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FINAL REPORT

on

IONIZATION IN GASES

For Period Thru

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FINAL REPORT OF RESEARCH ON THE IONIZATION
OF GASES AND THE AVERAGE ENERGY TO MAKE
AN ION PAIR

William P. Jesse

All the experiments of this year on the ionization of gases were carried out in the high temperature chamber, which has been developed and was described in some detail in the report of last year. In spite of formidable difficulties the chamber with its teflon insulators has performed with reasonable reliability.

IONIZATION MEASUREMENTS IN MERCURY VAPOR WITH BETA
PARTICLES AND THE MEAN ENERGY TO FORM AN ION PAIR

The results of these experiments were discussed in some detail in our last report and have since been published [Jour. Chem. Phys. 55, 3603, October 1971]. A reprint of this paper is included in this report. Any further discussion here would thus seem superfluous.

IONIZATION MEASUREMENTS IN WATER VAPOR WITH BETA
PARTICLES AND THE MEAN ENERGY TO FORM AN ION PAIR

As was pointed out in our last report, it should be of interest to biologists to have a reliable value of W , the mean energy to form an ion pair in water vapor.

To this end measurements were made in the high temperature chamber on the vapor of water which had been distilled into the chamber. These measurements followed the technique used for pure mercury vapor. The ionizing agent was again the beta particles from ^{63}Ni and a comparison in relative ionization was made with the chamber filled with pure argon. The best values obtained were $W_{\text{H}_2\text{O}} = 29.7 \pm 0.2$ eV/ion pair, relative to argon taken as $W = 26.4$ eV/ion pair.

This is slightly lower value than the value of 29.9 eV/ion pair obtained by Adler and Bothe [Z. Naturforsch 20a, 1700 (1965)] with the beta particles from ^{63}Ni . Here a relative ionization comparison was made with air with W taken to be 33.8 eV/ion pair.

A similar result of 29.9 ± 0.5 eV/ion pair was obtained by Booz and Ebert [Strahlen-therapie 120, 7 (1963)] obtained relative to air ($W = 33.8$ eV/ion pair). The ionizing source in this case consisted of X-rays of 100 to 300 KeV.

For comparison with the ionization values for H_2O vapor in our experiments a few tentative measurements were made with the vapor of D_2O under the same conditions. The isotopic purity of the D_2O was estimated as 99.7% by the supplier.

The ionization vs vapor pressure curves for D_2O were found to be about two percent higher than those for H_2O in the plateau region. This is in general agreement with the ratio obtained in a similar comparison of deuterated and undeuterated hydrocarbon gases [Jour. Chem. Phy. 38, 2774 (1963)]. The present measurements in water vapor, however, do not have the very high precision attained in the hydrocarbon gases.

IONIZATION STUDIES IN MIXTURES OF ARGON AND MERCURY VAPOR

These experiments were discussed at some length in our last years report. They would seem of some importance, since they are the first where the lower excited states of argon can be discharged by the ionization of a monatomic contaminant.

A pool of mercury is enclosed in an atmosphere of argon in the high temperature test chamber, and the total ionization in the mixture is measured as the vapor pressure of mercury increases with the rising chamber temperature. The ionization, relative to that in pure argon, is then plotted as in previous experiments against the atomic concentration of mercury in argon as in Fig 1.

In calculating such a concentration one makes an estimate of the vapor pressure of mercury from a thermal couple temperature reading at the base of the chamber. As before (see enclosed reprint) the mercury pool is maintained at the coolest part of the chamber. To obtain the desired concentration of mercury in argon one then divides the estimated mercury vapor pressure by the pressure of argon corresponding to the temperature of the mercury vapor. This is, of course, calculated from the initial measured argon pressure at room temperature by the use of Charles Law.

Characteristic curves for the relative ionization measured in mercury argon mixtures against the atomic concentration of mercury argon are shown in Fig 1. As in previous experiments [Phy. Rev. 100, 1755 (1955)], as the concentration of mercury molecules increases the observed ionization increases over that found in pure argon. This increase is at first rapid and then slower until finally a relatively constant ionization current

value is attained. This maximum value has been unexpectedly hard to determine with exactness, since somewhat varying values have been obtained. This maximum value would seem however, to be approximately about 30 percent higher than that for pure argon. Such an increase is somewhat less than the 40 percent predicted by Platzman's approximate formula. This is not astonishing since the formula represents only a rough approximation.

It is interesting to note that the 30 percent maximum increase is almost the same as that obtained by Hurst and his co-workers and by ourselves for acetylene in argon. This was the highest increase for any hydrocarbon contaminant so far found by the Hurst group.

