**On the Application of Van der Waals' Equation to the
Compression of Ordinary Liquids. By Prof. Tait.**

(Read June 4, 1894.)

In a paper, read for me to the Society in January last (*ante*, p. 245), I pointed out the difficulties I had met with in trying to reconcile Van der Waals' equation with Amagat's experimental data for common liquids, and I promised to recur to the question when the state of my health should permit. I now find that, as I had then only surmised, the constants in Van der Waals' equation necessarily become non-real when we try to adjust it to Amagat's data.

The proof of this assertion is very simple. Suppose the equation

$$\left(p + \frac{A}{v^2}\right)(v - \beta) = BT$$

to hold for any three pairs of values of p and v ; say p and a , q and b , r and c . Eliminating BT among the three resulting equations, we have

$$\beta = \frac{\left(pa + \frac{A}{a}\right) - \left(qb + \frac{A}{b}\right)}{\left(p + \frac{A}{a^2}\right) - \left(q + \frac{A}{b^2}\right)} = \frac{\left(qb + \frac{A}{b}\right) - \left(rc + \frac{A}{c}\right)}{\left(q + \frac{A}{b^2}\right) - \left(r + \frac{A}{c^2}\right)}.$$

The values of A are therefore to be found from the quadratic

$$A^2 \frac{(a-b)(b-c)(c-a)}{a^2 b^2 c^2} + A \Sigma \left(p \frac{b-c}{b^2 c^2} (ab - bc + ca) \right) - \Sigma (pq(a-b)) = 0.$$

Write, for brevity,

$$P = p \frac{b-c}{b^2 c^2}, \quad Q = q \frac{c-a}{c^2 a^2}, \quad R = r \frac{a-b}{a^2 b^2};$$

so that one at least of P , Q , R is essentially negative, if p , q , r be all positive. The condition that the values of A shall be real is

$$\{\Sigma(P(ab - bc + ca))\}^2 + 4\Sigma(PQ(a-b)^2 c^2) > 0.$$

But it is an obvious theorem of ordinary algebra, that, whatever be the quantities involved, the two expressions

$$(lx + my + nz)^2 + (xy(l - m)^2 + yz(m - n)^2 + zx(n - l)^2)$$

and

$$(x + y + z)(l^2x + m^2y + n^2z)$$

are absolutely identical except in form.

Hence the condition for real values of A is simply that

$$(P + Q + R) \left(P(ab - bc + ca)^2 + Q(ab + bc - ca)^2 + R(-ab + bc + ca)^2 \right)$$

shall be positive :—i.e. that its factors shall have the same sign.

To compare with experiment, let us take $r = 1$ atm., $c = 1$; and find the relation between the values of p and q , the pressures when the volume is reduced to $a = 0.9$, and $b = 0.95$, respectively.

The factors of the above quantity are

$$-p \frac{0.05}{(0.95)^2} + q \frac{0.1}{(0.9)^2} - \frac{0.05}{(0.95)^2(0.9)^2}$$

and

$$-p \frac{0.05(0.805)^2}{(0.95)^2} + q \frac{0.1(0.905)^2}{(0.9)^2} - \frac{0.05(0.995)^2}{(0.95)^2(0.9)^2}$$

or, quite approximately enough for our purpose,

$$-p + 2.228q - 1.234$$

and

$$-p + 2.816q - 1.886.$$

In the latter form each has been divided by the (essentially positive) multiplier of p ; and, as p and q are each of the order 1000 atm., the last terms may usually be disregarded. Thus it appears that the values of A cannot be real if p/q lie between the approximate limits 2.23 and 2.82. But from Amagat's data we easily calculate the following sufficiently accurate values :—

Ratio of Pressures at 0° C. for Volumes 0.9 and 0.95.

Water.	Bisulphide of Carbon.	Methylic Alcohol.	Ethylic Alcohol.	Chloride of Ethyl.	Propylic Alcohol.	Ether.
2.51	2.61	2.65	2.65	2.69	2.71	2.73

[The values of q range from 458 atm. in the case of ether to 1166 atm. in that of water.] All of these ratios lie well within the limits

of the region in which the constants of Van der Waals' equation are non-real; though they are, as a rule, nearer to the upper than to the lower limit.

But it is well to inquire what values A assumes at the limits of this region, when it has just become real. A rough calculation shows that when $p/q = 2.23$ we have $A = -18.1q$ (a *tension*); and for $p/q = 2.82$, $A = 20q$. Outside these limits A has of course two values.

It thus appears that Van der Waals' equation becomes altogether meaningless except for liquids in which the compressibility alters very much with increase of pressure:—*i.e.* for substances which have *just* assumed the liquid form under considerable pressure. For, of course, under the lower limit we are dealing with substances naturally in a state of tension. As I said in my previous paper, this state of things is due mainly to the factor $1/v^2$ with which A (if taken as corresponding to my Π) is affected. There is little doubt that the Π term in my formula does increase as the volume is diminished, but much more slowly than in the inverse ratio of the square of the volume.

(Added, 6/6/94.) It may be interesting to look at the above result from a different point of view, so as to find *why* it is impossible to reconcile the general equation of Van der Waals with the experiments of Amagat.

For this purpose let us take β as independent variable, and (using the same data as before) find the value of p/q . Eliminating BT and A , we obtain the equation

$$\Sigma \left(p \frac{b^2 - c^2}{b^2 c^2} (a - \beta) \left(\frac{bc}{b+c} - \beta \right) \right) = 0;$$

from which, at once,

$$-\frac{p}{q} = \frac{b^2(c^2 - a^2)(b - \beta) \left(\frac{ca}{c+a} - \beta \right)}{a^2(b^2 - c^2)(a - \beta) \left(\frac{bc}{b+c} - \beta \right)} + \frac{r}{q} \frac{c^2(a^2 - b^2)(c - \beta) \left(\frac{ab}{a+b} - \beta \right)}{a^2(b^2 - c^2)(a - \beta) \left(\frac{bc}{b+c} - \beta \right)}.$$

In the further discussion of this equation we may neglect the last term (which is usually *very* much smaller than the preceding term, and becomes infinite for the same values of β). Its only

noticeable effect is to *slightly* alter the values of β for which p/q vanishes. We therefore have, to a quite sufficient approximation,

$$\frac{p}{q} = 2.1712 \frac{(b - \beta) \left(\frac{ca}{c + a} - \beta \right)}{(a - \beta) \left(\frac{bc}{b + c} - \beta \right)}$$

where the literal factors have been retained in the more important portion. The value of $\frac{p}{q}$ in terms of β is thus seen to be a

numerical multiple of the ratio of the corresponding ordinates of two equal and similarly situated parabolas, whose vertices do not

coincide. The first cuts the axis of x at b and $ca/(c+a)$, the second at a and $bc/(b+c)$, so that the second lies wholly within the first while y is negative. They intersect in the single point whose abscissa is $abc/(ab+bc+ca)$. These parabolas are shown in the cut opposite.

The values of p/q are the ordinates of the chief curve. This has three asymptotes :—two parallel to y , and cutting x at a and $bc/(b+c)$ respectively ; and the third at a constant distance, 2·1712, from the axis of x . Its maximum ordinates are given by the equation

$$0 = \frac{d}{dx} \frac{(b-x)\left(\frac{ca}{c+a} - x\right)}{(a-x)\left(\frac{bc}{b+c} - x\right)},$$

or
$$0 = (ab+bc+ca)x^2 - 2abcx.$$

Thus the maximum (at A in the cut) is on the axis of y ; and the minimum (at B) corresponds to $x = 0\cdot6321$. Their values are 2·228 and 2·816 respectively ; and the ordinate of the point of intersection of the construction-parabolas lies midway between them.

Thus, since the minimum numerically exceeds the maximum, the curve has no ordinate intermediate to these values ; and therefore no selection of real constants can make Van der Waals' equation applicable to a liquid in which the pressure, required to reduce its volume by 10 per cent., exceeds that required for a 5 per cent. reduction, in any ratio between 2·228 and 2·816.

Moreover, in accordance with what has been said above about the term A/v^2 , it is only while the ratio of pressures exceeds the higher of these limits that this term represents a pressure, and not a tension. For the graph of A/q in terms of β is easily seen to be a rectangular hyperbola whose asymptotes are parallel to the axes ; cutting x at $bc/(b+c)$, and y at $b^2c^2/(b^2-c^2)$. The curve cuts x at b , and so its ordinates are positive from $bc/(b+c)$ to b , only.