MOLECULAR ATTRACTION. X. A REPLY TO CRITICISM

BY J. E. MILLS

The primary object of this paper is to reply to an article by Dr. A. P. Mathews¹ containing a discussion of the author's views and work on molecular attraction.

The articles which I have published² on molecular attraction and related subjects were written as the work proceeded. These papers are now being revised but the revised work is not suitable for publication in a journal. Therefore a reply here.

First. The Correctness of the Fundamental Equation,

$$1. \quad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant, or } \lambda = \mu' (\sqrt[3]{d} - \sqrt[3]{D}),$$

has been brought into question.

Here L is the heat of vaporization of 1 gram of the liquid, E_E is the energy spent in overcoming the external pressure as the liquid expands to the volume of the saturated vapor. $L - E_E$ is therefore the so-called internal heat of vaporization and is called λ . d and D are the densities of the liquid and saturated vapor, respectively, at the temperature of the vaporization. The constant given by the equation I have called μ' .

A summary of the evidence is given in the papers cited, particularly Jour. Phys. Chem., 13, 512 (1909) and Phil.

¹ Jour. Phys. Chem., 17, 520 (1913).

² Ibid., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909); 15, 417 (1911); Jour. Am. Chem. Soc. 31, 1099 (1909); Phil. Mag., Oct. (1910); July (1911); Oct. (1912); Trans. Am. Electrochem. Soc., 14, 35 (1908); Chem. News, 102, 77 (1910); and related papers, Mills and MacRae: Jour. Am. Chem. Soc., 32, 1162 (1910); Jour. Phys. Chem., 14, 797 (1910); 15, 54 (1911).

Mag., July (1911) and Oct. (1912). Mathews,¹ after stating that the equation gives a constant except in the neighborhood of the critical temperature, says that I "ascribed the fall of the constant near the critical temperature to the inaccuracy of the data." This statement is misleading. *What I did was to prove beyond any question that the Biot formula used to calculate the $\frac{dP}{dT}$ necessary in calculating the latent heat did not correctly represent the observed data, and that the deviations were practically always in a definite direction causing the constant given by the equation to be too low near the critical temperature. This fact must be admitted by anyone who attempts to make the Biot formula fit the observations. It simply will not fit near the critical temperature.*

Now for the three substances where more direct observations of the $\frac{dP}{dT}$ were obtainable at the critical temperature, equation 1 showed agreement to within the limit of error of the measurements. Without going here into evidence formerly published in part, and later to be published in full, I will only say that there is no evidence to show, and no reason to suppose, that equation 1 is not exactly correct at the critical temperature for non-associated substances. There is, moreover, strong evidence to show that it is certainly correct, even at the critical temperature, to within 2 percent for non-associated substances.

The observations of Young and his co-workers are remarkably correct and I have often expressed my admiration of their work. The fact that these observations permit of a universal accuracy in the constant only to within 2 percent

¹ Dr. Mathews writes, "If you have read my last paper (Jour. Phys. Chem., Oct., 1913) you will have noticed that I there accept your equation,

$\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, as probably correct clear to the critical temperature.

You think that Biot's formula gives incorrect results close to the critical temperature, and in this I think you are right; at least I wish that you may be right. Were I rewriting my paper which you answer I should change this part of the paper, which after all was a very subordinate point," etc.

is due largely, as often explained before, to an enormous multiplication of error in the necessary calculations. Yet in spite of this multiplication of error only 17 values of the constant out of 431 for 25 substances, diverge from the average value (except at 0° C and near the critical temperature for explained causes) by more than 1.5 percent.

