Initial Ionization Rates in Shock-Heated Argon, Krypton, and Xenon

KENNETH E. HARWELL* AND ROBERT G. JAHN†
Daniel and Florence Guggenheim Jet Propulsion Center,
California Institute of Technology, Pasadena, California
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The rate of ionization behind strong shock waves in argon, krypton, and xenon, is observed by a transverse microwave probe, over a range of electron densities low enough that atom-atom inelastic collisions are the rate-determining mechanism. Shocks of Mach number 7.0 to 10.0 propagate down a 2-in. sq. aluminum shock tube into ambient gases at pressures of 3.0 to 17.0 mm. Hg, heating them abruptly to atomic temperatures of 5500°K to 9600°K. The subsequent relaxation toward ionization equilibrium is examined in its early stages by the reflection, transmission, and phase shifts of a 24.0 Ge/sec (1.25 cm) transverse microwave beam propagating between two rectangular horns abreast a glass test section. The data yield effective activation energies of 11.9 ± 0.5 eV for argon, 10.4 ± 0.5 eV for krypton, and 8.6 ± 0.5 eV for xenon. These coincide, within experimental error, with the first excitation potentials, rather than the ionization potentials of the gases, indicating that in this range ionization proceeds via a two-step process involving the first excited electronic states of which the excitation step is rate controlling.

I. INTRODUCTION

The purpose of the experiment reported here is to study the initial ionization of shock-heated argon, krypton, and xenon. "Initial" ionization refers to that regime of very low ionization, proposed by Bond and others, wherein the relatively efficient electron-atom collision processes are so rare that the gas must have recourse to much less effective heavy particle collisions to generate its first few ions. A variety of reaction schemes can be proposed for this regime. For example, in pure gases, the ionization may be achieved by single atom-atom collisions:

$$A + A \rightarrow A^+ + e + A,$$

or by successive atom-atom collisions, involving an intermediate excited state, $A^*$:

$$A + A \rightarrow A^* + A,$$

$$A + A^* \rightarrow A^+ + e + A,$$

$$[A^* \rightarrow A + h\nu].$$

Here $k_1$, $k_2$, $k_3$, $k_4$, symbolize reaction rates in the usual chemical sense, and $k_4$ is a composite rate discussed below. Because of the relatively high atomic levels and small collision cross sections of these pure gas "reactions," a very small amount of impurity may participate significantly, either by directly ionizing the test gas:

$$I + A \rightarrow A^+ + e + I,$$

or, more likely, by becoming ionized itself, and possibly undergoing subsequent charge exchange with the test gas:

$$A + I \rightarrow I^+ + A + e,$$

$$I^+ + A \rightarrow A^+ + I.$$  

The impurity particle involved, I, may be either in the gas or on the wall of the container.

The theoretical formulation of any of these reactions is quite similar. For example, the frequency with which process (1) proceeds in a gas whose atoms are in Maxwellian equilibrium may be written:

$$\frac{d}{dt} (N_A) = \frac{1}{2} N_A^2 \left( \frac{M}{2\pi K T} \right)^{3/2} \int_0^\infty e^{-\mu + \epsilon/K T} 4\pi v_0^2 dv_0$$

$$\cdot \int_{v_0}^\infty e^{-\mu + \epsilon/K T} Q_1(v) dv = k_1(I)N_A,$$

where $N_A$, $M$, and $T$ are the atomic particle density, mass, and temperature, $K$ is Boltzmann's constant, $v_0$ is the center of mass speed of two colliding atoms, and $g$ their relative speed, which has a minimum value $g_0$ corresponding to the threshold energy for ionization, $E_i$,

$$g_0 = (4E_i/M)^{1/2}.$$  

The magnitude of $d(N_A)/dt$ hinges on the dependence of the ionization cross section, $Q_1$, on the relative particle speed at impact. Weymann assumes

$$k_1 = k_1 (E_1).$$

However, most of the ionization energy dependence depends on $Q_1$. Since we will be concerned with $K T \ll E_1$, we set $Q_1$ by a linear Richardson model above threshold:

$$Q_1 = C_1 T.$$

Taking the natural logarithm with respect to the temperature,

$$\ln \left[ \frac{d}{dt} (N_A) \right] = C_1 e - (E_1 / K T),$$

for $K T \ll E_1$.

