

Electron Removal in Krypton Afterglows*

JOHN M. RICHARDSON†

Department of Physics, Harvard University, Cambridge, Massachusetts

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The decay of the electrodeless microwave discharge in samples of Kr at 0.5- to 25-mm Hg was studied by the recently developed techniques of electron-concentration, optical spectrographic, and optical photometric measurements as a function of time after termination of the exciting fields out to a maximum of 15 msec. The Kr samples unavoidably contained traces of Xe estimated to be of the order of 0.01 to 0.1 mole percent, and such quantities of Xe were found to enter importantly into the afterglow processes of recombination and radiation in the pressure range 6 to 25 mm Hg. The observations are interpreted in terms of dissociative recombination of the molecular ions Kr_2^+ or $(\text{MXe})^+$ (where M is an undertermined atom, either Kr or Xe) with subsequent atomic radiation by an excited dissociation product. For Kr, one quantum from various $2p$ to $1s$ transitions appears to be associated with each recombination event. Recombination coefficients of approximately 0.6×10^{-6} and 2×10^{-6} cm³/electron-sec are obtained for the Kr and Xe recombination process, respectively. These values do not appear to be pressure-dependent. Results of ambipolar diffusion measurements are also stated.

I. INTRODUCTION

CONSIDERABLE experimental data dealing with electron removal from the afterglows of gas discharges have recently been obtained by microwave, spectrographic, and photometric means. Gases previously reported have been He,^{1,2} Ne,³⁻⁵ A,^{3,6} Hg,⁷ Cs,⁸ H₂,^{3,9,10} N₂,^{3,11} and O₂.^{3,11} The present article describes results obtained in Kr and certain inferences concerning Xe. These results are of dual interest because they both augment the list of gases studied and give information about Kr which has been the subject of virtually no previous investigation of this type.

Since the experimental portion of this work was completed, two significant advances in the subject have been reported. These are the identification of the recombination process as dissociative recombination of molecular ions proposed by Bates^{12,13} and experimentally shown by Biondi,^{14,15} and the analysis of ionic recombination including ion production during measurement by Kunkel.¹⁶ It is thus possible to make use of these results in the interpretation of the present work, and to show that Kr behaves essentially like gases previously observed.

Of equal fundamental interest with the mechanism of recombination (the event by which a free electron

passes to any bound state of either atom or molecule) are the mechanisms by which the recombined electron eventually passes to the ground state, and indeed these mechanisms may often give some clue as to the mechanism of recombination. The spectrography and photometry of the afterglow therefore, combined with electron loss measurements, give valuable additional information about these secondary processes.

II. METHOD AND APPARATUS

The method and apparatus are substantially as previously described.^{2,4,6,7} The experiment is arranged so that the electron concentration at the center of the sample, here designated by n , is proportional to the shift in resonant wavelength, $\Delta\lambda$, of an S -band cavity (2800 Mc). The sharpness of the resonance presentation in time is improved by sweeping the low-power search signal through resonance at a rate large (say 4 Mc per 60 μ sec) compared to the rate of change of resonance due to dn/dt instead of using the transient decay of the electron concentration to plot a resonance indication. This sweep is centered about any desired time in the afterglow. Figure 1 shows the circuits used. The breakdown pulse was of 10 μ sec duration and a few hundred watts peak power. In the absence of cavity resonance, a signal of varying frequency but of substantially constant amplitude is delivered to the first detector, so that a plot of the i - f response (4-Mc band width) is made on the indicator. If the occurrence of this pattern is adjusted either in frequency or time to embrace cavity resonance and if the probe is properly positioned, essentially the admittance curve of the cavity (~ 1 Mc band width) is superimposed on the indicator. In order to mark the position in time of a particular frequency differing a known amount from the indication of the frequency meter, a low-level marker signal in the i - f band (11 Mc) accurately known to 0.01 Mc is injected into the i - f amplifier. This signal produces a zero beat with the output of the first detector and is readily recognized on the indicator.

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† Now at the National Bureau of Standards, Boulder, Colorado.