The statement made by Mathews¹ that "in ether and ethyl acetate there is a pretty steady fall in the constant through-out" is correct as regards ethyl acetate and wrong as regards ether.² I quote further from Mathews:³ "The apparently negative value of b_v is found closer to the critical temperature in the esters which are known to associate slightly." I also believe that there is slight association in the esters and that the constant of equation 1 for them should decrease slightly with the temperature. But after allowing for the known sources of error and considering the esters as a whole such decrease must be slight, probably not more than 2 percent, and therefore within, or so nearly within, the error of the observations as used, as to render a certain statement impossible at this time. The best evidence upon this point comes from a comparison of equation 1 with Dieterici's equation at the critical temperature,

$$2. \quad \lambda = CRT \ln \frac{d}{D}.$$

For the esters there is a divergence shown on comparison of the two equations at the critical temperature ranging from 2.2 percent with methyl formate, to 4.5 percent with propyl acetate. Probably at least half of this divergence is due to Dieterici's equation which is also affected by molecular association, and some of it seems certainly due to another known source of error.

Second. Van der Waals' Equation.—Much of Mathews' article consists in a more or less direct judgment of the fundamental equation 1 and derived conclusions from the stand-

¹ Loc. cit., p. 524.

² Jour. Phys. Chem., 13, 518 (1909).

³ Loc. cit., p. 526.

point of van der Waals' equation and views. Van der Waals' equation is not correct, and it is not only not correct, but it is nowhere near correct when viewed as a whole. Dieterici expresses exactly my own attitude toward van der Waals' equation when he says,¹ "Nach der Nobelpreisrede² von van der Waals ist es nicht mehr nötig, auf die schwachen Punkte in Studium dieser Zustandsgleichung aufmerksam zu machen; viel näher liegt es, die Frage, die van der Waals selbst aufwirft, 'gibt es einen besseren Weg?' zu verfolgen." Mathews himself confesses to the situation when he says, on page 530, "As a matter of fact $L - E_E / \left(\frac{1}{V_I} - \frac{1}{V_v} \right)$ (from van der Waals' equation, J. E. M.) *does not equal a constant*, hence our assumption must be wrong. But if the assumption is wrong then the fact that $L - E_E / \left(\frac{1}{V_I^{1/3}} - \frac{1}{V_v^{1/3}} \right)$ *happens to equal a constant* cannot be adduced as evidence that molecules attract inversely as the square of the distance." (Italics mine, J. E. M.) I will not, therefore, follow Mathews' discussion in detail. My own equation and views could not be correct if they agreed with van der Waals' equation in its usual form, and I pointed out, at the end of my first paper in 1902, "that the law of attraction assumed does not lead to the equation of van der Waals'." When any one has succeeded in modifying van der Waals' equation so as to make it correctly represent the facts, then perhaps my equation and views will not be found irreconcilable.

Third. The fundamental equation not empirical.—Mathews, in several places, refers to equation 1 as an "empirical relationship." A little history will perhaps be pardoned as it will serve to bring out several facts clearly.

The fundamental equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, was not derived as an empirical equation in the usual sense of that

¹ Drude's Ann., 35, 220 (1911).

² Van der Waals: "Die Zustandsgleichung," Leipzig Akadem. Verlagsges. (1911).

term. When an undergraduate in college on working out a problem in calculus involving the velocity, and hence the energy, of a cannon ball shot upwards from the earth, the idea occurred to me that possibly the much desired law of molecular attraction could be found by a similar process. I asked two of my instructors at that time, without stating the reason for the question, if there "was any reason for supposing the energy *per se* of the molecules of a liquid and its vapor to be the same, or any method for arriving at the energy *per se* of the molecules of the liquid?" Of course the information desired was unknown. But this first step will surely make clear the fact that I could never later have overlooked the fundamental importance of the question as to the relative energy of the liquid and vapor molecules in obtaining the law of attraction. (See later.) It was perhaps five years afterwards when I obtained some idea as to the correct answer to the question above stated and only then did I even attempt the next step. Meanwhile, I was interested in the cause of gravitational and chemical attraction, and it is interesting to myself at least, that during that time I recorded in an old note book on the subject a suspicion as to the correctness of the *numerator factor* of Newton's law of gravitation.