Expressing the logarithm of the left side of the above equation in terms of $1/K T$ gives the ionization energy for the gas, which in this case is the temperature.

An identical approach to the reaction (2), except now the excitation cross section involved is the state $A^*$:

$$[A^* \rightarrow A + h\nu].$$

The second step is written in terms of a cross section for a two-step process:

$$k_1 = k_1 (E_1).$$

The effective ionization cross section, and the total ionization rate dependence, are given in terms of the composite two-step cross section $k_1$, which in this case is the mean free path.

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* Present address: Department of Aerospace Engineering, Auburn University, Auburn, Alabama.
† Present address: Department of Aeronautical Engineering, Princeton University, Princeton, New Jersey.
\[ Q_1 = C_1(E - E_v) = \frac{1}{2}MC_1(g^2 - g_0^2), \]  

in terms of which the ionization frequency becomes:

\[ \frac{d}{dt}(N_*) = 4C_1(\pi M)^{1/2}N^2(KT)^{3/2}(E_v/2KT + 1)e^{−E_v/KT}. \]

Taking the natural logarithm, and differentiating with respect to \(1/KT\) yields

\[ \frac{d}{dt}(N_*) \]

\[ \frac{d}{d(1/KT)} \]

\[ = -E_v\left[1 + \frac{3}{2} \frac{KT}{E_v} - \frac{1}{E_v/KT + 2}\right]. \]

For \(KT < E_v\)

\[ \frac{d}{d(1/KT)} \]

\[ \approx -E_v, \]

expressing the familiar result that the slope of a graph of the logarithm of the rate of ionization, \(\ln dN_*/dt\) vs \(1/KT\) is approximately the activation energy for the process being considered, \(E_v\), in this case the ionization potential.

An identical relation prevails for the first step of reaction (2), except that the threshold energy is now the excitation potential, \(E_v\), and the cross section involved is that for excitation to the excited state \(\Lambda^*\):

\[ Q_* = \frac{C_2(E - E_v)}. \]

The second step, (2b) would be similarly described in terms of a threshold energy, \(E_v - E_v^*\), and a cross section for ionization from the excited state

\[ Q_v = C_v(E - (E_v - E_v^*)]. \]

The effective activation energy, the density dependence, and the relative efficiency of the composite two-step process all depend strongly on the lifetime of the excited state, \(\Lambda^*\), in comparison to the mean free time for ionization by process (2b).

Since for the noble gases even the lowest excited states have energies well above half the ionization potentials, the energy increments involved in the second step, \((E_v - E_v^*)\) will be substantially less than those for the first step, \(E_v\). Also, the geometrical “size” of an excited noble gas atom presumably exceeds that of its ground state, and a continuum of final states is available for the second step compared to a discrete level for the first. It is thus reasonable to anticipate significantly higher collision efficiencies for the second step, i.e., \(k_v \gg k_v^*\).

The efficiency of the two-step process thus hinges on the level of “steady state” concentration of \(\Lambda^*\) which can be sustained. This in turn depends on the relative rates of collisional de-excitation \((k'\Lambda^*)\), and radiative decay \((k_\Lambda^*)\), to the ionization step \((k_v)\). The natural lifetime of a normal excited state against radiative decay \((\sim 10^{-9}\) sec) is probably inadequate to support this process. However, the gas could possibly make use of a longer-lived metastable level, or of a resonance trapping mechanism\(^\text{3,4}\), wherein the photon emitted on radiative decay is captured and re-emitted many times by adjacent atoms before escaping from the gas. In this way the effective lifetime of the excited state would be substantially protracted. In either case, the process is symbolized by equation (2c) where \(k_v\) represents the effective reaction rate coefficient for decay of \(\Lambda^*\) by spontaneous radiation, and may depend on the gas density and total sample size, as well as the temperature.

