The Variation with the Density of Mercury Vapor of the Intensity of the Spectral Lines of Mercury Excited by Electron Impact

O. S. DUFFENDACK AND O. G. KOPPIUS*
University of Michigan, Ann Arbor, Michigan
(Received May 1, 1939)

The variation in the intensities of mercury lines with the abundance of mercury present was investigated experimentally both for mercury alone and for mercury vapor in a mixture with another gas. The source consisted of a normal low voltage arc and this source was used because it closely approximates the simple ideal source desired; namely, one in which electrons of definite and controlled energy are projected through a space containing mercury and possibly other atoms so that an electron may not make more than one exciting or ionizing collision in its passage through the gas. Tests indicated that the ideal conditions were closely approximated. Theoretical formulae were developed for the relationship between the intensities of the mercury lines and the density of the mercury vapor (abundance of mercury). The measured values were found to be in good agreement with those given by the formulae. The relation of this investigation to the practices of quantitative spectrochemical analysis is pointed out. An analytical curve for the determination of mercury in such mixtures as were employed can be gotten from the data and the equation of the curve can be derived from the formulae derived from the theory given.

A. INTRODUCTION

EXPERIMENTS have brought to light many methods for the production of spectra. In former years the analysis and classification of spectra were some of the most important problems. The type of discharge which would produce the spectra was of secondary importance. The knowledge gained about the spectra and the extensive development of spectral theory now make it possible to use spectroscopic methods for the investigation of phenomena in the discharge of electricity through gases.

In this investigation one would, ideally, like to project into an extended region containing gas atoms a large number of electrons of definitely controlled energy. Within this region the electrons should be free and gain no more energy. Their energy should be such that upon an occasional exciting collision, the electron would lose most of its energy and could not excite any other atom upon which it might make an impact.

The low voltage arc[1] was chosen as a discharge source because it offers the simplest means of excitation by electron impacts. The reasons are as follows: (1) In the normal low voltage arc, after the discharge has reached a steady state, the whole fall in potential between the filament and the anode is concentrated in a thin sheath close to the cathode. The rest of the space is field free and is known as the plasma. (2) The current through the tube and the potential difference applied to the electrodes can be changed independently. This mode of discharge permits the mechanism for excitation to be adjusted so that the primary electrons have only one exciting collision. Further, this method facilitates an exact control of a given excitation condition.

Any investigation of a discharge as a source of light must involve radiation processes and the mechanism of the discharge. In fact, as C. G. Found[2] has stated, "Any discussion of the production of light in a gaseous discharge must involve a consideration of such a discharge as a conductor of electricity, since the fundamental function of the applied voltage is to establish a passage of current. Any light produced is merely incidental to and a by-product of the processes which render the tube conducting."

Although the production of light does not constitute a major role of a gaseous discharge, nevertheless, the mode in which light is produced is utilized in the field of quantitative spectrochemical analysis. This field of investigation presents numerous problems in which the conduction of electricity through gases plays a major role. Besides the more obvious value, the field of quantitative spectrochemical analysis affords, and is affording, an accurate quantitative

* Now at the Mathieson Alkali Works, Inc., Niagara Falls, New York.

[1] O. S. Duffendack, Phys. Rev. **20**, 665 (1922); K. T. Compton, Phys. Rev. **15**, 30 (1920).

[2] C. G. Found, Gen. Elec. Rev. **37**, 269 (1934).

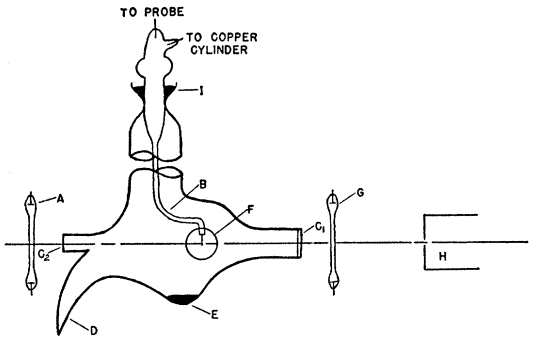

FIG. 1. Diagram of apparatus. *A*, mercury glow tube. *B*, probe. C_1, C_2, quartz windows. *E*, mercury reservoir. *F*, plate (anode). *G*, helium glow tube. *H*, spectrograph. *I*, mercury seal.

check of some phases of the extensive spectral theory and a correlation of this theory with discharge phenomena. Through extensive developments in quantitative spectrochemical analysis and in other fields by many investigators, the technique of spectral photometry has been improved to a high degree of reliability so that repeat measurements of a single plate agree within ± one percent. The principal problem in the development of the technique of spectrochemical analysis lies in a better understanding of the mechanism occurring in a gaseous discharge and its relation to spectral theory.

