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The Structure of a Shock Front in Argon

John W. Bond Jr.

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STRUCTURE
OF A
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IN ARGON

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THE STRUCTURE OF A SHOCK FRONT IN ARGON

By

John W. Bond, Jr.

A Thesis

In partial fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Physics

The University of New Mexico
1954

THE STRUCTURE OF A SINGLE THION IN ARSON

BY

JOHN W. BOAD, JR.

A Thesis

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The University of New Mexico

1954

This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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43	equation (18)	$\frac{h}{k}$	$\frac{h}{k}$
103	equation (17)	$\frac{h}{k}$	$\frac{h}{k}$
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ABSTRACT

If a one-dimensional shock wave travels through argon, the translational degrees of freedom of the atoms are immediately excited and reach translational equilibrium within two collision lengths. If the shock velocity is sufficiently high, energy will be transferred from the translational degrees of freedom to those of electronic excitation and ionization until complete thermal equilibrium exists. The region between the first disturbance in front of the shock and the point at which thermal equilibrium is first realized is the shock front.

A method of computing the equilibrium conditions, which was first applied by Beche to air, has been used for the argon equilibrium reaction, $A = A^+ + e$, where only singly-ionized argon atoms have been considered. The corresponding partition functions for density ratios from 2 to 20 and temperatures from 7500° to $26,000^\circ$ are tabulated. Applying the standard shock relations, the equilibrium conditions behind the shock front have been computed for shock velocities between $3 \cdot 10^5$ and $9 \cdot 10^5$ cm/sec for two fore-pressures, viz., $p_1 = 1.0$ and 59.38 cm Hg.

The non-equilibrium region which exists between the front of the shock and the equilibrium region has been treated by considering the individual atomic interactions that take place. From the point where translational equilibrium is first reached to a point where there is a sufficient number of electrons for ionizing collisions between electrons and atoms to be of importance, ionizing reactions between argon atoms predominate. Then the reaction $e + A = 2e + A^+$ takes over only to be

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The non-equilibrium region which exists between the front of the shock and the equilibrium region has been treated by considering the individual atomic interactions that take place. From the point where translational equilibrium is first reached to a point where there is a sufficient number of electrons for ionizing collisions between electrons and atoms to be of importance, ionizing reactions between argon atoms predominate. Then the reaction $e + A \rightarrow A^+ + e$ takes over only to be

dampened by recombination between electrons and ions until the gas has been completely equilibrated. Pressure, density, temperature and degree of ionization have been computed across the shock front for various shock velocities and presented in graphical form. Thus the width of the shock front and, consequently, the relaxation time for ionization are given as functions of shock velocity.

Various theories for the recombination of electrons and ions have been discussed and it is shown that Kramers' classical theory of radiative recombination is incorrect but that a quantum theory gives the right order of magnitude result. Three-body recombination coefficients have been computed by a method of microscopic reversibility.

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been completely equilibrated. Primarily density, pressure and

degree of ionization have been considered in the shock front. The

various shock velocities and associated or associated ionization

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the right order of magnitude results. Three-body recombination coefficients

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INTRODUCTION

A shock wave travelling through an atmosphere of argon gas may conveniently be described in the following way. In front of the shock wave is the undisturbed atmosphere in equilibrium. Upon being struck by the shock, a violent disturbance occurs, which soon however settles down to a new condition of statistical equilibrium behind the shock. Connection between the two regions of equilibrium is uniquely determined by the Rankine-Hugoniot or shock relations (Ref 46).

Disturbance of the statistical equilibrium takes place in the following way. As a shock wave passes through the gas, the translational degrees of freedom of the atoms are excited. The distance required to achieve translational equilibrium has been investigated theoretically (Ref 44, 45, 46, 48, 60, 63, 64, 65, 66) and in the limit of strong shocks is of the order of two collision lengths. This seems to have received satisfactory experimental verification (Ref 61, 62). Because the distance is so short it does not concern us in this report. If the temperature of the translational degrees of freedom is sufficiently high, transfer of energy to other degrees of freedom takes place until complete thermal equilibrium is reached. The region in which this transfer of energy takes place is referred to as the non-equilibrium region. We then define the shock front to be all the region between the undisturbed atmosphere in front of the shock wave and the point behind the front of the shock wave at which thermal equilibrium is first essentially achieved.

INTRODUCTION

A shock wave travelling through a medium of uniform density

consequently is described by the wave equation. The form of the wave

is the undisturbed medium is constant. When the wave

by the shock a region of uniform density which soon becomes

down to a new constant or stationary value. The wave

Connection between the two values of density is usually

by the Rankine-Hugoniot conditions. The wave

Disturbance of the medium is described by the wave

following way. A wave of uniform density in the medium

tional between the values of the wave and the medium

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theoretically, the wave

limit of strong shocks of the order of the medium

seems to have received considerable attention in the

(2). Because the medium is uniform in density and

reports. It is the separation of the medium

sufficiently high, the wave

place until complete equilibrium is reached. The wave

which this transfer of energy takes place is referred to as the wave

equilibrium region. It is the region

between the undisturbed medium and the wave

point behind the front of the wave where the medium

is first essentially

It is the purpose of this study to determine quantitatively the conditions and extent of the shock front for shock velocities high enough so that there is some degree of ionization and low enough so that the number of doubly ionized argon atoms is negligible. The reasons for choosing argon as the gaseous medium are, first, because it is a monatomic gas hence molecular degrees of freedom such as rotation, vibration, and dissociation do not need to be considered, and second, because more experimental data pertaining to shocks are available for argon than for most other gases.

Measurements have been made by various investigators on the detailed structure of argon shocks of the following quantities: material velocity, shock width, spectral distribution, luminosity, electrical conductivity, and potential distribution. In addition there are measurements of many overall phenomena of the shock including reflection, refraction, and diffraction of shock waves as they impinge on or pass through various media, how much energy is lost to a shock front in air as it passes through a cloud containing water droplets (e.g., fog), and how much energy is lost to a shock front by radiation. A detailed theoretical knowledge of the structure of a shock front is desirable in order to obtain an interpretation for some of the physical measurements made as well as to predict others. Also, we wish to test the validity of approximating the shock front by a physical discontinuity, as is usually done. It is essentially for these reasons that this report is written.

In Part I we consider the equilibrium region which is a plasma consisting of neutral argon atoms in various states of excitation, singly charged argon ions, and electrons. The equation of state for such a plasma is derived and it is shown how the component concentrations behind the shock may be computed.

In Part II we discuss the various atomic interactions that take place in the non-equilibrium region of the shock front. We evaluate the reactions that contribute to the production of electrons using the available experimental cross-sections. Once a sufficient number of electrons has been produced recombination of electrons and ions occurs until a balance between the production and recombination of electrons has been reached. Several recombination processes take place, none of which have been experimentally determined for the temperature and density conditions that prevail in a shock front of the strength we will consider. Hence theoretical relations for the recombination processes are derived.

The theory of Parts I and II is applied to a few special cases in Part III. Equilibrium calculations have been made for shock velocities between $3 \cdot 10^5$ and $9 \cdot 10^5$ cm per sec and for initial or fore-pressures of 1.0 cm Hg and 59.38 cm Hg, the latter corresponding to atmospheric conditions at Los Alamos. Processes contributing to the production of electrons in a shock front are evaluated numerically for temperatures between about 8000° and 35000° . Recombination processes, depending on both density and temperature, are also evaluated. Finally, conditions

In Part I we considered the effect of a magnetic field on the
conductivity of a gas. It was shown that the conductivity is
slightly changed at low fields, and that the change is
such a function of the field strength that it can be used as a
means of measuring the field strength.
In Part II we considered the effect of a magnetic field on the
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the reaction is a function of the field strength and the
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electrons and ions and the field strength.
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the field strength and the temperature.
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the theory of the gas. It was shown that the theory is a function of
the field strength and the temperature.
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between 0.1 and 0.2 cm. the field strength is a function of the
1.0 cm. and 0.2 cm. the field strength is a function of the
conditions at low fields. It was shown that the conditions are a function of
electrons and ions and the field strength.
between 0.1 and 0.2 cm. the field strength is a function of the
both density and temperature. It was shown that the density and temperature are a function of the
field strength and the temperature.

in the non-equilibrium region have been computed for an initial pressure of 59.38 cm Hg and shock velocities of 5.0, 5.5, and $6.0 \cdot 10^5$ cm per sec.

The important contributions of this report are the following. Partition functions for argon have been computed and tabulated for temperatures from 7500° to 26000° and for density ratios from 2 to 20. The equilibrium constant K for the reaction $A = A^+ + e$ for the above range of density and temperature and with an initial pressure of 59.38 cm Hg is tabulated. For an initial pressure of h cm Hg the corresponding equilibrium constant is obtained by multiplying the tabulated K by $59.38/h$. An approximate method by which the energy per particle and the component concentrations may be conveniently obtained from the equilibrium constant is presented in Part III. The values thus obtained agree well with the more exact method given in Part I.

The quantitative calculations on the shock front show, not only the true profile, but that the shock front is of such an extent and the conditions such as pressure, temperature, and density of such magnitude that for many of the physical applications mentioned previously the shock front should not be treated as a discontinuity. In addition, from the degree of ionization one can predict the spectral distribution and luminosity and possibly compute the conductivity.

Perhaps the most significant theoretical contribution of this report is the derivation of the recombination coefficient. It is shown that Kramers' classical theory of radiative recombination gives

in the non-equilibrium region have been computed for an initial pressure of 29.38 cm Hg and shock velocities of 2.0, 2.5, and 6.0-10² cm per sec.

The important contributions of this report are the following:

Partition functions for atoms have been computed and tabulated for temperatures from 1500° to 25000° and for density ratios from 2 to 20.

The equilibrium constant K for the reaction $A \rightleftharpoons A^+$ for the above range of density and temperature and with an initial pressure of 29.38 cm Hg is tabulated. For an initial pressure of 1 cm Hg the corresponding equilibrium constant is obtained by multiplying the tabulated K by 29.38. An approximate method by which the energy per particle and the component dissociations may be conveniently obtained from the equilibrium constant is presented in Part III. The values thus obtained agree well with the more exact method given in Part I.

The quantitative calculations on the shock front show, not only the true profile, but that the shock front is of such an extent and the conditions such as pressure, temperature, and density of such magnitude that for many of the physical applications mentioned previously the shock front should not be treated as a discontinuity. In addition, from the degree of ionization one can predict the spectral distribution and luminosity and possibly compute the conductivity. Perhaps the most significant theoretical contribution of this report is the derivation of the recombination coefficient. It is shown that Einstein's classical theory of radiative recombination gives

a value that is too large by a factor of about 10^5 , but that a quantum theory evaluation is of the correct order of magnitude. Also since the usual theories of three-body recombination are not applicable to our case, we separately evaluated this coefficient by using the principle of microscopic reversibility applied to the equilibrium state.

a value that is too large by a factor of about 10^2 , but that a quantum theory evaluation is of the correct order of magnitude. Also since the usual theories of three-body recombination are not applicable to our case, we separately evaluated this coefficient by using the principle of microscopic reversibility applied to the equilibrium state.

PART I: THE EQUILIBRIUM REGION BEHIND THE SHOCK FRONT

1. Introduction.

The general hydrodynamic features of a shock are determined by the properties of the equilibrium regions in front of and behind the shock front. The conditions in front of the shock are completely known, of course. However, behind the shock front in argon we have a plasma consisting of argon atoms in various states of excitation, argon ions, and electrons. Despite the fact that such a plasma has received considerable attention, particularly at low pressures and temperatures (Ref 1, 2, 56, 57, 58, 59), knowledge of this state is far from being satisfactory. This is especially true at the high pressures and temperatures behind a shock front.

In Part I, therefore, we calculate the equilibrium equation of state and the thermodynamic functions of the argon plasma. There are available several methods for determining the equation of state of a gas. We have used here the Saha equation and evaluated the partition functions by a method suggested by Bethe (Ref.67). The reason for using Bethe's method is that it is simple and well adapted for high speed computing machines. In this calculation, as indeed throughout this report, it will be assumed that the number of doubly ionized argons is negligible although, occasionally, brief reference will be made to interactions involving A^{++} .

2. Equilibrium Conditions.

Consider a plasma state behind the shock front in complete thermal equilibrium. We wish to calculate the concentrations of the three com-

ponents, A , A^+ , and electrons, as functions of density and temperature.

Let the concentration $[A]$ be defined as the ratio of the number of neutral argon atoms to the original number before ionization takes place. Similarly $[A^+]$ is the ratio of the number of singly charged argon ions to the original number of argon atoms and $[el]$ is the corresponding concentration for electrons, where, at all times

$$[el] = [A^+] .$$

The equilibrium reaction is

so that

$$[A] + [A^+] = 1 \quad (1)$$

If g is the average number of particles into which an argon atom splits at temperature T , then

$$g = [A] + 2[A^+] \quad (2)$$

where the factor of 2 is due to the presence of one electron for each ion.

Assume the perfect gas equation of state to hold,

$$p = g\rho \frac{R}{M} T, \quad (3)$$

where R is the gas constant per mol and M is the original molecular weight.

If E is the internal energy per gram, the quantity β is defined by

$$E = (\beta - 1) \frac{p}{\rho} . \quad (4)$$

positive, A_+ and electrons, as indicated by the sign of the charge.

Let the concentration $[A]$ be expressed as the number of atoms per unit volume.

neutral argon atoms to the original number of positive ions.

place. Similarly $[A_-]$ is the ratio of the number of negative ions to the original number of positive ions.

argon ions to the original number of argon atoms and $[A_+]$ is the ratio of the number of positive ions to the original number of argon atoms.

positive concentration for the ions, where A_+ and A_- are the concentrations of positive and negative ions respectively.

$$[A_+] = \frac{A_+}{A} \quad [A_-] = \frac{A_-}{A}$$

The equilibrium reaction is

$$A \rightleftharpoons A_+ + A_-$$

so that

$$[A] = [A_+] + [A_-]$$

If α is the average number of particles per unit volume, then

applied at temperature T , then

$$[A_+] = \alpha e^{-\frac{E_+}{kT}} \quad [A_-] = \alpha e^{-\frac{E_-}{kT}}$$

where the factor of α is due to the probability of finding a particle in a unit volume.

ion.

Assume the perfect gas equation of state to be

$$p = \alpha kT$$

where R is the gas constant per mole and N is the number of molecules per mole.

weight.

If E is the internal energy per gram, then

by

$$E = \frac{3}{2} kT$$

Then from the relation

$$E = \frac{P}{(\gamma-1)\rho}, \quad (5)$$

γ is given by

$$\gamma = \frac{\beta}{\beta-1}. \quad (6)$$

For a perfect gas γ is equal to the ratio of specific heats, although, in general, particularly for a solid, this is not true.

Following Bethe we define a quantity ϵ from the enthalpy i , i.e.,

$$i = E + \frac{P}{\rho} = \frac{R}{M} T \epsilon = \beta \frac{P}{\rho}. \quad (7)$$

From (3) and (7),

$$E = (\epsilon - g) \frac{R}{M} T = \left(\frac{\epsilon}{g} - 1 \right) g \frac{R}{M} T,$$

or

$$\beta = \frac{\epsilon}{g}. \quad (8)$$

The quantities β and ϵ have been defined for computational purposes. We can define a parameter analogous to β separately for atoms, ions, and electrons. This parameter $\beta(q_1)$ will include the energy of translation and electronic excitation, hence for each species

$$\beta(q_1) - 1 = \frac{E(q_1)}{kT} \quad (9)$$

where $E(q_1)$ is the internal energy per particle and where q_1 stands for a particular particle which, in our case may be an argon atom, A, an argon ion, A^+ , or an electron, e ; i.e.,

Then from the relation

$$E = \frac{h\nu}{\lambda}$$

λ is given by

For a perfect gas λ is equal to the ratio of specific heats, γ , in general, γ is given by

Following Boltzmann's theory γ is given by

$$\gamma = \frac{f+2}{f}$$

From (3) and (4)

$$T = \frac{h\nu}{k \ln \left(\frac{1}{1 - e^{-h\nu/kT}} \right)}$$

or

The quantities λ and γ are determined by the temperature of

the gas. We can define a parameter θ by the relation $\theta = h\nu/k$

Then, and also γ is a function of θ and θ is a function of T

transformation and electric field, and hence for each substance

$$h\nu/k$$

$$\theta = \frac{h\nu}{k}$$

where E_{ion} is the ionization energy per electron and θ is a function of T

a particular substance which is only a function of T and θ

where E_{ion} is the ionization energy per electron and θ is a function of T

$$\beta(A)^{-1} = \frac{E(A)}{kT},$$

$$\beta(A^+)^{-1} = \frac{E(A^+)}{kT},$$

$$\beta(\mathcal{E}l)^{-1} = \frac{E(\mathcal{E}l)}{kT}.$$

If n, n^+ and n_e are the number of neutral atoms, the number of ions, and the number of electrons per cm^3 then the internal energy per gram is

$$E = \frac{nE(A) + n^+ \{E(A^+) + I\} + n_e E(\mathcal{E}l)}{\rho}.$$

Substitute the following quantities in E,

$$\rho = m(n+n^+), \quad [A] = \frac{n}{n+n^+}, \quad [A^+] = \frac{n^+}{n+n^+}, \quad [\mathcal{E}l] = \frac{n_e}{n+n^+}.$$

Then

$$E = [A] \frac{E(A)}{m} + [A^+] \frac{\{E(A^+) + I\}}{m} + [\mathcal{E}l] \frac{E(\mathcal{E}l)}{m}.$$

If we now substitute this into (7) using (3) we have

$$[A] \frac{E(A)}{m} + [A^+] \frac{\{E(A^+) + I\}}{m} + [\mathcal{E}l] \frac{E(\mathcal{E}l)}{m} + g \frac{R}{M} T = \epsilon \frac{R}{M} T.$$

We now divide through by $RT/M = kT/m$ obtaining

$$[A] \frac{E(A)}{kT} + [A^+] \frac{\{E(A^+) + I\}}{kT} + [\mathcal{E}l] \frac{E(\mathcal{E}l)}{kT} + g = \epsilon.$$

Using (2), (9), and the fact that $[\mathcal{E}l] = [A^+]$ we finally have

If a, b and c are real numbers, then

and the same is true for a, b and c .

is

$\frac{1}{2}$

Substituting $\frac{1}{2}$ for a and b in (1)

$\frac{1}{2} = \frac{1}{2}$

Then

$\frac{1}{2}$

If

$\frac{1}{2}$

We now divide (1) by (2) and get

$\frac{1}{2}$

Using (2) in (1) we get

$$\epsilon = \beta(A) [A] + \beta(A^+) [A^+] + \frac{I(A)}{kT} [A^+] + \beta(\epsilon l) [\epsilon l]$$

where $I(A)$ is the ionization energy for argon and $\beta(A)$ means β for neutral argon and includes the energy of translation and excitation. $\beta(A^+)$ is similarly defined for singly ionized argon. Since, for a free particle the energy is $3/2 kT$, from (9), we have

$$\beta(\epsilon l) = 2.5,$$

hence

$$\epsilon = \beta(A) [A] + [A^+] \left\{ \beta(A^+) + \frac{I(A)}{kT} + 2.5 \right\}. \quad (10)$$

The equilibrium constant for the argon interaction is

$$K = \frac{[A^+] [\epsilon l]}{[A]} \quad (11)$$

or, if $x = [A^+]$,

$$K = \frac{x^2}{1-x}. \quad (12)$$

3. The Partition Functions.

Once the equilibrium conditions have been defined, then, for an ionizing reaction the Saha equation may be used to write the equilibrium constant in terms of the partition functions. The Saha equation for the argon equilibrium reaction may be written

$$K = \left(\frac{2\pi k\mu}{h^2 N_0} \right)^{3/2} \cdot \frac{1}{n_1} \cdot \frac{T^{3/2}}{\gamma} \cdot \frac{Z_n(A^+) \cdot Z(\epsilon l) \cdot e^{-I/kT}}{Z(A)}, \quad (13)$$

where μ is the reduced mass, i.e.,

$$C = \frac{1}{2} \left(\frac{1}{\lambda} + \frac{1}{\lambda'} \right) \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right)$$

where $\lambda(\lambda')$ is the wavelength of the incident (reflected) light and C is the constant of proportionality.

$\delta(\lambda)$ is the difference between the incident and reflected wavelengths.

Free particles are assumed to be in thermal equilibrium with the radiation.

hence

$$e^{-\delta(\lambda)/kT} = \frac{\lambda}{\lambda'} \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right)$$

The equilibrium constant for the reaction is

$$K = \frac{\lambda}{\lambda'}$$

$$\text{or, if } x = \frac{\lambda}{\lambda'}$$

3. The reaction equilibrium

Once the equilibrium constant has been determined, the reaction

ionizing reaction can be determined and the reaction equilibrium

constant in terms of the reaction equilibrium constant can be

derived. The reaction equilibrium constant can be written as

$$K = \frac{\lambda}{\lambda'} \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right) = \frac{\lambda}{\lambda'} \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right) \frac{1}{\lambda}$$

where λ is the wavelength of the incident light.

$$\mu = \frac{m^+ m_e}{m}, \quad m = m^+ + m_e \quad (14)$$

and

n_1 = number of argon atoms in one cm^3 of the undisturbed gas in front of the shock

η = density ratio = ρ_4/ρ_1

ρ_1 = density of the undisturbed gas (cf Fig. 1, Part II)

ρ_4 = density in the equilibrium region behind the shock

k = Boltzmann's const

h = Planck's const

N_0 = Avogadro's number

T = temperature in degrees absolute

I = first ionization potential of argon

$Z(A^+)$ = internal partition function for the argon ion

$Z(A)$ = internal partition function for the neutral argon atom

$Z(e)$ = internal partition function for the electron.

The density ratio η is used in (13) in place of the corresponding pressure ratio ξ because η varies between 1 and about 10 across the shock front whereas ξ may become very large and, in fact, is set equal to ∞ in the strong shock approximation.

The internal partition functions are defined by

$$Z = \sum_n g_n e^{-E_n/kT} \quad (15)$$

where n corresponds to a state of the system with energy E_n and sta-

and

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tistical weight g_n (the energy of the ground state is arbitrarily set equal to zero). The internal partition function of the electrons reduces simply to the degeneracy 2. Hence, if

$$f = f(T, \eta) = \left(\frac{2\pi k\mu}{h^2 N_0} \right)^{3/2} \cdot \frac{1}{n_1} \cdot \frac{T^{3/2}}{\eta}, \quad (16)$$

then

$$K = 2f \frac{Z(A^+) \cdot e^{-I/kT}}{Z(A)}. \quad (17)$$

At high temperatures the higher excited states of the atom become numerous and may contribute appreciably to the partition function. The summing over these higher states could become quite laborious but even worse would be the overlapping of the higher quantum states of neighboring atoms. Therefore, a cut-off must be made. This cut-off successively eliminates the high quantum states of the atom as the density is increased. The corresponding process is termed pressure ionization.

The radius of a hydrogen-like electron orbit is

$$a_n = a_0 n^2 \quad (18)$$

where a_0 is the first Bohr radius and n is the principal quantum number. We now assume all electron orbits to be suppressed whose radius a_n exceeds half the average distance between atoms. Let this half-distance be r_0 ; then, if L is the number of atoms per cm^3 in front of the shock,

$$\frac{4\pi}{3} r_0^3 = \frac{1}{L\eta}$$

or

statistical weight of the evidence is not equal to unity. The statistical weight of the evidence is equal to unity only if the evidence is not ambiguous.

then

At high concentrations of the evidence, the evidence is not ambiguous. At low concentrations of the evidence, the evidence is ambiguous. At intermediate concentrations of the evidence, the evidence is ambiguous.

eliminate the evidence. The evidence is not ambiguous. The evidence is ambiguous. The evidence is ambiguous.

The evidence is not ambiguous. The evidence is ambiguous. The evidence is ambiguous.

where a is the evidence. We now assume that the evidence is not ambiguous. We now assume that the evidence is ambiguous. We now assume that the evidence is ambiguous.

$$r_o = \left(\frac{3}{4\pi L \eta} \right)^{1/3}.$$

From (18), the limiting value of n is

$$n = \left(\frac{r_o}{a_o} \right)^{1/2} = \frac{1}{a_o^{1/2}} \left(\frac{3}{4\pi L \eta} \right)^{1/6}$$

$$n_\eta = D \cdot \eta^{-1/6}, \quad D = \text{const} = \frac{1}{a_o^{1/2}} \left(\frac{3}{4\pi L} \right)^{1/6}. \quad (19)$$

As n_η is non-integer, g is reduced proportionately in the following way:

For $n > n_\eta + \frac{1}{2}$ the state will be completely cut off and for $n \leq n_\eta - \frac{1}{2}$

the state will be fully counted in the partition function. In between

these values of n the multiplicity is adjusted according to the formula

$$g_{\text{effective}} = g_n \left\{ \frac{(n_\eta + 1/2) - n}{(n_\eta + 1/2) - (n_\eta - 1/2)} \right\} = g_n (n_\eta + 1/2 - n) \quad (20)$$

Hence, the internal partition function of the atom depends not only on the temperature but to a small extent on the density, i.e.,

$$Z = Z(T, \eta).$$

The effect of the above approximation is discussed in Ref 69 where it is pointed out that the partition function of the free electrons is underestimated, since their potential energy is neglected. Also, the integration over phase space is not carried out properly. While it is difficult to estimate the size of the error, it can not be large since theory and experiment are in good agreement (cf Part III, section 3). In addition, the above theory agrees with more precise calculations made at Los Alamos.

From (12), the characteristic equation is

$$\lambda^2 + 2\lambda + 1 = 0$$

As $\lambda = -1$ is a root of the characteristic equation, the general solution of the homogeneous equation is

$$y_h = C_1 e^{-x} + C_2 x e^{-x}$$

The state will be stable if the real part of the eigenvalues is negative. Thus we have

Therefore, the system is stable.

Hence, the system is stable.

The characteristic equation is

$$\lambda^2 + 2\lambda + 1 = 0$$

The roots of the characteristic equation are

$$\lambda = -1, -1$$

It is pointed out that the system is stable if the real part of the eigenvalues is negative. Thus we have

understanding of the system is essential for the design of the controller. The system is stable if the real part of the eigenvalues is negative. Thus we have

Integration over time and the system is stable. Thus we have

difficult to achieve for the system. Thus we have

theory and experimental results. Thus we have

In addition, the system is stable. Thus we have

at Los Angeles.

The contribution to the partition function from the low states is easy to obtain because of their small number. However, the contributions from the higher states which have one electron excited to $n \geq 4$ is a different matter both because of the great number available and because of the cut-off that must be made. Hence the partition function for the neutral atom may be written as

$$Z = Z_{\text{low}} + Z_{\text{high}} \quad (21)$$

where Z_{low} is summed over the low states ($n = 3$) as in (15).

The ground state of argon is a $(3p)^6 {}^1S_0$ level with a multiplicity of one and an energy by convention equal to zero. There is also a level from the configuration $(3p)^5(3d)$, observed spectroscopically, which has a relatively high energy, viz, 113000 cm^{-1} or $162,500$ degrees. This level has a multiplicity 60. Levels with two excited electrons have such high energies as to be unimportant in the partition function. Using these levels the evaluation of Z_{low} is shown in the following table: (cf Table IV, Part III)

Table I

(A I at $T = 25000^\circ$)

State	g_n	$E_n (\text{cm}^{-1})$	$E_n (\text{degrees})$	$g_n e^{-E_n/kT}$
$3p^6 {}^1S$	1	0	0	1
$3p^5 d$	60	113,000	162,500	.0902

From this table it is seen that $Z_{\text{low}} = 1.0902$ when $T = 25000^\circ$.

We now evaluate Z_{high} by the following approximation: Consider a highly excited atom as an ion with an electron moving around the ion in a large orbit. The spectrum will be alkali-like and the energy E_{nl} , of a state of principal quantum number n and orbital quantum number l , will be

$$E_{nl} = I + E_{\text{ion}} - E'_{nl} \quad (22)$$

where

E_{ion} = excitation energy of the ion ($\gg 0$)

E'_{nl} = binding energy of the electron.

If (22) is substituted in (15) Z_{high} becomes

$$Z_{\text{high}} = Z_{\text{ion}} \cdot e^{-I/kT} \cdot z_{\text{high}} \quad (23)$$

Z_{ion} is determined similarly to Z_{low} although the low states are more numerous for A II than for A I. z_{high} is the partition function for the (one electron) high excited states of the neutral argon atom, neglecting the multiplicity of the core configuration (which is included of course in Z_{ion}). It is given by

$$z_{\text{high}} = \sum g_{nl}(\gamma) e^{+E'_{nl}/kT} \quad (24)$$

where $g_{nl}(\gamma)$ is the adjusted multiplicity, eq. (20). As shown by (22) E'_{nl} corresponds to a positive binding energy which is subtracted from the energy of the ion, i.e.,

$$E'_{nl} = I - E_n$$

where E_n is the excitation energy. The high excited states of the ion

have not been included because their contribution to the partition function is negligible in the temperature range with which we are concerned.

4. The Energy Content.

Knowing the partition function it is possible to obtain the various other thermodynamic functions. The energy content is of particular interest because of its importance in determining the shock conditions (section 5).

The average energy per particle in units of kT is

$$\beta(q_1) - 1 = \frac{3}{2} + \frac{\sum g_n \frac{E_n}{kT} e^{-E_n/kT}}{Z} \quad (25)$$

where $3/2$ represents the translational energy, E_n the internal energy per particle for the remaining degrees of freedom and Z is the corresponding partition function.

Let

$$W = \sum g_n \frac{E_n}{kT} e^{-E_n/kT} \quad (26)$$

then

$$\beta = \frac{5}{2} + \frac{W}{Z} \quad (27)$$

W may be evaluated in the same way as Z , i.e.,

$$W = W_{\text{low}} + W_{\text{high}} \quad (28)$$

where W_{low} is given by (26) but summed over just the low states. W_{high} is obtained by substituting (22) in (26):

have not been included because their contribution to the partition function is negligible in the temperature range with which we are concerned.

4. The Energy Content

Knowing the partition function it is possible to obtain the various other thermodynamic functions. The energy content is of particular interest because of its importance in determining the shock conditions (section 5).

The average energy per particle is given by

$$\bar{E} = \frac{\sum E_n \frac{e^{-E_n/kT}}{Z}}{\sum \frac{e^{-E_n/kT}}{Z}} \quad (25)$$

where $3/2$ represents the translational energy, E_n the internal energy per particle for the remaining degrees of freedom and Z is the corresponding partition function.

Let

$$W = \sum E_n \frac{e^{-E_n/kT}}{Z} \quad (26)$$

then

$$\bar{E} = \frac{W}{Z} \quad (27)$$

W may be evaluated in the same way as Z , i.e.,

$$W = W_{\text{low}} + W_{\text{high}} \quad (28)$$

where W_{low} is given by (26) but summed over just the low states.

is obtained by substituting (26) in (25).

$$W_{\text{high}} = \frac{I}{kT} Z_{\text{high}} + e^{\frac{-I}{kT}} (W_{\text{ion}} z_{\text{high}} - w_{\text{high}} Z_{\text{ion}}) \quad (29)$$

where

$$W_{\text{ion}} = \sum g_n \frac{E_{\text{ion}}}{kT} e^{\frac{-E_{\text{ion}}}{kT}} \quad (30)$$

and

$$w_{\text{high}} = \sum g_{nl}(\gamma) \frac{E'_{nl}}{kT} e^{\frac{E'_{nl}}{kT}} \quad (31)$$

and Z_{high} , Z_{ion} , z_{high} are determined according to (23) and (24).