To outline the various possible ionization profiles, consider the kinetic rate equations appropriate to the “reactions” (2a)–(2c):

\[ \frac{d}{dt}(N_*) = k_vN^2 - (k_v + k_*^*)NN_* - \hat{k}_vN_*, \]

\[ \frac{d}{dt}(N_*) = k_v^*NN_*. \]

For the low-level regime, \(N_v\) greatly exceeds \(N_*\) and \(N_v\), and may be regarded as constant here. The solution to (14) is then

\[ N_* = \frac{k_*^*}{k_v^*}N^2(1 - e^{-t/\tau}), \]

\[ \tau = [(k_v + k_v^*)N + \hat{k}_v]^{-1}. \]

and thus the build-up of ion density by this mechanism becomes

\[ N_* = k_vk_v^*N^3[t - \tau(1 - e^{-t/\tau})]. \]

Table I. Characteristics of various ionization routes in the atom–atom regime.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>COLLISION D.E.-EXCIT.</th>
<th>RAD. DECAY</th>
<th>PHASE</th>
<th>ORDER</th>
<th>TIME DEP.</th>
<th>ACT. ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-STEP</td>
<td>$k_\phi k_p/N &lt; k_p$</td>
<td>$k_\phi/N &lt; k_N$</td>
<td>$t &lt;&lt; 1/k_N$</td>
<td>$N^3$</td>
<td>$t^2$</td>
<td>$E_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t &gt; 1/k_N$</td>
<td>$N^3$</td>
<td>$1$</td>
<td>$E_i$</td>
</tr>
<tr>
<td></td>
<td>$k_\phi/N &gt; k_N$</td>
<td>$t &lt;&lt; 1/k_\phi$</td>
<td>$N^3$</td>
<td>$t^2$</td>
<td>$E_i$</td>
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<tr>
<td></td>
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<td></td>
<td>$t &gt; 1/k_\phi$</td>
<td>$N^3$</td>
<td>$1$</td>
<td>$E_i$</td>
</tr>
<tr>
<td>1-STEP</td>
<td>$k_\phi/N &gt; k_p$</td>
<td>$k_\phi/N &lt; k_N$</td>
<td>$t &lt;&lt; 1/k_N$</td>
<td>$N^3$</td>
<td>$t^2$</td>
<td>$E_i$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t &gt; 1/k_N$</td>
<td>$N^3$</td>
<td>$1$</td>
<td>$E_i$</td>
</tr>
</tbody>
</table>

Suppose first that collisional deexcitation is negligible, and that the resonance radiation is effectively trapped, or that the excited state is metastable, i.e., $k_\phi/N < k_p$, and $k_\phi/N < k_N$. Then,

$$N_\ast \approx k_\ast N^2 \left[ t - \frac{1}{k_N} (1 - e^{-k_N t}) \right].$$  \hspace{1cm} (18)

In this case, for times up to $t \approx 1/k_N$, the reaction is in an inception phase, building up the $A^\ast$ population to some steady state level, after which ions are generated at a constant rate

$$\frac{d}{dt} (N_\ast) \rightarrow k_\ast N$$

$$= 4C_\ast N^2 (KT)^{-1} \pi M^{-1} \left(\frac{E_\ast}{2KT} + 1\right) e^{-E_\ast/KT},$$  \hspace{1cm} (19)

where $C_\ast$ and $E_\ast$ are coefficients for the particular specific process, and $T$ and $M$ are the temperatures and masses for the colliding species. The existing data suggest a reasonable assumption that even ionization in these conditions is a conservative condition for the ionization velocity hypothesis.

The desired experimental conditions are samples of very high pressure $n \approx 10^5$ atm, temperatures in the range up to $1000$ K and levels below $10^{-5}$, long enough time for the reaction to be determined. Shocks of 5 to 10 propagating through times of a few mm Hg and temperatures of $1000$ K establish a few mm Hg as a diagnostic device for the lower level below $10^{13}$ cm$^{-3}$ possible. Spatial and temporal gradients establish a lower limit of a reaction time of $1.25$ cm wavelet, as described in detail.

II. APPENDIX

The shock tube setup is designed to combine the high shock strengths of the high level of electronic energy. The shock tube was assembled from the transition of wall aluminum plates.

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where $n$, $m$, and $\alpha$ are the density, mass, and cross section coefficients.

Similar relationships can be derived for the two-step electron transfer processes, as described in Table I, that the ionization process is the determining one of the reaction route. The steady state level should be on the order of $A^\ast$.

$$N_\ast \approx k_\ast k_p k_N\left[ t - \frac{1}{k_\ast N} (1 - e^{-k_\ast N t}) \right].$$  \hspace{1cm} (22)

Here the inception phase is again shorter: $t \approx 1/k_N N \ll 1/k_\ast$, and is again followed by a linear phase, quadratic in neutral density.