B. Purpose of Investigation

The purpose of the investigation was threefold: First, to make a quantitative study of the variation of intensity of the spectral lines of an element present alone in the discharge as a function of the amount. Second, to make a quantitative study of the variation of intensity of the spectral lines of one element, in the presence of definite amounts of foreign gas, as a function of the amount of the element present. Third, to tie up the general problem stated above to the more practical problem of quantitative spectrochemical analysis.

C. Experimental Procedure

Figure 1 gives a detailed view of the Pyrex experimental tube, also a schematic arrangement of the experimental tube, two auxiliary tubes *G* and *A*, and the spectrograph, *H*.

The experimental tube was constructed so as to carry out several different types of measurements without disturbing the discharge. The electrons from the hot tungsten filament were accelerated toward the nickel plate, *F*, a distance, $d=3$ cm, from the filament. The radiation from the discharge could be studied by allowing it to pass through a quartz window, C_1, and thence finally to a medium quartz spectrograph, *H*. A movable probe, *B*, was provided to determine the discharge conditions electrically. It could be set at any point within the discharge by turning the probe through the mercury seal, *I*. The light trap, *D*, served to eliminate reflections of the radiation from the back wall. In direct line with the main quartz window, C_1, but on the opposite side of the experimental tube was another quartz window, C_2. *E* is a reservoir containing the excess mercury.

Two magnetically controlled traps were provided to insure that whatever gas was admitted to the tube would remain at constant density as the temperature was changed. Both traps could be lifted by means of solenoids placed around the side tubes. The discharge tube was connected to a high vacuum system. A second mercury diffusion pump permitted the gases to be circulated through a charcoal trap, a hot copper oxide trap, a liquid-air trap, and through the experimental tube. Since there are no wax joints on this tube, contamination from this source was avoided.

The auxiliary tubes, *A* and *G*, were constructed similarly; both have fused quartz center sections. The electrodes were made of nickel. After the tubes were well outgassed, *G* was filled with pure helium to a pressure of 5 mm and *A* with pure argon to a pressure of 3 mm and an excess of redistilled mercury. Both tubes were then sealed off from the vacuum system.

The probe design has been described before by Sloane and Emeleus.[3] The probe wire was tungsten, five mm in length and three mm in diameter.

The electrical connections for the experimental tube were arranged so that the plate voltage and filament current could be changed independently. An adequate power source insured a plate current

[3] R. H. Sloane and K. G. Emeleus, Phys. Rev. **44**, 333 (1933).

which did not fluctuate more than ± one percent.

The method of measuring relative intensities of spectral lines was that given by Thomson and Duffendack.[4] Eastman Polychrome plates were used throughout this investigation.

The gases used in this investigation were helium, argon and mercury vapor. No impurities were found in any of these gases when spectroscopically examined.

The auxiliary helium discharge tube, *G*, served as a standard reference of intensity for the investigation of the test element, mercury. The constancy of the auxiliary discharge tubes was tested as will be described later. As shown in Fig. 1, the standard helium tube was placed in direct line with the spectrograph. Thus one could photograph simultaneously the radiation emitted by inelastic impacts of the electrons within the experimental tube and the radiation emitted by the standard helium lamp. This procedure permitted a study to be made of the dependence of relative intensities of mercury transitions to that of a particular helium transition = 2945.11A. This dependence was studied under constant excitation conditions as the density of mercury was changed.

The density of the mercury in the discharge was changed by simply varying the temperature of the water bath. In this investigation the temperature was changed from 0°C to 40°C; this corresponds to a change in pressure (reduced to 0°C) from 1.8×10^{-4} mm to 53×10^{-4} mm of mercury.

A medium quartz spectrograph, Hilger E2, was used throughout this investigation. It was adjusted so that the contribution from every portion of the discharge was always taken into consideration.

