

support for the hypothesis that the volume of material is essentially dependent upon the internal pressures existing within that material, because it explains some of the most palpable exceptions shown by the first crude test of that hypothesis.

Summary.

1. The compressibilities of twelve salts have been determined—the chlorides, bromides, and iodides of sodium, potassium, silver, and thallium. The values between 100 and 500 megabars (*c. g. s.* "atmospheres") pressure are as follows:

Sodium chloride, 0.0000041; sodium bromide, 0.0000051; sodium iodide, 0.0000069; potassium chloride, 0.0000050; potassium bromide, 0.0000062; potassium iodide, 0.0000086; silver chloride, 0.0000022; silver bromide, 0.0000026; silver iodide, 0.0000039; thallos chloride, 0.0000047; thallos bromide, 0.0000051; thallos iodide, 0.0000067.

2. The relative values of the compressibilities of these salts have been correlated systematically with the volatility, surface tension, internal stress and heat of formation of the salts, as well as with the compressibility of the elements and the contraction which occurs during the formation of the salts from their elements.

3. It is shown that the new facts support the hypothesis that the volumes of liquids and solids are essentially dependent upon the chemical and cohesive affinities existing within them, and hence afford new evidence of the significance of changing atomic volume.

AN EXPLANATION OF THE NEGATIVE COEFFICIENT OF EXPANSION OF SILVER IODIDE.

By GRINNELL JONES.

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Silver iodide has the remarkable and almost unique property of decreasing in volume when its temperature is raised. Fizeau¹ has measured the coefficient of expansion of three different varieties, by a reliable optical method, and found the coefficient to be negative in every case. A cylinder of silver iodide, which had been previously fused and therefore consisted of closely-packed small crystals, was found to have a linear coefficient of expansion -0.00000139 (mean temperature 40°). Precipitated silver iodide which had been compressed until it was compact and coherent and took a good polish, but still retained its amorphous structure, was found to have the same linear coefficient of expansion -0.00000137 (mean temperature 40°). The linear coefficient of expansion of a single large hexagonal crystal was found to be -0.000003966 in the direction of the principal axis and $+0.000000647$ in a direction at

¹ Fizeau, *Pogg. Ann.*, 132, 292 (1867).

right angles to the principal axis. The cubic coefficient of expansion is therefore $-0.000003966 + 2 \times 0.00000647 = -0.00000267$, which is less than that observed for the other varieties ($3 \times -0.00000138 = -0.00000414$). Both the amorphous and the crystalline varieties possess this very unusual property. This abnormal behavior was observed through the range -10° to $+70^\circ$, and was found to be reversible. The numerical magnitude of the coefficient increases with rise in temperature, at least through the range of temperatures studied by Fizeau. Fizeau confirmed the sign of the coefficient by means of a lever comparer.

The observations of Fizeau are confirmed, at least as regards the sign of the coefficient of expansion and its change with the temperature by the observations of Rodwell¹ made by an entirely different and apparently less reliable dilatometer method. Rodwell's results are -0.00000718 between -18° and 0° , -0.00003297 between 0° and 21° and -0.00005570 between 21° and 67° .

The only other cases which I have been able to find of a decrease in volume with rise in temperature are water between 0° and 4° , liquid bismuth² for about 8° above its melting point, previously fused quartz³ below -80° , and a nickel-steel.⁴

For beryl, Fizeau⁵ found a negative linear coefficient of expansion in the direction of the principal axis, but at right angles to the axis the coefficient is positive and larger. The cubic coefficient of expansion is positive. Calcite behaves similarly.

Fizeau⁶ estimated from the change in the coefficient of expansion that diamond would have a density maximum at -42.3° , and below this temperature a negative coefficient of expansion and that crystallized copper oxide has a density maximum at -4.3° , and below this temperature a negative coefficient of expansion. This is, however, a guess based on extrapolation and not an observed fact.

As far as I know the only attempt which has been made to explain the remarkable behavior of silver iodide is due to H. Sainte-Claire Deville,⁷ who attempts to connect it with the expansion which occurs during the formation of silver iodide from its elements. He makes the supposition that two elements at any given temperature are allowed to combine adiabatically and that the compound formed is heated to a higher temperature t° by the heat evolved. "Experience shows that in

¹ Rodwell, *Chem. News*, **31**, 5 (1875).

