

parable intensity ratios were observed was very much lower in the liquid He cooled cathode. If it is assumed that the behavior of the relative intensities depends only on the average time between collisions, then it ought to be possible to scale the measurements. It is well known that in a gas, the mean time between collisions is proportional to the square root of the temperature. Taking for the temperatures in the discharge region in the two cases, the temperature determined from the width of the He I $1s2p\ ^3P_0-1s4s\ ^3S_1$ line of the 4713 Å multiplet (100°K for liquid nitrogen and 35°K for liquid helium), one finds that the pressures measured in the liquid helium cooled cathode should be multiplied by a factor of about 1.7 in order to scale them to the conditions in the liquid nitrogen cooled cathode. Using this factor we find general agreement, but not exact coincidence, and conclude that there are other processes, not clearly understood, which must be taken into account.

G. Summary of Intensity Study

Within the experimental uncertainty the results of the intensity study can be summarized as follows:

So long as the pressure in the discharge region is high enough, the levels are populated according to their statistical distributions.

At low pressures, the population of an excited level

depends upon the product of its rate of excitation and its lifetime.

The usual multiplet intensity rules are satisfied.

The excitation function of a level with a specified n depends only on its l value.

There is no mixing between the nearly degenerate states with the same j but different l .

The relative rates of excitation for the various levels may change if the average electron energy changes.

To at least a fair approximation, the transition between dynamical and statistical intensities depends only on the average time between collisions.

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Primary Ionization Coefficient Measurements in Penning Mixtures

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Measurements have been made of the electron ionization coefficient η in helium-hydrogen and neon-hydrogen gas mixtures over an extended range of E/p_0 values. The present results show a variation of η with E/p_0 and hydrogen concentration similar to that previously obtained by Kruithof and Penning for the case of neon-argon mixtures. The maximum values of η observed of 0.0302 and 0.0285 V^{-1} were obtained for hydrogen concentrations of 0.1% and at E/p_0 (V/cm \times Torr) values of 15.0 and 3.0 for helium-hydrogen and neon-hydrogen mixtures, respectively. Comparison is made of these results with the neon-argon measurements of Kruithof and Penning. In addition, the present data are compared with ionization measurements obtained using other techniques.

I. INTRODUCTION

IN a binary gas mixture if the energy of the metastable state of the main constituent exceeds the ionization energy of the minor component, such a mixture is generally referred to as a Penning mixture. One of the most significant characteristics of such a mixture is the enhancement of the ionization coefficient of the resulting mixture over that of either constituent. This property was demonstrated in detail in the measurements of Kruithof and Penning¹ for the case of neon-argon mixtures. In the present investigation measure-

ments were made of the ionization coefficient η in helium-hydrogen and neon-hydrogen mixtures. The electron ionization coefficient η is defined as the average number of ionizing collisions for each volt potential difference through which an electron has fallen. The present paper describes the results of these measurements and discusses the enhancement of the ionization coefficient for various Penning mixtures.

II. APPARATUS

The apparatus and technique used in the present studies have been described² in detail previously, hence

¹ A. A. Kruithof and F. M. Penning, *Physica* **6**, 430 (1937).

² L. M. Chanin and G. D. Rork, *Phys. Rev.* **132**, 2547 (1963).

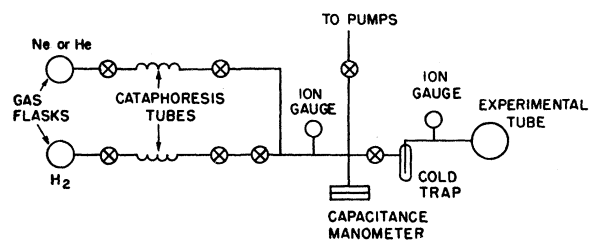


FIG. 1. Schematic diagram of the high-vacuum gas-handling system.

