

THE GENERAL THEORY OF MOLECULAR FORCES.

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Received 31st July, 1936.

Following Van der Waals, we have learnt to think of the molecules as centres of forces and to consider these so-called *Molecular Forces* as the common cause for various phenomena: The deviations of the gas equation from that of an ideal gas, which, as one knows, indicate the identity of the molecular forces in the liquid with those in the gaseous state; the phenomena of capillarity and of adsorption; the sublimation heat of molecular lattices; certain effects of broadening of spectral lines, etc. It has already been possible roughly to determine these forces in a fairly consistent quantitative way, using their measurable effects as basis.

In these semi-empirical calculations, for reasons of simplicity, one imagined the molecular forces simply as rigid, additive central forces, in general cohesion, like gravitation; this presumption actually implied

a very suggestive and simple explanation of the parallelism observed in the different effects of these forces. When, however, one began to try to explain the molecular forces by the general conceptions of the electric structure of the molecules it seemed hopeless to obtain such a simple result.

§ 1. Orientation Effect.¹

Since molecules as a whole are usually uncharged the *dipole moment* μ was regarded as the most important constant for the forces between molecules. The interaction between two such dipoles μ_I and μ_{II} depends upon their relative orientation. The interaction energy is well known to be given to a first approximation by

$$U = -\frac{\mu_I \mu_{II}}{R^3} (2 \cos \theta_I \cos \theta_{II} - \sin \theta_I \sin \theta_{II} \cos (\phi_I - \phi_{II})) \quad (1)$$

where $\theta_I, \phi_I; \theta_{II}, \phi_{II}$ are polar co-ordinates giving the orientation of the dipoles, the polar axis being represented by the line joining the two centres, R = their distance. We obtain attraction as well as repulsion, corresponding to the different orientations. If all orientations were equally often realised the average of μ would be zero.

But according to Boltzmann statistics the orientations of lower energy are statistically preferred, the more preferred the lower the temperature. Keesom, averaging over all positions, found as a result of this preference:

$$\bar{U} = -\frac{2}{3} \frac{\mu_I^2 \mu_{II}^2}{R^6} \frac{1}{kT} \quad (\text{valid for } \frac{\mu_I \mu_{II}}{R^3} \ll kT). \quad (2)$$

For low temperatures or small distances ($kT \lesssim \frac{\mu_I \mu_{II}}{R^3}$) this expression does not hold. It is obvious that the molecules cannot have a more favourable orientation than parallel to each other along the line joining the two molecules, in which case one would obtain as interaction energy (see (1)):

$$\bar{U} = -\frac{2\mu_I \mu_{II}}{R^3} \quad (\text{valid for } \frac{\mu_I \mu_{II}}{R^3} \gg kT) \quad (3)$$

which gives in any case a lower limit for this energy. (2) and (3) represent an attractive force, the so-called *orientation effect*, by which Keesom tried to interpret the Van der Waals attraction.

§ 2. Induction Effect.²

Debye remarked that these forces cannot be the only ones. According to (2) they give an attraction which vanishes with increasing temperature. But experience shows that the empirical Van der Waals corrections do not vanish equally rapidly with high temperatures, and Debye therefore concluded that there must be, in addition, an interaction energy independent of temperature. In this respect it would not help to consider the actual charge distribution of the molecules more in detail,

¹ W. H. Keesom, *Leiden Comm. Suppl.*, 1912, **24a**, **24b**, **25**, **26**; 1915, **39a**, **39b**. *Proc. Amst.*, 1913, **15**, 240, 256, 417, 643; 1916, **18**, 636; 1922, **24**, 162. *Physik. Z.*, 1921, **22**, 129, 643; 1922, **23**, 225.

² P. Debye, *Physik. Z.*, 1920, **21**, 178; 1921, **22**, 302. H. Falckenhagen, *Physik. Z.*, 1922, **23**, 87.

e.g. by introducing the quadrupole and higher moments. The average of these interactions also would vanish for high temperatures.

But by its charge distribution alone a molecule is, of course, still very roughly characterised. Actually, the charge distribution will be changed under the influence of another molecule. This property of a molecule can very simply be described by introducing a further constant, the *polarisability* α . In an external electric field of the strength F a molecule of polarisability α shows an *induced* moment

$$M = \alpha \cdot F \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(in addition to a possible *permanent* dipole moment) and its energy in the field F is given by

$$U = -\frac{1}{2}\alpha \cdot F^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now the molecule I may produce near the molecule II an electric field of the strength

$$F = \frac{\mu_I}{R^3} \sqrt{1 + 3 \cos^2 \theta_I} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This field polarises the molecule II and gives rise to an additional interaction energy according to (5)

$$U = -\frac{1}{2}\alpha_{II}F^2 = -\frac{\alpha_{II}}{2} \frac{\mu_I^2}{R^6} (1 + 3 \cos^2 \theta_I) \quad . \quad . \quad . \quad (7)$$

which is always negative (*attraction*) and therefore its average, even for infinitely high temperatures, is also negative. Since $\cos^2 \theta = \frac{1}{3}$ we obtain :

$$\bar{U}_{I \rightarrow II} = -\alpha_{II} \frac{\mu_I^2}{R^6}$$

A corresponding amount would result for $\bar{U}_{II \rightarrow I}$, i.e. for the action of μ_{II} upon α_I . As total interaction of the two molecules we obtain :

$$\bar{U} = -\frac{1}{R^6} (\alpha_I \mu_{II}^2 + \alpha_{II} \mu_I^2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If the two molecules are of the same kind ($\mu_I = \mu_{II} = \mu$ and $\alpha_I = \alpha_{II} = \alpha$) we have

$$\bar{U} = -\frac{2\alpha\mu^2}{R^6} \quad . \quad . \quad . \quad . \quad . \quad (8')$$

This is the so-called *induction effect*.

In such a way Debye and Falcckenhagen believed it possible to explain the Van der Waals equation. But many molecules have certainly no permanent dipole moment (rare gases, H_2 , N_2 , CH_4 , etc.). There they assumed the existence of quadrupole moments τ , which would of course also give rise to a similar interaction by inducing dipoles in each other. Instead of (8) this would give :

$$\bar{U} = -\frac{3}{2} \frac{\alpha\tau^2}{R^8} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Since no other method of measuring these quadrupoles was known, the Van der Waals corrections (second Virial coefficient) were used in order to determine backwards τ , which, after μ and α , has been regarded as the most fundamental molecular constant.

§ 3. Criticism of the Static Models for Molecular Forces.

The most obvious objection to all these conceptions is that they do not explain the above mentioned parallelism in the different manifestations of the molecular forces. One cannot understand why, for example, in the liquid and in the solid state between all neighbours simultaneously practically the same forces should act as between the occasional pairs of molecules in the gaseous state. All these models are very far from simply representing a general additive cohesion :

Suppose that two molecules I and II have such orientations of their permanent dipoles that they are attracted by a third one ; then between the two former molecules very different forces are usually operative, mostly repulsive forces. Or, if the forces are due to polarisation, the acting field will usually be greatly lowered, when many molecules from different sides superimpose their polarising fields. One should expect, therefore, that in the liquid and in the solid state the forces caused by induced or permanent dipoles or multipoles should at least be greatly diminished, if not by reasons of symmetry completely cancelled.