² Ludeking, *Wied. Ann.*, **34**, 21 (1888).

³ Dorsey, *Physical Rev.*, **25**, 101 (1907). Scheel, *Ber. deut. physik. Ges.*, **5**, 718 (1907).

⁴ Guillaume, *C. R.*, **136**, 303 (1903).

⁵ Fizeau, *Pogg. Ann.*, **128**, 584 (1866).

⁶ Fizeau, *Ibid.*, **128**, 585 (1866).

⁷ H. Sainte-Claire Deville, *Ibid.* **132**, 307 (1867).

very many cases the volume of the product, taken at the temperature t° , which the act of combination produces is very little different from the sum of the volumes of the components" (taken at the original temperature). If, then, the silver iodide contracted in the usual way on cooling to the original temperature, the volume of the silver iodide produced at the original temperature would be less than the sum of the volumes of the elements before combination. But, as a matter of fact, the volume of the silver iodide is greater than the sum of the volumes of the elements. From these premises Deville reasons that silver iodide must expand when cooling. Deville does not give the slightest evidence in support of the remarkable statement quoted above, which serves as the first premise.

T. W. Richards,¹ in a series of papers on the "Significance of Changing Atomic Volume," has shown that there is no evidence in support of the old assumption that the atoms are incompressible. This assumption was originally made to simplify the mathematical treatment of molecular physics. He gives strong reasons for believing that, in liquids and solids, the atoms and molecules are closely packed and in actual contact and that the "free space" has usually been greatly overestimated.² He then proposes the hypothesis that the atoms are compressible, *i. e.*, subject to changes in volume and shape under the influence of either external pressure or the pressure exerted by the mutual attraction of the molecules (cohesion), or by the attraction of the atoms within the molecule (chemical affinity). If the atoms are closely packed, such changes in the volume of the atoms would produce changes in the volume of the substance. Richards has shown clearly that the volumes of substances are influenced by these forces. He has also deduced many other consequences of this hypothesis of compressible atoms and shown that they agree very well with the facts.

The hypothesis of compressible atoms furnishes a new means of searching for an explanation of negative coefficients of expansion, which the old hypothesis of the incompressible atom has been unable to explain. The common and accepted explanation of the increase in volume which nearly all substances undergo when heated is that the increased violence of the molecular vibrations produces an increased intramolecular space. This is clearly the case in the expansion of a gas by rise in temperature under constant pressure and the same conception has been applied to liquids and solids. While this is probably one of the causes of a change in volume with rising temperature, it can be deduced from the hypothesis

¹ Richards, *Proc. Am. Acad.*, 37, 3 (1901); 37, 399 (1902); 38, 293 (1902); 39, 581 (1904).

² See *Proc. Am. Acad.*, 37, 407-9 for the first statement of this conclusion, although all the papers referred to above should be consulted for a complete statement of the evidence which has been published.

of compressible atoms that there must be at least two other influences at work.

It is well known that surface tension decreases with rise in temperature and since surface tension and cohesion are very closely connected we can conclude that cohesion also decreases with rise in temperature. Since Richards has proven that cohesion has a marked influence on volume, it follows that at least a part of the expansion of substances with rise in temperature is due to decrease in the cohesion.

If atoms are really compressible and if the volume of the molecules is influenced by the pressure of affinity, as Richards has suggested, it follows that any change in the affinity or attraction from any cause will be accompanied by a change in volume. Since the affinities of the elements for each other change with changes in temperature, there must be still a third cause for changes in the volume of substances with changes of temperature. Since in some cases the affinity is increased and in others decreased by rising temperature, the effect would have opposite signs in different cases.

In gases the effect of variations in cohesion and affinity (except in a few cases where dissociation takes place) is negligible in comparison with the effect of variations in the molecular velocity, which explains the fact that the coefficients of expansion of all gases are very nearly the same. In liquids and solids, on the other hand, the three influences are superposed on one another, producing the great differences between the coefficients of expansion of various liquids and solids. Furthermore, since the variations in molecular vibration and in cohesion probably always tend to produce a positive coefficient of expansion and since usually the effect of changes in cohesion on the volume is greater than the effect of variations in affinity, it is only in rare cases that the increase in affinity would be sufficient to overcome the two opposing tendencies and produce a negative coefficient of expansion.

