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TEMPERATURE DEPENDENCE OF DISSOCIATIVE RECOMBINATION COEFFICIENTS IN ARGON[†]

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The unexpectedly high values of recombination coefficients in inert gases obtained by Biondi and Brown[1] and Johnson, McClure, and Holt[2] were shown to be theoretically possible by Bates,[3] assuming dissociative recombination involving the molecular ion

$$AB^+ + e \rightleftarrows AB^* \rightarrow A^* + B^*.$$

Subsequent measurements[4] have established the dissociative process as the dominant recombination mechanism in inert gases at 20-30 mm Hg. Most measurements have been conducted close to 300°K, but Chen, Leiby, and Goldstein[5] have reported that the recombination coefficient in helium varies as $T_e^{-3/2}$ with electron temperature over the range 300 to 1500°K. Hess[6] has reported recently that in neon the dependence with electron temperature in the range 300 to 600°K is $T_e^{-0.25}$, and between 900 and 2400°K is $T_e^{-0.4}$. In both of these experiments the electron temperature was raised by selective heating, using a low-power microwave signal.

Bates and Dalgarno[7] state that if the process

$$AB^* \rightarrow A^* + B^*$$

is the significant limitation to the over-all rate of reaction, then a temperature dependence of $T^{-3/2}$ would be obtained. If, however, the rate-limiting step is

$$AB^+ + e \rightleftarrows AB^*,$$

then at high temperatures a $T^{-1/2}$ law might be anticipated after a more complex initial dependence. They suggest that the $T^{-1/2}$ law is probably more common.

The experiment briefly described here was carried out to resolve this uncertainty.

A shock wave is produced in a 1-cm internal-diameter pressure-driven glass shock tube, shown schematically in Fig. 1. The temperature of the shock-heated gas is taken to correspond to the shock velocity, which may be readily varied by using diaphragms of different thicknesses and appropriate driver gases. The shock tube passes through a section of X-band wave guide in which electrical breakdown of a volume of gas, limited to the dimensions of the wave guide and guard rings, can be produced by a 0.5-μsec pulse from a magnetron. This section of wave guide operates essentially as a low-Q cavity. The position of the shock front is determined from the response of thin platinum-film thermal transducers formed on the inside wall of the shock tube. The signal from

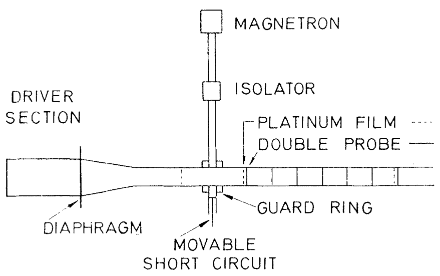

FIG. 1. Experimental apparatus.

a transducer upstream of the cavity can be time delayed and used to initiate the magnetron pulse. By this means, a volume of ionized gas can be created at any desired position before or behind the shock front. In this experiment the ionized slice is generated immediately behind the shock front and travels down the tube in the shock-heated gas. Previous experiments in this shock tube have demonstrated the time-dependent behavior of a slice of ionized gas in a shock wave.[8] After a period of about 50 μsec from breakdown, it is assumed that the electron temperature will have relaxed to the gas temperature and that all atomic ions will have formed molecular ions. Investigation of this latter assumption is to be carried out later using a mass spectrometer. The temporal variation of ion number density in the ionized slice is measured by the insertion of double probes into the shock tube[9,10] at positions indicated in Fig. 1.

The measurements are made in argon at an initial pressure of 3 mm Hg. The temperature range covered is from 1000 to 3000°K, produced by shocks in the range Mach 3 to Mach 5. Under these conditions the corresponding pressure in the shocked gas is between 30 and 90 mm Hg. In order to obtain absolute values of ion number density, corrections must be applied to the raw probe data to allow for collection under high-pressure conditions and in a high-velocity gas flow. The theory of Su and Lam,[11] applicable to spherical probes operating at high pressures, shows that because of collisions with neutral atoms, the ion-current density collected at the probe surface is less than the random ion-current density in the ionized gas. The correction terms corresponding to various conditions are presented in Ref. 11. The mean free path used here is that for the molecular ion and has been deduced from the mobility data of Beaty[12] and Biondi and Chanin.[13] In addition to this, and because of the motion of the shocked gas relative to the probe, the ion current collected is enhanced by a further factor, and this has been analyzed by Oppenheim.[14] In this experiment the probes have cylindrical rather than the spherical geometry which was considered by Su and Lam; but this is considered to have only a marginal effect on the overall result.

McLaren and Hobson[10] have found that under conditions similar to those encountered in this experiment, the Su and Lam correction may be too severe within a factor of 2.

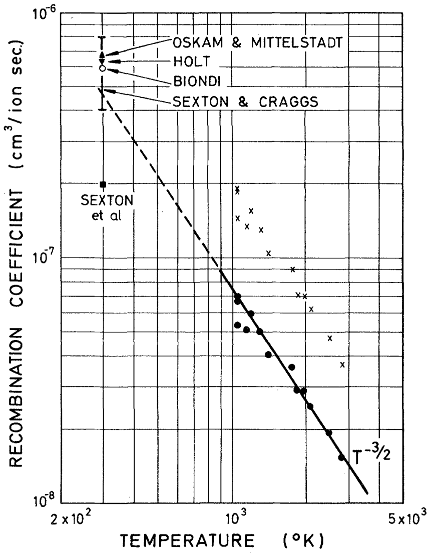

FIG. 2. Variation of recombination coefficient with temperature. × points are obtained from the uncorrected probe data, ● points from the corrected probe data.

Plots of reciprocal electron number density with time, assuming the electron and molecular-ion number densities to be equal, give a linear relationship for about 300 μsec after the ionizing pulse. Subsequent to this the experimental points depart from the linear plot. Impurities in the spectroscopically pure test gas and impurities outgassed from the walls before the shock wave passes amount to 8 parts per million. During the transit of the shocked gas down the tube, further impurities from the walls will be contained in the boundary layer, clear of the slice of gas under examination.

The recombination coefficients measured, after correction of the raw probe data, are shown in Fig. 2. They follow a $T^{-3/2}$ dependence which extrapolates close to the values obtained by others at 300°K. Coefficients calculated from the uncorrected number-density measurements have also been plotted to indicate that although there is an uncertainty within a factor of 2 as to the absolute values of the recombination coefficients obtained, there is little doubt that under these conditions the temperature dependence is $T^{-3/2}$.

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RESONANT SCREENING OF FOREIGN ATOMS IN METALS*

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The nonmonotonic variation found by Asik, Ball, and Slichter for the strength of the p wave inside a foreign impurity atom dissolved in lithium or sodium metal can be fit by a simple resonance formula. A crucial test of the resonance hypothesis is the predicted spin-flip scattering cross section of $(4\pm1)\times10^{-17}$ cm^2 for bismuth in sodium.

Asik, Ball, and Slichter[1] have recently reported some measurements of the cross section for spin-flip scattering of conduction electrons by foreign-atom impurities dissolved in alkali metals. ABS have measured the cross sections for numerous different atoms dissolved at exceedingly small concentrations in the host metals lithium and sodium. As they explain, the observed spin-flip cross sections can be used to infer the strength of the conduction-electron p waves within the foreign atoms. A simple perturbation-theory treatment establishes the proportionality of the spin-flip cross section to the fourth power of the amplitude of the p-wave wave function close to the impurity nucleus. Alternatively, the cross section is proportional to the square of the probability of finding an electron of unit orbital angular momentum inside the foreign atom. Viewed in this way, the experiments indicate the variation in the p-wave strength as an impurity is replaced by its neighboring element in the periodic table. ABS have discovered unexpectedly that this variation from one element to the next is not a monotonic function of the atomic number. Quite to the contrary, each series of impurity elements dissolved in a given host metal (either lithium or sodium) exhibits a maximum within the series, surrounded by lower cross-section values at both higher and lower atomic numbers. ABS have attempted to relate this variation to the changes in the screening of the impurity which occur as the atomic number is varied, but were unable to deduce any variation other than a monotonic one from their theoretical treatment.

The purpose of this note is to propose a simple interpretation of the nonmonotonic variation of the p-wave strength observed by ABS. Our explanation follows immediately from the observation that the Friedel sum rule[2] requires relatively large values for the partial-wave phase shifts, especially for the higher valence impurities. Thus, it is not to be excluded that the p-wave phase shift may become as large as 90° and in effect be associated with a resonant condition. It is, therefore, worthwhile to recall some simple properties of resonances