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THE PRESENT ASPECT OF THE HYPOTHESIS OF COMPRESSIBLE ATOMS.¹

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Speculation concerning the ultimate nature of the material Universe goes far back into the early history of mankind. As soon as several of the ancient Greek philosophers perceived that some kind of atomic hypothesis is the simplest method of accounting for things, they attempted to imagine the nature of the ultimate particles. The apparent permanence of the Universe suggested that these particles could never become worn out, and hence the ancients naïvely conceived of them as being infinitely hard. Newton inherited this idea, and speaks more than once of "hard, massy particles." Not much over a hundred years ago, Dalton brought forth convincing quantitative evidence in favor of the atomic theory, putting it thus upon a firm basis; and the theory was later adopted by physicists to explain the pressure of gases. Throughout these considerations the notion of hard, incompressible (but perfectly resilient) atoms persisted, partly because this assumption served as a convenient basis for mathematical analysis.

According to the tenets generally held during the last fifty years, solids and liquids, as well as gases, are supposed to be constituted of small, hard

¹ Presidential address, written for the Montreal meeting of the Society, which was to have been held in September, 1914. Because of the abandonment of this meeting on account of the European War, this address was not delivered.

atoms (or complexes of hard atoms called molecules) with wide, empty spaces between them—these particles being supposed to be each for itself in violent irregular motion to and fro, due to heat. There is, however, nothing in this philosophy to distinguish solids and liquids from gases, although in reality they are very different indeed. Such a conception gives a very reasonable picture of the state of a gas, but does not explain the fixed bulk of liquids nor the rigidity and impermeability of solids. To overcome these difficulties, it was necessary, in discussing solids and liquids, to add to the hard imaginary incompressible particle a magic "sphere of influence" surrounding it, which would prevent its touching other atoms; but how this "sphere of influence" was constituted no one was quite prepared to say.

About fifteen years ago, in studying the behavior of gases, I came to the conclusion that, even with this dilute form of matter, the imaginary particles (although here widely separated) were still surrounded by "spheres of influence," somewhat but not very much larger than those imagined to exist in liquids. This conclusion raised a serious question as to the real boundary of the space occupied by the atom itself. It seemed that since a "sphere of influence" appears always to accompany the atom, the little hard particle in the middle might have no real physical significance; this imaginary hard particle appeared to be a purely arbitrary assumption. The so-called "sphere of influence" in all its relations acts as if it were really the important thing to be considered. Hence the question was proposed: Why should we not call this "sphere of influence" the atom itself, since it always accompanies the atom; why should we pretend to know anything about how the material is distributed within its limits? The gain in this point of view is twofold. In the first place it concentrates the interest and attention upon the entity which actually comes into consideration; on the other hand, it abolishes an arbitrary hypothesis. Moreover, since the so-called "sphere of influence" appears to be rarely spherical, even the designation of the old idea is of doubtful legitimacy.

If then, we consider this space which the atom actually occupies in liquids and solids as being the bulk of the atom, we must admit that the atom is compressible; for this space is diminished by increasing pressure. In other words, liquids and solids are actually compressed when pressure is applied to them.

Such atoms, compressible and elastic throughout their substance, would be capable of sustaining and transmitting heat-vibration, even if closely packed together; hence this conception of solids and liquids does not interfere with the mechanical conception of heat.

One can easily see that the new hypothesis is suggestive. If atoms are compressible, and are packed closely together in solids and liquids

may we not trace, through the alteration in bulk of substances during chemical change, the action of the chemical and cohesive affinities which hold the atoms together? May we not with the help of this study interpret anew the mysterious symmetry of crystals? May we not correlate numerous properties in relation to one another and by means of the fundamental conception show the mutual dependence of all the properties of matter?

In this brief address I shall not attempt to present all the far-reaching applications of the theory of compressible atoms, but I shall endeavor to show how the new conception explains many apparent inconsistencies in the earlier interpretation, and how it presents the picture of the manifold phenomena of the physico-chemical Universe in a new and more reasonable light. In so far as is possible in a brief presentation, the endeavor will be made to discuss systematically the most important applications of the theory which have thus far been made. Let us begin with the properties of gases, which, as I have said, first suggested the idea.

To the layman, the attempt to discover anything whatever from the properties of gases as to the spaces occupied by molecules themselves might at first seem quite hopeless, for everyone agrees that in gases (at least under ordinary pressure) there must be wide, empty spaces between the molecules, so that the total bulk occupied by the gas as a whole must be made up of the sum of the comparatively small space actually occupied by the molecules and the much greater spaces between them.

The task would indeed be hopeless except for the existence of the well-known, simple laws of Boyle (or Mariotte) and Charles (or Gay-Lussac) governing gases. These laws, we have every reason to believe, should apply with absolute precision to a perfect gas—an abstraction which may be defined for the present purpose as a gas in which the molecules are imagined as mathematical points without any attractive affinities. They tell us, as you well know, that the volume of a perfect gas ought to be exactly proportional to the absolute temperature, and inversely proportional to pressure. If these laws apply exactly to the imaginary case in which the molecules occupy no space whatever, it is evident that any deviation from them ought to afford a clue as to the actual bulk occupied by the molecules in any given gas. This aspect of the question was first pointed out by Budde in 1874; and three years afterwards, van der Waals saw clearly, for the first time, that not only the bulk occupied by the molecules, but also the attractive affinities between them must affect the volume of a gas. This latter agency would diminish the outward pressure (and, therefore, the volume under constant pressure) by pulling the particles inward. Taking account of these two tendencies, namely, the tendency of the molecule itself to occupy space and its tendency to attract other molecules, van der Waals constructed his well-known equation, which

modifies the simple gas-law by making a definite allowance for both, $(p + a/v^2)(v - b) = nRT$.

Now it is well known that nobody has ever been able to find for any gas a perfectly constant quantity (b) which will serve in this equation to represent (for all temperatures and pressures) the exact amount of space occupied by the molecules themselves. Fifteen years ago, this inadequacy in van der Waals' equation excited my interest, and I sought to discover, if possible, the reason for the lack of the exact fulfilment of the mathematical expression. The matter is complicated by the coëxistence of the two effects mentioned in the preceding paragraph; it is difficult to be sure that the affinity-effects have been entirely eliminated from the estimate of the bulk. Nevertheless, careful study made it seem highly probable that at least one reason for the inconsistency is simply a real changeableness in the space occupied by the molecules under varying circumstances.

In other words, it seemed as if the molecules sometimes occupy more space and sometimes less, as if they might be diminished in bulk by pressure (in other words, compressed); and as if they might be affected in size also by changing the temperature.

At that time, however, although the results were suggestive and led to a search for signs of atomic compressibility among other phenomena, they did not seem to be conclusive, for two reasons: In the first place one could not be sure, as already stated, that the effect of affinity had been entirely allowed for; and in the next place one could not feel sure whether the compression affected the atoms themselves, or only molecules built of several atoms. In order to obtain conclusive evidence on these points, one must study some gas which has only a single atom in each molecule, and which has practically no cohesive tendency. In such a gas any change in the calculated bulk of the molecules must be referred directly to the atoms, because here in this special case the molecule and the atom are identical; and the lack of cohesiveness or self-affinity would eliminate the complication affecting the pressure, thus going back to Budde's original idea.

Fortunately just such a gas exists in helium; and the recent data of Kamerlingh-Onnes show indeed that helium atoms in all probability change their apparent bulk with changing conditions.¹ One can easily compute the quantity b (which must be a function of the apparent collision-bulk² of the molecules) from these data; thus it is found that at 0° C. the quantity b is 12 cc., and at 100° C. it is only 10.4 cc. per 4 g. of helium under moderate pressure.

¹ Richards, THIS JOURNAL, 36, 617 (1914).

² The apparent collision-bulk is the bulk which is made up of imaginary spheres with the radius of half the apparent distance between atomic centers on nearest approach during collision. It includes an effect due to the time of collision.

Evidently, then, the apparent collision-bulk of the molecules in helium must be smaller at high temperatures than at low temperatures, and the only satisfactory way of accounting for this is to suppose that the greater velocity of the colliding atoms at high temperatures produces a greater compressing effect upon them, so that at high temperatures they seem to occupy less space than at low temperatures. The data are not as plentiful as one would like; but the laboratory work seems to have been carefully done by the great Dutch experimenter, and the evidence is strong. If the helium atoms are thus capable of compression, it is only fair to assume that other atoms are also compressible; and one is given immediately an adequate and satisfactory qualitative explanation for the deviations of all gases from the exact requirements of the equations of van der Waals. If the molecules and atoms are compressible, of course no constant value could be found for their bulk under varying conditions.

Not only the equation of van der Waals, but also that of corresponding states (a mathematical deduction evolved from the former equation) has its difficulties of interpretation smoothed away by this assumption of atomic compressibility. The reason why this equation also is by no means exact, applying only with similar substances, is made clear.

But these interesting conclusions are not the only outcomes of this discussion, for the idea that atoms are compressible at once leads to the conviction that the atoms in gases are much larger than van der Waals supposed them to be. All his conclusions referred to the apparent collision bulk, which must needs (in compressible atoms) be considerably smaller than the true bulk, because of the great velocity with which the colliding molecules in a gas are known to strike one another. Those who are interested will find the argument rather fully set forth in the recent article already mentioned; there is no time here to go into detail, but the outcome may be stated. This is, that the bulk of the molecules, when not compressed, may perhaps be about that of the so-called critical volume. This idea gives us a new definition of the critical point—one of the most puzzling phenomena concerning the relations of liquids and vapors.

The study of the critical point brings us naturally to the next heading of the discourse, namely, the application of this idea of atomic compressibility to liquids and solids. It has just been pointed out that the logical discussion of the properties of aeriform matter indicates that the bulk of the uncompressed molecules in gases is much larger than had previously been expected. Indeed, as stated above, it appears that the actual bulk of the molecule in a gas is to be considered as about the critical volume, which is of course considerably larger than the space occupied by the liquid under ordinary conditions. That is to say, we must imagine the atoms in a liquid as being not only packed closely together, but packed so closely that every atom is much compressed by the force of the cohesion.

This seems revolutionary indeed. It was formerly thought that the atoms, even in liquids, were as far apart, relatively to their size, as the planets in the solar system. Van der Waals, to be sure, did away with this extreme view by his equation, giving good evidence that the atoms were at least as large as one-third of the space occupied by the liquid; but the new conception now advocated makes them much larger still.

In what direction must we seek for further evidence of the close-packing and compression of atoms in liquids and solids? Much is at hand. Striking support for this hypothesis is seen in the slight contraction which liquids and solids suffer on being cooled to the absolute zero. If the atoms really have wide spaces between them in solids, these spaces should disappear at the absolute zero, where heat-energy is supposed no longer to exist; but no substance known to me contracts anything like as much on cooling to very low temperatures as it should to correspond with the requirements even of van der Waals' theory.¹ Evidently something very different from heat vibration is the chief tendency which maintains the bulk of liquids and solids.

Precisely in line with this conclusion is the inference to be drawn from the compressibility of matter at low temperatures. If the ordinary conception of matter is true, it should be wholly incompressible at the absolute zero; on the other hand, if the theory of compressible atoms is true, matter should be almost as compressible at the absolute zero as it is at ordinary temperatures. I pointed out in the Faraday Lecture of 1911 that the latter is probably the case, basing the conclusion on an extrapolation of the results of Grüneisen obtained at very low temperatures. In this crucial case again the facts decide in favor of the theory of compressible atoms.

Yet another obvious argument among many may be cited. The ordinary theory demands that all material should be porous with large spaces between actively moving molecules. This idea is so interwoven in the science of today that most text-books on physics name porosity as one of the universal properties of matter. Now as a matter of fact in very many cases porosity is conspicuous by its absence. Liquid has been imprisoned in quartz and other materials for countless ages; many solids indeed (especially crystals) are thoroughly impervious both to liquids and to gases. This could hardly be the case if there were wide spaces between the rapidly moving molecules. Other instances are cited in the Faraday Lecture of 1911, to which those interested may be referred.

That an occasional substance, such as monoclinic sulfur which has been metamorphosed into the rhombic form at low temperatures, or iron (which undergoes a well-recognized solid transition below its melting point), or amorphous fused silica, might have minute pores within its fabric is only to be expected; this fact does not militate at all against the theory.

¹ THIS JOURNAL, 36, 626 (1914).

From another point of view also, the ordinary conception of a solid has always seemed to me little short of an absurdity. A gas, indeed, may very properly be imagined as consisting of moving particles independent and far apart from one another, but how can a rigid solid like steel possess such an unstable structure?

These and many other considerations, then, lead me to conclude that in solids and liquids not only are the atoms packed closely together to form molecules, but that also these molecules are packed closely together to form the material solid and liquid substances which we can see and handle. We must conclude that heat vibration occurs in these closely packed molecules by a somewhat different mechanism from the rectilinear motion which we all imagine to be the carrier of heat energy in gases. We must imagine that these compressible molecules are working upon one another in somewhat the fashion discernible in the microscope among small floating particles and called the "Brownian movements." Of course, the molecular upheavals must take place on a much smaller scale, but the analogy is illuminating. Such a motion would obviously turn into a rectilinear one if a molecule were freed from its bondage to other molecules, that is to say, vaporized.

Having thus step by step come to the conclusion that the atoms in liquids and solids must be packed closely together and that they must be compressed in this close contact by the forces which hold them together, we are immediately stimulated to study in detail the effect which cohesion and chemical affinity may have on these compressible objects, the atoms. May not the study of the changes exhibited by the volumes of liquids and solids under varying conditions be able to throw much light on the forces which hold solids and liquids together if all this be true?

Chemical affinity and cohesion are phenomena of the utmost importance in our daily life. The existence and stability of all the complex molecules which make up our bodies and our environment depend upon the chemical affinity; and cohesion is the agency which causes these molecules to assume the solid and liquid states, without which the world would be indeed "without form and void." Therefore, the study of these agencies is highly important to anyone interested in man's relation to the physical universe in which he has been placed.

We know very little about the nature of the forces which produce these effects, and every phenomenon which can throw light upon them should be eagerly pressed into service.

The first question which demands answer before any conclusions can be drawn is the question whether chemical affinity and cohesion exert pressure in their action, or whether they merely hold the atoms and molecules together without pulling them toward one another. I am aware of no adequate discussion concerning this point, important as it is; and I

doubt if there is unanimity among chemists and physicists concerning it. Of course, all know that gravitation, at least, acts at a distance and pulls objects together. When two objects are in contact, gravitation causes their surfaces to press on one another. Undoubtedly gravitation has something to do with cohesion and chemical affinity, but it is equally certain that some agency besides gravitation comes into play. Does this other force or concatenation of forces also pull inward?

Clearly the theory of compressible atoms gives us a means of finding an answer to this question. For if the atoms are compressible, a force which pulls them together will diminish the volume of the system by pressing them upon one another. But a force which merely holds the atoms together, without pulling inward, could have no such effect. Hence, assuming pragmatically that the practicable bulk of an atom is compressible, we may infer that cohesion exerts pressure if we find diminished volume in cases where great cohesion is known to exist. Precisely the same argument may also be applied to chemical affinity. Consistency in the outcome must afford strong support for the assumption on which the inference was based.

Plentiful data exist supporting this point of view. Although it is somewhat difficult in a brief lecture of this sort to present clearly the situation (because the variables are so many that no feasible mode of representation can make all of the relationships clear at once) it is hoped that the following explanation may be comprehensible and convincing:

Let us first study the behavior of cohesion, because some knowledge of cohesion is necessary in order to interpret chemical affinity. Cohesion manifests itself in various ways. The most obvious is the mechanical resistance to the separation of one part of a substance from another. Thus it appears, often modified, in the properties of ductility, malleability, tenacity, hardness, and may be supposed to be concerned with surface tension and with resistance to evaporation. There are, therefore, many guides which afford an approximate idea of the magnitude of the cohesive tendency which may exist in a substance.

We may then ask ourselves: Do bodies having great cohesive affinity act as if they were under great internal pressure? If this is the case, it would not be unreasonable to ascribe the great pressure to great cohesion.

What now are our guides as to the presence of pressure in a given system? The most obvious is the diminution of the volume, because pressure always produces decreased volume. Diminishing volume of course means that the density of the substance in question is increased. Hence, other things being equal, if the external pressure is constant, at least one of the causes of the appearance of a greater density in a given substance may be the existence of a greater internal pressure within it.

Another evidence that pressure exists within a given system is to be found in the slight effect of further additional pressure. From this tentative clue, based upon experience, one may infer that the existence of only a slight compressibility in any system probably signifies the residence already in that substance of considerable internal pressure, upon which the slight added increment will have but little percentage effect.

Yet another still more subtle evidence of great pressure in any system is the constancy of the compressibilities under changing pressure. In a system already under great pressure each small successive addition of pressure will be nearly the same percentage of the whole, and, therefore, each like addition would be expected to have very nearly the same effect upon the volume. On the other hand, if the substance is under small pressure, each successive equal addition of pressure will be a much smaller percentage than the preceding and would, therefore, have a greatly diminished effect upon the volume. Thus if the compressibility decreases greatly with increasing pressure, one may infer that but little pressure was present in the first case, but if a body possesses a small compressibility which is nearly constant over a wide range of pressure, we should feel obliged to believe that a great internal pressure was already present in some form within the substance.

A fourth means of guessing as to the presence of internal pressure may be inferred qualitatively from the effect of temperature upon the body being studied. Where a rise of temperature produces a very marked effect upon the volume, we may guess that there are only gentle forces holding the body together; but where the effect of rising temperature is slight, we may suppose the internal pressure to be great.

We have, then, in addition to the several criteria indicating a tendency to *hold* together, four different methods of evaluating a tendency to *pull* together. If the phenomena show that these tendencies all go hand in hand the presumption would be very strong that great cohesion produces pressure, and that this pressure is actually effective in reducing the volume of solid and liquid substances.

Because of the many variables involved, it is clear that our safest conclusions are to be drawn from the comparison of isomers; here we can compare a number of substances having exactly the same components.

The following table compares seven properties of two typical organic isomers. In every case the relation is exactly in accord with the theory in question. The denser has the less compressibility, the less decrease of compressibility with pressure, the less coefficient of expansion, the higher boiling point, the greater surface tension and the greater heat of vaporization. That this solidarity of all the properties should be due to chance is extremely improbable.

PROPERTIES OF ETHYL BUTYRATE AND ISOBUTYRATE.

	Ethyl butyrate.	Ethyl isobutyrate.
Density.....	0.8785	0.8710
Compressibility $\times 10^6$	76.9	80.8
Decrease of compr. (per 200 atm.) $\times 10^6$	13.6	15.0
Coeff. of expansion ¹	0.001247	0.001294
Boiling point.....	120.8°	109.8°
Surface tension.....	24.58	23.3
Heat of vaporization (kilojoules per mol).....	34.7	33.9

Many other such tables might be given; and although in some cases deviations from the theory appear, the percentage of agreement among the many substances which I have thus far compared is so very great that the evidence is overwhelming.

Let us now change our method of comparison. Instead of comparing many properties of two substances, let us compare two properties of many substances. For example let us compare the boiling points and densities of substances having the formula $C_7H_{14}O_2$.² Here it is seen that the greater density follows closely the higher boiling point, exactly as the theory suggests. (The diagram is given on the opposite page.)

Again, the comparison of the surface tensions and compressibilities of a number of compounds of carbon, hydrogen, nitrogen, and oxygen chosen at random shows a marked tendency to grouping in a definite curve of the kind predicted.³ This is very striking, especially when one considers the great variety of substances discussed. The relation between the compressibility and its decrease with pressure is also striking.⁴ Here again, although there is some scattering, the points are all grouped near a definite curve, showing that there is a real relation of exactly the sort indicated by the theory of compressible atoms. It is clear that all these phenomena taken together constitute so strong a basis of fact that one can hardly avoid the conviction that they are due to a common cause; and the only reasonable cause seems to be the action of cohesion, which is thus shown to exert pressure.

These considerations led to the actual experimental study of compressibility because, as a rule, it is a mistake for anyone to theorize greatly

¹ These data were determined as follows: The rise of temperature needed to make each liquid expand 3.42% of its original volume (in a calibrated dilatometer allowing for the expansion of the glass) was found by repeated experiments to be 27.2° for the butyrate and 26.2° for the isobutyrate. The initial temperature was 21.5°, and the coefficients are referred to the volume at this temperature. The result is, therefore, the mean value over this range (or about that at 35°) referred to the volume at 21.5°. As comparative results alone are needed, this suffices.

² Richards, *Proc. Am. Acad.*, **39**, 594 (1904). A somewhat similar comparison is made by W. A. Noyes in his *Organic Chemistry*, p. 368 (1902).

³ Richards and Mathews, *THIS JOURNAL*, **30**, 11 (1908).

⁴ Richards, Stull, Mathews and Speyers, *Ibid.*, **34**, 990 (1912).

about a series of phenomena, with which he has not come face to face in the laboratory. This work, as well as much other work conducted in this laboratory, has been generously subsidized by the Carnegie Institution of Washington. The already existing methods for determining compressibility having been found inadequate, a new and convenient method for determining this somewhat elusive property was devised. With the help of this method the compressibilities of about forty elements have been determined at Harvard—only two or three having been known before.

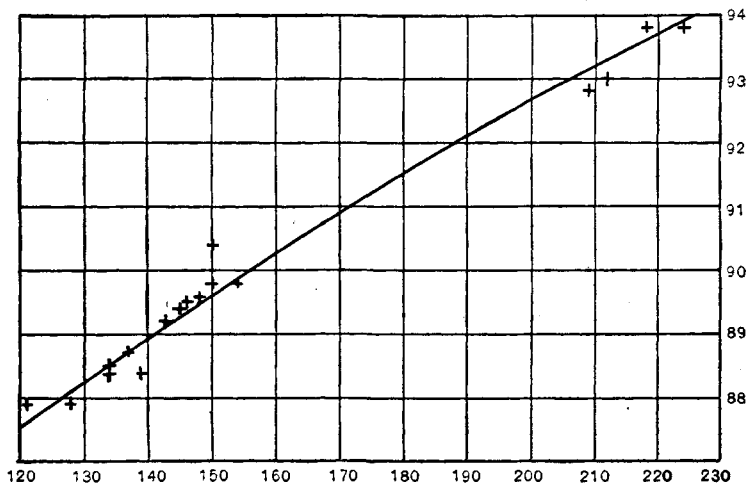
BOILING POINTS AND DENSITIES OF SUBSTANCES $C_7 H_{14} O_2$.

Fig. 1.

The divergent point on the ordinate 150° represents methyl caproate, and that less divergent on the ordinate 139° , isoamyl acetate.

The other substances, named in order, are isopropyl isobutyrate, isopropyl butyrate, propyl isobutyrate, ethyl isovalerate, butyl propionate, propyl butyrate, ethyl valerate, isobutyl propionate, amyl acetate, methyl isobutyl acetate, hexyl formiate, isoamylacetic acid, isoheptylic acid, iso-onanthic acid, and heptylic acid.

It was found that in the case of the solid elements the compressibility shows periodic fluctuation as the atomic weight increases, and that in general, with elements as with compounds, the bulky volatile substances are the most easily compressible. This was new—neither the facts nor the explanation had been available before. Obviously the explanation is exactly like that applied to the isomers above. When a substance is held firmly together by cohesion, that is to say, when it is non-volatile, one would expect it to be much compressed by this great cohesion. Therefore, it should be dense, that is to say, have small atomic volume; it should be slightly compressible, and should possess only a small coefficient of expansion. This is precisely the case.

Consistently, elements with great atomic volumes show, in general, also great volatility, great compressibility, great coefficient of expansion, and great change of compressibility with increasing pressure. The accompanying diagram, taken from the Faraday Lecture of 1911, clearly indicates the relation of atomic volume to compressibility in the cases of those solid elements which have been measured.

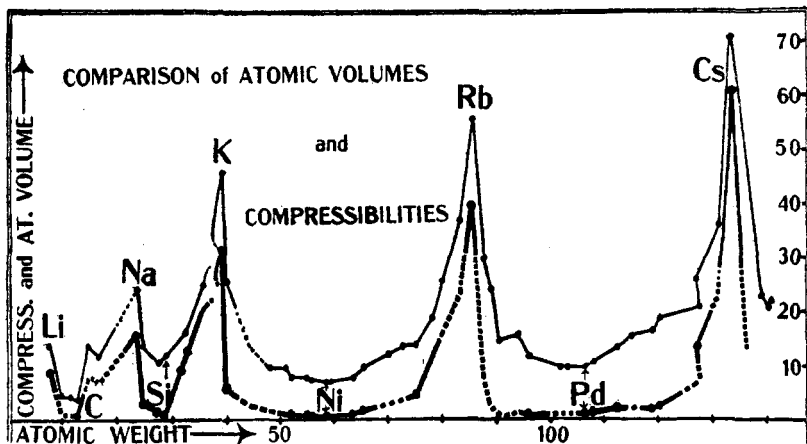


Fig. 2.

It is true that the regularity is not perfect, but the small discrepancies may often, if not always, be explained through taking account of the undoubted fact that the tendency even of elementary atoms to cling to one another manifests itself in diverse ways. Thus many elements make polyatomic molecules, and the internal pressures within the molecule must be greater than those which bind the separate molecules together. This latter cohesive tendency is that which has to do with volatility, whereas the other properties are usually determined by a net effect due to both. On the whole, then, the evidence becomes extremely strong that cohesion exerts pressure.

Let us now turn to chemical affinity.

If cohesion produces compression, must not the far stronger aggregation of forces which (for lack of a better name) we call "chemical affinity" also produce compression? If this is the case, must not chemical affinity be one of the essential factors in determining the volume of all liquid and solid substances? This is a highly important question, the answer to which brings with it quite a new interpretation of the mechanism of chemical action.

Since, as we have seen, cohesion is an important influence in determining liquid and solid volumes, we can only hope to trace the further effect of chemical affinity after we have made allowance for such an effect as

cohesion may produce. Because as a rule both occur together and the total volume must be fixed by superposition of the two effects, it is hard to discriminate between the two. We can, therefore, expect to trace the relative compressing effect of affinity most satisfactorily by comparing cases in which the effects of cohesion in both factors and products are not very different. To cite a definite example, a good case to compare would be the contractions which occur on forming the chlorides of strontium and lead, for the two metals are not very different in boiling point (a fact which shows that their internal cohesive affinity is not very different); moreover, the resulting compounds also are neither of them very volatile; and chlorine is common to each reaction. Hence one may have a reasonable expectation that a comparison of these two substances should yield some clue as to the relative compressing effect of the affinity of chlorine for the two metals.

What are the facts? A gram-atom of strontium occupies 34.5 cc., and two gram-atoms of chlorine occupy 50 cc., or 84.5 cc. in all. But a gram-molecule of strontium chloride occupies only 51.9 cc.; hence in the act of its formation there has been a contraction of 32.6 cc. Similarly, when a gram-atom of lead unites with chlorine there is a contraction of 20.1 cc.; distinctly less than in the former case. This is just what we should expect if affinity causes compression, for the affinity of strontium for chlorine is undoubtedly much greater than that of lead for chlorine. The heats of formation of these chlorides (which in parallel cases of this kind give a roughly approximate idea of the relative free-energy changes involved) are 772 and 346 kilojoules per mol, respectively; moreover, strontium will replace lead in this compound.

Many other similar cases have been noticed from time to time. The first seems to have been pointed out by Humphry Davy in a footnote to one of his papers,¹ and figures of this sort have been quoted occasionally by others (especially Müller-Erzbach, Hagemann, and Traube) as showing that high chemical affinity is associated with small volume. Nevertheless none of the earlier observers succeeded in convincing the chemical public of the generality of the proposition, perhaps for the reason that there appeared to be altogether too many exceptions to the rule; moreover, the argument was logically incomplete. According to the present theory, the supposed exceptions are seen, usually if not always, to support the rule; indeed they are really necessary consequences of the rule. The effect of cohesion may entirely mask the effect of affinity, especially when some of the factors or products are volatile substances in which the cohesive internal pressure is slight; again, one must obviously take into account the compressibility of the bodies under examination. Both these modifying tendencies were entirely ignored by the earlier experimenters; but the prob-

¹ Humphry Davy's "Collected Works," 5, 133 (1840).

able influence of each tendency is now clear, and their existence explains many apparent irregularities which are now seen to be due, not to accident, but merely to the necessarily confusing superposition of the several effects.

The example cited above (namely, the comparison of the chlorides of strontium and lead) was especially chosen because the compressibilities of the elements (lead and strontium) are not far apart: the difference in the contraction may therefore be ascribed chiefly to the difference in affinity. The effect of compressibility, on the other hand, is best seen by comparing the contractions occurring during the formation of similar compounds of elements having large and widely different compressibilities, but similar affinities. The series of five alkaline chlorides is especially suitable for this purpose; the elements are all fairly similar to one another as to their cohesiveness (that is to say, their boiling points, except in the case of lithium, are not very far apart) and their affinities for chlorine also are not very different;¹ but their compressibilities vary widely. The following table and diagram compare the latter data with the contraction on combination. It is clear that the greater the compressibility of the metal, the greater is its contraction on combination.

COMPRESSIBILITIES OF METALS OF THE ALKALIES COMPARED WITH THE CONTRACTION OCCURRING DURING THE FORMATION OF THEIR CHLORIDES.

	Compressibilities ($\times 10^6$) of elements.	Contraction on for- mation from elements. Cc. per 1 mol.
Lithium.....	9.0	17.6
Sodium.....	15.6	21.5
Potassium.....	31.7	33.1
Rubidium.....	40	36.8
Caesium.....	61	53.6

Many comparisons of this sort might be cited, for example, the behavior of the several halides of any single alkali metal is equally striking, but these typical examples indicate sufficiently for a brief discourse the important relation of the compressibilities of the elements to the volumes of their compounds. No more convincing argument in favor of the theory of compressible atoms could be desired.

When the elements entering into such a comparison are widely different in cohesive affinity, or when the resulting compounds are not fairly comparable in this regard, the effect of chemical affinity may be masked by the differences of cohesiveness. Thus the comparison of volatile with non-volatile substances cannot be expected to yield results as consistent as those given above. Enthusiasts or critics interested in the details will find a discussion of typical cases of this kind in previous papers concerning the significance of changing atomic volume.²

¹ See the Faraday Lecture of 1911 (Richards), especially the diagram given on page 1215 (*J. Chem. Soc.*, 99, 1201 (1911)).

² *Proc. Am. Acad.*, 39, 590, 592 (1904); *THIS JOURNAL*, 31, 190 (1909).

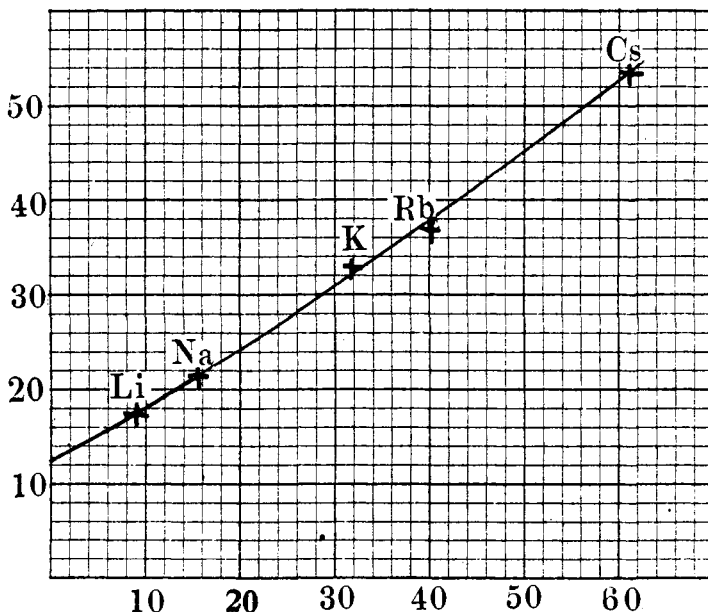


Fig. 3.—Diagram depicting data in table opposite. Contraction on combination (in cc. per mol) is plotted ordinately; compressibilities (of the elements) are plotted as abscissae.¹

¹ An interesting corollary suggested by this diagram is to be found in the extrapolation of the curve toward the left. The point where the abscissa becomes zero indicates the hypothetical contraction which would take place if an imaginary incompressible element were combined with chlorine by an affinity about equal to that of the others to form a compound similar to lithium chloride. Since, in this case, the contraction of 12.5 cc. must be due to the 25 cc. of chlorine alone, we may suppose that in each of the actual cases of the alkali chlorides the contraction must be about the same, and that in each case the chlorine occupies about $25 - 12.5 = 12.5$ cc. From this assumption and the actual total contractions, the table which follows (given here for the first time) has been computed.

APPROXIMATE DETAILED VOLUME-RELATIONS OF SOLID ALKALI CHLORIDES ON THE ASSUMPTION THAT THE CHLORINE IN EACH OCCUPIES ABOUT 12.5 Cc.

	Actual total mol. vol. of salt.	Hypothetical at. vol. of metal in salt.	Hypothetical contraction of metal on combination.
Lithium chloride.....	20.5	8.0	5.1
Sodium chloride.....	27.2	14.7	9.0
Potassium chloride.....	37.3	24.8	20.6
Rubidium chloride.....	44.0	31.5	24.3
Caesium chloride.....	42.4	29.9	41.1

These values do not pretend to be absolutely precise, and their interpretation is complicated by differences in the cohesive properties of the molecules concerned; but they are nevertheless interesting, because they give a clue to the mechanism of the reaction.

The theory has had another interesting outcome, which bids fair to bear much fruit in the future. If atoms are compressible, the uneven compression caused by differently applied chemical affinities might be supposed to restrict the heat-vibration existing within their elastic boundaries. This restriction would lessen their heat capacities (which are measured by the quantities of heat needed to cause a given change of temperature) and, therefore, expel some heat-vibration already present which could no longer be accommodated by the system; for diminished heat capacity at ordinary temperatures probably indicates diminished average heat capacity over the whole range down to the absolute zero.¹

Since the heat energy contents of any system must be supposed to be represented by the product of the absolute temperature into the integral heat capacity over the whole range (plus the latent heat involved in any change of phase which may have occurred), a diminution of the heat capacity at ordinary temperatures must expel some of this contained heat energy. Thus the theory predicted that, when during a given reaction the heat-capacities of the substances concerned were diminished, one would expect also to find an output of heat during this reaction in excess of that corresponding to the chemical work. Thermal energy thus displaced at constant temperature could not be expected to be capable of doing work; and we may reasonably ascribe to this cause at least a part of the well-known difference between the total-energy change and the free-energy change of an isothermal reaction.² Moreover, it seemed probable that some of the driving energy of the reaction might be needed to accomplish this effect, and, therefore, not be able to perform outside work. These two considerations together might account for the puzzling "bound-energy" of chemical change, which was recognized but not explained by thermodynamics. The mathematical analyses of Helmholtz and Lewis (afterwards confirmed by Haber) had shown the problem to be beyond the power of contemporary thermodynamics alone; but the idea seemed so plausible that an effort was immediately made to submit it to practical verification. I was able to show, in cases of certain typical reversible gal-

¹ The somewhat academic theory of the equipartition of energy suggests a difficulty in the situation, demanding that such a system (*i. e.*, one continuously deformable) should possess an infinite heat capacity. But this theorem notoriously fails at low temperatures, and even at high temperatures it is very arbitrary in its assumptions concerning restraints; hence its demands may be set aside in this case. Lack of space forbids here any further discussion of the relative magnitudes of potential and kinetic energy in a condensed system.

² Helmholtz had proved that a thermodynamically indeterminate integration-constant was involved in this relation, and Lewis at Harvard had shown mathematically that change of heat capacity must be concerned in "bound-energy;" but neither proposition was sufficiently definite to lead to much outcome. See Haber, "Thermodynamics of Technical Gas Reactions," translated by A. B. Lamb, p. 45, 1911, also G. N. Lewis, *Proc. Am. Acad.*, 35, 7 (1899).

vanic cells, that when free energy change increases with rising temperature, total energy change decreases, and *vice versa*.¹

From this interesting discovery two fundamental conclusions were then drawn: first, that "When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and total-energy changes of the reaction are equal and unchangable with the temperature;" and secondly, that "the sign and magnitude of the difference between the free and total energy changes is dependent upon the sign and magnitude of the change of the heat capacity of the system."² When the heat capacity decreases (as is more usual) during the reaction, the total energy change exceeds the free energy change, and *vice versa*. It was further pointed out that the difference between these two must diminish as the temperature approached the absolute zero, where the two must become identical, running into one another almost if not quite asymptotically.³ All these ideas were afterward (1906) adopted unchanged by Nernst in his recent development of the "Wärmethorem" usually named after him.

The next step was obviously to determine the actual amount of heat displaced by change of heat capacity, in order to determine whether or not this was exactly equal to the bound-energy (that is, the difference between the free- and total-energy change). To do this, one must know the specific heats of factors and products over the whole range of temperature; but data were lacking. Hence a new method was devised at Harvard, and the preliminary results showed that the specific heats of solids at low temperatures are much smaller than had been supposed.⁴ The intention had been to continue with this highly interesting and significant discovery; but before this could be done, these various ideas also were taken up by Nernst and incorporated into the new "Wärmethorem."

It is, perhaps, not out of place to point out here that the new feature

¹ That is to say, expressed mathematically $dA/dT = -n dU/dT$, in which A represents free energy, U total energy, and n a number, which was found often to be about 2. Of course dU/dT is nothing more nor less than the change of the heat capacity during the reaction. J. M. Bell has questioned the sufficiency of the evidence, but he has neglected to note that although Marignac's data (upon which I relied) were perhaps absolutely not very accurate, they are relatively to one another much more to be depended upon; and in this question relative accuracy alone is concerned (*J. Phys. Chem.*, 9, 402 (1906)). Brönsted has evidently quite failed to understand the original idea although he has provided much of interest as to its later development (*Z. Phys. Chem.*, 56, 653 (1906)); but van't Hoff (*Boltzmann Festschrift*, p. 233 (1904)) and Haber (*loc. cit.*) saw its significance.

² Richards, *Proc. Am. Acad.*, 38, 307, 300; *Z. physik. Chem.*, 42, 143, 136 (1902).

³ This is explicitly stated (*Proc. Am. Acad.*, 38, 301 (1902); *Z. physik. Chem.*, 42, 138 (1902)). The mathematical expression of the latter alternative (complete tangency) is, of course, that later written by Nernst, namely $(dU/dT)_{T=0} = (dA/dT)_{T=0}$.

⁴ Richards and Jackson, *Z. physik. Chem.*, 70, 450 (1909).

first introduced by the mathematical physicist was the arbitrary assumption of the simplified equation $U - \beta T^2 = A + \beta T^2$. This assumption,¹ since abandoned, introduced the great convenience of making the situation amenable to mathematical treatment. Qualitatively the Nernst proposition especially in its recent more complex form, is identical with that older American one from which it was derived; the only essential difference is the assumed quantitative formulation.² In 1902 any such attempt at greater definiteness seemed unwarranted by either fact or theory.

In the intervening years, much experimental work has been performed in many laboratories, stimulated by the theorem. So far as I know, all, or nearly all, of these investigations have supported the idea of 1902; but by no means all of them have supported exactly Nernst's later additions to that idea.³ Nevertheless, the latter has certainly done good service by stimulating research. Moreover, even if the final word upon the groundwork of the theory has not been spoken, the complicated mathematical superstructure reared by Nernst upon the earlier concepts must be conceded to be exceedingly clever and ingenious.

When the exact quantitative statement of the fundamental principle underlying these phenomena is discovered, it will be worthy of ranking with the great laws of thermodynamics; and even now it is possible to make a general statement (like that made in 1902) which may not need revision when the details are mastered, as follows: *Apart from concentration effects, the bound energy change of a chemical reaction is essentially dependent in sign and magnitude upon the change of heat capacity. When the latter is negative the former is positive, and vice versa.*

The theory of compressible atoms was thus the starting point of a long train of thought and experiment.

The suggestion that the idea of atomic compressibility might explain the previously incomprehensible volume changes which occur on dissolving salts in water has recently been discussed by Baxter.⁴ He has successfully elucidated, through the comparison of the densities of solutions of alkaline halides, the tendencies at work; and he finds that the facts entirely accord with the predictions of the present theory.

Another suggestive application of the hypothesis concerns the idea of the

¹ See Nernst, "Theoretical Chemistry" (translated by Tizard, p. 712 (Macmillan, 1911)). Later developments have shown the need of more terms; but no attempt will be made here to enter into a discussion of the complex mathematical development of them. Some of the latest curves look very like those published in my early paper of 1902, differing only in details.

² Nernst has admitted this identity in one of his American publications. "Thermodynamics and Chemistry," Silliman lectures, p. 56 (1907).

³ See for example, Naumann, *Z. Electrochem.*, **16**, 778 (1910).

⁴ Baxter, *THIS JOURNAL*, **33**, 922 (1911).

“asymmetric” carbon atom of van't Hoff and Le Bel, which is the basis of so much of modern organic chemistry. The observed phenomena are exactly what one would expect if a compressible carbon atom were unequally compressed on four different sides by the four different affinities inherent in four other dissimilar atoms. An atom, spherical in the first place, would thus be compressed into an irregular twisted tetrahedron, which would have its attached atoms securely held on its faces, and not impossibly perched on its projecting angles. Geometrically an arrangement of this new kind answers the requirements as well as the old conception; and it is certainly more plausible from a mechanistic point of view. That such a twisted structure should rotate the plane of polarized light seems only natural. Moreover, would not the flexible nature of the system make possible just such changes as are manifest in the well-known but not satisfactorily elucidated Walden inversion?

One of the yet more recently developed aspects of the hypothesis is its interpretation of crystal form. The application of the idea to this field was suggested at the beginning; and in two papers which have not long since appeared in our journal, various phenomena exhibited by crystals—such as their definite angles, the similarity of forms assumed by analogous substances, and other details concerning their highly symmetrical shapes—are all accounted for in a fashion which seems (at least to the author) to be more satisfactory than any other thus far suggested. It has long been assumed by most speculators upon the chemical mechanism of crystallization that the spheres of influence of the atoms must be closely packed; but usually these “spheres” are assumed to remain spherical, or nearly so. The present theory greatly modifies this notion by pointing out that the so-called spheres of influence (the atoms themselves, according to the present definition) must be greatly distorted by the affinity exerted in the act of their combination. Thus the atoms must be more closely compacted in some directions than in others. The total result of the crystal-unit or solid molecule thus formed must be a definitely constituted aggregate of closely tied atoms; and the shape in which this crystallographic unit can best fit together with others must determine the crystal form. Specific cases have been worked out with this idea in mind; and the conception has shown itself to be consistent with the known facts of crystallography.¹

We may well ask: what is the distending tendency, which prevents the affinities of the atoms from contracting all solids and liquids into a mathematical point? I have found it convenient to speak of the boundary of this distending or repelling tendency as the surface of the atom, because it seems to accompany the atom wherever it goes. The present investigation does not attempt to decide how the atom may be constituted within;

¹ THIS JOURNAL, 35, 382 (1913); 36, 1686 (1914).

it seeks simply to study and draw inferences from its outward behavior.

Let us review the essential characteristics of the boundary of this distending effect which surrounds the atomic center. In the first place the distending tendency begins to be apparent at about the distance from the atomic center which is defined by the critical volume. It accompanies the atom wherever it goes, under all temperatures and pressures. Existing both in non-electrified substances, and between electrically dissimilar atoms, it is not apparently connected with electric repulsions or with any other manifestation of energy which may be perceived upon a larger scale. Pressure, whether from the chemical attracting of two atoms by one another, or from the cohesive action of molecules upon one another's surfaces, or from impact of collision, or from outside compression, all tend to contract this field of influence at the place or places where the pressure is applied. In liquids and solids this distending tendency has been counteracted by affinity and cohesion; and in extreme cases the surface of the atom may, perhaps, be compressed until the atomic diameter is about half of that corresponding to the critical volume. This is, after all, a comparatively small range of compression; evidently the "spring of the atom," whatever it is, increases very rapidly as the atomic centers approach one another. As regards the nature of this distending tendency, it is clearly not directly dependent in any way upon heat vibration. This is shown by the behavior of solids at very low temperatures, at which neither their bulk nor their compressibility are greatly diminished.

These are almost inevitable inferences as regards the outside of the atom, but how the interior may be constituted, other investigations must decide. The present theory makes no necessary postulate as to how the atomic bulk of this so-called "sphere of influence," which I have ventured to call the atom because of its persistence, may be filled. Many sorts of hypotheses will equally satisfy the requirements. There may, indeed, be no such thing as the so-called "substance" in the atom. If, as Larmor and others have suggested, the atom is a minute vacuous space in a prodigiously dense ether, the boundary of the vacuum may be that surface of demarcation capable of being compressed. If, as J. J. Thomson and Rutherford propose, the atom consists of positive and negative corpuscles or electrons held apart by repulsions within themselves and pulled together by an inscrutable attraction, the boundary of this complicated entity (or at least the boundary of the unknown repelling forces which abide in it) must constitute the atom. Such a system would be supposed to be compressible, and all the facts presented in the present discourse seem only what would be expected. According to either point of view or to any other which may be brought forward, it is not necessary to assume that the boundary consists of a perfectly sharp defining surface. Whether the atom consists of "substance," of whirling electrons, of complete vacuity, or merely

of a repellent force, this boundary need not be considered as perfectly sharp. It may gradually diminish with distance without a sharp defining line; but the present research shows that the effect increases inversely as the very high power of the distance; and because we know of no such repelling force on a larger scale (excepting perhaps magnetism, which does not seem to be greatly involved in most cases) it seems not unreasonable to imagine that there is a fairly concrete surface which defines the atom.

The really essential part of the whole discussion lies in the strong evidence that *where affinities are great the atomic centers come closer together, and that where the affinities are slight they are further apart*. This causes each atom to occupy an irregular and distorted space, the shape of which is accountable for many of the properties of matter. The "hard massy particle" of the ancients appears to be a figment of the imagination.

Perhaps to some of you an investigation of this sort may seem very remote from the pressing problems of everyday life. Although we have every reason to believe that we are made of atoms, we do not commonly think of them either in relation to ourselves or to our surroundings. They seem to be an abstract philosophical notion, of little significance in human life; and if atoms themselves are of little significance, why should we bother about their compressibility, or the way in which they fill the space allotted to them? Plausible as this argument may seem, it is really a very short-sighted one. Our dominance over the forces of nature depends primarily upon our understanding of them; and this matter of atomic compressibility, inessential although it may seem, is bound up fundamentally with the very nature of the atoms themselves and the affinities which bind them together. It can afford us new clues as to the intimate working of the Universe; and in that way the conception may open up in the future perhaps unexpected and otherwise unattainable insight, and, therefore, unexpected and otherwise unattainable power.

You have doubtless noticed that much of the subject matter of this address has concerned itself with properties and relations which would ordinarily be called physical, although the audience as well as the lecturer are all primarily chemists. There is no anomaly in this. Physics and chemistry are inextricably woven together; they are indeed parts of one science. The organic chemist who would freely use a thermometer for identifying his substance may look with disfavor upon a compression-pump, counting the latter as purely physical implement; but after all the pump is no more physical than the thermometer. The intricacy of the make-up of this world is so great that every means must be sought to help in its untangling, and we may safely say in these days that the chemist who looks askance upon physics is only half a chemist.

The applications of the theory of compressible atoms to the interpretation of chemical phenomena and to the suggestion of new research are by

no means exhausted by this brief discussion. No significant objection to it has thus far been encountered; but even supposing that the idea should be supplanted in the future by something yet more satisfactory—and this is always a possibility in the progress of scientific thought—one would be inclined to say that the theory had already justified its existence. The saying of Scripture “By their fruits ye shall know them” applies in full force to theories as well as to persons, and in the short span of its existence the theory has been fruitful. It has “acquired merit” in the only way open to any such hypothesis, namely, by stimulating new experimentation and thus leading to the discovery of facts and laws previously unknown.

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CAMBRIDGE, MASSACHUSETTS, Sept., 1914.

STUDIES OF THE VAPOR PRESSURE OF SOLUTIONS. A STATIC METHOD FOR THE DETERMINATION OF THE DIFFERENCE BETWEEN THE VAPOR PRESSURE OF SOLUTION AND THAT OF SOLVENT.

By J. C. W. FRAZER AND B. F. LOVELACE.

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The fundamental importance of accurate determinations of the effect of dissolved substances on the vapor pressure of solvents, and the lack of agreement of results obtained by different workers using dynamic methods, led the authors, in the spring of 1912, to undertake the problem of improving the static method with the view of making it a method of precision. After some preliminary experiments, they decided to apply the principle of the Rayleigh manometer.¹

This instrument was designed by Lord Rayleigh for the purpose of measuring small differences in gas pressure. It is used by the authors to measure the difference between the vapor pressure of the solution and that of the pure solvent. The work so far has been limited to aqueous solutions of mannite at 20°.

The essential features of the manometer are shown in Fig. 5. R R are glass bulbs, about 39 mm. in diam., blown on a glass fork. This is connected by means of a rubber tube with a mercury reservoir which may be adjusted very accurately at any desired height by means of the screw I. At the centers of the bulbs are set two glass points. The side limbs P P communicate with the systems, the relative pressures in which are to be measured.

¹ *Z. physik. Chem.*, **37**, 713 (1901); *Trans. Royal Soc.*, **196**, 205 (1901).