This hypothetical analysis of the coefficient of expansion based on the hypothesis of compressible atoms is thus consistent with the great uniformity of the coefficients of expansion of gases and the differences between the coefficients of various liquids and solids and also with the very rare occurrence of a negative coefficient of expansion.

In order to test this hypothesis an attempt will be made to apply it to the specific case of silver iodide. Since the free energy of formation furnishes the best clue as to the intensity of chemical affinity we must first calculate the free energy of formation of silver iodide. For comparison the cases of silver chloride and bromide will also be considered.

The free energy of formation of silver chloride is equal to the energy output of a cell consisting of a silver electrode and chlorine electrode in a solution of potassium chloride which is saturated with silver chloride.

When the current passes through this cell silver chloride is produced reversibly without any other work being done. Cells of exactly this type have not actually been measured, but there are sufficient data available to make it possible to calculate the potential of such a cell producing silver chloride, silver bromide or silver iodide.¹

Goodwin² has measured the potential of a cell consisting of a silver electrode in a 0.1 normal solution of potassium chloride saturated with silver chloride against a silver electrode in a 0.1 normal solution of silver nitrate.

(1) Ag, KCl 0.1*n* AgCl sat., KNO₃ 0.1*n*, AgNO₃ 0.1*n*, Ag: E = +0.449.

For the potential of the silver electrode I accept the result obtained by Lewis,³ who has found that the potential of the silver electrode in tenth-normal silver nitrate against the normal calomel electrode (N.E.) is -0.451 volt.

(2) Ag, AgNO₃ 0.1*n*, N. E.: E = -0.451.

Erich Müller⁴ found that the cell composed of hydrogen and chlorine, both at atmospheric pressure, with normal hydrochloric acid as the electrolyte, gives a potential of 1.366. He then calculated the potential of these electrodes against a solution normal with respect to the ions, assuming that the normal acid is 78 per cent. dissociated, obtaining 1.353.

(3) H₂ (1 atm.) H⁺*n*, Cl⁻*n*, Cl₂ (1 atm.): E = +1.353.

Wilsmore⁵ has shown that

(4) N.E., H⁺*n*, H₂ (1 atm.): E = -0.283.

The potential of the following cell has been calculated by the aid of the Nernst formula on the assumption that tenth-normal potassium chloride is 86 per cent. dissociated.

(5) Cl₂ (1 atm.) Cl⁻*n*, KCl 0.1*n*, Cl₂ (1 atm.): E = RT/*n*F log C₁/C₂ = -0.0591 log 0.081 = +0.063.

In order that the result may be more nearly comparable with the free energy of formation of silver bromide and iodide, we will calculate the free energy of formation of silver chloride from liquid chlorine and silver. Since according to Knietsch⁶ liquid chlorine at 25° is in equilibrium with chlorine gas at 7.63 atm. the free energy of formation from liquid chlorine would be the same as from chlorine gas at 7.63 atm. Hence

¹ All the data to be used refer to 25° unless otherwise stated. E is given the positive sign when the positive current tends to pass within the cell from the first electrode to the second. E will be given exclusive of any potentials between the electrolytes of the cell.

² Goodwin, *Z. physik. Chem.*, 13, 645 (1894). In this and in other data quoted from Goodwin, a correction of -0.001 volt has been applied on account of the potential at the liquid-liquid junctions.

³ Lewis, *THIS JOURNAL*, 28, 168 (1906).

⁴ Müller, *Z. physik. Chem.*, 40, 159 (1902).

⁵ Wilsmore, *Ibid.*, 35, 291 (1900).

⁶ Knietsch, *Ann.*, 259, 124 (1890).

(6) Cl_2 (1 atm.), KCl 0.1*n*, Cl_2 (liquid): $E = 0.0591/2 \log 7.63/1 = +0.026$.

Adding these six equations we have

(7) Ag , KCl 0.1*n*, AgCl sat., Cl_2 (liquid): $E = 1.157$ volt.

The free energy₃₀ of formation of silver chloride at 25° is $A = nEF = 1.157 \times 96.58 = 111.7$ kilojoules.