only a brief description will be given here. The apparatus is a modern version of that previously used³ by numerous workers in the field. The experimental tube was constructed primarily of stainless steel. The electrodes were 8-cm-diam nickel disks; the electrode separation could be varied out to 2.0 cm with an accuracy of 10^{-3} cm. Photoelectric current densities $\sim 10^{-11}$ A/cm² were created at the cathode by means of a constant ($\sim 1\%$) external source of ultraviolet radiation which passed through a 2-cm-diam nickel mesh at the center of the anode. The gas pressures were measured with a bakeable capacitance type of manometer with an accuracy of 0.5%. The gas concentrations are believed accurate to within 5%. The voltage and currents were read with accuracies of 0.25% and 2%, respectively. The total estimated accuracy of the η measurements was $\sim 10\%$.

The experimental tube was mounted on a high vacuum gas handling system.⁴ Following extended bake-out at temperatures $\sim 400^\circ\text{C}$ the system achieved rates of rise of contamination pressures $\sim 10^{-10}$ Torr/min. In view of important effects which minor impurities have on the ionization coefficient measured in helium and neon, steps were taken to remove contamination prior to mixing with hydrogen. Figure 1 shows a schematic drawing of the gas handling system. The gas purification methods involved the combined use of cataphoretic cleaning of both constituents before mixing and final introduction into the experimental tube through a liquid-nitrogen-cooled cold trap.

The $\ln I(x)$ versus x (current versus electrode separation) data were analyzed using a three-point method² which took into account the effect of secondary electron emission on the prebreakdown current. In the helium-hydrogen mixtures the total pressure range investigated varied from 12.3–54.0 Torr; for the case of neon-hydrogen mixtures the range varied from 9.35–66.1 Torr. The ionization coefficient η was measured over as wide a range of E/p_0 (electric field to normalized pressure ratio) values as possible, with the restriction that measurements were not made at high E/p_0 values, where evidence² indicated that the electrons were not

³ An excellent summary of work in this field is given in L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955), Chap. VIII.

⁴ D. Alpert, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 12.

TABLE I. He + $a\%$ H₂.

E/p_0 (V/cm) \times Torr	$\eta(\text{V})^{-1}$					
	$a=0$	$a=0.01$	$a=0.1$	$a=1$	$a=10$	$a=100$
3	0.00027	0.00194	0.00242	0.00150
5	0.00119	0.0176	0.0198	0.0117	0.000237	...
7	0.00250	0.0211	0.0244	0.0179	0.00107	...
10	0.00513	0.0225	0.0285	0.0239	0.00367	...
15	0.00753	0.0226	0.0302	0.0285	0.00871	...
20	0.00943	0.0190	0.0290	0.0287	0.0137	0.000205
30	0.0114	0.0154	0.0270	0.0273	0.0181	0.00179
50	0.0126	0.0145	0.0212	0.0245	0.0203	0.0062
70	0.0131	0.0149	0.0185	0.0200	0.0186	0.0095
100	0.0131	0.0149	0.0155	0.0207	0.0175	0.0129

in equilibrium with the applied fields. Thus at E/p_0 values in excess of the Paschen minimum, where measurements of the ionization coefficient as a function of the relative electron collision number showed a consistent decrease of η with increasing collision number, the data were not believed to be significant due to nonequilibrium conditions.

III. RESULTS

Figure 2 shows a plot of the ionization coefficient η as a function of E/p_0 for various concentrations of hydrogen in helium. The data given in Fig. 2 are presented in tabular form in Table I. Figure 3 shows a plot of the corresponding measurements for the case of various concentrations of hydrogen in neon. Data shown in Fig. 3 are given in tabular form in Table II. It will be noted that for the case of helium-hydrogen

