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THE ELECTRIC MOMENT OF ALKALI ATOMS

BY J. J. WEIGLE

ABSTRACT

The electric moments of atoms can be calculated if we know the constant *a* of van der Waals. This constant can be obtained from the vapor pressure equation. Thus for all the substances for which the vapor pressure curve has been determined it is possible to calculate the electric moment or the electric moment of inertia. These computations have been made for the alkali atoms giving 0.18×10^{-18}, $0.24+10^{-18}$, 0.24×10^{-18}, $\mathrm{gr}^{1/2}\,\mathrm{cm}^{3/2}\,\mathrm{sec}^{-1}\epsilon$ as the electric moments of Na, K, Rb respectively. These values although not very accurate are interesting, for Bohr's picture of the alkali atom, with the penetrating orbit of the valence electron precessing around the nucleus, gives no electric moment. The values above are so small as to be negligible and thus in accord with the theory.

IT IS well known that if we consider the molecules or atoms as made up of movable electric charges, such molecules placed in an electric field will be polarized. Debye[1] has assumed that this polarization is directly responsible for the forces of cohesion of van der Waals, and has thus calculated the equation of state of the gases composed of such molecules. He obtained an expression for the coefficient *a* of van der Waals as a function of the polarizability of the molecule, and of the distribution of the charges in it. This polarizability is measured by the electric moment induced when the molecule is placed in an electric field and can be obtained experimentally by measuring the index of refraction of the substance or the variation of its dielectric constant with the applied field; for the polarizability is the property of the molecules which is responsible for the index of refraction being different from unity. However the dielectric constant may be different from unity for two reasons the first and most important being the orientation, in the field, of molecules having a permanent electric moment, the second being this polarizability. Following Debye the molecules can be classified in two groups according to their electrical symmetry. If r be the distance of a point from a molecule at the origin composed of z charges $e_k (k=1, 2, 3, \cdots, z)$ coordinates $x_k y_k z_k$ the potential at this distance $r=(x^2+y^2+z^2)^{1/2}$ is (as given by Debye)

$$\phi=\frac{\Sigma e_k}{r}+\frac{1}{r^2}\left\{\frac{x}{r}\Sigma e_k x_k+\frac{y}{r}\Sigma e_k y_k+\frac{z}{r}\Sigma e_k z_k\right\}$$
$$-\frac{1}{r^3}\left\{\left(\frac{1}{r}-\frac{3}{2}\,\frac{x}{r^2}\right)\Sigma e_k x_k{}^2+\quad\cdots\;+\cdots\right\}-\cdots$$

As $\sum e_k=0$ for a neutral molecule, ϕ depends on the electric moment of components $\sum e_k x_k$, etc., and on the electric moment of inertia of components

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[1] Debye, Phys. Zeits. **21**, 179 (1920).

(tensor) $\sum e_k x_k^2$, etc. If $\sum e_k \mathbf{r}_k \neq 0$ the molecule is called a dipole, as the centers of charge of the positive and negative charges do not coincide. If however the electric moment is zero (rare gases for instance) the potential is due to the electric moment of inertia, the molecule is called a quadrupole.

The van der Waals cohesive forces are not directly due to the attraction or repulsion of these electric moments, for on the average such actions would cancel each other; however when the polarizability of the molecule is taken into account the following processes take place: If two molecules are ordered in such a way that their permanent moments repel each other, each receives an additional moment (opposite to the first) because it is polarized by the field of the other molecule. As they move away this superimposed moment decreases (since the field decreases) and the force of repulsion becomes less or we may say that an attraction is superposed. If the two molecules had been disposed in such a way as to attract each other, the moment arising from the polarization would be in the same direction as the permanent moment and, when the two molecules move toward each other, this additional moment would become greater and so would the force of attraction. In both cases the effect of polarization is thus to produce attraction and, on averaging, this force cannot become zero. Falkenhagen[2] has calculated the second virial coefficient B of the equation of state of a gas formed of molecules having a permanent electric moment μ and a polarizability α. He obtained

$$B=\frac{2\pi}{3}Nd^3\left(1-b_1\frac{\theta}{T}-b_2\left(\frac{\theta}{T}\right)^2-\cdots\right) \tag{1}$$