The situation seemed to be still worse when wave mechanics showed that the rare gases are exactly spherically symmetrical, that they have neither a permanent dipole nor quadrupole nor any other multipole. They showed none of the mentioned interactions. It is true, that for H_2 , N_2 , etc., wave mechanics, too, gives at least quadrupoles. But for H_2 we are now able to calculate the value of the quadrupole moment numerically by wave mechanics. One gets only about 1/100 of the Van der Waals forces that were attributed hitherto to suitably chosen quadrupoles.

On the other hand, wave mechanics has provided us with a completely new aspect of the interaction between neutral atomic systems.

§ 4. Dispersion Effect ; a Simplified Model.³

Let us take two spherically symmetrical systems, each with a polarisability α , say two three-dimensional isotropic harmonic oscillators with no permanent moment in their rest position. If the charges e of these oscillators are artificially displaced from their rest positions by the displacements

$$\vec{r}_I = (x_I, y_I, z_I) \quad \text{and} \quad \vec{r}_{II} = (x_{II}, y_{II}, z_{II})$$

respectively, we obtain for the potential energy :

$$V = \underbrace{\frac{e^2 r_I^2}{2\alpha} + \frac{e^2 r_{II}^2}{2\alpha}}_{\text{Elastic Energy.}} + \underbrace{\frac{e^2}{R^3}(x_I x_{II} + y_I y_{II} - 2z_I z_{II})}_{\text{Dipole Interaction Energy (cf. (1)).}} \quad . \quad . \quad (10)$$

Classically the two systems in their equilibrium position

$$(x_I = x_{II} = . . . = z_{II} = 0)$$

would not act upon each other and, when brought into finite distance ($R > \sqrt[3]{2\alpha}$), remain in their rest position. They could not influence a momentum in each other.

³ F. London, *Z. physik. Chem.*, 1930. B, 11, 222.

However, in *quantum mechanics*, as is well known, a particle cannot lie absolutely at rest on a certain point. That would contradict the uncertainty relation. According to quantum mechanics our isotropic oscillators, even in their lowest states, make a so-called *zero-point motion* which one can only describe statistically, for example, by a probability function which defines the probability with which any configuration occurs; whilst one cannot describe the way in which the different configurations follow each other. For the isotropic oscillators these probability functions give a spherically symmetric distribution of configurations round the rest position. (The rare gases, too, have such a spherically symmetrical distribution for the electrons around the nucleus.)

We need not know much quantum mechanics in order to discuss our simple model. We only need to know that in quantum mechanics the lowest state of a harmonic oscillator of the proper frequency ν has the energy

$$E_0 = \frac{1}{2}h\nu \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the so-called *zero-point energy*. If we introduce the following co-ordinates ("normal"-co-ordinates):

$$\vec{r}_+ \equiv \begin{cases} x_+ = \frac{1}{\sqrt{2}}(x_I + x_{II}) \\ y_+ = \frac{1}{\sqrt{2}}(y_I + y_{II}) \\ z_+ = \frac{1}{\sqrt{2}}(z_I + z_{II}) \end{cases} \quad \vec{r}_- \equiv \begin{cases} x_- = \frac{1}{\sqrt{2}}(x_I - x_{II}) \\ y_- = \frac{1}{\sqrt{2}}(y_I - y_{II}) \\ z_- = \frac{1}{\sqrt{2}}(z_I - z_{II}) \end{cases}$$

the potential energy (10) can be written as a sum of squares like the potential energy of six independent oscillators (while the kinetic energy would not change its form):

$$\begin{aligned} V &= \frac{e^2}{2\alpha}(r_+^2 + r_-^2) + \frac{e^2}{2R^3}(x_+^2 + y_+^2 - 2z_+^2 - x_-^2 - y_-^2 + 2z_-^2) . \\ &= \frac{e^2}{2\alpha} \left[\left(1 + \frac{\alpha}{R^3}\right)(x_+^2 + y_+^2) + \left(1 - \frac{\alpha}{R^3}\right)(x_-^2 + y_-^2) + \right. \\ &\quad \left. \left(1 - 2\frac{\alpha}{R^3}\right)z_+^2 + \left(1 + 2\frac{\alpha}{R^3}\right)z_-^2 \right] \quad (10') \end{aligned}$$

The frequencies of these six oscillators are given by

$$\begin{aligned} \nu_{x^{\pm}} = \nu_{y^{\pm}} = \nu_0 \sqrt{1 \pm \alpha/R^3} &\approx \nu_0 \left(1 \pm \frac{\alpha}{2R^3} - \frac{\alpha^2}{8R^6} \pm \dots\right) \\ \nu_{z^{\pm}} = \nu_0 \sqrt{1 \mp 2\alpha/R^3} &\approx \nu_0 \left(1 \mp \frac{\alpha}{R^3} - \frac{\alpha_2}{2R^6} \mp \dots\right) \quad (12) \end{aligned}$$

Here $\nu_0 = \frac{e}{\sqrt{m\alpha}}$ is the *proper frequency* of the two elastic systems, if isolated from each other ($R \rightarrow \infty$), and m is their reduced mass. Assuming $\alpha \ll R^3$, we have developed the square roots in (12) into powers of (α/R^3) .

The lowest state of this system of six oscillators will therefore be given, according to (11), by:

$$\begin{aligned}
 E_0 &= \frac{h}{2} (\nu_x^+ + \nu_y^+ + \nu_z^+ + \nu_x^- + \nu_y^- + \nu_z^-) \\
 &= \frac{h\nu_0}{2} \left[6 + \left(\frac{1}{2} + \frac{1}{2} - 1 - \frac{1}{2} - \frac{1}{2} + 1 \right) \frac{\alpha}{R^3} - \left(\frac{4}{3} + \frac{2}{3} \right) \frac{\alpha^2}{R^6} + \dots \right] \\
 &= 3h\nu_0 - \frac{3}{4} \frac{h\nu_0 \alpha^2}{R^6} + \dots
 \end{aligned}$$

The first term $3h\nu_0$ is, of course, simply the internal zero-point energy of the two isolated elastic systems. The second term, however,

$$U = -\frac{3}{4} \frac{h\nu_0 \alpha^2}{R^6} \quad . \quad . \quad . \quad . \quad (13)$$

depends upon the distance R and is to be considered as an interaction energy which, being negative, characterises an attractive force. We shall presume that this type of force,⁴ which is not conditioned by the existence of a permanent dipole or any higher multipole, will be responsible for the Van der Waals attraction of the rare gases and also of the simple molecules H_2 , N_2 , etc. For reasons which will be explained presently these forces are called the *dispersion effect*.

§ 5. Dispersion Effect; General Formula.⁵

Though it is of course not possible to describe this interaction mechanism in terms of our customary classical mechanics, we may still illustrate it in a kind of semi-classical language.