Equation (25) follows from the formula for the internal energy per mol E_1 , i.e.,

$$E_1 = RT^2 \frac{d}{dT} \ln Z_1. \quad (32)$$

Other quantities of interest in shock propagation may be similarly determined. If F_1 is the free energy per mol, S_1 the entropy, and C_1 the heat capacity per mol, then

$$F_1 = -RT \ln Z_1 \quad (33)$$

$$S_1 = R \frac{d}{dT} (T \ln Z_1) \quad (34)$$

$$C_1 = R \frac{d}{dT} T^2 \frac{d}{dT} \ln Z_1 = \frac{dE_1}{dT}. \quad (35)$$

In equations (32) to (35) only the contributions from the internal degrees of freedom are included.

5. The Shock Front without Heat Conduction or Viscosity.

In sections 2 to 4 we have shown how component concentrations and energy content may be calculated in a gas which is in a state of complete thermal equilibrium. If we now specify this equilibrium state to be that which exists behind a shock front, then the density and temperature are determined by the conservation equations, the equation of state, the shock velocity, and the initial conditions. In this section we assume that heat conductivity and viscosity can be neglected which is perfectly valid if the conditions are those of equilibrium (cf section 6).

The procedure for calculating β for atoms and ions is given in section 4 and that for calculating ϵ and g in section 2. Then, from (8), the value of β for the gaseous mixture is given by

$$\beta = \frac{\epsilon}{g}. \quad (36)$$

Consider a one-dimensional shock for which the shock equations may be written:

Conservation of mass:

$$\rho v = m = \text{const} \quad (37)$$

where ρ is the density and v the velocity with respect to the shock front, i.e.,

$$v = u - U, \quad (38)$$

u being material velocity and U the shock velocity.

Conservation of momentum:

$$p + mv = mV, \quad V = \text{const} \quad (39)$$

Conservation of energy:

$$\beta \frac{p}{\rho} + \frac{1}{2} v^2 = \frac{1}{2} C^2, \quad C = \text{const.} \quad (40)$$

 

case of scattering.

The equation of state is given by (3), i.e.,

$$p = g \frac{R}{M} \rho T. \quad (41)$$

If we substitute (37) and (41) into (39) and (40) and divide through by ρ_1^2 we obtain

$$g \eta^2 \frac{R}{M} T - \frac{m}{\rho_1} v \eta + \left(\frac{m}{\rho_1} \right)^2 = 0$$

$$\beta g \frac{R}{M} \eta^2 T - \frac{1}{2} c^2 \eta^2 + \frac{1}{2} \left(\frac{m}{\rho_1} \right)^2 = 0.$$

We take the variable parameter, aside from the initial conditions, to be the shock velocity U . This is because it is the most accurately measured quantity in shock experiments. Also, in producing shock waves by high explosives, one method is to detonate a stick of high explosive in a gas chamber. In this case the detonation velocity and the shock velocity in the gas will be equal and detonation velocities are well known.

The last two equations are re-written as

$$g \eta^2 \frac{R}{M} T - UV \eta + U^2 = 0 \quad (42)$$

$$\beta g \frac{R}{M} \eta^2 T - \frac{1}{2} c^2 \eta^2 + \frac{1}{2} U^2 = 0 \quad (43)$$

The constants V and C are determined from the conditions in front of the shock. Then, for a given value of U , and if $\beta(\eta, T)$ and $g(\eta, T)$ are known, the quantities η , T , ξ and u may be uniquely determined in the shock front and behind the shock front.

The equation of state is given by (3), i.e.,

$$p = \epsilon \frac{E}{M} \quad (41)$$

If we substitute (37) and (41) into (39) and divide through by

ρ_1^2 we obtain

$$\frac{2E}{M} + \frac{1}{2} \left(\frac{u}{V_1} \right)^2 = 0$$

$$\frac{2E}{M} + \frac{1}{2} \left(\frac{u}{V_1} \right)^2 = 0$$

We take the variable parameter, aside from the initial conditions,

to be the shock velocity U . This is because it is the most accurately

measured quantity in shock experiments. Also, in producing shock waves

by high explosives, one wishes to produce a shock of high explosive

in a gas chamber. In this case the detonation velocity and the shock

velocity in the gas will be equal and detonation velocities are well

known.

The last two equations are re-written as

$$\frac{2E}{M} + \frac{1}{2} \left(\frac{u}{V_1} \right)^2 = 0 \quad (42)$$

$$\frac{2E}{M} + \frac{1}{2} \left(\frac{u}{V_1} \right)^2 = 0 \quad (43)$$

The constants V and U are determined from the conditions in front of the

shock. Then, for a given value of U , and if $\rho_1(T)$ and $g_1(T)$ are known,

the quantities $\rho_2(T)$ and u may be uniquely determined in the shock

front and behind the shock front.

In the above equation radiation has been neglected but a brief consideration shows that this is probably a good approximation for the range of shock strengths* we are considering. For example, if $\xi = 500$, $\gamma = 7$, and $\gamma = 4/3$ which is about right for $T = 20,000$ deg and $U = 6 \cdot 10^5$ cm/sec, then the energy density for internal degrees of freedom is 10^{11} ergs per gram. However, if we assume black-body radiation, the radiation density is only about 10^5 ergs per gram.

Assuming about 0.1 of the argon atoms are either excited or ionized (cf Part III, Table IV) and an average wave-length for emitted radiation of $2 \cdot 10^{-5}$ cm, we obtain a rate of radiation of about 10^{15} ergs per gm per sec (see eq (28), Part II). If we compare this with the internal energy, viz, 10^{11} ergs per gm we see that the relaxation time, $E/\dot{E}$, for radiation loss is of the order of 100μ secs. It may be seen from Fig 17, Part III, that this relaxation time is much longer than times of interest in the shock front. (As will be shown in Part III, times of interest are of the order of magnitude of 10^{-8} sec, which is also about the lifetime of a radiative transition.) Even the total shock width involves a time considerably less than the above relaxation time.

* Shock strength is defined here as the pressure ratio $\xi = p_4/p_1$ where p_4 is the equilibrium pressure and p_1 is the fore-pressure.

6. The Shock Front with Heat Conduction and Viscosity.

We have shown in section 5 how the equilibrium conditions behind a shock front may be determined; however thermal conductivity and viscosity have been omitted from the equations. In this section we will include these terms and briefly consider how the equations could then be treated.

In the temperature range of interest here (5000° to $30,000^{\circ}$) values of the heat conductivity K or the viscosity μ are not well known. But it has been indicated, eq (35), how the specific heat and, eq (6), γ may be determined. According to Chapman and Cowling (Ref 70) the quantity

$$f_1 = \frac{K}{\mu C_v} \quad (44)$$

is reasonably constant with temperature if γ is constant (see, also, Ref 71). It is doubtful that such a relation is valid if ionization is involved, i.e., if γ varies. However, if we knew the specific heat at constant volume C_v the ratio $\frac{K}{\mu}$ could, in principle, be obtained.

If heat conduction and viscosity are included in the conservation equations, (37) to (40), they may be written (Ref 63)

$$\rho v = m = \text{const} \quad (45)$$

$$mv + (p - \sigma) = mV = \text{const} \quad (46)$$

$$m \left(\frac{v^2}{2} + E \right) + v(p - \sigma) - H = \frac{1}{2} mC^2 = \text{const.} \quad (47)$$

6. The Shock Front with Heat Conduction and Viscosity

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$$\frac{K}{\eta} = \frac{1}{2} \frac{C_p}{C_v} \quad (44)$$

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If heat conduction and viscosity are included in the conservation equations, (37) to (40), they may be written (Ref 63)

$$\rho v = \rho = \text{const} \quad (45)$$

$$w + (p - \sigma) = w = \text{const} \quad (46)$$

$$n \left(\frac{1}{2} v^2 + \epsilon \right) + v(p - \sigma) - \frac{1}{2} \sigma = \text{const} \quad (47)$$

The equation of state is, again,

$$p = g \frac{R}{M} \rho T . \quad (48)$$

Assuming a γ -law and using (48), eq (47) becomes

$$m \left[\frac{v^2}{2} + (\beta - 1) g \frac{RT}{M} \right] + v(p - \sigma) - H = \frac{1}{2} m c^2 . \quad (49)$$

σ is the ordinary stress term due to viscosity and $-H$ is the heat flow intensity, i.e.,

$$H = K \frac{dT}{dx} , \quad \sigma = \frac{4}{3} \mu \frac{dv}{dx} \quad (50)$$

Putting the relation for σ into (46) and using (48) and (45) we get

$$\frac{4}{3} \frac{\mu}{m} \frac{dv}{dx} = v + \frac{gRT}{Mv} - v . \quad (51)$$

Substituting (46) into (49) and using the relation for H , (50):

$$\frac{K}{m} \frac{dT}{dx} = vV - \frac{1}{2} c^2 - \frac{v^2}{2} + (\beta - 1) \frac{gRT}{M} \quad (52)$$

Dividing (52) by (51):

$$\frac{dT}{dv} = \frac{4\mu}{3K} \frac{vV - \frac{v^2}{2} - \frac{1}{2} c^2 + (\beta - 1) \frac{gRT}{M}}{v + \frac{gRT}{Mv} - v} \quad (53)$$

Let

$$h(v, T) = v + \frac{gRT}{Mv} - v , \quad (54)$$

$$j(v, T) = \frac{4\mu}{3K} \left[vV - \frac{v^2}{2} - \frac{1}{2} c^2 + (\beta - 1) \frac{gRT}{M} \right] ,$$

The equation of state

Assume that the

is the constant

intensity of

$\mu = 2$

Putting the

Substituting

Dividing

Let

or using,

$$\beta - 1 = \frac{1}{\gamma - 1} ,$$

$$j(v, T) = \frac{4}{3} P_r \left[\frac{M (\gamma - 1)}{gR} \left(vV - \frac{v^2}{2} - \frac{1}{2} c^2 \right) + \frac{T}{\gamma} \right] \quad (55)$$

where P_r is a modified Prandtl's number (Ref 63), which is g times the usual Prandtl's number,

$$P_r = \frac{\gamma gR}{(\gamma - 1)M} \frac{\mu}{K} \quad (56)$$

If $h = 0$, conservation of momentum is obtained and $j = 0$ gives conservation of energy.

Letting

$$v^2 = z, \quad 2v dv = dz;$$

then (53) becomes, with (54), (55),

$$\frac{dT}{dz} = \frac{2}{3} P_r \frac{\left[\alpha (V \sqrt{z} - \frac{z}{2} - \frac{1}{2} c^2) + \frac{T}{\gamma} \right]}{z + \frac{gRT}{M} - V \sqrt{z}} = \frac{k_1}{k_2} \quad (57)$$

where

$$\alpha = \frac{(\gamma - 1)M}{\gamma gR}$$

$$k_1 = \frac{2}{3} P_r \left[\alpha (V \sqrt{z} - \frac{z}{2} - \frac{1}{2} c^2) + \frac{T}{\gamma} \right]$$

and

$$k_2 = z + \frac{gR}{M} T - V \sqrt{z}$$

Equation (57) has a singularity whenever the numerator and the denominator on the right-hand side go to zero simultaneously. The curve of $k_2 = 0$ in the z, T -plane intersects the z -axis at $z = 0$ and at $z = V^2$ and has its maximum value of T at $z = V^2/4$. It is concave toward the z -axis. Since V^2 is always greater than or equal to z , the curve of $k_1 = 0$ in the z, T -plane has a negative derivative and is convex toward the z -axis. It intersects the T -axis at

$$T = \frac{\gamma-1}{\gamma R} \frac{C^2}{2}$$

and has a minimum at $z = V^2$, intersecting the k_2 -curve in the two points (z_1, T_1) and (z_4, T_4) where $z_1 > z_4$, $T_1 < T_4$ (cf Fig. 1). The shock width is then the distance between points 1 and 4.

Fig. 1

From $k_1 = k_2 = 0$,

$$z \left(\frac{\gamma+1}{2} \right) - \gamma V \sqrt{z} + (\gamma-1) \frac{C^2}{2} = 0$$

or

$$\sqrt{z} = \frac{\gamma V \pm \sqrt{\gamma^2 V^2 - (\gamma^2 - 1)C^2}}{\gamma + 1} \quad (58)$$

This shows that z is a sensitive function of γ which, in turn, depends on say z and T . A method for determining γ has been discussed previously.

Also, for $k_1 = k_2 = 0$

$$T = \frac{M}{gR} (V\sqrt{z} - z) = \alpha \left(\frac{C^2}{2} - \frac{z}{2} \right) \quad (59)$$

One may obtain the integral curves for (57) by using the method of isoclines. Writing (57) as

$$\frac{dT}{dz} = \frac{2Pr}{3\gamma gR} \frac{T - T_a}{T - T_b} \quad (60)$$

where

$$T_a = \gamma \alpha \left(\frac{z}{2} - V\sqrt{z} + \frac{C^2}{2} \right) \quad (61)$$

$$T_b = \frac{M}{gR} (V\sqrt{z} - z) \quad (62)$$

γ and g vary across the shock front staying, for our temperature range, between 1 and 2. As the temperature increases γ decreases and g increases their product remaining approximately constant.

Let

$$G = \frac{2Pr}{3\gamma gR} = \frac{2}{3} \frac{\mu/K}{(\gamma - 1)} \quad (63)$$

then (60) becomes

$$\frac{dT}{dz} = G\lambda, \quad \lambda = \frac{T_\lambda - T_a}{T_\lambda - T_b}, \quad T_\lambda = \frac{T_a - T_b}{1 - \lambda} \quad (64)$$

The isocline for dT/dz is a curve of constant λ . If $\lambda = \infty$, $T_\lambda = T_b$ and if $\lambda = 0$, $T_\lambda = T_a$. If $\lambda = 1$, $T_a = T_b$ and we obtain (58) where the plus sign corresponds to z_1 and the minus sign to z_4 . Using additional values for λ it may be seen that point 1 is a nodal point and point 4 is a saddle point, i.e., an infinite number of integral curves pass through point 1 and a finite number (viz., 2) through point 4. If $\lambda = (\gamma - 1)$ we obtain the second equation of (59), i.e.,

$$T_\lambda = \frac{(\gamma - 1)M}{\gamma g R} \left(\frac{c^2}{2} - \frac{z}{2} \right) \quad (65)$$

which is a straight line connecting the points 1 and 4.

If these results are applied to the region in which complete thermal equilibrium exists then, since $dT/dz = 0$ here, equations (58) and (59) may be used to calculate the equilibrium conditions. Fortunately, the viscosity and heat conductivity drop out for $dT/dz = 0$ and the method of section 5 may be used to compute the equilibrium conditions behind the shock front.

Application of the theory given in sections 2 to 5 is made in Part III. The partition functions and equilibrium constants for a wide range of densities and temperatures have been computed and are tabulated in Table IV of Part III. Equilibrium conditions behind the shock front

then (60) becomes

$$\frac{dT}{dt} = \frac{1}{2} \left(\frac{dT}{dt} \right)_{\text{max}}$$

The fraction of the total area is $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

where the area is the area of the rectangle and the area of the rectangle is the area of the rectangle.

additional values of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

and points $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

curves have a slope of $\frac{1}{2}$ and a slope of $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

points $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

which is a constant value of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

if these results are compared with the results of the other experiments, it is found that

equilibrium values of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

may be used to determine the values of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

viscosity and a constant value of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

of section 2 may be used to determine the values of $\frac{1}{2}$ and $\frac{1}{2}$ of the total area is $\frac{1}{2}$ of the total area.

the shock front

Application of the theory of shock waves to the case of a shock wave moving through a medium

III. The pressure and density of the gas behind the shock front

of density and pressure of the gas behind the shock front

Table IV. The pressure and density of the gas behind the shock front

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for U between $3 \cdot 10^5$ and $9 \cdot 10^5$ cm/sec and for $p_1 = 1.0$ and 59.38 cm Hg have been calculated and are presented in both graphical and tabular form.

for 1 between 1.0 and 1.5 and 1.5 and 2.0
have been calculated and are given in Table I
form.

PART II: THE NON-EQUILIBRIUM REGION

1. Introduction.

In Part I it has been shown how the conditions in the region behind the shock where thermal equilibrium is assumed to be established may be completely determined. We now wish to look at the non-equilibrium portion of the shock, i.e., the part between the undisturbed gas in front of the shock and the equilibrated region behind the shock.

Although a true thermodynamic temperature does not exist in this region, the velocity distribution of the neutral atoms, the ions, and the electrons is at each point close to maxwellian. We may therefore introduce a local "temperature" which is characteristic of this distribution. The use of such a temperature is probably valid, since the high density and pressure involved cause a maxwellian distribution to be very quickly established.

Let us divide the shock front in the following way. Region 1 is the undisturbed part in front of the shock. Region 4 is the part behind the shock in which complete thermal equilibrium is assumed to

Fig. 1

be achieved and for which the conditions have been previously calculated. In region 2 we assume only elastic collisions and a width of about two

mean free paths, as it has been shown that equilibrium between translational degrees of freedom is established in about two collisions for strong shocks (Ref 44, 45, 46). Because of the small extent of region 2 and because its thickness does seem to be known reasonably well, we will not consider it further. We will be concerned only with region 3 in the following. This is the region in which excitation and ionization of the argon atoms takes place and we wish to calculate how long it takes to go from point A to point B (Fig. 1), i.e., from where there is complete equilibrium between translational degrees of freedom only, to where there is complete equilibrium between all degrees of freedom.

To obtain the conditions at point A we use the shock equations with the assumption, however, that the internal degrees of freedom are not excited. We therefore use a constant γ , viz., $\gamma = 5/3$ for argon. The temperature at point A is given by

$$T_A = T_1 \frac{(\gamma-1)}{(\gamma+1)^2} \frac{p_1}{\rho_1 U^2} \left\{ \frac{2\rho_1^2}{p_1^2} U^4 - \frac{\rho_1}{p_1} \frac{(\gamma^2 - 6\gamma + 1)}{\gamma - 1} U^2 - 2\gamma \right\}.$$

Pressure is determined from

$$\frac{p_A}{p_1} = \xi_A = \frac{2\rho_1}{p_1(\gamma+1)} U^2 - \frac{1}{\gamma_\infty}$$

and density from

$$\frac{\rho_A}{\rho_1} = \gamma_A = \frac{\gamma_\infty \xi_A + 1}{\xi_A + \gamma_\infty}$$

mean free path, as it has been shown that equilibrium between translational degrees of freedom is established in about two collisions for strong shocks (Ref. 44, 45, 46). Because of the small extent of region 2 and because its thickness does seem to be known reasonably well, we will not consider it further. We will be concerned only with region 3 in the following. This is the region in which excitation and ionization of the argon atoms takes place and we wish to calculate how long it takes to go from point A to point B (Fig. 1), i.e., from where there is complete equilibrium between translational degrees of freedom only, to where there is complete equilibrium between all degrees of freedom. To obtain the conditions at point A we use the shock equations with the assumption, however, that the internal degrees of freedom are not excited. We therefore use a constant γ , viz., $\gamma = 5/3$ for argon. The temperature at point A is given by

$$T_A = T_1 \frac{p_1}{p_2} \frac{(\gamma+1)}{(\gamma-1)} \left\{ \frac{p_1}{p_2} \frac{(\gamma+1)}{(\gamma-1)} - \frac{p_1}{p_2} \frac{(\gamma+1)}{(\gamma-1)} \frac{U_1^2}{U_2^2} \right\}$$

Pressure is determined from

$$\frac{p_A}{p_1} = \frac{p_1}{p_2} \frac{(\gamma+1)}{(\gamma-1)} \frac{U_1^2}{U_2^2} - \frac{1}{\gamma}$$

and density from

$$\frac{\rho_A}{\rho_1} = \frac{p_1}{p_2} \frac{(\gamma+1)}{(\gamma-1)} \frac{U_1^2}{U_2^2}$$

where

$$\gamma_{\infty} = \frac{\gamma+1}{\gamma-1}.$$

(Derivation of these equations is indicated in Part III, section 4.)

If we knew the cross-sections for all the various atomic interactions that take place in a shock front, it should be possible to compute the rate^{of} transfer of energy from the translational degrees of freedom to the other degrees of freedom, i.e., the rate at which true thermal equilibrium is established. For argon, the interactions involved are fairly simple and many of the cross-sections are known. In the following sections these interactions are considered in some detail and it is shown how they may be used to compute conditions in the non-equilibrium region.

If n_e is the electron concentration, the rate of change of the number of electrons per cm^3 is

$$\frac{dn_e}{dt} = q - p.$$

q represents the rate at which electrons are produced and p the rate at which recombination takes place. (See, however, Part III, section 4.)

2. Production of Electrons in the Shock Front.

We first consider the means by which electrons are produced in the shock front and then, in section 3, consider how they recombine with the argon ions. There are numerous processes by which electrons are produced in forming a plasma. Hence the production term is written

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$$q = \sum_i q_i$$

where the summing is over all possible processes. Some of the processes will be neglected because the concentrations of one or more of the interacting components is small and some will be neglected because the interaction is small. In the final computation (cf Part III) only the processes (1) and (3) listed below are used, although one could easily include others.

We start with a maxwellian distribution of neutral argon atoms with a sufficient number in the high-energy tail to produce ionization by the reaction

This produces small concentrations of electrons and argon ions, A^+ , which then enter into the following reactions:

Reactions (4) and (5) offer small contributions compared to (3) but their cross-sections are known.

The reaction

is not included because the concentration of each of the reactants is

where the summing is over all possible processes i and j of the process

will be neglected because the probability of such a process is small.

interesting components are small and some will be neglected because

interaction is small. The final equation for the reaction (1) may be

processes (1) and (2) which are small. Although the final equation

include other

We start with a generalized description of the reaction (1) and (2)

a sufficient number of the reaction (1) and (2) processes is required to

reaction (1) and (2) are small. The final equation for the reaction (1)

This process is a description of the reaction (1) and (2) and (3)

which then enter into the following reaction

Reaction (1) and (2) are small. The final equation for the reaction (1)

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Reaction (1) and (2) are small. The final equation for the reaction (1)

small. However, this reaction may be of more importance than (5) but the cross-section is not available.

The reactions

and

are neglected because of the higher ionization potential of A II (27.62 ev) compared to that of A I (15.76 ev) as well as the low concentration of one or both of the reactants. In addition, the cross-sections are not available.

Finally, the absorption reaction,

is neglected because of the long lifetime involved (cf Part I, section 5), and because the photons escape from the system.

Finally, the argon atom may be excited by processes similar to the ones listed above. Once excited it can drop into a meta-stable state from which ionization can take place either by collisions of the second kind or by a photo-process. In both cases radiative transitions are involved and, as pointed out above, the lifetimes of radiative transitions are of such lengths as to warrant neglect of excitation. It is possible, however, that excitation processes compete with some of the one-step processes but the cross-sections are not known very well (although cf Ref 76).

If all processes are included the production term is

small. However, this reaction is not observed in the

the cross-section of the reaction.

The reaction

is not observed in the

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is not observed in the

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If all reactions

$$q = \sum_{i=1}^9 q_i \quad (10)$$

where q_1, q_2, q_3 , etc., represent the reactions (1) to (9) respectively.

2.1. Collisions between Atoms and Ions.

Since, at the peak of the shock (point A, Fig 1), only the translational degrees of freedom are excited and there are no electrons present, we consider first the reactions between argon atoms. q_1 and q_2 and the cross-sections involved in (1) and (2) are similar so only q_1 need be discussed in detail.

We write

$$q_1 = \iint f(v_1) f(v_2) \sigma_1(v_r) v_r d\vec{v}_1 d\vec{v}_2 \quad (11)$$

where $f(v_1), f(v_2)$ are the maxwellian distributions for the two reactants (in this case, neutral argon atoms), $\sigma_1(v_r)$ is the ionization cross-section, v_r is the relative velocity, and $d\vec{v}_1, d\vec{v}_2$ are the elements of volume in velocity space. The use of maxwellian distributions here is particularly good because of the high shock velocities to be considered (Ref 48) and because the masses of the reactants are equal. However, the cross-section $\sigma_1(v_r)$ is not well known and some assumptions must be made.

Very* little theoretical work has been done for the case of two heavy atoms colliding and not much more experimental work. The observed cross-sections for argon in argon are sketched in Fig. 2.

*Text which is typed in single-space may be omitted without interrupting the continuity.

(10)

$$p = \frac{1}{2} \sum_{i=1}^2 p_i$$

where p_1, p_2, p_3 , etc., represent the reactions (1) to (3) respectively.

2.1. Collisions between Atoms and Ions

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We write

$$p_1 = \int \int \int f_1(v_1) f_2(v_2) Q_1(v_1, v_2) dv_1 dv_2 \quad (11)$$

where $f_1(v_1)$, $f_2(v_2)$ are the Maxwellian distributions for the two reactants

(in this case, neutral argon atoms), $Q_1(v_1, v_2)$ is the transition cross-

section, v_1 is the relative velocity, and dv_1, dv_2 are the elements of

volume in velocity space. The use of Maxwellian distributions here is

particularly good because of the high shock velocities to be considered

(Ref. 18) and because the masses of the reactants are equal. However,

the cross-section $Q_1(v_1, v_2)$ is not well known and some assumptions must

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Very little theoretical work has been done for the case of two heavy atoms colliding and not much more experimental work. The observed cross-sections for argon in argon are sketched in Fig. 2.

*Text which is typed in single-space may be omitted without interrupting the continuity.

Fig. 2

Since agreement between the various observers is not good, we consider the reasons for the discrepancies.

To obtain a source of fast neutral particles, use is made of the charge transfer process which occurs without the direction of the neutralized ion being altered. A source of the appropriate ion is obtained which is then accelerated to the desired energy by an ion gun and allowed to pass through a chamber of neutral atoms. Charge exchange takes place and a beam of neutral atoms is emitted and the ions remaining in the beam are removed by an electrical field. The energy of the neutral beam is nearly the same as that of the original ion beam.

For the detection of fast neutral beams, three methods have been used. In the ionization method a neutral beam enters an ionization chamber and the relative ionization is measured. In the thermal method the neutral beam is allowed to impinge on a thermo-element and the beam intensity determined by the heating effect produced. In the secondary emission method the neutral beam strikes a metal surface and the secondary electrons produced are collected by an electrode held positive with respect to the surface. These methods of detection give relative intensities but, since only total cross-sections are required here, this is sufficient. The discrepancy between the observed cross-sections as measured by different observers is probably due to employment of different methods of measuring the neutral beam intensity.

Of the numerous methods used for measuring the cross-sections, one will be briefly described. A homogeneous beam of ions, e.g. A^+ , is caused to enter a collision chamber which is filled with neutral atoms. If the beam energy is small, charge exchange without ionization will take place and the

Fig. 3

flux of slow ions produced may be measured. The slow ions are attracted to the collecting cylinder Z which has in front of it a grid R. The saturation current i_c represents slow

Fig. 4

ions produced by charge exchange.

If the beam energy is large, not only will charge exchange take place but there will be ionization. If Z is positive with respect to R the saturation value for the electron

Fig. 5

current i_I will be measured from which the ionization cross-section may be computed. If Z is negative with respect to R, the total current measured will be that due to charge exchange i_C plus that due to ionization i_I . Knowing i_I it is then possible to calculate i_C , thus both charge exchange and ionization cross-sections may be computed.

Actually, as indicated by Fig. 2, the measurement of accurate ionization cross-sections is extremely difficult for the following reasons. The ionization currents produced are small, and the electrons which have to be collected in order to measure the ionization are produced in the presence of large quantities of slow positive ions produced both in the ionization process itself, and, more often, by charge exchange. The positive ions, when collected, may give rise to considerable quantities of secondary electrons. Also, the saturation electron current must be measured at a potential below that needed to ionize the gas by electron impact. Finally, particularly in argon and other inert gas atoms and ions, metastable atoms may be present which have the property of freeing electrons from surfaces on which they are incident.

It is appropriate to mention here that the chief difficulty in measuring excitation cross-sections arises from the low intensity of the effects produced. There will, of course, be a loss in intensity due to the presence of the gas itself, but, in addition, there will be losses in intensity due to the necessity of spectral analysis of the radiation emitted. This partially explains why excitation cross-sections for very low energies have not been measured.

If v is the velocity of relative motion of the two colliding atomic systems and u the orbital velocity of the electrons concerned in the particular excitation process, then, in discussing inelastic collisions, two regions are distinguished, viz., $|v/u| \gg 1$ and $|v/u| \ll 1$. For the high-velocity region Born's approximation may be used but since we are primarily interested in the low velocity region for which no suitable theory exists, we must, as pointed out above, use the observed cross-sections. The low velocity or near-adiabatic region is defined such that collisions occur so gradually that the chance of any ultimate transfer of energy is slight.

As indicated in Fig. 6, the cross-section in the near-adiabatic region is extremely small. The correspondence principle argument for this is the following. If the collision time τ of the atomic systems is large compared to the period T of the electron involved in the particular excitation (or ionization) collision, then the orbital electrons have time to readjust themselves to the slowly changing conditions without a transition taking place. If a is the range of interaction between the atoms and v their relative velocity, the condition for weak excitation becomes

$$\frac{a}{v} \gg \frac{1}{\nu} .$$

The frequency ν is given by $\Delta E/h$ where ΔE is the internal energy involved in the electronic transition. The relative velocity is given by

$$v = 2\sqrt{\frac{e}{M}}$$

Fig. 6 Cross-sections for ionization by impact between two argon atoms or an argon atom and an argon ion. (Ref, 49)

where $\mathcal{E}$ is the relative kinetic energy and M is the mass of an argon atom.

The adiabatic condition then becomes

$$\frac{a}{2} \frac{\Delta E}{h} \sqrt{M} \gg \sqrt{\mathcal{E}}$$

or, using $a = 2 \times 10^{-8}$ cm, $h = 6.62 \times 10^{-27}$ erg sec, and expressing energies in electron-volts, the conditions becomes

$$16\Delta E \gg \sqrt{\mathcal{E}}$$

If ΔE is the ionization energy, then for argon $\mathcal{E} \ll 62$ kev. However, this is far from being a good criterion since for helium $\mathcal{E} \ll 15$ kev indicating the near-adiabatic region for argon should extend to about four times that of helium whereas experiment shows that it is less (cf Ref 52, p 530).

Since there is no reliable theory for the near-adiabatic region, one would be inclined to believe, on the basis of the above argument, that the ionization cross-section σ_1 should increase with $\mathcal{E}$ up to a rather flat maximum of the order of the gas-kinetic cross-section at $\mathcal{E} = 62$ kev at which energy the velocity of relative motion is comparable with the velocity of the atomic electrons concerned in the transition. It should then fall off perhaps with some v -power law. For the following reasons, however, the high-energy region need not concern us. First, the experimental values available extend only up to about 25 kev and, second, we are working with temperature distributions for which the number of particles in the high end of the maxwell tail is negligible.

where λ is the wavelength of the light
atom.
The relative velocity of the atom
or, using $v = \lambda f$,
energy is given by $E = hf$
It is the relative velocity
this is for the atom
indicating the atom
low, then the
(at $\lambda = 0.001$)
Since there is no relative motion
one would be surprised to find
that the frequency of the light
rather than the wavelength
 $\lambda = 0.001$ nm as which means
with the velocity of the atom
It should be noted that the
moving towards the observer
The relative velocity of the atom
and, hence, the frequency of the light
the number of waves per unit distance

In comparing the observed cross-sections as given in Fig. 2, it is evident that the results of two different observers may be off by a factor of two or more. The previously discussed experimental difficulties probably account for the discrepancies, with the error in measurement of the incoming flux being chiefly responsible. In view of the correspondence principle argument given above, the results of Berry showing a decrease in cross-section with increasing relative ion energy in the range 1 to 5 kev seem somewhat unlikely (Ref 52).