One may observe in Fig 1 the marked dependence of the measured ionization upon the pressure of the mixture in the chamber. The pressures noted in the diagram are the initial pressures of argon introduced into the chamber at room temperature. These pressures of course increase, as do those of the mercury component, as the temperature of the chamber is raised.

It is useful to plot ionization data of this sort in the form of a Stern-Volmer plot following the method outlined in some detail in our former paper [*Phy. Rev.* 100, 1755 (1955)]. This has been done in Fig 2 from a characteristic array of data comprising four initial argon pressures ranging from 89.3 cm to 36.5 cm of Hg.

From the resulting straight line plots in Fig 2 it has been shown in the reference cited that it is possible to determine values of K_i/K_d , where K_i is proportional to the probability of ionization of the contaminant molecule, and K_d is proportional to the probability for the alternative radiative process. The ratio K_i/K_d is in fact equal

to the ordinate intercept $\frac{1}{\alpha_0}$ divided by the slope of the straight line drawn for each pressure run. The results from such computations are shown in Table 1.

Table 1

Computation of K_i/K_d

Initial argon pressure at room temp. in cm of Hg	Intercept $\frac{1}{\alpha_0}$	Slope of line	Calculated K_i/K_d $= \frac{\text{intercept}}{\text{slope}}$
36.5	3.30	5.4×10^{-3}	611
70.4	3.30	3.83×10^{-3}	862
80.3	3.20	2.15×10^{-3}	1488
89.3	3.20	1.82×10^{-3}	1758

It will be seen that the calculated value of K_i/K_d rises continuously as the initial pressure of the added argon is increased. It should be noted that we have indicated in column one the initial pressure of the argon filling at room temperature. In the temperature range from 20°C to 200°C employed the argon pressure increases markedly as the temperature rises, as does of course the overall pressure of the mixture, which is approximately the same as the argon pressure.

In Fig 3 is plotted a composite of three separate runs showing this pressure variation of K_i/K_d . The agreement for the plotted points leaves something to be desired, but there seems to be no question qualitatively that there is a distinct pressure effect and

that K_i/K_d rises with the pressure.

The exact mathematical relation between the values for the ratio K_i/K_d and the pressure is harder to determine with certainty because of the scatter of experimental points. The direct proportionality between K_i/K_d and the pressure, as indicated by the straight line drawn on the diagram, would seem as good a guess as any available.

In this connection it is very interesting to mention a direct relation observed during the course of the experiments between the ionization measured relative to pure argon and the absolute vapor pressure of mercury measured in torr. This relation is plotted in Fig 4. Here experimental points with three initial pressures of argon are shown. Regardless of the pressure of the argon used all these points seem to cluster along the same curve shown drawn in the diagram. Here the ionization observed is within the limits of error of the measurements, quite independent of the pressure of argon employed. On the other hand when we plot the measured ionization against the relative concentration of mercury in argon (Fig 1) we get a marked difference in the curves for different argon pressures.

Discussion

The cause of this pressure effect with concentration of mercury in argon is still very puzzling. It should be noted that this is quite different from the results obtained with contaminants in helium (see 1955 paper noted) where the ratio K_i/K_d is either relatively constant or is even decreased as the pressure of the mixture increases. This decrease was explained in the paper cited from a three body reaction involving K_d .

The marked increase of K_i/K_d with mixture pressure in the present experiments may perhaps indicate an entirely different mechanism of interaction from the experiments in helium mixtures.

A truly valid explanation of the observed pressure effect must await intensive study of the results and of the literature bearing on the subject. One can at the moment indulge only in very vague speculations which are hardly profitable to discuss here at length.

LEGENDS FOR FIGURES

Fig 1.

A plot of the ionization measured in the mixture relative to that in pure argon against the concentration of Hg in Ar in parts per 10,000 by volume. Curves are shown for three initial argon fillings at room temperature at pressures 89.4 , 70.3 and 36.3 cm of Hg. Experimental points for several runs are indicated. Experimental points on the central curve have been omitted to avoid undue crowding in the diagram.

Fig 2.

Stern-Volmer plots where $1/(N_p - N_o)$ is plotted against $1/C$ the reciprocal of the concentration of mercury in argon. $(N_p - N_o)$, which follows the notation of a previous paper, is here essentially proportional to the increase of the measured ionization relative to argon which accompanies a given concentration of mercury in argon. The marked decrease of the slope of the lines with increased initial argon pressures should be noted.

Fig 3.

A composite curve showing the ratio K_i/K_d plotted against the initial mixture pressure in cms of Hg at room temperature. Three sets of data are shown.

Fig 4.

The ionization measured in the mixture, relative to pure argon, plotted against the absolute vapor pressure of mercury in torr for three different initial mixture pressures. Note that the experimental points for three different pressures follow the same curve.

Fig.1

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