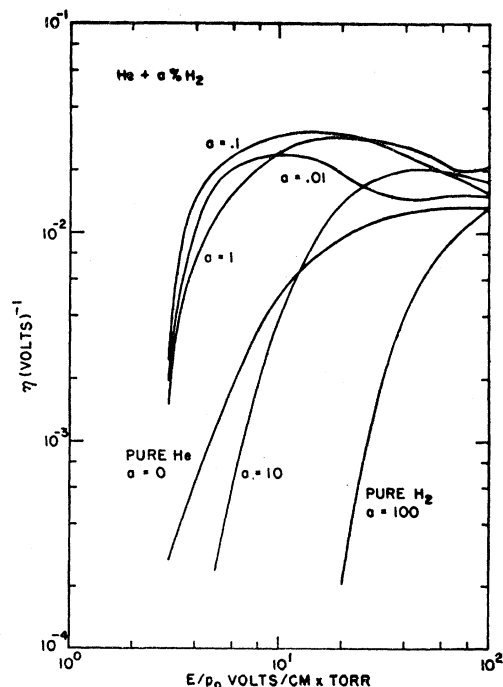


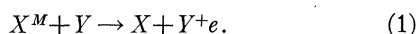
FIG. 2. The variation of η with E/p_0 in helium-hydrogen mixtures.

TABLE II. Ne + $a\%$ H₂.

E/p_0 (V/cm × Torr)	η (V) ⁻¹					
	$a=0$	$a=0.01$	$a=0.1$	$a=1$	$a=10$	$a=100$
1	...	0.0095	0.0106	0.00040
2	0.00025	0.0156	0.0260	0.0080
3	0.00050	0.0180	0.0285	0.0140
5	0.00150	0.0177	0.0283	0.0200	0.00138	...
7	0.00280	0.0170	0.0280	0.0230	0.00289	...
10	0.00460	0.0168	0.0283	0.0248	0.00640	...
15	0.00750	0.0162	0.0254	0.0263	0.00939	...
20	0.0097	0.0160	0.0245	0.0269	0.0120	0.00021
30	0.0120	0.0149	0.0238	0.0270	0.0172	0.00170
50	0.0138	0.0157	0.0202	0.0231	0.0202	0.00620
70	0.0149	0.0165	0.0194	0.0229	0.0208	0.00950
100	0.0154	0.0162	0.0161	0.0219	0.0197	0.0129

mixtures η has a maximum value of 0.0302 for concentrations of 0.1% hydrogen for $E/p_0=15$. For neon-hydrogen mixtures the maximum value attained by η is 0.0285 for hydrogen concentrations of 0.1% for $E/p_0=3$. From a comparison of Figs. 2 and 3, it will be noted that the maximum values of η for the mixtures are considerably in excess of those for either of the pure constituents, and in addition the maximum values are achieved at E/p_0 values considerably less than the corresponding values for the pure gases.

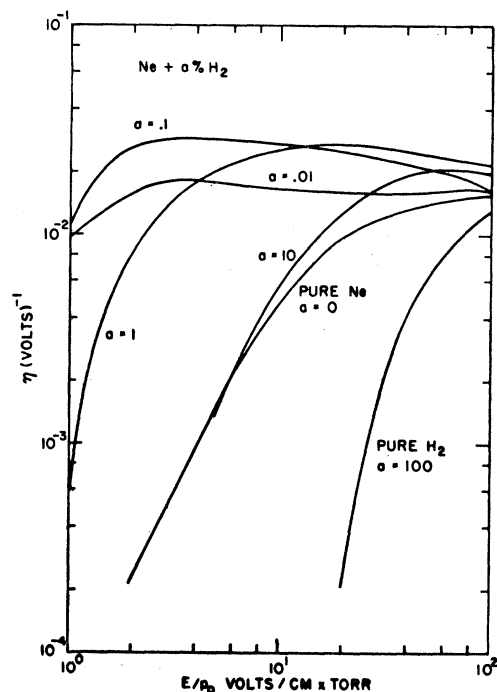
In the case of the mixtures the total measured η values may be regarded as the result of contributions to η via direct ionization and that resulting from metastable de-excitation via the Penning reaction