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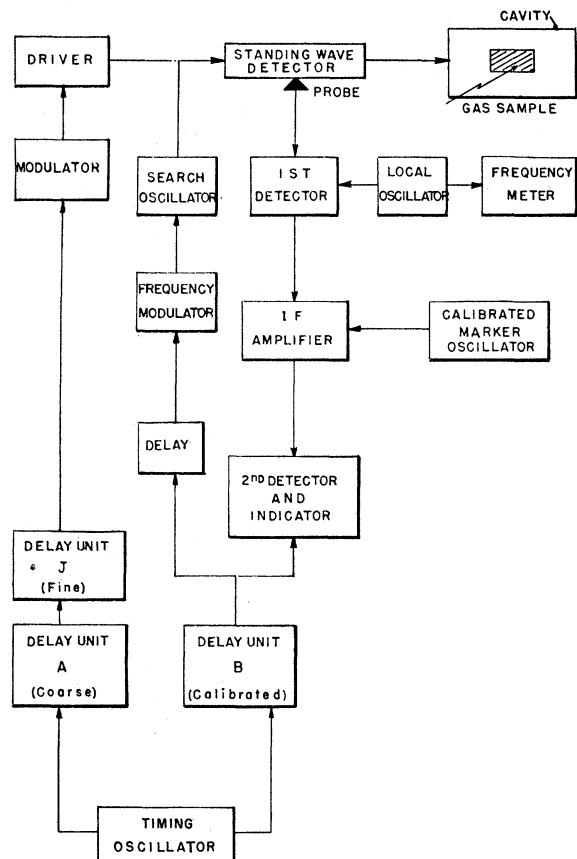


FIG. 1. Block diagram of electron-concentration apparatus, showing frequency-modulated search oscillator with sweep adjustable to occur at any desired afterglow time.

Measurements of n are limited by the smallest accurately detectable frequency shift (here ~ 0.1 Mc) and by the largest permissible concentration of electrons consistent with the derivation of the applicable equation connecting n and $\Delta\lambda$. In practice this means $2 \times 10^7 \text{ cm}^{-3} < n < 5 \times 10^{10} \text{ cm}^{-3}$. Times varied from 100 to 15,000 μsec .

Spectrograms of any 80- μsec interval of the afterglow period could be taken, intensity permitting, in the wavelength range 2000A to 8000A simultaneously with electron-concentration measurements.

The spectrographs could be replaced with a gated photomultiplier tube (1P28) for the purpose of making photometric measurements at any time in the afterglow of total light intensity within the 1P28 response band or within any smaller band defined by optical filters. A stepped attenuator (1000 Ω) was used before the amplifier-indicator chain to measure light levels. Advantages of the photomultiplier apparatus were that it supplied quick measurements, it enabled measurements very close (15 μsec) to the end of the main discharge to be made, and it was susceptible to an approximate calibration in absolute energy units if suitable cor-

rections were made for system response and spectral characteristics of the source.

Samples of Kr in the pressure range 0.5 to 25.4 mm Hg were prepared from Air Reduction Company supply flasks. Spectrographic examination under continuous 2.5-Mc electrodeless discharge showed traces of the Cameron bands of CO, which, however, did not appear under microwave excitation nor in the afterglow. Xenon was present as an impurity in amounts estimated at 0.1 mole percent in some samples and in amounts of less than 0.02 mole percent (limit of detectability by mass spectrographic analysis) in other samples prepared from reagent grade Kr.

III. RESULTS

A. Spectra

The optical spectra proved of prime importance in interpreting the results. In all cases the continuous and main pulsed discharge exhibited only the spectrum Kr I, except that in a few samples the strongest lines of Xe I were observed faintly after long exposure.

At pressures of 2.7-mm Hg and below (where diffusion predominated) only Kr I was observed even to 4000 μsec in one sample. However, at higher pressures Xe I was always detected. In the three purest samples Kr I in the visible predominated until at least 500 μsec , after which Xe I predominated. In the two most impure samples Xe I predominated at times as short as 300 μsec and thereafter.

