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# The equation of state for gases and liquids

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Now that I am privileged to appear before this distinguished gathering to speak of my theoretical studies on the nature of gases and liquids, I must overcome my diffidence to talk about myself and my own work. Yet the thought that you are entitled to expect that of me leads me to hope that you will forgive me if I state my views in this field with utter conviction, even in regard to aspects which are not yet universally known and which have so far not achieved universal recognition. I intend to discuss in sequence:
(1) the broad outlines of my equation of state and how I arrived at it;
(2) what my attitude was and still is to that equation;
(3) how in the last four years I have sought to account for the discrepancies which remained between the experimental results and this equation;
(4) how I have also sought to explain the behaviour of binary and ternary mixtures by means of the equation of state.

(1) The first incentive to this my life's work came to me when, after my studies at university, I learned of a treatise by Clausius (1857) on the nature of the motion which we call heat. In this treatise, which is now taught with negligible modifications in every highschool in Holland, he showed how Boyle's law can very readily be derived on the assumption that a gas consists of material points which move at high velocity, that this velocity is of the order of that of sound and increases in proportion to the square root of the absolute temperature. It was subsequently realized that this is only the root mean square of the velocities and that, as Maxwell stated, although he erroneously considered to have proved it, there is a law for the distribution of the velocities known as the Maxwell law. Boltzmann was the first to give the correct proof for this velocity distribution law. Clausius' treatise was a revelation for me although it occurred to me at the same time that if a gas in the extremely dilute state, where the volume is so large that the molecules can be regarded as points, consists of small moving particles, this is obviously still so when the volume is reduced; indeed, such must still be the case down to the maximum compression and also in liquids, which can only be re-

garded as compressed gases at low temperature. Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter - that the factors which, apart from the motion of the molecules, act to determine the pressure must be regarded as quantitatively different when the density changes and perhaps also when the temperature changes, but that they must be the very factors which exercise their influence throughout. And so the idea of continuity occurred to me. I then also asked myself how the solid state behaved. Although I have not as yet seriously gone into that question I do think that in the amorphous state the close proximity of the molecules impedes their mutual displacement. The crystalline state definitely behaves in a slightly different way. Actually I should still be silent on this question. Nevertheless it can now scarcely be doubted that continuity exists between the other two states of aggregation.

As you are aware the two factors which I specified as reasons why a non-dilute aggregate of moving particles fails to comply with Boyle's law are firstly the attraction between the particles, secondly their proper volume. Turning first to the second factor I should like to point out the following: originally I had anticipated that simply the total volume must be decreased with the total volume of the molecules to find the volume remaining for the motion. But closer examination showed me that matters were not so simple. To my surprise I realized that the amount by which the volume must be reduced is variable, that in the extremely dilute state this amount, which I have notated $b$, is fourfold the molecular volume - but that this amount decreases with decreasing external volume and gradually falls to about half. But the law governing this decrease has still not been found. This very point has proved to be the most difficult in the study of the equation of state. Korteweg, Lorentz, Boltzmann, Jeans, and of my pupils, Van Laar, my son, and Kohnstamm have subsequently worked on it. I had thought that it was simply a matter of studying how the mean free path decreases between the collisions of the molecules which are the consequence of their extensiveness, i.e. of the fact that they must not be considered material points but small particles with a real volume in common with all bodies known to us, and so I arrived at this formula:

$$b = b_g \left\{ 1 - \alpha \frac{b_g}{v} + \beta \left( \frac{b_g}{v} \right)^2 \text{etc.} \right\} \qquad \text{(A)}$$

where $b_g$ is fourfold the molecular volume.

Boltzmann has shown, however, that this is inadequate and later on Kohnstamm proved that the formula will be more complex and that for $b/b_g$ a quotient will be obtained of two series in which powers of $b_g/v$ occur. It is so difficult to determine the coefficients $\alpha$, $\beta$ etc. that Van Laar was compelled to carry out fearfully long calculations when determining the second coefficient $\beta$ by my method ($\alpha$ gave rise to far less trouble). This prevented me from proceeding further. And here I have come to the weak point in the study of the equation of state. I still wonder whether there is a better way. In fact this question continually obsesses me, I can never free myself from it, it is with me even in my dreams.