The next step in the discovery of this "empirical equation" came when I recognized the fact that Watterson's equation,

$$3. \quad \frac{\sigma_p}{\sigma_v} = \gamma = \frac{E_K + E_I + E_E}{E_K + E_I},$$

could be combined with the equations derived also from the kinetic theory and facts of gases

$$4. \quad E_K = \frac{3}{2} R,$$

$$5. \quad E_E = R,$$

for a difference in temperature of one degree, and written,

$$\gamma = \frac{\frac{3}{2} R + E_I + R}{\frac{3}{2} R + E_I} = \frac{\frac{5}{3} R + E_I}{\frac{3}{2} R + E_I}, \text{ or}$$

$$6. \quad E_I = \frac{R}{2} \frac{5 - 3\gamma}{\gamma - 1} \text{ or from 4}$$

$$7. \quad E_I = \frac{\frac{5}{3} - \gamma}{\gamma - 1} \cdot E_K.$$

In these equations σ_p and σ_v are the specific heat at constant pressure and constant volume of a gas. E_K is the kinetic energy of the molecules, E_I is the internal energy of the molecules (best defined from the equation $\sigma_v = E_K + E_I$) and E_E is the energy spent in overcoming the external pressure of the gas during expansion.

In words equation 7 means that for a perfect gas *the internal energy of the gas is proportional to the kinetic energy of the gas.*

Now I believe, and there is reason for the belief, that in the molecules of a liquid similarly, the internal energy E_I was proportional to the kinetic translational energy E_K .

The third step came practically at the same time when I recognized that the fact that cane sugar molecules dissolved in water caused an osmotic pressure similar to a gas pressure, indicated that the cane sugar molecules were behaving like gaseous molecules in part at least. This indicated a translational energy similar to the gas translational energy. The water molecules must have the same translational energy as the dissolved cane sugar molecules, a conclusion already drawn by Ostwald. The internal energy of the water molecules was, from equation 7, probably proportional to their translational energy. In short, it seemed that the molecular energy *per se* of molecules of a liquid and its vapor at the same temperature must be the same.

The same night that I reached this conclusion—the answer to my old question—I attacked the problem of molecular attraction, paralleling the cannon ball problem, and reached the fundamental equation essentially as stated in equation 1, without one particle of experimental evidence. The first experimental evidence in its favor was obtained that same night.

In obtaining the equation I assumed that the molecular attraction varied inversely as the square of the distance apart of the molecules. This seemed to me the most probable assumption for several reasons—primarily perhaps because the other attractive forces whose laws were known, magnetic,

electrical, and gravitational, varied in that way, and I suspected a close relationship among these forces. But also because any emanation or disturbance proceeding from a center seemed to me necessarily to be compelled to have an inverse square law of distance as *one of its factors*. Because I did not know the other factors, or the influence of temperature, I did not feel at all certain that the deduced equation would prove true, and intended to try other laws of force and modifications if the equation failed. *The equation proved true.* Moreover it is the only equation concerning molecular attraction that ever has proved true. It is rather important, therefore, to look carefully into the reasoning by which it was deduced before rejecting that reasoning.

Fourth. The role of mass in molecular attraction.—A little more history will help to throw light upon the equation. When sufficient experimental proof had accumulated to convince me that the equation was true, I set eagerly to work to extend the results in three directions. First,¹ I investigated the attraction itself, rather expecting the molecular attraction to behave as does the gravitational attraction as regards mass, having temporarily overlooked my suspicion above referred to of the gravitational law. I readily found on trying to compare the attractions of, let us say, oxygen molecules with carbon dioxide molecules (I have forgotten the gases actually used, I compared several I think) that these attractions did not vary as the masses of the molecules. Somewhat surprised, I contented myself with the statement made at the end of the first paper, "*The molecular attraction appears to resemble the attraction of gravitation in that it varies inversely as the square of the distance apart of the attracting molecules and does not vary with the temperature. It differs from the attraction of gravity in being determined primarily by the construction of the molecule and not by its mass.*"