Goodwin has also measured the cell

(8) Ag , KCl 0.05*n*, AgCl sat., KNO_3 0.05*n*, AgNO_3 0.05*n*, Ag : $E = +0.418$.

Then assuming that 0.05*n* silver nitrate is 86 per cent. dissociated and 0.1*n* silver nitrate is 81.5 per cent. dissociated we have

(9) Ag , AgNO_3 0.05*n*, AgNO_3 0.1*n*, Ag : $E = 0.0591 \log 0.0815/0.0429 = +0.016$.

Instead of equation (5) we use

(10) Cl_2 (1 atm.), Cl^- *n*, KCl 0.05*n*, Cl_2 : $E = 0.0591 \log 0.0445 = 0.080$.

By adding equations (8), (9), (2), (3), (4), (6), and (10), we obtain

(11) Ag , KCl 0.05*n*, AgCl sat., Cl (liquid): $E = 1.159$ volt and hence the free energy of formation of silver chloride is $1.159 \times 96.58 = 111.9$ kilojoules. The mean value is 111.8 kilojoules.

Goodwin¹ has found

(12) Ag , KBr 0.1*n*, AgBr sat., KNO_3 0.1*n*, AgNO_3 0.1*n*, Ag : $E = +0.598$.

Sammet's² measurements of the potential of a molal solution of free bromine against a normal solution of bromide ion against the normal calomel electrode give the result

$N. E.$, Br^- *n*, Br_2 (molal): $E = +0.807$.

The very similar measurements of Boericke³ give a potential of 0.810 for the same cell. The mean is accepted:

(13) $N. E.$, Br^- *n*, Br_2 (molal): $E = +0.808$.

Boericke found that the concentration of free bromine in solution in equilibrium with liquid bromine is 0.2125 mol. per liter. The potential of liquid bromine against normal bromide ions can therefore be calculated with the aid of the Nernst formula:

(14) Br_2 (molal), Br^- *n*, Br_2 (0.2125 molal): $E = 0.0591/2 \log 0.2125/1 = -0.020$.

Assuming that 0.1*n* potassium bromide is 86 per cent. dissociated we have

(15) Br (liquid), Br^- *n*, 0.1*n* KBr , Br (liquid): $E = -0.0591 \log 0.0861 = +0.063$.

By adding equations (10), (2), (13), (14) and (15) we obtain

(16) Ag , KBr 0.1*n*, AgBr sat., Br (liquid): $E = +0.998$.

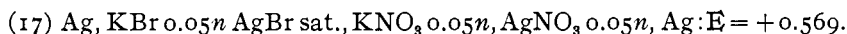
Hence the free energy of formation of silver bromide is $0.998 \times 96.58 = 96.4$ kilojoules.

¹ Goodwin, *Loc. cit.*

² Sammet, *Z. physik. Chem.*, 53, 681 (1905).

³ Boericke, *Z. Elektrochemie*, 11, 57 (1905).

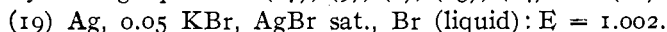
Goodwin also measured the cell



Assuming that 0.05*n* potassium bromide is 89 per cent. dissociated, we have



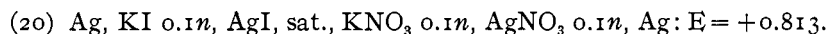
By adding equations (17), (9), (2), (13), (14) and (18) we have



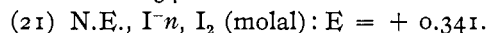
Hence the free energy of formation of silver bromide is $1.002 \times 96.58 = 96.8$ kilojoules.

The mean of these two results given is 96.6 kilojoules, as the free energy of formation of silver bromide at 25°.

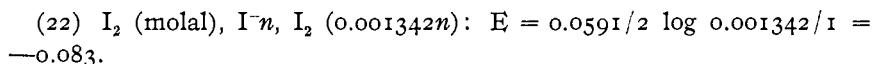
Goodwin has measured the cell



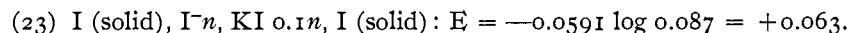
The measurements of Sammet¹ agree with the previous measurements of Crotogino² in showing that the potential of the cell consisting of the normal calomel electrode against molal free iodine in solution and normal iodide ion is 0.341 volt.



