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# Long Range Interactions Between Dipole Molecules

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The first-order van der Waals forces between symmetrical top molecules which carry a dipole along their figure axis are calculated. Their strength is compared with that of other interactions, and found to be greater than London's second-order effect for linear dipoles over the main part of the range of the latter. A simple preliminary theory of the effect of these forces on the width of spectral lines in bands of polyatomic molecules is given, and it is shown that they lead to results of the correct order of magnitude.

THE van der Waals forces between dipole molecules have been worked out on the basis of quantum mechanics, and classified in a systematic manner, chiefly by F. London.[1] He finds that, in general, greatest importance is to be ascribed to the attractive forces arising from the dispersion effect, the electronic perturbations of high frequency. This is common to all molecular interactions and is independent of the presence of permanent poles. The potential due to dispersion forces varies (asymptotically) like $-1/R^6$, $R$ being the distance between interacting partners.

Besides this, there are the following effects specifically connected with dipole molecules: (1) The induction of an additional dipole moment due to the permanent moment of a partner, producing a small potential proportional asymptotically to $-1/R^6$. (2) The effect of molecular alignment which depends on the rotational quantum number and hence on the temperature distribution of the molecules. Its potential varies, at large distances, as $\pm 1/R^6$, but for close approach becomes proportional to $-1/R^3$, and relatively strong, for molecules in the lowest rotational state. The transition from the $1/R^6$ to the $1/R^3$ law takes place at distances of approach for which the perturbation energy becomes comparable with the normal separation of the rotational levels. (3) Resonance forces due to the possibility of exchanging a quantum of radiation, come into play when two interacting partners have rotational quantum numbers, $J$, differing by unity. They correspond to first-order interactions, have a potential proportional to $\pm 1/R^3$, and produce a symmetrical splitting of the rotational levels, which are, however, in general also lowered as a result of the other types of interaction mentioned above. These forces, clearly, have therefore the longest range, but their average over all orientations of the molecules is zero. Thus they are unimportant when interest is confined to properties of a dipole gas which depend on long time averages. But phenomena like the broadening of spectral lines depend on them quite essentially.

The present classification is sufficient as long as one is dealing with linear or diatomic dipole molecules, which indeed London chose as the model for his calculations. These exhibit no first-order Stark effect; hence their interactions bring about no removal of space degeneracy. With polyatomic dipoles the situation is different, for the symmetrical top gives rise to a linear Stark effect. We expect, therefore, a first-order splitting of the rotational levels on approach of two symmetrical top molecules. A calculation of this effect will be presented below. Although the treatment has not been extended to asymmetrical molecules, the results obtained will hold qualitatively for such cases as well.

We suppose that the top carries a dipole of moment $\mu$ along its figure axis. If the axes of two similar tops make angles $\theta_1$ and $\theta_2$ with the line, of length $R$, joining the molecular centers, their azimuths being $\varphi_1$ and $\varphi_2$, then the classical perturbation energy is

$$V = -\mu^2/R^3[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)]. \quad (1)$$

To set up the secular equation it is necessary to calculate the matrix elements of (1) between the unperturbed degenerate states of the top. These depend on the three quantum numbers $J$, $K$, $M$

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[1] F. London, Zeits. f. Physik **63**, 245 (1930).

corresponding to the three Eulerian degrees of freedom $\theta$, $\varphi$, $\chi$.[2] $V$ does not contain $\chi$; the matrix elements are therefore diagonal in $K$.

If the two interacting molecules have quantum numbers $J, K, M$ and $J', K', M'$, the unperturbed function representing their combined state is

$$\psi_{J,\,K,\,M;\,J',\,K',\,M'}=N(J,\,K,\,M)N(J',\,K',\,M')\,\Theta_{J,\,K,\,M}(\theta_1)\,\Theta_{J',\,K',\,M'}(\theta_2)e^{i(M\varphi_1+M'\varphi_2+K\chi_1+K'\chi_2)},$$

where the $N$'s are normalizing factors. We require the matrix elements for fixed values of $J, K, J', K'$, between the various permitted sets $M_i$, $M'_i$ and $M_j$, $M'_j$. Since $M$ runs from $-J$ to $+J$ and $M'$ from $-J'$ to $+J'$, our secular determinant will have $(2J+1)(2J'+1)$ rows and columns. In forming the elements, the integrations over the $\chi$'s and $\varphi$'s can be carried out immediately, the result at that stage being:

$$\begin{aligned}V_{J,\,K,\,M_i,\,J',\,K',\,M'_i;\,J,\,K,\,M_j,\,J',\,K',\,M'_j}&\\=-(\mu^2/R^3)N(M_i)N(M'_i)N(M_j)N(M'_j)\{&32\pi^4I_1(J,\,K,\,M_i)I_1(J',\,K',\,M'_i)\delta(M_j,\,M_i)\delta(M'_j,\,M'_i)\\&-8\pi^4I_2(J,\,K,\,M_i)I_3(J',\,K',\,M'_i)\delta(M_j,\,M_i-1)\delta(M'_j,\,M'_i+1)\\&-8\pi^4I_3(J,\,K,\,M_i)I_2(J',\,K',\,M'_i)\delta(M_j,\,M_i+1)\delta(M'_j,\,M'_i-1)\}\end{aligned}\tag{2}$$

with the following definitions of the integrals:

$$\left.\begin{aligned}I_1(J,\,K,\,M_i)&=\int_0^\pi\cos\theta\,\Theta^2_{J,\,K,\,M_i}\sin\theta d\theta=2\int_0^1(1-2x)\,\Theta^2_{J,\,K,\,M_i}(x)dx,\\I_2(J,\,K,\,M_i)&=\int_0^\pi\sin\theta\,\Theta_{J,\,K,\,M_i}\Theta_{J,\,K,\,M_i-1}\sin\theta d\theta=4\int_0^1x^{\frac12}(1-x)^{\frac12}\,\Theta_{J,\,K,\,M_i}(x)\,\Theta_{J,\,K,\,M_i-1}(x)dx,\\I_3(J,\,K,\,M_i)&=\int_0^\pi\sin\theta\,\Theta_{J,\,K,\,M_i}\Theta_{J,\,K,\,M_i+1}\sin\theta d\theta=I_2(J,\,K,\,M_i+1).\end{aligned}\right\}\tag{3}$$

The $\Theta$ functions are Jacobi polynomials, and the transformation from $\theta$ to $x$ is the usual one: $x=\frac{1}{2}(1-\cos\theta)$. $I_1$ is the integral which appears in the theory of the linear Stark effect; it has been calculated by Reiche and Rademacher, and by Manneback.[2] Its value is given by

$$N^2(M_i)I_1(J,\,K,\,M_i)=KM_i/(4\pi^2J(J+1)).\tag{4}$$

We have calculated $I_2$ by the reduction method as explained by Reiche and Rademacher. The details of the calculation are straightforward and hardly of sufficient interest to be set down here. The result is

$$\begin{aligned}N(M_i)N(M_i-1)I_2(J,\,K,\,M_i)&\\=\frac{\pm K[(J-M_i+1)(J+M_i)]^{\frac12}}{4\pi^2J(J+1)}&.\end{aligned}\tag{5}$$

Here the $-$ sign holds if the numerically greater of $K$ or $M$ is positive, the $+$ sign if it is negative, or if $K=-M$. (Except for its sign, Eq. (5) may be checked against Dennison's[2] intensity formulae to which it is related by the definition (3) of $I_2$.)

On putting these values of $I_1$, $I_2$ and $I_3$ into (2) we find, leaving off the fixed subscripts from $V$,

$$\begin{aligned}V_{M_i,\,M'_i;\,M_j,\,M'_j}=\frac{\mu^2}{R^3}\frac{KK'}{J(J+1)J'(J'+1)}\{&-2M_iM'_i\delta(M_j,\,M_i)\delta(M'_j,\,M'_i)\\&\pm\tfrac{1}{2}[(J-M_i+1)(J+M_i)(J'-M'_i)(J'+M'_i+1)]^{\frac12}\delta(M_j,\,M_i-1)\delta(M'_j,\,M'_i+1)\\&\pm\tfrac{1}{2}[(J+M_i+1)(J-M_i)(J'-M'_i+1)(J'+M'_i)]^{\frac12}\delta(M_j,\,M_i+1)\delta(M'_j,\,M'_i-1)\}.\end{aligned}\tag{6}$$

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[2] Cf. the familiar papers by Reiche and Rademacher, Manneback, Kronig and Rabi, and Dennison. The present notation is illustrated in Pauling and Wilson, *Introduction to Quantum Mechanics*, p. 276. For references cf. D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

With the use of these matrix elements we wish to determine the roots $\Delta E$ of the secular equation, $\det(V_{ij}-\Delta E\delta_{ij})=0$. If arranged properly, all elements of the determinant will be zero except those in, and adjacent to, the principal diagonal. The most convenient way of factoring the determinant is the following.