These various regimes are summarized in Table I, in comparison with the single-step reaction (1).

The primary purpose of the experiment described is to measure the atom–atom ionization rates of various noble gases over a range of atomic temperatures and densities, and thereby to attempt to distinguish among the various mechanisms outlined above. To accomplish this purpose, it clearly is necessary to assure that the impurity reactions (3) and (4), and all electron–atom ionization reactions are rendered insignificant. Impurities reactions are well known to be troublesome in such studies, as could be anticipated from the comparatively low excitation and ionization potentials available in many metal and molecular vapors. It is found empirically in the course of the experiments described here that impurity levels above one part per million significantly bias the results. Impurity levels above ten parts per million completely obscure the reactions of interest.

The suppression of electron–atom reactions dictates an upper limit on the ionization density which can be tolerated. An analysis similar to that above yields an ionization rate for direct electron–atom ionization

$$\frac{d}{dt} (N_\ast) = 4C_s \left(\frac{2}{\pi m}\right)^{1/2} n_0 (KT)^{1/2} \left(\frac{E_i}{2KT} + 1\right) e^{-E_i/KT},$$  \hspace{1cm} (23)

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where \( n \), \( m \), and \( T \) are the free electron number density, mass, and temperature, and \( C_a \) is the cross section coefficient above threshold

\[
Q_a = C_a(E - E_a). \tag{24}
\]

Similar relations could also be expressed for the two-step electron-atom processes. If it is assumed that as the ion density grows, the first electron-atom process to compete successfully with the prevailing atom-atom process involves the same type of reaction route as the latter, then the break-even level should be defined, for \( T = T_a \), by:

\[
(2M/m)^3nC_a = NC_a \tag{25}
\]

where \( C_a \) and \( C_a \) here denote the cross section coefficients for the prevailing processes. Even if these specific processes were known, accurate numerical values for the coefficients would not be available. The existing data\(^7\) indicates \( C_a > (0.01) C_a \) is a reasonable assumption, on which basis the break-even ionization level is at least \( 10^4 \), a value quite conservative compared with the conventional equivalent velocity hypothesis.

The desired experiments therefore must provide samples of very pure gas of constant (translational) temperatures in which ionization proceeds at a level below \( 10^{-5} \), at a fast enough rate, yet for a long enough time that the rate can be precisely determined. Shock waves of Mach number range 5 to 10 propagating into monatomic gases at a few mm Hg ambient pressure in a shock tube, establish a few hundred microseconds of nearly isothermal flow at total densities \( \approx 10^{18} \) cm\(^{-3}\). A diagnostic device sensitive to free electron densities below \( 10^{13} \) cm\(^{-3}\) is thus required, with adequate spatial and temporal resolution to follow the axial gradients established by the prevailing ionization reaction rate in this zone of gas. The choice was a 1.25 cm wavelength transverse microwave probe, described in detail elsewhere.\(^8\)

**II. APPARATUS AND PROCEDURE**

The shock tube employed was specifically designed to combine the necessary ruggedness for high shock strength operation with a reasonable level of cleanliness. The major portion of the tube was assembled from lengths of cold-extruded, heavy-wall aluminum pipe (6006 - T5), having an interior cross section 2-in. sq., with \( \frac{1}{2}\)-in. flat corner fillets, and a \( \frac{1}{4}\) inch wall thickness (cf. Fig. 1).\(^9\) A rectangular channel was thus provided without the need for longitudinal seams. The lengths of tubing were joined with simple "O-ring" butt joints, constrained by split-ring flanges.\(^{10}\) Access ports to the tube were restricted to a minimum number and all were covered with cylindrical, "O-ring" flange fittings.

The test section was a 10-in length of heavy wall, precision bore, square pyrex pipe,\(^{11}\) whose interior surface, hot-formed over a stainless steel mandril, precisely matched the interior dimensions of the adjacent aluminum sections of the shock tube. This pyrex section was attached to the tube, 20 ft from the diaphragm, by means of a heavy steel yoke which permitted precise alignment of the inner walls at the junctions with the aluminum sections. Two feet beyond the test section, the tube terminated into a 10 ft stainless steel dump tank, needed to reduce the final pressure in the tube to a level tolerable to the glass pipe.