As regards the other cause underlying the non-compliance of real gases and liquids with Boyle's law, i.e. the mutual attraction of the molecules, the situation is somewhat better although here again the last word has not yet been spoken. Using the procedure adopted by Laplace in his capillarity theory, in my continuous theory I have reduced this attraction, which acts in the whole volume, to a surface force which acts towards the interior and thus, together with the external pressure, holds together the moving molecules. Laplace regards his liquid actually as a continuum; at the time he was still unaware of molecules. And if we were dealing with stationary molecules it would have been inadmissible to reduce the attracting forces in the interior to just a surface force. Yet since the molecules are in motion each point in the interior will certainly not be filled with matter at every moment. But space may be regarded as continuously filled with matter of mean - normal - density. I shall return to this point however when I speak of my studies in recent years. The above considerations brought me to the following formula:

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \qquad \text{(B)}$$

which became universally known only as a result of Eilhard Wiedemann's efforts.

(2) Having reached the second part of my lecture I must now mention my own attitude to this equation. It will be abundantly plain from my earlier comments that I never expected this equation, with $a$ and $b$ assigned a constant value, to give results numerically in agreement with experiment and yet people almost always act as though that were my opinion. This astonishes me as in my treatise of 1873 not only did I expressly emphasize the variability

of $b$ but also quoted a series of $b$-values from Andrews' experiment in which for small volumes the change in $b$ with the volume is calculated. For carbon dioxide I moved from the limiting value $b_g = 0.0023$ down to $b = 0.001565$. In this series of values the volumes of the liquid even go below the limiting value of $b_g$ for infinite volume.

Perhaps the reason why my opinion that $b$ is variable has rarely been regarded as seriously intended is to be found in the manner in which I calculated the critical parameters. In this calculation I had to assume $b$ as invariable. But that was because I believed that Andrews' values justified still assigning the limiting value $b_g$ to $b$ in the critical volume. But as I later showed that was a mistake; the value of $b$ in the critical volume has, of course, slightly decreased. Yet to determine the critical volume when $b$ changes with the volume, the first and second differential quotients $db/dv$ and $d^2b/dv^2$ also need to be known. To determine the critical volume, as I later showed, we obtain the equation:

$$\frac{v}{v-b}\left(1 - \frac{db}{dv}\right) + \frac{1}{2}\frac{v\dfrac{d^2b}{dv^2}}{1 - \dfrac{db}{dv}} = \frac{3}{2} \qquad (C)$$

Only when we neglect $db/dv$ and $d^2b/dv^2$ do we find $v_k = 3b$. And it can again be seen from this equation that what I have termed the weak point of my theory is actually responsible for the theoretical impossibility of calculating accurately the critical volume. Using an approximation formula for $b$ I was able to determine $v_k$ as about 2.2 $b_g$. This equation for determining the critical volume I gave and used in my paper in honour of Boltzmann; it was repeated in part in my 1910 treatises. When I had realized this large deviation in the critical volume I also feared a large deviation in the other critical data, i.e. non-compliance with the formulae:

$$RT_k = \frac{8}{27}\frac{a}{b_g} \text{ and } p_k = \frac{1}{27}\frac{a}{b_g^2} \qquad (D)$$

To my great joy, however, and not without astonishment, I found that the two equations used to calculate $a$ and $b$ from the critical data remain unchanged. That I was able to conclude from the results of Sydney Young's admirable experiments on the volumes of co-existing vapour and liquid

phases and on the saturation pressure level at various temperatures. I showed this recently in a treatise to which I shall refer again in the present lecture. However I can explain it as follows: Sydney Young determines inter alia the value of

$$\frac{pv}{RT} \qquad (D')$$

at the critical point and finds 1/3.77. If $p$ and $T$ have the same values as in my theory, providing $b$ is imagined to be constant, the difference from 3/8, the value which I found for $pv/RT$, can be ascribed wholly to the volume. And this, we can say, is entirely correct. The critical volume is not $3\ b_g$, but $(3/2)\ b_g = 2.125\ b_g$ (approximately). And the product $pv/RT$ is not 3/8 but $3/8\sqrt{2}$. For the value of

$$\left(\frac{T}{p}\frac{dp}{dT}\right)_k - 1$$

my equation gives $a/pv^2$. A value of about 6 is found for this value from Sydney Young's experiments. Therefore for $p_k$ we have the value: $p_k = a/6vk^2$, and with $v_k = (3/2)b_g$ the value $p_k = (1/27)a/b_g^2$, as was originally found, is again obtained for $p_k$.

It will thus be seen that I have never been able to consider that the last word had been said about the equation of state and I have continually returned to it during other studies. As early as 1873 I recognized the possibility that $a$ and $b$ might vary with temperature, and it is well known that Clausius even assumed the value of a to be inversely proportional to the absolute temperature. Thus he thought he could with probability account for the equation

$$\left(\frac{T}{p}\frac{dp}{dT} - 1\right)_k = 6$$

only the half being found when $a$ and $b$ are held constant. The foregoing remarks signify that this value does not arise from a change in $a$ with temperature, but merely from the change in $b$ with the volume.