If one were to take an instantaneous photograph of a molecule at any time, one would find various configurations of nuclei and electrons, showing in general dipole moments. In a spherically symmetrical rare gas molecule, as well as in our isotropic oscillators, the average over very many of such snapshots would of course give no preference for any direction. These very quickly varying dipoles, represented by the zero-point motion of a molecule, produce an electric field and act upon the polarisability of the other molecule and produce there induced dipoles, which are in phase and in interaction with the instantaneous dipoles producing them. The zero-point motion is, so to speak, accompanied by a synchronised electric alternating field, but not by a radiation field: The energy of the zero-point motion cannot be dissipated by radiation.

This image can be used for interpreting the generalisation of our formula (13) for the case of a general molecule, the exact development of which would of course need some quantum mechanical calculations.

We may imagine a molecule in a state k as represented by an orchestra of periodic dipoles μ_{kl} which correspond with the frequencies

$$\nu_{kl} = \frac{E_l - E_k}{h}$$

of (not forbidden) transitions to the states l . These "oscillator strengths," μ_{kl} , are the same quantities which appear in the "dispersion formula" which gives the polarisability $\alpha_k(\nu)$ of the molecule in the state k when acted on by an alternating field of the frequency ν .

$$\alpha_k(\nu) = \frac{2}{3\hbar} \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu^2} \quad . \quad . \quad . \quad (14)$$

⁴ This type of force first appeared in a calculation of S. C. Wang, *Physik. Z.* 1927, **2B**, 663.

⁵ R. Eisenschitz and F. London, *Z. Physik*, 1930, **60**, 491.

If the acting field of the frequency ν_0 has the amplitude F_0 , the induced moment M is given by

$$M = \alpha_k(\nu_0) \cdot F_0 = \frac{2}{3h} F_0 \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_0^2} \quad (4')$$

and the interaction energy between field and molecule by

$$U = -\frac{1}{2} \alpha(\nu_0) \cdot F_0^2 = -\frac{F_0^2}{3h} \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_0^2} \quad (5')$$

Now this acting field may be produced by another molecule by one of its periodic dipoles $\mu_{\rho\sigma}$ with the frequency $\nu_{\rho\sigma}$ and inclination $\theta_{\rho\sigma}$ to the line joining the two molecules. Near the first molecule (we call it the "Latin" molecule, using Latin indices for its states, and Greek indices to the other one) the dipole $\mu_{\rho\sigma}$ produces an electric field of the strength (compare (6)):

$$F_{\rho\sigma} = \frac{\mu_{\rho\sigma}}{R^3} \sqrt{1 + 3 \cos^2 \theta_{\rho\sigma}} \quad (6')$$

This field induces in the Latin molecule a periodic dipole of the amount:

$$M_{\rho\sigma}^k = \alpha_k(\nu_{\rho\sigma}) \cdot F_{\rho\sigma},$$

and an interaction energy (compare (5')):

$$-\frac{\alpha_k(\nu_{\rho\sigma}) F_{\rho\sigma}^2}{2} = -\frac{\mu_{\rho\sigma}^2}{3hR^6} (1 + 3 \cos^2 \theta_{\rho\sigma}) \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2}.$$

If we now consider the whole orchestra of the "Greek" molecule in the state ρ we have to sum over all states σ and to average over all directions $\theta_{\rho\sigma}$ ($\cos^2 \theta = 1/3$). This would give us the action of the Greek atom upon the polarised Latin atom:

$$U_{\rho \rightarrow k} = -\frac{2}{3hR^6} \sum_{l\sigma} \frac{\mu_{kl}^2 \mu_{\rho\sigma}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2}.$$

Adding the corresponding expression $U_{k \rightarrow \rho}$ for the action of the Latin molecule upon the Greek one, we obtain the total interaction due to the "periodic" dipoles of a molecule in the state k with another in the state ρ :

$$\begin{aligned} U_{\rho k} &= U_{\rho \rightarrow k} + U_{k \rightarrow \rho} = -\frac{2}{3hR^6} \sum_{l\sigma} \mu_{kl}^2 \mu_{\rho\sigma}^2 \left(\frac{\nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2} + \frac{\nu_{\rho\sigma}}{\nu_{\rho\sigma}^2 - \nu_{kl}^2} \right) \\ &= -\frac{2}{3hR^6} \sum_{l\sigma} \frac{\mu_{kl}^2 \mu_{\rho\sigma}^2}{\nu_{kl} + \nu_{\rho\sigma}} \quad (15) \end{aligned}$$

§ 6. Additivity of the Dispersion Effect.

Of course this reasoning does not claim to be an exact proof of (15), but it may perhaps illustrate the mechanism of these forces. It can be shown that the formula (15) has the peculiarity of *additivity*;³ this means that if three molecules act simultaneously upon each other, the three interaction potentials between the three pairs of the form (15) are simply to be added, and that any influence of a third molecule upon the interaction between the first two is only a small perturbation effect of a smaller order of magnitude than the interaction itself. These attractive

forces can therefore simply be superposed according to the parallelogram of forces, and they are consequently able to *represent the fact of a general cohesion*.

If several molecules interact simultaneously with each other, one has to imagine that each molecule induces in each of the others a set of co-ordinated periodic dipoles, which are in constant phase relation with the corresponding inducing original dipoles. Every molecule is thus the seat of very many incoherently superposed sets of induced periodic dipoles caused by the different acting molecules. Each of these induced dipoles has always such an orientation that it is attracted by its corresponding generating dipole, whereas the other dipoles, which are not correlated by any phase relation, give rise to a *periodic* interaction only and, on an average over all possible phases, contribute *nothing* to the interaction energy. So one may imagine that the simultaneous interaction of many molecules can simply be built up as an *additive* superposition of single forces between pairs.

§ 7. Simplified Formula ; Some Numerical Values.

For many simple gas molecules (*e.g.* the rare gases, H_2 , N_2 , O_2 , CH_4), the empirical dispersion curve has been found to be representable, in a large frequency interval, by a dispersion formula of the type (14) consisting of one single term only. That means that for these molecules the oscillator strength μ_{kl} for frequencies of a small interval so far exceed the others that the latter can entirely be neglected. In this case, and for the limiting case $\nu \rightarrow 0$ (polarisability in a *static* field) the formula (14) can simply be written :

$$\alpha_k \equiv \alpha_k(0) = \frac{2}{3h} \frac{\mu_k^2}{\nu_k} \quad . \quad . \quad . \quad (14')$$

(μ_k signifies the dipole-strength of the only main frequency ν_k) and formula (15) for the interaction of the two systems goes over into :

$$\begin{aligned} U_{\rho k} &= - \frac{2}{3hR^6} \frac{\mu_k^2}{\nu_k} \cdot \frac{\mu_\rho^2}{\nu_\rho} \cdot \frac{\nu_k \cdot \nu_\rho}{\nu_k + \nu_\rho} \\ &= - \frac{3h}{2R^6} \cdot \alpha_k \alpha_\rho \frac{\nu_k \cdot \nu_\rho}{\nu_k + \nu_\rho} \quad . \quad . \quad . \quad (13') \end{aligned}$$

This formula is identical with (13) in the case of two molecules of the same kind. It can, of course, only be applied if one already knows that the dispersion formula has the above-mentioned special form. But in any case, if the dispersion formulæ of the molecules involved are empirically known, their data can be used and are sufficient to build up the attractive force (15). No further details of the molecular structure need be known.