The desired shock strengths were generated by pressure bursting diagonally-scribed aluminum and copper diaphragms of various thicknesses by various types and pressures of driver gas. Hydrogen up to 1000 psi was needed to generate the stronger shocks in argon. Helium was used for the weaker shocks in argon, and for all of the shock strengths generated in krypton. Various helium-argon mixtures were used as drivers for xenon.

Thin platinum film gauges, mounted on small glass plugs, recorded the time of passage of the

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10 Professor D. Morelli and his students designed and implemented the mechanical details of the tube and its suspension.
11 Fischer-Porter Company.
Fig. 2. Two microwave circuits for transverse probe: (a) reflection detector; (b) reflection detector on directional coupler. Notation: RK, reflex klystron; EH, E and H plane tuner; FG, section of flexible waveguide; FI, ferrite isolator; VA, variable attenuator; CWM, cavity wave meter (absorption type); T, termination; ST, stub tuner; SS, straight section; TX, tunable crystal mount; H, horn; MT, magic tee; DC, directional coupler; TS, test section (pyrex).

Each these experiments, the shock over given positions along the tube. The amplified responses of two platinum film gauges adjacent to the test section, fed into a Berkeley 7200 time interval crystal counter, yielded the shock Mach number at the test section to better than 1%. The history of shock attenuation during its propagation down the tube was likewise determined by displaying the signals from a series of several film gauges directly onto a Tektronix 551 dual beam oscilloscope.

Largely by trial and error, the absolute leak rate of the tube and its associated gas handling equipment was reduced to less than $5 \times 10^{-4} \mu$/min, which was felt to be adequate in comparison with the outgassing rate of about $2 \times 10^{-2} \mu$/min which prevailed even after heating the entire tube to 100°C for several hours. To combat the introduction of impurities via the outgassing, the test gas was allowed to flow continuously down the shock tube from a valve near the mouth of the dump tank, to a valve near the diaphragm, at rates as high as 1000 times the outgassing. These valves remained open until slammed shut by the passage of the shock wave over their ports. The ultimate impurity level prevailing in the gas at the time of passage of the shock front was reducible by this technique to about 1 part in $10^7$.

The build-up of ionization density in the gas behind the shock front was observed by a transverse microwave probe, described in detail elsewhere. Briefly, a pair of rectangular horns face each other across the glass test section, matched to it and to each other with a VSWR of about 1.01. These are driven at 24.0 Gc/sec by one of two circuits of standard K-band components; one involving a directional coupler, the other a magic tee, as shown in Fig. 2.

Using these microwave circuits, the transmitted power amplitude, the reflected power amplitude, and the transmission phase were recorded as functions of time after passage of the shock wave, on a dual-beam Tektronix oscilloscope. A typical record is shown in Fig. 3. Using the process outlined in Ref. 8, the electron density time history $n(t)$ and the collision frequency $\nu$, were then determined from this data.

Corrections were applied to the raw microwave data for nonlinearity of the crystal detectors, refraction of the radiation patterns, and departures from the theoretically assumed plane slab geometry of the ionized gas sample, wherever needed, in accordance with calibration measurements and theoretical models described in Ref. 8. In addition, substantial corrections were made to compensate for the measured attenuation of the shock fronts. A shock varying in strength during its propagation down the tube leaves behind a body of shocked gas which is nonuniform in temperature. Since the ionization rates depend exponentially on this local temperature, there results a corresponding distortion of the ionization profile behind the shock from that which would have prevailed behind a constant strength shock producing an isothermal body of gas. The correction for this effect follows from a straightforward variation of the ionization rate integrals, and is described in detail elsewhere. It quite frequently alters the electron density by a factor of the order of $10^2$ to $10^3$. The correction, as shown in the data plots, rather than the actual density levels, would directly be the ionization densities above.

III. EXPERIMENTAL DATA

The corrected electron densities were determined to be linear in time throughout the range of ionization densities from $2 \times 10^{11} \leq n \leq 2 \times 10^{14}$ per cm$^3$. The electron temperatures in the range of $7500^\circ$ to $9600^\circ$K, these temperatures being confirmed through the time lag of the ionization rise time, the limit of experience being the time required to effect the "steady" gas temperature of the vessel in the range of $5800^\circ$ to $7500^\circ$K, there is evidence that the linear rise temperature is indicative of a marginal thermal equilibrium of the gas to these low electron temperatures. Strong gradients involved in these experiments are typical impurities in this low pressure gas, which will be subject to further study of the gas properties.

The absolute measurement of the electron temperature, summarized in Fig. 4, was accomplished by the associated gas temperature by a common method of gas temperature, for which a common method of gas temperature measurement is shown to be in agreement with electron temperatures of $9600^\circ$K, as shown in Fig. 3. The absolute measurement of the electron temperature, summarized in Fig. 4, was accomplished by the associated gas temperature by a common method of gas temperature measurement is shown to be in agreement with electron temperatures of $9600^\circ$K, as shown in Fig. 3.

![Fig. 3. Typical responses of microwave transmission and reflection detectors to build-up of ionization behind shock front. Total transmission ($T^2 = 1$) implies electron densities $n < 2 \times 10^{10}$ cm$^{-3}$; total reflection ($R^2 = 1$) implies $n > 10^{15}$ cm$^{-3}$.

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*Note: K. E. Harwell, Ph.D. Thesis, California Institute of Technology (1963).*
frequently altered the raw $n(t)$ data by a large fraction, and is regarded as the principal source of uncertainty in the results. In the worst cases, the 1% intrinsic inaccuracies in the response of the thin film gauges could be amplified to a 20% uncertainty in the ionization rate. Fortunately, this appears as a modest random scatter on the semilog data plots, rather than a systematic error which would directly bias the determination of the activation energies.

III. EXPERIMENTAL RESULTS

A. Argon

The corrected electron density profiles are found to be linear in time after passage of the shock front, over the range of sensitivity of the microwave probe ($2 \times 10^{11} \leq n \leq 1 \times 10^{13}$ cm$^{-3}$). For shocked gas temperatures in the range from about 5800°K to 9000°K, these linear profiles extrapolate back through the time origin at the shock front within the limit of experimental certainty, thus indicating that the "steady state" of the prevailing reaction (cf. Table I) is attained rapidly ($< 5$ usec). In a few very low temperature shots, $5400°K < T_2 < 5800°K$, there is evidence of a discernible intercept of the linear rise with the positive time axis, perhaps indicative of a more protracted inception phase, but the marginal sensitivity of the microwave probe to these low electron densities, the very small gradients involved, and the larger influence of impurities in this low temperature regime discourage further study of this possibility by the present experiment.

The absolute rates of ionization are found to be remarkably slow in high purity argon. Figure 4 summarizes the observed linear rates for various shocked gas temperatures $T_2$ at a preshock ambient pressure of 5 mm. It is found, for example, that for shocks producing temperatures $T_2 \approx 9000°K$, the theoretically predicted transition to the more efficient electron-atom phase ($n > 10^{13}$ cm$^{-3}$) is reached in about 300 usec, particle time. For $T_2 \approx 8000°K$, over a millisecond is required. In fact, for temperatures lower than 8200°K, the transition value is not reached in this shock tube before the arrival of the contact front terminates the hot flow. As an extreme case, for a temperature low enough that the equilibrium electron density lies below the transition value ($T_2 < 5500°K$), it would take about one second to reach that level via this atom-atom route.

The effective activation energy is obtained from the slope of the graph of $\ln(dN_e/dt)$ vs $(KT)^{-1}$, shown in Fig. 5 for $p_i = 5$ mm. Using a straight line fit to the data points, and iterating through the weak coefficient of relation (10) at $KT = \frac{1}{2}$ eV, the value is 11.9 ± 0.5 eV. This coincides, within the experimental uncertainty, to the first excitation potentials of argon, 11.55 - 11.83 eV, and differs distinctly from the ionization potential, 15.75 eV, thereby indicating that the ionization proceeds by a two-step mechanism involving negligible collisional deexcitation or radiative decay (cf. Table I).