We observe by inspecting (6) that a state function characterized by $M_iM'_i$ gives a nonvanishing matrix element only by combination with another state $M_jM'_j$ if $M_j+M'_j=M_i+M'_i$. Thus if the states $M\ M'$ are divided into sets so that, for each set, $M+M'$ is constant, and if we number the members of each set consecutively, the determinant consists of diagonal squares and hence factors immediately. Since there is but one member, namely $M=J$, $M'=J'$, in the set for which $M+M'=J+J'$, this particular state combines only with itself, and the corresponding matrix element is a root of the secular equation. Closer analysis shows that it is not in general the largest root, but that it lies near the edge of the pattern. It may therefore serve as an indication of the magnitude of the splitting. Its value is obtained, of course, from (6) by putting $M_i=M_j=J$, $M'_i=M'_j=J'$, which yields

$$\Delta E_1=-\frac{2\mu^2}{R^3}\frac{KK'}{(J+1)(J'+1)}. \tag{7}$$

This is a double root, because it results also from the diagonal element of the state $M=-J$ and $M'=-J'$. (7) suggests at once the formula for the linear Stark effect

$$\Delta E_1=\mu F\frac{KM}{J(J+1)}$$

and shows its relation with the interaction here considered, since the greatest Stark displacement is given by $\mu FK/(J+1)$ which is very similar to (7).

The arrangement of the elements in sets just discussed causes the determinant to consist of square blocks along the diagonal, increasing in size up to the $(2J+1)^{\text{rst}}$ which has the maximum number $(2J+1)$ of rows and columns.[3] They continue to have this size up to the $(2J'+1)^{\text{rst}}$ block and then decrease again. The entire determinant is symmetrical about the midpoint of the principal diagonal. Hence all roots, except those arising from the central block, are double.

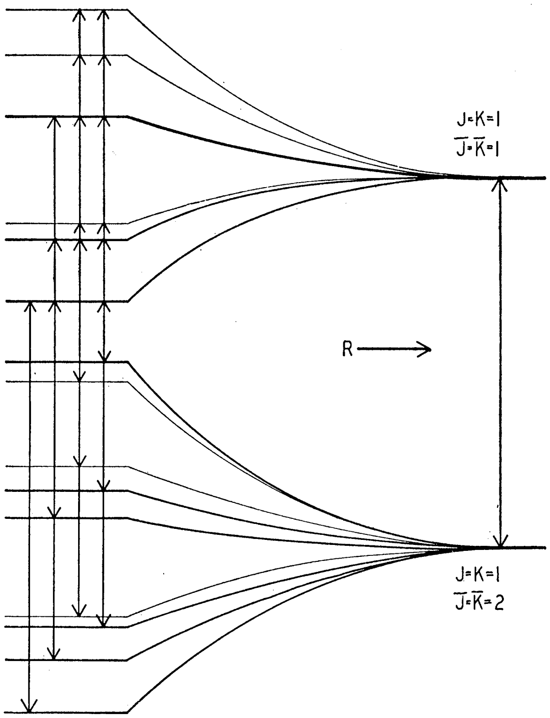

FIG. 1. Splitting of energy levels on approach of two molecules, one in the state $J=K=1$, the other in state $J'=K'=1$ for the upper diagram, $J'=K'=2$ for the lower diagram. Light lines indicate single levels, heavy lines double levels. The arrow heads on the vertical lines mark the allowed transitions (40 in all).

In the general case, many of the roots are irrational, and no closed formula can be given for the splitting of the levels. But it can always be computed with relative ease by the method just outlined. As seen from (6), the lowest level ($J=0$) undergoes no perturbation of the kind in question, because its $K$ value is zero. For the case of two tops, with $|K|=|K'|=1$, each having one quantum of rotational energy, the roots are

$$-2,\ -1,\ 1-\sqrt{3},\ +1,\ +2,\ 1+\sqrt{3}$$

in units $\mu^2/4R^3$. The first, second and fourth of these are double, the others single. This situation is illustrated in Fig. 1. In Fig. 1 we have also plotted as another example the splitting of the levels occurring when two molecules, one with $J=1$, the other with $J'=2$, approach each other.