Here X^M refers to a metastable state of the major gas component and Y refers to the minor constituent. The maximum value of η (η_{\max}) resulting from metastable de-excitation will occur at an E/p_0 value approximately corresponding to the electron energy for the optimum production of metastables. This will occur at moderately low E/p_0 values where the electron energy losses are predominantly due to the excitation of electronic states. With increasing electron energy (E/p_0) the losses due to excitation decrease, and those due to direct ionization increase, until at sufficiently high E/p_0 values the major energy loss is due to direct ionization. In general the decrease of η with decreasing E/p_0 from that corresponding to the η_{\max} can be attributed to increased elastic energy losses which dominate other

TABLE III. ΔE corresponds to the difference in energy between the metastable state of the major component and the ionization potential of the minor constituent. V corresponds to the potential difference through which an electron must pass in order to produce a new ion pair and is defined as $V = (1/\eta_{\max}) \ln 2$.

Gas	E/p_0 (V/cm × Torr)	Percent concentration	η_{\max} (V) ⁻¹	V (V)	Percent ionization efficiency	ΔE (eV)
He-H ₂	15.0	0.1	0.0302	22.95	68.0	4.20
Ne-H ₂	3.0	0.1	0.0285	24.3	64.2	1.02
Ne-Ar	3.0	0.1	0.037	18.7	84.0	0.865

FIG. 3. The variation of η with E/p_0 in neon-hydrogen mixtures.

losses at very low E/p_0 values. At a given E/p_0 value less than that corresponding to the maximum, the decrease of η for concentrations greater than the optimum may be understood since under these conditions elastic impacts and excitation losses due to the presence of hydrogen will become significant. The corresponding decrease of η , for concentrations less than the optimum concentration at a fixed E/p_0 value, may be attributed to the presence of fewer hydrogen molecules available to de-excite metastable states via reaction (1), thereby resulting in decreased contributions to the net ionization. For E/p_0 values in excess of that corresponding to η_{\max} , the value of η decreases as the result of the excitation of states with energies greater than the metastable state. In this energy range, as one would expect, increasing hydrogen concentrations lead to an η variation approximating that of pure hydrogen, while for decreasing concentrations η will approximate the behavior characteristic of the major component.

In both mixtures for each E/p_0 value and hydrogen concentration studied, measurements were made as a function of the total pressure. The total pressure variation in such measurements was at least a factor of 2. Analysis of the data failed to reveal any dependence of η on the total pressure. As a result we conclude that the principle of similitude is obeyed in these mixtures over the range of pressures investigated.

IV. DISCUSSION

Table III shows a comparison of the data obtained in the present measurements, with the characteristics

previously obtained by Kruthof and Penning for the case of neon-argon mixtures. Columns 2 and 3 give the E/p_0 values and the percent concentrations, respectively, corresponding to values for which η was found to be a maximum (η_{\max}). Here it will be noted that while η_{\max} is greatest for the case of neon-argon mixtures, the variation of η_{\max} between the mixtures under consideration is only $\sim 23\%$. From a comparison of columns 2 and 4 it will be noted that the E/p_0 values corresponding to η_{\max} are in agreement for the case of neon-hydrogen and neon-argon mixtures. Column 5 shows a comparison for the various mixtures, of the potential difference V through which an electron must pass in order to produce a new ion pair and column 6 gives the corresponding efficiencies of ionization. These values were calculated using Penning's⁵ convention where $V = (1/\eta_{\max}) \ln 2$, and the efficiency of ionization is defined as the ratio of the ionization potential of the minor component to the potential difference V .

It will be noted that the efficiencies of ionization for the mixtures given in Table III are relatively high. The corresponding efficiencies for the pure gases, helium, neon, argon, and hydrogen are 47, 44, 50.5, and 30%, respectively.^{2,6,7} For the case of helium, neon, argon, and hydrogen, the corresponding energies required to produce an ion pair are 52.1, 46.5, 31.2, and 52.5 eV, respectively. It is interesting to note that the energy V required to produce an ion pair (52.1 eV in the case of helium, for example) is in serious disagreement with the value of roughly 30 eV commonly found in the literature^{8,9} obtained from alpha-particle ionization studies. However, more recent studies¹⁰ using these techniques and more carefully controlled conditions of gas purity have yielded values as high as 46 eV.