Attempts to verify the quadratic density dependence appropriate to this reaction mechanism have been only modestly successful. The range of ambient pressures accessible to this experiment is restricted by the attainable shock strengths and by the microwave sensitivity belt to less than one order of magnitude. Consequently, the experimental un-
uncertainties associated with shock attenuation, gas impurity, and the microwave compensations which could be tolerated in the determination of the strong exponential temperature dependence of the ionization rate, become much more troublesome in the study of a mild density dependence. Typical results are displayed in Fig. 6, where the upper line reproduces the 5 mm data, traced from Fig. 5, and the other two lines are the 5 mm data normalized by the square of the indicated pressure ratios. The experimental data for \( p_1 = 5 \) mm support this quadratic scaling, but that for \( p_1 = 10 \) mm lie systematically below the corresponding line, in some cases in excess of the estimated experimental uncertainty. Since this departure is in the direction of a lower order density dependence, it favors none of the alternative reactions summarized in Table I.

**B. Krypton**

The original purpose of the experiment was a detailed study of the ionization kinetics in argon, and the various techniques involved in obtaining and reducing the data were developed solely with this gas. Only fairly late in the program did it become clear that application of these techniques to another gas would clarify certain of the crucial points in the data reduction, and for this reason, as much as to obtain information on other noble gases, were the studies of krypton, and later xenon undertaken. Since some two or three days are needed to obtain and reduce the data for any one experimental point, less total data was taken for krypton than for argon. By this time, however, the gas handling technique had been well developed, and the overall reliability of the results are felt to be comparable to those for argon.

As in argon, the ionization density in krypton is found to rise linearly in time after passage of the shock over the range of sensitivity of the microwave probe. The absolute rates are somewhat faster than those in argon at the same temperatures, but still very slow on a shock tube scale. For \( p_1 = 5 \) mm, for example, the transition to electron-atom processes would be reached in about 150 \( \mu \)sec at 9000\(^\circ\)K, and in about 550 \( \mu \)sec at 8000\(^\circ\)K (particle time).

The graph of \( \ln (dn_v/dt) \) vs \((KT)^{-1}\), shown in Fig. 7 yields 10.4 \( \pm \) 0.5 eV as the excitation potential for the ionization process, a step, trapped reaction being dominant.

The density dependence of the krypton rate is depicted in Fig. 8, where the higher pressure data (which support a temperature exponent of about 4) overlap the 3 mm data which are close to 1.5.

Even less data are available. Even if taken are felt to be consistent with what is known. The density dependence at rates slightly lower than those observed at the same temperature in argon is reported to be about 4000 \( \mu \)sec on the scale \( \ln (dn_v/dt) \) vs \((KT)^{-1}\), and about 400 \( \mu \)sec on the scale \( \ln (dn_v/dt) \) vs \((KT)^{-1}\) when the activation energy is taken to be 0.7 eV rather than 1.0 eV.

A very few shots are available at \( p_1 = 10 \) mm again indicating the data are weaker than quadratic.

The results described here were obtained using a multichannel mass spectrometer and a shock tube in the manner previously described, with comparison of the measured pressure rise and the maximum impurity concentrations.
Fig. 7. A density diagram showing the relationship between the density of krypton and xenon at different stagnation pressures. The density of krypton is higher than that of xenon at the same stagnation pressure.

D. Impurities

The results described above were obtained using pure xenon and krypton. The density of xenon was measured at 10 atm and 5 mm Hg, corresponding to the density of krypton at 100 atm and 5 mm Hg, respectively. The densities were measured using a capillary gas sampling method. The results showed that the density of xenon was higher than that of krypton at the same stagnation pressure.

Fig. 8. A density diagram showing the relationship between the density of xenon and krypton at different stagnation pressures. The density of xenon is higher than that of krypton at the same stagnation pressure.

A brief study of impurity effects in krypton indicated a more uniform increase in ionization rate with temperature. The samples were heated in an oven at 100°C for 24 hours prior to measurement. The ionization rates were then measured at 10 atm and 5 mm Hg, corresponding to the density of xenon at 100 atm and 5 mm Hg, respectively. The results showed that the ionization rate of xenon was lower than that of krypton at the same stagnation pressure.

Fig. 9. A density diagram showing the relationship between the density of xenon and krypton at different stagnation pressures. The density of xenon is higher than that of krypton at the same stagnation pressure.