Argon in definite amounts was admitted to the discharge tube in order to investigate the variation of intensity of the line spectra of mercury in the presence of a foreign gas, as a function of the amount of mercury present. Finally, as a check, the argon was removed and helium introduced.

A probe was used to determine the electrical conditions within the discharge. The theory and analysis by probe methods have been described before.[5]

The constancy of the auxiliary discharge tubes was tested photographically. A series of timed exposures were taken on one plate for the same setting of the auxiliary tube and spectrograph. The values of the blackening produced were then compared and were found to be constant to within ±3 percent. The helium lamp was tested over a 40-hour period; whereas the mercury lamp was tested over a 6-hour period.

D. Experimental Results

Transitions from both the singlet and triplet states to the 6^3P_2, 6^3P_1, 6^3P_0 states of mercury were investigated. Resonance radiation was not considered.

Two striking phenomena were observed: (1) All curves of intensity *versus* abundance of mercury (pressure) show saturation. That is, after a certain pressure of mercury in the discharge tube the intensity no longer increases when additional amounts of the element are added. This is true for both mercury alone and for mixtures. (2) All curves of intensity *versus* abundance of mercury (pressure) behave similarly but not identically. That is, the series $6^3P_2-n^3D_2$ behaves similarly to $6^3P_2-n^1D_2$.

Two different explanations for the observed phenomena suggested themselves and were critically checked. The first one, which proved false, was as follows: At low concentration of mercury in the discharge, the number of atoms in the metastable states (6^3P_2 and 6^3P_0) is small and thus the radiation passes directly out of the discharge. At higher densities of mercury vapor, the concentration of atoms in 6^3P_2 and 6^3P_0 states is large and the radiation does not immediately pass from the bulb. The radiation from the entire volume of the discharge passes through the quartz window at low pressures of mercury and the intensity *versus* abundance plot varies linearly with the pressure. Because of the scattering of radiation at the higher pressures of mercury, the radiation no longer comes from the entire volume, but from the outer layer of excited gas near the tube wall. Some of the radiation emitted within the center of the dis-

[4] K. T. Thomson and O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

[5] I. Langmuir and H. M. Mott-Smith, Gen. Elec. Rev. **27**, 732–770 (1924).

charge is trapped and lost. The mechanism in this case could be a collision of the second kind between an excited mercury atom and an electron. Depending on the energy of the electron, the excited atom could either be ionized or lowered to a metastable state. The energy of the metastable atoms and ions could then be dissipated in the form of heat at the walls of the discharge tube. Since, in the case of a high concentration of mercury within the discharge, the radiation comes only from the outer layer of excited gas near the tube wall, any further increase of pressure does not increase the area of excited vapor since the area is bounded by the tube container. Thus the intensity *versus* abundance plot shows saturation.

The following experiment was performed to test this hypothesis. Radiation from a constant auxiliary mercury tube was passed directly through the discharge of the experimental tube and the absorption determined for transitions of mercury ending in the metastable states. Table I shows the method of procedure and the results. These data were taken at a pressure of 30×10^{-4} mm at which, as the curves show, the intensity has reached nearly its maximum value.

The results of this experiment show that the saturation of the intensity versus abundance plots are not due to absorption and re-emission, and thus the hypothesis is false. Cumulative excitation and ionization is consequently very improbable due to the small concentration of atoms in the lower states (6^3P_2 and 6^3P_0).

The second explanation assumes that the excitation of the mercury lines is due solely to inelastic collisions between mercury atoms and primary electrons. It will be shown that upon this basis formulae can be deduced such that the experimental data fit the curves representing the formulae.

The proof of the second explanation comes from probe analysis. To establish the mechanism of the saturation effect observed, the solution of the following problems must be known. Do the primary electrons coming from the filament have enough energy left after exciting once to again excite? After exciting once, can the resulting secondary electrons gain enough energy from the field in the discharge to again excite? Consideration will now be given to data that answer these questions.

From the straightness of the lower end of the semi-logarithm probe characteristic plots one can conclude that one and only one Maxwellian distribution of electrons was found. Thus, only two groups of electrons need be considered; namely, the primary electrons and the Maxwellian group given by these data.

