This outline is, of course, merely a sketch of the method. It needs amplification with the help of many examples, which can easily be provided by anyone even moderately familiar with the principles evolved.

Summary.

To sum up briefly the contents of this note: the idea of the component is replaced by that of the "individual," which is defined in the simplest possible way as an undecomposed chemical substance necessary for constructing the system under consideration, and the number of individuals needed to satisfy the Phase Rule is taken as the least number of such "individuals" needed to construct the system. Into the equation representing the Phase Rule and expressing the number of degrees of freedom of the system is then introduced a term giving the maximum number of independent restrictions involved in the fixation either (*a*) of one or more of the intensity-factors of the forms of physical energy concerned, or (*b*) of some concentration-relation of the individuals in the variable phase. A somewhat obvious method of evolving the Phase Rule inductively for beginners is sketched.

This note is intended rather as the suggestion of an idea than as a final or complete statement of the case. The nomenclature is subject to change if better designations can be found. The object of the note is to remove, if possible, the most serious stumbling-block from the path of the beginner.

CAMBRIDGE, MASS.

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

THE COMPRESSIBILITY OF CERTAIN TYPICAL HYDROCARBONS, ALCOHOLS AND KETONES.

BY T. W. RICHARDS AND J. W SHIPLEY.

Received February 25, 1916.

This research was a continuation of work already published in several instalments during the last twelve years. The object was to ascertain a large number of compressibilities of pure organic substances under similar conditions. From a physicochemical point of view this is a desirable object, because compressibility has close relations to other properties and is directly concerned with the nature of the several substances.[1]

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attempt the application of the Phase Rule to such cases, which are full of pitfalls. A much simpler case is a dilute amalgam cell with two concentrations of amalgam as the two electrodes. Here the concentration of the electrolyte is without influence and does not form another restriction (Richards and Lewis, *Z. physik. Chem.*, **28**, 7 (1899)).

[1] Richards and Stull, *Pub. Carnegie Inst.*, **7** (1903); *Z. physik. Chem.*, **49**, 1 (1904); Richards, THIS JOURNAL, **26**, 399 (1904); Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst.*, **76** (1907); *Z. physik. Chem.*, **61**, 77 (1907); *Ibid.*, **61**, 183 (1907); THIS

The previous papers have so fully described the method that only a very abbreviated description will be given here, emphasis being laid merely upon the respects in which improvements have been introduced. The most important improvements were in the pressure gauge, the form of piezometer and the study of the hysteresis of glass.

It should be noted that the present research was completed before that carried out with the help of E. P. Bartlett[1] upon the compressibilities of several elements, and the experience gained in the present research was very useful in that one.

Pressure Gauge.

The absolute pressure gauge resembled in principle those of Amagat and Bridgman, but was smaller and comparatively inexpensive, although fully as accurate. It consisted simply of a steel attachment to be screwed upon the pressure-cylinder of the familiar Cailletet apparatus—the attachment being bored with a very even hole, into which ran a closely fitting cylindrical piston or plunger. The shaping of this attachment and the manner of screwing it in place upon the pressure cylinder are shown in the diagram (Fig. 1) which will be at once comprehensible to anyone familiar with the Cailletet apparatus. The projecting conical upper end of the plunger was fitted loosely into a conical bearing, and this supported a horizontal steel bar, from which was suspended a heavy scale pan made of oak, about 50 × 100 cm. in area, and capable of bearing weights to the extent of 200 kg. The plunger and cylindrical hole were about 0.63 cm. ($^1/_4$ inch) in diameter.

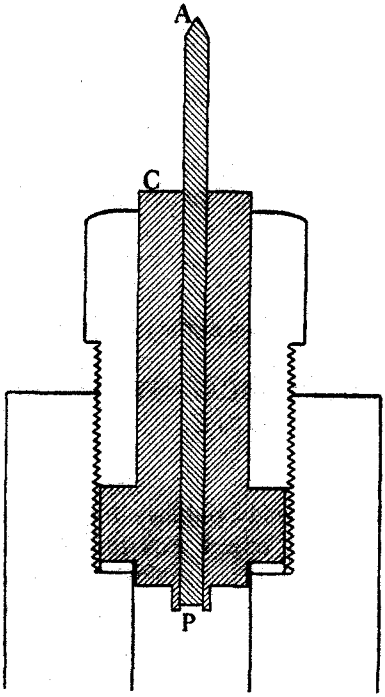

Fig. 1.—Plunger and cylinder of absolute pressure gauge. Plunger AP, cylinder C.

Two such attachments (A and B) were made for us with great care by the Taft-Pierce Mfg. Co. of Woonsocket, R. I., and their indications were found to be precisely identical when attached both at once to the same system.

Journal, **31**, 154 (1909); Richards and Mathews, *Ibid.*, **30**, 8 (1908); *Z. physik. Chem.*, **61**, 449 (1908); Richards and Jones, This Journal, **31**, 158 (1909); *Z. physik. Chem.*, **71**, 152 (1910); Richards, Stull, Mathews and Speyers, This Journal, **34**, 971 (1912).

[1] Richards and Bartlett, This Journal, **37**, 470 (1915).

Especial study was made of the heretofore doubtful question as to the actual working diameter of the plunger, compared with its carefully measured diameter when not in operation. The latter can be determined with great accuracy by means of a screw micrometer gauge, which gives very precise results; but the diameter while in operation is not so easily estimated, partly because the space between the plunger and the cylinder must be appreciable if the cylinder is to move easily, and partly because of the compression of the steel piston. The latter effect is negligible at 500 atmospheres, however, not exceeding 0.06%.

In practice, previous experimenters have usually accounted half of the width of the intervening space between plunger and cylinder as belonging to the plunger and half of it as belonging to the cylinder, thus accounting the effective diameter of the plunger as the mean between that of the cylinder and the plunger; but no one seems to have made a careful quantitative study as to the legitimacy of this procedure. We at first adopted the same method and determined the size of the annular space by exactly filling it with oil and then withdrawing and weighing the plunger. Several trials gave very consistent results, and the method (which depended upon the assumption that upon withdrawal half of the oil remained on the plunger and half on the cylinder) would doubtless have answered any ordinary purpose. Nevertheless, we were not satisfied, and proceeded to test the behavior of plungers B_1, B_2, B_3, of slightly different sizes in the same cylinder, comparing each with A_1 in a connected apparatus. The size of the bore at P was measured by means of a very slightly tapering plug made for this special purpose, and the plungers were measured with great care micrometrically. The following table contains the result of these measurements, together with the comparison of the calculated effective area with that actually found by the comparison of the pressures. It will be seen that the agreement is satisfactory—the greatest error being only 0.02%, except with the loosest piston, which gave a result well within 0.1%.

TABLE I.—EFFECTIVE PLUNGER AREA (IN INCHES).

Plunger.	Diameter of plunger.	Diameter of lower orifice of cylinder.	Double width of vacant annular space.	Assumed effective diameter.	Effective area calculated from assumed effective diameter.	Difference between calculated effective area and that of A_1.	Difference found in actual effec. area by direct compar. with A_1.
A_1	0.25040	0.25049	0.00009	0.25045	0.31784	0.00000	0.0000
B_1	0.24997	0.25000	0.00003	0.24999	0.31670	0.00114	0.0012
B_2	0.24970	0.25000	0.00030	0.24985	0.31630	0.00154	0.0016
B_3	0.24950	0.25000	0.00050	0.24975	0.31605	0.0018	0.0020

In a second trial these gauges were compared not only with one another, but also, taking great care and expenditure of time, with Dr. Bridgman's gauge. In this comparison the least accurate plunger (B_3) was not included, but the comparison of the other plungers was even more satisfactory than the figures in the table just given. B_1 was not taken as the standard, because it fitted very closely indeed. Assuming its area as 0.31670, Bridgman's piston was found to have the actual area calculated from the weights which it would support, of 0.31842, whereas we calculated its area by adding half the width of its annular space to its radius as 0.31845. In the same way for A_1 0.31785 was found as against the calculated 0.31784, and for B_2 the value 0.31627 instead of the calculated 0.31630. In no case does the deviation here amount to as much as 0.01%; the agreement is so close that it must have been partly due to accident. In any case the usual rule of accounting half of the width of the annular space as belonging to the piston is seen to be a safe and adequate rule. Moreover, it is clear that we had attained very exactly a knowledge of the diameters of our several pistons, and that, therefore, our standard of pressure was beyond reproach.

The details of the comparison of Bridgman's gauge with ours need not be dwelt upon. It is enough to say that all the pressures given in the present paper are determined by one or other of the pistons just described, and that all of these gave the same standard of pressure within the limit of error of the experiment, agreeing also with Bridgman's. The Bourdon gauge was used only as an approximate guide to the pressure and never as a final index.

Piezometer.

The piezometer for liquids was designed with the idea of securing the greatest possible convenience and accuracy. The principle is the same as that of the forms suggested in previous papers, but it is on the whole decidedly more convenient than most of those forms. It is shown in the diagram (Fig. 2). The platinum point (opposite P) must, as usual, be very finely sharpened. The most difficult part of the apparatus to adjust was the stopcock (S), which needed polishing, first with very fine emery and finally with rouge until it was perfectly smooth. It was lubricated with a trace of lubricant made of hard and soft paraffin and melted rubber, but this was scarcely necessary, and only a trace was used. The accuracy of the apparatus depends greatly upon having the stopcock ground with extraordinary fineness. The whole must be very carefully constructed of glass as nearly similar as possible, and must be annealed with the greatest care, because any strain in the glass may lead to rupture under pressure. When constructed in this way the apparatus proved to be exceedingly satisfactory. It was at first filled with mercury between S and P, and the compressibility of the mercury in glass was determined. Then the liquid to be studied was drawn in after the mercury, the latter being drawn up into the upper barrel (A). After the excess of mercury in A had been removed, the compression of the remaining mercury and the weighed amount of liquid was determined quantitatively in the usual manner by adding successive drops of mercury through the opening O and finding in each case the pressure needed to cause exact contact at the point P. The calculation was precisely as usual. Besides eliminating the objectionable stopper, which is the chief disadvantage in most of the other forms thus far suggested, this form of piezometer offered the further advantage in that the weight of the substance being compressed was determined immediately after being drawn into the apparatus.

The details of filling were as follows: After it had been thoroughly cleaned, dried, filled with mercury considerably above the platinum point and weighed, the point of the stopcock was inserted into an auxiliary vessel containing an accurately weighed quantity of mercury, together with about the desired quantity of the liquid (9 or 10 cc.) to be compressed. Enough mercury was expelled from the piezometer into the auxiliary vessel below to drive over all the air enclosed in the stopcock. Then most of the liquid to be studied (7 to 8 cc.) was drawn up into the apparatus, followed by mercury sufficient to form a seal 10 cm. long in the capillary above the stopcock. The mercury in the stopcock itself was then run back into the auxiliary vessel by turning the stopcock one-quarter way around until the interior hole was opposite to the aperture (H) drilled for this purpose, and the piezometer with its contents was reweighed. The residual lighter liquid remaining in the auxiliary vessel was removed, and the weight of the mercury in the auxiliary vessel was determined after thorough drying with filter paper. The gain of the weight of the piezometer vessel and total mercury before and after gave the weight of substance introduced into the piezometer. In practice this method was found to be very expeditious and exact and the manipulation easy and neat.

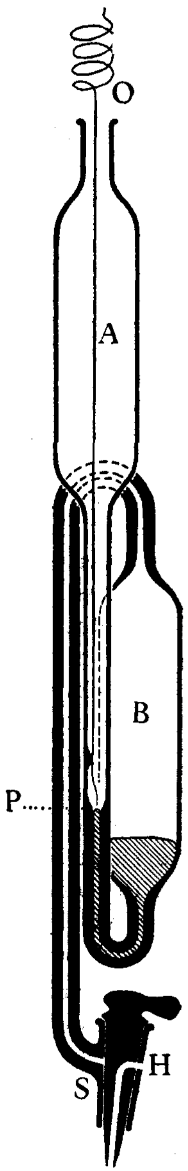

Fig. 2.—Piezometer for liquids. The platinum point which determines the attainment of definite volume is opposite P.

After the last weighing, the mercury in the upper barrel A was removed by a fine pipet down to the platinum point P. It is absolutely essential that the small mercury meniscus thus left should be perfectly clean. Otherwise good contact is not always obtained at the platinum point, and the indications of the instrument are uncertain. On the other hand, when it is perfectly clean, the pressure may be ascertained within 0.01 megabar. A brief description of the method of cleaning may be given in order to guide others in this important procedure. The barrel A was filled with water, and a drop or two of concentrated nitric acid introduced by means of a capillary pipet directly upon the surface of the mercury in the capillary. By alternately slightly warming and cooling the piezometer, the acid was drawn up and down the capillary past the platinum point. This was continued with fresh quantities of acid until the mercury moved up and down without any break in its surface or tendency to cling to the walls. The acid was then washed out by means of a very fine funnel tube, and the walls of the capillary and the platinum point scrubbed with a bit of chamois on the end of a wire.

Subsequently, of course, great pains must be taken to exclude the access of foreign matter to this carefully cleaned spot. The upper bulb A was plugged with cotton wool at its top (O), but even this does not wholly prevent the creeping of oil along the glass or wire when the instrument has been some time in use after filling. After each determination of the pressure the plug was removed, and the adhering oil dissolved with a little ether, care being taken that none of the latter approached the surface of the mercury. Since it is difficult to obtain ether pure enough to be wholly without action upon mercury, the water in bulb A must be completely renewed after each determination of pressure.

If these precautions are heeded, very constant results may be obtained· The mercury meniscus evidently takes exactly the same shape at each return to any definite pressure. The meniscus may still change slightly in shape at different pressures, but this makes no difference whatever in the result obtained by this method, for any changes of this sort are entirely eliminated in subtracting the values obtained with mercury alone from those obtained with the given liquid in the piezometer.

The bulb B was immersed wholly under mercury in the barrel of the compression apparatus, and was found to lose very quickly its heat of compression. If the pressure is slowly applied, the temperature of the whole apparatus never rises much above the constant temperature of the thermostat—an important condition on account of the thermal hysteresis of glass. The reading was always taken 15 minutes from the first application of pressure. The piezometer being always lighter specifically than mercury, it was necessary to push the instrument down beneath this liquid, and the pressure thus applied in mounting the instrument kept a platinum coil emerging from the top of A in good contact with a similar small coil attached to the movable top of the cylinder, so that electrical connection was easily obtained. This arrangement is the simplest and most convenient method of arranging the instrument and making contact thus far devised.

The capillary pipet employed for removing and adding mercury is worth a brief mention. The fine tube 25 cm. long was graduated in terms of grams of mercury, and was of such diameter that 2.5 cm. corresponded to one gram. This greatly facilitated removing or adding a definite amount of mercury to the piezometer. Before removing the pipet from the piezometer the mercury in the capillary pipet was always drawn up several centimeters from its lower end, in order to avoid the possibility of losing drops of mercury when transferring it to the weighing cup.

Two piezometers of this shape were used, designated IV and V. The latter contained the same stopcock as the former, which was accidentally broken in the middle of the research.

In connection with this work, a careful series of experiments on the pressure-volume hysteresis of glass was conducted. It was found that this may be very important, if the glass is exposed to high pressure for a long time. Glass slowly contracts under the continued pressure, so that the piezometer diminishes in volume. At first it would seem as if this pressure hysteresis would have a detrimental effect, but this is not the case. If the same time is always allowed between the first application of pressure and the final reading, and if on successive days the instrument is treated in essentially the same way with each successive liquid, as well as with the mercury used in standardizing it in the first place, all these hysteresis effects are eliminated, being the same in each case. Hence in working with the glass apparatus at pressures above 200 megabars, one must be careful to comply with these conditions if results of the highest accuracy are desired. Fortunately, this precaution has been observed in all the work of this sort at Harvard since the beginning in 1902. Of course, the slight volume changes caused by this continued action of pressure have very much less percentage effect upon organic liquids than upon mercury. Nevertheless, it is worth while so to arrange one's experiments as to avoid any error even in the present case.

The full details of the work on pressure-volume hysteresis of glass will be given in another place. They do not concern the present investigation, since the effect was here eliminated in the way just described.

Preparation and Purification of Materials.

Among aliphatic compounds, two nonanes, 2,5-dimethyl heptane and 2,4-dimethyl heptane, were studied, as well as methyl and ethyl alcohol, acetone and diethyl ketone. Eight homologous aromatic substances—benzene, toluene, ethyl benzene, isopropyl benzene (cumene), normal propyl benzene, tertiary butyl benzene, mesitylene and pseudocumene—were subjected to qualitative compression, as well as cyclohexane (hexamethylene) and two of its derivatives, cyclohexanol and cyclohexanone.

These substances were chosen partly to fill gaps in previous work, and partly because they represent a wide variety of carbon compounds.

The preparation and purification of the substances compressed took much time. Although they were secured in the purest condition obtainable yet in most cases they were many times further fractionated. In most cases the constancy of the boiling point and the density were taken as criteria; but in two cases the constancy of the freezing point as solidification progressed could be used as a yet safer assurance of the purity of the substance; in such cases the purification was best conducted by freezing. The full description of the preparation and purification of the substances would require too much space for this publication. Their degree of purity may be inferred from their physical constants given in the table immediately following.

The aromatic hydrocarbons were all the same preparations as those used in a recent paper by one of us and Dr. Frederick Barry.[1] *Methyl alcohol* was prepared in a very pure state through methyl oxalate, which was recrystallized from water until free from impurity and carefully saponified, when the alcohol was fractionally distilled, treated with iodine and sodium hydroxide, and again fractionally distilled. *Acetone* was purified through the acid sulfite addition-product, as was also *cyclohexanone*.

TABLE I.—PHYSICAL CONSTANTS OF SUBSTANCES EMPLOYED.

Name.	Boiling point.	Barometer.	Melting point.	Density 20°/4°.
Methyl alcohol	64.48° to 64.55°	760	...	0.7923
Ethyl alcohol	78.4°	753.5	...	0.7903
Acetone	55.8° to 55.9°	752.3	...	0.7915
Diethyl ketone	101.2° to 101.3°	760	...	0.8136
2,5-Dimethyl heptane	135.6° to 135.9°	760	...	0.7198
2,4-Dimethyl heptane (A)	132.9° to 133°	760	...	0.7158
2,4-Dimethyl heptane (B)	132.4° to 132.9°	760	...	0.7162
Benzene	79.70° to 79.71°	763	5.483°	c.8791
Toluene	110.3° to 110.4°	756	...	0.8649
Ethyl benzene (A)	136.3° to 136.4°	766.7	...	0.8678
Ethyl benzene (B)	136.4° to 136.5°	766.7	...	0.8697
Isopropyl benzene (cumene)	152.6° to 152.8°	759	...	0.8620
Normal propyl benzene (A)	157.9° to 158.2°	765	...	0.8616
Normal propyl benzene (B)	157.9° to 158.2°	765	...	0.8617
Tertiary butyl benzene	168.6° to 168.7°	759.0	...	0.8671
Mesitylene	164.8° to 164.9°	760	...	0.8634
Pseudo cumene	169.4° to 169.6°	764.8	...	0.8786
Cyclohexane (liquid)	81.3° to 81.5°	760	6.40°	0.7791
Cyclohexane (solid)	.. ..	...	6.40°	0.8230
Cyclohexanol (solid)[2]	.. ..	...	23.87°	0.9624
Cyclohexanone	155.6° to 155.7°	768.0	...	0.9466

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[1] Richards and Barry, THIS JOURNAL, **37**, 993 (1915).

[2] Furthermore, the density of liquid cyclohexanol at 40.0°/4° was found to be 0.9327, and at 34.16°/4°, 0.9369; and its boiling point 160.8°.

This latter substance, as well as *cyclohexanol* and *cyclohexane* were made for us by Dr. G. L. Kelley by the Sabatier-Senderens method. The former of the last two (which is very difficult to dry) was purified by 24 recrystallizations, and the latter by 4 recrystallizations. The *nonanes*, two in number, were kindly made by Dr. Latham Clarke[1] for this investigation. All these substances except cyclohexanol and cyclohexanone were scrupulously dried, usually by means of finely powdered fresh lime or sodium. *Mercury* and *water* were carefully purified by the recognized methods used in every laboratory.

In Table I the physical constants of the several substances are recorded. In three cases two samples were available. In only one of these cases, namely, that of ethyl benzene, were the properties of the two samples different to an important degree. Here, Sample A (made by the Fittig reaction) was purer than Sample B (made by the Friedel-Crafts reaction) for reasons explained in the paper with Barry. In the case of propyl benzene a similar difference of source made no difference in the resulting substance.

Data and Results.

Eight determinations of the compressibility of water were made from time to time in order to test the constancy of the method as well as the effect of dissolved air in water. These need not be given in detail here; they will be recorded in another place. It is enough to say that the average compressibility of water over 500 atmospheres remained constant within the limit of error of experiment throughout the whole time. This average was 43.26 between 100 and 300 megabars, 40.69 over the next 200 megabars or an average of 41.97 over the whole range. These determinations showed: first, that the effect of dissolved air in water is less than the error of the method; secondly, that the two pressure-gauge pistons gave essentially the same results; and thirdly (since the determinations were not made all at once, but rather at intervals between those of the organic substances), that the apparatus was functioning properly throughout the time of the research.

The results obtained with the several carbon compounds are shown in Table II. They are tabulated over the same ranges of pressure, with the exception of cyclohexane, in which case (because the substance solidified during compression) the result for the liquid is given only between 100 and 200 megabars and that for the solid only between 400 and 500 megabars. In almost every case at least two complete experiments were made with each substance; and in every case the work with each substance was continued until there could be no reasonable doubt of the result. The total number of experiments made with the fifteen carbon compounds was thirty-seven.

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[1] Latham Clarke, THIS JOURNAL, 34, 60 (1912).

The complete data occupy so much space that there is not room for them here; but they will be published in full in a monograph soon to be published by the Carnegie Institution of Washington, with complete details describing the purification of the substances.

Table II.—Summary: Compressibility of Carbon Compounds.
Temperature 20.00° (except with cyclohexanol).
Unit of pressure = megabar = megadyne per sq. cm. = 0.987 atmosphere, approximately.

	P. range 100–500.	P. range 100–300.	P. range 300–500.	Diff. between ranges.
Methyl alcohol	87.67	95.81	79.53	16.28
Ethyl alcohol	81.60	88.69	74.51	14.18
Acetone	90.09	98.72	81.46	17.26
Diethyl ketone	76.98	83.60	70.36	13.24
2,5-Dimethyl heptane	85.82	94.93	76.71	18.22
2,4-Dimethyl heptane	*87.12*	*95.58*	*78.65*	*16.73*
Benzene	72.09	77.66	66.52	11.14
Toluene	69.00	74.07	63.93	10.14
Ethyl benzene	65.94	70.84	60.97	9.87
Isopropyl benzene	65.37	70.34	60.40	9.94
Normal propyl benzene	64.91	69.73	60.09	9.64
Tertiary butyl benzene	63.44	68.23	58.65	9.58
Mesitylene	62.86	67.41	58.31	9.10
Pseudo cumene	60.18	64.26	56.10	8.16
Cyclohexane (liquid)	...	[92.56]	...	...
Cyclohexane (solid)	...	...	[49.04]	...
Cyclohexanol (liquid) (40.0°)	...	55.58	...	...
Cyclohexanol (liquid) (34.16°)	...	53.96	...	...
Cyclohexanol (solid)	...	...	34.81	...
Cyclohexanone	54.41	57.76	51.06	6.70

A complete discussion of these results in relation to one another and to other similar data as well as to the other related properties of material is a subject too large for the present paper, but a few points are worthy of emphasis. The first relation which is obviously to be drawn from the data is the remarkable parallelism between change of compressibility with pressure and the magnitude of the compressibility itself. In almost every case greater compressibility goes with greater change of compressibility under increasing pressure. This is shown by the accompanying diagram, in which the compressibility over the whole range is plotted in the direction of abscissae and the difference between the result for the upper and lower halves in the direction of ordinates. Only one point is markedly distant from the fairly regular curve, namely, that corresponding to 2,5-dimethyl heptane. Whether this single discrepancy has real meaning or is due to impurity in the substance, it is impossible as yet to say. A single deviation of this kind, however, does not greatly injure the verdict of the others, since the relationship can make no claim to precise accuracy, but only stands as an indication of a general tendency. The results clearly justify the similar but less consistent curve shown in an earlier

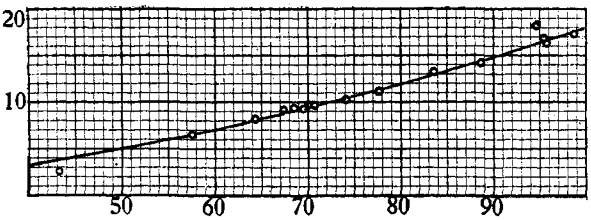

Fig. 3.—Change of compressibility with pressure compared with magnitude of compressibility. Changes of compressibility with pressure are plotted as ordinates; compressibilities are plotted as abscissae. The 16 different substances include paraffin and aromatic hydrocarbons, alcohols, ketones and cyclohexane derivatives, as well as water.

article.[1] That this new curve, which depicts more accurately determined values of a wide variety of substances, should be yet better than the earlier one is interesting and significant.

Attention should also be called to the fact that in general the more compressible substance of a given type has the lower boiling point. Compare, for example, methyl and ethyl alcohol, acetone and diethyl ketone, the two nonanes, the benzene series, and so on. Here, of course, the specific nature of the substance makes the parallelism between different classes less striking, and in the comparison of densities also the different effects of different elements prevent indiscriminate comparison. When a large number of accurate data have been obtained, these matters, none of which have as yet been fully treated, will be made the subject of an especial communication, in which the various contributory effects will be discussed in detail. We are glad to express indebtedness to the Carnegie Institution of Washington for the generous pecuniary assistance which made this work possible.

Summary.

The present paper recounts the following experimental details: First, an accurate but simple pressure gauge is described; secondly, the usual practise with regard to allowing for the space between piston and cylinder in such a gauge is justified by experiment; thirdly, data for the compressibility of 15 organic liquids are recorded, some of them for the first time; fourthly, the striking relation between the magnitude of the compressibility and the change of this compressibility with pressure is pointed out; and, fifthly, attention is called, briefly, to relationships to other properties.

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[1] Richards, Stull, Matthews and Speyers, THIS JOURNAL, 34, 990 (1912).