I never myself forgot that statement, nor intended to

¹ The other investigations dealt with specific heats and the equation of state.

change it. Some subsequent rather carelessly worded statements of mine mislead others. Thus it will be seen that the first idea that I obtained as to the true relation of mass in molecular attraction had nothing whatever to do with the correctness of the equation. Mathews says¹ "That Mills' expression, $\mu' \left(\frac{1}{V_1^{1/3}} - \frac{1}{V_2^{1/3}} \right)$, does not represent the work done in overcoming molecular cohesion may be shown, also, if the attempt is made to deduce the formula on this basis, assuming the attraction to vary inversely as the square of the distance. A value is obtained for μ' widely different from that found. Mills realized this difficulty and tried to avoid it by assuming that the law that matter attracted itself as the product of the masses was incorrect." This statement hardly expresses the situation correctly and the facts cannot be disposed of so briefly.

In the sixth paper² I corrected an error made in the derivation of the fundamental equation from the assumed law of attraction,

$$8. \quad f = \frac{\mu^2 m^2}{s^2},$$

obtaining as the complete expression,

$$9. \quad \frac{M(L - E_E)}{\sqrt[3]{d} - \sqrt[3]{D}} = \frac{M^2 \mu^2 C}{n^2 \sqrt[3]{m}} = m^{2/3} \mu^2 C,$$

where n is the number of molecules in a gram, m is the molecular weight, $nm = M$, and C was a constant only when the number of molecules was constant. For a constant mass the equation reduces to the form previously given in this paper,

$$1. \quad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

Now one has a perfect right to start with a constant mass and to continue the investigation with a constant mass. By so doing one will obtain for μ' exactly the values given as proof of equation 1. The statement of Mathews that by using the

¹ Loc. cit., p. 530.

² Jour. Phys. Chem., 11, 132 (1907).

gravitational law of force, equation 8, "a value is obtained for μ' widely different from that found" is therefore misleading. The gravitational law of attraction produces equation 1 by the *strictest* mathematics if we deal always with the same mass originally used on starting the investigation. To make this point doubly sure I used¹ Helmholtz's equation for the heat given out by the contraction of the sun under gravitational attraction and showed that this equation, obtained by a totally different mathematical treatment, also reduced to the form of equation 1 for a constant mass. But, *vary the mass and the equation shows that the heat given out should vary as the 5/3 power of the mass.* Now we know as a matter of fact that the heat of vaporization of 2 grams of liquid is just twice the heat of vaporization of one gram of liquid and not $2^{5/3}$ times as much.

In other words, the important fact is that the gravitational law of attraction applied to molecular attraction gives a true equation if we keep the mass investigated constant, which we have a perfect right to do; and gives a false equation if we allow the mass under investigation to vary, which we have an equal right to do. I would write these words in capitals if that would serve better to focus attention upon the fact they set forth.

It seems so clear to me, without mathematics, that, if a variation in the *mass* of liquid taken causes the difference above mentioned, the trouble is due to the numerator factor of the above assumed gravitational law of force (the only part concerned with mass), and not to the denominator of the law (which is concerned with distance apart only), that I cannot realize where the doubt expressed by others can creep in. Mathematically, it is easy to show that an assumed law of molecular force,

$$10. \quad f = \frac{\mu m}{s^2},$$

will give an equation,

$$11. \quad M\lambda = M\mu'(3\sqrt{d} - 3\sqrt{D}),$$

equally true for a constant or for a variable mass.

¹ Jour. Phys. Chem., 11, 147 (1907).

My assumption that matter (molecules) did not attract as the product of their masses was made for the compelling reasons set forth above, and not as alleged by Mathews to account for variations in μ' . I now realize that this conclusion was foreshadowed by the investigation so briefly reported in the first paper as indicating that "molecular attraction is determined primarily by the construction of the molecule and not by its mass," and that it receives further support from many facts dimly recognized even before the fundamental equation was discovered.