We give, in Table I., a list of theoretical values for the attractive constant c (*i.e.* the factor of $-1/R^6$ in the above interaction law) for rare gases and some other simple gases where the refractive index can fairly well be represented by a dispersion formula of one term only. The characteristic frequency ν_D multiplied by h is in all these cases very nearly equal to the ionisation energy $h\nu_I$. This may, to a first approximation, justify using the latter quantity in similar cases where a dispersion formula has not yet been determined. It is seen that the values of

c vary in a ratio from 1 to 1000, and this wide range of the order of

TABLE I.—DISPERSION EFFECT BETWEEN SIMPLE MOLECULES.

	$h\nu_f$ (e. Volts).	$h\nu_D$ (e. Volts).	$\alpha \cdot 10^{24}$ [cm. ³].	$c \cdot 10^{48} = \frac{3}{2} \alpha^2 h\nu_0 \cdot 10^{48}$ [e. Volts . cm. ⁶].
He .	24.5	25.5	0.20	0.77
Ne .	21.5	25.7	0.39	2.93
Ar .	15.4	17.5	1.63	34.7
Kr .	13.3	14.7	2.46	69
Xe .	11.5	12.2	4.00	146
H ₂ .	16.4		0.81	8.3
N ₂ .	17	17.2	1.74	38.6
O ₂ .	13	14.7	1.57	27.2
CO .	14.3		1.99	42.4
CH ₄ .	14.5		2.58	73
CO ₂ .		15.45	2.86	94.7
Cl ₂ .	18.2		4.60	288
HCl .	13.7		2.63	71
HBr .	13.3		3.58	128
HI .	12.7		5.4	278
Na .		2.1	29.7	960

magnitude makes even a very crude experimental test of these forces instructive (see § II).

J. E. Mayer⁶ has shown that, for the negative rare-gas-like ions, one is not justified in simplifying the dispersion of the continuum by assuming one single frequency only. He used a simple analytical expression for the empirical continuous absorption and replacing the sums in (15) by integrals over these continua he gets the following list of c values for the 29 possible pairs of ions (Table II.) :

Starting from a different method (variation method) and using some simplifying assumptions as to the wave functions of the atoms (products of single electronic wave functions) Slater and Kirkwood^{6a} have also calculated these forces. They found the following formula :

$$U = - \frac{1}{R^6} \frac{3eh}{8\pi} \sqrt{\frac{N\alpha^3}{m}} \quad . \quad . \quad . \quad (13'')$$

(N = number of electrons in the outer shell.)

This expression usually gives a somewhat greater value than (13) and may be applied in those cases in which the characteristic frequencies in (13) are not obtainable. But at present it is difficult to say how far one may rely on formula (13'').

TABLE II.—DISPERSION EFFECT BETWEEN IONS.

($c \cdot 10^{48}$ in units [$e \cdot \text{volts cm.}^6$]).

	F-.	Cl-.	Br-.	I-.	
Li ⁺ .	$c_{-+} = 0.13$	3.2	4.0	5.4	$c_{++} = 0.11$
Na ⁺ .	7.14	17.8	22.2	30.3	2.68
K ⁺ .	31.0	76.3	95.3	130	38.6
Rb ⁺ .	49.2	125	157	214	94.3
Cs ⁺ .	82.5	205	259	356	247
	$c_{--} = 23.30$	176.206	294.332	600.676	

⁶ J. E. Mayer, *J. Chem. Physics*, 1933, **1**, 270.

^{6a} J. C. Slater and J. G. Kirkwood, *Physic. Rev.*, 1931, **37**, 682.

§ 8. Systematics of the Long Range Forces.⁷

The formula (15) applies quite generally for freely movable molecules so long as the interaction energy can be considered as small compared with the separation of the energy-levels of the molecules in question; *i.e.* so long as

$$\frac{\mu_{kl}\mu_{\rho\sigma}}{R^3} < |E_k - E_l + E_\rho - E_\sigma| \quad . \quad . \quad (16)$$

With this restriction, the formula (15) holds for freely movable dipole molecules, as well as for rare gas molecules. There is therefore always a minimum distance for R up to which we can rely on (15).

The difference between a molecule with permanent dipole and a rare gas molecule consists in the following: A rare gas molecule has such a high excitation energy (electronic jump) that for normal temperatures we can assume that all molecules are in the ground state; therefore we have forces there independent of temperature. For a dipole molecule, on the other hand, we have to consider a Boltzmann distribution over at least the different rotation states, because the energy difference between these states is usually small in comparison with kT .

Let us at first consider an *absolutely rigid dipole* (dumb-bell) molecule (*i.e.* a molecule without electronic or oscillation states). Then the probability $p_{\rho k}$ that the Greek molecule is in the pure rotation state ρ and the Latin one in the pure rotation state k is given by

$$p_{\rho k} = A e^{-\frac{1}{kT}(E_k + E_\rho)}$$

where

$$A^{-1} = \sum_{k\rho} e^{-\frac{1}{kT}(E_k + E_\rho)}.$$

The mean interaction between two such molecules is accordingly

$$\bar{U} = \sum_{\rho k} p_{\rho k} U_{\rho k} = -\frac{2A}{3R^6} \cdot \sum_{\sigma l} \frac{\mu_{kl}^2 \mu_{\rho\sigma}^2}{E_l - E_k + E_\sigma - E_\rho} e^{-\frac{E_k + E_\rho}{kT}}. \quad (17)$$

If in this expression we interchange the notation of the summation indices ρ and k with σ and l , the value of the sum of course remains unchanged. Therefore, taking the average of these two equivalent expressions we can write (since $\mu_{kl} = \mu_{lk}$):

$$\bar{U} = -\frac{A}{3R^6} \sum_{\substack{\sigma l \\ \rho k}} \mu_{kl}^2 \mu_{\rho\sigma}^2 \frac{e^{-\frac{E_k + E_\rho}{kT}} - e^{-\frac{E_l + E_\sigma}{kT}}}{E_l + E_\sigma - E_k - E_\rho}. \quad (17')$$

Developing the exponentials into powers of $1/kT$ we notice that the constant terms cancel each other (no interaction for high temperature as in § 1). The first and the only important term of the development of (17') yields:

$$\bar{U} = -\frac{A}{3R^6} \frac{1}{kT} \sum_{\substack{kl \\ \rho\sigma}} \mu_{kl}^2 \mu_{\rho\sigma}^2 + \dots = -\frac{2\mu_I^2 \mu_{II}^2}{3kTR^6} + \dots \quad (18)$$

Here we designate by μ_I and μ_{II} the permanent moments of the dipole molecule, which for an absolutely rigid molecule are of course independent

⁷ F. London, *Z. Physik*, 1930, **63**, 245.

of the state. We therefore obtain exactly the same result as Keesom did from classical mechanics. One can, by the way, show that whilst the validity of (15) is bounded by the condition (16) the result (18) is only bounded by the weaker condition

$$\frac{\mu_I \mu_{II}}{R^3} < kT$$

which was also the limit for the validity of the classical calculation.