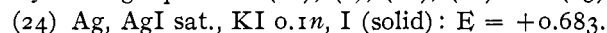
According to Noyes and Seidensticker,³ the concentration of free iodine in solution in equilibrium with solid iodine is 0.001342 mol. per liter. The potential of solid iodine against normal iodide ion can, therefore, be calculated



Assuming that 0.1*n* potassium iodide is 87 per cent. dissociated, we have

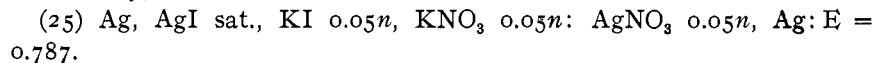


By adding equations (20), (2), (21), (22) and (23) we have

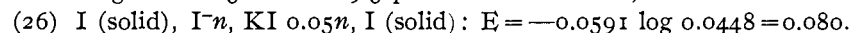


Hence the free energy is $0.683 \times 96.58 = 66.0$ kilojoules.

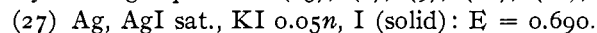
Similarly, Goodwin has measured the cell



Assuming that 0.05*n* KI is 89.5 per cent. dissociated, we have



By adding equations (25), (2), (9), (21), (22), and (26), we obtain



Hence the free energy is $0.690 \times 96.58 = 66.6$ kilojoules.

¹ Sammet, *Z. physik. Chem.*, 53, 674 (1905).

² Crotogino, *Z. anorg. Chem.*, 24, 250 (1900).

³ Noyes and Seidensticker, *Z. physik. Chem.*, 27, 357 (1898).

Taking the mean we have 66.3 kilojoules as the free energy of formation of silver iodide from silver and solid iodine.

Goodwin calculated from his potential measurements, the solubility of the three silver salts. Thiel,¹ who measured the solubility of these salts by a different method, obtained results which agree essentially with those of Goodwin and we may, therefore, consider them confirmation of Goodwin's potential measurements.

For the heat of formation of the three silver halogen salts, I accept the results of Thomsen.² In the case of silver chloride, the heat of vaporization of chlorine as determined by Knietzsch³ (9.3 kilojoules) must be subtracted. These values are probably less reliable than the values of free energy which have already been calculated.

We are now able to calculate the change in the free energy with the temperature by the use of the well-known expression

$$A - U = T dA/dT.$$

The following table gives the free energy (A) and the heat of formation (U) and the change in the free energy with the temperature expressed in kilojoules per degree or kilomayers (dA/dT) and the cubic coefficient of expansion (3α).

	A.	U.	dA/dT .	3α .
AgCl.....	111.8	114	-0.006	+0.0000988
AgBr.....	96.6	95	+0.005	+0.0001041
AgI.....	66.3	58	+0.028	-0.0000041

Although little accuracy can be claimed for these temperature coefficients and in the cases of silver chloride and bromide, the sign may not be significant, there can be no doubt that the sign is significant in the case of silver iodide.

We may, therefore, conclude that the attraction of silver and iodine for each other increases with rise in temperature and that in other cases the effect of temperature on the attraction is much less.

A study of this table confirms, in a striking manner, the deduction from Richards' hypothesis of compressible atoms that an increase in the attraction (or affinity) with temperature must tend to decrease the coefficient of expansion and, in extreme cases, even produce a negative coefficient of expansion. In all three cases, according to the hypothesis which has been proposed, there is a tendency toward expansion due to an increase in the intramolecular space and to a decrease in the cohesion. In the case of silver iodide, the increase in the attraction of the silver

¹ Thiel, *Z. anorg. Chem.*, **24**, 57 (1900).

² Thomsen, *Thermochemische Untersuchungen*, III, 380. The changes in the heat capacities are so small that the differences between the heats of formation at 18° and 25° are within the limit of experimental error and therefore we can use Thomsen's data without applying a correction.

³ Knietzsch, *Z. Elektrochemie*, **9**, 847 (1903).

and the iodine for each other, according to this hypothesis, produces a contraction more than sufficient to overcome the other two influences.