N is Avogadro's number, d the diameter of the molecules, $\theta=\mu^2/kd^3$ where k is Boltzman's constant, $b_1=4z$, $b_2=3.33\ 10^{-1}+3.27z^2\cdots$ where $z=\alpha/d^3$. The value of α can be computed from the molecular refraction P_0 by using the equation

$$P_0=4\pi\alpha/3 \tag{2}$$

Falkenhagen compared the value of B obtained experimentally from the isothermals of a gas with that calculated from (1), knowing μ from the variation of the dielectric constant with the temperature. He found a very satisfactory agreement. If we want to express B as a function of van der Waals constants a and b we have to transform slightly the equation of state. Instead of

$$(p+a/v^2)(v-b)=RT$$

we can write for small densities

$$\frac{pv}{RT}=1+\frac{b-a/RT}{v}+\frac{b^2}{v^2}+\cdots.$$

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[2] Falkenhagen, Phys. Zeits. **23,** 87 (1922).

and comparing with the virial equation of Kammerlingh Onnes

$$\frac{pv}{RT}=A+\frac{B}{v}+\frac{C}{v^2}+\cdots.$$

we find

$$B=b-(a/RT) \tag{3}$$

and we know that $b=(2\pi/3)Nd^3$, that is 4 times the volume of the molecules. Thus the experimental values of a and b, or B may be used to calculate the electric moment μ of the molecules.

For the metals we do not possess any experimental data concerning their equation of state, but we do have their vapor pressure curves. Now Planck[3] has given an equation for the vapor pressure as a function of van der Waals constants. This expression is easily obtained by integrating the relation

$$p=\frac{1}{v_1-v_2}\int_1^2 pdv$$

where the indexes 1 and 2 refer to the liquid and gaseous states. By using van der Waals expression for p, van Laar[4] obtains

$$\log p=-a/v_0RT-B\log T-CT+D$$

where v_0 is the volume of the gas at $T=0$, B, C and D are constants.

Thus by means of (3), (2) and (1), if we assume

$$(2\pi/3)Nd^3=4v_0$$

we can calculate the electric moment of the atoms from their vapor pressure curves. Van Laar[5] has already calculated v_0 and a for the alkali atoms from the experimental values of the vapor pressure p and we shall use his result to carry the calculations further. Table I shows the values of v_0 of a and of P_0.

TABLE I

van der Waals constants for alkali metals

v_0(cm^3/mole)	a(dynes cm^4/mole^2)		P_0(cm^3/mole)
	Na	K	Rb
v_0	22.25	43.25	52.35
$a\times10^{-10}$	3.365	5.250	5.825
P_0	62.7	107	110

The values of the molecular refraction P_0 are taken from Herzfeld.[6] With these values we obtain for $10^{18}\mu$ in gr$^{1/2}$ cm$^{3/2}$ sec^{-1} ϵ the following values .18, .24, and .27 for Na, K and Rb respectively. It is true that this is a

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[3] Planck, Thermodynamik p. 282 (6th edition).

[4] van Laar, Zustandgleichung p. 267.

[5] van Laar, Zeit. fur Anorg. Chemie 146, 263, and 148, 235 (1925).

[6] Herzfeld, Phys. Rev. **29**, 701 (1927).

very inaccurate way of determining the electric moment of atoms, for it is well known that the sodium vapor for instance, is composed of molecules Na_2 and of atoms. However, an investigation of the dielectric constant of metallic vapors is being carried out at the present time in our department and it is hoped that it will yield much more accurate values of the electric moment.

It is interesting to compare the values obtained above with those calculated from Bohr's theory of the atom. The valence electron of the alkalis is on a very elliptical orbit (for sodium a 3_1 orbit) which goes far outside of the other electronic shells. This orbit, being of the penetrating type, precesses very rapidly around the rest of the atom as Hoyt[7] has shown and thus the electrical dissymmetry of the atom is destroyed on the average by this precession and we would expect no electric moment. The values we have obtained above are so small, as will be shown below, as to be negligible and are thus more or less a verification of the theory of precessing penetrating orbits. If the orbit had not been precessing we would have expected an electric moment approximately equal to $e\bar{r}$ where e is the charge of the electron, and $\bar{r}$ its average distance from the nucleus. The value of $\bar{r}$ is[8]

$$\bar{r} = a(1+\tfrac{1}{2}\epsilon^2)$$

where ϵ is the eccentricity of the ellipse and a the major axis. If we take for a the value 10^{-8} cm and for ϵ, $(8/3)^{1/2}$ for a 3_1 orbit, we find $\bar{r} = 1.44\ 10^{-8}$ cm and

$$\mu = e\bar{r} = 6.9 10^{-18} gr^{1/2} cm^{3/2}\ \mathrm{sec}^{-1}\epsilon.$$

which is obviously incompatible with the electric moment of sodium derived above.

If we had assumed that the electric moments of the alkali atoms were zero, we could have calculated instead the electric moments of inertia by the method of Debye.[1]

Physics Department
University of Pittsburgh
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[7] Hoyt, Phys. Rev. **25,** 174 (1925).

[8] Born, Vorlesungen uber Atommechanik p. 164.