In order to obtain an integrable function approximating Rostagni's results, the curve (Fig. 6) was fitted in the following way. The zero-value was obtained by simply extrapolating the experimental values. The maximum cross-section was assumed to be at $\mathcal{E} \doteq 62$ kev at which point the slope is zero. In Table I, σ_1 and σ_2 are the cross-sections for reactions (1) and (2), $\mathcal{E}_a$ is the initial relative kinetic energy in electron volts and v is the relative velocity in cm per sec where

$$v = 3.106 \cdot 10^5 \mathcal{E}_a^{1/2}$$

Table I

$\mathcal{E}_a$ (ev)	$v \left(\frac{\text{cm}}{\text{sec}} \right)$	$\sigma_1 (\text{cm}^2)$	$\sigma_2 (\text{cm}^2)$
60	$2.406 \cdot 10^6$	0	0
100	$3.106 \cdot 10^6$	$.119 \cdot 10^{-16}$	$.129 \cdot 10^{-16}$
500	$6.945 \cdot 10^6$	1.140	1.280
1000	$9.822 \cdot 10^6$	1.891	2.174
62000	$7.734 \cdot 10^7$		

A cubic equation was fitted to these values where

$$\sigma_1(v) = a_1 v^3 + b_1 v^2 + c_1 v + d_1 \quad (12)$$

$$\sigma_2(v) = a_2 v^3 + b_2 v^2 + c_2 v + d_2 \quad (13)$$

with the constant factors being given in Table II.

Table II

	a	b	c	d
$10^{16} \cdot \sigma_1$	-2.948×10^{-23}	1.897×10^{-15}	2.355×10^{-7}	$-.5772$
$10^{16} \cdot \sigma_2$	-5.602×10^{-23}	4.949×10^{-15}	2.397×10^{-7}	$-.6045$

Above $\epsilon_a = 62$ kev σ_1 was assumed to drop off as $1/v$ which is perhaps incorrect but not important anyway, as will be shown below. In the neighborhood of $\epsilon_a = 62$ kev the cross-section should have approximately its gas-kinetic value. Equations (12) and (13) give for this energy, $\sigma_1 = 15 \times 10^{-16} \text{ cm}^2$ and $\sigma_2 = 21 \times 10^{-16} \text{ cm}^2$, values of the same order of magnitude as the gas-kinetic values.

By carrying out the integration in (11) using (12) it was found that energies above 1000 ev give no contribution. Hence we only need to use the cross-sections over their experimentally determined energy range. This is because the number of particles in the high end of the maxwell distribution is insignificant above 1000 ev for the range of temperatures involved. (Actually, 100 ev is probably high enough.)

A cubic equation was solved for the roots of the characteristic equation

$$\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0 = 0$$

$$a_2 = -\frac{1}{\tau_1} - \frac{1}{\tau_2} - \frac{1}{\tau_3}$$

with the constant terms a_1 and a_0 given by

λ_1	λ_2	λ_3
$-\frac{1}{\tau_1}$	$-\frac{1}{\tau_2}$	$-\frac{1}{\tau_3}$
$\frac{1}{\tau_1\tau_2}$	$\frac{1}{\tau_1\tau_3}$	$\frac{1}{\tau_2\tau_3}$
$-\frac{1}{\tau_1\tau_2\tau_3}$		

where τ_1, τ_2 and τ_3 are the time constants of the system

perhaps interpreted as the time constants of the system

the relationship between the time constants and the system parameters

namely the gain, the time delay, and the time constant of the system

energy, O_2 is the energy of the system, O_1 is the energy of the system

order of magnitude of the energy of the system

By carrying out the integration in the Laplace transform

that energy is about 1000 units, and the energy of the system

to use the cross-section of the system, and the energy of the system

range. This is because the energy of the system is about 1000 units

maxwell distribution in the system, and the energy of the system

temperatures involved in the system, and the energy of the system

Rostagni's results have been used for two reasons. First, his measurements on other gases are in agreement with other observers, indicating his method is good. And second, his measurements are in the lowest energy range, which is desirable for our problem.

In the very low energy range, say below 100 ev, the measurement of the cross-section is particularly difficult because the chance of energy transfer is so minute that it is not easy to reduce background effects to an unimportant magnitude. Wayland (Ref 72) found a low energy tail with a threshold value of 48 ev; however, this has not been incorporated into our computations. This should be done because of the maxwellian distributions involved. But, as yet, there is no satisfactory theoretical calculation available (Ref 75). The values we use in this range will not have much effect on the actual shock structure but are important in determining the shock width (cf Part III, section 7). As will be shown in the next section, reaction (3) offers the most important contribution to the electron production as soon as a sufficient number of free electrons are produced from reactions (1) and (2).

Inserting the expressions for the distribution functions into (11),

$$q = A \iint e^{-\frac{mv_1^2}{2kT}} e^{-\frac{mv_2^2}{2kT}} \sigma(v) v d\vec{v}_1 d\vec{v}_2 \quad (14)$$

where A is the normalizing factor. Change to relative coordinates v, V , the relative velocity and the center of mass velocity respectively:

$$\begin{aligned} \vec{v} &= \vec{v}_1 - \vec{v}_2 \\ \vec{V} &= \frac{1}{2} (\vec{v}_1 + \vec{v}_2). \end{aligned}$$

Since the Jacobian is unity,

$$d\vec{v}_1 d\vec{v}_2 = d\vec{v} d\vec{V}.$$

We then have

$$q = A \iiint e^{-\frac{m}{2kT} (2V^2 + \frac{1}{2} v^2)} \sigma(v) v d\vec{v} d\vec{V} \quad (15)$$

or, integrating out the center of mass,

$$q = 4\pi A \left(\frac{\pi kT}{m} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{mv^2}{4kT}} \sigma(v) v^3 dv \quad (16)$$

The integration over v is carried from the minimum ionizing velocity to infinity although, as pointed out above, 1000 ev is sufficient for the upper limit.

The normalizing factor A is determined from

$$\mathcal{V}^2 A \iint e^{-\frac{mv_1^2}{2kT}} e^{-\frac{mv_2^2}{2kT}} d\vec{v}_1 d\vec{v}_2 = 1$$

or

$$A = \frac{1}{\mathcal{V}^2} \left(\frac{m}{2\pi kT} \right)^3 \quad (17)$$

where $\mathcal{V}$ is the volume per particle. If n is the number density of particles at an arbitrary point in the shock front then

$$q_1 = \frac{\pi}{2} n^2 \left(\frac{m}{\pi kT} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{mv^2}{4kT}} \sigma_1(v) v^3 dv \quad (18)$$

where we have now written q_1 , since this derivation holds for reaction (1).

Since the Jacobian is

We then have

$$\frac{\partial(x, y)}{\partial(u, v)} = \begin{vmatrix} \frac{\partial x}{\partial u} & \frac{\partial x}{\partial v} \\ \frac{\partial y}{\partial u} & \frac{\partial y}{\partial v} \end{vmatrix}$$

or, integrating over the region

The integration over the region is carried out by changing the order of integration to

upper limit

The lower limit is

$$y = \frac{1}{2}x^2$$

or

where S is the region in the xy -plane bounded by the parabola $y = \frac{1}{2}x^2$ and the line $y = 1$.

particular case of the general case where the region is bounded by the parabola $y = \frac{1}{2}x^2$ and the line $y = 1$.

where we have the region

(1).

Only a minor change is necessary in (18) to write the corresponding expression for q_2 . For reaction (2) the normalizing factor, eq (17), becomes

$$A = \frac{1}{\mathcal{V}\mathcal{V}^+} \left(\frac{m}{2\pi kT} \right)^{3/2} \left(\frac{m^+}{2\pi kT^+} \right)^{3/2}$$

$\mathcal{V}^+$, m^+ , T^+ are the volume, mass, and mean temperature of the argon ions; however, under our assumptions $T^+ = T$. Also $m^+ \doteq m$ and

$$\mathcal{V}^+ = \frac{1}{n^+} = \frac{1}{n_e}$$

where n^+ is the number density for the argon ions and n_e that for the electrons. Hence

$$q_2 = \frac{\pi}{2} n n_e \left(\frac{m}{\pi kT} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{mv^2}{4kT}} \sigma_2(v) v^3 dv \quad (19)$$

In the relations for q_1 , q_2 , the quantities n, n_e , and T occur outside the integral and T also occurs inside each integral. These quantities all vary across the shock front as shown in the following table:

Only a minor change is necessary in (16) to write the corresponding

expression for q_2 . For reaction (2) the normalizing factor, eq (17),

becomes

$$A = \frac{1}{V_+} \left(\frac{n}{2\pi kT} \right)^{3/2} \left(\frac{n}{2\pi kT} \right)^{3/2}$$

V_+ , m_+ , T are the volume, mass, and mean temperature of the argon ions;

however, under our assumption $T = T_+$. Also $n_+ = n$ and

$$V_+ = \frac{1}{n} = \frac{1}{n_+}$$

where n is the number density for the argon ions and n_+ that for the

electrons. Hence

$$q_2 = \frac{n}{2} \int_{v_1}^{\infty} \left(\frac{n}{\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}} \frac{1}{v} dv \quad (19)$$

In the relations for q_1 , q_2 , the quantities n , n_+ , and T occur

outside the integral and T also occurs inside each integral. These

quantities all vary across the shock front as shown in the following

table:

Table III

Position on the Shock Front (cf Fig. 1) } → Quantity	Shock Velocity, $U = 6 \times 10^5$ cm/sec		
	1	A	B
T (degr)	285	32741	18400
$\gamma = \rho/\rho_1$	1	3.9674	7.123
$n_e(\text{cm}^{-3})$	0	0	$.160n = 1.974 \cdot 10^{19}$
γ	5/3	5/3	1.3216
ξ	1	456	523

(γ is the ratio of specific heats, and ξ the pressure ratio.)

2.2 Collisions between Electrons and Atoms.

Once electrons have been produced by the A+A reaction, then reactions between electrons and atoms take place. We consider reactions(3), (4), and (5), although, as pointed out previously, (3) is by far the most important reaction. It is sufficient to discuss q_3 in detail as q_4 and q_5 may be written immediately from q_3 .

As in (11), q_3 may be written

$$q_3 = B \iint f(v_1) f(v_2) \sigma_3(v) v d\vec{v}_1 d\vec{v}_2 \quad (20)$$

where B is the normalization factor, v_1 is the electron velocity, and v_2 the velocity of the neutral atoms. The relative and center-of-mass velocities are

(8)

S.S. Collisions

Once

along

(1)

most

of

As

where

v

velocities

$$\vec{v} = \vec{v}_1 - \vec{v}_2$$

and

$$\vec{V} = \frac{m_e}{M} \vec{v}_1 + \frac{m}{M} \vec{v}_2, \quad M = m_e + m.$$

Substituting these relations in (20) and remembering that the Jacobian for the transformation is one,

$$q_3 = B \iint e^{-\frac{1}{2kT} (MV^2 + \mu v^2)} \sigma_3(v) v d\vec{v} d\vec{V}.$$

μ is the reduced mass,

$$\mu = \frac{m_e m}{M}. \quad (21)$$

Integrating over V ,

$$q_3 = 16\pi^2 B \sqrt{\frac{\pi}{2}} \left(\frac{kT}{M}\right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{\mu v^2}{2kT}} \sigma_3(v) v^3 dv.$$

The normalization factor is obtained as before and is

$$B = n_e n \frac{(m_e m)^{3/2}}{(2\pi kT)^3} \quad (22)$$

v_1 is the minimum ionizing velocity, which, in this case, corresponds to the first ionization potential. n_e is the number density for electrons and n is the number density for the argon atoms. Thus we have

$$q_3 = \sqrt{\frac{2}{\pi}} n_e n \left(\frac{\mu}{kT}\right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{\mu v^2}{2kT}} \sigma_3(v) v^3 dv \quad (23)$$

and

have

Similarly,

$$q_4 = \sqrt{\frac{2}{\pi}} n_e n \left(\frac{\mu}{kT} \right)^{3/2} \int_{v_i'}^{\infty} e^{-\frac{\mu v^2}{2kT}} \sigma_4(v) v^3 dv \quad (24)$$

and

$$q_5 = \sqrt{\frac{2}{\pi}} n_e n \left(\frac{\mu}{kT} \right)^{3/2} \int_{v_i''}^{\infty} e^{-\frac{\mu v^2}{2kT}} \sigma_5(v) v^3 dv \quad (25)$$

v_i' corresponds to the second ionization potential, 44.0 ev, and v_i'' to the third ionization potential, 88 ev. The observed cross-sections, σ_3 , σ_4 , and σ_5 are shown in Fig. 7 (Ref 53). Because of the greater weight attached to the low energy cross-sections, values for σ_3 and σ_4 near the threshold are shown in Figs. 8A and 8B (Ref 54).

3. Recombination Processes.

After some electrons have been created by ionizing impacts between heavy particles, electron production increases with extreme rapidity due to the processes discussed in section 2.2. However, there are opposing processes, viz, recombination between electrons and ions. These are the following:

(a) Dielectronic recombination

Similarly,

$$Q_4 = \sqrt{\frac{2}{\pi}} n_0 \left(\frac{h}{kT} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{mv^2}{2kT}} Q_4(v) v^3 dv \quad (24)$$

and

$$Q_5 = \sqrt{\frac{2}{\pi}} n_0 \left(\frac{h}{kT} \right)^{3/2} \int_{v_2}^{\infty} e^{-\frac{mv^2}{2kT}} Q_5(v) v^3 dv \quad (25)$$

v_1 corresponds to the second ionization potential, 44.0 ev, and v_2 to the third ionization potential, 88 ev. The observed cross-sections, Q_3 , Q_4 , and Q_5 are shown in Fig. 7 (Ref. 23). Because of the greater weight attached to the low energy cross-sections, values for Q_3 and Q_4 near the threshold are shown in Figs. 2A and 2B (Ref. 24).

3. Recombination Processes

After some electrons have been created by ionizing impacts between heavy particles, electron production increases with extreme rapidity due to the processes discussed in section 2.5. However, there are opposing processes, viz, recombination between electrons and ions. These are the following:

(a) Dielectronic recombination

$A^+ + e \rightarrow A^* + \gamma$ (doubly excited atom, i.e., two electrons are excited)

Fig. 7 Cross-sections for ionization by impact between an argon atom and an electron. (Ref. 53)

Fig. 1. Cross-sections for ionization of atoms and on electron (Ref. 22)

Fig. 8A Threshold cross-section for the reaction $e + A \rightarrow e + A^+ + e$ (Ref. 54)

(4.5.199) $9.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \rightarrow A + 2$ polycrystalline for polycrystalline - 2000 bladed 17 40.0 m

Electron energy (eV)

Fig. 8B Threshold cross-section for the reaction $e + A \rightarrow e + A^{++} + 2e$ (Ref. 54)

80

(End)
E.O. 11-01

(b) Dissociative recombination

(c) Radiative recombination

(d) Three-body recombination

The first three processes, being two-body processes, are most important at low pressures whereas the fourth process becomes most important at higher pressures.

The recombination term p in equation (4) becomes

$$p = \sum_i p_i$$

where p_i is summed over all possible processes, i.e.,

p_1 = dielectronic recombination

p_2 = dissociative recombination

p_3 = radiative recombination

p_4 = three-body recombination.

3.1 Dielectronic Recombination.

When an electron recombines with an ion some energy is released.

If this energy is taken up by a second atomic electron, a doubly excited atom will be formed,

Because of the length of the lifetimes involved, we will probably not be interested in how A'' decays. That is, A'' will either revert to its ini-

(b) Dissociative recombination

(c) Radiative recombination

(d) Three-body recombination

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3.1 Dielectronic Recombination

When an electron recombines with an ion some energy is released.

If this energy is taken up by a second atomic electron, a doubly excited

atom will be formed,

because of the length of the lifetimes involved, we will probably not be

interested in how A^{**} decays. That is, A^{**} will either revert to the ion

tial state, ejecting one electron and leaving the other excited electron in its initial bound state,

or, the doubly excited atom will undergo a radiative transition going over to a stable, singly excited state,

We have then

It has not been possible to obtain an accurate cross-section for this process but we can gain some information by using a computation of Massey and Bates (Ref 22). There is a chance that the lifetime of A'' for decay to $A^+ + e$ is much greater than the time required for a radiative transition, i.e., 10^{-8} sec. Assuming such a possibility, then we may compute the contribution in the following way: The Saha equation may be written

$$\frac{n''}{n_e n^+} = \frac{1}{K} = \left(\frac{h^2}{2\pi\mu kT} \right)^{3/2} \frac{Z_n(A'')}{Z_n(e) Z_n(A^+)}$$

where K is the equilibrium constant and the Z_n are the partition functions described in Part I. This of course assumes the process is one of equilibrium which is not strictly true.

Each time an electron disappears a doubly excited complex appears,

that state, and it is not possible to find a single example of it in the United States. It is not only a matter of fact, but of law, that the country is not a single entity, but a collection of many different states, each with its own laws and customs. This is the reason why it is so difficult to find a single example of it in the United States. It is not only a matter of fact, but of law, that the country is not a single entity, but a collection of many different states, each with its own laws and customs. This is the reason why it is so difficult to find a single example of it in the United States. It is not only a matter of fact, but of law, that the country is not a single entity, but a collection of many different states, each with its own laws and customs. This is the reason why it is so difficult to find a single example of it in the United States.

hence

$$\left(\frac{dn_e}{dt}\right)'' = -\frac{dn''}{dt} = -\frac{n''}{\tau} = -p_1$$

where τ is the lifetime. In case there is more than one state for A'' then

$$p_1 = \left(\frac{h^2}{2\pi\mu kT}\right)^{3/2} \frac{\sum_s \frac{w_s e^{-\frac{E_s}{kT}}}{\tau_s}}{2w^+} \cdot n_e^2 \quad (\text{since } n_e = n^+)$$

w_s is the statistical weight of the collision complex A'' , w^+ is the statistical weight of the ion, and E_s is the energy excess of A'' above A^+ .

Substituting numerical values and assuming $\tau = 10^{-8}$ sec., $T = 20,000^\circ$, and that the statistical weights are of the order of unity then

$$p_1 \approx 10^{-14} n_e^2 \sum_s e^{-\frac{E_s}{kT}}$$

The lowest state for A'' will have an energy such that $\left(\frac{E_s}{kT}\right)$ is about 5, hence

$$p_1 \approx 10^{-16} n_e^2.$$

As will be seen later, this term can be neglected compared to p_3 and p_4 .

If the cross-section for this case is σ_{r1} then, neglecting the velocity distribution,

$$p_1 = \sigma_{r1} v n_e^2$$

and, for $T = 20,000^\circ$,

hence

where $\bar{t}$ is the

then

$$D = \frac{1}{2} \left(\frac{1}{\bar{t}} + \frac{1}{\bar{t}_0} \right)$$

w is the

statistical

A

Substituting

$T = 20,000$ and

then

The

The

hence

As

if

velocity

and

for

and

for

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for

for

for

for

$$\sigma_{r1} \approx 10^{-24} \text{ cm}^2.$$

On the basis of the above computation and because the concentrations of the reactants is small, this reaction will not be included in the final calculations of Part III.

3.2 Dissociative Recombination.

An argon atom and an argon ion may unite in a triple impact to form a molecular ion, A_2^+ . Because of the short duration of the time of formation, the process

could be of considerable importance. And, in fact, at low temperatures this is thought to be the case (Ref 30, 31, 32). However, molecular binding energies are low and since the mean temperatures we are considering are in the range from 2 to 3 electron volts, it is probably safe to assume that the concentration of A_2^+ is negligibly small.

3.3 Radiative Recombination.

In the previous sections two types of recombination processes have been briefly considered and it was indicated that their contribution to the total recombination process could be neglected. This will be verified by the discussion of the present and the following sections.

Radiative capture of an electron by an argon ion is a two-body process and may be represented by the reaction

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fied by the discussion of the present and the following sections.

Radiative capture of an electron by an argon ion is a two-body

process and may be represented by the reaction

where A' may be the ground state or any excited state of an argon atom. This can be regarded as a radiative transition of an electron from an unquantized (free) state to a bound state.

There is also the possibility of the attachment of an electron to an argon atom to form a negative ion. However, the cross-section for such a process is small, particularly for inert gas atoms (Ref 52), hence will be ignored.

So far observations of recombination rates have not been very successful for two reasons. First, as has been pointed out before, it is difficult to separate the various mechanisms involved. At low pressures and temperatures dissociative recombination occurs. As the temperature increases radiative recombination plays an increasingly important role and with increase in pressure, the three-body process enters.

The second difficulty lies in the order of magnitude of the effects produced. This may be indicated by the following consideration. The lifetime of an excited state of an atom is observed to be approximately 10^{-8} sec. This means that an electron must remain in an excited state in the neighborhood of an ion as long as 10^{-8} sec before there is considerable chance of its undergoing a radiative collision. Then if τ sec is the collision time, $\tau/10^{-8}$ is the chance of emission of radiation during an encounter. Collision times are of the order of a/v where a is the range of interaction and v is the relative velocity of the incoming electron. Taking $a = 10^{-8}$ cm and $v = 10^8$ cm/sec gives $\tau = 10^{-16}$ sec, hence the chance of capture to a particular quantum state is 10^{-8} , i.e., 10^8 encounters are required before an electron is captured.

where A may be ...
This can be ...
quantities (1) ...
There is ...
an error ...
such a process ...
hence will be ...
So for ...
for ...
it is ...
temperature ...
these ...
and with ...
The ...
process ...
the ...
in ...
alterable ...
I see ...
from ...
is the ...
coming ...
hence the ...
8
10

In the first experiments in which recombination was studied (Ref 35, 55) a discharge tube was employed. After short-circuiting the discharge the decay of electron density in the afterglow was investigated by visual intensity, by spectrophotometric measurements, and by probe measurements. Recently, a microwave technique has been employed (Ref 24, 26, 30, 32). The gas in a microwave cavity is ionized by the microwaves and the decay time for the electrons measured by observing the change in the resonant wave-length of the cavity. However, the recombination coefficients as measured by the microwave method are 10 to 100 times greater than those measured by the probe technique. This is probably due to dissociative recombination, as the experiments were done at relatively low temperatures.

Since experimental cross-sections are not available, it is necessary to develop a theoretical expression for the radiative reaction (26). What is needed is a relation for α as a function of temperature for the range $T \leq 3$ ev where

$$\left. \frac{dn_e}{dt} \right|_{\text{radiative}} = -\alpha_3(T) n_e^2$$

and $\alpha_3(T) = \sigma_r v$; or, if maxwell distributions are used, $\alpha_3(T) = \overline{\sigma_r v}$. v is the relative velocity of the incoming electron and σ_r is the cross-section for radiative capture.

It would be possible to use the inverse process, viz, photo-ionization,

by applying the theory of detailed balancing. But this reaction has neither been computed or measured (see, however, Part III, section 6).

An accurate theoretical derivation has been made only for hydrogen (Ref 36, 42). An approximate (classical) theory has been given by Kramers (Ref 41) and applied by Eddington (Ref 27) and Biondi (Ref 24). Biondi found that Kramers' theory gave a result for argon that was higher than

in the first experiment, the results were as follows:
(Ref. 35) a series of experiments were conducted to determine the effect of temperature on the rate of reaction between a certain substance and a certain reagent. The results showed that the rate of reaction increased with increasing temperature. The data are given in the following table:

Temperature (°C)	Rate of Reaction (g./hr.)
20	0.5
30	1.0
40	1.5
50	2.0
60	2.5

The above results are in good agreement with the theoretical predictions. The rate of reaction is proportional to the absolute temperature raised to the power of 1.5.

Since experimental conditions are not identical in all cases, it is not possible to compare the results of different experiments directly. However, the general trend of the results is the same. The rate of reaction increases with increasing temperature.

For the purpose of this study, the following data were obtained:

Temperature (°C)	Rate of Reaction (g./hr.)
20	0.5
30	1.0
40	1.5
50	2.0
60	2.5

and it is found that the rate of reaction is proportional to the absolute temperature raised to the power of 1.5. This is in good agreement with the theoretical predictions.

It would be possible to compare the results of different experiments by applying the theory of reaction rates. However, this would require a knowledge of the activation energy of the reaction.

Neither the experimental results nor the theoretical predictions are in good agreement with the results of the present study. This is due to the fact that the experimental conditions are not identical in all cases.

(Ref. 36) The results of the present study are in good agreement with the theoretical predictions. The rate of reaction is proportional to the absolute temperature raised to the power of 1.5.

the experimental value by a factor of ten; however, it has been pointed out that the measured recombination coefficients may include several processes whose contribution is unknown. Hence the theory could well be in error by several orders of magnitude.

To restate the problem, we have a plasma consisting of free electrons and neutral and singly-ionized argon atoms in various states of excitation with respective concentrations n_e , n and n^+ where $n^+ = n_e$ and the velocity distributions are maxwellian. The radiative capture cross-section for an electron by an argon ion, reaction (26), is to be estimated.

Classical Theory. When an electron passes through an electric field in which the charge distribution is uniform, it loses energy at a rate dependent upon the square of the acceleration. If the accelerating force is exerted by a positive charge, the path of the electron will be hyperbolic and such that the greatest acceleration, and consequently the greatest energy loss, will be at the point of closest approach to the positive charge. Kramers used this classical picture to develop the following theory for radiative recombination. Let us assume a uniform charge distribution to surround each argon nucleus. This charge distribution may be obtained by taking the self-consistent field calculations of Hartree (Ref. 43) for a neutral argon atom and reducing the outer orbital charge by unity with appropriate adjustment of the radius and charge density. The result is shown in Figs. 9, 10, 11. When the electron penetrates this charge distribution, it radiates energy at a

the experimental value by a factor of ten; however, it has been pointed

out that the measured recombination coefficients may include several

processes whose contribution is unknown. Hence the theory could well

be in error by several orders of magnitude.

To restate the problem, we have a plasma consisting of free electrons

and neutral and singly-ionized argon atoms in various states of excita-

tion with respective concentrations $n_1, n_2, \dots, n_n$ and n_0 and the

velocity distributions are Maxwellian. The radiative capture cross-

section for an electron by an argon ion, reaction (20), is to be esti-

mated.

Classical Theory. When an electron passes through an electric

field in which the charge distribution is uniform, it loses energy at

a rate dependent upon the square of the acceleration. If the accelera-

tion force is exerted by a positive charge, the path of the electron will

be hyperbolic and even though the greatest acceleration, and consequently

the greatest energy loss, will be at the point of closest approach to

the positive charge, Kramers used this classical picture to develop

the following theory for radiative recombination. Let us assume a uni-

form charge distribution to surround each argon nucleus. This charge

distribution may be obtained by taking the self-consistent field cal-

culation of Hartree (Ref. 43) for a neutral argon atom and reducing the

outer orbital charge by unity with appropriate adjustment of the radius

and charge density. The result is shown in Figs. 9, 10, 11. When the

electron penetrates this charge distribution, it radiates energy at a

Fig. 9 Charge distribution for a singly-ionized argon atom.

55

56

57

Fig. 10 Charge distribution for a singly-ionized argon atom.

Fig. 10. Dependence of the critical temperature T_c on the concentration of the monomer ϕ_1 for the system $\text{CH}_2=\text{CHCl}-\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CHCl}-\text{CH}=\text{CH}_2$ in the presence of $\text{CH}_2=\text{CHCl}$.

(ϕ_1 in mole fraction)

Fig. 11 Charge distribution for a singly-ionized argon atom.

(atomic units)

6.5

6.0

5.5

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

rate given by

$$R = \frac{2}{3c^3} |\ddot{\vec{D}}|^2 \left(= \frac{2e^2 \dot{v}^2}{3c^3} \right) \quad (28)$$

where $\vec{D}$ is the dipole moment. For a spherical charge distribution the dipole moment is zero, hence the only contribution to $\vec{D}$ is from the incoming electron, i.e.

$$\vec{D} = e\vec{r} \quad (29)$$

where $\vec{r}$ is the distance between the center of the atom and the impinging electron.

The equation of motion is

$$\mu \ddot{\vec{r}} = -e^2 Z_e \frac{\vec{r}}{r^3} \quad (30)$$

Z_e is the effective charge as seen by the electron as it passes through the charge cloud. This has been estimated on the basis of the Thomas-Fermi model to be between 11e and 13e (Ref 24). The self-consistent field gives the distribution shown in Fig. 12.

From (28) - (30),

$$R = \frac{2}{3c^3} \frac{e^6 Z_e^2}{\mu^2 r^4} \quad (31)$$

Since the incoming electron and the atomic ion are oppositely charged, the path of the electron through the charge cloud will be an hyperbola, the equation of which is

$$r = \frac{A}{1 - \epsilon \cos \phi} \quad (32)$$

where A and ϵ are constants, ϵ being the eccentricity.

are given by

$$E = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

where ϕ is the scalar potential and $\mathbf{E}$ is the electric field. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

where $\mathbf{E}$ is the electric field and $\mathbf{B}$ is the magnetic field. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

is the total energy of the system. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

where $\mathbf{E}$ is the electric field and $\mathbf{B}$ is the magnetic field. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

where $\mathbf{E}$ is the electric field and $\mathbf{B}$ is the magnetic field. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

Since the electric field and the magnetic field are related by

$$\mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}$$

where $\mathbf{A}$ is the vector potential, the total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

where $\mathbf{E}$ is the electric field and $\mathbf{B}$ is the magnetic field. The total energy of the system is then given by

$$U = \frac{1}{2} \epsilon_0 \int_{-\infty}^{\infty} \left(\frac{\partial \phi}{\partial t} \right)^2 + (\nabla \phi)^2 dV$$

Fig. 12 Effective charge as a function of radius for singly-ionized argon.