Figure 2 shows spectra obtained with one of the least pure samples. In the afterglow period centered at 90 μsec the enhancement of Xe I is well established. At 200 μsec , Xe I is greatly enhanced. At later times (600 to 1000 μsec), depending upon purity and pressure the only atomic lines which persisted were the strong lines of Xe I at 4624A and 4671A. (At still later times, using a wide spectrograph slit, a continuum was photographed, which is believed to be extraneous light possibly caused by the fluorescence of container walls. This view is substantiated by the character of the photometric curves at long times.) These spectral shifts are confirmed by other spectrograms in the red and in the near ultraviolet.

Examination of the entire set of spectrograms indicated that the process leading to Xe I is enhanced by increasing total pressure (relative concentrations being equal), and furthermore that the substitution of Xe I for Kr I occurs at later times in the red than in the violet. These results demand that interpretation of the electron removal and photometric data be made in terms of a process leading to xenon light at long times and in terms of a process leading to krypton light at short times, the transition time being that at which the complete spectral change occurs.

B. Electron Removal

At low pressures (0.5- to 2.7-mm Hg) electron removal was found to be predominantly by diffusion, as shown

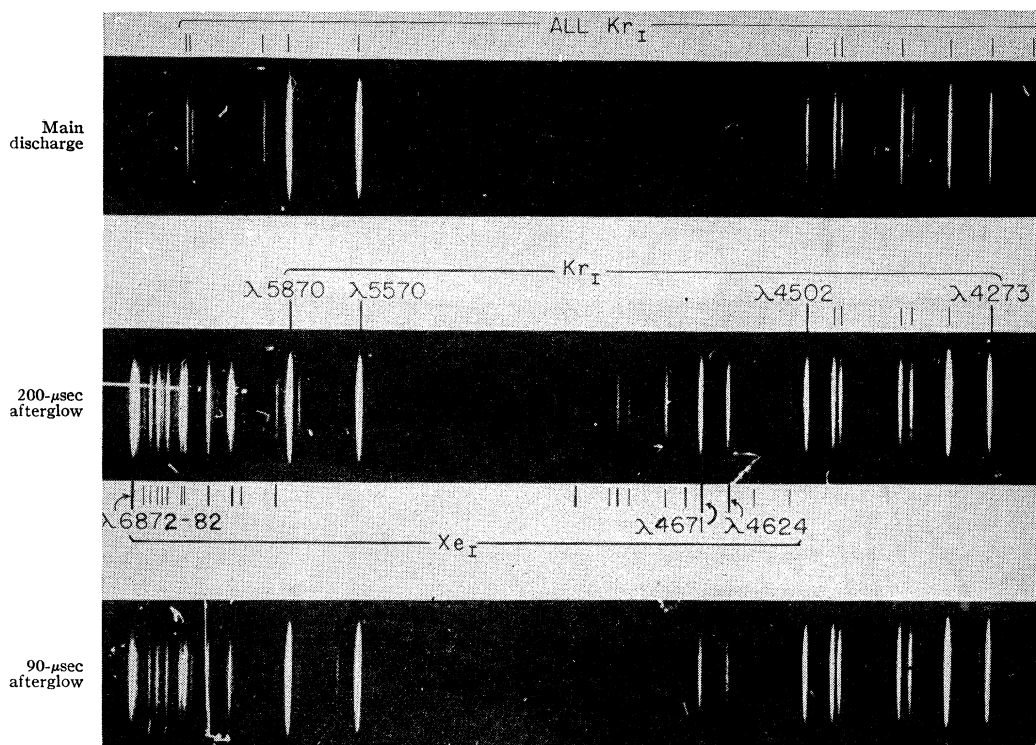


FIG. 2. Main discharge and afterglow spectra in one of the least pure samples, at 7.4 mm Hg. Eastman type 103a-F emulsion. Repetition rate ~ 240 pps; shutter speed 10, 80 and 80 μ sec, respectively; exposure periods 90, 3180, and 715 sec, respectively.