For a long time I searched for a definite characteristic to find whether just making $b$ variable is sufficient to bring about complete agreement between

my formula and experiment, and in the case of remaining discrepancies, whether perhaps it is necessary to assume variability o f $a$ and $b$ with temperature; and now I come to my latest studies on the equation of state.

(3) In 1906 before the Royal Academy of Sciences in Amsterdam I gave a lecture entitled: pseudo association. At the time, however, I contented myself with an oral communication. But one of my pupils, Dr. Hallo, took it down in shorthand and later Dr. Van Rij incorporated it in his inaugural dissertation and developed the theme further. As the criterion whether the variability of $b$ with the volume would be sufficient to bring about agreement between my formula and Sydney Young's experimentally determined liquid and vapour volumes I used in my lecture the Clapeyron principle which, with $b$ varying only with $v$ and not with $T$, and with $a$ constant, leads to the equation

$$\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T} - 1\right) p = \frac{\frac{a}{v_1} - \frac{a}{v_2}}{v_2 - v_1} = \frac{a}{v_1 v_2}$$

or

$$\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T} - 1\right) p v_1 v_2 = a$$

To ensure that only parameters are involved which are directly determinable by experiment, we may also write

$$\frac{\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T} - 1\right) p v_1 v_2}{\left(\frac{T}{p}\frac{\mathrm{d}p}{\mathrm{d}T} - 1\right)_k p_k v_k^2} = 1 \qquad \text{(E)}$$

All the parameters on the left of this equation were accurately determined by Sydney Young for a series of substances. At the critical temperature the value of the left-hand side is, of course, equal to unity; but what is the value at temperatures that are only a fraction of $T_k$? Here it appears that as the temperature decreases the value of the left-hand side increases, very rapidly at first, then at an imperceptible rate.

Sydney Young's experiments only go as far as a value o f $T/T_k = 2/3$. The right-hand side has then increased to 1.4 and seems to be approaching asymptotically the value 1.5. The value of the right-hand side may very accurately be represented by the empirical formula

$$1 + \sqrt{1 - m} - \frac{1 - m}{2} \qquad (F)$$

where $T/T_k = m$.

At a temperature very close to the critical, e.g. $m = 0.99$, the increase in this expression is as much as 0.1 whereas if the square root of $1 - m$ did not occur in the formula and the increase were only to be represented by $1 - m$, it would be less by a factor of ten.

I then had to examine whether the assumption that $a$ or $b$ is temperature-dependent could account correctly for this increase of the right-hand side; and were such not the case, whether another expression for the internal pressure, which I have always written as $a/v^2$, could explain it. As a result of this examination it was found that each temperature function for $a$ and $b$ compatible with such a rapid initial increase of the right-hand side, must contain $\sqrt{1 - m}$. Yet above the critical temperature that would give imaginary values for $a$ and $b$ and is obviously at variance with the whole behaviour of gases. It also appeared that no other assumption for the internal pressure can lead to such a rapid initial increase as the one under discussion. It should not be forgotten that the critical temperature is actually not a special temperature. At this temperature the co-existing densities are equal in magnitude. That alone gives this temperature a meaning which under all other circumstances it does not have. An abrupt jump, a rapid increase either in $a$ or $b$ would make the temperature quite a special one at any level of compression and its determination would then be possible at any density level. In fact, bluntly speaki ng, the result would be: an equation of state compatible with experimental data is totally impossible. No such equation is possible, unless something is added, namely that the molecules associate to form larger complexes ; this year, therefore, I have given two treatises at the Academy in Amsterdam on this possible association. I have termed it "pseudo association" to differentiate it from the association which is of chemical origin. The possible formation of larger molecular complexes, particularly in the liquid state, has frequently been emphasized and the finding that the assumption is necessary to achieve agreement between the state equation

and experiment will hence cause no surprise. Unfortunately my examination is still incomplete. I have found it arduous. And I have had to make use of every piece of evidence to derive something concrete. Nevertheless so much has emerged that it will have to be assumed that a large number of single molecules are required to form a new group which holds together and behaves as a new, larger unit in the molecular motion.