50
50

If $\vec{n}_r$ and $\vec{n}_\phi$ are unit vectors in the direction of increasing r and ϕ , then

$$\begin{aligned}\vec{r} &= r\vec{n}_r \\ \dot{\vec{r}} &= \dot{r}\vec{n}_r + r\dot{\phi}\vec{n}_\phi \\ \ddot{\vec{r}} &= \ddot{r}\vec{n}_r + 2\dot{r}\dot{\phi}\vec{n}_\phi + r\ddot{\phi}\vec{n}_\phi - r\dot{\phi}^2\vec{n}_r.\end{aligned}\tag{33}$$

Substituting in (30) the radial equation of motion is

$$\mu(\ddot{r} - r\dot{\phi}^2) = -\frac{e^2 Z_e}{r^2}.\tag{34}$$

For the angular momentum

$$L = \mu r^2 \dot{\phi} = \text{constant}.\tag{35}$$

Let

$$r = \frac{1}{u}, \quad \dot{r} = -\frac{1}{u^2} \frac{du}{dt},\tag{36}$$

then, from (35),

$$\mu\dot{\phi} = Lu^2, \quad \dot{r} = -\frac{L}{\mu} \frac{du}{d\phi}, \quad \ddot{r} = -\left(\frac{L}{\mu}\right)^2 u^2 \frac{d^2 u}{d\phi^2}.\tag{37}$$

Substitute in (34) obtaining,

$$\frac{d^2 u}{d\phi^2} + u = e^2 Z_e \frac{\mu}{L^2}.\tag{38}$$

From (32),

$$u = \frac{1 - \epsilon \cos \phi}{A}, \quad \frac{d^2 u}{d\phi^2} = \frac{\epsilon}{A} \cos \phi.\tag{39}$$

Hence, from (38) and (39),

$$A = \frac{L^2}{e^2 Z_e \mu},\tag{40}$$

If $\vec{r}$ and $\vec{p}$ are unit vectors in the direction of increasing r and ϕ , then

$$\begin{aligned} \vec{r} &= r\hat{r} \\ \vec{p} &= \dot{r}\hat{r} + r\dot{\phi}\hat{\phi} \\ \vec{L} &= r\dot{\phi}\hat{\phi} \times r\hat{r} = r^2\dot{\phi}\hat{\phi} \times \hat{r} = r^2\dot{\phi}\hat{z} \end{aligned} \quad (32)$$

Substituting in (30) the radial equation of motion is

$$m\ddot{r} = -\frac{dV}{dr} + \frac{L^2}{mr^3} \quad (33)$$

For the angular momentum

$$L = \mu r^2 \dot{\phi} = \text{constant} \quad (34)$$

Let

$$u = \frac{1}{r}, \quad \frac{dr}{dt} = -\frac{1}{u^2} \frac{du}{dt} \quad (35)$$

then, from (32),

$$\frac{d\phi}{dt} = \frac{L}{\mu r^2} = \frac{L}{\mu} u^2, \quad \frac{dr}{dt} = -\frac{1}{u^2} \frac{du}{dt} \quad (36)$$

Substituting in (33) we obtain

$$\frac{d^2u}{d\phi^2} + u = \frac{\mu}{L^2} \left(-r^2 \frac{dV}{dr} \right) \quad (37)$$

from (32),

$$u = \frac{1 - \epsilon \cos \phi}{A}, \quad \frac{dr}{dt} = \frac{L}{\mu} \frac{du}{d\phi} \quad (38)$$

Hence, from (35) and (36)

$$A = \frac{L^2}{\mu k} \quad (39)$$

and, for the equation of path,

$$u = \frac{e^2 Z_e \mu}{L^2} (1 - \epsilon \cos \varphi). \quad (41)$$

We now assume the total radiative energy loss to be given by

$$W = \int_{+\varphi_0}^{2\pi - \varphi_0} R dt$$

where $2\varphi_0$ is the angle between the asymptotes. Actually, if the electron loses energy, the incoming angle must differ from the outgoing angle; however, the assumption of equality is approximately justified classically as will be seen below. And, quantum mechanically, the assumption is even better. Substituting (31), (37), and (41) in W ,

$$W = \frac{4}{3c^3} \frac{e^{10} Z_e^4 \mu}{L^5} \left[\left(1 + \frac{\epsilon^2}{2} \right) (\pi - \varphi_0) + 2\epsilon \sin \varphi_0 - \frac{\epsilon^2}{4} \sin 2\varphi_0 \right]. \quad (42)$$

If v is the initial velocity and b the impact parameter, the angular momentum is

$$L = b\mu v.$$

The total energy of the system is

$$E = \frac{\mu}{2} (\dot{r}^2 + r^2 \dot{\varphi}^2) - \frac{e^2 Z_e}{r}.$$

From (41),

$$\frac{du}{d\varphi} = + \frac{\epsilon e^2 Z_e \mu}{L^2} \sin \varphi,$$

and, for the equation of path,

$$u = \frac{S}{L} (1 - \epsilon \cos \phi) \quad (41)$$

We now assume the total radiative energy loss to be given by

$$W = \frac{1}{2} \epsilon^2 \frac{S^2}{L^2} \sin^2 \phi_0$$

where ϕ_0 is the angle between the asymptotes. Actually, if the electron

loses energy, the incoming angle must differ from the outgoing angle;

however, the assumption of equality is approximately justified classically

as will be seen below. And, quantum mechanically, the assumption is even

better. Substituting (31), (37), and (41) in W,

$$W = \frac{1}{2} \epsilon^2 \frac{S^2}{L^2} \left[1 + \frac{\epsilon^2}{2} \right] (1 - \epsilon \cos \phi_0) + 2\epsilon \sin \phi_0 - \frac{\epsilon^2}{2} \sin 2\phi_0 \quad (42)$$

If v is the initial velocity and b the impact parameter, the angular

momentum is

$$L = bmv$$

The total energy of the system is

$$E = \frac{1}{2} m v^2 (1 + \epsilon^2 \sin^2 \phi_0) - \frac{e^2}{r}$$

from (41),

$$\frac{d\phi}{d\phi_0} = 1 + \frac{\epsilon^2 S^2}{L^2} \sin \phi_0$$

and, using (37),

$$\dot{r} = - \frac{\epsilon e^2 Z_e \sin \varphi}{L}, \quad r\dot{\varphi} = \frac{e^2 Z_e}{L} (1 - \epsilon \cos \varphi).$$

Substituting in E,

$$E = \frac{e^4 Z_e^2}{\mu b^2 v^2} \left(\frac{\epsilon^2 - 1}{2} \right).$$

Since

$$E = \frac{1}{2} \mu v^2,$$

and, from (32),

$$\epsilon = \frac{1}{\cos \varphi_0},$$

$$b = \frac{e^2 Z_e}{\mu v^2} \tan \varphi_0. \quad (43)$$

Eliminating ϵ and L in (42),

$$W = \frac{2}{3c^3} \frac{e^{10} Z_e^4}{\mu^4 b^5 v^5} \left[(\sec^2 \varphi_0 + 2)(\pi - \varphi_0) + 3 \tan \varphi_0 \right]. \quad (44)$$

Substitution of (43) into (44) shows that for our range of temperatures ($T \lesssim 3$ ev) φ_0 is close to zero, hence, to this approximation,

$$W = \frac{2\pi e^{10} Z_e^4}{3c \mu^4 b^5 v^5}. \quad (45)$$

The assumption is now made that if the energy lost by radiation W is greater than the initial kinetic energy of the electron, then capture takes place. Quantum mechanically this means that if the incoming angle differs from the outgoing angle, the electron falls into some quantum

and, when (2) is substituted in (1), we get

Substituting in (1)

Since

and, from (2)

Eliminating ϕ and ψ from (1), (2) and (3)

we get

Substituting (4) in (1) and (2)

Thus (1) and (2) are satisfied

The summation is positive and it is greater than the sum of the squares of the terms in the series

Take place

different from the series

state n, ℓ .

Let $W = \frac{1}{2}\mu v^2$ and solve for b :

$$b = \frac{(4\pi)^{1/5} Z_e^{4/5}}{\beta^{7/5}} r_o = \frac{217.68 Z_e^{4/5}}{v^{7/5}} \quad (46)$$

where

$$r_o = \frac{e^2}{mc^2}, \quad \beta = \frac{v}{c}.$$

The cross-section is

$$\sigma(v) = \pi b^2 = \frac{1.4885 \cdot 10^5 Z_e^{8/5}}{v^{14/5}} \quad (47)$$

in agreement with Ref 24.

Up to now the variation of Z_e has not been taken into account. Combining equation (46) and Fig. 12, Z_e may be obtained as a function of v . This is plotted in Fig. 13. Similarly $\sigma(v)$ is shown in Fig. 14.

The recombination term p_3 is

$$p_3 = \iint f(v_1) f(v_2) \sigma(v) v d\vec{v}_1 d\vec{v}_2$$

where the notation is the same as in section 2.2. Changing to relative coordinates, from equation (23)

$$p_3 = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT} \right)^{3/2} n_e^2 \int_0^\infty e^{-\frac{\mu v^2}{2kT}} \sigma(v) v^3 dv. \quad (48)$$

It will be shown in Part III that the above result is incorrect;

state n, l

Let $V = \frac{1}{2} \mu v^2$ and solve for v

$$v = \frac{h}{m \lambda} \quad (40)$$

where

$$\lambda = \frac{h}{m v}$$

The cross-section is

$$\sigma(v) = \pi r_0^2 \left(1 + \frac{1}{2} \left(\frac{v_0}{v} \right)^4 \right) \quad (41)$$

in agreement with Ref. 24.

Up to now the variation of σ has not been taken into account.

Combining equation (40) and Eqs. 12, 13, σ may be obtained as a function

of v . This is plotted in Fig. 13. Similarly $\sigma(v)$ is shown in Fig. 14.

The recombination term p_3 is

$$p_3 = \int_0^\infty \sigma(v) n_1(v) n_2(v) dv$$

where the notation is the same as in section 2.2. Changing to rela-

tive coordinates, from equation (23)

$$p_3 = \int_0^\infty \sigma(v) n_1(v) n_2(v) dv \quad (42)$$

It will be shown in Part III that the above result is incorrect.

Fig. 13 Effective charge as a function of relative velocity for radiative capture of an electron by a singly charged argon ion.

Fig. 14 Cross-section for radiative capture of an electron by a singly charged argon ion. (Classical theory)

hence, we present below the quantum theory which should give the correct answer but for which accurate computations have not been made.

Quantum Theory. Following the radiative capture of an electron by an argon ion, as indicated by (26), the resulting argon atom may be in its ground state which is a $3p^6$ level with an occupation number $1/Z(A)$ (cf Table IV, Part III), or in any one of its discrete excited states. The reaction is a transition of a free electron of energy $1/2\mu v^2$ to a bound state for which quantal theory gives an effective cross-section of

$$\sigma_e(n, l) = \frac{64\pi^4 e^2 \nu^3}{3h\nu c^3} |\vec{M}|^2.$$

The bound state is specified by the quantum numbers n, l , and v is the initial relative velocity, ν the frequency of the emitted radiation and $e\vec{M}$ the dipole moment where

$$\vec{D} = e\vec{M} = \int \psi_f e\vec{r} \psi_i^* d\tau.$$

The distance between the incoming electron and the center of the atom is $\vec{r}$, ψ_f is the normalized wave function for the bound state, and ψ_i is the wave function for the initial free state which is normalized to have the asymptotic form of a modified plane wave and the corresponding scattered wave. The amplitude of the plane wave is normalized for a flux of one electron/cm²/sec in the direction of the wave so that

$$\psi_i = \frac{N}{v^{1/2}} \left[e^{ikz} + \frac{e^{ikr}}{r} f(\theta) \right]$$

where $N/v^{1/2}$ is the normalization factor, $k = mv/\hbar$, e^{ikz} is the plane wave travelling in the z -direction, $\frac{e^{ikr}}{r} f(\theta)$ represents the scattered

hence, we present below the quantum theory which should give the correct answer but for which accurate computations have not been made.

Quantum Theory Following the radiative capture of an electron by

an argon ion, as indicated by (20), the resulting argon atom may be in its

ground state which is a $3p^6$ level with an occupation number $1/\chi(A)$ (cf

Table IV, Part III), or in any one of its discrete excited states. The

reaction is a transition of a free electron of energy $1/2mv^2$ to a bound

state for which quantum theory gives an effective cross-section of

$$\sigma_0(a, \lambda) = \frac{64\pi^2 a^3}{3} \frac{v^3}{c^3} |\tilde{M}|^2$$

The bound state is specified by the quantum numbers n, l , and m is the

initial relative velocity, λ the frequency of the emitted radiation and

$\tilde{M}$ the dipole moment where

$$\tilde{M} = e\hbar \int \psi_f^* \psi_i d\tau$$

The distance between the incident electron and the center of the atom is

$\tilde{\psi}_f$ is the normalized wave function for the bound state, and $\tilde{\psi}_i$ is the

wave function for the initial free state which is normalized to have the

asymptotic form of a modified plane wave and the corresponding scattered

wave. The amplitude of the plane wave is normalized for a flux of one

electron/cm²/sec in the direction of the wave so that

$$\psi_i = \frac{1}{\sqrt{v}} \left[e^{ikx} + \frac{ik}{k} f(\theta) e^{ikr} \right]$$

where $1/\sqrt{v}$ is the normalization factor, $k = mv/\hbar$, x is the plane

wave travelling in the x -direction, $\frac{ik}{k} f(\theta)$ represents the scattered

wave and $f(\theta)$ gives the angular dependence of the scattered wave. The total radiative capture cross-section will then be

$$\sigma_r = \sum_{n,l} \sigma_e(n,l)$$

where the summation is over all possible bound states of the argon atom. In Part I we saw that the number of bound states is limited by pressure ionization such that, for our range of temperature and pressure, there is no state for which $n > 8$.

We now assume (Bates et al, Ref 78) that for all excited states the wave functions ψ_f may be taken as those of the hydrogen atom since, for the excited states, the effective core charge is about one. However, the ground state wave function and the initial wave function must be evaluated numerically. The wave function for the ground state of the argon atom has been computed by Hartree using the method of self-consistent fields and is tabulated in Ref 8.

The initial wave function may be represented by

$$\psi_i = \sum_l (2l+1) \psi_i^l(r) P_l(\cos \theta).$$

$P_l(\cos \theta)$ is the l th Legendre coefficient with l the orbital quantum number. The ground state of argon, being a 3p level, can combine only with an s or a d state, hence only ψ_i^0 and ψ_i^2 need be determined. The wave functions ψ_i^l may be found by solving the Schrödinger equation

$$\frac{d^2}{dr^2} (r \psi_i^l) + \frac{2\mu}{\hbar^2} \left[(E-V) - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] (r \psi_i^l) = 0$$

wave and ϕ is the phase of the wave. The total potential energy is

where the summation is over all the particles. In this case the potential energy is

is no case for the potential energy. We now assume that the wave function is

For the case of a plane wave, the wave function is given by

everywhere. The wave function is then given by

be evaluated numerically. The wave function is then given by

constant. The wave function is then given by

The initial value of the wave function is given by

number. The wave function is then given by

with an error of order ϵ . The wave function is then given by

The wave function is then given by

where E is the kinetic energy of the incident electron and V the potential energy of interaction between an electron and an argon atom. In Ref 78 computations were made for hydrogen and oxygen, and for the latter the unmodified potential energy of the ionic field as given by Hartree was used. However, for argon, as well as other inert gas atoms, polarization effects are important (compare the discussion of the diffusion cross-section in section 3.4), hence the Hartree field should be correspondingly modified. Using such a modified V the above equations could be integrated numerically.

Normalization of the argon wave functions has not been considered; however, this is discussed for oxygen in the above reference. Once the normalized wave functions ψ_i and ψ_f , have been obtained the cross-section for capture into the ground state, $\sigma_e(3p)$, may be computed by performing another numerical integration.

In the self-consistent field approximation used by Hartree the complete wave function is the product of wave functions for each separate electron. In evaluating $\vec{M}$ the integral is over the coordinates of the incoming electron and this is independent of the other electronic coordinates. In obtaining $\sigma_e(3p)$ above the effect of the other electrons was omitted. Bates has shown that this omission may be approximately corrected for by multiplying by a numerical factor which for oxygen is .93.

The ground state cross-section for both hydrogen and oxygen amounts to about one-fourth of the total cross-section. The two cross-sections are not far different, that for oxygen being slightly smaller than that

where E is the kinetic energy of the incident electron and V the poten-

tial energy of interaction between an electron and an argon atom. In

Ref. 18 computations were made for hydrogen and oxygen, and for the latter

the unmodified potential energy of the ionic field as given by Hartree

was used. However, for argon, as well as other inert gas atoms, polar-

ization effects are important (compare the discussion of the diffusion

cross-section in section 3.4), hence the Hartree field should be cor-

respondingly modified. Using such a modified V the above equations

could be integrated numerically.

Normalization of the argon wave functions has not been considered;

however, this is discussed for oxygen in the above reference. Once the

normalized wave functions ψ_1 and ψ_2 have been obtained the cross-

section for capture into the ground state, $\sigma_0(p)$, may be computed by

performing another numerical integration.

In the self-consistent field approximation used by Hartree the com-

plete wave function is the product of wave functions for each separate

electron. In evaluating $\hat{H}$ the integral is over the coordinates of the

incoming electron and this is independent of the other electronic co-

ordinates. In obtaining $\sigma_0(p)$ above the effect of the other electrons

was omitted. Bates has shown that this omission may be approximately

corrected for by multiplying by a numerical factor which for oxygen is

93.

The ground state cross-section for both hydrogen and oxygen amounts

to about one-fourth of the total cross-section. The two cross-sections

are not far different, that for oxygen being slightly smaller than that

for hydrogen. We will use these facts in estimating the total cross-section for argon.

In evaluating the cross-sections for capture into excited states the assumption is made that the wave functions are hydrogen-like. If the energy E of the incoming electron is small, then this assumption is good. This is because, for small E , the phase shift produced by the inner field of the ion is also small. Hence if ψ_f for an excited state is large, then ψ_i will not differ much from the corresponding function for atomic hydrogen. This point was considered in Part I.

The computations made by Bates were for energies of less than .28 ev. His results are plotted in Fig. 18 of Part III where it is seen, that for this energy range, σ decreases with energy. This is to be expected because the wave-length of the incoming electron is large compared to the dimensions of the atomic system upon which it impinges. However, for our energy range, i.e., one to three electron volts, the electron wave-length becomes comparable to the size of the atomic system. In such a case one or more complete wave-lengths of zero angular momentum may be obtained within the range of the potential well without affecting waves of higher angular momentum. This means that at an energy of approximately one electron volt, the capture cross-section should show a sharp increase (Ref 79). In Part III, section 6, a method of detailed balancing is used to compute the capture cross-section for energies between .1 and 3.0 electron volts. The results are plotted along with those of Bates, where it may be seen that the

predicted increase of cross-section with energy is not obtained.

Unfortunately, experimental values are unavailable for either oxygen or argon. Also, computations have not been made for energies greater than .28 ev for oxygen and none for argon. However, the method of detailed balancing used to obtain the argon cross-sections has received a fair amount of verification in its application to the shock front. This will be discussed in greater detail in Part III.

It has been suggested by Morse and Stueckelberg (Ref 28) that the cross-section $\sigma_r(Z, n, l, v)$ for capture of electrons of velocity v by a heavy ion of charge Ze into a state of quantum numbers n, l is related to that $\sigma_r(1, n, l, v)$ for capture into the corresponding state for a hydrogen atom by (see also Ref 52)

$$\sigma_r(Z, n, l, v) = Z^2 \sigma_r(1, n, l, v).$$

This formula does not apply to the ground state for which separate computations must be made as explained previously. In order to apply this formula to our case the computations for hydrogen need to be extended to higher energies. In addition, as will be pointed out in Part III, the argon calculations for the equilibrium region need to be extended; however, this is at present limited by the equation of state used here.

3.4 Three-body Recombination.

There are two ways in which electrons can be lost from the plasma:

- (1) by the electron being captured in a two-body collision, the excess energy being removed by photons, or by excita-

predicted increase of cross-section with energy is not obtained.

Unfortunately, experimental values are unavailable for either

oxygen or argon. Also, computations have not been made for energies greater than 28 eV for oxygen and none for argon. However, the method

of detailed balancing used to obtain the argon cross-sections has re-

ceived a fair amount of verification in its application to the shock

front. This will be discussed in greater detail in Part III.

It has been suggested by Morse and Brackebart (Ref. 28) that the

cross-section $\sigma_c(Z, a, l, v)$ for capture of electrons of velocity v by a

heavy ion of charge Z into a state of quantum number n, l is related

to that $\sigma_c(Z, a, l, v)$ for capture into the corresponding state for a

hydrogen atom by (see also Ref. 22)

$$\sigma_c(Z, a, l, v) = Z^2 \sigma_c(1, a, l, v)$$

This formula does not apply to the ground state for which separate

computations must be made as explained previously. In order to apply

this formula to our case the computations for hydrogen need to be ex-

tended to higher energies. In addition, as will be pointed out in

Part III, the argon calculations for the equilibrium region need to be

extended; however, this is at present limited by the extension of state

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3.4 Three-body Recombination

There are two ways in which electrons can be lost from the plasma:

(1) by the electron being captured in a two-body collision,

the excess energy being removed by photon, or by excita-

tion of the atom, and

- (2) by the electron being captured in a three-body collision, the excess energy being given to the third particle.

The first of these has been discussed in the previous sections and the cross-sections given. The second will be considered in the present section.

Theory of J. J. Thomson. We consider first the theory developed by Thomson for a plasma of oppositely charged ions A and B and neutral atoms C, and later modify the theory to apply to our plasma of ions, electrons, and atoms. We wish to find the condition that an ion B should, after making a collision with a neutral atom, proceed to describe a closed orbit around A. Assume that just after the collision the kinetic energy of the B ion is equal to the mean kinetic energy of an atom at the temperature of the gas. If m_1, m_2 are the masses of the A and B ions, then if B makes a collision at a distance r from A, the ions will describe closed orbits around each other if r is less than r_0 where r_0 is prescribed by

$$\frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} v^2 = \frac{e^2}{r_0} \quad (49)$$

and v is the relative velocity of the ions at a separation r_0 . This follows since a bound orbit is one for which the total energy, $E = T + V$, is negative.

The inherent assumption here that the attractive energy e^2/r for $r > r_0$ is lost upon collision with a neutral atom seems rather drastic;

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$$\frac{1}{2} \frac{m_1^2 v^2}{m_1^2 v^2} = \frac{e^2}{r_0}$$

(2)

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is negative.

The inherent assumption here that the attractive energy e^2/r for

$r > r_0$ is lost upon collision with a neutral atom seems rather drastic;

however, in support of this is the moderate agreement between theory and experiment under conditions for which the theory seems valid. In addition, we have previously adopted the concept of a local temperature, hence

$$r_o = \frac{2e^2}{3kT} \quad (50)$$

Draw a sphere of radius r_o about ion A (cf Fig. 16). Then the number of times per second that ion B comes within a distance r_o of an A ion is $\pi r_o^2 v n_A$ where n_A, n_B are the number of A, B ions per cm^3 . Ion B will have acquired an additional amount of kinetic energy equal to e^2/r_o by the time it approaches ion A within a distance r_o , i.e., if ϵ_∞ represents the kinetic energy of B at a distance $r = \infty$ from A and ϵ_o is the kinetic energy of B at $r = r_o$, then

$$\epsilon_\infty = \epsilon_o - \frac{e^2}{r_o}$$

But $\epsilon_\infty = \frac{3}{2} kT$ and from (50), $e^2/r_o = 3/2 kT$, hence $\epsilon_o = 2\left(\frac{3}{2} kT\right)$.

Thus, for recombination to take place, we require that B lose an amount of energy of order kT when within a distance r_o of A. We have assumed that this amount of energy is lost upon collision with a neutral atom. If B and C have equal masses, then, on the average, this assumption is exactly obeyed, which can be shown as follows: Let m_1, m_2 be two particles where, initially, m_2 is at rest and m_1 has velocity v_1 . After the particles collide, m_1 has velocity v_1' and is moving at an angle θ with its original direction. m_2 has final velocity v_2' and

however, in support of this is the moderate agreement between theory and experiment under conditions for which the theory seems valid. In addition, we have previously adopted the concept of a local temperature, hence

$$(50) \quad \frac{1}{2} m_0 v_0^2 = \frac{3}{2} kT$$

Draw a sphere of radius r_0 about ion A (cf Fig. 1c). Then the number of times per second that ion B comes within a distance r_0 of an A ion is $\pi r_0^2 v_{AB}$, where v_{AB} is the number of A-B ions per cm³. Ion B will have acquired an additional amount of kinetic energy equal to $\frac{1}{2} m_0 v_0^2$ by the time it approaches ion A within a distance r_0 , i.e., if $\frac{1}{2} m_0 v_0^2$ represents the kinetic energy of B at a distance $r = \infty$ from A and $\frac{1}{2} m_0 v_0^2$ is the kinetic energy of B at $r = r_0$, then

$$\frac{1}{2} m_0 v_0^2 = \frac{1}{2} m_0 v_0^2 + \frac{e^2}{r_0}$$

$$\text{But } \frac{1}{2} m_0 v_0^2 = \frac{3}{2} kT \text{ and from (50), } \frac{e^2}{r_0} = \frac{3}{2} kT, \text{ hence } \frac{1}{2} m_0 v_0^2 = 2 \left(\frac{3}{2} kT \right).$$

Thus, for recombination to take place, we require that B lose an amount of energy of order kT when within a distance r_0 of A. We have assumed that this amount of energy is lost upon collision with a neutral atom. If B and C have equal masses, then, on the average, this assumption is exactly obeyed, which can be shown as follows: Let m_1, m_2 be two particles where, initially, m_1 is at rest and m_2 has velocity v_1 . After the particles collide, m_1 has velocity v_1' and is moving at an angle θ with its original direction. m_2 has final velocity v_2' and

Fig. 15

angle ϕ . Then, from conservation of energy,

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_1 v_1'^2 + \frac{1}{2} m_2 v_2'^2, \quad (51)$$

and, from conservation of momentum,

$$m_1 v_1' \sin \theta = m_2 v_2' \sin \phi,$$

$$m_1 v_1 = m_1 v_1' \cos \theta + m_2 v_2' \cos \phi.$$

Eliminating ϕ ,

$$m_1^2 \left[v_1'^2 \sin^2 \theta + v_1^2 + v_1'^2 \cos^2 \theta - 2v_1 v_1' \cos \theta \right] = m_2^2 v_2'^2.$$

Combine this with (51) obtaining

$$m_1(v_1^2 + v_1'^2 - 2v_1 v_1' \cos \theta) - m_2(v_1^2 - v_1'^2) = 0, \quad (52)$$

from which,

$$\frac{v_1'}{v_1} = \frac{m_1}{m_1 + m_2} \cos \theta + \frac{m_2}{m_1 + m_2} \left[1 - \frac{m_1^2}{m_2^2} (1 - \cos^2 \theta) \right]^{1/2}.$$

Before collision

After collision

angle θ from horizontal

and, from conservation of momentum

Eliminating v_2 from the above

$$m_1 v_1 = m_1 v_1' \cos \theta + m_2 v_2'$$

Combine this with the above

from which

$$v_1' = \frac{m_1 v_1}{m_1 + m_2} \left(\frac{1 + \cos \theta}{\cos \theta} \right)$$

If $m_1 \ll m_2$, then, to the order of terms in $(m_1/m_2)^2$,

$$\frac{v_1'}{v_1} = \frac{m_1 \cos \theta + m_2}{m_1 + m_2} . \quad (53)$$

Since

$$\frac{\Delta E}{E} = \frac{2\Delta v}{v} ,$$

$$\frac{\Delta E}{E} = \frac{2(v_1 - v_1')}{v_1} = 2 \left(1 - \frac{v_1'}{v_1} \right) = \frac{2m_1}{m_1 + m_2} (1 - \cos \theta), \quad (m_1 \ll m_2). \quad (54)$$

The average energy loss is, since $\overline{\cos \theta} = 0$,

$$\frac{\overline{\Delta E}}{E} = \frac{2m_1}{m_1 + m_2} . \quad (55)$$

This follows also from (52), i.e.,

$$\frac{\overline{\Delta E}}{E} = \frac{\frac{1}{2} m_1 v_1^2 - \frac{1}{2} m_1 v_1'^2}{\frac{1}{2} m_1 v_1^2} = 1 - \left(\frac{v_1'}{v_1} \right)^2 = \frac{2m_1}{m_1 + m_2} .$$

Hence we need to calculate the chance that ion B suffers an elastic collision with a neutral atom C within a distance r_0 of A and such that B loses an appreciable amount of energy and recombines in a closed orbit with A. Let this chance be s_B and let s_A be the chance for A colliding with C and recombining with B. The chance that ion B should be at a distance between ρ and $\rho + d\rho$ from a line drawn through A parallel

11

Since

$$\frac{\Delta L}{L} = \frac{\Delta v}{v}$$

$$\frac{\Delta L}{L} = \frac{\Delta v}{v} = \frac{\Delta v}{c} \quad (1)$$

The average

$$\frac{\Delta L}{L} = \frac{\Delta v}{c}$$

The following

$$\frac{\Delta L}{L} = \frac{\Delta v}{c}$$

collision with a

is found an

with A. Let

and with C and

a distance

Fig. 16

to the relative velocity of the two ions is $2\rho d\rho/r_0^2$ and the chance that B will go through the sphere of radius r_0 drawn about A at this distance without a collision is

$$e^{-\frac{2\sqrt{r_0^2 - \rho^2}}{l_B}}$$

where l_B is the mean free path for ions B in a collection of atoms C. If B and C are of approximately equal masses equation (55) and the preceding argument show that, since, on the average, the energy lost in a collision is about kT , the energy-loss mean free path l_B is, to a sufficient degree of approximation, equal to the geometric mean free path. Thus the chance that ion B should pass without making a collision is

$$Q = \int_0^{r_0} e^{-\frac{2\sqrt{r_0^2 - \rho^2}}{l_B}} \cdot \frac{2\rho d\rho}{r_0^2} = \int_0^1 e^{-\frac{2r_0}{l_B} (1-z^2)^{1/2}} \cdot 2z dz$$

Fig. 18

to the relative velocity of the two ions is $2v_0/r$ and the chance that B will go through the sphere of radius r drawn about A at this distance without a collision is

$$\frac{2\sqrt{1-r^2}}{r}$$

where λ is the mean free path for ion B in a collection of atoms of mass M . If B and C are of approximately equal mass, equation (55) and the preceding argument show that, since, on the average, the energy loss in a collision is about $4T$, the energy-loss mean free path λ is, to a sufficient degree of approximation, equal to the geometric mean free path. Thus the chance that ion B should pass without making a collision is

$$Q = \int_0^{\infty} e^{-\lambda x} \frac{2\sqrt{1-r^2}}{r} dx = \frac{2\sqrt{1-r^2}}{r} \lambda$$

where $z = \rho/r_0$. Let $y = \frac{2r_0}{l_B} (1-z^2)^{1/2}$, $2zdz = -\frac{l_B^2 y dy}{2r_0^2}$, then

$$Q = -\frac{l_B^2}{2r_0^2} \int_{g_B}^0 e^{-y} y dy.$$

Let

$$J = \int_0^y e^{-ay} dy = \frac{1}{a} (1 - e^{-ay}),$$

$$\frac{\partial J}{\partial a} = - \int_0^y e^{-ay} y dy = -\frac{1}{a^2} (1 - e^{-ay}) + \frac{y}{a} e^{-ay};$$

hence

$$Q = -\frac{2}{g_B} \left[g_B e^{-g_B} + e^{-g_B} - 1 \right].$$

Thus the chance that ion B will make a collision is

$$s_B = 1 + 2 \left(\frac{e^{-g_B}}{g_B} + \frac{e^{-g_B}}{g_B} - \frac{1}{g_B} \right) \quad (56)$$

with a similar expression for s_A and where

$$g_B = \frac{2r_0}{l_B}, \quad g_A = \frac{2r_0}{l_A}. \quad (57)$$

It should be kept in mind that l_A, l_B are really the energy mean free paths and not the geometric mean free paths. The relation between the two is, from (55),

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$$(57) \quad \epsilon_B = \frac{\epsilon_0}{\lambda_B}, \quad \epsilon_A = \frac{\epsilon_0}{\lambda_A}.$$

with a similar expression for ϵ_A and where

$$(56) \quad \epsilon_B = 1 + 2 \left(\frac{\epsilon_0}{\epsilon_B} + \frac{\epsilon_0}{\epsilon_A} - \frac{1}{2} \right)$$

Thus the chance that ion B will make a collision is

$$Q = -\frac{2}{\epsilon_B} \left[\epsilon_B e^{-\epsilon_B} + e^{-\epsilon_B} - 1 \right]$$

hence

$$\frac{dQ}{d\epsilon} = - \int_0^\infty e^{-\epsilon y} dy = - \frac{1}{\epsilon} (1 - e^{-\epsilon y})$$

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Let

$$Q = - \frac{\epsilon_0}{\epsilon_B} \int_0^\infty e^{-\epsilon y} dy$$

where $\epsilon = \epsilon_0/\lambda_B$. Let $y = \frac{\epsilon_0}{\lambda_B} (1-z)$, $\epsilon dz = -\frac{\epsilon_0}{\lambda_B} dy$, then

$$l_{\text{energy}} = \frac{(m_1 + m_2)}{2m_1} l_{\text{geom.}} \quad (58)$$

This is because $1/\frac{\Delta E}{E}$ collisions are required for the particle m_1 to lose an amount of energy about equal to E .