The variation of electron temperature as a function of the abundance of mercury for the probe fixed at the center of the tube shows that the inelastic impacts made by the ultimate electrons can be neglected. The highest electron temperature observed was 11,000°K in mercury alone. The electron temperature drops quickly as the pressure of mercury is increased until at 20×10^{-4} mm it is 4000°K. For the mixtures of mercury and foreign gas the curves are similar to those for mercury alone. In this case the curves start initially at a much lower value of the electron temperature, and decrease rapidly to about 4000°K as the pressure of mercury is increased. A change of 7000°K in electron temperature corresponds approximately to a decrease of 10^5 in the number of electrons available for excitation. In contrast one observes a maximum value of the intensity in the region where the electron temperature is the lowest. Hence, only an extremely small fraction of this group of Maxwellian electrons have enough energy to again excite. A special tube was constructed to lend experimental proof to this fact. A cold cathode discharge tube was made containing a mixture of argon and excess mercury. The electron temperature was measured in the region of the Faraday dark space. In this region, prac-

TABLE I. *Measurements to detect absorption. For no absorption $a=b+c$ and this is found to be true.*

Experimental Arrangement	Intensity 2697A $6^3P_0-7^3D_1$	Intensity 3341A $6^3P_2-7^3S_1$
	Units	*Units*
(a) Radiation from the experimental tube plus radiation of standard mercury lamp	3.01	3.67
(b) Radiation from standard mercury lamp alone	1.65	2.65
(c) Radiation from experimental tube alone	1.49	1.11

tically no excitation takes place yet electron temperatures of the order of 8000 to 9000°K were observed.

The electron temperature was approximately a constant throughout the plasma for any given pressure of mercury in the discharge tube. A sharp increase in temperature was observed in the vicinity of the filament. This was due to the fact that the probe was collecting some primary electrons. The maximum drop in potential observed within the plasma was less than one volt. Thus the electrons after exciting once cannot gain enough energy from the field within the plasma to excite again.

The results of this experiment show that the primary electrons either have no inelastic impacts, or one and only one inelastic impact while going from the cathode to the anode. The radiation is produced solely by the inelastic impacts of primary electrons with mercury atoms.

Formulae accounting for the variation of the intensities of the spectral lines can be deduced in the following way. When the discharge is in a steady state, the intensity of a spectral line due to the transition from state j to state k of the atom will be proportional to the concentration N_j, of atoms in the state j, the probability of transition A_{jk}, and the magnitude of the light quantum, $h\nu$, that is $I_{\nu j}\alpha N_j \cdot A_{jk} \cdot h\nu$. For one type of atom and for one transition N_j is the only parameter. Since it was shown that no cumulative impacts occur, N_j is proportional to the number of inelastic impacts made by the primary electrons. Formulae determining N_j can be derived in the following manner. Let n_0 = total number of electrons per square centimeter per second which are accelerated across the cathode fall in potential; p = pressure of mercury vapor (corrected to 0°C); λ_E = average mean free path of an electron in mercury vapor for the excitation of any level in the mercury atom; λ_{1E} = average mean free path for the excitation of the mercury atom at unit pressure (0°C and 1 mm pressure), (thus $1/\lambda_E = p/\lambda_{1E}$); P_j = probability that an electron upon exciting the mercury atom will excite the particular state j; d = distance from cathode to anode and x = distance of any electron from the cathode. Hence, dx/λ_E = probability that an electron will have an inelastic collision within the interval dx. $-dn = ndx/\lambda_E$ is the number of ultimate electrons formed by inelastic impacts of high energy electrons with mercury atoms per unit area per element of distance in the direction of motion.

Integrating this expression from $x=0$ to $x=d$ we have the total number of electrons which suffer no inelastic impacts.

$$n' = n_0 e^{-d/\lambda_E}.$$

Consequently the number having inelastic collisions is simply $n = n_0(1-e^{-d/\lambda_E})$. Upon multiplying this expression by P_j we have the number of these excited atoms, N_j, which are in state j. In terms of pressure of mercury vapor and the current, i, passing through the discharge tube, the equation can be written

$$I_{\nu j} = A \cdot i(1-e^{-dp/\lambda_{1E}})P_j. \qquad (1)$$

Where A is a multiplicative constant, i is the tube current in milliamperes, p is the pressure of mercury in millimeters, P_j is a constant for any one particular state j.

