Similarly

$$C_1 = \frac{CK_1(H_2PO_4^-)}{1 + K_1(H_2PO_4^-) + K_2(H_3PO_4)} \qquad (13)$$

and

$$C_2 = \frac{CK_2(H_3PO_4)}{1 + K_1(H_2PO_4^-) + K_2(H_3PO_4)} \qquad (14)$$

Combination of equations 9, 12, 6 and 14 gives

$$\epsilon_0 = \frac{\epsilon_1 K_1(H_2PO_4^-) + \epsilon_2 K_2(H_3PO_4^-) + \epsilon_3}{1 + K_1(H_2PO_4^-) + K_2(H_3PO_4)} \qquad (3)$$

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[CONTRIBUTION FROM MOUND LABORATORY, A. E. C. INSTALLATION[1a]]

The Vapor Pressures of Tellurium and Selenium

BY L. S. BROOKS[1b]

The vapor pressures of tellurium and selenium have been measured with quartz Bourdon gages, with the following results:

	A	B	T_b	L_v
Tellurium	7.5999 ± 0.0136	5960.2 ± 14.5	989.8 ± 3.8	27.26 ± 0.07
Selenium	8.0886 ± 0.0048	4989.5 ± 4.5	684.9 ± 1.0	22.82 ± 0.02

in which A and B are constants in the equation $\log p = A - B/T$, p is the pressure in mm., T the absolute temperature, T_b the boiling point in degrees centigrade and L_v the latent heat of vaporization in kcal./mole, the probable errors being stated in each case.

Introduction

The vapor pressures of tellurium and selenium have been measured with quartz Bourdon gages, at pressures up to about one-third atmosphere for tellurium, and just over one atmosphere for selenium. Earlier work with tellurium was done by Doolan and Partington[2] with a transport method that yielded values at 0.46, 3.34 and 14.1 mm., and by Schneider and Schupp[3] with the same method with improvements, in the range 8.15 to 67.2 mm. The vapor pressure above the solid was observed by Niwa and Sibata[4] between 0.887 and 45 × 10^{-3} mm. Selenium was studied by Le Chatelier[5] who obtained a boiling point of 688°, followed by Berthelot,[6] Preuner and Brockmöller,[7] Dodd,[8] Neumann and Lichtenberg,[9] Niwa and Sibata[10] and Selincourt.[11] Of these, only Preuner and Brockmöller worked over an extended range (3 to 970 mm.), and their results differ from those of Selincourt in the vicinity of the boiling point. The results of the present work, which covers the range from about 0.4 to 786 mm., are in agreement with those of Selincourt.

Experimental

Tellurium was measured with a quartz spiral gage[12] and a sickle gage, identified as P and Q, respectively, and selenium with three different sickle gages, M, N and O. The general design of the sickle gage apparatus is shown in Fig. 1 with the gage assembly directly above the temperature control apparatus in which it is placed for a run. The gage is used as a deflection instrument at low pressures and as a null device at higher pressures as described below.

Temperature Control.—The sample bulb with its thermocouple well at G, Fig. 1, is placed in a copper cylinder 20 cm. long and 7.5 cm. in diameter, in which the temperature is maintained stable and uniform in a region centered about point W. A smaller cylinder, 10 cm. long and 5 cm. in diameter, was used for the first tellurium experiment with the spiral gage, and a check performed after completing the measurements showed that temperature gradients of several tenths of a degree per cm. existed along the axis of the block, enough to allow temperature uncertainties of a degree or two to exist. The large cylinder was used thereafter, and tests under simulated operating conditions showed that a temperature uniform within 0.1° could be maintained over a region of 8 cm. along the axis, centered on point W, the location of the sample thermocouple junction. Auxiliary windings on the ends of furnace B were used to control the temperature distribution.

During operation the temperature of the cylinder as indicated by a thermocouple at K and that of the sample at W were brought into equilibrium within 0.1°. The absence of a temperature gradient between points U and V in the cylinder was checked during each measurement with a movable thermocouple. Additional thermocouples at L and J were used to ascertain that the temperatures of the connecting tubing and the gage bulb were above that of the sample bulb. Furnace A was used to keep the gage bulb at a constant high temperature, generally 750°. The connecting furnace C prevented the occurrence of a cold spot between furnaces A and B.

The platinum-10% rhodium thermocouples used to measure the temperature at W were calibrated by the procedure of Roeser and Wensel[13] with standard melting point samples of metals from the National Bureau of Standards.

Pressure Measurements.—The deflection of the sickle gage pointer was observed through a quartz window at Y by means of a viewing telescope with a micrometer eyepiece. The sensitivity of each gage was about 0.02 mm. per scale division as calibrated by introducing air into the jacket surrounding the gage bulb with the sample bulb cold. Deflections of the gage were used to measure pressures up to about 3 mm. Above that value, the pressure was balanced by admitting air or nitrogen, the balancing pressure being measured with a closed tube mercury manometer that had a precision of 0.05 mm. The manometer readings were reduced to equivalent mercury columns at 0° and corrected

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[1] (a) Operated by Monsanto Chemical Company, Miamisburg, Ohio, under Contract AT-33-1-GEN-53; (b) Physics Department, University of Michigan, Ann Arbor, Michigan.

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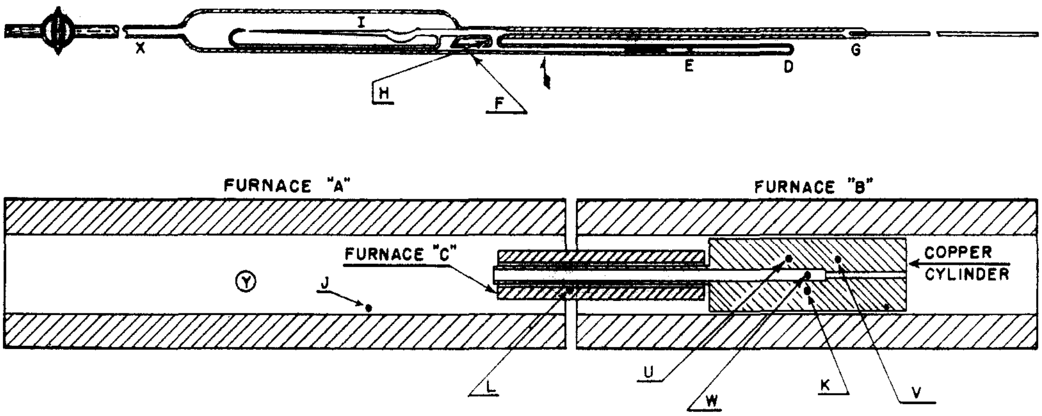

Fig. 1.—Quartz sickle gage with preparation tube and temperature control apparatus.

for the amount of unbalance indicated by deflections of the gage.

The null positions of the gages were observed at the beginning and end of each day's measurements when the metal was cold and the gage bulb was at the constant temperature used during the measurements. The null positions for sickle gages M, N and O, which were kept at 750°, remained constant within a distance equivalent to 0.1 mm. of pressure. The null position for spiral gage P which was kept at 880° drifted a distance equivalent to about 2 mm. during the first 2 days and about 5 mm. during the third day. The null position for gage Q drifted a distance equivalent to about 0.6 mm. pressure each day on days 1, 2, 4 and 5 when the sickle manometer was at 760°, and it shifted a distance equivalent to about 4 mm. pressure during the third day when the gage was at 860°. The drift of the null positions was the major uncertainty in the measurements. In order to correct as well as possible for the change of null position during a day's measurements, a correction was applied based on the assumption that the drift occurred uniformly with time.

Sample Preparation.—The tellurium used in gages P and Q was first purified by L. Marchi by the method of E. Keller.[14] It was then volatilized for 45 hours at 500° and at a pressure of 0.2 mm. or less. It formed large silvery rhombohedral crystals. A spectrographic analysis showed the presence of 0.001 ± 0.0005% copper. The sample for gage Q was further fractionally distilled in a vacuum, reduced in a hydrogen atmosphere for 4 hours while heated to 450° in a final preparation tube, evacuated to 8×10^{-8} mm. and sealed into a preparation tube as shown at ED in Fig. 1.

The selenium used in gages M, N and O was supplied by Eimer and Amend Co. with the description "Selenium, Powder (N free), Special for Micro Analysis." It was further purified by the method described by Neumann and Lichtenberg[15] which yielded selenium in the black crystalline form. A spectrographic analysis showed 0.02 ± 0.01% silicon, 0.008 ± 0.004% boron and 0.003 ± 0.0015% copper. Portions of the crystals for gages M and N were placed in quartz distillation tubes and heated to 350° while evacuated to about 10^{-6} mm. In each case, the selenium condensed in a single ring on the unheated portion of the tube leaving no visible residue behind. The distilled samples were sealed in tubes like ED of the preparation tube shown in Fig. 1. The crystals which were used for gage O were given a preliminary distillation and heated to 200° for 4 hours while being evacuated in order to remove any selenium oxide, before being handled as described above.

The preparation tube was sealed on to the gage assembly at the arrow in Fig. 1. The apparatus was then placed in furnaces extending from G to X, attached to a vacuum system through stopcock S, and outgassed. Gages M, N and P were outgassed by heating to 800° for an hour while being evacuated to 10^{-5} mm. However, consideration of the findings of Biltz and Müller[16] led to a more thorough outgassing treatment of gages O and Q. Gage O heated to 800°, and Q to 900° were evacuated to 10^{-4} mm. for 14 hours, filled with oxygen to 620 mm. pressure, evacuated and flushed twice with dry nitrogen, and evacuated to less than 10^{-5} mm. for 6 hours. After the evacuated apparatus cooled, the crack-off tip at E was broken with the striker, and the tubing was sealed shut at F. The sample was moved to end G of vessel G-H-I by distillation. The tubing at H was then sealed, and the preparation tube was sealed off and removed.

The present measurements[17] of the vapor pressure of tellurium and selenium, respectively, are represented by the equations

$$\log p = \frac{-5960.2 \pm 14.5}{T} + 7.5999 \pm 0.0136$$

$$\log p = \frac{-4989.5 \pm 4.5}{T} + 8.0886 \pm 0.0048$$

in which p is the pressure in mm., T is the absolute temperature, and the probable errors are stated. The equations were computed from the experimental data by the method of least squares, weighting the pressure according to the square of the pressure. Latent heats of vaporization computed from the equations are 27.26 ± 0.07 kcal./mole for tellurium and 22.82 ± 0.02 kcal./mole for selenium.

The equation for tellurium represents 30 determinations with gage Q of the vapor pressure between 1.1 and 161 mm. Extrapolation with this equation yields a boiling point of 989.8 ± 3.8° in contrast with the value of 1390° quoted by Yost and Russell.[18] Earlier measurements of the vapor pressure of tellurium were made by observing the loss of weight of a sample of metal in a silica boat when a measured quantity of a carrier gas passed over the sample. The earlier measurements neither gave results consistent with each other nor with the present results and were widely scattered above and below the vapor pressure curve for the present data, which is both consistent and obtained from a more direct measurement.

The equation for selenium represents 48 measurements of the vapor pressure with three gages between 0.06 and 786.3 mm. The equation gives a boiling point of 684.9 ± 1.0° in comparison with Selincourt's[10] value of 684.8 ± 0.1°. The fact that the present measurements are confirmed at the boiling point by the careful determinations of Selin-

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court but are, in general, higher than those of Preuner and Brockmöller sustains their suggestion of a systematic error in their temperature measurements.

MIAMISBURG, OHIO RECEIVED APRIL 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

The Inductive Effect and Chemical Reactivity. II. Reactions of Halides with Sodium Atoms[1]

BY RICHARD P. SMITH[2] AND HENRY EYRING

The application of the theory presented in the first paper of this series to the calculation of charge distributions in halogen-substituted alkanes is discussed. Net charges on halogen atoms in a number of aliphatic halides, as well as X_2 and HX molecules, are calculated and used for a discussion of heats of activation for the sodium "flame" reactions. It is found that, for molecules having C–X and H–X bonds, the heats of activation are linear in the halogen net charges divided by the C–X or H–X bond polarizabilities. Possible reasons for this correlation are discussed.

Introduction

In the first paper of this series,[3] hereafter referred to as Part I, we have shown, with two others, how approximate charge distributions may be calculated for molecules in which the bonds are essentially localized, such as saturated molecules and molecules with isolated multiple bonds. Qualitatively, the theory relates bond dipole moments primarily to the different effective nuclear charges of the atoms concerned, the effective nuclear charges themselves decreasing as the electron densities on the atoms increase, and *vice versa*. Thus while methyl chloride and chloroform would have the same dipole moments if there existed additive "bond dipole moments," chloroform has a much lower moment because three chlorine atoms cannot remove from the central carbon atom three times as much charge as can one chlorine atom, since as the carbon effective nuclear charge is increased by the removal of negative charge from the atom, it becomes increasingly difficult to remove electronic charge from the carbon. In Part I this viewpoint was mathematically formulated, using a simple model as a guide. Electric dipole moments were calculated for a number of haloalkanes, the only parameters needed being estimated from established covalent bond radii, lengths and longitudinal polarizabilities, screening constants, and electric dipole moments of methyl halides, together with an assumed value for the moment of the C–H bond in methane. In general the agreement with experiment was satisfactory, being as good for an assumed zero C–H bond moment in methane as for other values of this quantity; hence, for simplicity, we have based all calculations in this paper upon a zero methane C–H bond moment. All constants used here are those determined in Part I in connection with this choice of C–H moment.

Having developed a method for estimating net electronic charges on atoms in a wide variety of molecules, we are now in a position to extend the earlier work of Ri and Eyring,[4] showing that net atomic charges are, in many cases, basic in determining relative rates of reactions, and are therefore useful for the correlation, interpretation and prediction of reaction rates and mechanisms. It seems desirable to begin with a consideration of the gas phase reaction of sodium atoms with halides of various types, since the reaction seems simple from a theoretical standpoint and many experimental studies of it have been made. The reaction is purely a bimolecular gas reaction, having no solvent complications, and steric hindrance can be completely excluded as a factor affecting the rate.[5] Hence we expect electrical effects, particularly the halogen net charge, to predominate in determining relative rates. We turn now to a discussion of the charge-distribution calculations, before returning to a consideration of the factors directly affecting the relative rates.

The Calculation of Charge Distributions in Halides

The halides considered here are the halogen molecules, the hydrogen halides and alkyl halides. For the halogen molecules the net charges are of course zero; for the hydrogen halides we divide the electric dipole moments by the interatomic distances to obtain the net charges. The alkyl halide charge distributions are calculated from the theory developed in Part I. It seems worthwhile to point out here some simplifications in the actual application of the theory.

As discussed above, we take the methane C–H bond moment to be zero; hence, in the notation of Part I, $\gamma_{HC} = 0$. This approximation has the advantage of greatly simplifying charge-distribution calculations, not only in that many terms in the calculations become zero, but net charges on adjacent atoms in many cases become related by simple ratios, as we now demonstrate. Consider first C–H bonds. From equation (15) of Part I we have

$$\epsilon_H = \gamma_{HC} + \beta_{HC}\epsilon_C \qquad (1)$$

where ϵ_C is the net charge on the particular carbon to which the hydrogen under consideration, with net charge ϵ_H, is attached. Now with $\gamma_{HC} = 0$ and β_{HC} as determined in Part I, we find

$$\epsilon_H = 0.13\ \epsilon_C \qquad (2)$$

a relation holding for all C–H bonds.

Consider next the linkage

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[1] Presented in part before the Physical–Inorganic Division of the American Chemical Society, Cleveland, Ohio, April, 1951.

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