If A,B are of approximately equal masses then, as they approach each other they each acquire additional kinetic energy due to their attraction which is then lost upon collision. Hence the chance that when the two ions come within a distance r_0 one or the other of them should make a collision within this distance is

$$s_A + s_B - s_A s_B$$

where $s_A s_B$ is the chance that they both make collisions within this distance, and this has been included in both s_A and s_B . In case the mass of the incoming ion B is much greater than the mass of A most of the attractive energy will go into increasing the kinetic energy of A and the velocity of B will remain about the same; hence, upon collision only A will lose energy. Therefore, in this case, the chance of making a recombining collision is simply s_A or s where

$$s = 1 + 2 \left(\frac{e^{-g}}{g^2} + \frac{e^{-g}}{g} - \frac{1}{g^2} \right) \quad (59)$$

and, from (57), (58),

$$g = \frac{2r_0}{l_{\text{geom}}} \cdot \frac{2m_e}{M} = \frac{4r_0 m_e n \sigma_d}{M} \quad (60)$$

where

(53)

$$E_{\text{energy}} = \frac{(m_1 + m_2) v^2}{2}$$

This is because $\frac{1}{E} \Delta E$ collisions are required for the particle m_1 to

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$$s_A^2 + s_B^2 = s_{AB}^2$$

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of making a recombinant collision is simply s_A or s_B where

(54)

$$s = 1 + 2 \left(\frac{e^{-8}}{8} + \frac{e^{-8}}{8} + \frac{1}{8} \right)$$

and, from (57), (58),

(55)

$$E = \frac{Z_1 Z_2 e^2}{r_0} \ln \frac{2m}{M} = \frac{Z_1 Z_2 e^2}{r_0} \ln \frac{2m}{M}$$

where

m_e = mass of electron,

$$M = m + m_e,$$

m = mass of argon atom,

σ_d = diffusion cross-section (see below) ,

n = number of gas atoms,

and, the geometric mean free path is

$$l_{\text{geom}} = \frac{1}{n \sigma_d} . \quad (61)$$

Finally, then, the rate at which electrons recombine with argon ions by three-body collisions is given by the number of times per second an electron comes within a distance r_o of an argon ion, $\pi r_o^2 v n^+$, times the chance of making a recombining collision, s , times the number of electrons, n_e , or

$$p_4 = \pi r_o^2 s v n_e n^+ = \pi r_o^2 s v n_e^2 \quad (62)$$

where

n^+ = number of argon ions per cm^3 ,

n_e = number of electrons per cm^3 ;

and

$$n_e = n^+.$$

In case $g \ll 1$,

$$s = \frac{2g}{3} = \frac{8}{3} \frac{r_o m n \sigma_d}{M}$$

and

$$p_4 = \frac{8\pi}{3} r_o^3 \frac{m n \sigma_d}{M} v n_e^2 , \quad (63)$$

and the above is a generalization of the result obtained in the case of a single electron.

It is now necessary to consider the case of a multi-electron system. In this case the wave function is a function of the coordinates of all the electrons, and the above result is generalized to

where ψ is the wave function of the system, and ∇^2 is the Laplacian operator with respect to the coordinates of all the electrons.

Finally, it is noted that the above result is valid for any system of particles, whether they are electrons or not, provided the wave function satisfies the appropriate boundary conditions.

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where ψ is the wave function of the system, and ∇^2 is the Laplacian operator with respect to the coordinates of all the electrons.

from which

$$\sigma_4 = \frac{8\pi}{3} r_o^3 \frac{m_e n \sigma_d}{M}, \quad (g \ll 1). \quad (64)$$

At a temperature of $30,000^\circ$ and a compression ratio of 5, $\sigma_4 = 10^{-22} \text{ cm}^2$ which is much less than the classical cross-section for radiative capture (see, however, Part III, section 6).

To complete the discussion of the Thomson theory its limitations should be considered and, in addition, use of the diffusion cross-section, σ_d , should be justified.

No allowance has been made for the possibility of more than one collision while the electron is still within a distance r_o of the ion and before it has recombined. If such a collision could restore the original hyperbolic motion and if the chance of such an occurrence were high, then the above theory would not give the correct result. This is born out experimentally since theory and experiment agree at low pressures where σ_4 shows an increase with pressure. However, at high pressures the theory breaks down and since pressures are high in a shock front (in our case between 100 and 1000 atmospheres), it is necessary to obtain a pressure limit for the theory. This is done by defining a saturation condition such that $r_o = \ell$. The corresponding saturation pressure then lies at the upper limit of the conditions considered in this report.

Langevin's Theory. Thomson's theory verifies the increase of the three-body recombination coefficient α_4 with pressure in the low-

from which

$$C_4 = \frac{8\pi}{3} \frac{e^2}{M} \frac{1}{v_0} \quad (3 \ll 1) \quad (64)$$

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by defining a saturation condition such that $r_0 = 1$. The corres-

ponding saturation pressure then lies at the upper limit of the con-

ditions considered in this report.

Langevin's Theory. Thomson's theory verifies the increase of the

three-body recombination coefficient C_4 with pressure in the low-

pressure region; however, at high pressures α_4 drops off with pressure. Hence we consider a theory due to Langevin (Ref 52, 58) which predicts α_4 nicely in this region. In this theory the electrons are attracted toward the ions by the respective coulomb fields. They attain a relative drift velocity which is inhibited by collisions with neutral gas atoms. If k_A and k_B are the respective mobilities of ions and electrons, then the relative drift velocity at a distance r will be

$$\left(k_A + k_B\right) \frac{e}{r^2} .$$

The number of electrons drifting radially inwards across a spherical surface of radius r about an ion is then

$$4\pi n_B e(k_A + k_B) .$$

The electrons will drift up to and neutralize the ions unless deflected by collisions with other charged particles. Assuming small ion density and isotropic distribution, this possibility can be neglected, hence the rate of recombination is given by

$$4\pi e(k_A + k_B) n_A n_B$$

and

$$\alpha_4 = 4\pi e(k_A + k_B) .$$

Evaluation of the mobilities for the plasma state behind the shock front has not been made, however, for normal conditions it is found that k drops off with pressure, verifying the decrease of α with pressure (at high pressures).

pressure regions near the surface of the liquid.

Hence we consider the theory of the surface of the liquid.

of the surface of the liquid. The surface of the liquid is

toward the surface of the liquid. The surface of the liquid is

drift velocity of the surface of the liquid. The surface of the liquid is

If k and k' are the respective velocities of the surface of the liquid.

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The number of electrons which are emitted from the surface of the liquid is

surface of the liquid. The surface of the liquid is

The electrons will drift toward the surface of the liquid. The surface of the liquid is

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and isotropic distribution of the surface of the liquid. The surface of the liquid is

the rate of recombination of the surface of the liquid. The surface of the liquid is

and

Evaporation of the surface of the liquid. The surface of the liquid is

front has not been reached. The surface of the liquid is

is proportional to the surface of the liquid. The surface of the liquid is

(at high pressure).

The Diffusion Cross-Section. As indicated above, we wish to justify use of the diffusion cross-section in the Thomson theory. If velocity distributions are used, the recombination rate would be expressed as

$$p_4 = \iint \sigma_4(v) f_e(\vec{v}_1) f^+(\vec{v}_2) d\vec{v}_1 d\vec{v}_2$$

where $f_e(\vec{v}_1)$ is the maxwellian velocity distribution for electrons and $f^+(\vec{v}_2)$ that for the argon ions. σ_4 is given by (64) and contains the diffusion cross-section $\sigma_d(v)$. It would be convenient if an analytic expression for $\sigma_d(v)$ were available, hence we examine this possibility.

The elastic scattering cross-section may be written as

$$\sigma = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \eta_l$$

where

$$k = \frac{\sqrt{2m_e E}}{\hbar}$$

and η_l is the phase shift produced in the de Broglie waves of angular momentum $[l(l+1)]^{1/2} \hbar$. We wish an analytic expression for σ which is explicit in v . However, η_l will depend on the scattering potential $V(r)$ which, for argon, is quite complicated. This was discussed in section 3.3. Holtsmark (Ref 16), using the Hartree field modified by a polarization effect, was able to obtain a theoretical value for σ which agreed well with the observed σ in the low energy range, i.e., his results led to the Ramsauer-Townsend effect. He was able to show that

$$\sigma_{\text{expt}} \doteq \sigma_{\text{theor}} = \sum_{l=2}^{\infty} (2l+1) \sin^2 \eta_l \quad (\text{for } .3 \text{ ev} < E < 13 \text{ ev});$$

The Diffusion Cross-Section. As indicated above, we wish to justify use of the diffusion cross-section in the Thomson theory. If velocity distributions are used, the recombination rate would be expressed as

$$R = \int \int \int C_1(v_1) C_2(v_2) v_1 v_2 dv_1 dv_2$$

where $C_1(v_1)$ is the Maxwellian velocity distribution for electrons and $C_2(v_2)$ that for the argon ions. C_2 is given by (6a) and contains the diffusion cross-section $\sigma_D(v)$. It would be convenient if an analytic expression for $\sigma_D(v)$ were available, hence we examine this possibility. The elastic scattering cross-section may be written as

$$\sigma = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l$$

where $k = \frac{\sqrt{2mE}}{\hbar}$ and δ_l is the phase shift produced in the scattering waves of angular momentum $\hbar k l$. We wish an analytic expression for σ which is explicit in v . However, δ_l will depend on the scattering potential $V(r)$ which, for argon, is quite complicated. This was discussed in section 3.3. Holtsmark (Ref. 10), taking the Hartree field modified by a polarization effect, was able to obtain a theoretical value for σ which agreed well with the observed σ in the low energy range, i.e., the results led to the Ramsauer-Townsend effect. He was able to show that

$$\sigma_{\text{calc}} = \sigma_{\text{obs}} = \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l \quad (\text{for } 0.5 \text{ ev} < E < 1.5 \text{ ev})$$

Fig. 17 Diffusion cross-section for electrons in argon.

$(\text{mol})_g$
 $10^{-12} \times 10^1$

Δ 13.8
 $\circ$ 13.9

but in order to obtain values for γ_e ($\ell = 0, 1, 2, \dots$) a numerical integration was necessary.

Thus it is possible to obtain an empirical relation for $\gamma_e(v)$ but not an analytic expression. Hence we may fit an empirical curve directly to the observed values for σ_d (cf Fig. 17). There is some disagreement between observers, particularly in the region below 1 ev, so an approximate curve is used.

The value for the cross-section at zero energy is given as about $7 \times 10^{-16} \text{ cm}^2$ (Ref 18, 19) while Wahlin (Ref 20) measured $\sigma_d = .73 \times 10^{-16} \text{ cm}^2$ at $\xi = .03 \text{ ev}$. Again because of the nature of the maxwell distribution, it is somewhat immaterial what $\sigma_d(0)$ is; so we use $\sigma_d(0) = 1 \times 10^{-16} \text{ cm}^2$.

The interest here is only in low-energy cross-sections hence we do not need to discuss inelastic, superelastic, or radiative cross-sections, i.e. only elastic collisions are to be considered. A superelastic collision occurs between an electron and an excited atom where the electron gains energy from the internal motion of the atom. Collisions involving radiation are rare compared with other types of collisions and have been previously considered.

If σ_o is the total elastic cross-section and $I_o(\theta)$ the differential cross-section for elastic scattering then

$$\sigma_o = \int_0^\pi \int_0^{2\pi} I_o(\theta) \sin \theta d\theta d\phi.$$

but in order to obtain values for $\sigma_e = 0.1, 2, \dots$ a numerical inte-

gration was necessary.

Thus it is possible to obtain an empirical relation for $\sigma_e(v)$ but

not an analytic expression. Hence we may fit an empirical curve directly

to the observed values for σ_e (cf. Fig. 11). There is some disagreement

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cross-section for elastic scattering then

$$\sigma_e = \int_0^\pi I_e(\theta) \sin \theta d\theta$$

If σ is the total collision cross-section where

$$\sigma = \sum_{n=0}^n \sigma_n$$

is summed over all types of collision, then in the energy range of interest $\sigma_0 = \sigma$.

The total collision cross-section may be measured by the following method (cf Fig. 18). Electrons are ejected photoelectrically from a source F into a circular collimating channel with a magnetic field directed perpendicular to the paper. Electrons which suffer no collision enter a collector at C, while those which are scattered fail to pass through the slits and those which collide inelastically move in new circular paths of smaller radii.

Fig. 18

If i_C is the current to C alone and i_B the current to B alone then $i_{C1} =$

$$i_{BC1} e^{-\alpha p_1 x} \text{ where } i_{BC1} =$$

$i_{B1} + i_{C1}$, α is the absorption coefficient, and p_1 is the pressure. Similarly at a pressure p_2 ,

$$i_{C2} = i_{BC2} e^{-\alpha p_2 x}$$

and

$$\alpha(p_1 - p_2)x = \ln \frac{i_{C2}}{i_{BC2}} \frac{i_{BC1}}{i_{C1}}.$$

Hence α may be determined and consequently σ .

In case the electrons are very slow (say ~ 1 ev) it is possible to use the Townsend method (Ref 21) (cf Fig. 19) in which a swarm of electrons is introduced into a diffusion chamber through a slit A across which an electric field F is directed as shown. The current may then be measured at C_1 , B, and C_2 . Guard rings 2, 3, 4 may be added to insure uniformity of the field.

Fig. 19

Now, as the electrons diffuse through the chamber they gain energy from the field but, in the steady state, this gain in energy is equal to the loss in energy by collision with the gas atoms. (We are assuming the electron energy so low that only elastic collision with gas atoms need be considered). Let the drift velocity be u in the direction x of the field and assume a definite mean energy ϵ for the electrons.

Let the mean free path ℓ and the fractional energy loss λ be constant. Then, if c is the mean velocity of the random motion of the electron, the actual path length is cx/u and the number of collisions made in travelling a distance x is $cx/u\ell$. Then, from conservation of energy,

$$\lambda \epsilon \frac{cx}{u\ell} = Fex,$$

or, if $\epsilon = 1/2 m_e c^2$,

$$\frac{\lambda c^3}{u} = 2 \frac{Fe\ell}{m_e}.$$

If δt is the time between collisions then $u\delta t$ is the mean distance travelled in the direction of the field in this time. Assuming isotropic scattering then

$$u\delta t = \frac{1}{2} \frac{Fe}{m} (\delta t)^2,$$

or, if $\delta t = \ell/c$,

$$2uc = Fe\ell/m.$$

In case the electrons are very slow (say $v \ll v_{th}$) it is possible to use the Townsend method (see Fig. 12) in which a

swarm of electrons is introduced

into a diffusion chamber

through a slit across

which an electric field E

is directed as shown. The

current may then be measured

at C , B , and A . Good

results may be obtained

to insure uniformity of the

field.

Fig. 12

Now, as the electrons diffuse through the chamber they gain energy from the field but, in the steady state, this gain in energy is equal to the loss in energy by collision with the gas atoms. (We are assuming the electron energy so low that only elastic collision with gas atoms need be considered.) Let the drift velocity be u in the direction of the field and assume a definite mean energy ϵ for the electrons.

Let the mean free path λ and the fractional energy loss δ be constant. Then, if c is the mean velocity of the random motion of the electron, the actual path length is $c\lambda/u$ and the number of collisions made in traveling a distance x is cx/λ . Then from conservation of energy,

$$cx \frac{d\epsilon}{dx} = \epsilon \frac{cx}{\lambda} \delta$$

$$\text{or } \epsilon = \frac{1}{2} \delta \lambda c^2$$

$$\frac{\lambda c^2}{u} = \frac{2\epsilon}{\delta}$$

If δt is the time between collisions then u is the mean distance travelled in the direction of the field in this time. Assuming isotropic scattering then

$$u = \frac{1}{2} \delta t c$$

$$\text{or } \delta t = \frac{2\epsilon}{\delta c^2}$$

$$\text{and } \lambda = \frac{2\epsilon}{\delta c^2}$$

Now $\ell \sim 1/p$ where p is the pressure, hence u should be a linear function of $\frac{F}{p}$.

u may be determined by directing a magnetic field H perpendicular to the electric field F . Then the stream of electrons will be deviated through an angle θ such that

$$\tan \theta \sim \frac{Hu}{F}.$$

If u is plotted against F/p , the mean free path ℓ may be computed from the slope of the curve.

In this discussion the effect of diffusion is neglected; however, the method is discussed in more detail in Ref 52, Chapter I.

If we assume that in the electron swarm the mean energy is so small that inelastic collisions with gas atoms do not occur, then the only energy loss will occur in elastic collisions and will be due to the finite ratio of the masses, m_e/M . Also, we assume the electron concentration in the stream to be so small that interaction between electrons can be ignored.

Considering only elastic impacts between electrons and atoms, then since $m_e \ll m$, the fractional energy loss per impact by an electron is (cf eq (54))

$$2(1-\cos \theta) \frac{m_e}{m}$$

where terms of order $(m_e/m)^2$ have been dropped.

If $p(\theta)d\Omega$ is the probability that the electron will be scattered into a solid angle $d\Omega$ then the mean fractional energy loss per impact will be

$$2 \frac{m_e}{m} \int (1-\cos \theta) p(\theta) d\Omega.$$

But the differential cross-section for elastic scattering into the solid angle $d\Omega$ is given by

Now λ will be a
linear function of

it may be better to
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elementary with the

Let λ be

It is a problem
computed from the

In this direction
however, the method
Chapter 1

If we assume that
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A. Also, the
system to be
be ignored.

Considering only

Since λ is a

(or ed (2))

where some of

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will be

But the difference

solid angle Ω

$$I_0(\theta)d\Omega = \sigma_0 p(\theta)d\Omega$$

where σ_0 is the total cross-section for elastic scattering. The mean fractional energy loss per impact then becomes

$$2 \frac{m_e}{m} \frac{\sigma_d}{\sigma_0}$$

where

$$\sigma_d = \int_0^\pi \int_0^{2\pi} I_0(\theta)(1-\cos \theta) \sin \theta d\theta d\phi.$$

σ_d is the diffusion or momentum transfer cross-section.

The fractional amount of energy lost by an electron in moving a distance x is then

$$2 \frac{m_e}{m} \frac{\sigma_d}{\sigma_0} \cdot n x \sigma_0 = 2 \frac{m_e}{m} \cdot n \sigma_d \cdot x.$$

Hence for elastic collisions the mean free path should be $\ell = 1/n\sigma_d$ and the mean fractional energy loss $\lambda = 2m_e/m$.

4. Summary.

In the above sections the individual atomic interactions that take place in an argon shock front have been detailed. It has been indicated that the production of electrons is a two-stage process. First, starting from a state of translational equilibrium where only argon atoms exist, electrons are produced by ionizing collisions between the argon atoms. Once a sufficient number of electrons have been produced, then ionizing collisions between argon atoms and electrons predominate. If maxwell distributions are replaced by averages, then the two production

coefficients for the above reactions may be written as $\overline{\beta}_1 = \overline{\sigma}_1 v$ and $\overline{\beta}_3 = \overline{\sigma}_3 v$ where β_1 and β_3 are functions of temperature only. Theoretical values for these cross-sections have not been derived, hence we have used the experiment cross-sections. Other production reactions have been considered and assumed to be unimportant.

As soon as electrons have been produced in quantity, recombination processes must be considered. It was shown that, for the pressure and temperature conditions existing in a shock front, only two recombination processes are of importance. The first is radiative recombination which depends on temperature only, and the second is three-body recombination which depends on temperature and pressure.

Experimental values for the cross-sections corresponding to the two recombination reactions are unavailable, hence theoretical derivations have been made. Radiative capture of electrons by argon ions has been considered both classically and quantum mechanically. It is indicated that the classical theory gives too large an answer by several orders of magnitude. Thomson's theory for the three-body process has been presented and its limitations discussed.

If we combine the above processes the source term which expresses the rate of production of electrons may be written as

$$S = \frac{dn_e}{dt} = \beta_1 n^2 + \beta_3 n n_e - \alpha n_e^2.$$

Quantitative evaluation of $\beta_1(T)$, $\beta_3(T)$ and $\alpha(n,T)$ is made in Part III.

coefficients for the above
 $\bar{A}_3 = 0.5$ when $\bar{A}_1 = 1$
cal values for the above
used the experimental
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dependence on
which depends on
Experimental
recognition that
have been made
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Part III

PART III: COMPUTATIONS AND RESULTS

1. Introduction.

In Parts I and II the theoretical basis for the computations involved has been presented in some detail. In Part III the theory will be applied to a few special cases. It should be remembered that the theory is somewhat limited, viz, there is an upper limit to the temperature because doubly ionized argon has been ignored and there is a lower limit to the pressure and temperature due to effects discussed in the sections on recombination. Also, as pointed out in Part I, if the degree of ionization is too high, the method used to calculate the partition functions breaks down. The theory as presented is probably good for shock velocities in argon between 3 and 9 times 10^5 cm per sec.

If higher shock velocities are of interest then doubly ionized argon must not be neglected which means a different equation of state than the one used here (cf Ref 69). However, one would still be limited because there is not sufficient cross-section data available for reactions involving multiple-ionized atoms.

The extension to lower shock velocities is not difficult for argon because, below about $3 \cdot 10^5$ cm per sec the ionization is negligible, i.e., only translational degrees of freedom are important. This case has been thoroughly treated as we have previously indicated.

2. Equation of State of Argon.

Using the method of Part I, sections 2-4, we write down the complete equation of state for argon for a rather wide range of density

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2. Equation of State of Argon

Using the method of Part I, sections 2-4, we write down the complete equation of state for argon for a rather wide range of density

and temperature. The partition functions are given by eqs I: (22) to I: (24). The energy levels and multiplicities for the low states of the neutral argon atom A and the argon ion A^+ are listed in Table II. This table enables us to calculate $Z_{\text{low}}(T)$ and $Z_{\text{ion}}(T)$. There are a number of higher levels for the argon ion which are not listed in the Table. These levels are fairly closely spaced with an average number of levels per degree, $\bar{n}$, and an average multiplicity $\bar{g}$. Then, for Z_{ion} ,

$$Z_{\text{ion}} = \sum_{n(E_1)}^{n(E_2)} g_n e^{-E_n/T} + \int_{E_2}^{E_3} \bar{n}\bar{g} e^{-E/T} dE$$

where the energies are expressed in degrees. For argon we have used $E_1 = 0$, $E_2 = 268920$, $E_3 = 320800$ and $\bar{n}\bar{g} = 4.05 \cdot 10^{-3}$. The integral on the right represents a correction to the higher states which is small but is easy to make. Because the ion is more tightly bound than the atom, pressure ionization will not be important and no correction has been made for this.

Z_{high} , eq I: (24), is not only a function of temperature but is also a function of density. Values of the energy E_{nl} and the effective multiplicity are listed in Table III.

Using Tables II and III the partition functions for the atoms and ions have been calculated and are listed in Table IV as functions of the temperature and density ratio. The equilibrium constant K, eq I: (17), is given in Table IV* for the initial condition of 59.38 cm Hg,

* Actually, K divided by the partition function for electrons is listed, or, for our case, $K/2$.

and temperature. The partition functions are given by eqs 1: (22) to

1: (24). The energy levels and multiplicities for the low states of

the neutral argon atom A and the argon ion A⁺ are listed in Table II.

This table enables us to calculate Z_{ion}^{+} and Z_{ion}^{-} . There are a

number of higher levels for the argon ion which are not listed in the

Table. These levels are fairly closely spaced with an average number

of levels per degree $\bar{n}$ and an average multiplicity $\bar{g}$. Then for

$$Z_{ion}^{+} = \sum_{n(E)} n(E) e^{-E/T} + \int_{E_2}^{\infty} \bar{n} \bar{g} e^{-E/T} dE$$

where the energies are expressed in degrees. For argon we have used

$E_1 = 0$, $E_2 = 268600$, $E_3 = 320800$ and $\bar{g} = 4.5 \cdot 10^{-3}$. The integral on

the right represents a correction to the higher states which is small

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atom, pressure ionization will not be important and no correction has

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Using Tables II and III the partition functions for the atoms and

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(17), is given in Table IV for the initial condition of 59.38 cm Hg.

Actually, K divided by the partition function for electrons is listed
or, for our case, K/Z_e .

which is local atmospheric pressure at Los Alamos, (see Table I).

From equations (16) and (17) in Part I it is clear that the equilibrium constant for an initial pressure of h cm Hg can be obtained from the value of K in Table IV by multiplying by $59.38/h$. (Although, the internal partition functions may change slightly due to the cut-off criterion.) The concentrations, $[A]$ and $[A^+]$, of course depend upon the initial conditions through the equilibrium constant.

The energy content of the neutral argon atoms is given by

$$\beta(A) = 2.5 + \frac{W}{Z}$$

and that for the argon ions by

$$\beta(A^+) = 2.5 + \frac{W_{\text{ion}}}{Z_{\text{ion}}} .$$

3. Shock Conditions in the Equilibrium Region.

It has been shown in Part I, section 6, that heat conduction and viscosity do not enter into the shock conditions in the equilibrium region. It has already been indicated that the equations to be used are those of Part I, section 5, and specifically, equations (42) and (43) of that paragraph. These two equations are solved simultaneously for η and T with the shock velocity U as a parameter. The quantities g and β occur in these equations and are rather complicated functions of η and T . They are obtained from the equation of state as explained in Part I.

It is possible to simplify the computation of β considerably by the

which is local atmospheric pressure at Los Alamos, (see Table I).
From equations (16) and (17) in Part I it is clear that the equilib-

rium constant for an initial pressure of 1 cm Hg can be obtained from
the value of K in Table IV by multiplying by 29.38/n. (Although, the

internal partition functions may change slightly due to the cut-off
criterion.) The concentrations, $[A]$ and $[A^*]$, of course depend upon the

initial conditions through the equilibrium constant.

The energy content of the neutral argon atoms is given by

$$\bar{\epsilon}(A) = 2.5 + \frac{W}{2}$$

and that for the argon ions by

$$\bar{\epsilon}(A^+) = 2.5 + \frac{W_{ion}}{2}$$

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of that paragraph. These two equations are solved simultaneously for
 γ and T with the shock velocity U as a parameter. The quantities ϵ
and $\bar{\epsilon}$ occur in these equations and are rather complicated functions of
 γ and T . They are obtained from the equation of state as explained in

Part I.

It is possible to simplify the computation of $\bar{\epsilon}$ considerably by the

following approximation. The ionization ratio x is given by

$$x = \frac{n_e}{n+n_e} = \frac{n_e/n}{1+n_e/n} \quad (1)$$

and the average number of particles per original atom by

$$g = 1+x. \quad (2)$$

x may be computed directly from the equilibrium constant (listed in Table IV) by the relation

$$K = \frac{x^2}{1-x}.$$

Since the temperatures we are considering are low enough so that the number of singly ionized argon atoms in higher excited states is small, it is a good assumption that

$$\beta(A^+) = 2.5.$$

Then, from eq I: (10),

$$\epsilon = \beta(A)(1-x) + \beta(A^+)x + \beta(\epsilon l) \cdot x + \frac{I}{kT} \cdot x$$

or

$$\epsilon = \beta(A)(1-x) + 5.0x + \frac{183000}{T} \cdot x \quad (3)$$

where $\beta(\epsilon l) = 2.5$ and the first ionization potential for argon is $I = 183,000$ degrees. If we knew $\beta(A)$, we could obtain ϵ and hence β from

$$\beta = \frac{\epsilon}{g}.$$

$\beta(A)$ has been calculated and a good fit is

$$\beta(A) = \frac{1}{2} \left(\frac{5+x}{1-x} \right). \quad (4)$$

following approximation

$$\frac{1}{x} \approx \frac{1}{x_0} - \frac{(x - x_0)}{x_0^2}$$

and the average number of particles

x may be computed directly from the data in Table IV by the relation

Table IV by the relation

Since the temperature is not too high

the number of particles is small, it is a good approximation to

small, it is a good approximation to

Then, from (10)

where $\lambda(0) = 0.5$ and the first term is

or

$$\epsilon = \lambda(0) - \lambda(1)$$

where $\lambda(0) = 0.5$ and the first term is

$I = 183,000$ degrees. If we know λ , we can find ϵ and vice versa.

λ from

$$\lambda(x) = \lambda(0) - \epsilon x$$

If (4) is substituted in (3),

$$\epsilon = 2.5 + 5.5x + \frac{183000}{T} x,$$

or

$$\beta = \frac{2.5 + 5.5x + \frac{183000}{T} x}{1+x} \quad (5)$$

If we substitute the relations for $\beta(A)$ and $\beta(A^+)$ given in section 2 into ϵ ,

$$\epsilon = \left(2.5 + \frac{W}{Z}\right) (1-x) + \left(2.5 + \frac{W_{ion}}{Z_{ion}}\right) x + 2.5x + \frac{I}{kT} x,$$

or

$$\epsilon = 2.5 + 2.5x + \frac{I}{kT} x + \frac{W}{Z} - x \left(\frac{W}{Z} - \frac{W_{ion}}{Z_{ion}} \right).$$

Thus we see that our approximation is that

$$3x = \frac{W}{Z} + x \left(\frac{W_{ion}}{Z_{ion}} - \frac{W}{Z} \right)$$

or

$$x = \frac{W/Z}{3 + \frac{W}{Z} - \frac{W_{ion}}{Z_{ion}}}.$$

If

$$\epsilon' = 2.5 + 2.5x + \frac{I}{kT} x$$

then

$$\epsilon = \epsilon' + 3x.$$

The term $3x$ is less than 10% of ϵ' in even the most extreme case.

Hence, as shown in the following table, the maximum error made in com-

If (4) is substituted in (3),

$$E = 2.5 + 2.5x + \frac{103000}{T} x$$

or

$$(2) \quad E = \frac{2.5 + 2.5x + \frac{103000}{T} x}{1+x}$$

If we substitute the relations for $\delta(A)$ and $\delta(A')$ given in

section 2 into (2),

$$E = \left(2.5 + \frac{W}{T}\right) \cdot (1-x) + \left(2.5 + \frac{W}{T}\right) x + 2.5x + \frac{1}{K} x$$

or

$$E = 2.5 + 2.5x + \frac{1}{T} x + \frac{W}{T} x - \left(\frac{W}{T} - \frac{W}{T}\right) x$$

Thus we see that our approximation is

$$2x = \frac{W}{T} + x \left(\frac{W_{ion}}{W_{ion}} - \frac{W}{W_{ion}} \right)$$

or

$$x = \frac{W_{ion}}{2 + \frac{W}{T} - \frac{W_{ion}}{W_{ion}}}$$

If

$$E' = 2.5 + 2.5x + \frac{1}{T} x$$

then

$$E = E' + 3x$$

The term $3x$ is less than 10% of E in even the most extreme case.

Hence, as shown in the following table, the maximum error made in com-

puting ϵ by this method is not more than .5% and will, in most cases, be far less.

T	$\frac{W}{Z}$	$\frac{W_{ion}}{Z_{ion}}$	x (correct)	x (approximate)
16000	.12	.04	.05	.04
19000	.45	.04	.12	.13
22000	.97	.05	.22	.24
24000	1.46	.08	.28	.33

Results of the computations for the two initial conditions, $p_1 = 59.38$ cm Hg and $p_1 = 1$ cm Hg are plotted in Figs. 1 to 6 and listed in Table V.

Some measurements have been made on strong shocks in argon at Los Alamos (Ref 74). The shocks were produced by high explosives for which the detonation velocities are known and the material velocity u behind the shock front was measured. The results are plotted along with the theoretical curve in Fig. 1.

4. Electron Balance in the Shock Front.

The equation for the rate of electron production, i.e., the source term, is given in Part II, section 1. In order to apply this equation to the non-equilibrium part of the shock front, we need to incorporate a term that expresses the change in macroscopic density. This comes about as follows: Let S represent the source term, i.e.,

$$S = q - p,$$

or,

$$S = \beta_1(T)n^2 + \beta_3(T)nn_e - \alpha(T)n_e^2. \quad (6)$$

(Note that α has been written as a function of temperature only.

This is not quite correct but is discussed further in section 6.)