In reality a dipole molecule cannot, of course, be treated as a simple rigid dumb-bell. It has *electronic* and *oscillation* transitions as well. Let us, for sake of simplicity, assume that kT is big in comparison to the energy differences for pure rotation jumps, but small for all the other jumps.

In this general case we have again formula (17), but here it is sufficient to extend the Boltzmann sum $\sum$ only over those states which imply pure rotation jumps from the ground state, since the thermo-dynamical probability of the other states being occupied is negligible. We now divide the sum over σ and l in (17) into four parts

$$\bar{U} = U_{rr} + U_{rg} + U_{gr} + U_{gg}$$

in the following way :

(1) In U_{rr} both, σ and l , shall be restricted to those values which differ from the ground-state only by a pure rotation transition. For this sum (with certain uninteresting reservations) the above calculation for the rigid dipoles remains valid. Accordingly we get (18)

$$U_{rr} = -\frac{2}{3R^6} \frac{\mu_I^2 \mu_{II}^2}{kT},$$

i.e. *Keesom's orientation effect*.

(2) In U_{rg} the summation over σ as before shall be extended only over those terms which differ from the ground state by a pure rotation jump; but l shall designate a great (not a pure rotation-) jump. Then we may neglect $E_\sigma - E_\rho$ in comparison with $E_l - E_k$ in the denominators of (17) and can write

$$U_{rg} = -\frac{2A}{3R^6} \left(\sum_{kl} \mu_{kl}^2 e^{-\frac{E_k}{kT}} \right) \cdot \left(\sum_{\rho\sigma} \frac{\mu_{\rho\sigma}^2}{E_\sigma - E_\rho} e^{-\frac{E_\rho}{kT}} \right).$$

Comparison with (14) shows that the terms of the second sum on the right-hand side can be represented by the static polarisability $\alpha_\rho = \alpha_\rho(o)$ of the second molecule which will depend very little on the state of rotation ρ of the molecule so that we may signify it simply by α_{II} ; whereas the first sum again gives the square of the permanent dipole moment of the first molecule, of which we also may assume that it is approximately independent of the state of rotation. We obtain

$$U_{rg} = -\frac{2}{3R^6} \cdot \mu_I^2 \cdot \frac{2}{3} \alpha_{II}(o) = -\frac{\mu_I^2 \alpha_{II}}{R^6}.$$

(3) Correspondingly

$$U_{gr} = -\frac{\mu_{II}^2 \alpha_I}{R^6}$$

(2) and (3) are exactly *Debye's induction effect*.

(4) In U_{gg} finally both, σ and l , shall differ from the ground state by a great (not a pure rotation-) jump. If we assume that the transition

probabilities of such a jump do not depend noticeably on the state of rotation, we can take simply the ground state for ρ and k and obtain

$$U_{\sigma\sigma} = -\frac{2}{3hR^6} \sum_{\sigma} \frac{\mu_{\sigma\sigma}^2 \mu_{\sigma\sigma}^2}{\nu_{\sigma\sigma} + \nu_{\sigma\sigma}}.$$

i.e. the *dispersion effect*. If the conditions for (13') are fulfilled we may join the three effects in the form

$$\bar{U} = -\frac{1}{R^6} \left(\frac{2}{3} \frac{\mu_I^2 \mu_{II}^2}{kT} + \mu_I^2 \alpha_{II} + \mu_{II}^2 \alpha_I + \frac{3h}{2} \alpha_I \alpha_{II} \frac{\nu_I \nu_{II}}{\nu_I + \nu_{II}} \right) \quad (19)$$

We give, in Table III., a short list for the three effects of some dipole molecules :

TABLE III.—THE THREE CONSTITUENTS OF THE VAN DER WAALS' FORCES.

	$\mu \cdot 10^{18}$.	$\alpha \cdot 10^{24}$.	$h\nu_0$ (Volts).	Orientation Effect $\frac{2}{3} \frac{\mu^4}{kT^2} \cdot 10^{60}$ [erg cm. ⁶].	Induction Effect $2\mu^2\alpha \cdot 10^{60}$ [erg cm. ⁶].	Dispersion Effect $\frac{2}{3} \alpha^2 h\nu_0 \cdot 10^{60}$ [erg cm. ⁶].
CO .	0.12	1.99	14.3	0.0034	0.057	67.5
HI .	0.38	5.4	12	0.35	1.68	382
HBr .	0.78	3.58	13.3	6.2	4.05	176
HCl .	1.03	2.63	13.7	18.6	5.4	105
NH ₃ .	1.5	2.21	16	84	10	93
H ₂ O .	1.84	1.48	18	190	10	47

It is seen that the induction effect is in all cases practically negligible, and that even in such a strong dipole molecule as HCl the permanent dipole moments give no noticeable contribution to the Van der Waals' attraction. Not earlier than with NH₃ does the orientation effect become comparable with the dispersion effect, which latter seems in no case to be negligible.

§ 9. Limits of Validity.

We have yet to discuss the physical meaning of the condition (16).

In quantum mechanics, in characteristic contrast to classical mechanics, a freely movable polyatomic molecule has a centrally symmetric and, particularly in its lowest state, a spherically symmetric structure, *i.e.* a spherically symmetric probability function. That means that on the average, even in its lowest state, a free molecule does not prefer any direction, it changes its orientation permanently owing to its zero-point motion. If another molecule tries to orientate the molecule in question a compromise between the zero-point motion and the directing power will be made, but only for

$$\frac{\mu_I \mu_{II}}{R^3} > |E_0 - E_1| . \quad . \quad . \quad . \quad (20a)$$

the directive forces preponderate over the zero-point rotation. Accordingly, in this case, the motion of the dipoles becomes more similar to a vibration near the equilibrium orientation of the dipoles (parallel to each other along the line joining the two molecules) and the interaction will then be of the nature of orientated dipoles, *i.e.* of the order of magnitude of

$$-\frac{2\mu_I \mu_{II}}{R^3}.$$

In quantum mechanics, we learn, in contrast to (3), the condition

$$\frac{\mu_I \mu_{II}}{R^3} > kT \quad . \quad . \quad . \quad (20b)$$

is not sufficient for the molecules being orientated. The orientating forces have not only to overcome the temperature motion but in addition the zero-point motion also. If Θ is the moment of inertia of the molecule the right-hand side of (20a) becomes equal to $\frac{h^2}{4\pi\Theta}$; and using this one can easily show that, for example, for HI molecules, at the distances they have in the solid state, the directive forces of the dipoles are still too weak to overcome the zero-point rotation. One has therefore to imagine these molecules always rotating even at the absolute zero in the solid state. But HI is certainly rather an exceptional case.

It is obvious that for larger molecules and for small molecular distances in the solid and liquid state the directive forces are quite insufficiently represented by the dipole action. For these one has simply to replace the left-hand side of (20) by the classical orientation energy in order to obtain a reasonable estimate for the limit of free motion.

As long as we are within the limits of (16) our argument in § 6 as to the additivity holds quite generally for all the three effects collected in formula (19). Only if, in consequence of (20), the free motion of the molecules is hampered does the criticism of § 3 apply, and this concerns the non-additivity of the direction effect as well as of the induction effect.

The internal *electronic* motion of a molecule, however, will not appreciably be influenced when the rotation of the molecule as a whole is stopped. Thus one is justified in applying the formula for the dispersion effect for non-rotating molecules also.

It is obvious, however, that only the highly compact molecules, as listed in Tables I. and II., can reasonably be treated simply as force centres. For the long organic molecules it seems desirable to try to build up the Van der Waals' attraction as a sum of single actions of parts of the molecules. As it is rather arbitrary to attribute the frequencies appearing in (15) or (13) to the single parts of a molecule, it has been attempted⁸ to eliminate them by making use of the approximate additivity of the atomic refraction as well as of the diamagnetic susceptibility.

If there is one single "strong" oscillator μ_k only (*cf.* 14') the diamagnetic susceptibility has simply the form :

$$\chi_k = -\frac{\mu_k^2 N_L}{6mc^2} (< 0) \quad (N_L \text{ Loschmidt's number})$$

therefore, because of (14'),

$$\nu_k = \frac{2}{3h} \frac{\mu_k^2}{\alpha_k} = \frac{4mc^2}{hN_L} \frac{\chi_k}{\alpha_k}$$

We can therefore write, instead of (13'),

$$\begin{aligned} U_{kp} &= \frac{3}{2} \frac{h}{R^6} \alpha_k \alpha_p \frac{4mc^2}{hN_L} \frac{\frac{\chi_k}{\alpha_k} \frac{\chi_p}{\alpha_p}}{\chi_k/\alpha_k + \chi_p/\alpha_p} \\ &= \frac{1}{R^6} \frac{6mc^2}{N_L} \frac{\alpha_k \alpha_p}{\alpha_k/\chi_k + \alpha_p/\chi_p} \quad . \quad . \quad . \quad (13''') \end{aligned}$$

⁸ J. G. Kirkwood, *Physik. Z.*, 1932, **33**, 57; A. Müller, *Proc. Roy. Soc. A*, 1936, **154**, 624.

In this formula the interaction energy is represented by approximately additive atomic constants, and it seems quite plausible to build up in such a way the Van der Waals' attraction of polyatomic molecules from single atomic actions. But the comparison given in Table IV. shows that the exactitude of this method is apparently not very great.

For the *dispersion effect* also, the condition (16) indicates a characteristic limit. The quantity $\frac{\mu^2_{kl}}{E_k - E_l}$ is practically identical with the polarisability α , if $E_k \rightarrow E_l$ is the "main" electronic jump (compare 14'). Accordingly, instead of (16) we may roughly write

$$\alpha < R^3 \quad . \quad . \quad . \quad (16')$$

as condition for the validity of our formulæ for the dispersion effect. What $\alpha > R^3$ would mean can easily be inferred from considering our simple model (§ 4): Some of the proper frequencies (12) would become imaginary, and that indicates that for these short distances the rest positions of the electrons would no longer be positions of stable equilibrium.

Some time ago Herzfeld⁹ noticed that if R_0 is the shortest possible atomic distance (atomic diameter) the alternative " $\alpha > R_0^3$ or $\alpha < R_0^3$ " nearly coincides with the alternative "*metal* or *insulator*." Accordingly, for the non-metallic atoms and molecules listed in Table I. one is always within the limits of (16).

§ 10. Higher Approximations. Repulsive Forces.

The formula (15) is very far from completely representing the molecular forces, even of the rare gases, for all distances. It can be considered as a first step of a calculus of successive approximation. The state of a molecule is of course only quite roughly characterised by its orchestra of periodic dipoles; there are obviously also periodic quadrupoles and higher multipoles, which give rise to similar interactions proportional to R^{-8} , R^{-10} , etc. For big distances these terms are in any case smaller than the R^{-6} forces, and there one may rely on formula (15). For He and H-atoms one¹⁰ could calculate the R^{-8} term and could show that for small distances it can give rise to a contribution comparable with the R^{-6} term. But the R^{-10} term seems always to be negligible.

For these small distances, however, quite another effect has also to be considered. Even if a molecule does not show any permanent multipole but has, on an average, an absolutely spherically symmetrical structure, *e.g.* like the rare gases, quite apart from all effects due to the internal electronic motion, the mean charge distribution itself gives rise to a strong, so to speak "static," interaction, simply owing to the fact that by penetrating each other the electronic clouds of two molecules no longer screen the nuclear charges completely and the nuclei repel each other by the electrostatic Coulomb forces. In addition to this, and simultaneously, a second influence is to be considered. Already the

TABLE IV.

	$\frac{3mc^2}{N_L} \alpha_X \cdot 10^{48}$.	$c \cdot 10^{48}$ (Table I.).
He .	0.84	0.77
Ne .	4.94	2.93
A .	69.0	34.7
Kr .	180	69
X .	448	146

⁹ K. F. Herzfeld, *Physic. Rev.*, 1927, **29**, 701.

¹⁰ H. Margenau, *ibid.*, 1931, **38**, 747.

penetration of the two electronic clouds is hampered by the Pauli Principle: two electrons can only be in the same volume element of space if they have sufficiently *different velocity*. This means that for the reciprocal penetration of the two clouds of electrons the velocity and therefore also the kinetic energy of the internal electronic motion must be augmented: energy must be supplied with the approach of the molecules, *i.e.* repulsion.

This repulsion corresponds to the *homopolar attraction* in the case of unsaturated molecules. In an unsaturated molecule there are electrons with unsaturated spin and of these, when penetrating the cloud of a corresponding other molecule, the Pauli Principle no longer demands "sufficiently different" velocity but *only different spin orientation*. In that case, consequently, one has a repulsion only for much smaller distances.

The actual calculation of the repulsive forces needs of course a very exact knowledge of the charge distribution on the surface of the molecules, and therefore presents considerable difficulties; hitherto, a detailed calculation could only be carried out for the very simplest case¹¹ of He. The most successful attempts¹² in this direction so far have applied the ingenious Thomas-Fermi method which takes the Pauli Principle directly as a basis and is accordingly able, neglecting many unessential details, to account for just that effect which is characteristic of this penetration mechanism.

It is impossible here to reproduce the results of these numerical methods. Up to now the repulsive forces have been successfully calculated only for the interaction between the rare gas-like ions, not yet for the rare gases themselves. This is not because the repulsive forces between the neutral rare gas molecules constitute a very different problem, but because a considerably smaller degree of exactitude of the repulsive forces gives a useful description, when they are balanced by the strong ionic attractive forces instead of the weak molecular forces only.