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[3] We are assuming here that $J'>J$. There are thus altogether $2\sum_{n=1}^{2J} n+(2J'-2J+1)(2J+1)=(2J+1)(2J'+1)$ rows.

That the present effect cannot take place for molecules with only one moment of inertia is clear. The eigenfunctions and energies of a symmetrical top go over into those of a linear molecule if we let $K$ be zero. But then all the matrix elements (6) vanish.

## II

To calculate the second-order interactions between two symmetrical tops would not be difficult. But one would expect the result to be very similar to that obtained by London[1] for diatomic molecules. Let us then, in order to arrive at an estimate of relative magnitudes, compare the present results with those of London. For the lowest rotational state, the second-order forces are the only ones present. If $J=1$, $J'=1$, however, the first-order forces here computed are generally predominant. To illustrate this we recall that, for $|K|=|K'|=1$, (taking the second largest root)

$$|\Delta E^{(1)}|=\frac{1}{2}\frac{\mu^2}{R^3}, \tag{8}$$

while

$$|\Delta E^{(2)}|=\frac{1}{6B}\frac{\mu^4}{R^6},\quad B=\frac{h^2}{8\pi^2 A}. \tag{9}$$

Both these formulae are valid only as long as the perturbation energy is considerably smaller than the normal separation of the lines; i.e., if $\Delta E<B$. What happens on closer approach is discussed by London. Now

$$\frac{|\Delta E^{(1)}|}{|\Delta E^{(2)}|}=3B\frac{R^3}{\mu^2}.$$

If we assume $B=1.8\times 10^{-15}$ ergs, $\mu=1.5\times 10^{-18}$ e.s.u., this ratio is unity for $R\approx 7$A. Thus for distances greater than this, $\Delta E^{(1)}$ predominates, and $\Delta E^{(2)}$ becomes rapidly insignificant in comparison with it. It might also be remarked that at $R=7$A, $\Delta E$ is already greater than $B$, so that there is in this example no range at all in which formula (9) is both accurate and important. This situation is quite general for large values of $K$ and $K'$, as may be seen from (7).

The equation of state of dipole gases is not affected by the interactions considered in this paper, except at low temperatures. It is known that for ordinary temperatures, at which most measurements are made, the sum of state is sufficiently well approximated by the classical phase integral.

The influence on the broadening of molecular band lines should be more appreciable. The present inquiry has indeed been stimulated by a suggestion due to Watson[4] who concludes, on the basis of a survey of experimental data regarding pressure effects, that the lines of some polyatomic molecules seem more effectively broadened than those of linear ones. The experimental data are as yet very qualitative. Great difficulties arise from lack of resolution of the lines and from the fact that an exact assignment of quantum numbers has not been achieved. Moreover, in the case of parallel type bands, where the structure is most intelligible, the band lines are composite, consisting of a superposition of lines for all values of $K$. Since the splitting of the levels is proportional to $K$, the broadening of a spectral line is due to a superposition of patterns of the type shown in Fig. 1, but on different scales. For each value of $K$, the actual pattern is further greatly complicated by the velocity effect.

To get a rough measure of line widths, we first calculate the average spread of a pattern for given $J$, $J'$, $K$, $K'$. Let the roots of the secular determinant whose matrix elements are given by (6), if measured in units of

$$\frac{\mu^2}{R^3}\frac{KK'}{J(J+1)J'(J'+1)},$$

be denoted by $\epsilon_1, \epsilon_2, \cdots \epsilon_n$, where

$$n=(2J+1)(2J'+1),$$

and each root is counted as many times as it occurs. Then the secular equation becomes

$$\det(V_{ij}-\epsilon\delta_{ij})=\prod_{i=1}^{n}(\epsilon-\epsilon_i)$$
$$=\epsilon^n-a\epsilon^{n-1}+b\epsilon^{n-2}-\cdots+x=0. \tag{10}$$

The form of the determinant shows at once that

$$a=\sum_i \epsilon_i=\sum_i V_{ii}.$$

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[4] W. W. Watson, J. Phys. Chem. **41**, 61 (1937), especially symposium discussion in later issue. We wish to express our thanks to Professor Watson for many interesting discussions.