S is the number of electrons produced per cm^3 per sec by interatomic collision processes. If ΔX is the Eulerian element of displacement perpendicular to the shock

front, then the number of

electrons in the volume ele-

ment $\Delta X \Delta A$ is

$$N_e = n_e \cdot \Delta X \Delta A$$

and the number of argon

atoms is

$$N = n \cdot \Delta X \Delta A.$$

Hence the electron flux

through ΔA is

$$\frac{\Delta(N_e/\Delta A)}{\Delta t} = S \Delta X - \Delta(un_e).$$

Dividing through by ΔX and taking limits, we obtain the ordinary continuity equation expressed in terms of electron density

$$\frac{\partial n_e}{\partial t} + \frac{\partial(un_e)}{\partial X} = S,$$

or,

$$S = p \cdot q$$

or,

$$S = \Delta_1(T)n_2 + \Delta_2(T)n_3 - \alpha(T)n_2^2 \quad (6)$$

(Note that α has been written as a function of temperature only.)

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Dividing through by ΔX and taking limits, we obtain the ordinary con-

tinuity equation expressed in terms of electron density

$$\frac{dn_e}{dt} + \frac{d(n_e u)}{dx} = S$$

or,

$$\frac{\partial n_e}{\partial t} + u \frac{\partial n_e}{\partial X} = S - n_e \frac{\partial u}{\partial X}.$$

If x is the Lagrange coordinate, then

$$\frac{\rho_1}{\rho} = \frac{\partial X}{\partial x}$$

and

$$\left(\frac{\partial n_e}{\partial t} \right)_x = S - n_e \frac{\rho}{\rho_1} \frac{\partial u}{\partial x}.$$

To an observer on the shock front the shock wave appears stationary, hence we may make the similarity transformation,

$$f(t) \longrightarrow f(\tau) = f\left(t - \frac{x}{U}\right) \quad (7)$$

and obtain

$$\frac{dn_e}{d\tau} = S + \frac{n_e \rho}{U \rho_1} \frac{du}{d\tau} = S + \frac{n_e \rho}{M} \frac{du}{d\tau} \quad (8)$$

where

$$M = \rho_1 U.$$

The Rankine-Hugoniot equations may also be transformed as follows:

$$\rho_1 \frac{\partial u}{\partial t} = - \frac{\partial p}{\partial x} \text{ becomes } M \frac{du}{d\tau} = \frac{dp}{d\tau},$$

$$\rho_1 \frac{\partial v}{\partial t} = \frac{\partial u}{\partial x} \text{ becomes } M \frac{dv}{d\tau} = - \frac{du}{d\tau},$$

and

$$\rho_1 \frac{\partial}{\partial t} \left(E + \frac{u^2}{2} \right) = - \frac{\partial}{\partial x} (pu) \text{ becomes } M \frac{d}{d\tau} \left(E + \frac{u^2}{2} \right) = \frac{d(pu)}{d\tau}$$

where v is the specific volume. These last three equations lead to the

$$\frac{\partial u}{\partial x} = \frac{\partial u}{\partial x} + \frac{\partial u}{\partial x} = \frac{\partial u}{\partial x}$$

If x is the Lagrangian coordinate, then

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial x} + \frac{\partial}{\partial x} = \frac{\partial}{\partial x}$$

and

$$\frac{\partial u}{\partial x} = \frac{\partial u}{\partial x} + \frac{\partial u}{\partial x} = \frac{\partial u}{\partial x}$$

To an observer on the shock front the shock wave appears stationary,

hence we may make the following transformation,

$$x' = x - ut \quad (1)$$

and obtain

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} + \frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} \quad (2)$$

where

The Rankine-Hugoniot equations may also be transformed as follows:

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} + \frac{\partial u}{\partial t} = \frac{\partial u}{\partial t}$$

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} + \frac{\partial u}{\partial t} = \frac{\partial u}{\partial t}$$

and

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial t} + \frac{\partial u}{\partial t} = \frac{\partial u}{\partial t}$$

where v is the specific volume. These last three equations lead to the

ordinary shock conditions discussed previously, viz,

$$Mu = p - p_1,$$

$$M(v - v_1) = -u,$$

and

$$M(E - E_0 + \frac{u^2}{2}) = pu.$$

From the γ -law equation for the energy,

$$E = \frac{p/\rho}{\gamma - 1},$$

and the three shock equations we obtain the following relations given in Part II, section 1:

$$\xi = \frac{2\rho_1 u^2}{p_1(\gamma + 1)} - \frac{1}{\gamma_\infty} \quad (9)$$

and

$$\eta = \frac{\gamma_\infty \xi + 1}{\xi + \gamma_\infty} \quad (10)$$

where

$$\gamma_\infty = \frac{\gamma + 1}{\gamma - 1}.$$

From the equation of state

$$p = gR^* \rho T$$

we have that

$$T = \frac{\eta_A T_A}{\xi_A} \cdot \frac{\xi}{\eta_B} \quad (11)$$

ordinary shock conditions discussed previously, viz.,

$$M u = p - p_1$$

$$M(v-v_1) = -u$$

and

$$M(E-E_0 + \frac{u^2}{2}) = pu$$

From the γ -law equation for the energy,

$$E = \frac{p}{\gamma - 1}$$

and the three shock equations we obtain the following relations given

in Part II, section I:

$$\frac{p}{p_1} = \frac{2\gamma u^2}{\gamma + 1} \quad (9)$$

and

$$\frac{v}{v_1} = \frac{\gamma + 1}{2\gamma} \quad (10)$$

where

$$\gamma = \frac{\gamma + 1}{\gamma - 1}$$

from the equation of state

$$p = \gamma \rho \epsilon$$

we have that

$$T = \frac{p}{\rho} = \frac{\gamma}{\gamma - 1} \frac{p}{\rho} \quad (11)$$

These relations enable us to calculate p, ρ, T as well as other quantities at any point in the shock front provided γ is known (assuming the shock velocity U and the initial conditions in front of the shock to be given). To calculate γ we return to the equation for the electron balance (8) into which we first substitute

$$\frac{1}{M} \frac{du}{dt} = - \frac{dv}{dt}.$$

This gives

$$\frac{1}{n_e} \frac{dn_e}{dt} + \frac{1}{v} \frac{dv}{dt} = \frac{S}{n_e}.$$

Using (6) we obtain

$$\frac{d \ln(n_e v)}{dt} = \beta_1(T) \frac{n}{n_e} + \beta_3(T)n - \alpha(T)n_e. \quad (12)$$

n is the number density of argon atoms at temperature T and n_1 is the corresponding value at T_1 . Also, n_e is the number density of electrons, which, of course, is equal to the ion density. Conservation of mass may be written

$$(n+n_e)V = n_1 V_1 = k. \quad (13)$$

From (1) and (13)

$$n_e V = kx, \quad n = \frac{k(1-x)}{V}. \quad (14)$$

Substituting in (12),

$$\frac{dx}{dt} = \frac{\beta_1 k}{V} + x \left(\frac{\beta_3 k - 2\beta_1 k}{V} \right) + x^2 \left(\frac{\beta_1 k - \beta_3 k - \alpha k}{V} \right). \quad (15)$$

These relations enable us to calculate p, T , as well as other quantities at any point in the shock front provided γ is known (assuming the shock velocity U and the initial conditions in front of the shock to be given). To calculate γ we return to the equation for the electron balance (8) into which we first substitute

$$\frac{1}{n} \frac{dn}{dt} = - \frac{dv}{dt}$$

This gives

$$\frac{1}{n} \frac{dn}{dt} + \frac{1}{v} \frac{dv}{dt} = \frac{S}{n}$$

Using (6) we obtain

$$\frac{dn}{dt} = \frac{A_1(T) \frac{n}{n_0} + A_2(T) n^{-\alpha(T)}}{A_3(T) \frac{n}{n_0}} \quad (12)$$

n is the number density of argon atoms at temperature T and n_0 is the corresponding value at T_0 . Also, n_0 is the number density of electrons which, of course, is equal to the ion density. Conservation of mass may be written

$$(n+n_0)V = n_0 V_0 = K \quad (13)$$

From (1) and (13)

$$n_0 V = Kx, \quad n = \frac{K(1-x)}{V} \quad (14)$$

Substituting in (12),

$$\frac{dx}{dt} = \frac{A_1 K}{V} + x \left(\frac{A_2 K}{V} - \frac{A_3 K(1-x)}{V} \right) \quad (15)$$

This equation can be integrated by completing the square. Let

$$a' = \frac{(\beta_1 - \beta_3 - \alpha)k}{V}, \quad b' = \frac{(\beta_3 - 2\beta_1)k}{V}, \quad c' = \frac{\beta_1 k}{V}.$$

Then

$$\Delta t = \int_{x_1}^{x_2} \frac{dx}{a'x^2 + b'x + c'} = \frac{1}{a'} \int_{x_1}^{x_2} \frac{dx}{\left(x + \frac{b'}{2a'}\right)^2 - \left[\left(\frac{b'}{2a'}\right)^2 - \frac{c'}{a'}\right]}.$$

Let

$$a = \left[\left(\frac{b'}{2a'}\right)^2 - \frac{c'}{a'}\right]^{1/2} = \left[b^2 - \frac{c'}{a'}\right]^{1/2}$$

and

$$b = \frac{b'}{2a'}.$$

The integral then becomes

$$aa' \Delta t = \tanh^{-1} \left(\frac{x_1 + b}{a} \right) - \tanh^{-1} \left(\frac{x_2 + b}{a} \right)$$

or

$$x_2 = -b + a \tanh \left[\tanh^{-1} \left(\frac{x_1 + b}{a} \right) - aa' \Delta t \right]. \quad (16)$$

This equation enables us to compute the degree of ionization x_2 at a point specified by an interval Δt seconds behind a point at which the degree of ionization x_1 is known. In this time interval β_1 , β_3 , and α are assumed to be constant. In the integration one iteration was used.

This equation can be integrated by completing the square. Let

$$s' = \frac{(b_1 - b_2 - ac)k}{V}, \quad b' = \frac{(b_2 - 2b_1)k}{V}, \quad c' = \frac{b_1 k}{V}$$

Then

$$\Delta t = \int_{x_1}^{x_2} \frac{dx}{s'x^2 + b'x + c'} = \frac{1}{a'} \left[x_1 \left(x + \frac{b'}{2a'} \right) - \left[\left(\frac{b'}{2a'} \right)^2 - \left(\frac{c'}{a'} \right) \right]^{1/2} \right]$$

Let

$$a = \left[\left(\frac{b'}{2a'} \right)^2 - \left(\frac{c'}{a'} \right) \right]^{1/2} = \left[b^2 - \frac{c^2}{a^2} \right]^{1/2}$$

and

$$b = \frac{b'}{2a'}$$

The integral then becomes

$$a' \Delta t = \tanh^{-1} \left(\frac{x_1 + b}{a} \right) - \tanh^{-1} \left(\frac{x_2 + b}{a} \right)$$

or

$$x_2 = -b + a \tanh \left[\tanh^{-1} \left(\frac{x_1 + b}{a} \right) - a' \Delta t \right] \quad (16)$$

This equation enables us to compute the degree of ionization x_2 at a point specified by an interval Δt seconds behind a point at which the degree of ionization x_1 is known. In this time interval Δt , b_1 , and b_2 are assumed to be constant. In the integration one iteration was

used.

5. Production of Electrons in the Shock Front.

We have previously discussed how electrons are produced (Part II, section 2). It remains here only to evaluate the electron production coefficients, β_1 and β_3 .

Initially there are no electrons, hence the only means by which electrons are produced is by ionizing collisions between argon atoms. The cross-section for this reaction has a relatively high threshold value, hence the coefficient β_1 is quite small for the temperatures we are considering. This means that γ remains essentially constant until a sufficient number of electrons are present for the ionizing collisions between electrons and atoms to predominate. This point is called the onset of ionization.

From eq (18), Part II, β_1 is given as

$$\beta_1 = \frac{\pi}{2} \left(\frac{m}{\pi kT} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{mv^2}{4kT}} \sigma_1(v) v^3 dv \quad (17)$$

and is plotted in Fig. 7. As will be shown in section 7 β_1 is the most important quantity in determining the actual width of the shock front.

Once the onset of ionization has been reached reactions between electrons and atoms take over and β_3 becomes the important production coefficient. β_3 is defined from eq (23), Part II, to be

$$\beta_3 = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT} \right)^{3/2} \int_{v_1}^{\infty} e^{-\frac{\mu v^2}{2kT}} \sigma_3(v) v^3 dv. \quad (18)$$

We have previously

section 2. It remains to be seen

coefficient β and β'

Initially there are no electrons

electrons are produced in the

The cross-section for the

value, hence the coefficient

we are considering. This

until a sufficient number of

collisions between electrons

called the critical value

from eq. (10), and

and is plotted in Fig. 1

important quantity in determining

Once the critical value is

electrons and their number

coefficient β is determined

A graph of $\beta_3(T)$ is shown in Fig. 8.

In the computations to follow only the two reactions discussed above have been considered. In a more refined analysis some of the other reactions listed in Part II might be included; however, because of the approximate nature of some of the quantities involved and because their contribution is small, this was not done.

6. The Recombination Coefficient.

There appear to be no experimental measurements of the recombination coefficient in the temperature and density regions of importance in the shocks we are considering. We therefore consider the theoretical formulae for radiative recombination derived by Kramers, and for three-body recombination as given by the Thomson theory. These formulae were discussed in sections (3.3) and (3.4) of Part II. We shall see later in this section, however, that the region of validity of the Thomson theory does not include the conditions of interest, hence its use would be suspect. Moreover, we will also show that the Kramers' theory gives values for the radiative recombination coefficient which are much too large to permit the equilibrium degree of ionization behind the shock. We must therefore proceed in a different manner to obtain the recombination coefficients. Our method will be to use recombination coefficients determined by detailed balancing from the inverse reactions.

We can readily see that Kramers' formula for the radiative recombination coefficient gives values which are too large. His values, which we denote by $\alpha_3(cl)$, as discussed in Part II, are considerably

A graph of $\lambda(T)$ is shown in Fig. 8.

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larger than the corresponding values obtained from the theoretical three-body recombination coefficient $\alpha_4(\text{theor})$. If Kramers' formula were correct, we could neglect α_4 and simply replace α by α_3 where

$$\alpha_3 = \sqrt{\frac{2}{\pi}} \left(\frac{\mu}{kT} \right)^{3/2} \int_0^{\infty} e^{-\frac{\mu v^2}{kT}} \sigma_r(v) v^3 dv, \quad (19)$$

$\sigma_r(v)$ being the cross-section for radiative capture of electrons by argon ions given by Kramers' classical relation (eq II: (47) or Fig. II: 13). A plot of $\alpha_3(\text{cl})$ is shown in Fig. 9. With our assumption that α may be replaced by $\alpha_3(\text{cl})$ in eq (15), the production and recombination coefficients, β_1 , β_3 and α are all known as functions of temperature and the equation could be numerically integrated across the shock front. If this is done, we obtain a degree of ionization in the steady state region behind the shock (region 4 of Fig. II; (1)) which is smaller than that computed in section 3 by a factor of about 10^4 .

In view of the failure of Kramers' classical theory for the radiative recombination coefficient, we turn to the quantum theory for this process. Usually the cross-section σ_{ph} for the inverse process; that is, photoelectric absorption, is what is calculated. This causes but little difficulty, for the radiative capture cross-section σ_r can be obtained from it by detailed balancing. In fact (Ref 82)

$$\frac{\sigma_r}{\sigma_{\text{ph}}} = \frac{p_{\text{ph}}^2}{p_{\text{el}}^2} = \frac{(h\nu)^2}{2mc^2 E}, \quad (20)$$

larger than the corresponding values obtained from the theoretical three-body recombination coefficient α_3 (theor). If Kramers' formula were correct, we could neglect α_1 and simply replace α by α_3 where

$$\alpha_3 = \sqrt{\frac{2}{\pi}} \left(\frac{u}{kT} \right)^{3/2} \int_0^\infty e^{-\frac{u}{kT}} Q_T(v) v^3 dv \quad (19)$$

$Q_T(v)$ being the cross-section for radiative capture of electrons by argon ions given by Kramers' classical relation (eq. II: (4)) or Fig. II: (13). A plot of $\alpha_3(c_1)$ is shown in Fig. 9. With our assumption that α may be replaced by $\alpha_3(c_1)$ in eq. (15), the production and recombination coefficients, β_1 , β_3 and α are all known as functions of temperature and the equation could be numerically integrated across the shock front. If this is done, we obtain a degree of ionization in the steady state region behind the shock (region 4 of Fig. II: (1))

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$$\frac{Q_T}{Q_{ph}} = \frac{p_{ph}}{p_{el}} = \frac{p_{ph}}{p_{el}} \frac{(h\nu)^2}{8\pi^2 c^2} \quad (20)$$

where $P_{ph} = h\nu/c$ is the photon momentum and $P_{el} = \sqrt{2mE}$ is the electron momentum, E being the electron kinetic energy.

It is possible to use a rather simple approximation for the photoelectric cross-section, for we are interested in processes where the kinetic energy of the electron in the ionized state is small compared to the ionization energy. For this case it is valid to expand the continuum wave function occurring in the matrix elements of the transition probability about the function for zero energy. If a similar expansion (which is a priori much less justified, but which nevertheless gives good numerical results) is used for the bound state functions, and the resulting cross-section averaged over all values of the orbital angular momentum of the bound state, we obtain the cross-section derived by Menzel and Pekeris (Ref 80) and discussed by Mayer (Ref 81, p 12),

$$Q_{ph}(n \rightarrow f) = \frac{2^5 \pi}{3\sqrt{3}} \alpha^3 a_0^2 \frac{mc^2 (Rhc)^2}{(h\nu)^3} \frac{Z_n^{*4}}{n^5}.$$

Here $\alpha = e^2/\hbar c \sim 1/137$ is the fine structure constant,

a_0 is the first Bohr radius,

Rhc is the Rydberg energy (13.61 ev),

n is the principle quantum number of the photoelectron in its bound state, and

Z_n^* is the effective nuclear charge which the photoelectron feels.

This formula is derived using the approximation to hydrogenic wave functions, and the only adjustment possible to take into account the actual form of the wave functions is Z_n^* .

where $p = mv/c$ is the photon momentum, $\hbar$ being the Planck constant,

It is possible to show that the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

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α_0 is the first Bohr radius, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

R_{∞} is the Rydberg constant, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

n is the principal quantum number of the final state, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

bound state, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

E_{∞} is the effective ionization energy, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

This formula is derived from the theory of the photoelectric effect, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

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actual form of the wave function, and the probability of the photoelectric cross-section, for a given frequency of the incident light, is proportional to the kinetic energy of the electron, and hence to the frequency of the light, to the power $3/2$.

Using (20) the radiative capture cross-section for an electron of kinetic energy E in its initial state making a transition to a bound state of principle quantum number n is

$$\sigma_r(f \rightarrow n) = \frac{2^4 \pi}{3\sqrt{3}} \alpha^3 a_0^2 \frac{(Rhc)^2}{E(I_n + E)} \frac{Z_n^{*4}}{n^5}, \quad (21)$$

where we have substituted $h\nu = I_n + E$, I_n being the ionization potential of the electron in its bound state. We are interested in capture from states near the ionization limit, and hence we can neglect E compared to I_n . Further, putting

$$I_n = \frac{Z_n^{*2}}{n^2} Rhc,$$

(21) becomes

$$\sigma_r(f \rightarrow n) = \frac{2^4 \pi}{3\sqrt{3}} \alpha^3 a_0^2 \frac{Rhc}{E} \frac{Z_n^{*2}}{n^3}. \quad (22)$$

To get the total radiative capture cross-section, we must sum (22) over all available bound states. For the argon ion it is possible to capture an electron into one 3p orbital, or into $2n^2$ orbitals of n greater than 3. For the latter orbitals we use an effective nuclear charge $Z_n^* = 1$. For the 3p orbital, the device of the effective nuclear charge is only approximate, since the orbital is far from hydrogenic. However, we will not be making order of magnitude errors if we choose $Z_{3p}^* = 5$, a value gotten by using the screening constants in Mayer's paper.

Using (20) the relative energy levels of the system are calculated. The kinetic energy of the electron is given by

$$E_k = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{h}{m \lambda} \right)^2 = \frac{h^2}{2 m \lambda^2}$$

where we have used the relation $\lambda = h/mv$. The energy of the electron in the potential well is given by

$$E_p = -\frac{e^2}{4 \pi \epsilon_0 r}$$

(21) becomes

$$E_k + E_p = -\frac{e^2}{4 \pi \epsilon_0 r} + \frac{h^2}{2 m \lambda^2}$$

To get the total relative energy of the system, we add the energy of the electron in the potential well to the kinetic energy. For the total energy to be a minimum, we differentiate the total energy with respect to λ and set it equal to zero. This gives us the following equation:

$$-\frac{e^2}{4 \pi \epsilon_0 r} + \frac{h^2}{m \lambda^2} = 0$$

Solving for λ , we get:

$$\lambda = \frac{h}{m v} = \frac{h}{m \sqrt{\frac{e^2}{4 \pi \epsilon_0 r}}}$$

Substituting this value of λ into the total energy equation, we get the total energy of the system:

$$E_{total} = -\frac{e^2}{4 \pi \epsilon_0 r} + \frac{h^2}{2 m \lambda^2} = -\frac{e^2}{4 \pi \epsilon_0 r} + \frac{h^2}{2 m} \left(\frac{m \sqrt{\frac{e^2}{4 \pi \epsilon_0 r}}}{h} \right)^2 = -\frac{e^2}{4 \pi \epsilon_0 r} + \frac{e^2}{4 \pi \epsilon_0 r} = 0$$

Thus, the total energy of the system is zero.

Finally, we apply the quantum cut-off, equation (19) of Part I, in summing (22). For our range of shock strengths and for a fore-pressure $p_1 \sim 60$ cm Hg we can, to a good approximation, assume that states for which $n \geq 7$ are non-existent. This cuts the series off so that it is finite and thus convergent. However, convergence of the sum is only an apparent difficulty of our formula (22). For higher values of n the approximation that $h\nu \doteq I_n$ is no longer valid, and we must keep the kinetic energy term, as included in (21). In this case the sum over n even if it were infinite clearly converges.

Making the above substitutions in (33) we obtain for the total capture cross-section

$$\sigma_r = \frac{3.018 \times 10^{-21}}{E} \text{ cm}^2 \quad (23)$$

with E in electron volts. Values for σ_r are plotted in Fig. 18 where it is seen that they are in good agreement with values for argon obtained by adjusting Bates' results on hydrogen and oxygen as discussed in Part II, section 3.3.

If we substitute (23) into (19) we obtain the coefficient for radiative recombination α_3 where

$$\alpha_3 = \frac{2.174 \times 10^{-11}}{T^{1/2}}, \quad (24)$$

with T in degrees absolute. This relation is plotted in Fig. 19. Comparison with $\alpha_3(\text{cl})$ of Fig. 9, shows our new result to be smaller by a factor of about 10^5 . This invalidates our previous integration of

Finally, we apply the same method to the case of a
in a medium (22). The results are shown in Table I.
pressure of 1000 cm. Hg. The results are shown in Table I.
states for which $n = 1$ and $n = 2$. The results are shown in Table I.
that it is finite and that the results are shown in Table I.
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Making the above assumption in the results are shown in Table I.
capture cross-section
$$\sigma = \frac{4\pi e^2}{m^2 v^2} \frac{Z^2}{v^2} \frac{1}{v^2}$$

with E in electron volts. The results are shown in Table I.
it is seen that the results are shown in Table I.
calculated by the method of the results are shown in Table I.
in Part II, section 1, the results are shown in Table I.
If we substitute (22) in the results are shown in Table I.
radiative recombination of the results are shown in Table I.
with T in degrees absolute. The results are shown in Table I.
portion with α_1 of the results are shown in Table I.
a factor of about 10. The results are shown in Table I.

the ionization density through the shock front in which $\alpha_3(\text{cl})$ was used.

With this new value of the radiative recombination coefficient, we can no longer neglect the three-body recombination process. We therefore consider the range of applicability of Thomson's theory of three-body recombination. On the low pressure side the pressure must be sufficiently high so that the chance for the neutral atom involved in the collision to be in the neighborhood of the interacting ion and electron is large enough. This means that the distance between an ion and a neutral atom must be less than $r_0 = 2e^2/3kT$; e.g., at $T = 12000^\circ$ and $p_1 = 59.3$ cm Hg the compression η^* must be greater than about 60 (η^* of course increases as T^3). In terms of the atom density n this says that, for our range of temperatures and pressures, n must be greater than about 10^{22} atoms per cm^3 . On the high pressure side we have already indicated that Thomson's theory breaks down for atom densities greater than $n \sim 10^{24}$ in the temperature range of 1 to 3 ev. Whereas the Thomson theory is applicable for atom densities per cm^3 $10^{22} \leq n \leq 10^{24}$, the atom densities achieved in the shocks we are treating lie in the range 10^{18} to 10^{20} per cm^3 .

In view of the inapplicability of the Thomson theory, we turn to another method aimed at finding the recombination coefficient α . To do this let us reconsider the derivation of the source term, equation (6). We assume the only important reactions occurring in our plasma, which consists of argon atoms A , argon ions A^+ , and electrons e , are

the following:

The electron production rates are given by the β 's and the recombination rates by the α 's. From these reactions we write the source term as

$$\frac{dn_e}{dt} = \beta_1 n^2 + \beta_3 n n_e + \beta_9 n n_\nu - \alpha_4' n n_e^2 - \alpha_5' n_e^3 - \alpha_3 n_e^2 \quad (28)$$

where all the coefficients are functions of temperature only and where $\alpha_4' = \alpha_4/n$ and $\alpha_5' = \alpha_5/n$. The atom density is n , electron density n_e , photon density n_ν , and electron and ion densities are equal. If we compare eq (24) with eq (6) we see that

$$\alpha = \alpha_4' n + \alpha_5' n_e + \alpha_3. \quad (29)$$

In the equilibrium state $dn_e/dt = 0$ or, from (28), using the asterisk to denote equilibrium values,

$$\alpha^* = \alpha_4' n^* + \alpha_5' n_e^* + \alpha_3 = \frac{n^{*2}}{n_e^{*2}} \left(\beta_1 + \beta_3 \frac{n_e^*}{n^*} + \beta_9 \frac{n_\nu^*}{n^*} \right).$$

the following:

$$(25) \quad \frac{dA_1}{dt} = \alpha_1 A_1 + \beta_1 A_2 + \gamma_1 A_3$$

$$(26) \quad \frac{dA_2}{dt} = \alpha_2 A_1 + \beta_2 A_2 + \gamma_2 A_3$$

$$(27) \quad \frac{dA_3}{dt} = \alpha_3 A_1 + \beta_3 A_2 + \gamma_3 A_3$$

The electron production rates are given by the β 's and the recombination rates by the α 's. From these reactions we write the source terms

$$(28) \quad \frac{dn_e}{dt} = \beta_1 A_1 + \beta_2 A_2 + \beta_3 A_3 - \alpha_1 n_e - \alpha_2 n_e - \alpha_3 n_e$$

where all the coefficients are functions of temperature only and where $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$. The atom density is n_a electron density n_e , photon density n_γ , and electron and ion densities are equal. If

we compare eq (28) with eq (5) we see that

$$(29) \quad \alpha = \alpha_1 n_a + \alpha_2 n_e + \alpha_3 n_\gamma$$

In the equilibrium state $dn/dt = 0$ or, from (28), using the asterisk

to denote equilibrium values,

$$\alpha^* = \alpha_1 n_a^* + \alpha_2 n_e^* + \alpha_3 n_\gamma^* = \frac{n_e^*}{n_a^*} \left(\beta_1 + \beta_2 + \beta_3 \right)$$

From eq (1)

$$\frac{n^*}{n_e} = \frac{1-x}{x},$$

hence

$$\alpha^* = \alpha_4' n^* + \alpha_5' n_e^* + \alpha_3 = \beta_1 \left(\frac{1-x}{x}\right)^2 + \beta_3 \left(\frac{1-x}{x}\right) + \beta_9 \frac{n_2^*}{n^*} \left(\frac{1-x}{x}\right)^2. \quad (30)$$

By the principle of microscopic reversibility, not only must the overall production of electrons be zero in the equilibrium state, but each individual reaction (25) to (27) must be balanced. Hence we have

$$\alpha_4' = \frac{1}{n^*} \beta_1 \left(\frac{1-x}{x}\right)^2,$$

$$\alpha_5' = \frac{1}{n_e^*} \beta_3 \left(\frac{1-x}{x}\right),$$

$$\alpha_3 = \frac{n_2^*}{n^*} \beta_9 \left(\frac{1-x}{x}\right)^2.$$

We can therefore obtain the non-equilibrium recombination rate α of (29) from knowledge of the equilibrium concentrations, and β_1 and β_3 (giving α_4' and α_5') and from the quantum formula for radiative recombination (giving α_3), i.e.,

$$\alpha = \frac{n}{n^*} \beta_1 \left(\frac{1-x}{x}\right)^2 + \frac{n_e}{n_e^*} \beta_3 \left(\frac{1-x}{x}\right) + \alpha_3. \quad (31)$$

Actually it is unnecessary to use this general formula for many of the conditions with which we are dealing. The main point here is

From eq (1)

$$\frac{n}{n_0} = \frac{1-x}{x}$$

hence

$$\alpha^* = \alpha_1^* n_1 + \alpha_2^* n_2 + \alpha_3^* n_3 = \alpha_1^* \left(\frac{1-x}{x} \right) + \alpha_2^* \left(\frac{1-x}{x} \right) + \alpha_3^* \left(\frac{1-x}{x} \right) \quad (30)$$

By the principle of microscopic reversibility, not only must the overall production of electrons be zero in the equilibrium state, but each individual reaction (25) to (27) must be balanced. Hence we have

$$\alpha_1^* = \frac{1}{n_1} \left(\frac{1-x}{x} \right)$$

$$\alpha_2^* = \frac{1}{n_2} \left(\frac{1-x}{x} \right)$$

$$\alpha_3^* = \frac{1}{n_3} \left(\frac{1-x}{x} \right)$$

We can therefore obtain the non-equilibrium recombination rate of (29) from knowledge of the equilibrium concentrations, and α_1^* and α_2^* (giving α_1^* and α_2^*) and from the quantum formula for radiative recombination (giving α_3^*), i.e.,

$$\alpha = \frac{n}{n_0} \left(\frac{1-x}{x} \right) + \frac{n_0}{n} \left(\frac{1-x}{x} \right) + \alpha_3^* \quad (31)$$

Actually it is unnecessary to use this general formula for many of the conditions with which we are dealing. The main point here is

that in the region in which the ionization is relatively low the recombination rate αn_e^2 is negligible, hence the value of α is unimportant. The recombination rate does become important after considerable ionization has taken place. Then, however, the coefficients of the terms β_1 and β_3 in (31) become comparable at least to within several orders of magnitude and since β_3 is between 10^{11} to 10^{14} times β_1 (see Figs. 7 and 8), we may neglect the term in β_1 . Moreover, as can be seen from Figs. 11, b and c, for temperatures of $15,000^\circ$ and $18,000^\circ$ the radiative recombination term α_3 is small compared to $\beta_3 \left(\frac{1-x}{x} \right)$ for a considerable range of densities. Hence in (31) we can neglect α_3 for values of n_e in the neighborhood of n_e^* . (For the 12000° case, Fig. 11a, the radiative recombination term is dominant and the approximation we make here does not apply.) Hence over a considerable range of densities and temperatures ($n > 5 \cdot 10^{19}$ and $T > 16000^\circ$) we can approximate α by

$$\alpha \sim \frac{n_e}{n_e^*} \beta_3 \left(\frac{1-x}{x} \right). \quad (32)$$

Actually in the integrations following the degree of ionization through the shock front the value $\alpha = \beta_3 \left(\frac{1-x}{x} \right)$ was used (cf section 7). This is satisfactory in the most important region near equilibrium where n_e/n_e^* is close to unity, and makes some allowance for the other terms in (31) for regions far from equilibrium.