The chemist at present must be satisfied with the knowledge that the repulsive forces depend on rather subtle details of the charge distribution of the molecules, and that consequently there is no reason to hope that one might connect them with other simple constants of the molecules, as is possible for the far-reaching attractive forces. Their theoretical determination is in any special case another problem of pure numerical calculations. But what really will interest the chemist is the fact that it can generally be shown that these homopolar repulsive forces (in characteristic contrast with the above-mentioned homopolar binding forces) have also the property of additivity, in the same approximate sense as the R^{-6} forces are additive, and that, therefore, to a first approximation, it will be quite justified to assume for the repulsive forces also simple analytical expressions, to superpose them simply additively and so to try to determine them from empirical data of the liquid or solid state. Whereas formerly one used to presume a power-law of the form b/R^n for these repulsive forces, quantum mechanics now shows that an exponential law of the form

$$be^{-R/\rho}$$

gives a more appropriate representation of the repulsion.

¹¹ J. C. Slater, *Physic. Rev.*, 1928, **32**, 349; see also W. E. Bleand J. E. Mayer, *Journ. chem. Physics*, 1934, **2**, 252.

¹² H. Jensen, *Z. Physik.*, 1936, **101**, 164; P. Gombar, *ibid.*, 1935, **93**, 378.

In this form one now usually presumes the repulsive forces and determines the constants b and ρ empirically.

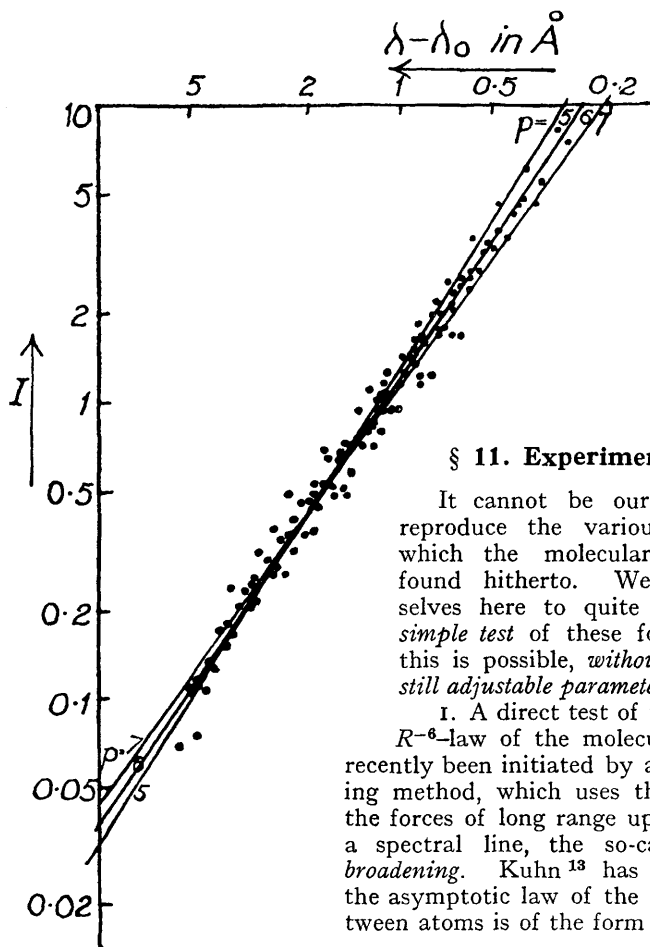
For the attraction one uses the expression (15) or (13) possibly completed by a term proportional to R^{-8} . The factor R^{-8} supplies a third constant which also has to be empirically determined. For rare-gas like ions of the charges e_1, e_2 , finally, one has of course to add the Coulombian term $+\frac{e_1 e_2}{R}$.

Thus, altogether one usually now takes, for the simplest molecules, an expression of the form

$$U = be^{-R/\rho} - c/R^6 - d/R^8 + \frac{e_1 e_2}{R} \quad (21)$$

as a reasonable basis, where b, ρ, d are adjustable parameters, whereas

c, e_1, e_2 are regarded as theoretically given. Thus, in all applications of the Van der Waals' forces a considerable freedom remains, and this is to be noticed when one wishes to test the theory.



§ 11. Experimental Test.

It cannot be our task here to reproduce the various applications which the molecular forces have found hitherto. We confine ourselves here to quite a rough and *simple test* of these forces so far as this is possible, *without adapting the still adjustable parameters* in (21).

1. A direct test of the asymptotic R^{-6} -law of the molecular forces has recently been initiated by a very interesting method, which uses the influence of the forces of long range upon the form of a spectral line, the so-called *pressure-broadening*. Kuhn¹³ has shown that if the asymptotic law of the interaction between atoms is of the form

$$U \approx \frac{c}{R^p}$$

FIG. 1.—Intensity distribution and molecular forces.

¹³ H. Kuhn, *Phil. Mag.*, 1934, **18**, 987; *Proc. Roy. Soc. A*, 1936 *in print*; see also H. Kuhn and F. London, *Phil. Mag.*, 1934, **18**, 983.

the intensity in a certain region of the spectral line is given by

$$I(\nu) = \frac{k}{(\nu_0 - \nu)^{\frac{p+3}{p}}}.$$

Thus the inclination of $\log(I)$ as a function of $\log \nu$ gives immediately the exponent p . Thereupon Minkowski¹⁴ has discussed his measurements of the broadening of the D-lines of Na by Argon. He gives the following figure of his measured values of $\log(I)$ (Fig. 1). In addition, we have drawn the lines corresponding to $p = 5$, $p = 6$ and $p = 7$. One sees that the accuracy of the measurements does not yet permit an exact determination of p . But in any case we may say that $p = 6$ fits much better than $p = 5$ or $p = 7$, and that $p = 8$ and $p = 4$ can be excluded with certainty.

2. Testing the theory by the *gas equation* we shall restrict ourselves here to a quite rough check by means of the Van der Waals' a and b only. If this test has a satisfactory result, the exact dependence of the second virial coefficient on temperature may be used for determining *backwards* the still adjustable parameters in (21). But since it is always possible to get a fairly good agreement with the second virial coefficient by adjusting an expression like (21) it seems desirable to simplify the situation in such a way that, if possible, no adjustable parameters would be involved.

Accordingly, we replace (21) by :

$$U = \begin{cases} -c/R^6 & \text{for } R \geq R_0 \\ +\infty & \text{for } R < R_0 \end{cases} \quad (22)$$

That means we idealise the molecules as infinitely impenetrable spheres, and neglect for $R > R_0$ the two adjustable terms $be^{-R/b}$ and $-d/R^8$ entirely. For large values of R the term $-c/R^6$ is certainly the only noticeable one. For mean distances $R \gtrsim R_0$ the two neglected terms, having different sign, may to a large extent cancel each other. For $R < R_0$ the very sudden increase of the exponential repulsion is replaced by an infinitely sudden one. By this procedure the order of magnitude of the minimum of U may be affected by a common factor, but will not be completely mutilated. Instead of the three adjustable parameters of (21) we have now only one : the size R_0 .

The second virial coefficient B_2 is defined by the development of the gas equation into powers of $\frac{1}{V}$.

$$\frac{pV}{NkT} = 1 + \frac{B_2(T)}{V} + \frac{B_3(T)}{V^2} + \dots,$$

and is given theoretically by

$$B_2 = 2\pi N \int_0^\infty (1 - e^{-\frac{U}{kT}}) r^2 dr \quad (23)$$

In the development of B_2 into powers of $\frac{1}{V}$, the first two terms can be identified with the corresponding terms of Van der Waals' equation :

$$\frac{pV}{NkT} = \frac{V}{V-b} - \frac{a}{VNkT} \approx 1 + \frac{1}{V} \left(b - \frac{a}{NkT} \right) + \frac{1}{V^2} (\dots) + \dots$$

¹⁴ R. Minkowski, *Z. Physik*, 1935, **93**, 731.

The comparison gives:

$$B_2 = b - \frac{a}{N_L k T} + \dots,$$

and if we now substitute (22) into (23) and consider that for high temperatures $U \gg -kT$ for all values of R , we obtain:

$$b = \frac{2\pi N_L R_0^3}{3}$$

$$a = -2\pi N_L^2 \int_{R_0}^{\infty} U R^2 dR = \frac{2\pi N_L^2 c}{3R_0^3}.$$

In these two equations we may eliminate R_0^3 and obtain:

$$ab = \frac{4\pi^2 N_L^3}{9} \cdot c = 1.51 \times 10^{54} \cdot c \quad (24)$$

Here the numerical factor is so determined that a , as usual, is measured in $[\text{atm. cm.}^6 \text{ g.}^{-2}]$ and c in the units of Table I.

If b is taken from the experimental gas equation the relation (24) can be used for predicting the constant a . These values are listed as $a_{\text{theor.}}$ in Table V., where they can be compared with the experimental values $a_{\text{exp.}}$

TABLE V.—VAN DER WAALS a -CONSTANT AND HEAT OF SUBLIMATION.

	$b_{\text{exp.}}$ [cm ³].	$a_{\text{theor.}} \cdot 10^{-4}$ [atm. cm. ⁶ g. ⁻²].	$a_{\text{exp.}} \cdot 10^{-4}$ [atm. cm. ⁶ g. ⁻²].	ρ .	$L_{\text{theor.}} \cdot 10^{-3}$ cal. mol.	$L_{\text{exp.}} \cdot 10^{-3}$ cal. mol.
He .	24	4.8	3.5			
Ne .	17	26	21	1.46	0.47	0.59
Ar .	32.3	163	135	1.70	1.92	2.03
Kr .	39.8	253	240	3.2	3.17	2.80
Xe .	51.5	430	410			
H ₂ .	26.5	46	24.5			
N ₂ .	39.6	147	135	1.03	1.64	1.86
O ₂ .	31.9	135	136	1.43	1.69	2.06
CO .	38.6	166	144	1.05	1.86	2.09
CH ₄ .	42.7	256	224	0.53	2.42	2.70
CO ₂ .	42.8	334	361			
Cl ₂ .	54.8	680	632	2.00	7.18	7.43
HCl .	40.1	283	366	1.56	3.94	5.05
HBr .	44.2	510	442	2.73	4.45	5.52
HI .				3.58	6.65	6.21

It is needless to say how inadequate the use of the critical data is for determining the limiting values for $T \rightarrow \infty$ of the second virial coefficient. These inadequacies may produce an uncertainty of perhaps 30 per cent., and our simplified expression (22) may also introduce an error of such an order of magnitude. But these uncertainties will presumably give rise only to a common systematic error for all molecules considered, and though the good absolute agreement found in the list is to be regarded as a lucky chance the relative agreement between theoretical and experimental a -values over such a wide range is certainly not disputable. That may justify trying to improve our knowledge of the Van der Waals

forces by adjusting the expression (21) by means of the empirical second virial coefficient. Hitherto this has only been tried¹⁵ by adding a law of the form b/R^n for the repulsion. But this procedure inevitably gives too small a molecule size, as it must attribute to the R^{-6} -forces what is due to the neglect of the R^{-8} -forces and of the sudden decrease of the exponential repulsion.

3. In Table V. is also listed the *lattice energy* L (sublimation heat extrapolated to absolute zero after subtraction of the zero-point energy) for some molecule lattices, calculated on the basis of the same simplified formula (22). In all cases we have assumed closest packed structure, as this structure is at least approximately realised in the molecular lattices in question. The summation of (22) over the lattice gives

$$L = 8.36 \cdot N L^2 \frac{c}{v^2} 10^4 \left[\frac{\text{cal}}{\text{mol}} \right] = 3.04 \times 10^{52} \frac{c \cdot \rho^2}{M^2} \left[\frac{\text{cal}}{\text{mol}} \right]. \quad (25)$$

Here c is to be taken from Table I., v is the experimental mol. volume, ρ = density, M = molecular weight.

This test is instructive in so far as it shows plainly the additivity of the forces, and particularly the increase of L from HCl to HI with decreasing dipole moments clearly demonstrates the preponderance of those forces which are not due to the permanent moments.*

When the full expression (21) will be determined, say, from the experimental second virial coefficient it will be possible to calculate all constants (compressibility, elastic constants, etc.) of these molecular lattices.

For the constitution of the *ionic* lattices also, the Van der Waals attraction has been found to be a very decisive factor. We know the forces at present much better for these ions than for the neutral molecules. Using an interaction of the form (21), Born and Mayer¹⁶ have calculated the lattice energy of all alkali halides for the NaCl-type and simultaneously for the CsCl-type and comparing the stability of the two types they could show quantitatively that the relatively great Van der Waals attraction between the heavy ions Cs^+ , I^- , Br^- , Cl^- (cf. Table II.) accounts for the fact that CsCl, CsBr, CsI, and *these only*, prefer a lattice structure in which the ions of the same kind have smaller distances from each other than in the NaCl-type. The contribution of the Van der Waals' forces to the total lattice energy of an ionic lattice is of course a relatively small one, it varies from 1 per cent. to 5 per cent., but just this little amount is quite sufficient to explain the transition from the NaCl-type to the CsCl-type.

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¹⁵ K. Wohl, *Z. physik. Chem. B*, 1931, **41**, 36; J. E. Lennard-Jones, *Proc. Physic. Soc.*, 1931, **43**, 461.

* In Table V. the lattice energies of He and H_2 have been omitted, because in these lattices the zero-point energy of the nuclear motion gives such a great contribution that it cannot be neglected. Therefore H_2 and He cannot immediately be compared with the other substances. See F. London, *Proc. Roy. Soc. A*, 1936, **153**, 576.

¹⁶ M. Born and J. E. Mayer, *Z. Physik*, 1932, **75**, J. E. Mayer, *J. Chem. Physics*, 1933, **1**, 270.