Fifth. Is the internal heat of vaporization spent solely in overcoming molecular attractive forces?—A rough copy of my first paper contained a good deal about specific heats. Before publishing it I discovered that my ideas regarding the specific heats were not in accord with the facts. I therefore eliminated from the paper all discussion of specific heat and contented myself with the statement made at the end of that paper, "The argument pursued might lead one to suspect that the entire increase of the specific heat of a liquid over that of a gas at constant volume must be spent in increasing the distance apart of the molecules. Investigation shows that this is not always, if it is ever the case, and herein possibly lies the true cause of the discrepancies from the theory." The true cause of the discrepancies referred to were later in all cases discovered and had nothing to do with the specific heat problem. A reviewer of the first paper criticised it for not pointing out certain simple specific heat relations which should follow. The truth is that the simple specific heat relations that I had expected did not follow. I did not know, at the time of publication of the first paper, that specific heat relations could be shown to contradict the belief that the energy of the molecules of a liquid and its vapor were the same, but I discovered the fact later and in the sixth paper (1907) stated,¹ "As regards now the first step—the equality of the energy *per se* of a molecule of a liquid and

¹ Loc. cit., p. 156.

of a molecule of its vapor—we have already stated in outline the facts which lead us to that belief. This first step is the most fundamental and important step in our work and is the most open to doubt. The fact that using this belief as a basis we derived an equation that appears to be true, is perhaps again the best evidence that the belief expresses, at least partly, the truth. But only in part, for in attempting to derive a direct method for testing this belief we find that it will require some modification. An account of this work could not be introduced within the limits of this paper and we hope shortly to publish this investigation in a separate article. Recognizing the doubt, we would state that any errors introduced by our statement have undoubtedly canceled, since one is certainly able to calculate the energy given out by the contraction of a vapor into a liquid from the same formula used to calculate the energy given out by the contraction of the sun." Surely this statement is evidence sufficient to show that after I recognized the fact that the energy *per se* of the molecules of a liquid and its vapor were not the same, the fact was not concealed. And I will repeat again that Mathews is exactly right in his belief that the energy *per se* of the molecules of liquid and vapor are not the same. I reached this conclusion by the simple process of adding up all of the energy added to a substance from the absolute zero to its condition as liquid. That is, I summed up the specific heat energy added and the latent heat of fusion. Then, allowing for the energy necessary to produce the slight expansion of the solid and liquid (this can be done either from my own theory or thermodynamically), I compared the remainder with the energy which the substance would have as a perfect gas at the given temperature. The result shows that the molecules of the liquid have *per se* far more energy than the molecules of the gas are popularly supposed to possess. So very much more that it was fruitless to consider the difference as by any possibility due to the experimental uncertainties which are usually large. By this time (probably 1906) I had accumulated so much evidence as to the truth of the fundamental equation

that I myself placed absolute confidence in its correctness. Moreover, the argument quoted above, involving the osmotic pressure of cane sugar molecules, was even stronger than before, the excellent work of Morse and his co-workers having begun to appear. I contented myself therefore with the paragraph already quoted from the sixth paper and set about a study of the situation.

An enormous amount of data on specific heats was collected, sifted, and studied. I thought at first that the trouble might lie with our ideas of temperature (which do require clarification). Then since the facts apparently indicated that always when particles were closer together they, in some way, retained or possessed more energy, I considered the possibility of a change of inertia (mass). This supposition is not so easy to reject in view of the facts as one might suppose. I was aware of T. W. Richards' work upon the compressibility of the molecules, and the possibility that molecular expansion would require energy. For several years nothing was published on the subject because I could not even satisfy myself. Finally light began to dawn upon the situation and I recognized that *the gravitational law of attraction necessitated that whenever two bodies came together from an infinite distance and formed a stable system of moving bodies that these bodies retain exactly as much energy as they gave out*. The law of gravitation necessitates the *retention of energy* in a stable system of moving particles just as much as it *necessitates the giving out of energy* when the stable system is formed.