7. Structure of the Shock Front.

The main purpose of this report is to describe quantitatively the structure of a shock front in argon when the shock strength is high enough so that ionization takes place. The previous sections have prepared us for such a computation and in this section we present the results.

All conditions at the peak of the shock (point A, Fig. 1 of Part II) may be obtained from the ordinary shock equations with $\gamma = 5/3$, provided we know the shock velocity U and the conditions in front of the shock. The conditions thus obtained will be expressed in terms of compression η , shock strength ξ and temperature ratio T/T_1 . Thus, knowing the conditions at point A and in front of the shock and numerical relations for β_1 , β_3 and α we may integrate equation (15) across the shock front. The method of integration is outlined in section 4 with the relations for β_1 , β_3 and α being given in sections 5 and 6. Since specific volume V and temperature T which occur in equation (15) are slowly varying functions of time, they were replaced by an average constant value across the small interval of integration $\Delta t = t_2 - t_1$. The average was determined by an iteration procedure and one iteration was sufficient. The criterion used in determining the interval Δt was that the corresponding temperature change ΔT must be less than 100° . This integration carried out in equation (16) gives a value for the degree of ionization x at t_2 knowing conditions at t_1 . From x at t_2 we computed β , equation (5), and hence γ . The shock equations

7. Structure of the Shock Front

The main purpose of this report is to describe qualitatively the

structure of a shock front in air when the shock strength is high

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results.

All conditions at the rear of the shock (point A, Fig. 1 of Part

II) may be obtained from the ordinary shock equations with $\gamma = 5/3$, pro-

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shock. The conditions thus obtained will be expressed in terms of com-

pression p , shock strength ϵ , and temperature ratio T/T_1 . Thus,

knowing the conditions at point A and in front of the shock and numeri-

cal relations for β_1 , β_2 and α , we may integrate equation (15) across

the shock front. The method of integration is outlined in section 4

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t_2 we computed β_2 , equation (5), and hence γ . The shock equations

(9), (10) and equation (11) then give ξ , η and T respectively at the time t_2 , and the Eulerian increment of distance in this time interval is given by $\Delta X = U\Delta t/\eta$. Starting at the head of the shock (point A) we thus proceed by successive small steps Δt until we arrive at what is sensibly the equilibrium condition B (Fig. 1 Part II).

The electron production coefficients β_1 and β_3 are given as functions of temperature in Figs. 7 and 8 but, for purposes of calculation, exponential type empirical formulas were fitted to these curves. The recombination coefficient α , equation (31) depends on the atom and electron densities n and n_e , as well as on the temperature. This could be incorporated into the integration where, to even a better approximation than for V used above, n could be considered as constant across the integration interval Δt . Actually equation (31) was not used, but instead the quantity $\beta_3\left(\frac{1-x}{x}\right)$ plotted in Fig. 10 was used for the recombination coefficient α . This gives substantially the correct value for α in the region near the equilibrium position B where recombination has the greatest effect on the shock structure. In the less important regions away from the equilibrium position α is incorrectly represented by $\beta_3\left(\frac{1-x}{x}\right)$ both because of the neglect of radiative and other recombination processes, and because the density dependence of this function is incorrect.

The numerical work of this integration (as well as all other computations in this paper) was done on the IBM card programmed electronic computer (CPC) through the courtesy of Los Alamos Group T-1. A typical

(9), (10) and equation (11) then give ξ , η and τ respectively as the time t_2 and the Eulerian increment of distance in this time interval is given by $\Delta X = U \Delta t$. Starting at the head of the shock (point A) we thus proceed by successive small steps Δt until we arrive at what is essentially the equilibrium condition B (Fig. 1 part II).

The electron production coefficients δ_1 and δ_3 are given as functions of temperature in Figs. 7 and 8 but, for purposes of calculation, exponential type empirical formulae were fitted to these curves.

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The numerical work of this integration (as well as all other computations in this paper) was done on the IBM card programmed electronic computer (CPC) through the courtesy of Los Alamos Group T-1. A typical

integration through the shock front may take from 2 to 3 hours.

The structure of the shock obtained from this integration is given in Table VI and is plotted in Figs. 12 to 17.

We have previously described the sort of behavior to be expected in a shock front and now, on the basis of the above computations, we review this description. First let us recall that our calculations apply to a monatomic gas, viz, argon, where the initial pressure is 59.38 cm Hg and for which the shock velocity is high enough so that some ionization takes place but low enough so that the number of doubly ionized atoms may be ignored.

When such a shock wave passes a point X the translational degrees of freedom of the gas are first excited and translational equilibrium is achieved within about two collisions. This point is referred to here as the peak of the shock. The time required for translational equilibration is small compared to that for the remaining processes involved in the shock front, hence is not included in our computations. The local temperature at the peak of the shock is high enough so that a significant amount of energy may be transferred from the translational degrees of freedom to those of electronic excitation and ionization. This is clearly indicated in Fig. 12 where it is seen that the equilibrium temperature T^* is considerably lower than that at the peak of the shock T_A . This is particularly true for increasing shock velocity as shown in the following table:

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The structure of the shock obtained from this integration is given in Table VI and is plotted in Figs. 12 to 14.

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When such a shock wave passes a point K the translational degrees of freedom of the gas are first excited and translational equilibrium is achieved within about two collisions. This point is referred to here as the peak of the shock. The time required for translational equilibrium is small compared to that for the remaining processes involved in the shock front, hence is not included in our computations. The local temperature at the peak of the shock is high enough so that a significant amount of energy may be transferred from the translational degrees of freedom to those of electronic excitation and ionization. This is clearly indicated in Fig. 15 where it is seen that the equilibrium temperature T^* is considerably lower than that at the peak of the shock T_s . This is particularly true for increasing shock velocity as shown in the following table:

U(cm per sec)	T_A/T^*
$5.0 \cdot 10^5$	1.46
$5.5 \cdot 10^5$	1.60
$6.0 \cdot 10^5$	1.78

The only reactions available at first are collisions between argon atoms for which the corresponding ionization cross-section is quite small. This means that the transfer of energy takes place rather slowly until the point we have called the onset of ionization is reached. Thus the values at the peak of the shock remain approximately unchanged for some distance, resulting in a rather flat region in the shock front. This is true for all the shock parameters as Figs. 12 to 17 show (cf the table below). We refer to this distance as the onset width. If we call the relaxation point that point at which 63% of the equilibrium ionization is achieved, it may be seen that the onset width offers the most important contribution to the total relaxation width.

In determining the onset width β_1 is the most significant quantity because the degree of ionization x is small in this region. Hence, by considering the leading term in eq (15), we see that the onset width scales inversely with initial density ρ_1 (or pressure p_1) at constant initial temperature T_1 .

Once the onset of ionization is reached transfer of energy from translational degrees of freedom to electronic excitation and ionization proceeds quite rapidly. This results in a sudden change in the

$U(\text{cm per sec})$	T_A/T^*
$5.0 \cdot 10^2$	1.46
$5.5 \cdot 10^2$	1.60
$6.0 \cdot 10^2$	1.78

The only reactions available at first are collisions between argon atoms for which the corresponding ionization cross-section is quite small. This means that the transfer of energy takes place rather slowly until the point we have called the onset of ionization is reached. Then the values at the peak of the shock remain approximately unchanged for some distance, resulting in a rather flat region in the shock front. This is true for all the shock parameters as Figs. 12 to 15 show (cf. the table below). We refer to this distance as the onset width. If we call the relaxation point that point at which 6% of the equilibrium ionization is achieved, it may be seen that the onset width offers the most important contribution to the total relaxation width.

In determining the onset width δ_1 is the most significant quantity because the degree of ionization x is small in this region. Hence, by considering the leading term in eq (15), we see that the onset width scales inversely with initial density ρ_1 (or pressure p_1) at constant initial temperature T_1 .

Once the onset of ionization is reached transfer of energy from translational degrees of freedom to electronic excitation and ionization proceeds quite rapidly. This results in a sudden change in the

shock parameters, especially the temperature (Fig. 12) and the degree of ionization (Fig. 16). Again we see that the effect is more violent for higher shock velocities, e.g, if the distance in which this sudden change takes place is ΔX , then for $U = 6 \cdot 10^5$ cm per sec, $\Delta X \doteq .001$ cm, while for $U = 5 \cdot 10^5$ cm per sec, $\Delta X \doteq .007$ cm. At first the electron production term involving β_3 is most important but soon the recombination term takes over and equilibrium is quickly achieved. The shape (or profile) of this region is rather sensitive to the value of α but because the region is relatively narrow α does not have much effect on determining the total relaxation width of the shock front.

If λ_x is the relaxation width for the shock front, λ_t the relaxation time, and x_r the corresponding degree of ionization, we find the following approximate values for the case $p_1 = 59.38$ cm Hg:

$U \left(\frac{\text{cm}}{\text{sec}} \right)$	Onset width (cm)	λ_x (cm)	λ_t (sec)	x_r
$5.0 \cdot 10^5$	$10.5 \cdot 10^{-3}$	$13.7 \cdot 10^{-3}$	$1.15 \cdot 10^{-7}$	.045
$5.5 \cdot 10^5$	$1.6 \cdot 10^{-3}$	$2.45 \cdot 10^{-3}$	$2.0 \cdot 10^{-8}$	.065
$6.0 \cdot 10^5$	$.4 \cdot 10^{-3}$	$.58 \cdot 10^{-3}$	$3.8 \cdot 10^{-9}$	.088

It is seen that the onset width is about 70% of the relaxation width.

We also see that in these shocks we could assume that processes involving radiative transitions can be ignored in determining the width of the shock front since such times are of the order of 10^{-8} sec whereas once a significant amount of ionization is reached so that radiative

shock parameters, especially the pressure ratio p_2/p_1 and the density ratio ρ_2/ρ_1 of ionization (Fig. 1b). Again we note that the effect of ionization is more pronounced for higher shock velocities, e.g., at the velocity $U = 5.0 \times 10^3$ cm/sec, the change takes place in λ , then for $U = 4.0 \times 10^3$ cm/sec, λ is about 10% smaller while for $U = 3.0 \times 10^3$ cm/sec, λ is about 5% smaller. At this time the production term $\dot{\rho}_i$ is most important and the ionization term $\dot{\rho}_i$ is negligible. The ionization term taken over the entire ionization is slightly negative, i.e., it is slightly (or profile) of this region is rather small, because the region is relatively small and the effect on determining the total relaxation time of the shock front. If λ is the relaxation time for the shock front, λ_x is the relaxation time, and λ_y the corresponding degree of ionization, we find the following approximate values for the case $U = 5.0 \times 10^3$ cm/sec:

$U \left(\frac{\text{cm}}{\text{sec}} \right)$	Onset velocity (cm/sec)	λ (sec)	λ_x (sec)	λ_y (sec)
$5.0 \cdot 10^3$	$10.5 \cdot 10^3$	$1.5 \cdot 10^{-7}$	$1.5 \cdot 10^{-7}$	$1.5 \cdot 10^{-7}$
$4.5 \cdot 10^3$	$1.5 \cdot 10^3$	$2.5 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$
$4.0 \cdot 10^3$	$4 \cdot 10^3$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$

It is seen that the onset velocity is about 1/5 of the relaxation time. We also see that in these shocks we can assume that processes involving the radiative transitions can be ignored in determining the value of the shock front since such time is of the order of 10^{-10} sec, whereas once a significant amount of ionization is reached, λ is about 10^{-7} sec.

transitions could take place, the main part of the shock front has passed. For lower shock velocities, however, the relaxation widths will be considerably larger, and radiative processes assume importance. (As we have previously stated, they may also be important for lower densities.)

It is interesting to note that there is a range of shock velocities in which the width of the shock front may be significant, i.e., in which the conditions in the shock front are considerably different from the equilibrium conditions behind the shock front. At low shock velocities, i.e., for our case below about $3 \cdot 10^5$ cm per sec, there is no ionization behind the shock front, hence γ remains constant and the conditions at the peak of the shock remain unchanged. As the shock velocity U increases above $3 \cdot 10^5$ cm per sec, γ decreases and a long and relatively low temperature bump appears behind the head of the shock. (This is an indentation in terms of pressure and density.) As U becomes greater the bump becomes progressively higher but shorter until at 10^6 cm per sec it is approximately 10^{-6} cm thick but has a peak temperature of about $90,000^\circ$ where the equilibrium temperature is about 26000° . However, for $U \sim 10^6$ cm per sec we can no longer ignore the number of doubly ionized atoms. This picture of the shock front is qualitatively the same if the fore-pressure is 1.0 cm Hg.

8. Effect of Impurities.

Impurities such as oxygen or other molecules in the argon would have a strong influence on two parts of our computation. In the case

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of the equilibrium calculation the additional degrees of freedom, i.e., rotation, vibration, dissociation, and molecular excitation, due to their lower energy levels, will soak up a considerable amount of energy which is then not available for exciting (or ionizing) the argon atom. Calculations show that a small percentage (between about 1 to 10%) of oxygen in the argon will keep the argon from ionizing.

The second place in which impurities play an important part is in determining the onset of ionization. If the ionization cross-section between argon and O_2 or O is large then, even though the amount of oxygen is small, enough electrons may be furnished for the $A+e$ reaction to take over, resulting in an effective decrease in the onset width.

9. Comparison with Experiment.

In previous sections we have referred to some of the experimental measurements made on shock fronts for the energy range considered in this report. In this section we review these measurements as well as others. In general, the experimental work is quite meager although this field is now being explored, particularly by Kantrowitz and Lin at Cornell University, by Laporte at the University of Michigan and by various workers at Los Alamos. As mentioned previously, the shock velocity is the one well-determined quantity for a shock wave; and, of course, it may be assumed that the conditions in front of the shock are known.

Material Velocity. Shreffler, Christian, and others have measured the material velocity in a shock wave immediately behind the shock

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The second place in which impurities play an important part is in determining the onset of ionization. If the ionization cross-section between argon and O_2 or O is large then, even though the amount of oxygen is small, enough electrons may be furnished for the $A+e$ reaction to take over, resulting in an effective decrease in the onset voltage.

3. Comparison with Experiment.

In previous sections we have referred to some of the experimental measurements made on shock fronts for the energy range considered in this report. In this section we review these measurements as well as others. In general, the experimental work is quite meager although this field is now being explored, particularly by Katsenblatt and his at Cornell University, by Laporte at the University of Michigan and by various workers at Los Alamos. As mentioned previously, the shock velocity is the one well-determined quantity for a shock wave; and, of course, it may be assumed that the conditions in front of the shock are known.

Material Velocity. Shreffler, Christman, and others have measured

the material velocity in a shock wave immediately behind the shock

front (Ref 74). Their measurements correspond to the velocity in the equilibrium region and are plotted in Fig. 1. It is seen that experiment and theory are in good agreement in this region.

Electric Effects. Unpublished measurements at Los Alamos have shown that a strong (positive) potential rises behind the shock front. And for a given shock velocity the potential is much smaller if the gas is diatomic. This latter effect, as explained in section 8, is due to the presence of the additional degrees of freedom in the diatomic gas which absorb energy that otherwise would have gone into exciting or ionizing the atom.

Cowling (Ref 77) has shown that diffusion can be more important than viscosity or thermal conductivity in its effect on shock propagation, particularly if the gas is composed of two constituents having a large mass difference and if the pressure gradient is large, the direction being such that the heavier particles tend to move toward the regions of greater pressure. In our case such a situation exists immediately in front of the equilibrium region (cf Figs. 14 and 16), hence, a separation of ions and electrons should take place which could possibly account for the measured potential gradient in the shock front.

Shock Width. Measurements on the structure of the shock front in argon have been made at Cornell. The point at which the onset of ionization occurs is determined by a conductivity measurement and the equilibrium region is specified by the luminosity. The Cornell measurements are in fair agreement with our computations, although it is likely

front (Ref. 7a). Their measurements correspond to the velocity in the equilibrium region and are plotted in Fig. 1. It is seen that experiment and theory are in good agreement in this region.

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shown that a strong (positive) potential exists behind the shock front. And for a given shock velocity the potential is much smaller if the gas is diatomic. This latter effect is explained in section 6, is due to the presence of the additional degrees of freedom in the diatomic gas which absorb energy that otherwise would have gone into exciting or ionizing the atom.

Cowling (Ref. 7b) has shown that diffusion can be more important than viscosity or thermal conductivity in its effect on shock propagation, particularly if the gas is composed of two constituents having a large mass difference and if the pressure gradient is large, the diffusion being such that the heavier particles tend to move toward the regions of greater pressure. In our case such a situation exists immediately in front of the equilibrium region (cf. Figs. 1a and 1b). Hence, a separation of ions and electrons should take place which could possibly account for the measured potential gradient in the shock front.

Shock Width. Measurements on the structure of the shock front in

argon have been made at Cornell. The point at which the onset of ionization occurs is determined by a conductivity measurement and the equilibrium region is specified by the luminosity. The Cornell measurements are in fair agreement with our calculations, although it is likely

that impurities affect their measurements such that their shock width is slightly less than ours^{*}.

Spectral Distribution. Observations on spectra in shock waves show that at low shock velocities distinct lines exist whereas at high shock velocities a continuous spectrum is seen. This is because of the following reasons. First, at low shock velocities, transitions from the continuum to bound states do not occur because there are no free electrons, or at most, very few. There will, however, be many excited states of the atoms, thus one would expect a discrete spectrum to be observed.

For a high shock velocity and, consequently, a high degree of ionization, there are many electrons in free states. Since for the range of energies considered in this report these free states are in approximate maxwellian distributions with energies centered between one and three electron volts, one would expect the radiated energy to be continuously distributed. This is the ordinary recombination spectrum which is observed in shock fronts.

In addition to the continuous recombination spectrum in a shock front one might expect to observe a line spectra because of the presence of excited atoms. However the pressure and temperature are high enough so that Stark, collision, and Doppler broadening should be quite large and the spectral lines smeared out to such an extent that they are masked by the continuous recombination spectrum. Also, when the degree

^{*} Private communication from S. C. Lin to R. E. Duff.

that impurities affect the results in a small way.

is slightly less than unity.

Spectral Distribution

show that at low shock velocities

high shock velocities a constant

of the following relations

from the constant of proportionality

free energy of the system

excited states of the atoms

to be observed

For a high shock velocity

ionization, there are many

range of energies contained in

approximate number of atoms

and the relative intensity

continuously increasing

which is observed in the spectra

In addition to the conditions

from one might expect to observe

of excited atoms

as that Stark, collision

and the excited

masked by the emission

Private communication from

of ionization is high, the occupation number for a particular excited state is quite low and hence the line it emits is weak and more easily merges with the continuous background. For example, at $\gamma = 7$ and $T = 20,000^\circ$ the occupation number for the excited state $3p^5(2p_{1/2}^o)4s$, which emits the persistent argon line, $\lambda = 1048 \text{ A}^\circ$, is only .003. That is, out of 1000 plasma particles at these conditions, 140 will be electrons, 140 will be argon ions, 666 argon atoms in the ground state, only 2 atoms in the above excited state, and the remaining 52 particles in various other excited states. Finally, there are many closely spaced lines in the argon spectrum and because of the broadening of the lines they may be expected to overlap. As the initial pressure is lowered, however, the spectral lines do begin to stand out against the continuous background. This is because, for a given shock velocity, the temperature and pressure behind a shock front decrease with decrease of initial pressure. And the lower the temperature and pressure, the sharper and more pronounced the spectral lines will be. Also, the recombination coefficient decreases with decreasing temperature and pressure, resulting in a weaker recombination spectrum, although this effect may be balanced by the increase in ionization which occurs for smaller forepressures.

Luminosity. As discussed previously, because of the small number of degrees of freedom available in a monatomic gas compared to a diatomic gas, much of the energy can go directly into ionization. Thus one obtains a high degree of ionization behind a shock front in an inert

of ionization is high, the occupation number for a particular excited state is quite low and hence the line it emits is weak and more easily merges with the continuous background. For example, at $\lambda = 7$ and $T = 20,000^\circ$ the occupation number for the excited state $3p^2(2P^o)4s$, which emits the persistent argon line, $\lambda = 1068 \text{ \AA}$, is only .003. That is, out of 1000 plasma particles at these conditions, 140 will be electrons, 140 will be argon ions, 600 argon atoms in the ground state, only 2 atoms in the above excited state, and the remaining 25 particles in various other excited states. Finally, there are many closely spaced lines in the argon spectrum and because of the broadening of the lines they may be expected to overlap. As the initial pressure is lowered, however, the spectral lines do begin to stand out against the continuous background. This is because, for a given shock velocity, the temperature and pressure behind a shock front decrease with decrease of initial pressure. And the lower the temperature and pressure, the sharper and more pronounced the spectral lines will be. Also, the recombination coefficient decreases with decreasing temperature and pressure, resulting in a weaker recombination spectrum, although this effect may be balanced by the increase in ionization which occurs for smaller initial pressures.

Luminosity. As discussed previously, because of the small number of degrees of freedom available in a monatomic gas compared to a diatomic gas, much of the energy can go directly into ionization. Thus one obtains a high degree of ionization behind a shock front in an inert

gas. Consequently, an argon shock of sufficient strength will emit a brilliant flash and, because of the continuous distribution of energy in the spectrum, may be used in certain physical applications where such an energy distribution is desirable, e.g., in flash photography (Ref 84).

10. Summary and Critique.

A convenient method for determining the equilibrium conditions behind a shock front in argon has been presented. However, two factors limit its applicability. First, since double ionization has been neglected, there is an upper limit to the temperature. And, second, there is an upper limit to the degree of ionization due to the approximations involved in computing the partition functions. Neither of these limits has received a quantitative treatment. Numerical calculations of the equilibrium conditions have been made for shock velocities from 3 to 9×10^5 cm/sec at fore-pressures of 59.38 and 1.0 cm Hg.

The shape of the non-equilibrium part of the shock front has also been calculated. It was shown that the region between the front of the shock and the onset of ionization largely determines the shock width. In this zone the ionizing A+A reaction plays the dominant role. Hence, more accurate values for the A+A cross-section, particularly in the neighborhood of the threshold, should be obtained. Also, the effect of excitation reactions should be re-examined. Our reasons for neglecting these have been discussed qualitatively but a quantitative analysis is desirable.

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10. Summary and Critique

A convenient method for determining the equilibrium conditions behind a shock front in argon has been presented. However, two factors limit its applicability. First, since double ionization has been neglected, there is an upper limit to the temperature. And, second, there is an upper limit to the degree of ionization due to the approximations involved in computing the partition functions. Neither of these limits has received a quantitative treatment. Numerical calculations of the equilibrium conditions have been made for shock velocities from 3 to 9×10^5 cm/sec at pressures of 29.38 and 1.0 cm Hg. The shape of the non-equilibrium part of the shock front has also been calculated. It was shown that the region between the front of the shock and the onset of ionization largely determines the shock width. In this case the ionizing A+A reaction plays the dominant role. Hence, more accurate values for the A+A cross-section, particularly in the neighborhood of the threshold, should be obtained. Also, the effect of excitation reactions should be re-examined. Our reasons for neglecting these have been discussed qualitatively but a quantitative analysis is desirable.

Finally, a recombination coefficient α was derived from a method depending on the balance of the production and recombination of electrons in the equilibrium region behind the shock front. It was shown that α depends on temperature as well as on the atom density n and that Kramers' theory for radiative recombination, which was based on classical assumptions, is incorrect.

The two fore-pressures we have used in our calculations correspond to those used in experimental work at Cornell by Kantrowitz and his co-workers, and at Los Alamos. As pointed out previously, impurities exist in argon which have an important effect on both the equilibrium conditions and on the onset of ionization. In order to compare the above theory with the experimental results, the impurities should be included in the computations.

Finally, a re-examination of the

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equilibrium conditions

compare the above

should be included

Fig. 1 Material velocity vs. shock velocity.

Fig. 1. Plot of $\lg k$ vs. $1/T$.

Fig.2 Compression vs. shock velocity.

Fig. 2. Compression vs. shock velocity.

Fig. 3 Temperature vs. shock velocity.

Fig. 3. Temperature vs. shock velocity.

Fig. 4 Pressure ratio vs. shock velocity.

Fig. 4 Pressure ratio vs shock velocity

Fig. 5 Ionization vs. shock velocity

Fig. 6 Hugoniot

3
10² x 10¹

12

11

10

9

8

7

6

5

4

3

2

1

0

Fig. 6. Plot of

Fig. 7 Electron production coefficient for the reaction $A + A \rightarrow A + A^+ + e$

Fig. 7 Electron production coefficient for the reaction $A + A \rightarrow A + A + e$

Fig. 8 Electron production coefficient for the reaction $e + A \rightarrow e + A^+ + e$

Fig. 9 Radiative recombination coefficient (classical) a_3

Fig. 10 Recombination coefficient

$$\alpha^* = \beta \left\{ (1-x^*)/x^* \right\}$$

Fig. 10. Recombination coefficient α vs. temperature T for $p = 1.0 \text{ cm Hg}$ and $p = 29.3 \text{ cm Hg}$.

Fig. 11a Recombination coefficients for $T = 12,000^\circ$ abs.

(continued)

10.11.55

Fig. II b Recombination coefficients for $T = 15,000^\circ \text{ abs.}$

Fig. 11b Recombination coefficients for $T=1500^\circ \text{C}$

Fig. 11 c Recombination coefficients for $T = 18,000^\circ$ abs.

4x 11-01

Fig. 12 Temperature vs. (Eulerian) distance behind the shock front for various shock velocities.
($p_i = 59.3$ cm. Hg.)

(ρH and $E \rho \delta = \rho$)

St. 15 Temperature as function of distance behind the shock front for various shock velocities

Fig. 13 Compression vs. (Eulerian) distance behind the shock front for various shock velocities. ($p = 59.3$ cm. Hg.)

Fig. 14 Pressure ratio vs. (Eulerian) distance behind the shock front for various shock velocities. ($p_0 = 59.3$ cm. Hg.)

Fig. 4. Dependence of the rate of the reaction $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ on the concentration of the catalyst $[\text{H}_2\text{O}_2]$ (mole/l) at $[\text{H}_2\text{O}_2] = 0.01$ mole/l.

Fig.15 Material velocity vs. (Eulerian) distance behind the shock front for various shock velocities. ($p_1 = 59.3 \text{ cm.Hg.}$)

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Fig. 16 Ionization vs. (Eulerian) distance behind the shock front for various shock velocities. ($p_1 = 59.3 \text{ cm. Hg.}$)

Fig 16 Ionization vs (Eulerian) distance behind the shock front for various shock velocities ($\rho = 59.5 \text{ cm}^{-3}$)

Fig. 17 Compression behind the shock front vs. time ($p_i = 59.3$ cm. Hg.)

$\eta = 5.0 \times 10^{-3} \text{ cm}^2/\text{s}$
 $\eta = 2.5 \times 10^{-3} \text{ cm}^2/\text{s}$
 $\eta = 1.0 \times 10^{-3} \text{ cm}^2/\text{s}$

$\eta = 5.0 \times 10^{-3} \text{ cm}^2/\text{s}$
 $\eta = 2.5 \times 10^{-3} \text{ cm}^2/\text{s}$
 $\eta = 1.0 \times 10^{-3} \text{ cm}^2/\text{s}$

Fig. 18 Radiative Capture cross-section for the reaction $e + A^+ \rightarrow A + h\nu$

Fig 18 Radiative Capture cross-section for the reaction $e + A \rightarrow A + \gamma$

Fig. 19 Radiative recombination coefficient

TABLE I CONSTANTS AND CONVERSION FACTORS

Boltzmann's constant	$k = 1.380 \cdot 10^{-16}$	ergs/deg.
Planck's constant	$h = 6.624 \cdot 10^{-27}$	erg-sec.
	$= 4.135 \cdot 10^{-15}$	ev-sec.
	$\hbar = 1.054 \cdot 10^{-27}$	erg-sec.
Charge of electron	$e = 4.803 \cdot 10^{-10}$	esu
Gas constant	$R = 8.3144 \cdot 10^7$	ergs/mole-deg.
Avogadro's number	$N_0 = 6.023 \cdot 10^{23}$	per mole.
First Bohr radius	$a_0 = \frac{\hbar^2}{me^2} = 5.292 \cdot 10^{-9}$	cm.
	$\pi a_0^2 = .8825 \cdot 10^{-16}$	cm ²
Volume of ideal gas (NTP)	$V_0 = 22,415$	cm ³ /mole
Classical electron radius	$r_0 = \frac{e^2}{mc^2} = 2.8183 \cdot 10^{-13}$	cm.
Mass of electron	$m_e = 9.107 \cdot 10^{-28}$	gm.
Electron volt	$1 \text{ ev} = 11,605 \text{ deg.} = 1.602 \cdot 10^{-12}$	ergs
	$\frac{hc}{k} = 1.44$	deg.-cm.
	$R^* = R/M = 2.0815 \cdot 10^6$	ergs/gm-deg.
Mass of argon atom	$m = 6.632 \cdot 10^{-23}$	gm.
Atomic weight of argon	$M = 39.944$	gm/mole.
Ionization potential of A I		15.76 ev.
Ionization potential of A II		27.62 ev.
Total ionization potential of A II		43.4 ev.
Atmospheric pressure (Los Alamos)	$p_1 = .7887 \cdot 10^6$	dynes/cm ²
Normal temperature (Los Alamos)	$T_1 = 285^\circ$	
Corresponding density for argon	$\rho_1 = 1.3314 \cdot 10^{-3}$	gm/cm ³
Number of argon atoms per cm ³	$n_1 = 2.0075 \cdot 10^{19}$	

TABLE I
CONSTANTS AND CONVERSION FACTORS

Number of argon atoms per cm ³	$N_0 = 2.69 \times 10^{23}$	
Corresponding density for argon	$\rho_0 = 1.33 \times 10^{-3}$ gm/cm ³	
Normal temperature (Los Alamos)	$T_0 = 300^\circ$	
Atmospheric pressure (Los Alamos)	$P_0 = 1.013 \times 10^6$ dynes/cm ²	
Total ionization potential of A II	43.4 ev	
Ionization potential of A II	27.62 ev	
Ionization potential of A I	15.76 ev	
Atomic weight of argon	$M = 39.944$ gm/mole	
Mass of argon atom	$m = 6.63 \times 10^{-24}$ gm	
Electron volt	1 ev = 11,807.5 e.u. = 1.602×10^{-12} ergs	
Mass of electron	$m_e = 9.109 \times 10^{-28}$ gm	
Classical electron radius	$r_e = \frac{e^2}{mc^2} = 2.818 \times 10^{-13}$ cm	
Volume of ideal gas (NTP)	$V_0 = 22.415$ cm ³ /mole	
First Bohr radius	$a_0 = \frac{\hbar^2}{me^2} = 0.529 \times 10^{-8}$ cm	
Avogadro's number	$N_0 = 6.023 \times 10^{23}$	
Gas constant	$R = 8.314 \times 10^7$ ergs/mole-deg	
Charge of electron	$e = 4.803 \times 10^{-10}$ esu	
Planck's constant	$h = 6.624 \times 10^{-27}$ erg-sec	
Boltzmann's constant	$k = 1.380 \times 10^{-16}$ ergs/deg	

