerce having been shown to be altogether too impure to give significant results. The method of Richards and Stull[2] was used for determining the compressibilities, and with some modifications the method of Ramsay and Shields,[3] for determining the surface tensions; the boiling-points were corrected for the projecting thread of the thermometer, and the specific gravities were determined with great care by means of the Ostwald pycnometer. All the data given below except the heats of vaporization were made in the Harvard Laboratory, some of them as parts of another investigation by one of us in collaboration with Dr. Stull, the rest by the present authors. Each figure is suitably designated in order to show who found it. The heats of vaporization are taken from the work of

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[1] Proc. Amer. Acad. Arts and Sciences, **39,** 581 (1904); also, Z. physik. Chem., **49,** 15 (1904). This Journal, **26,** 399.

[2] Z. physik. Chem., **49,** 1 (1904); also, Pub. No. 7 Carnegie Institution of Washington.

[3] Z. physik. Chem., **12,** 433 (1893).

others, as tabulated in the well-known tables of Landolt and Börnstein. The compressibilities are expressed in terms of the kilograms per square centimeter, which is 0.967 atmosphere; that is to say, a substance having a compressibility of $\beta = 80 \times 10^{-6}$ would be altered in volume by the

Substance	Compressibility. $\beta \times 10^6$.	Boiling point.	Density $20^\circ/1^\circ$.	Surface tension γ.	Vapor pressure at 20°.	Molecular heat of vaporization.	$K = 1000\beta\gamma^{4/3}$.
Methyl aniline	41.87	195.7°	0.9865	39.46	..	42.67	2.6
Dimethyl aniline	47.98	193.7	0.9555	36.50	..	40.19	2.8
Ethyl aniline	45.89	206.5	0.9625	36.58	..	..	2.6
Diethyl aniline	49.79	217.5	0.9344	34.17	..	..	2.6
Toluidine (ortho)	40.43	196.5	0.9986	39.76	..	42.67	2.5
Toluidine (meta)	41.89	199.0	0.9887	36.92	..	..	2.4
Cresol (ortho)	42.24	187.0	1.0482	—	..	..	..
Cresol (meta)	42.58	201.0	1.0341	36.82	..	45.17	2.4
Cresol (para)	42.14	200.5	1.0347	36.58	..	..	2.4
Benzyl alcohol	40.20	204.5	1.0463	38.11	..	..	2.4
Ethyl acetate	81.6[1]	77[1]	0.8990[1]	23.87	72.8	30.94	2.6
Propyl formate	78.3[1]	81[1]	0.8982[1]	24.45	63.9	31.37	2.6
Ethyl benzene	64.8[1]	136[1]	0.8759[1]	28.90	8.2	33.88	2.7
Xylene (ortho)	64.4[1]	142[1]	0.8633[1]	28.40	5.8	..	2.6
Xylene (meta)	64.6[1]	139[1]	0.8642[1]	28.48	6.7	34.72	2.6
Xylene (para)	65.7[1]	138[1]	0.8612[1]	28.24	7.5	..	2.6
Isoamyl formate	72.8[1]	123[1]	0.8706[1]	24.58	9.4	34.72	2.4
Methyl isovalerianate	74.6[1]	116[1]	0.8808[1]	24.10	14.15	33.88	2.4
Ethyl butyrate	76.9[1]	120[1]	0.8785[1]	24.44	11.9	34.72	2.5
Isobutyl acetate	78.6[1]	116.5[1]	0.8711[1]	23.62	14.1	33.88	2.5
Ethyl isobutyrate	80.8[1]	110[1]	0.8710[1]	23.26	18.8	..	2.5
Ethyl propionate	78.8[1]	99[1]	0.8907[1]	23.32	28.4	33.05	2.4
Methyl isobutyrate	80.4[1]	92[1]	0.8906[1]	23.72	42.0	32.21	2.5
Methyl butyrate	75.8[1]	102[1]	0.8982[1]	..	24.3	33.05	..
Valerianic acid	69.4	175	0.9301	25.23	..	43.92	2.4
Methyl acetate	78.7	57	0.9286	24.58	..	29.07	2.6
Ethyl acetate	81.6[1]	77[1]	0.8990[1]	23.87	72.8	30.94	2.6
Methyl alcohol	85.7	66	0.7940	22.39	(88.6)[2]	35.14	2.5
Ethyl alcohol	72.75	78	0.8040	22.68	44.0	39.74	2.2
Propyl alcohol (norm)	71.2	97	0.8044	24.23	15.8	41.41	2.3
Butyl alcohol (norm)	69.2	117	0.8094	24.25	(5.0)[2]	44.34	2.3
Butyl alcohol (tert)	79.6	83	0.7887	20.44	31.75	40.37	2.1
Isoamyl alcohol	75.6	131	0.8121	23.56	..	52.94	2.4
Ethyl bromide	89.5	38.0	1.4307	23.23	(387)[2]	27.61	2.8
Ethyl iodide	74.4	72.2	1.9330	28.24	(110)[2]	30.54	3.0
Ethylene chloride	61.5	83.7	1.2569	32.50	62.0	..	3.0
Ethylene bromide	50.5	131.7	2.1823	38.83	9.2	34.30	3.0

Average value of K = 2.53

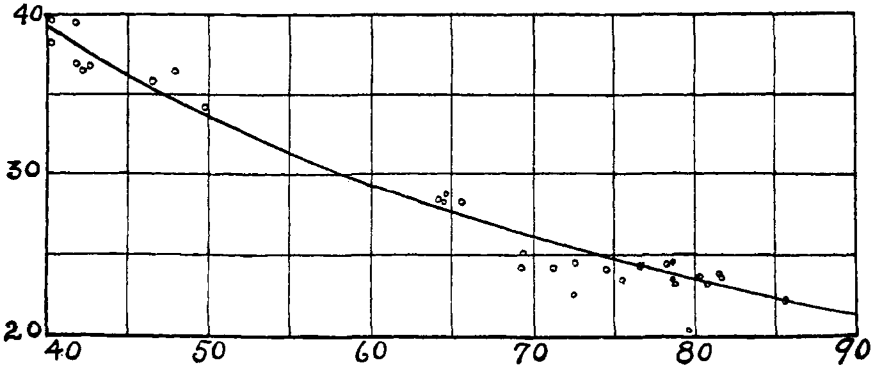
[1] Richards and Stull

[2] From Landolt and Börnstein.

addition of 0.967 atmosphere, 0.08 milliliter in one liter. This particular value is about double that for water.