But the sum of the diagonal elements of (6) is

$$\sum_{M_i=-J}^{J}\ \sum_{M'_i=-J'}^{J'} 2M_iM'_i=0.$$

We see thus that there is no shift in the weighted mean of the perturbed energy levels. Next, let us find the root mean square displacement. Consider the coefficient $b$ of (10).

$$\begin{aligned} b&=\sum_{i>j}(V_{ii}V_{jj}-V_{ij}^2)\\ &=\tfrac{1}{2}\sum_i\epsilon_i\sum_j\epsilon_j-\tfrac{1}{2}\sum_i\epsilon_i^2=-\tfrac{1}{2}\sum_i\epsilon_i^2. \end{aligned}\tag{11}$$

On the other hand,

$$\sum_{i>j}(V_{ii}V_{jj}-V_{ij}^2)=\sum_{i,\,j}\tfrac{1}{2}V_{ii}V_{jj}-\sum_i\tfrac{1}{2}V_{ii}^2-\sum_{i>j}V_{ij}^2.$$

If now we insert values from (6) we obtain

$$\begin{aligned} b&=2\sum_{M_i,\,M_j}\ \sum_{M'_i,\,M'_j} M_iM'_iM_jM'_j-2\sum_{M_i,\,M'_i}M_i^2M'^2_i\\ &\quad-\tfrac{1}{4}\sum_{M'_i,\,M'_i}(J^2-M_i^2+J+M_i)(J'^2-M'^2_i+J'-M'_i)\\ &=0-\tfrac{2}{9}J(J+1)(2J+1)J'(J'+1)(2J'+1)\\ &\quad-\tfrac{1}{4}[(J^2+J)(2J+1)-\tfrac{1}{3}J(J+1)(2J+1)]\\ &\qquad\times[(J'^2+J')(2J'+1)-\tfrac{1}{3}J'(J'+1)(2J'+1)]\\ &=-\tfrac{1}{3}J(J+1)(2J+1)J'(J'+1)(2J'+1). \end{aligned}$$

By reason of (11), this expression, if multiplied by $-2$, is the sum of the squares of all the roots. To get the root mean square spread of the levels, we divide by $n$ and extract the square root. Hence

$$\begin{aligned} (\epsilon_i^2)_{\mathrm{Av}}^{\frac{1}{2}}&=[\tfrac{2}{3}J(J+1)J'(J'+1)]^{\frac{1}{2}},\\ [(\Delta E)^2]_{\mathrm{Av}}^{\frac{1}{2}}&=\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{\mu^2}{R^3}\frac{KK'}{[J(J+1)J'(J'+1)]^{\frac{1}{2}}}. \end{aligned}\tag{12}$$

Inasmuch as the present type of interaction causes no mean shift, and is proportional to $R^{-3}$, it is very similar to resonance forces between atoms. But if spectral lines are broadened by resonance interactions for which the potential has the form

$$\Delta E=\pm B/R^3,$$

the lines are known[5] to have an approximate half-width $\Delta\nu_{\frac{1}{2}}\approx\frac{4}{3}\pi^2B/h\cdot N$, where $N$ is the number of atoms per cc. Now while it is indefensible in detail to identify the splitting patterns calculated in part I with *any* pattern which has the same standard deviation, an approximate estimate of the line width may certainly be obtained by identifying the constant $B$ in the law for resonance forces with the constant

$$\left(\frac{2}{3}\right)^{\frac{1}{2}}\frac{\mu^2}{h}|KK'|[J(J+1)J'(J'+1)]^{-\frac{1}{2}}$$

in (12). We find

$$\Delta\nu_{\frac{1}{2}}\approx\pi^2\frac{\mu^2}{h}N|KK'|[J(J+1)J'(J'+1)]^{-\frac{1}{2}}.\tag{13}$$

This is, approximately, the line width caused by the effect here considered. Its isolation from other effects is, of course, an idealization, since line widths due to various causes may not be simply added. But at lower pressures it is likely to be the dominant cause of line broadening in polyatomic molecules.