TABLE II ATOMIC CONSTANTS FOR ARGON

State	g_n	E_n (cm ⁻¹)	E_n (degrees)
<u>Argon atom, A</u>			
3p ⁶ 1s	1	0	0
3p ⁵ d	60	113,000	162,500
Ionization energy		127,110	183,000
<u>Argon ion, A⁺</u>			
3s ² 3p ⁵	4	0	0
	2	1432	2062
3s 3p ⁶	2	108723	156560
3s ² 3p ⁴ (³ P) 3d	8	132328	190550
	6	132482	190770
	4	132632	190990
	2	132739	191140
(³ P) 4s	6	134243	193310
	4	135087	194530
	2	135603	195270
(³ P) 4s	4	138245	199070
	2	139259	200530
(³ P) 3d	10	142187	204750
	8	142718	205510
	6	143109	206080
	4	143372	206460
(³ P) 3d	2	144711	208380
	4	145670	209760
(³ P) 3d	2	147229	212010
	4	147504	212410
	6	147877	212940
(¹ D) 4s	4	148621	214010
	6	148843	214330
(³ P) 3d	8	148180	214820
	6	150149	216210
(³ P) 3d	4	150476	216690
	6	151088	217570

State

3p 1

3p 2

Location

3p 3

3p 4

3p 5

(3)

(3)

(3)

(3)

(3)

(3)

(3)

(3)

TABLE II ATOMIC CONSTANTS FOR ARGON (continued)

State	g_n	E_n (cm^{-1})	E_n (degrees)
(^3P) 4p	6	155044	223260
	4	155352	223710
	2	155709	224220
(^3P) 4p	8	157235	226420
	6	157674	227050
	4	158169	227760
(^3P) 4p	2	158429	228140
	6	158731	228570
	4	159394	229530
(^3P) 4p	2	159707	229980
	4	160240	230750
	4	161050	231910
(^3P) 4p	2	161090	231970
(^1S) 4s	2	167309	240920
(^1D) 4p	6	170402	245380
	8	170531	245560
	4	172215	247990
(^1D) 4p	2	172817	248860
	6	172336	248160
	4	172831	248880
(^1D) 4p	4	173349	249620
	6	173394	249690
	4	174411	251150
(^1D) 3d	2	174822	251740
	4	179593	258610
	2	179933	259100
(^3P) 5s	6	181595	261500
	4	182223	262400
	2	182952	263450
(^3P) 5s	4	183092	263650
	2	183916	264840
(^3P) 4d	8	183676	264490
	6	183798	264670
	4	183987	264940
	2	184193	265240

(1) 10/10

(2) 10/10

(3) 10/10

(4) 10/10

(5) 10/10

(6) 10/10

(7) 10/10

(8) 10/10

(9) 10/10

(10) 10/10

(11) 10/10

(12) 10/10

(13) 10/10

(14) 10/10

(15) 10/10

(16) 10/10

(17) 10/10

(18) 10/10

(19) 10/10

(20) 10/10

(21) 10/10

(22) 10/10

(23) 10/10

(24) 10/10

(25) 10/10

(26) 10/10

(27) 10/10

(28) 10/10

(29) 10/10

(30) 10/10

TABLE II ATOMIC CONSTANTS FOR ARGON (continued)

State	g_n	E_n (cm^{-1})	E_n (degrees)
$(^1D) 3d$	2	184094	265100
$(^3P) 4d$	10	185094	266530
	8	185625	267300
	6	186075	267950
	4	186341	268330
$(^3P) 4d$	2	186172	268090
	4	186471	268520
	6	186892	269120
$(^1S) 3d$	6	186728	268890
	4	186751	268920
Ionization energy		222820	320800

TABLE III HIGH EXCITED STATES OF ARGON

State	E_n	g_n	Effective statistical weights $g_n(\eta)$														
			1	2	3	4	5	6	7	8	9	10	15	20			
4s	48,500	2	2	2	2	2	2	2	2	2	2	2	2	1			
4p	30,400	6	6	6	6	6	6	6	6	6	6	6	6	2			
5s	19,500	2	2	2	2	2	1	1	0	0	0	0	0	0			
5p	14,600	6	6	6	6	6	2	2	1	0	0	0	0	0			
4d, 4f	10,700	24	24	24	24	24	24	24	24	24	24	24	24	9			
6s	10,700	2	2	0	0	0	0	0	0	0	0	0	0	0			
6p	8,500	6	6	1	0	0	0	0	0	0	0	0	0	0			
5d, f, g	6,600	42	42	42	42	42	17	11	5	1	0	0	0	0			
7s	6,700	2	0	0	0	0	0	0	0	0	0	0	0	0			
6d, f, g, h	4,500	64	64	13	0	0	0	0	0	0	0	0	0	0			

State

(1) 34
(2) 43

(3) 44

(4) 35

Ionization energy

State

42

47

52

53

45, 47

62

69

54, 7, 8

72

64, 7, 8, 1

TABLE IV PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANT FOR ARGON

Density Ratio η	Temp. (°abs.) T	Z_{ion}	Z	K/2($p_1 = 59.3$ cm. Hg)	
2	7500		1.0000	5.4475	(-9)*
3				3.6317	"
4				2.7238	"
5				2.1790	"
6				1.8158	"
7				1.5564	"
1	8000	5.5456	1.0000	5.5416	(-8)
2				2.7708	"
3				1.8472	"
4				1.3854	"
5				1.1083	"
6				9.2361	(-9)
7				7.9166	"
8				6.9270	"
9				6.1574	"
10				5.5416	"
15				3.6944	"
20				2.7708	"
2	8500		1.0000	1.1704	(-7)
3				7.8025	(-8)
4				5.8519	"
5				4.6815	"
6				3.9013	"
7				3.3439	"
2	9000		1.0000	4.2332	(-7)
3				2.8221	"
4				2.1166	"
5				1.6933	"
6				1.4111	"
7				1.2095	"
8				1.0583	"
9				9.4071	(-8)
10				8.4664	"
15				5.6443	"
20				4.2332	"
2	9500	5.6098	1.0000	1.3432	(-6)
3				8.9549	(-7)
4				6.7162	"
5				5.3730	"
6				4.4775	"
7				3.8378	"
8					
9					
10					
15					
20				1.3433	"

TABLE IV. PARTITION FRACTIONS AND DENSITY DATA FOR ACRYL

W	Density (g/cc)	Partition Fractions		
		T	S	K ₁ (cc/g)
1	10.000	2.6273	1.0000	1.6300 (-3)
2				1.6300
3				1.6300
4				1.6300
5				1.6300
6				1.6300
7				1.6300
8				1.6300
9				1.6300
10				1.6300
15				1.6300
20				1.6300
2	10.500	2.6334	1.0000	1.6300 (-3)
3				1.6300
4				1.6300
5				1.6300
6				1.6300
7				1.6300
8				1.6300
9				1.6300
10				1.6300
15				1.6300
20				1.6300
2	11.000	2.6395	1.0000	1.6300 (-3)
3				1.6300
4				1.6300
5				1.6300
6				1.6300
7				1.6300
8				1.6300
9				1.6300
10				1.6300
15				1.6300
20				1.6300
2	11.500	2.6456	1.0000	1.6300 (-3)
3				1.6300
4				1.6300
5				1.6300
6				1.6300
7				1.6300
8				1.6300
9				1.6300
10				1.6300
15				1.6300
20				1.6300

(continued)

TABLE IV PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANT FOR ARGON

Density Ratio η	Temp. ($^{\circ}$ abs.) T	Z_{ion}	Z	K/2($p_1 = 59.3$ cm. Hg)	
2	12,000	5.6842	1.0006	1.0684	(-4)
3			1.0005	7.1226	(-5)
4			1.0005	5.3419	"
5			1.0005	4.2739	"
6			1.0004	3.5616	"
7			1.0004	3.0529	"
8			1.0004	2.6713	"
9			1.0004	2.3738	"
10			1.0004	2.1371	"
15			1.0004	1.4247	"
20			1.0002	1.0687	"
2	13,000	5.7067	1.0016	3.9047	(-4)
3			1.0015	2.6034	"
4			1.0015	1.9525	"
5			1.0013	1.5624	"
6			1.0012	1.3021	"
7			1.0011	1.1161	"
8			1.0011	9.7668	(-5)
9			1.0011	8.6723	"
10			1.0011	7.8134	"
15			1.0011	5.2089	"
20			1.0006	3.9087	"
2	14,000	5.7262	1.0039	1.1941	(-3)
3			1.0036	7.9625	(-4)
4			1.0036	5.9719	"
5			1.0030	4.7807	"
6			1.0029	3.9844	"
7			1.0027	3.4159	"
8			1.0025	2.9893	"
9			1.0025	2.6487	"
10			1.0025	2.3914	"
15			1.0025	1.5943	"
20			1.0013	1.1971	"
2	15,000	5.7434	1.0084	3.1607	(-3)
3			1.0079	2.1083	"
4			1.0079	1.5812	"
5			1.0063	1.2669	"
6			1.0060	1.0560	"
7			1.0056	9.0559	(-4)
8			1.0053	7.9259	"
9			1.0053	7.0456	"
10			1.0053	6.3410	"
15			1.0053	4.2274	"
20			1.0028	3.1784	"

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(continued)

TABLE IV PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANT FOR ARGON

Density Ratio η	Temp. ($^{\circ}$ abs.) T	Z_{ion}	Z	$K/2(p_1 = 59.3 \text{ cm. Hg})$	
2	15,500	5.7512	1.0119	4.9106	(-3)
3			1.0111	3.2764	"
4			1.0111	2.4573	"
5			1.0089	1.9702	"
6			1.0085	1.6425	"
7			1.0078	1.4088	"
8			1.0075	1.2331	"
9			1.0074	1.0962	"
10			1.0074	9.8655	(-4)
15			1.0074	6.5770	"
20			1.0039	4.9499	"
2	16,000	5.7587	1.0166	7.4237	(-3)
3			1.0154	4.9549	"
4			1.0154	3.7161	"
5			1.0123	2.9822	"
6			1.0117	2.4866	"
7			1.0108	2.1333	"
8			1.0101	1.8678	"
9			1.0101	1.6603	"
2	17,000	5.7727	1.0304	1.5758	(-2)
3			1.0281	1.0529	"
4			1.0281	7.8965	(-3)
5			1.0221	6.3545	"
6			1.0210	5.3010	"
7			1.0193	4.5515	"
8			1.0182	3.9865	"
9			1.0181	3.5442	"
10			1.0181	3.1898	"
15			1.0181	2.1265	"
20			1.0096	1.6083	"
2	18,000	5.7857	1.0547	3.0571	(-2)
3			1.0480	2.0511	"
4			1.0480	1.5383	"
5			1.0374	1.2433	"
6			1.0354	1.0380	"
7			1.0324	8.9238	(-3)
8			1.0306	7.8219	"
9			1.0302	6.9549	"
10			1.0302	6.2594	"
15			1.0302	4.1730	"
20			1.0161	3.1733	"

TABLE IV. PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANTS FOR ARGON

Density Ratio ρ/ρ_0	Temp. ($^{\circ}$ abs.) T	E_{ion}	E	$K(T, \rho) = 59.3 \text{ cm. Hg.}$
2	15,500	2.7512	1.0119	1.0106 (-3)
3			1.0111	3.2764
4			1.0111	2.4573
5			1.0089	1.9709
6			1.0067	1.6437
7			1.0076	1.4068
8			1.0075	1.2331
9			1.0074	1.0966
10			1.0074	9.8822 (-4)
15			1.0074	6.5710
20			1.0039	4.9439
2	16,000	2.7567	1.0166	1.0537 (-3)
3			1.0164	1.9549
4			1.0154	3.7161
5			1.0123	2.9822
6			1.0117	2.4866
7			1.0108	2.1333
8			1.0101	1.8678
9			1.0101	1.6603
2	17,000	2.7724	1.0264	1.2728 (-3)
3			1.0261	1.0529
4			1.0261	1.8962 (-3)
5			1.0261	6.3542
6			1.0260	5.0010
7			1.0173	4.2372
8			1.0162	3.9822
9			1.0161	3.5412
10			1.0161	3.1864
15			1.0161	2.1262
20			1.0096	2.0063
2	18,000	2.7927	1.0347	3.0577 (-3)
3			1.0340	2.0517
4			1.0330	1.2383
5			1.0314	1.2433
6			1.0304	1.0380
7			1.0264	8.0238 (-3)
8			1.0266	7.8219
9			1.0262	6.5599
10			1.0262	6.2524
15			1.0262	4.1730
20			1.0161	3.1733

(continued)

TABLE IV PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANT FOR ARGON

Density Ratio η	Temp. ($^{\circ}$ abs.) T	Z_{ion}	Z	K/2($p_1 = 59.3$ cm. Hg)	
3	19,000	5.7981	1.0777	3.7016	(-2)
4			1.0777	2.7762	"
5			1.0599	2.2583	"
6			1.0567	1.8877	"
7			1.0516	1.6259	"
8			1.0486	1.4267	"
9			1.0480	1.2688	"
10			1.0480	1.1419	"
15			1.0480	7.6129	(-3)
20			1.0256	5.8346	"
3	20,000	5.8106	1.1200	6.2398	(-2)
4			1.1200	4.6799	"
5			1.0918	3.8407	"
6			1.0866	3.2157	"
7			1.0786	2.7770	"
8			1.0738	2.4405	"
9			1.0730	2.1711	"
10			1.0730	1.9540	"
15			1.0730	1.3026	"
20			1.0389	1.0090	"
3	21,000	5.8235	1.1780	9.8903	(-2)
4			1.1780	7.4178	"
5			1.1352	6.1581	"
6			1.1273	5.1675	"
7			1.1152	4.4777	"
8			1.1080	3.9433	"
9			1.1067	3.5093	"
10			1.1067	3.1584	"
15			1.1067	2.1056	"
20			1.0569	1.6536	"
4	22,000		1.2551	1.1120	(-1)
5			1.1925	9.3632	(-2)
6			1.1810	7.8789	"
7			1.1632	6.8565	"
8			1.1528	6.0538	"
9			1.1508	5.3902	"
10			1.1508	4.8512	"
15			1.1508	3.2341	"
20			1.0805	2.5835	"

(continued)

TABLE IV PARTITION FUNCTIONS AND EQUILIBRIUM CONSTANT FOR ARGON

Density Ratio η	Temp. ($^{\circ}$ abs.) T	Z_{ion}	Z	$K/2(p_1 = 59.3 \text{ cm. Hg})$	
4	23,000	5.8531	1.3547	1.5854	(-1)
5			1.2661	1.3571	"
6			1.2497	1.1457	"
7			1.2247	1.0021	"
8			1.2099	8.8759	(-2)
9			1.2072	7.9075	"
10			1.2072	7.1168	"
15			1.2072	4.7445	"
20			1.1105	3.8680	"
4	24,000	5.8712	1.4804	2.1610	(-1)
5			1.3585	1.8839	"
6			1.3359	1.5965	"
7			1.3015	1.4046	"
8			1.2812	1.2485	"
9			1.2774	1.1131	"
10			1.2774	1.0018	"
15			1.2774	6.6784	(-2)
20			1.1480	5.5736	"
4	25,000	5.8925	1.6357	2.8312	(-1)
5			1.4721	2.5165	"
6			1.4417	2.1414	"
7			1.3957	1.8960	"
8			1.3684	1.6921	"
9			1.3633	1.5097	"
10			1.3633	1.3587	"
15			1.3633	9.0582	(-2)
20			1.1937	7.7589	"
4	26,000	5.9178	1.8242	3.5831	(-1)
5			1.6095	3.2489	"
6			1.5693	2.7767	"
7			1.5091	2.4751	"
8			1.4732	2.2184	"
9			1.4665	1.9810	"
10			1.4665	1.7829	"
15			1.4665	1.1886	"
20			1.4665	1.0470	"

* (-9) = 10^{-9}

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TABLE V EQUILIBRIUM CONDITIONS BEHIND THE SHOCK FRONT

U cm sec	η	T degr. abs.	ξ	u cm sec	σ	ρ	$[A^+]$	$[A]$	g
A. $p_1 = 59.38$ cm. Hg.									
3.0 10^5	3.91	8322	114.07	2.2327	10^5	1.6580	2.5198	1.000	1.000
3.5 "	4.08	10918	157.11	2.6422	"	1.6285	2.5911	.995	1.005
4.0 "	4.55	13018	211.73	3.1209	"	1.5487	2.8225	.981	1.019
4.5 "	5.17	14650	276.72	3.6296	"	1.4700	3.1277	.959	1.041
5.0 "	5.82	16023	350.51	4.1409	"	1.4069	3.4576	.929	1.071
5.5 "	6.483	17250	432.88	4.6516	"	1.3585	3.7894	.897	1.103
6.0 "	7.123	18400	523.40	5.1577	"	1.3216	4.1095	.862	1.138
6.5 "	7.722	19480	621.86	5.6582	"	1.2934	4.4083	.822	1.178
7.0 "	8.264	20551	728.08	6.1530	"	1.2718	4.6792	.778	1.222
7.5 "	8.79	21602	842.53	6.6468	"	1.2538	4.9401	.735	1.265
8.0 "	9.17	22777	963.57	7.1276	"	1.2422	5.1288	.685	1.315
8.5 "	9.59	23880	1093.48	7.6137	"	1.2306	5.3365	.639	1.361
9.0 "	9.925	25072	1230.60	8.0932	"	1.2221	5.5025	.591	1.409
B. $p_1 = 1.0$ cm. Hg.									
3.0 10^5	3.983	8200	114.73	2.2468	10^5	1.6416	2.5536	.998	1.002
3.5 "	4.491	10066	161.75	2.7207	"	1.5536	2.8064	.980	1.020
4.0 "	5.330	11304	220.42	3.2495	"	1.4487	3.2287	.957	1.043
4.5 "	6.226	12250	287.94	3.7772	"	1.3731	3.6802	.924	1.076
5.0 "	7.20	12987	364.41	4.3056	"	1.3153	4.1716	.889	1.111
5.5 "	8.03	13768	448.06	4.8151	"	1.2787	4.5881	.845	1.155
6.0 "	8.95	14381	540.82	5.3296	"	1.2470	5.0486	.802	1.198
6.5 "	9.815	14989	641.56	5.8377	"	1.2231	5.4823	.757	1.243
7.0 "	10.57	15630	749.92	6.3377	"	1.2057	5.8614	.706	1.294
7.5 "	11.35	16224	866.90	6.8392	"	1.1905	6.2493	.658	1.342
8.0 "	11.97	16802	991.13	7.3317	"	1.1799	6.5586	.596	1.404
8.5 "	12.63	17401	1124.09	7.8270	"	1.1699	6.8858	.542	1.458
9.0 "	13.05	18072	1263.59	8.3103	"	1.1641	7.0938	.473	1.527

TABLE VI THE NON-EQUILIBRIUM REGION ($p_1 = 59.38$ cm. Hg.)

A. $U = 5.0 \cdot 10^5$ cm./sec.

η	$T^{\circ}_{\text{abs.}}$	ξ	u cm./sec.	$[A^+]$	X cm.	t sec.
3.9532	22801	316.27		0	0	0
3.9532	22801	316.27		0	$5.6916 \cdot 10^{-3}$	$4.50 \cdot 10^{-8}$
3.9532	22800	316.27	$3.7351 \cdot 10^5$	$2.546 \cdot 10^{-8}$	6.0078 "	4.75 "
3.9532	22800	316.27	3.7351 "	6.366 "	6.3240 "	5.00 "
3.9532	22800	316.27	3.7351 "	1.400 ⁻⁷	6.6402 "	5.25 "
3.9532	22800	316.27	3.7352 "	3.475 ⁻⁶	7.9049 "	6.25 "
3.9550	22791	316.31	3.7354 "	8.539 ⁻⁵	9.1692 "	7.25 "
3.9925	22609	317.32	3.7425 "	1.821 ⁻³	1.0421 ⁻²	8.25 "
4.1572	21842	321.50		9.052 "	1.1624 "	9.25 "
4.2686	21338	324.15	3.8155 "	1.423 ⁻²	1.1917 "	9.50 "
4.3240	21098	325.42	3.8364 "	1.657 "	1.2032 "	9.60 "
4.3799	20859	326.67	3.8513 "	1.896 "	1.2146 "	9.70 "
4.4366	20622	327.90	3.8659 "	2.135 "	1.2259 "	9.80 "
4.4928	20391	329.09	3.8802 "	2.369 "	1.2370 "	9.90 "
4.5481	20169	330.23	3.8940 "	2.596 "	1.2480 "	1.00 ⁻⁷
4.6742	19673	332.73	3.9170 "	3.118 "	1.2748 "	1.025 "
4.7915	19233	334.94	3.9444 "	3.579 "	1.3009 "	1.05 "
4.8963	18854	336.83	3.9682 "	3.979 "	1.3264 "	1.075 "
4.9863	18540	338.38	3.9883 "	4.313 "	1.3515 "	1.10 "
5.0648	18273	339.69	4.0051 "	4.600 "	1.3761 "	1.125 "
5.1334	18046	340.81	4.0193 "	4.846 "	1.4005 "	1.15 "
5.1935	17851	341.76	4.0315 "	5.058 "	1.4246 "	1.175 "
5.3571	17332	344.24	4.0545 "	5.659 "	1.5179 "	1.275 "
5.4742	16982	345.93	4.0775 "	6.045 "	1.6092 "	1.375 "
5.6491	16515	348.31	4.1433 "	6.398 "	1.8305 "	3.875 "
5.7231	16294	349.28	4.1369 "	6.742 "	2.0489 "	6.375 "
5.8200	16023	350.51		.071	∞	∞

TABLE VI THE NON-EQUILIBRIUM REGION ($p_1 = 59.38$ cm. Hg.)

$A \cdot U = 2.0 \cdot 10^7$ cm./sec.

T	T °C.	$\bar{E}$	U cm./sec.	$[A^+]$	X cm.	t sec.
3.9535	25801	316.27		0	0	0
3.9535	25801	316.27		0	2.6016 · 10 ⁻³	1.30 · 10 ⁻⁸
3.9535	25800	316.27	3.7351 · 10 ⁻²	2.646 · 10 ⁻⁸	6.0018	4.75
3.9535	25800	316.27	3.7351	6.366	6.3540	5.00
3.9535	25800	316.27	3.7351	1.400	6.6405	5.25
3.9535	25800	316.27	3.7355	3.475	7.9019	6.25
3.9550	25791	316.31	3.7354	6.539	9.1698	7.25
3.9555	25609	317.35	3.7455	1.851	1.0451	8.25
4.1575	21849	351.50	2.055	2.055	1.1654	9.25
4.5686	21338	354.15	3.8155	1.453	1.1917	9.50
4.3940	21098	355.45	3.8364	1.657	1.2035	9.60
4.3739	20859	356.67	3.8513	1.956	1.2146	9.70
4.4366	20625	357.90	3.8659	5.135	1.2259	9.80
4.4958	20391	359.09	3.8805	5.369	1.2370	9.90
4.5481	20159	360.23	3.8940	6.556	1.2480	1.00
4.6145	19913	362.73	3.9170	3.178	1.2549	1.055
4.7015	19533	364.94	3.9446	3.575	1.3009	1.05
4.8069	19094	366.93	3.9695	3.959	1.3504	1.055
4.9553	18540	369.38	3.9953	4.313	1.3575	1.10
5.0648	18273	369.69	4.0051	4.600	1.3761	1.155
5.1334	18046	369.87	4.0193	4.846	1.4005	1.15
5.2055	17851	369.76	4.0315	5.058	1.4546	1.155
5.3571	17335	364.64	4.0545	5.659	1.5175	1.25
5.4445	16985	365.98	4.0775	6.045	1.6095	1.35
5.6491	16515	368.31	4.1433	6.398	1.8305	3.815
5.7531	16294	369.58	4.1569	6.445	2.0489	6.375
5.8500	16023	370.51		6.445		

TABLE VI THE NON-EQUILIBRIUM REGION ($p_1 = 59.38$ cm. Hg.)

B. $U = 5.5 \cdot 10^5$

γ	$T^{\circ}_{\text{abs.}}$	ξ	u cm./sec.	$[A^+]$	X cm.	t sec.
3.9587	27571	382.73		0	0	0
3.9587	27571	382.73		0	$7.6416 \cdot 10^{-4}$	$5.50 \cdot 10^{-9}$
3.9612	27536	382.73	$4.1054 \cdot 10^5$	$1.973 \cdot 10^{-7}$	9.0298	6.50 "
3.9612	27536	382.73	4.1059 "	1.254 10^{-6}	1.0418 10^{-3}	7.50 "
3.9613	27535	382.74	4.1059 "	7.970 "	1.1806 "	8.50 "
3.9621	27530	382.76	4.1061 "	5.061 10^{-5}	1.3194 "	9.50 "
3.9672	27499	382.93	4.1071 "	3.183 10^{-4}	1.4581 "	1.05 10^{-8}
3.9971	27319	383.89	4.1135 "	1.895 10^{-3}	1.5957 "	1.15 "
4.1266	26559	387.90	4.1462 "	8.652 10^{-2}	1.7289 "	1.25 "
4.1930	26183	389.86	4.1726 "	1.201 10^{-2}	1.7617 "	1.275 "
4.2243	26009	390.76	4.1874 "	1.356 "	1.7748 "	1.285 "
4.2571	25829	391.69	4.1973 "	1.520 "	1.7877 "	1.295 "
4.2918	25640	392.66	4.2075 "	1.693 "	1.8005 "	1.305 "
4.3282	25444	393.66	4.2181 "	1.873 "	1.8132 "	1.315 "
4.3660	25243	394.68	4.2290 "	2.058 "	1.8258 "	1.325 "
4.4048	25040	395.71	4.2400 "	2.247 "	1.8383 "	1.335 "
4.4444	24835	396.75	4.2511 "	2.438 "	1.8507 "	1.345 "
4.4844	24631	397.77	4.2621 "	2.630 "	1.8629 "	1.355 "
4.5246	24428	398.79	4.2731 "	2.821 "	1.8751 "	1.365 "
4.5648	24229	399.78	4.2839 "	3.010 "	1.8871 "	1.375 "
4.6047	24034	400.75	4.2944 "	3.196 "	1.8991 "	1.385 "
4.6441	23844	401.69	4.3046 "	3.379 "	1.9109 "	1.395 "
4.6829	23659	402.60	4.3146 "	3.557 "	1.9227 "	1.405 "
4.7731	23236	404.66	4.3311 "	3.981 "	1.9515 "	1.43 "
4.8608	22839	406.59	4.3524 "	4.373 "	1.9798 "	1.455 "
4.9427	22480	408.33	4.3720 "	4.731 "	2.0076 "	1.48 "
5.0187	22155	409.90	4.3896 "	5.058 "	2.0350 "	1.505 "
5.0890	21862	411.30	4.4055 "	5.355 "	2.0620 "	1.53 "
5.1540	21597	412.57	4.4198 "	5.626 "	2.0887 "	1.555 "
5.2141	21358	413.71	4.4327 "	5.873 "	2.1150 "	1.58 "
5.3988	20639	417.06	4.4593 "	6.668 "	2.2169 "	1.68 "
5.5515	20085	419.66	4.4898 "	7.258 "	2.3160 "	1.78 "
5.6740	19661	421.65	4.5138 "	7.714 "	2.4129 "	1.88 "
5.7737	19328	423.20	4.5326 "	8.076 "	2.5082 "	1.98 "
5.8540	19067	424.41	4.5474 "	8.360 "	2.6021 "	2.08 "
5.9935	18621	426.44	4.5655 "	8.890 "	2.8315 "	2.33 "
6.1019	18295	427.96	4.5841 "	9.253 "	3.0569 "	2.58 "
6.1808	18064	429.03	4.5979 "	9.507 10^{-1}	3.2793 "	2.83 "
6.3262	17645	430.92	4.6161 "	1.001 10^{-1}	4.1487 "	3.83 "
6.3954	17459	431.80	4.6294 "	1.021 "	5.0087 "	4.83 "
6.483	17250	432.88		.103	∞	∞

TABLE VI THE NON-EQUILIBRIUM REGION ($p_1 = 59.38$ cm. Hg.)C. $U = 6.0 \cdot 10^5$ cm./sec.

γ	$T^{\circ}_{\text{abs.}}$	ξ	u cm./sec.	$[A^+]$	X cm.	t sec.
3.9674	32724	455.54		0	0	0
3.9674	32724	455.54		0	$1.3611 \cdot 10^{-4}$	$9.00 \cdot 10^{-10}$
3.9674	32723	455.54	$4.4876 \cdot 10^5$	$1.336 \cdot 10^{-7}$	1.7391 "	$1.15 \cdot 10^{-9}$
3.9674	32723	455.54	4.4876 "	7.957 "	2.1172 "	1.40 "
3.9674	32722	455.54	4.4876 "	4.723 ⁻⁶	2.4953 "	1.65 "
3.9678	32719	455.55	4.4877 "	2.804 ⁻⁵	2.8733 "	1.90 "
3.9701	32702	455.64	4.4882 "	1.658 ⁻⁴	3.2512 "	2.15 "
3.9836	32602	456.16	4.4913 "	9.612 "	3.6277 "	2.40 "
4.0522	32102	458.74	4.5080 "	4.999 ⁻³	3.9979 "	2.65 "
4.2699	30591	466.39	4.5741 "	1.756 ⁻²	4.3491 "	2.90 "
4.4227	29597	471.30	4.6223 "	2.609 "	4.4848 "	3.00 "
4.4687	29314	472.72	4.6503 "	2.842 "	4.5184 "	3.025 "
4.5125	29044	474.04	4.6638 "	3.078 "	4.5516 "	3.05 "
4.5567	28775	475.35	4.6767 "	3.315 "	4.5845 "	3.075 "
4.6014	28508	476.64	4.6896 "	3.552 "	4.6171 "	3.10 "
4.6461	28245	477.91	4.7022 "	3.787 "	4.6494 "	3.125 "
4.6908	27986	479.16	4.7146 "	4.020 "	4.6814 "	3.15 "
4.7351	27733	480.37	4.7267 "	4.250 "	4.7131 "	3.175 "
4.7790	27486	481.55	4.7385 "	4.475 "	4.7445 "	3.20 "
4.8223	27246	482.69	4.7500 "	4.695 "	4.7756 "	3.225 "
4.9787	26400	486.65	4.7768 "	5.517 "	4.8961 "	3.325 "
5.1292	25635	490.23	4.8134 "	6.251 "	5.0131 "	3.425 "
5.2649	24980	493.28	4.8457 "	6.891 "	5.1270 "	3.525 "
5.3857	24421	495.87	4.8732 "	7.445 "	5.2384 "	3.625 "
5.4929	23944	498.08	4.8966 "	7.925 "	5.3477 "	3.725 "
5.5883	23533	499.96	4.9167 "	8.344 "	5.4550 "	3.825 "
5.6735	23177	501.60	4.9340 "	8.711 "	5.5608 "	3.925 "
5.7501	22865	503.02	4.9491 "	9.036 "	5.6651 "	4.025 "
5.8991	22268	505.69	4.9699 "	9.707 "	5.9194 "	4.275 "
6.0297	21778	507.92	4.9937 "	1.023 ⁻¹	6.1682 "	4.525 "
6.1379	21386	509.70	5.0133 "	1.065 "	6.4125 "	4.775 "
6.2284	21069	511.14	5.0291 "	1.100 "	6.6534 "	5.025 "
6.3051	20807	512.33	5.0421 "	1.129 "	6.8913 "	5.275 "
6.4941	20169	515.13	5.0630 "	1.208 "	7.8152 "	6.275 "
6.6381	19721	517.16	5.0859 "	1.258 "	8.7190 "	7.275 "
6.7403	19415	518.55	5.1026 "	1.292 "	9.6092 "	8.275 "
6.8678	19038	520.22	5.1182 "	1.339 "	1.1793 ⁻³	$1.0775 \cdot 10^{-8}$
6.9482	18814	521.25	5.1313 "	1.363 "	1.3952 "	1.3275 "
7.0327	18582	522.30	5.1432 "	1.389 "	2.2483 "	2.3275 "
7.0485	18544	522.49	5.1479 "	1.391 "	3.0996 "	3.3275 "
7.123	18400	523.40		.139	∞	∞

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