Column 7 in Table III shows the differences in energy between the metastable states of the main constituent and the ionization energies of the minor component. In the Penning process this excess energy is removed as kinetic energy by the electron formed in the reaction. It will be noted that while the change of internal energy is approximately five times greater for the case of helium-hydrogen compared to neon-argon mixtures, the maximum value of η is only $\sim 23\%$ less. According to Massey and Burhop,¹¹ for the case of neon-argon mixtures, the chance of reaction (1) occurring is of the order of unity per collision.

⁵ The expression $V = (1/\eta_{\max}) \ln 2$, for the potential difference through which an electron must pass in order to produce a new ion pair, follows directly from the simplified electron multiplication equation $n = n_0 e^{\eta V}$.

⁶ A. A. Kruthof and F. M. Penning, *Physica* **6**, 515 (1936).

⁷ L. M. Chanin and G. D. Rork, *Phys. Rev.* **133**, A1005 (1964).

⁸ W. J. Price, *Nuclear Radiation Detection* (McGraw-Hill Book Company, Inc., New York, 1958).

⁹ H. Bethe and J. Ashkin, *Experimental Nuclear Physics* (John Wiley & Sons, Inc., New York, 1953), Vol. 1.

¹⁰ T. E. Bortner and G. S. Hurst, *Phys. Rev.* **90**, 160 (1953).

¹¹ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952).

In addition they regard the reaction as one of exact resonance as far as the relative translational energy of the heavy particles is concerned. On the basis of these considerations, one would therefore expect, as observed in the present studies, that the value of η_{\max} would be relatively independent of the excess energy ΔE .

The relatively close agreement between the η_{\max} values, for the same minor constituent concentrations, implies that the corresponding cross sections for the various Penning reactions are of comparable magnitude at their respective E/p_0 values for which η is a maximum. This is consistent with the experimental results of Benton¹² *et al.* on the de-excitation cross sections of helium metastables for various Penning helium mixtures. These investigators found that the de-excitation cross sections for a number of Penning mixtures, including minor molecular constituents, varied at most by a factor of 2.

Recently Jesse and Sadauskis¹³ made measurements of the relative ionization (the ionization in a mixture relative to that in the pure gas) produced by the passage of alpha particles in various gas mixtures. These investigators obtained values of the relative ionization of 1.316 and 1.274 for hydrogen concentrations of 0.1% for the case of helium-hydrogen and neon-hydrogen mixtures, respectively. From the present measurements the relative ionization values for the case of helium-hydrogen and neon-hydrogen mixtures are respectively 2.27 and 2.12. Part of this discrepancy may be accounted for on the basis that the gases used by Jesse and Sadauskis were subject to impurities. The discrepancy may also in part be attributed to basic differences between the two types of measurements. Thus, in the present studies, the maximum value of η occurs when the average electron energy is such that metastable de-excitation is at an optimum. By contrast, in the ionization by alpha-particle measurements the average energies of alpha particles (1–5.3 MeV) are sufficiently great to result both in the production of metastables and direct ionization. In such studies, therefore, the measured ionization is the net result of contributions integrated over a wide range of energies. On this basis it seems reasonable to expect that the relative ionization obtained from the alpha-particle measurements would be considerably less than in the present studies, where the electron energy is controlled, thus enabling one to determine the maximum difference in ionization between the mixture and pure gas case.

Note added in proof. Recent measurements of η as a function of pressure have been made at E/p_0 values of 3.0 and 15.0 V/cm \times Torr for 0.1% neon-hydrogen and helium-hydrogen mixtures, respectively. The resulting data indicate η is constant over a total pressure range

¹² E. E. Benton, E. E. Ferguson, F. A. Matsen, and W. W. Robertson, *Phys. Rev.* **128**, 206 (1962).