The following consideration needs to be taken into account when the discharge tube contains a mixture of mercury and helium or argon. The electrons that excite atoms other than mercury are no longer available to excite mercury. The fraction of electrons that hit mercury atoms in a mixture of gases will be the ratio of the excitation cross section for collision with mercury atoms to the total excitation cross section. Thus, the intensity of a particular mercury transition in a mixture of mercury and argon or helium will be

$$I_{\nu j} = Ai\frac{1/\lambda_E}{1/\lambda_E + 1/\lambda_A}(1-e^{-dp/\lambda_m})P_j. \qquad (2)$$

λ_A is the average mean free path of an electron for excitation of a foreign atom. λ_m is the average mean free path of an electron for excitation of either a mercury or a foreign atom. All the other symbols have the same meaning as defined before. In this investigation the quantity measured was J = log (ratio of intensity of a Hg line to the intensity of a He line). Hence, calling

$$B = (A/I_{\mathrm{He}})P_j, \quad a = d/\lambda_{1E}, \quad b = (p_A/\lambda_{1A})\lambda_{1E},$$

Eqs. (1) and (2) become

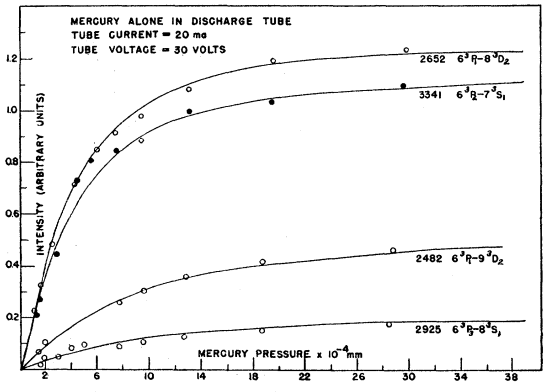

FIG. 2. Variation of intensity with abundance. Mercury alone.

$$e^J = Bi(1-e^{-ap_{Hg}}), \tag{3}$$

$$e^J = Bi\frac{1}{1+(b/p_{Hg})}(1-e^{-dp_{Hg}/\lambda_m}). \tag{4}$$

In all figures e^J was designated as "Intensity (Arbitrary units)" and is spoken of hereafter as intensity.

Equation (3) is valid for one element alone in the discharge tube; whereas Eq. (4) applies for the mixtures. B is a multiplicative constant which depends upon the geometry of the experimental tube, arrangement of spectrograph, position of helium lamp, the amount of absorption in the quartz and air of the particular wave-length of light under investigation, the probability of transition A_{jk}, and the magnitude of the light quantum $h\nu$. The constant, a, depends only upon the distance, d, and upon the probability of exciting the mercury atom. It should change only slightly for the various mercury transitions. By a suitable choice of constants the data for all the spectral lines, both when excited in mercury alone and when excited in mixtures, can be made to fit the curves representing Eqs. (3) and (4).

In the discussion that follows only typical sets of data will be considered. The experimental points and the theoretical curve are given in each case.

E. Discussion and Interpretation of Results for Mercury Alone

Equation (3) gives the relation between the intensity (e^J) of any particular transition of mercury, the current through the tube, and the abundance of mercury (pressure). For large values of the pressure, the intensity approaches a constant value. Fig. 2 shows this to be correct for transitions considered.

Table II gives a typical set of constants for eight different transitions. The classification includes transitions from both singlet and triplet states of mercury. Thus, in general, all transitions behave similarly, but not identically. The constant, a, is approximately a constant for all term values. This follows naturally due to the fact that, a, is proportional to the probability of exciting the mercury atom by electrons of a definite energy.

The value of λ_{1E} is of the same order of magnitude as the kinetic theory values. The value of d is uncertain due to the fact the trajectory of the electrons is altered by the many elastic collisions. Due to the zigzag motion of the electrons, the effective distance traversed is actually greater than the distance from cathode to anode. An increase in the value of d would cause the experimental value of λ_{1E} given in Table II to approach more nearly kinetic theory values. Exact agreement cannot be expected. The kinetic theory values were computed upon the false assumption that the cross section of the atom was the same for both high and low energy electrons.