by exponential or nearly exponential decay; and simultaneous spectrograms indicated that the xenon impurity had no effect on the process in that no lines of Xe I were observed. As the pressure was increased within this range, deviation from pure exponential decay occurred and the equation¹⁷

$$-\dot{n} = 0.49\alpha n^2 + n/\tau \quad (1)$$

derived by Redfield and Holt⁶ was assumed to apply, where n is the electron concentration at the center of the cavity, and τ is the time constant of the decay due to diffusion. Figure 3 shows a typical run at 0.9 mm Hg with the experimental points obeying the integral of Eq. (1):

$$\frac{n}{1+0.49\alpha\tau n} = \left\{ \frac{n(t_1)}{1+0.49\alpha\tau n(t_1)} \right\} \exp[-(t-t_1)/\tau]. \quad (2)$$

The constants α and τ were fitted from two experimental points in addition to the point $[t_1, n(t_1)]$.

Results are summarized in Table I, from which it is noted firstly that the product $D_a\bar{p}$ ($=\Lambda^2\bar{p}/\tau$, where D_a is the ambipolar diffusion coefficient, \bar{p} is the pressure, Λ is a characteristic diffusion length dependent on the geometry and particular solution of the diffusion

¹⁷ Redfield and Holt publish the constant in this equation as 0.54. After performing the integration which they indicate, the constant actually emerges as 0.49.

equation employed) was not constant as found in He, Ne, and A. Secondly, α at low pressures was considerably below that observed at higher pressures (as was the case with argon); and within the limited range presented here, the values of α can be roughly fitted to a p^2 law.

At higher pressures (6.3- to 25.4-mm Hg) measurements were made over the time range of 200 to 5000

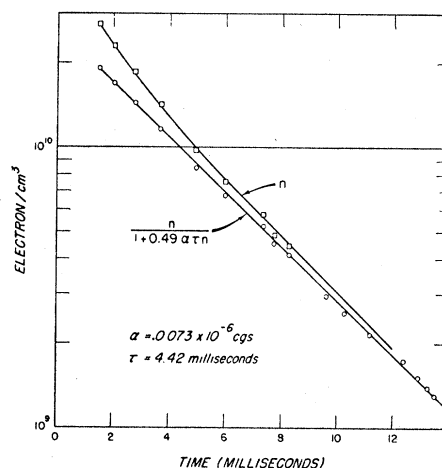


FIG. 3. Typical decay of electron concentration at low pressure (0.9 mm Hg) showing separation of α and τ according to Eq. (2).

TABLE I. Average diffusion measurements in krypton.

| Pressure (mm Hg) | $10^6\alpha$ ($\text{cm}^3/\text{electron-sec}$) | τ (μsec) | D_0p ($\text{cm}^2-\text{mm Hg}/\text{sec}$) |
|---------------------|---|-------------------------------|---|
| 0.5 | 0.0071 | 4150 | 50.8 |
| 0.9 | 0.0084 | 4540 | 82.6 |
| 2.7 | 0.14-0.19 ^a | 2260 | 504 |

^a Range of the average is the result of uncertainty of spatial distribution of electrons, whether of the cosine-bessel type or the uniform type.

μsec and electron-concentration range of 8×10^7 to $5 \times 10^9 \text{ cm}^{-3}$. The plots of $1/n$ vs t were characterized by a linear region at long times preceded by an initial region of either upward concavity or nearly constant slope distinct from that of the later region. An example is shown in Fig. 4. The time of transition was variously 500 to 2500 μsec , apparently influenced by pressure, purity and initial conditions. The slopes of the later regions give rise to negative $1/n$ intercepts, making it physically impossible to assign only the quadratic loss mechanism, $\dot{n} = -\alpha n^2$, throughout the afterglow period. Diffusion is excluded since here $\alpha \tau n \gg 1$, so that some complex mechanism such as outlined in the discussion below must be invoked. For impure samples (7.4 to 19 mm Hg) at long times where the xenon processes were presumably well established, the slopes of the $1/n$ vs t curves ranged from 1.4×10^{-6} to $2.1 \times 10^{-6} \text{ cm}^3/\text{electron-sec}$. The range is ascribed to slight variations in the predominance of the xenon recombination process. Surely no pressure variation as strong as the first power of pressure exists, and the coefficient may be taken as pressure-independent. For purer samples (6.3 to 25.4 mm Hg) at long times when the xenon processes predominated but were perhaps not so well-established as above, the apparent coefficient ranged from 1.2×10^{-6} to $1.9 \times 10^{-6} \text{ cm}^3/\text{electron-sec}$, again probably due to initial conditions and again pressure-independent. Thus the coefficient descriptive of the process leading to the spectrum Xe I may be taken roughly as 2×10^{-6} , and no greater accuracy is available from these experiments.