¹³ W. P. Jesse and J. Sadauskis, *Phys. Rev.* **100**, 1755 (1955).

from 24.7–675.0 and 5.3–103.0 Torr, respectively, for neon-hydrogen and helium-hydrogen mixtures. However, at the higher pressures (>150 Torr for neon-hydrogen mixtures, >70 Torr for helium-hydrogen mixtures) an apparent violation of Paschen's law was observed; thus for constant p_0x values the breakdown potential increased significantly over its value at lower pressures.

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Final-State Effects in Atomic Processes: Photodetachment*†

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A formalism which corrects Born-approximation amplitudes for final-state effects in atomic scattering and detachment processes is developed from use of Jost function enhancement factors. The method leads to soluble integral equations of the Omnès type. Application is made to the photodetachment of negative oxygen ions ($\gamma + O^- \rightarrow O + e^-$), yielding an improved fit to recent experimental data. The theory is compared with earlier work of Klein and Brueckner.

I. INTRODUCTION

FINAL-state effects in atomic reactions may exert considerable influence on observed spectra. As a model we shall consider the effects of the interaction between the ejected electron and the residual atom in the photodetachment process $\gamma + O^- \rightarrow O + e^-$. Klein and Brueckner¹ studied this process using asymptotic phase-shifted continuum wave functions. Since their work, there has been considerable development in the theory of final-state interactions evolving from the early work of Watson,² and exploiting the analytic structure of scattering amplitudes and Jost functions. Although most of the formalism was developed for high-energy physics, it is equally applicable to other domains. Apart from the work of Gerjuoy and Krall³ stemming from the investigations of Klein and Zemach,⁴ little use of these recent methods has been made in atomic physics. The adaptation presented here is designed to provide maximum computational ease for low-energy processes.

Appendix A contains a brief review of the Jost function formalism and its relation to final-state interactions. In Sec. II the final-state corrections to the Born amplitude are shown to yield soluble integral equations of the Omnès type. Section III presents the solutions

which are based on plausible assumptions for the analytic structure of the amplitude. An alternative method facilitates computation in some cases. The photodetachment process is formulated in Sec. IV as an example. Results of a sample numerical calculation are contained in Sec. V together with a comparison of the methods with those of Klein and Brueckner. Appendix B discusses alternate forms of the Born amplitude which may improve the accuracy of the formalism.

II. FINAL-STATE CORRECTIONS TO BORN AMPLITUDES

For processes such as detachment of a bound system, the scattering amplitude is given by

$$T = \int d^3r \psi_i^-(q, r) V(r, k) \phi_B(r), \quad (1)$$

where ψ_i^- is the continuum wave function for the detached system with momentum q , ϕ_B the bound state, and V the interaction depending parametrically on the incident momentum k . Energy conservation relates q , k , and the binding energy. Generally, the integral (1) is terminated at small r by the spatial extent of ϕ_B , or of the interaction V (as will be the case for large momentum transfers). In this case, the relation (A4) permits the substitution

$$\psi_i(q, r) \approx f_i^{-1}(-q) \psi_i^{(0)}(q, r) \quad (2)$$

which gives us the final-state enhancement

$$T(q) = f_i^{-1}(-q) T^B(q), \quad (3)$$

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† Portions of this work were reported in University of California Lawrence Radiation Laboratory Report UCRL 10762 (1963), and in Bull. Am. Phys. Soc. **8**, 621 (1963).

¹ M. M. Klein and K. A. Brueckner, Phys. Rev. **111**, 1115 (1958).

² K. M. Watson, Phys. Rev. **88**, 1163 (1952).

³ E. Gerjuoy and N. A. Krall, Phys. Rev. **119**, 705 (1960); **127**, 2105 (1962).

⁴ A. Klein and C. Zemach, Ann. Phys. (N. Y.) **7**, 365 (1959).