What is the origin of this complex formation, this pseudo association? I was compelled to assume it because it seemed to me the only way to make an equation of state - whichever it is - compatible with the results of measurements. However, as a result of a remark by Debye in last month's *Annalen der Physik,* I remembered a phrase of Boltzmann's. When a few years ago I was privileged to have him with me for some days, among the many matters which we discussed he told me in passing that he was unable to reduce the attraction of molecules to a surface force. At the time the significance of this remark of Boltzmann's did not dawn on me - only now do I think I appreciate what he meant. As far back as in my treatise of 1873 I came to the conclusion that the attraction of the molecules decreases extremely quickly with distance, indeed that the attraction only has an appreciable value at distances close to the size of the molecules. At the time this even prompted me to state that in the case of gases the collisions alone are responsible for their exhibiting an attraction. And it must have been Boltzmann's view that it is only admissible to adopt Laplace's procedure and assume a surface force as a consequence of the attraction provided it does not fall off so rapidly.* Debye's remark implied that Boltzmann had predicted the formation of a complex. Thus, so I believe, the assumption of pseudo association is justified from the theoretical standpoint. And now I think I may state how I proceeded in my latest treatise which appeared in November of this year. Pseudo association differs from true association in that the latter is the result of new chemical forces which arise only when molecules are combined to form e.g. double molecules, whereas pseudo association must be ascribed wholly to the normal molecular forces. Now, since this force diminishes so quickly, it has two consequences. Firstly it results in the formation of a complex, but that is not all. Secondly it leads to a surface pressure, although a lower one. And this is precisely what I was compelled to assume in my calculations were I to have some prospect of accounting for the cited differences. I thus sought to make this clear in the following manner. Let the number of molecules that have combined into a complex be so large that it

* Cf. L. Boltzmann, *Gastheorie,* I I, p. 176.

is possible to speak of a molecule at the centre surrounded by a single layer containing almost as many other molecules as is possible simultaneously. Then, for the surrounding molecules the attraction directed towards the interior acts only to maintain the complex; and this part of its attraction is lost for the surface pressure. Only the forces acting outwards from these molecules can contribute to the formation of the internal pressure. But of course, for pseudo association as for true association the number of formed complexes increases with decreasing temperature and volume. At the critical point, so I was compelled to conclude, only a very small part of the weight is present as complexes.

If pseudo association exists in a substance, there are at least two types of molecules, namely simple and complex. I say at least two types because it cannot be assumed that all complexes are of equal size. But as a first step I have assumed only two types, i.e. simple molecules and $n$-fold molecules. For a really scientific treatment, of course, it would be necessary to assume all values of $n$ as possible and to seek the law of distribution for these values. For the time being, however, I have confined myself to assuming only a single type of complex. We then have a binary mixture. It was very fortunate that for many years I had made a serious study of the laws of binary mixtures - and so I come to the fourth point of my lecture. Not to demand too much of your attention, however, I promise to be quite brief.

(4) When I first conceived the idea of utilizing my equation to study the properties of binary mixtures I can no longer say. But even 20 years ago, at the insistence of my friend Kamerlingh Onnes, I was able to publish a complete theory for binary mixtures. My "Théorie moléculaire d'une substance composée de deux matières différentes" (Molecular theory of a substance made up of two different constituents) appeared in the *Archives Néerlandaises* for 1890. I had written it in Dutch but my esteemed friend Bosscha undertook the difficult task of rendering it into French, a task which was all the more exacting as I had written it in an extremely concise form and the mathematical treatment led to particular points (plait points) and particular curves which at the time had rarely been examined in detail. Previously, however, my friend Korteweg, to whom I had communicated in broad outlines the outcome of my examinations, had studied the mathematical properties of these points and curves, a study which I have often found of great use. The reasons why I hesitated so long over publication were many and it would serve little purpose to enumerate them here. But one of the

reasons of scientific importance was the question which I kept asking myself: is it any use, until the study of the equation of state has been completed, applying it to mixtures ? I appreciated in advance that as long as I was ignorant of the law governing the variability of $b$ and hence had to assume that $b$ did not vary with the volume, the results for many parameters would yield values exhibiting numerically large differences as compared with the values of these parameters as determined by experiment. Nevertheless, the consideration that even with $b$ constant my theory had not been unimportant in the case of a single substance gave me the hope that many phenomena would be explained qualitatively provided that a suitable value for $a$ and $b$ were introduced for mixtures. It was of great importance for me to be acquainted with Gibbs' treatises on the equilibrium of heterogeneous substances which he had sent me immediately after their appearance. I made use inter alia of his principle that for a given amount of substance equilibrium sets in if the free energy is minimum for the given temperature and volume. In his honour I named the equilibrium surface for a binary system the $\psi$-surface. For, the free energy whose significance for the equilibrium he was the first to recognize, he always represents by the sign $\psi$.