On the other hand, at short times before the transition of slopes and when the Kr I spectrum predominated, the slopes had a range of 0.7×10^{-6} to $1.2 \times 10^{-6} \text{ cm}^3/\text{electron-sec}$ for impure samples, and 0.6×10^{-6} to 1.0×10^{-6} for purer samples. Thus the coefficient descriptive of the process leading to the spectrum Kr I may be taken roughly as $0.6 \times 10^{-6} \text{ cm}^3/\text{electron-sec}$ and is similarly pressure-independent.

C. Photometric Measurements

Photometric measurements on samples in which diffusion mainly occurred showed that there was a region of time where the light decay was exponential and of time constant about one-half that observed for electron decay. This result was not in exact agreement over the entire observed range because of the existence of the aforementioned extraneous light ascribed to container

fluorescence, but it nevertheless indicated that the light intensity was proportional to n and was intimately connected with the small amount of volume recombination which proceeds simultaneously with diffusion.

Photometric measurements on samples in which recombination mainly occurred were of greatest interest. As shown in Fig. 5, there was a region extending from extremely short times (15 μsec) to about 300 or 400 μsec in which the light very accurately followed the law

$$I^{-1/2} = I_0^{-1/2} + At \quad (3)$$

over a range of 400:1 in intensity. This behavior suggests that the recombining positive ions were well established at the end of the exciting pulse, and there was not significant production of ions during the range of this measurement. For otherwise the observed light intensity would indicate the local maximum observed by Johnson *et al.*² in He. At long times the intensity was found experimentally to be very roughly proportional to n^3 . Both in the absence of any simple interpretation of this fact and for the reason mentioned above under spectra, this intensity was considered to be extraneous and so great as to mask the more rapidly decaying intensity due to Xe I. Photometric measurements at long times were therefore ignored.

The fact that the law in Eq. (3) is maintained even though in some cases the light consisted of both Kr I and Xe I implies substantially similar rates of recombination for both types of ion, since the reasonable assumption may be made that substantially the same numbers and types of quanta in each case are emitted per recombination event. The law (3) establishes, avoiding the effect of extraneous light, that the light from the

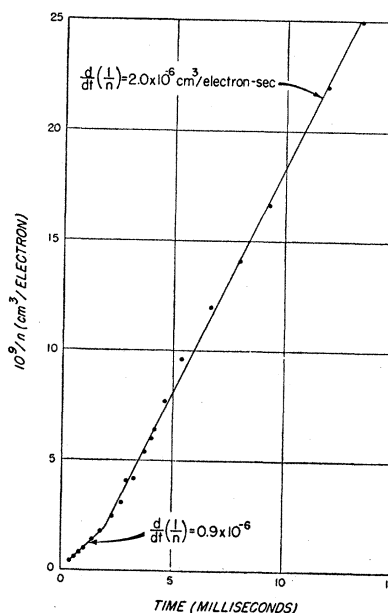
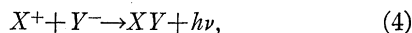


FIG. 4. Decay of electron concentration in sample emitting Kr I at short times and Xe I at long times. Pressure = 19 mm Hg. Two distinct line segments are apparent.

discharge tube from the very beginning is the result of a two-body process:



where X^+ and Y^- are charged particles, each of concentration N . This follows if intensity is assumed proportional to \dot{N} , because \dot{N} in the process (4) must be proportional to N^2 . It is possible to establish that the negative particle in the above reaction is an electron by calculating α from the slope of the $I^{-1/2}$ plot from the relation:

$$\alpha = -\dot{n}/n^2 = d(1/n)/dt = (1/C)dI^{-1/2}/dt, \quad (5)$$

where $C^2 = n^2/I$ and is evaluated by a simultaneous measurement of n and I at any one time. The necessary proportionality between I and n^2 was established experimentally over the range 200 to 600 μsec . Results of such calculations showed that the effective α in the short-time region inaccessible to direct observation of electron decay ($t < 200 \mu\text{sec}$) was very nearly the same as that obtained by the later observation of n as a function of t .