Having thus briefly stated the nature of the results, the table containing them may be given at once. In this table, the results are classified according to the composition of the substances, isomeric bodies being placed together. A glance at the table will show that in general the compressibility is large when the surface tension is small, and *vice versa.* Empirically it was found, especially among similar substances, that if the four-thirds power of the surface tension is multiplied by the compressibility, very nearly a constant value is found, especially among similar substances. This approximately constant value is given in the last column.

The results tabulated in the first and fourth columns of figures in this table may well be plotted in a diagram, showing the relation between compressibility and surface tension. As has been said, the general tendency of this curve is expressed by the equation $\beta \gamma^{4/3}$ = constant.



Comparison of the surface tensions and compressibilities of thirty-one compounds of carbon, hydrogen and nitrogen or oxygen. Surface tension (γ) is plotted in the direction of ordinates, compressibility (β) in the direction of abscissae. The curve represents the equation $\beta \gamma^{4/3}$ = constant.

This diagram contains all the results, excepting the four halogen compounds, which have surface tensions too high to correspond with their compressibilities—that is to say, where the value for the constant (3.0) is considerably above the average, 2.5.

That the relationship should be affected by the specific nature of the material need cause no surprise. Indeed it is surprising that the parallelism should be so great as it is. The surface tension may be supposed to be determined chiefly by the cohesive affinity of the substance, or from the molecular point of view, by the attraction between one molecule and another. We have shown that this attraction is probably *one* of the factors entering into the compressibility of a substance, but it is not the only one. Obviously, not all substances have the same compressibility when subjected to the same increase of pressure, even when they were at first under the same internal tension. Moreover, we must suppose that the compressibility includes within its magnitude not only the change in volume of the outside portions of the molecule, affected by the physical pressure of cohesion, but also the internal alteration of the molecule as well. Hence it is not at all surprising that the specific nature of the substance exercises a distinct effect upon this latter property, and therefore upon the relationship between it and surface tension.

In endeavoring to connect the other properties of material we see in the same way that the specific nature of the substance conceals in part relationships which might otherwise become manifest. For example, the specific gravity would naturally be supposed to be greater in compounds with great surface tension and small compressibility, than in those with small surface tension and great compressibility. The latter substances should be compressed into smaller bulk by the energy of their own cohesive affinity. Such substances also should have high boiling-points and high molecular heats of vaporization. To a certain extent one may trace this connection of properties upon comparing the data for a number of substances taken at random, but it is evident that the matter is not quite so simple as would appear from the above statement. Clearly the specific gravity is enormously affected by the nature of the elements which build up the atom, and variation in the composition may wholly conceal the effect due to surface tension or cohesive affinity. For example, the average specific gravity of hydrogen in an organic compound appears to be only 0.18, because the atomic volume of hydrogen is 5.5, while the specific gravity of carbon in an organic compound is 1.09, and that of oxygen varies between 1.3 and 2.0 on the usually accepted basis. These values are simply obtained by dividing the atomic weight by the usually accepted atomic volume.

On the other hand, in cases of isomeric compounds, regularities appear in the expected direction, except indeed where methyl compounds are concerned. Take for example the substances with the formula $C_6H_{12}O_2$, ethyl butyrate and its isomers. From the figures given in the table it is clear that the order of magnitude in the case of all these properties places ethyl butyrate on one extreme and ethyl isobutyrate on the other extreme with isobutyl acetate in the middle; and that the direction is always that demanded by the reasoning above.

It is not, however, our purpose in the present paper to attempt to sift out and explain all the perplexities of these data. That, when sufficient knowledge is obtained concerning them, the variations will be capable of explanation, at least in a qualitative way, we have no doubt, and indeed most of them are at present explicable. The object of the present paper is to point out the particular relationship between surface tension and compressibility, and to call attention to the fact that we are working further upon this relationship and other relationships concerning other allied properties of substance.

We are greatly indebted to the Carnegie Institution of Washington for generous aid in this research.

Summary.—(1) In this paper are given a number of new results on the compressibility, surface tension, boiling point, specific gravity and the vapor pressure at 20° of a number of organic substances.

(2) It is shown that approximate relationships exist between some of these quantities, particularly that as a rule substances with large surface tension possess small compressibility.

(3) This relationship is discussed briefly from the point of view of the theory of compressible atoms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS, No. 4.]

THE ATOMIC WEIGHT OF CHLORINE.

BY WILLIAM A. NOYES AND H. C. P. WEBER.

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The ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells,[1] the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver: oxygen :: 107.93: 16 is correct. Guye and Ter-Gazarian[2] have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107.89. The newly accepted value, 14.01 for nitrogen also points to the lower value of 107.89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes[3] and by Richards and Jones[4] that the value, 107.93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar.[5] In this determina-

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[1] This Journal, **27,** 459.

[2] Compt. rend., **143,** 411.

[3] This Journal, **29,** 808.

[4] *Ibid.*, **29,** 826.

[5] Phil. Trans., **205,** 169. Series A., Chem. News, **91,** 263. The determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations.