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THE CRITICAL POINT, AND THE SIGNIFICANCE OF THE QUANTITY b IN THE EQUATION OF VAN DER WAALS.[1]

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The equation of van der Waals has excited wide interest and received well-deserved recognition on all sides for over thirty years. The genius of this great Hollander emphasized, for the first time, the important effect upon the volume of a gas probably caused by the cohesive tendency of the molecules, and pointed out that, when this tendency is taken into account, the earlier equation of Budde for hydrogen (namely, $p(v - b) = n\mathrm{RT}$) may be extended so as to apply fairly well to other gases.

The well known equation thus modified—namely, $(p + a/v^2)(v - b) = n\mathrm{RT}$—is widely used, although its limitations and its lack of exact fulfilment are generally recognized. That it is not merely an abstract mathematical formula, but is also concretely if somewhat vaguely concerned with the most important influences determining the volume of a gas, will probably be admitted by most physical chemists. Therefore the significance of its terms is a matter of interest and importance. The

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[1] A preliminary treatment of this subject was given in a course of Lowell lectures in Boston in 1908, and again presented in a paper read at the meeting of the Eighth International Congress of Applied Chemistry, at New York, in September, 1912.

present paper concerns the meaning of the quantity b, or "co-volume"—the rather small quantity which must be subtracted from the volume of a gas in order that the remainder may correspond reasonably well with the requirements of the gas-law. The treatment of this topic will be essentially non-mathematical, partly because the situation seems at present too complex for really precise mathematical treatment. It is hoped that the discussion which follows will be comprehensible both to mathematical and to non-mathematical readers.

In an attempt at interpretation of this kind, the first step is to study the behavior of the given quantity under changing conditions. Although b is often assumed to be constant, much evidence is at hand which seems to prove that it probably varies under varying conditions. This possibility was suggested by van der Waals in his first paper long ago,[1] but the inference was complicated by the fact that the calculated value for b depends upon that assumed for a, and the change in the values of b seemed to be no greater than might have been due to uncertainty in this assumption. Hence physical chemists as a rule have been content to assume constancy in both a and b.

About fourteen years ago a few tentative unpublished calculations seemed to show me distinctly that b really varies, and these calculations drew my attention again to the original paper by van der Waals. They formed indeed the first clue which called to my notice the probable compressibility of atoms, and the outcome was summed up very briefly in the third item of the summary in the second paper concerning the significance of changing atomic volume,[2] as follows:

"3. That it (*i. e.*, the theory of compressible atoms) is able to interpret the actual deviations from the gas laws better than any other theory, retaining the essential import of the equation of van der Waals and modifying this equation only as regards the changeability of a and b." After thoughtful consideration of the whole subject for twelve years, I hope to explain the main idea somewhat more fully in the present communication, which does not pretend to be a final treatment of the matter.

Let us review here typical figures taken from the first paper of van der Waals.[3] First may be given a brief table showing the change of b (in the case of carbon dioxide) with temperature. In this table b is expressed first as a fraction of the total volume at 0° under one atmosphere's pressure calculated upon the assumption that $a = 0.00874$, and then in cubic centimeters in a gram-molecule of gas.

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[1] Van der Waals, "Over de Continuiteit van den Gas en Vloeistoftoestand," p. 77 (Leiden, 1873, translated by Roth, p. 81 (Leipzig, 1881)).

[2] *Proc. Am. Acad.*, **37**, 409 (1902); *Z. physik. Chem.*, 40, 607 (1902).

[3] See pp. 81, 85, and 86 of the German translation, 77 of the original Dutch already quoted.

THE EFFECT OF TEMPERATURE ON *b*.

Temperature.	*b* if *v* at 0° and 760 mm. = 1.0000.	*b* in cc. per mol.
0°	0.0023	51
13°	0.0024	53
34°	0.0026	58
50°	0.0027	60
100°	0.0029	64

Evidently *b* seems to change distinctly with the temperature, increasing as the temperature rises. Similar figures are given in the same paper for nitrous oxide and ethylene, from which it is seen that these two gases also have slight but somewhat less strongly marked positive temperature coefficients for *b*.

But, although the consistency of these results makes them mutually confirmatory, it is still undeniably the case that all the figures depend upon the values chosen for *a*;. a change in this other "constant" might have led to a different conclusion about the changeability of *b*. Hence another confirmation is welcome; that, namely, to be obtained by studying the effect of pressure upon *b*, a proceeding which subjects the variability of the quantity *a* to a searching test. The following table contains the appropriate figures.

THE EFFECT OF PRESSURE ON *b* (32.5°).

v at 32.5° if *v* at 0° C and 760 mm. = 1.00.	*b* if *v* at 0° C and 760 mm. = 1.000.	*b* in cc. mol.
1.130	(0.00255)	57
0.013	0.00251	56
0.0080	0.00254	57
0.0072	0.00252	56
0.0070	0.00251	56
0.0063	0.00248	55
0.00427[1]	...	..
0.0038	0.00216	48
0.0032	0.00199	44
0.0029	0,00190	42

Thus *b* seems to remain essentially constant over a wide range of pressures, but suddenly begins to diminish when very high pressures and very small volumes are attained. The constancy of *b* under low pressures seems to indicate at least that if *a* and *b* vary, their variations must exactly counterbalance. There is no evident reason why *b* should change over a wide range of pressure until one reaches the neighborhood of the bulk of *b* itself, whether the molecules are compressible or not. On the other hand, the sudden decrease of *b* under high pressures (when the volume of the gas has been brought almost down to the bulk of *b* itself) may

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[1] This is the critical volume. The density of carbon dioxide at the critical point (31.35°) is 0.464 (Amagat, *Compt. rend.*, 114, 1093 (1892)). Keesom found 0.0042 to 0.0044 according to the method used. See his thesis for doctorate, Amsterdam, 1904.

indicate that then the entity represented by b is really being compressed. It is perhaps not an accident that the bulk at which this compression begins to be manifest is about the critical volume, as will be shown later.

Van der Waals, returning to this subject after more than a quarter of a century,[1] came to the conclusion that his old value for a might be somewhat too large—the more accurate value seeming to be nearer 0.0085 than 0.00874; and his further calculations, while too complicated to review here, led him to think that the expansion of b with temperature was less and the compression of b at high pressures was greater than he had supposed at first. Although the usual value for b seemed to be as large as 0.0023, the smallest possible value of b under great pressure might be as small as 0.0007—only one-third of the value usually credited to this so-called constant. It matters little here which alternative is chosen. Although the situation is by no means clear, and van der Waals himself was evidently puzzled by some of the results of his own calculations, one leaves the perusal of his paper with a feeling of agreement with van der Waals' own conclusion that whatever reasonable value one may choose for a, the value of b must be assumed to shrink under very high pressures, and to change slightly with increasing temperatures. Moreover, besides van der Waals, many others, especially Ramsay and Young, have furnished further considerations which may be interpreted to signify the changeability of b.[2] Van der Waals suggested tentatively (on p. 284, *l. c.*) that the assumption of molecular compressibility might help in the explanation, but neither he or any other seems to have carried this idea to its logical conclusion.

In almost all cases the value assigned to b depends essentially (as in the case above) upon the value chosen for a. Because even the constancy of b over a large range of moderate pressures affords no certain criterion as to whether or not the choice is correctly made, it is manifestly desirable that we should obtain, if possible, data free from dependence upon the affinity-constant. Fortunately there exist two elementary substances, hydrogen and helium, having values of a so unusually small that as a first approximation this quantity may be considered as wholly negligible in the gases under atmospheric pressure. These elementary gases ought, therefore, to afford valuable and interesting information bearing upon the present problem, and their evidence is especially significant because the former of these gases contains two atoms to the molecule and the latter only one. The comparison of the two, then, ought not only to tell us whether b changes with the temperature, but also to decide whether this

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[1] Van der Waals, *Z. physik. Chem.*, 38, 257 (1901). See also *Chem. Weekblad*, 10, 624; reviewed in *C. A.*, 8, 598 (1914).

[2] Ramsay and Young, *Phil. Mag.*, p. 196 (1887).

change is entirely a question of the space between the atomic centers in the molecule, or whether the atoms themselves are compressed. If helium exhibits a change of b with the temperature, we cannot but think that its atom may actually be changed in volume by changing conditions.

Fortunately modern accurate data exist both for hydrogen and helium.[1] From among the wealth of available figures, in order to eliminate a change in a as much as possible from consideration, the value of b should evidently be calculated from the results obtained under comparatively small pressures and at temperatures not too low, so that the volume of the gas shall be fairly large and the term a/v^2, shall be as small as possible. The following table contains comparable results at 0° and 100° for both helium and hydrogen. The actual value of pv for 0° and atmospheric pressure is taken as equal exactly to unity.

TABLE I.—HELIUM.

Temperature.	p.	pv.
0°	1	1.0000
	26.634	1.0139
100.35°	1	1.3674
	42.574	1.3873
	Hydrogen	
0°	1	1.0000
	30.00	1.0181
100°	1	1.3661
	30.00	1.3858

From these figures (on the assumption that a in each case is so small as to be negligible when v exceeds 0.7 liter per mol) the value of b is easily calculated with close approximation from the equation of Budde: $p'(v'-b) = RT = p(v-b)$; whence $b = (pv - \mathrm{RT})/p$; or $b = (p'v' - pv)/(p' - p)$. The resulting values are given in the following table.[2]

TABLE II.

Values for b for helium and hydrogen.

(Expressed in terms of cubic centimeters per mol of gas.)

Temperature.	Hydrogen.	Helium.
100°	15.1	10.4
0°	13.8	12.0

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[1] Hydrogen.—Witkowski, *Krak. Anz.*, 1905, 305–338. Helium.—Kamerlingh-Onnes, *Proc. Sci. Akad. Amsterdam*, Jan. 23 (1908), p. 448, March 28, 1908, p. 741–742; Comm. Leiden, number 102*a*.

[2] If a is not so small as to be negligible, the result of this calculation is, of course, not b, but a virial of the approximate form $b - a/pv$. For hydrogen and helium over ordinary low pressure and high-temperature ranges this may be taken numerically as $b - a/\mathrm{RT}$ without important error. Thus if a is thought to be large in these gases, b with helium must be conceded to possess an even greater increase with falling temperature than that indicated above; and in the case of hydrogen the temperature-coefficient of b may become negative, like helium. If with hydrogen a is assumed to exceed

The interesting and striking point about these figures is that, whereas with rising temperature the value of b for hydrogen increases, the value of b for helium decreases. Perhaps, it is true, one might ascribe these small differences to error of experiment, but the consistency of the figures for hydrogen at even higher pressures leads one to believe that the experimental error is much smaller than these[1]. Calculated in the same way the value of b for hydrogen between 30 and 60 atmospheres is 15.2 at 100° and 14.2 at 0°, agreeing reasonably well with the values given in the table for much lower pressures. In the case of helium, it is true, the results at higher pressures do not seem to be quite so consistent. If we take the extreme range of pressure studied by Kamerlingh-Onnes (about 50 atmospheres at 0° and 66 atmospheres at 100°) the results are 10.8 at 100° and 11.5 at 0°. Although the difference is less between these figures than between those for the lower pressures given in the table,[2] the qualitative conclusion is the same; the value of b seems to decrease as the temperature rises, instead of increasing as in the case of hydrogen.

The most probable explanation for the opposite characters of the two gases is not far to seek. Let us consider first the case of helium. The quantity b is generally admitted to be a function of the bulk of the molecules themselves, therefore changes in b must be referred back to changes in this bulk. Thus, from the table above, when the molecules of a gas are single isolated atoms, their available bulk seems to decrease with rising temperature. Since we must look upon b as a function of some-

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0.0002, b will exceed 0.0008 (or 18 cc. per mol) and its temperature-coefficient will become negative. Since this paper was sent to the press Mr. R. H. Kent, of the Physics Department of Harvard University, has kindly brought to my notice strong evidence, worked out mathematically but not yet published by him, tending to show that this is really the case with hydrogen and argon, and probably also with carbon dioxide and many other gases. This conclusion intensifies the argument of the present paper. Nevertheless, for the present, I prefer to leave my original statements as they stand, accepting the usual values given to a and b, because then there is no risk of exaggerating the evidence. It is enough for the present argument that a single gas should show a definite decrease of b with rising temperature. No assumption whatever with regard to the value of a can change this conclusion. The question as to whether the others have a positive or negative temperature-coefficient is merely a question as to whether the positive or negative effect (each of which must be present) happens to predominate. Incidentally, the appearance of a positive plug-effect with hydrogen may perhaps be explained, in part, by the inherent distending tendency of atoms now under discussion; in most gases, of course, it must be supposed to be hidden and masked by the greater negative plug-effect due to cohesion.

[1] The excellent data of Kamerlingh-Onnes for hydrogen lead to the same conclusion. *Proc. Sci. Kon. Akad Wetensch. Amsterdam* X^2, 420 (1908).

[2] The reason for the disagreement is not easy to find. At low temperatures, too, helium is irregular. It is possible that helium has a tendency to form double molecules under high pressure and at low temperatures. The singular maximum in its liquid density at 2.2° absolute (Kamerlingh-Onnes) points in this direction.

thing which may be termed the "effective collision-bulk" of the molecules, does not this contraction with rising temperature signify that isolated atoms of helium are more compressed by collision, the greater the kinetic energy of the moving molecules? It would be highly desirable to verify this tentative conclusion with other gases, but unfortunately all other monatomic gases have large values for a.[1]

The quite different case, illustrated by hydrogen and carbon dioxide, is equally easy to explain upon the same basis; and probably most other substances fit into this latter category, since most other substances have polyatomic molecules. Here the coefficient of expansion of b is positive, or at any rate (even if we imagine that a and b are both decidedly larger than here assumed) distinctly less markedly negative than in the case of helium. Is it not likely that two opposing effects occur in these polyatomic molecules? Increased compression on impact with increasing temperature must be supposed to occur in hydrogen as well as in helium, but the effect is concealed, because, at the same time, the centers of the atoms in any given molecule are probably separated more widely, as the temperature rises, by the rotation of the diatomic molecule—which may affect the apparent size. Thus these two effects, the decrease in effective collision-bulk of the atom due to more violent impact, and the increase due to the expanded rotating state of the molecule, seem almost to balance one another, the latter slightly predominating if a is small.

The conclusion that atoms, when free and uncombined as in helium, expand but little, if at all, as the temperature rises, is entirely in harmony with the well known tenet of the kinetic theory of gases that all the heat-energy of a monatomic gas is translational and none of it is internal. The apparent expansion of the hydrogen molecule with heat is equally in accord with this theory, because the increased specific heat of hydrogen, and of other gases with polyatomic molecules, points to consumption of energy within the molecule in rotation, as usually assumed, or otherwise.

Thus the evidence is very strong and very consistent that b changes with changing conditions, and the most reasonable explanation of the facts seems to indicate that not only the molecules but also the atoms themselves are compressible.

If, then, molecules are capable of changing their volume under changing conditions, and are deformed or distorted during the violent impact caused by their mutual collisions when flying about in a confined space, one inevitably infers further that *time* must be consumed in the act of collision.

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[1] Compare Stefan (*Wiener Sitz. ber.*, **45**, *Abth.*, **2**, 339 (1872); also O. E. Meyer (Baynes) "Kinetic Theory," p. 166 (1899). Stefan imagined a compressible environment, but still conceived of the imaginary hard core.

The relation of this time spent in collision to that required in flight over the mean free path between collisions is an important item to be considered. The mean free path of hydrogen under ordinary conditions has been calculated to be as much as 0.000185 mm. whereas the diameter of the hydrogen molecule is supposed to be not much over 0.0000001 mm., an amount less than 0.1 of 1% of the free path. This being the case, the time spent in collision, even if the molecule were considerably deformed by the force of the impact, could hardly be a very important percentage of the whole time, although the deformation might correspond to a very appreciable percentage of the diameter of the atom. For the present discussion it is important to note that the time of collision is probably the same, no matter what the temperature may be, for the time spent in the actual collision of an elastic ball with an elastic barrier is independent of the velocity of the striking ball. This being the case, the figures just mentioned, especially those for helium, which are more simply interpreted, must refer to a real increase in compression in the atom as the temperature rises, because the falling off of *b* could not be ascribed to any increase of time of impact.

Several months before van der Waals' above-mentioned paper[1] had appeared, I tentatively brought forward a number of arguments of quite different sort, indicating that atoms (and therefore molecules) may well be supposed to be compressible; and the data pointing in this direction have multiplied greatly during the last ten years.[2] In the most recent

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[1] Van der Waals, *Z. physik. Chem.*, **38**, 283 (1901).

[2] Following are the titles of the several recent papers bearing upon the theory of compressible atoms with references:

"The Possible Significance of Changing Atomic Volume," *Proc. Am. Acad.*, **37**, 1 (1901); *Z. physik. Chem.*, 40, 169 (1902); *Chem. News*, **86**, 81 (1902).

"The Significance of Changing Atomic Volume. II. The Probable Source of the Heat of Chemical Combination and a New Atomic Hypothesis," *Proc. Am. Acad.*, **37**, 399 (1902); *Z. physik. Chem.*, 40, 597 (1902).

"The Significance of Changing Atomic Volume. III. The Relation of Changing Heat Capacity to Change of Free Energy, Heat of Reaction, Change of Volume and Chemical Affinity," *Proc. Am. Acad.*, **38**, 293 (1902); *Z. physik. Chem.*, 42, 129 (1902).

"New Method of Determining Compressibility, with Application to Bromine, Iodine, Chloroform, Bromoform, Carbon Tetrachloride, Phosphorus, Water and Glass," THIS JOURNAL, **26**, 399 (1904); *Z. physik. Chem.*, **49**, 1 (1904).

"The Significance of Changing Atomic Volume. IV. The Effects of Chemical and Cohesive Internal Pressure," *Proc. Am. Acad.*, **39**, 581 (1904); *Z. physik. Chem.*, **49**, 15 (1904).

"The Relation of the Hypothesis of Compressible Atoms to Electrochemistry," *Trans. Internat. Electr. Congress*, **2**, 7 (1905).

"Densities of Lithium, Sodium, Potassium, Rubidium, and Caesium," THIS JOURNAL, **29**, 117 (1907).

"The Compressibility of Lithium, Sodium, Potassium, Rubidium, and Caesium," *Publ. Carnegie Inst. Wash.*, **76**, 9 (1907); *Z. physik. Chem.*, **61**, 77 (1907).

"The Compressibility of Carbon, Silicon, Phosphorus, Sulfur, and Selenium," work at the highest pressures as yet attained in accurate experiments on compressibility, Bridgman admits that atoms must probably be imagined to be compressible, in order to explain his results.[1] Hence there is now a great bulk of testimony which is irreconcilable with the early assumption of van der Waals that molecules are incompressible and that the rebound after a collision between them is truly instantaneous.

In thus describing atoms as compressible I do not mean to make any assumption whatever with regard to the mode of distribution of their "substance" (whatever that may be) within their boundaries. I mean merely to declare that there seems to be a distending tendency in each atom, entirely different from and unconnected with the vibration of heat, and that this distending tendency seems to have a fairly well-marked boundary which is compressed by the application of pressure. Heat seems to distend this boundary only when atoms are combined chemically or cohesively with other atoms. It may be, of course, that the atom, as Larmor and others have suggested, is a vacuous space in an extremely dense ether. If so, this boundary must be supposed to be the boundary of that vacuous space. Again, the idea of atomic compressibility is quite combatible with the recent hypothesis which postulates a composite structure containing electrons. Many other suppositions might also comply with the requirements, but so far as I can see there is nothing in any of the facts demanding the assumption of the small, hard, incompressible core which has been the subject of so much speculation and often fruitless mathematical analysis in the past.

Publ. Carnegie Inst. Wash., **76**, 29 (1907); *Z. physik. Chem.*, **61**, 77 (1907).

"The Linear Compressibility of Copper and Iron, and the Cubic Compressibility of Mercury," *Publ. Carnegie Inst. Wash.*, **76**, 44 (1907); *Z. physik. Chem.*, **61**, 183 (1907).

"The Compressibilities of the more Important Solid Elements and their Periodic Relations," *Publ. Carnegie Inst. Wash.*, **76**, 56 (1907); *Z. physik. Chem.*, **61**, 183 (1907).

"The Compressibilities of the Elements and their Periodic Relations," THIS JOURNAL, **31**, 154 (1909).

"The Compressibilities of the Chlorides, Bromides, and Iodides of Sodium, Potassium, Silver, and Thallium," THIS JOURNAL, **31**, 158 (1909); *Z. physik. Chem.*, **71**, 152 (1910).

"The Fundamental Properties of the Elements," Faraday Lecture, *J. Chem. Soc.*, 100, 1201 (1911); *Science, N. S.*, **34**, 537 (1911); *Proc. Chem. Soc.*, **27**, 177 (1911); *Revue scientifique*, 50, 321 (1912); Smithsonian Report, p. 199 (1912).

"Compressibilities of Certain Hydrocarbons, Alcohols, Esters, Amines, and Organic Halides," THIS JOURNAL, **34**, 971 (1912).

"Die Bestimmung der Kompressibilität flüssiger und fester Substanzen.," Handbuch der Arbeitsmethoden in der anorganischen Chemie., p. 247, Leipzig, 1912.

"The Chemical Significance of Crystalline Form," THIS JOURNAL, **34**, 381 (1913).

"The Theory of Compressible Atoms," *Harvard Graduates' Magazine*, **21**, 595 (1913).

[1] Bridgman, *Proc. Am. Acad.*, **47**, 549 (1912).

Most, if not all, other investigators seem to have overlooked a very simple means of testing whether or not molecules and atoms (as conceived by van der Waals) are held apart merely by the vibration of heat, as most people suppose. If this were the case, the particles should lie closely packed when all heat is removed from a body, because then the vibration is supposed to cease. Therefore, the smallest possible bulk which molecules could be made to occupy might be inferred from their bulk at the absolute zero, upon the assumption that no kinetic energy remains at that temperature. Let us take the case of mercury, which is especially suitable for discussion, because of its monatomic nature. The volume of a gram atom of mercury at its boiling point, 357°, is 15.7 cc. At —39° when solid, its volume is 14.1 cc.; at —188° it is 13.9. Extrapolating linearly to the absolute zero, the value is found there to be not less than 13.8. The total decrease in volume from the boiling point to the absolute zero is about 12%, or 1.9 cc. per gram atom; but if a system of incompressible spheres (as assumed by van der Waals) were pressed into its most closely packed assemblage, the loss of volume would be not 12 but at least 40%.[1] Evidently, then, something not indicated in the equation of van der Waals and independent of heat, prevents the atomic cores usually imagined from approaching one another.

This case of mercury is not an unique or unusual one. The same phenomenon is to be observed in most, if not all, other substances. For example, Roth has extrapolated the density of common ice to the absolute zero, and finds the molecular volume at this temperature to be 19.2. This is actually larger than the bulk of the same amount of water at its boiling point (18.8). In general the contraction of substances on cooling to the absolute zero is found to be very small. For example, Cohen and Olie[2] find that at low temperatures the density of diamond is almost independent of temperature, and graphite also has a very small temperature-coefficient. White tin falls off less than 1% in volume in going from the temperature of the room to —163°, and gray tin loses only about one-third of 1% of its volume over that range. The bulk of gray tin at the absolute zero is much greater than that of liquid tin at the highest temperatures thus far studied; for according to Day and Sosman[3] the density (6.16) of tin at 1600° C. is nearly 6% greater than that (5.75) of gray tin at —163°. It is true that tin and ice are exceptional substances, but the fact remains that in general the contraction suffered by all substances on cooling is (so far as I can discover) much less than that required by the small incompressible cores of van der Waals. Clearly the compressible

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[1] The bulk of van der Waals' molecule ($^1/_4\ b$) for mercury is taken, as usual, to be 0.3 times the volume of the liquid at the boiling point, or 4.7 cc.; and the closest packed system of small spheres occupies about 57% of the bulk of its containing vessel.

[2] *Z. physik. Chem.*, 71, 400 (1910).

[3] Private communication to the editors of Landolt-Börnstein's Tables, p. 168 (1912).

"sphere of influence" accompanies the atom wherever it goes; the imaginary incompressible core simply marks the limit of the compression in each particular case. The puzzling changes exhibited by this imaginary core need therefore occasion no surprise.

Let us now inquire what bearing molecular compressibility may have upon the significance of the quantity *b*.

At the outset we perceive the inevitable error of a familiar proposition of van der Waals, namely, that the quantity *b* represents four times the actual bulk of the molecules. This tenet seems to have been accepted by everyone without much question, but it loses all authority if molecules are compressible, because incompressibility of the molecules was assumed in its ingenious deduction.[1] Fairness to the brilliant Hollander demands the statement of the fact that he himself accepted his own proposition with some reserve; this is clear from his statements showing that the supposed relation cannot possibly hold in greatly compressed gases.[2]

Further study seems to suggest that the molecules really occupy much more than one-fourth of the space *b*. Two causes would tend to reduce the apparent size of *b* if the molecules are compressible. In the first place the mutual compression of two molecules on collision would make their apparent diameter during contact less than it is when each molecule is free. Secondly, the time consumed in this collision would make the centers of the molecules seem to approach even more closely to one another than they really do. From the first cause alone a diminution in the diameter of only one-third would make the bulk of the molecules appear to be almost as small as a quarter of their true bulk. Let us suppose, for a moment, that this is really the extent of compression on collision; then if *b* is to be taken as four times the *apparent* bulk, its magnitude calculated from these data, although quadruple the apparent size, would not be far from the actual space occupied by the molecules. Thus if one admits that the molecules are compressible, it seems easily possible that the space occupied by the molecules is really at least as large as *b*.

Let us review briefly the results for carbon dioxide with this in mind. From van der Waals' table on the effect of pressure, already cited, one finds that at 32.5° *b* remains essentially constant with decreasing volume, until the gas has been compressed to a bulk only one hundred and sixtieth of its bulk under atmospheric pressure. When this bulk is halved yet again, bringing the volume down into the neighborhood of that *b*, its *b* is seen at last to diminish. Interpreting, we may infer that as long as the molecules are fairly far apart in the gas, the volume-effect ascribed to *b*

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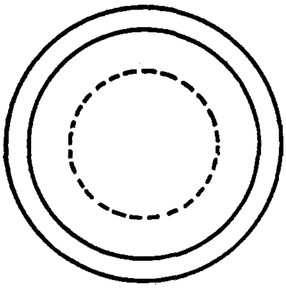
[1] Van der Waals, "Over de Continuiteit, Etc.," p. 52 (1873). This chapter was much expanded in the German translation, and the incompressibility of the molecules, at first tacitly assumed, was explicitly stated (pp. 46, 57, 59 of German translation) (1885).

[2] Van der Waals, "Die Continuiteit, Etc.," trans. by R. Roth, Leipzig, 1881, p. 55.

depends only upon single collisions, and these at a given temperature cause no more change in volume in a much compressed gas than in a comparatively rare one. On the other hand, when the bulk of the gas is reduced to the neighborhood of the bulk of the molecules themselves, these will begin to be compressed by the outside pressure, the whole situation will be changed, *a* may be supposed to increase rapidly, and the total effect of the compression will be greater than that due to collision alone. At this point, according to the theory above advocated, the pressure must be supposed to be no longer due primarily to free collisions with the walls, but rather to the above-discussed distending tendency of the atoms themselves, assisted by the infinitesimal impacts of such an elastic movement as is visible in magnified form in the Brownian movements. From the constancy of *b* down to a definite point, and its sudden decrease afterwards, one may conclude that the volume in which the molecules themselves begin to be compressed (that is to say, the critical volume) is not very far from the actual bulk of the molecules. This in the case of carbon dioxide is about 5/3 *b* at 31.35°.

The accompanying diagram is intended to show cross-sections of the three volumes under consideration, which have been imagined to occupy spheres, although of course in an irregular molecule exact spherical form can hardly be attained. The actual experimental volume of 44 grams of carbon dioxide at the critical point is 94.8 cc., and the value of *b* as calculated from the gas at the same temperature is 57 cc. One-quarter of *b* is therefore 14.25. The radii of three spheres having these relative volumes are to one another as 1.86 : 1.55 : 1, respectively, and the circles drawn with these radii give a rough idea of the relations under discussion.



In this diagram, the outermost ring indicates the actual critical volume, the next ring indicates *b* at the critical temperature, and the innermost dotted ring indicates the imaginary $^1/_4\, b$ demanded by the original hypothesis of van der Waals. The volumes are 95, 57, and 14.2 cc., respectively, per gram molecule of carbon dioxide.

Another more striking fact which supports the conclusion that the actual bulk of the molecules is greater than *b* (instead of being only one-quarter *b* as van der Waals assumed) is the well known but often overlooked fact that the quantity *b*, as computed from the behavior of a gas, is not very far from the actual volume of the liquid to be obtained from that gas.

A few data will demonstrate this nearness of the quantity *b* to the actual volume of the liquid. In the first place, the classic case of carbon dioxide may be quoted; its value of *b*, calculated at 13° from the behavior of the gas and expressed in terms of cubic centimeters per mol of gas is

53 cc. But the actual molal volume of liquid carbon dioxide at 13° is also about 53 cc.[1] Thus in the case of carbon dioxide *b* equals the actual volume of the liquid at 13°. At lower temperatures the volume of the liquid becomes less than that of *b*, at high temperatures the volume of the liquid becomes greater than *b*.

Other significant data of the same kind are not plentiful, because *b* is not often calculated as above from the behavior of the gas. This was done by van der Waals in his original paper for nitrous oxide and ethylene, but unfortunately our knowledge of the densities of these gases in a liquefied condition is not very comprehensive. The molecular values for *b* calculated by van der Waals for these two substances (about 42 and 56 cc. per gram molecule) would correspond to densities probably attained by the liquid at a boiling point under pressure greater than atmospheric pressure, but considerably below the critical pressure.

Although data for *b* obtained from the state of gas are far from plentiful, very many values for this so-called constant have been calculated from the critical data according to the equation of van der Waals. For our present purpose this procedure is unsatisfactory, for it assumes the accuracy of an equation which is really only an approximation. Moreover, in those cases where a comparison is made between the values obtained in two different ways, the values for *b* do not exactly agree. The first comprehensive collection of such data was compiled by Guye and Friedrich,[2] and a still larger collection of data is given by Landolt-Börnstein's tables.[3] As an example of the order of disagreement the case of carbon dioxide may be cited. The gas gives a molecular value for *b* between 51 and 64 according to the temperature, but the value calculated from the critical data according to van der Waals' equation is only 42.8.

Assuming, however, that the values given by van der Waals' equation are at least of the right order of magnitude, it is interesting to note that as a general rule *b* has a volume of about 1.2 times that of the liquid at the boiling point under atmospheric pressure. The parallelism of nearly all liquids in this respect has already been noticed[4] by others, although it is usually stated in another form as follows: "Assuming the actual bulk of the molecules to be one-quarter of *b*, this actual bulk is found to be almost universally three-tenths of the bulk of the liquid at the boiling point under atmospheric pressure."

Disregarding, as we have been led to do in this paper, the ill-founded assumption that $b = 4$ times the actual bulk of the molecules, the data have new interest in showing that the bulk of the liquid under pressure

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[1] Amagat found its density at 13° to be 0.831 (see Landolt and Börnstein, **1912**, p. 155).

[2] Guye and Friedrich, *Arch. sci. phys. nat.*, **9**, 505–531 (1900).

[3] Landolt-Börnstein, *Physikalisch-chemische Tabellen*, fourth edition, p. 439 (1912).

[4] For example, Nernst, *Theoretische Chemie*, p. 225 (1907).

somewhat above the boiling point attains a value exactly equal to b. If we allow the inference that b as found from the critical point with the help of van der Waals' equation is somewhat too small, the general principle probably still holds true, although the exact form of statement may somewhat alter.

The supposition that b is really not far from the space actually occupied by the molecules finds its analogy in the approximate regularity found by H. N. Morse in osmotic pressures, which conform approximately to the regular rule only when the actual bulk of the dissolved substance is subtracted from the total volume.

Although these considerations undermine confidence in the ingenious mathematical deductions of van der Waals—not because of any mathematical fault but only because of his probably erroneous premise of atomic incompressibility—the essential ideas embodied in van der Waals' equation as applied to *gases* are untouched and left as probable as ever. These essential ideas are, of course; first, that the molecules in a gas occupy space and that some allowance must be made for this space; secondly, that they attract one another, and that this attraction diminishes the pressure due to the outward momentum of the particles striking the enclosing wall.

If the equation of van der Waals thus gives a plausible and still valid, if somewhat crude, conception of the nature of a gas, its application to *liquids* is far more questionable. It is especially faulty in giving no explanation whatever of the evaporation of liquids and the condensation of vapors, one of the commonest of physico-chemical equilibria. Indeed, as is well known, it demands, in the region where liquid and vapor exist together, a state of affairs which is physically impossible, indicated by the reflex curve in the familiar low-temperature isothermals.

One may well ask how it is that van der Waals' equation can apply to the critical point, if at its best it fails to explain evaporation, and if besides we must conclude that all the mathematical considerations upon which it rests need modification. As a matter of fact, however, the application of the equation to the critical point is by no means satisfactory. Even in the case of carbon dioxide it applies only very roughly—for example, it demands a critical pressure of 50 atmospheres instead of the true value 73.[1] Most physical chemists will be inclined to

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[1] As is well known, the calculation is as follows: $p_c = a/27b^2 = 0.00874/27(0.00255)^2$. The difficulties and inconsistencies of the equation of van der Waals are interestingly reviewed in the masterly treatment of the theory, published by H. Kamerlingh-Onnes and W. H. Keesom in the Supplement 23, Volume 11, of the Communications from the Physical Laboratory of the University of Leiden. The page is numbered 799 above and 185 below. The possible compressibility of molecules is suggested not only there, but also on the page numbered 704 above and 90 below. This monograph was also published by the *Encycl. der Math. Wissenschaften*, 1912, pp. 615–945, and the page numbers on the top of the separate reprint are those in the encyclopedia.

admit that the equation of van der Waals cannot be expected to apply exactly to very condensed material. In order to explain the partial agreement at the critical point, it is only necessary to assume that the circumstances of collision are such as to make the compressible molecule appear, through its compression, to occupy a smaller space than that which it occupied before the collision, and that this smaller space happens to be approximately that which was required by van der Waals' first erroneous assumption. It is only reasonable that this volume should appear to be constant in gases not greatly compressed, for when collisions were not too frequent, the compression produced by each individual collision would be the same, as has already been suggested.

The existence of the critical point, at which it is possible to pass continuously from a state of liquid to a state of gas without any visible sign of the transition, has always been imagined to be one of the strongholds of the old theory. It was undoubtedly the approximate but perhaps accidental efficacy of the theory at this point which stimulated many to apply the kinetic theory of gases to liquids, supposing that if continuous transition exists from one to the other, the two forms of matter must necessarily be of the same structure. I shall endeavor, however, to show that this is not a necessary consequence, and that the fact of continuous transition from the liquid to the gaseous state at this particular point does not by any means necessarily fasten upon liquids and solids the same interpretation as that which applies to gases. As a matter of fact, a vapor and its liquid are not continuous under pressures below the critical pressure; and true continuity exists only at the critical point itself.

May not the critical point be explained on the basis of the hypothesis of compressible atoms as follows? A substance in the state of gas, at a temperature above its critical point, may be imagined to be gradually compressed by outside pressure until it occupies the volume which the liquid might be expected to occupy. The pressure will then be much above the critical pressure. According to the theory of compressible atoms, the spaces between the molecules would hereby be reduced to nothing, that is to say, the molecules would be packed in closely together, not only by their own attraction but also by outside pressure. If the pressure were removed, they would fly apart as a gas, because the energy of their vibration would be enough at this high temperature to overcome cohesion and to cause this effect. No sign of any liquid would be manifest. If, on the other hand, the substance were cooled, while thus compressed, to a temperature below the critical temperature, it is obvious that no change in appearance could be expected; the molecules, being already closely pressed together, could not combine into separate drops under the effect of the cooling. Each would remain in its old position, but if the pressure were now removed at this lower temperature the cohesion would be enough to withstand the diminished vibratory energy, so that a liquid would remain in the vessel. The transition would be continuous only because the molecules had been pressed so closely together by outside pressure that they could get no closer.

The critical point may obviously be supposed to be merely the dividing point between the first and the second of these alternatives. Thus, according to this explanation, the boiling point is that point at which the effect of the thermal tendency of the liquid to fly apart is exactly balanced by the sum of the effects of cohesion and vapor pressure, while the critical point is that at which, still fulfilling these conditions, the molecules in the vapor are forced by outside pressure into juxtaposition.[1]

The extreme sensitiveness of the critical point and the enormous volume-changes which take place in its vicinity, are quite in accord with this explanation. The equilibrium between an attracting or cohesive tendency (which may be supposed to grow with proximity) and a thermal disintegrating influence which is just able on the average to withstand this binding effect superposed on top of the distending effect of the compressed molecules, would naturally be a highly unstable one.

The equation of corresponding states about which much is written is not at all inconsistent with this conception of the nature of b and of the imagined mechanism of the critical phenomena. On the other hand, the present point of view provides a flexibility, lacked by preceding generalizations, which affords a reasonable explanation for the fact that the equations of van der Waals and of corresponding states are only approximate generalizations.

The immense multiplicity and variety of the published theories and facts concerning the critical point and the theory of van der Waals make it entirely impossible for any single individual to have made even a passing acquaintance with all. I have endeavored to seek information from many sources both by reading and by personal inquiry, and have sought to do justice to every earlier suggestion known to me, but some important contributions may have been overlooked. Therefore this essay is not intended in any way to claim ultimate priority with regard to any of the ideas advanced in it, although some of them may be new. The attempt has been made rather to show the modifications which seem to me to be needed in some commonly accepted notions, as well as to point out the consistency of all the facts with the theory of compressible atoms.

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[1] A briefer statement of this definition will be found in one of the earlier papers on changing atomic volume, *Proc. Am.*, **37**, 409 (1902); *Z. physik. chem.*, 40, 606 (1902).

Summary.

In this paper the following facts and interpretations are set forth:

1. The value of *b* in carbon dioxide must be admitted to vary according to conditions in such a way that, although fairly constant under moderate pressures, it diminishes greatly with very high pressures.

2. The value of *b* in hydrogen and carbon dioxide is probably affected by temperature, the nature of this effect being dependent on the value assumed for *a*. Both of these probabilities seem to be accepted by van der Waals himself.

3. The value of *b* with the monatomic gas helium is found to have a decidedly negative temperature coefficient.

4. This decrease in *b* with rising temperature seems to imply that the helium atoms are compressed by collision, the greater compression taking place at high temperatures because of the greater kinetic energy of collision. This conclusion suggests further that uncombined atoms are not expanded by rise of temperature—a conclusion in keeping with the solely translatory effect of heat on monatomic gases.

5. In polyatomic molecules this effect may be supposed to be partly counteracted by some sort of expansion of the molecule due to the energy expended within the molecule, as indicated by the larger specific heat of polyatomic molecules.

6. Therefore, since *b* may be supposed to be a function of the actual size of the molecules, one is driven to conclude that molecules may change the effective size which they assume under collision.

7. If the atoms and molecules are thus compressible, van der Waals's conclusion that *b* is equal to four times the actual molecular bulk falls to the ground; one must assume that the molecules really occupy considerably more space. It is not unreasonable to imagine that the actual molecular bulk (when the molecules are not compressed by collision or cohesion) is probably even larger than *b*, perhaps about the critical volume.

8. It is pointed out that as a matter of fact *b* occupies very nearly the bulk of the corresponding liquid at a temperature somewhat above the boiling point in many cases. This again shows that in the state of gas, when not compressed by cohesion, the molecules must be somewhat larger than *b*.

9. The approximate, although often unsatisfactory, agreement of the equation of van der Waals at the critical point is perhaps less significant than usually imagined; the continuity between the liquid and the gaseous states may be supposed to exist only at the critical point.

10. The critical temperature is defined by supposing that it is the point where the kinetic energy of the molecules is just barely enough to separate them when the outside pressure is sufficient to bring on the average the molecular surfaces into contact. Therefore the critical

volume may be about the true volume of the non-cohering molecules, as stated above.

11. From these conclusions it is evident that the theory of compressible atoms affords a satisfactory explanation for the inadequacy of the equation of van der Waals and the equation of corresponding states derived from it. The latter equation would be expected to hold better than the former, because the same kinds of deviations often exist in different gases, and the method of comparison may eliminate these.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

THE DOUBLE SULFATES OF SAMARIUM WITH SODIUM AND AMMONIUM.

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The solubility curves of the sulfates of samarium, gadolinium, yttrium and ytterbium in sodium sulfate seem to be of special interest. Samarium can be looked upon as being the first element whose double sulfate with sodium sulfate is distributed between the insoluble double sulfates and the more soluble ones. The solubility curve of gadolinium sulfate in sodium sulfate should show the reasons why some writers claim that gadolinium may be separated from the yttrium earths by this process, while others state that it can be separated from the cerium earths by this very method. Yttrium, possessing the average properties of the yttrium rare earths, as far as these compounds are concerned, shows the best concentrations under which the most complete separation can be obtained.[1] The curve given by ytterbium sulfate under these conditions would indicate, very nearly, the extreme solubilities. It would also show whether a concentrated solution of sodium sulfate would leave the members of the rare earth series, possessing the highest atomic weights, in solution accompanied by smaller amounts of the other yttrium earths.

This present communication deals with the compounds formed by samarium sulfate with the sulfates of sodium and ammonium.

The pure samarium sulfate was prepared in the following manner: Samarium oxalate was ignited and the oxide dissolved in hydrochloric acid. To the cool solution there was added a little more sulfuric acid than was required to unite with the samarium present, after which the mixture was poured into a large excess of alcohol. The precipitated sulfate was filtered off, washed with alcohol and rendered anhydrous by heating. The anhydrous sulfate was dissolved in water, filtered, and the filtrate evaporated upon the steam bath. The purified salt was then dried and very finely powdered.

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[1] This has been worked out by C. James and H. C. Holden. THIS JOURNAL, **35**, 559.