Finally, when applied to short times and pure samples where the spectrum Kr I is the end product of the recombination process, the photometric measurements provided an estimate of how much radiant energy (within the band of the apparatus) appeared per disappearing electron, and this value may be compared with that expected from a consideration of the possible transitions from the ionized state to the ground state.

Using a photomultiplier tube whose sensitivity was calibrated in absolute units by means of a standard lamp, and making suitable corrections for viewing geometry, spectral distribution, and photosurface response, it was found that the radiant energy in the band 3300A to 6500A (3.72 eV to 1.90 eV) was of the order of 0.1 to 0.2 eV per disappearing electron, or one quantum of the average energy of 2.81 eV for every 14 to 28 disappearing electrons. Furthermore, the strong group of red lines, 7587A to 8928A, also contributed to the radiant energy per disappearing electron, but was not included in the above measurement since it lay outside the response band of the phototube. Therefore, the above estimate was extended to include the contribution of these red lines. Pairs of spectrograms of the two regions which applied to identical experimental conditions at 100 μsec in the afterglow where the krypton spectrum predominated were selected. Using previously published relative intensities within each group,^{18,19} to define the relative power in the two groups of lines and correcting for different emulsion sensitivities, different observed densities of lines in each group of the same relative intensity, and different exposure

¹⁸ Meggers, de Bruin, and Humphreys, J. Research Natl. Bur. Standards, **7**, 643 (1931).

¹⁹ W. F. Meggers and C. J. Humphreys, J. Research Natl. Bur. Standards, **10** 427 (1933).

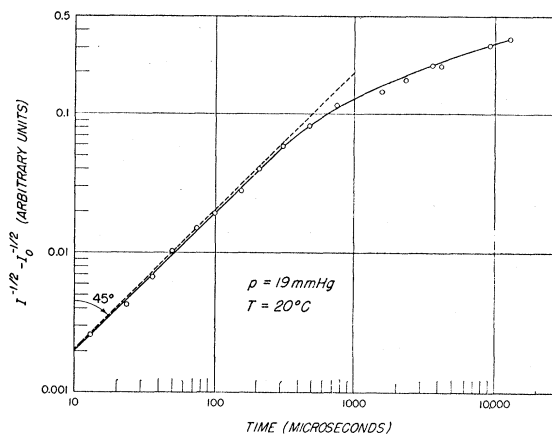


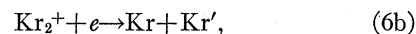
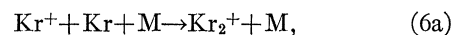
Fig. 5. Typical decay of visible intensity at high pressure ($> 6 \text{ mm Hg}$) showing region where $I \propto n^2$.

times, it was found that the radiant energy per disappearing electron in the band 7587A to 8928A (1.63 eV to 1.38 eV) was some 40 or 50 times that found in the shorter wavelength band with an uncertainty of perhaps a factor of 5. This result corresponds to one quantum of average energy of 1.5 eV for at most every 2 disappearing electrons, and strongly indicates that *every* recombination event is followed by the transition leading to one of these red lines. No such pronounced enhancement of the intensity of this red group relative to that of the shorter wavelengths was apparent in spectra of the main discharge.

IV. DISCUSSION

From the foregoing experimental results it is evident that several processes occurred either in turn or simultaneously, depending on conditions of purity, pressure, initial ion concentrations, and time of observation. The task of quantitatively separating these processes on the basis of the limited data obtained here does not appear promising. Instead, a few qualitative and semiquantitative conclusions based mainly on the high pressure measurements and consistent with recent work will be drawn.