The fact that the coefficient of expansion of silver bromide is not intermediate between that of the chloride and iodide shows that great caution must be used in drawing conclusions from these data. However, this unexpectedly large value of the coefficient of expansion of silver bromide is not inexplicable. We can infer from the smaller surface tension,¹ the greater volatility² and the greater compressibility³ that the cohesion of silver bromide is less than the cohesion of silver chloride. It is, therefore, to be expected that variations in the violence of the molecular vibrations and in the surface tension would have a greater effect on the volume in the case of silver bromide than in the case of silver chloride. The fact that the coefficients of expansion are very nearly the same in spite of these influences indicates that in the chloride there is some other cause of expansion not present in the bromide, namely, the decrease in the affinity with rising temperature.

Fizeau found that a hexagonal crystal of silver iodide has a negative linear coefficient of expansion in the direction of the principal axis and a much smaller positive coefficient at right angles to the principal axis. These facts can be explained in a simple manner with the aid of the hypothesis of compressible atoms. If we assume that in the crystals the atoms are so arranged that the affinity acts in a direction parallel to the principal axis, an increase in the affinity with rising temperature would tend to produce a contraction in this direction accompanied by a small bulging in a direction at right angles to the line of compression. It seems to me that this explanation of the facts is more rational than to postulate a more fundamental change in crystal form and molecular arrangement, since such changes do not occur reversibly over a wide range of temperature.

Of course it can not be claimed that a single case is sufficient to prove a relation between the temperature coefficient of the free energy and the coefficient of expansion. I have as yet found no other case for which the data are sufficient to make a quantitative test of the relation possible. A little qualitative evidence which supports the hypothesis may be added. The most conspicuous examples of substances with a comparatively small coefficient of expansion are amorphous quartz, diamond, copper oxide, glass, porcelain, platinum and silicon. Although it is not possible to calculate the temperature coefficient of the free energy of these substances, we can judge from the comparative stability of these substances at high temperatures that the affinity does not decrease as rapidly as usual with

¹ Quincke, *Pogg. Ann.*, 138, 141 (1869).

² Baxter, *THIS JOURNAL*, 27, 885 (1905).

³ T. W. Richards and Grinnell Jones, see preceding paper.

the temperature. The coefficient of expansion of arsenic is quite small. Although arsenic is volatile at comparatively low temperatures, the vapor of arsenic has four atoms in each molecule, whereas the molecules of most metals in the state of vapor are monatomic. Arsenic, therefore, is not a real exception to the requirements of the hypothesis, since the affinity is not overcome by a rise in temperature but only the cohesion.

The negative coefficient of expansion of water between 0° and 4° C. is undoubtedly due to a progressive change of associated into simple molecules.¹ The case of bismuth is probably very similar. The negative coefficient of expansion and the other anomalous properties of nickel-steel are considered by Guillaume² to be due to a reversible change of the state of the iron.

Conversely, the solids with the largest coefficients of expansion are certain hydrated salts $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, yellow phosphorus, ammonium chloride, and a great number of organic compounds, urea, naphthalene, rubber, etc. These substances are unstable at slightly elevated temperatures as required by the hypothesis which has been proposed. The large coefficient of expansion of phosphorus is probably due to its low cohesion.

Summary.

From Richards' hypothesis of compressible atoms it is deduced that changes in the volume of substances with rise in temperature must be made up of three components: 1st, an increase in the "intramolecular" space (or at least the space between the centres of the molecules) on account of the increased violence of the molecular vibrations; 2nd, an increase in volume of the molecules due to a decrease in cohesion; 3rd, a change in volume of the molecules due to a change in the chemical attraction of the atoms for each other.

It is shown that the affinity of silver and iodine increases with rising temperature, a circumstance which, according to the hypothesis proposed, would tend to produce a decrease in volume. As a matter of fact, silver iodide contracts when heated.

It is pointed out that, in general, substances with a low coefficient of expansion are stable at high temperatures and conversely, substances with a high coefficient of expansion are unstable.

Additional evidence is furnished in favor of Richards' interesting and fruitful hypothesis of compressible atoms.

THE UNIVERSITY OF ILLINOIS, URBANA, ILL.

¹ Richards, *Proc. Am. Acad.*, 39, 594 (1904), gives an explanation of this phenomena based on his hypothesis of compressible atoms.

² Guillaume, *C. R.*, 136, 1638 (1903).