When I did recognize the above fact I found it very much more difficult than one would suppose (since the problem of two bodies under gravitational attraction had been completely solved) to give the exact mathematical proof of the statement finally made,¹ "*The energy given out by any two bodies originally at rest at an infinite distance apart in forming any stable configuration (circular, elliptical, or limited linear orbit) under the action of gravitational attraction is equal to the kinetic*

¹ Phil. Mag., July, 1911, p. 105. This paper also contains the proof of the statement.

energy which they retain, and is, for either body, inversely proportional to its mean distance from their common center of mass."

In the paper referred to, I was unable to extend this conclusion to n particles as a mathematical proposition. During the last summer I have extended the proof to n particles and shown that this proof holds for the molecular law of attraction. This work has not yet been published.

Mathews has this to say¹ regarding this phase of my work, "While Mills states, in a recent paper, that not all the internal heat may be used in doing this work, and attempts to show that this is not incompatible with this conclusion, the conclusion nevertheless depends on the assumption that it is so used and that there is no change in the internal energy of the molecules on passing from the liquid to the vapor. It is clear that if this premise be not true, then the conclusion does not follow." "This premise I believe to be certainly erroneous."

The premise certainly is erroneous as I pointed out six years ago in the quotation given above. *It is in fact a contradiction of the law of attraction assumed.* The law of attraction assumed compels the freely moving molecules of the liquid to retain a given amount of orbital energy absolutely as much as it compels energy to be given out on the approach of the molecules. When the freedom of motion of the liquid molecules is checked, then some of this orbital energy which they retain is given out as latent heat of fusion. Some more of it is probably given out as the temperature is lowered. I doubt if all of it ever is surrendered even at the absolute zero. (See later.)

The moon is obliged to retain a given amount of energy as orbital energy if it is to continue in its orbit about the earth. It retains as a matter of fact exactly as much energy as it gave out when assuming that orbital position. How it happens that "all of us" scientists have considered the particles of a liquid to be freely moving under an attractive force and have failed

¹ Loc. cit., p. 524.

to consider the obvious fact that they must retain orbital energy is hard to see.

Of course, since this retained orbital energy is due to the attractive forces, I was, throughout all of my previous papers, really dealing with one-half of the result of the attractive force instead of with the total result as I had supposed.

Sixth. The volume actually occupied by the molecules and the change of this volume with temperature and pressure.

In the article cited on Chemical Energy¹ I have given the data to prove the statement that "*The 16 grams of oxygen and the 2.016 grams of hydrogen together at -273° C occupy 34.78 cubic centimeters, and when occupying this volume at that temperature they contain 67,300 calories more of energy than do the 18.016 grams of ice which they form if united, and which occupies a volume of 19.21 cc.*

No supposition and no uncertainty whatever is involved in this statement except the slight uncertainty of the measurements. More accurate measurements are now available but the result is not materially changed.

There is a good deal of food for thought in the above facts. In the first place we have no evidence whatever as to the energy retained by the molecules of the water at 0° absolute. Patterson² estimates the potential energy of charge on 16 grams of oxygen and 2.016 grams of hydrogen at 640,000 calories and Arrhenius¹ at 636,100 calories, both on the basis of the electron theory. At any rate, we can content ourselves with the statement that the energy retained by the molecules of water at 0° absolute may be very large. We do know positively that the oxygen and hydrogen at that temperature possessed 67,300 calories more of energy than does the 18.016 grams of water which they form if united. Now in what form is that energy? It has been pointed out long ago, by Clausius I think, that under Newtonian mechanics, energy cannot be retained in a system wholly as kinetic or wholly as potential

¹ Trans. Am. Electrochem. Soc., 14, 35 (1908).