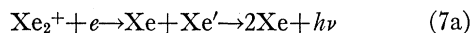
The excited states of Kr at short times in the afterglow are believed to arise by dissociative recombination of the molecular ion according to the scheme:



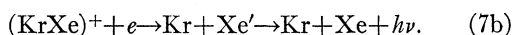
where M is a third body. Because of the aforementioned linearity of $I^{-1/2}$ from zero time, the ion Kr_2^+ probably is well-established in the main discharge. (Contrariwise, the pressure dependence of α at low pressures indicates that the molecular ion is there not so well-established, and that Eq. (6a) is operative.) The occurrence of two distinct slopes connected by a curved region in the $1/n$ plots is probably due to the xenon contamination

rather than to production of Kr_2^+ ions during measurement. It is, therefore, reasonable to assume that electrons disappear according to the quadratic law at the beginning and to assign the lowest observed $d(1/n)/dt$ as the recombination coefficient for process (6b). The large fraction (near unity) of $2p-1s$ transitions per disappearing electron indicates that the most probable state of the excited dissociation product is one of the $2p$ states, or possibly a higher state leading to the $2p$ states. A few afterglow transitions from initial $4p$ states were observed very weakly, and transitions from $3p$ levels were observed moderately from 4273A to 4502A.

The excited states of Xe are believed to arise from similar dissociative recombination of a molecular ion containing Xe, since the metastable states of Kr are not sufficiently energetic to raise Xe to the highest observed radiating levels. The same type of behavior as described above for Kr I was observed for Xe I when the latter spectrum appeared. The reaction might be either



or



The molecular ion in (7a) or (7b) must be produced during measurement, for the hypothesis that both the krypton and xenon ion are initially present in a given ratio cannot lead to the observed form of the electron decay curves. This production is believed to account for the curvature in the $1/n$ vs t plots according to an analysis similar to that of Kunkel.¹⁶ Once this ion predominates, the quadratic law again applies as shown by the new linearity of the $1/n$ plots at long times, with the observed $d(1/n)/dt$ at these times as the coefficient for process (7a) or (7b).

Recalling that initially there is no evidence for ionized xenon, a mechanism for producing the molecular ion in (7a) or (7b) must be postulated. It is possible that the Xe_2^+ ion might be formed in two steps by first a charge exchange between Kr^+ and Xe and subsequent collision between Xe^+ and Xe. The second step of this process is considered very improbable because of the low experimental concentration of Xe. The ion $(\text{KrXe})^+$ might be formed (a) by a two-stage process involving collisions of Xe^+ (as formed above) with Kr, (b) by direct combination of Kr^+ and Xe or (c) by an exchange of Xe for Kr in the molecular ion Kr_2^+ . There is as yet insufficient data to identify the recombining xenon ion or its origin, and all that can be said is that (c), above, is to be intuitively preferred. (See Note added in proof.)

V. SUMMARY

At low pressures (0.5- to 2.7-mm Hg) characteristic ambipolar diffusion behavior was observed, and possible

xenon contamination did not appear to influence the results. In this pressure region the effective recombination coefficient for krypton lies two orders of magnitude below its pressure-independent value for higher pressures, and apparently varies as p^2 , lending support to the hypothesis of Eq. (6a). The product $D_a p$ was found to increase with pressure.

At higher pressures (6.3- to 25-mm Hg) recombination behavior was observed, but with the evident superposition of two recombination processes because of contamination of the samples with xenon. One of these is ascribed to Kr_2^+ and the other to an unknown molecular ion containing Xe. Coefficients for the two processes are respectively set at $(0.6 \pm 0.2) \times 10^{-6}$ cm³/electron-sec and $(2 \pm 0.5) \times 10^{-6}$ cm³/electron-sec, of the same general magnitude as recent similar observations in other gases. These figures were observed for the extremes represented, respectively, by the purest samples at shortest afterglow times emitting only Kr I, and the most impure samples at longest afterglow times emitting only Xe I. Better accuracy awaits the results of new work in which the contamination problem is avoided.