Earlier data, obtained with pure gas samples, showed significant variations in the absolute ionization rates between 10 atm and 5 mm Hg. These variations are thought to be due to impurities present in the gas samples. The results described above were obtained using pure xenon and krypton. The density of xenon was measured at 10 atm and 5 mm Hg, corresponding to the density of krypton at 100 atm and 5 mm Hg, respectively. The densities were measured using a capillary gas sampling method. The results showed that the density of xenon was higher than that of krypton at the same stagnation pressure.

C. Xenon

The density of xenon was measured at 10 atm and 5 mm Hg, corresponding to the density of krypton at 100 atm and 5 mm Hg, respectively. The densities were measured using a capillary gas sampling method. The results showed that the density of xenon was higher than that of krypton at the same stagnation pressure.

Fig. 10. A density diagram showing the relationship between the density of xenon and krypton at different stagnation pressures. The density of xenon is higher than that of krypton at the same stagnation pressure.
Clearly, these data permit little conclusion regarding the effect of controlled amounts of given impurities on ionization rates—an interesting problem in its own right. They do emphasize, however, the general requirement for impurity levels below one part per million if significant “pure gas” ionization data are to be obtained.

IV. DISCUSSION AND CONCLUSIONS

Within the limits of their accuracy, the experiments described above indicate that the initial ionization of shock-heated argon, krypton and xenon proceeds by a two-step atom-atom process

\[ A + A \rightarrow A^* + A, \]  
\[ A + A^* \rightarrow A^+ + e + A, \]

where the effective lifetimes of the excited states against radiative decay and collisional de-excitation are sufficiently long to sustain their population at a level to make the first step rate-controlling. The measured activation energies indicate that the predominant excited states involved are the lowest available, namely the electronic configurations \( 3s^2 3p^5 4s^1 \) in argon, \( 4s^2 4p^5 5s^1 \) in krypton, and \( 5s^2 5p^5 6s^1 \) in xenon. Actually, each of these involves four separate levels, two of which are spectroscopically accessible to the ground state and are the origin of the principal resonance lines, and two of which are metastable, with transitions to or from the ground state forbidden by virtue of the \( J \) selection rules.\(^{13}\) The metastable levels may, however, be accessible by atom-atom collisions, and since the energy separations between them and their allowed neighbors are too small to be distinguished by the above experiments, two alternative interpretations must be admitted: (1) the first atom-atom collision elevates one particle to one of the metastable levels, whose lifetimes are inherently long enough to await a second, ionizing collision; (2) the first collision elevates one atom to one of the spectroscopic resonance levels, whose lifetimes, although much shorter, are effectively protracted by trapping of the resonant photon by adjacent atoms, prior to the subsequent ionizing collision.

In either case, the inception phase for build-up of the excited state concentration to its steady state value is very brief—less than 5 \( \mu \)sec for temperatures above 5800°K. The subsequent linear ionization rate is comparatively slow, ranging from \( 2 \times 10^{12} \text{ cm}^{-3} \text{ sec}^{-1} \) at 5500°K to \( 6 \times 10^{16} \text{ cm}^{-3} \text{ sec}^{-1} \) at 9500°K in argon.

The quadratic density dependence appropriate to this reaction scheme is qualitatively confirmed, although some slightly weaker dependence may be implicit in the data. Unknown impurities in the test gases are found to have profound effects on the ionization rates at concentrations as low as a few parts per million.

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\[ L \hat{x} = \sum e^{\gamma t} \]  
\[ F(x) \]  
\[ f(x) \]

The quantity \( x \) is also the displacement of an electron in a Knudsen number. The field is expressed in terms of a wavenumber \( k \) by the angular frequency \( \omega \) as follows:

\[ \frac{\omega}{k} = \frac{\omega}{k} \]  
\[ \frac{\omega}{k} \]

The operator \( L \) is then defined as

\[ L \hat{x} = \sum e^{\gamma t} \]  
\[ F(x) \]  
\[ f(x) \]

The quantity \( p \) is also the displacement of an electron in a Knudsen number. The field is expressed in terms of a wavenumber \( k \) by the angular frequency \( \omega \) as follows:

\[ \frac{\omega}{k} = \frac{\omega}{k} \]  
\[ \frac{\omega}{k} \]  
\[ \frac{\omega}{k} \]