The phenomena are really not complex in the case of a simple substance and it is an easy matter to obtain a general picture of them. It is therefore very surprising that in a mere binary mixture they become so complex that they have often been compared with a labyrinth. This is particularly so where three-phase pressure can exist. And it has now become clear that they are at least qualitatively in agreement with the "Théorie moléculaire, etc." from which they can be derived and indeed often predicted. Owing to the many experimental studies to which it has given rise I have frequently found the opportunity of discussing it closely in special communications. Thus in the years 1907 to 1909 about 15 treatises of this nature have appeared in the proceedings of the Academy at Amsterdam. It would be an impressive number were I just to mention the names of the physicists and chemists who, guided by this theory, have studied and still are studying binary mixtures. It begins with Kuenen and ends with Dr. Jean Timmermans of Belgium whose studies have still to be completed but which have already been published in part.

And if now I may be permitted to look back on the way I have come, I must confess that it may fairly be called a detour. Immediately the necessity of assuming association became clear to me I extended my equation of state

analogously to the formula for a binary mixture and introduced a new parameter, the degree of association. This degree of association is determined by means of Gibbs' equation to which I have referred. The degree of association thus determined must then be introduced into the equation of state. And I confess that this is a detour. Perhaps there is a direct way. That this way is seriously being sought I know from those in direct contact with me. In the search for this way Gibbs' *Elementary Principles of Statistical Mechanics* will be a necessary guide. In this lecture, I have only given the history of the origin and further elaboration of my theoretical studies and therefore had to speak of the difficulties that had to be surmounted. Consequently I could not, or only meagrely, discuss how they have assisted in correctly understanding the phenomena. One of the main conclusions, which I have termed the "Law of corresponding states", has, I may say, become universally known. Nor have I discussed how this law was a potent contributory factor in Dewar's determination of the method of liquefying hydrogen, and particularly in Kamerlingh Onnes' determination of the method of liquefying helium. I have also forgone detailed discussion of the temperature at which, to use Regnault's nomenclature, a gas starts to behave like a "pluperfect gas" (gaz plus que parfait), which temperature has been found to have a value of (27/8) $T_k$ - besides the temperature at which it may be stated that the Joule-Kelvin effect reverses: its value is found to be (27/4 ) $T_k$

Neither have I spoken of my perhaps somewhat overhasty efforts to determine the equation of state of the molecule itself. I have even omitted to say why I thought I had to go to such trouble to determine the relation between $p$, $v$ and $T$ for a substance. The formulae of thermodynamics are effective and can actually be applied in all problems, even to determining thermal parameters, only when this relation is known, otherwise they can be regarded as just *one* equation between two unknowns. I have explicitly emphasised this in the book in commemoration of Kamerlingh Onnes published in 1904.

But it was not my intention to discuss all that and I would not have had sufficient time. Yet it does not seem to me superfluous, perhaps it is even necessary, to make a general observation. It will be perfectly clear that in all my studies I was quite convinced of the real existence of molecules, that I never regarded them as a figment of my imagination, nor even as mere centres of force effects. I considered them to be the actual bodies, thus what we term "body" in daily speech ought better to be called "pseudo body". It is an aggregate of bodies and empty space. We do not know the nature of a

molecule consisting of a single chemical atom. It would be premature to seek to answer this question but to admit this ignorance in no way impairs the belief in its real existence. When I began my studies I had the feeling that I was almost alone in holding that view. And when, as occurred already in my 1873 treatise, I determined their number in one gram-mol, their size and the nature of their action, I was strengthened in my opinion, yet still there often arose within me the question whether in the final analysis a molecule is a figment of the imagination and the entire molecular theory too. And now I do not think it any exaggeration to state that the real existence of molecules is universally assumed by physicists. Many of those who opposed it most have ultimately been won over, and my theory may have been a contributory factor. And precisely this, I feel, is a step forward. Anyone acquainted with the writings of Boltzmann and Willard Gibbs will admit that physicists carrying great authority believe that the complex phenomena of the heat theory can only be interpreted in this way. It is a great pleasure for me that an increasing number of younger physicists find the inspiration for their work in studies and contemplations of the molecular theory. The crowning of my studies by the esteemed Royal Swedish Academy affords me satisfaction and fills me with gratitude, a gratitude which I cannot call eternal and in my old age I cannot even promise that it will be of long duration, but perhaps for this very reason my gratitude is all the more intense.