Formula (13) refers only to one set of values $J, K, J', K'$, whereas a spectral line involves two, the one just mentioned, and $J\pm1$ or 0, $K\pm1$ or 0, $J', K'$. The diffuseness of both will appear in the line. The exact manner in which they are to be combined is complicated. For the present purpose it will suffice to regard the quantum numbers appearing in (13) as mean values for the two states in question, since they do not differ by more than unity. The breadth is seen to depend on $J, J'$ in a different way than it does for linear molecules.[6]

In any practical application of formula (13) to the spectra of polyatomic molecules one is confronted with the difficulty that the quantum numbers are not in general known, and that a single line may involve numerous different values of $K$. It will be observed, however, that the factor $|KK'|[J(J+1)J'(J'+1)]^{-\frac{1}{2}}$ is always smaller than unity and has a weighted mean around $\frac{1}{2}$. Remembering this, the effect (13) is found to be about 20 times as weak as the self-broadening of atomic resonance lines.

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[5] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 43 (1936).

[6] Line widths for linear dipole molecules were discussed recently by W. W. Watson and H. Margenau, Phys. Rev. **51**, 48 (1937).

For $NH_3$ at atmospheric pressure, the value of $\Delta\nu_{\frac{1}{2}} \approx \frac{1}{2}\pi^2(\mu^2/h)N$ comes out to be $4.5\times10^{10}$ sec.$^{-1}$ $=1.5$ cm$^{-1}$. Cornell,[7] in measurements made in this laboratory, finds an average half-width of 1.45 cm$^{-1}$ in the 7920A band of $NH_3$, and of 0.81 in the 10,230A band. The agreement as to order of magnitude is gratifying in view of the present inaccuracies in both experiment and theory.

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[7] S. D. Cornell, Phys. Rev. this issue. We are indebted to Mr. Cornell for the use of his material before publication.

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# Vapor Pressure of Caesium by the Positive Ion Method

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The positive ion currents from pure tungsten filaments in saturated caesium vapor at bulb temperatures from −35°C to +73°C were measured for filament temperatures from 1000° to 1800°K. The results were corrected for the cooling effect of the leads and for photoelectric emission from the caesium film on the platinum deposited on the bulb which was used as an ion collector. The vapor pressures in mm of Hg are given for solid Cs ($T<302°$K) by

$$\log_{10}p_S=10.5460-1.00\log_{10}T-4150/T$$

and for liquid Cs ($T>302°$K) by

$$\log_{10}p_L=11.0531-1.35\log_{10}T-4041/T.$$

The vapor pressures given by these equations are believed to be accurate to within one percent from 220° to 350°K, within 3 percent up to 600° and within about 8 percent at 1000°K.

In some early studies of the effects of caesium vapor on thermionic phenomena[1, 2] it was observed that with a negatively charged cylinder surrounding a hot filament, positive ion currents were obtained which are independent (over wide ranges) of filament temperature and of voltage, but increase rapidly as the caesium vapor pressure is raised. These results were interpreted as indicating that every caesium atom which strikes a filament (above about 1200°K) is converted into an ion. The ion current thus serves as a measure of the pressure.

The vapor pressure $p$ of caesium, in baryes, was found to be accurately expressed (in a temperature range from 0 to 40°C) by the equation

$$\log_{10}p=10.65-3992/T. \tag{1}$$

The experimental data and the details of the method by which this equation was obtained have not been published.

These results have been criticized by Rowe[3] who compared them with measurements of Kröner[4] in the range from 250° to 350°C. Rowe found that Kröner's data could be expressed by

$$\log_{10}p_{mm}=7.165-3966/T, \tag{2}$$

while Eq. (1) expressed in the same units is

$$\log_{10}p_{mm}=7.525-3992/T. \tag{3}$$

The Langmuir-Kingdon (L-K) values of Eq. (3) are greater than those calculated from Kröner's data by a factor that varies from 1.85 at 27°C to 2.02 at 327°C. Rowe believed that the positive ion method is at fault, and that the discrepancy can be explained by assuming that the caesium ions that leave the filament have a double charge.

More recently Taylor and Langmuir[5] have measured the limitations of the caesium ion current by space charge in a cylindrical collector.

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* Dr. Taylor died January 22, 1937.

[1] I. Langmuir and K. H. Kingdon, Phys. Rev. **21**, 380 (1923) and Science **57**, 58 (1923).

[2] I. Langmuir and K. H. Kingdon, Proc. Roy Soc. **A107**, 61 (1925).

[3] H. Rowe, Phil. Mag. **3**, 544 (1927).

[4] A. Kröner, Ann. d. Physik (4) **40**, 438 (1913).

[5] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933); see especially p. 442.