² Chem. News, 102, 77 (1910).

energy, but must exist partly as kinetic energy and partly as potential energy. This being true, one is compelled to conclude that the oxygen and hydrogen molecules (or parts of molecules) must be in motion with terrific speed even at the absolute zero. I, at least, have never been able to escape this conclusion, and I think the atoms of hydrogen and oxygen in water, and the atoms of other compounds travel at great speed. We get some evidence of this sort of activity in radium and radioactive compounds.

If when we talk about the "real" volume occupied by molecules we mean the volume taken up because of these motions, I have no objection to the phrase, and if, when we speak of the compressibility of the atoms and molecules, we have in mind the compression of these rapidly moving parts closer together, I again have no objection to the idea. I do object to all ideas which leave out of consideration the atomic and interatomic motion. My position as to the necessity of considering such molecular volumes, or molecular changes in volume, in studying molecular attraction can now be understood.

The energy relations of the heavenly bodies have nothing to do with the volume occupied by the heavenly bodies but are determined by their attractions. Now in my work upon molecular attraction I have been considering energy relations, and these energy relations are similarly determined by attractive forces which have nothing to do with volumes as above defined. The influence of volume is brought into play only when freedom of motion is destroyed.

The internal energy of atoms changes with the temperature. But in nearly all of my published work I have been dealing solely with the energy of vaporization and *here the temperature is precisely the same before as after the expansion.*

It will again be argued that the change of internal energy with temperature must alter the molecular attraction. I think this is true. But the alteration for the chemically stable substances studied throughout the range of temperature studied is very small. Suppose 18.016 grams of water

really represents some 640,000 calories of energy as hinted. The addition of a few hundred calories of energy within the atoms as the temperature is raised does indeed alter the molecular attraction somewhat but not greatly. It would alter the attraction greatly if the temperature range were continued to 1800° C. Perhaps by some such study one might finally prove that molecular attraction was only the "left over" chemical attraction. Mathews' remarks, as to the influence upon molecular attraction of valence and number of atoms, are interesting in this connection.

Mathews thinks that changes of pressure would also cause changes in molecular volume. Perhaps so, but it must be remembered that *there is no change in external pressure during vaporization*. The changes in internal pressure, caused by the attractive forces, are precisely what the calculation of the attraction takes into account, if you choose to look at it in that way.

After all, Mr. Mathews' views are closely akin to my own. He thinks magnetism and molecular attraction closely related and magnetic attraction is popularly supposed to follow an inverse square law. Also he quotes somewhat approvingly the idea that molecular cohesion is delimited by the surrounding molecules. But this idea is practically nothing more than putting into words the numerator factor of the proposed molecular law.

Summary

(1) It is shown that the decrease shown by the constant of the equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, near the critical temperature was not attributed to errors in the observations used, but to the fact that the Biot formula used did not, and could not be made to represent the observations correctly.

(2) Emphasis is laid on the fact that my equation and views could not agree with the equation of van der Waals if mine were correct, since van der Waals' equation, in its present form, is known not to represent the facts accurately.

(3) Attention is called to the fact that the above equa-

tion is not an "empirical equation" but was derived theoretically by an argument still worthy of careful consideration. Afterwards the equation was proved from the experimental data.

(4) It is shown that the idea that the molecules did not attract as the product of the masses was introduced because of the important fact that "the gravitational law of attraction applied to molecular attraction gives a true equation if we keep the mass investigated constant, which we have a perfect right to do; and gives a false equation if we allow the mass under investigation to vary, which we have an equal right to do."

(5) It is pointed out that both the law of gravitation and the law of molecular attraction given, necessitate the retention of energy in a stable system of moving particles just as much as they necessitate the giving out of energy when the stable system is formed.

(6) Reasons are given for believing that it is not necessary to consider molecular volumes or changes in molecular volumes, in the interpretation of the fundamental equation,

$$\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

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