The Electron Affinity of Bromine Atoms from SpaceCharge Effects

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The Electron Affinity of Bromine Atoms from Space-Charge Effects

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The electron affinity of bromine atoms has been determined from the space-charge effects of a hot tungsten filament in bromine vapor and is found to be 88±3.4 kilocalories.

INTRODUCTION

THE electron affinity of bromine atoms has been determined by the method previously used with iodine.[1] The experimental set-up and methods of procedure were the same as those described. If it is assumed that equilibrium is attained between bromine atoms, electrons and bromine ions on the surface of the filament then the electron affinity ($-\Delta E_0$) of bromine is given by the expression

$$-\Delta E_0 = 4.575 T_s(\log F - \log P\ (Br_2, \text{mm}) + 2 \log T_s + 0.972),$$

where T_s = temperature of the filament, F = ratio of currents carried by bromide ions and electrons and P (Br_2, mm) = the pressure of bromine molecules in the reaction tube in mm Hg.

RECENT DETERMINATIONS

The electron affinity of bromine atoms is given by Mayer and Helmholz[2] as 81.5 kilocalories or 3.55 electron volts on the basis of thermochemical calculations involving the lattice energies of several alkali bromides. Piccardi[3] determined the conductivity of a flame fed with ethyl bromide and he reports 86.7 kilocalories or 3.76 electron volts for the electron affinity of bromine atoms.

EXPERIMENTAL RESULTS

The first determinations were carried out with bromine purified by shaking with several portions of normal potassium hydroxide solution and drying by distilling twice through phosphorus pentoxide. The last fractions of bromine were kept in the hope that the more volatile chlorine would be removed by this treatment. The bromine was distilled into small tubes carrying a breaking device through which they could be attached to the diode.[1] On breaking the shut-off, with liquid air on the bromine, a pressure developed in the experimental tube. The plate current was high and unsteady. The current-potential curves ($\log i - \log V$) showed a discontinuity at about 18 ev because of ionization of gas in the tube. This jump was far too great to correspond to the bromine pressure, judging from the experiments on iodine. Finally the conclusion was reached that the method of purification employed was insufficient to remove all the chlorine present as an impurity. The scheme adopted for the complete separation of the chlorine was to pump off all residual gases from the bromine supply at −100°C where the chlorine pressure is still about 4 mm Hg. The experiments reported in Table I were carried out on bromine purified in this manner.

A sample run is shown in Fig. 1 where the logarithm of the current in milliamperes is plotted as a function of the logarithm of the plate voltage. The three-half-power law is not obeyed but the relations between the currents in vacuum and with bromine in the tube and the

TABLE I.

Bromine °C	Bromine P(mm)×10⁵	Filament Temperature T_s	Current Ratio F×10⁵	Electron Affinity $-\Delta E_0$
−99.5	94	2310	1164	92.5
"	94	2410	276	90.5
−94.5	242	2419	190	84.6
"	242	2293	303	82.0
−99.5	94	2308	362	86.0
"	94	2432	370	92.0
−94.5	242	2432	748	91.5
"	242	2324	1288	89.5
−78.0	3350	2324	3550	82.0
−77.5	3610	2463	6270	89.6
				88.0±3.4 kilocalories

[1] G. Glockler and M. Calvin, J. Chem. Phys. **3**, 771 (1935).
[2] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).
[3] G. Piccardi, Atti acad. Lincei [6] **3**, 566–8 (1926).

plate voltage are sufficiently linear to permit extrapolation and determination of the constants of the diode.

Discussion of Results

It is seen that the value found for the electron affinity of bromine atoms in the present experiments agrees with the only other *direct* experimental determination of Piccardi.[3] However it was hoped that the indirectly found value of Mayer and Helmholz[2] could be checked, because they obtained their result from several bromides. It is conceivable that the bromine used by us was not of sufficient purity. The experiments reported here will be repeated at some future time and it is hoped that by using further extraordinary precautions it will be possible to give a definite answer. Since it is impossible to tell at the moment when this research can be continued, it was thought proper to report the present findings.

We are indebted to the research grant committee of the Graduate School of the University of Minnesota for financial assistance which enabled us to carry out this investigation.

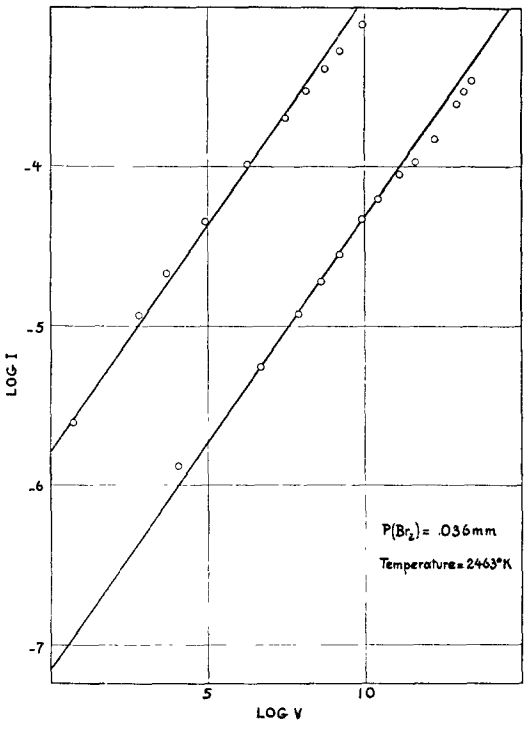

Fig. 1. Current-potential curve in vacuum and in bromine gas.

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The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

VI. The Methanol Equilibrium[1]

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The entropy of methanol and the equilibrium constant for methanol synthesis are calculated for two molecular models, one of which rotates freely about the CO bond, while the other possesses a torsional oscillation of frequency 700 cm^{-1} about that bond. The latter model is indicated by spectroscopic evidence and gives an entropy in close agreement with the third law value and an equilibrium constant close to the mean of the widely scattered experimental results. The former model is supported strongly by valence theory; it can be made to agree with the third law entropy by assuming a zero-point entropy of $R \log 3$, and its rather poor agreement with experimental equilibrium data is not conclusive evidence against it. The true equilibrium constant probably lies between these two calculated values, or at worst slightly beyond one of them.

THE equilibrium constant for the reaction

$$2H_2+CO=CH_3OH$$

has been determined many times. The extreme values at a single temperature are in some cases in the ratio of eight to one, and there is little reason to have confidence in the average values. This is particularly so because of the occurrence of undesired side reactions. It is

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