For large values of the pressure Eq. (1) reduces to $I_{\nu j}=A\cdot i\cdot P_j$.

The difference in intensity of two mercury transitions should be a constant in the region where the above-made assumption is valid, for $I_{\nu j_1}-I_{\nu j_2}=Ai(P_{j_1}-P_{j_2})=\text{const.}$ The exact difference in the P_j's cannot be determined since nothing is known of the magnitude of the constant, A. The differences in intensities should

TABLE II. *Mercury alone in the discharge tube. Kinetic theory value for $\lambda_{1E}=9\times10^{-3}$ centimeter. Tube voltage = 30 volts. Tube current = 20 ma.*

WAVE-LENGTH	CLASSIFICATION	B	a	λ_{1E} CM
3021A	$6^3P_2-8^3D_3$	1.045	0.20×10^4	1.5×10^{-3}
2803A	$6^3P_2-9^3D_3$	0.368	0.12×10^4	2.5×10^{-3}
2652A	$6^3P_1-8^3D_2$	1.20	0.20×10^4	1.5×10^{-3}
2482A	$6^3P_1-9^3D_2$	0.475	0.10×10^4	3.0×10^{-3}
3341A	$6^3P_2-7^3S_1$	1.09	0.18×10^4	1.66×10^{-3}
2925A	$6^3P_2-8^3S_1$	0.368	0.16×10^4	1.88×10^{-3}
2655A	$6^3P_1-8^1D_2$	1.15	0.24×10^4	1.25×10^{-3}
2483A	$6^3P_1-9^1D_2$	0.348	0.18×10^4	1.66×10^{-3}

TABLE III. *Intensities of mercury transitions for various pressures of mercury in the discharge. Tube voltage = 30 volts. Tube current = 20 ma.*

Mercury Pressure $\times 10^{-4}$ mm	Intensity (Arbitrary Units)														
	2652A		3341A		2482A		2925A	2655A		3021A		2803A		2483A	
6	0.84	0.08	0.76	0.53	0.23	0.14	0.09	0.79	0.88	0.16	0.72	0.49	0.23	0.03	0.20
10	1.05	.14	.91	.60	.31	.185	.125	.905	1.03	.13	.90	.61	.29	.01	.28
14	1.13	.15	.98	.62	.36	.22	.14	.95	1.09	.11	.98	.67	.31	.01	.30
18	1.16	.14	1.02	.63	.39	.23	.16	.96	1.12	.11	1.01	.68	.33	.01	.32
22	1.19	.15	1.04	.62	.42	.225	.165	.965	1.13	.11	1.02	.68	.34	.01	.33
26	1.21	.15	1.06	.62	.44	.27	.17	.97	1.14	.11	1.03	.69	.34	.00	.34
30	1.22	.14	1.08	.63	.45	.27	.18	.97	1.15	.11	1.04	.69	.35	.00	.35
34	1.22	.13	1.09	.62	.47	.29	.18	.98	1.16	.12	1.04	.69	.35	.01	.36

approximately be zero for transitions starting on levels having approximately the same energy value and ending on the same state. Several examples are 2483A *vs.* 2482A, 2655A *vs.* 2652A, 3341A *vs.* 3021A etc.

Table III shows a typical set of data illustrating these points. For the various transitions indicated the intensity is given for several pressures of mercury in the discharge tube.

In order to illustrate the first point, consider the difference of intensities for 2652A and 3341A. This gives 0.08, 0.14, 0.15, 0.15, 0.14 and 0.13 intensity units. This relationship holds generally for the differences of any two transitions. The differences between the intensities of the lines in adjacent columns in Table III are given by the numbers between the columns.

At the lowest pressures the above simplified equation is no longer valid, and the values of the differences are no longer constant. The numbers in the table for the lowest pressures indicate that such a condition was being approached. The second point becomes obvious upon examining the intensity values in the table for the examples given.

F. Discussion and Interpretation of Results for Typical Cases for Mercury Mixed with Helium or Argon

Equation (4) was found to be applicable to all cases investigated. It was found that d/λ_m was of the order of magnitude of 8×10^4 to 10^5 for all transitions and for the different pressures of argon and helium. For example, at the lowest pressure of mercury investigated, the value of the exponential term was found to be 3×10^{-4} which is negligible compared with unity. