129. *On the Characteristic Equation of Gases.*¹⁾

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In a previous paper²⁾, the present author has given, as the next approximation of van der Waals' equation of state,

$$p + \frac{a}{v^2} + c \frac{ab}{v^3} = \frac{RT}{v} \left(1 + \frac{b}{v} + \frac{5}{8} \frac{b^2}{v^2} \right), \quad \dots \dots (1)$$

where c is a numerical coefficient, between $\frac{1}{4}$ and $\frac{5}{8}$, which depends on the law of intermolecular force and on the temperature, but whose dependency on the temperature is so slight that it may be neglected; and

$$\begin{aligned} a &= \frac{2\pi}{3m^2} \int_{\sigma}^{\infty} r^2 f(r) e^{-2h \int_r^{\infty} f(x) dx} dr \\ &= \phi(T) = a_{\infty} + \frac{a_1}{RT} + \dots \end{aligned}$$

so that at sufficiently high temperatures a may also be taken as a constant.

Now we consider the case in which cohesion is more effective than the molecular volume. Then (1) can be written in the form

$$p + \frac{a}{v^2} + \frac{cab}{v^3} = \frac{RT}{v} \left(1 + \frac{b}{v} \right),$$

or, to the same order of approximation,

$$\left\{ p + \frac{\phi(T)}{(v - \frac{c}{2}b)^2} \right\} (v - b) = RT. \quad \dots \dots (2)$$

In the first place, this equation resembles that of Clausius³⁾, which is got empirically,

1) Details will be given in Nippon Sôgaku-Buturigakkwai Kizi (3d. Ser.)

2) Nippon Sôgaku-Buturigakkwai Kizi 3d. Ser. 8 (1926), 31.

3) Ann. d. Phys. u. Chem. 9 (1880), 337.

$$\left\{ p + \frac{a_c}{T(v+\beta)^2} \right\} (v-b_c) = RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since both constants b and b_c are of the same meaning as van der Waals' volume correction b_w , they must be approximately equal, provided that (2) and (3) are the next approximation of van der Waals' equation; but the observation shows that b differs slightly from b_w , while b_c is of a different order of magnitude, as shown in the table below. Thus, we see that Clausius' equation can not be taken as a corrected van der Waals' equation, and the resemblance between (2) and (3) is merely in form.

In the second place, at sufficiently high temperatures, (2) coincides with Goebel's equation¹⁾, got under some unnatural assumptions,

$$\left\{ p + \frac{a}{(v-a)^2} \right\} (v-b) = RT,$$

where $a = 0.35 v_m$ according to Goebel, v_m being the total molecular volume. But, from the meaning of b , we have $b = 4 v_m$; so that we should have $\frac{a}{b} = 0.0875$, while the numerical values of a and b deduced by Goebel himself from experimental data give much greater values for a/b as shown in the table below.

In my theory, on the other hand, we have from (2), $a = \frac{c}{2} b$; so that $\frac{1}{8} \leq \frac{a}{b} \leq \frac{5}{16}$. It will be noticed that these inequalities are satisfied by all values of a/b in the table.

Lastly we can get a rough estimation of the law of intermolecular force when the accurate value of a/b is known. Assuming the law of force to be $\frac{\lambda_n}{r^n}$, we can find the corresponding value of a/b as shown in my previous paper, so that conversely from the value of a/b we can get the value of n . The values of n thus obtained are given in the last column of the table below. Since the accurate values of a and b are, in general, difficult to obtain, the values of n estimated by the above mentioned method are not much reliable ones. But it may be not without interest to notice that the values of $n = 8$ or 9 for CO_2 etc. coincide approximately with the result of Debye's theory.²⁾

1) Zeits. f. Phys.-Chem. **47** (1904), 471; **49** (1904), 129.

2) Phys. Zeits. **20** (1919), 178.

	$\alpha \times 10^5$	$b \times 10^5$	α/b	$b_W \times 10^5$	$b_C \times 10^5$	n
CO ₂	44	233	0.185	228	86.6	8
C ₂ H ₄	68	329	0.207	251*	96.7	9
N ₂ O	44	233	0.185	184*	—	8
N ₂	68	246	0.276	255	135.9	20
O ₂	60	201	0.299	223	89.0	46

The values of α and b are taken from Goebel's paper. The values with * are calculated from critical data by the aid of van der Waals' equation.