Photometric measurements in the early afterglow indicated light arising from a two-body process, the absolute decay of which, further, was consistent with the above coefficient as to order of magnitude. Coupled with rough spectrographic intensity estimates, these measurements strongly indicate that each recombination event gives rise to a transition from the $2p$ levels to the $1s$ levels with radiation in the band 7587A to 8928A, from which it is inferred that the most probable state of the excited dissociation product is a $2p$ state. Further spectroscopic studies of the afterglows of both Kr and Xe with improved apparatus in which relative intensities of afterglow and discharge spectra are emphasized should provide valuable information as to the radiation processes subsequent to recombination.

The author is indebted to Professor R. B. Holt for his guidance and to the AEC for fellowship aid granted during a portion of this research.

Note added in proof:—Professor O. Oldenberg has stressed to me that the existence of ions of the type $(\text{KrXe})^+$ is questionable. The remaining alternative is that the positive carrier at long times is the atomic xenon ion, produced most likely by charge exchange. This ion would directly give the observed xenon spectrum and would disappear by ambipolar diffusion in Kr similarly to the behavior of A^+ in He as observed by Biondi. Although the present data favor the interpretation of Eq. (7b), it is recognized that a clear choice between the alternative processes was possibly prevented by the rather small time range of 5 msec. The conclusions regarding the recombination of xenon are correspondingly weakened.

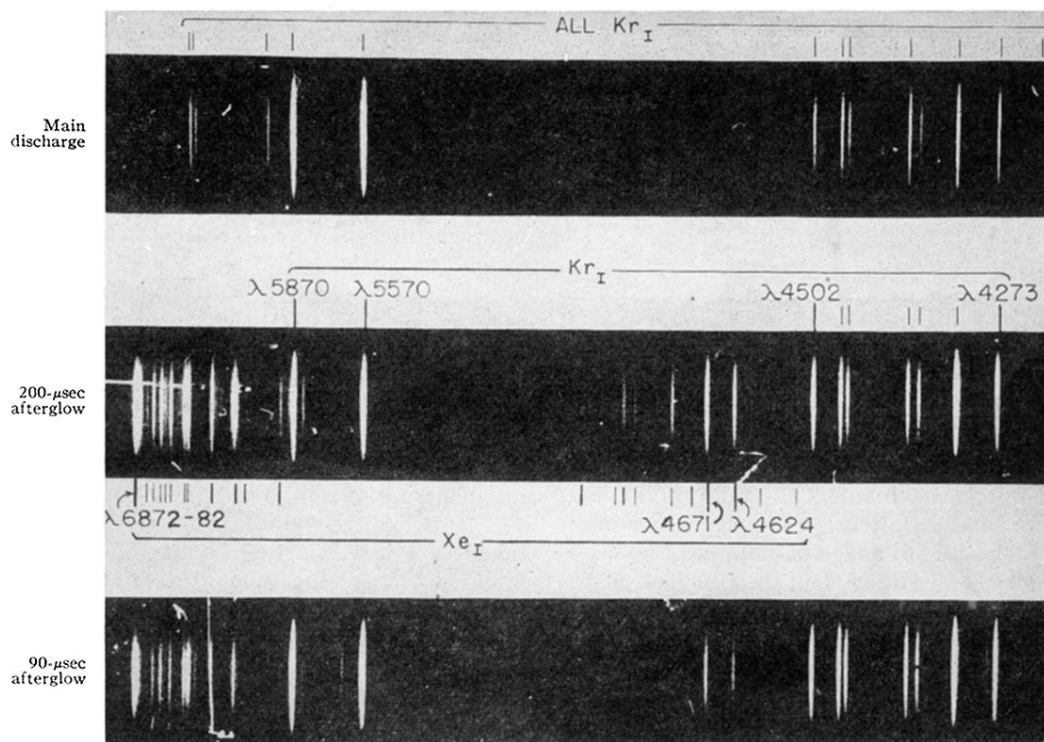


FIG. 2. Main discharge and afterglow spectra in one of the least pure samples, at 7.4 mm Hg. Eastman type 103a-F emulsion. Repetition rate ~ 240 pps; shutter speed 10, 80 and 80 μ sec, respectively; exposure periods 90, 3180, and 715 sec, respectively.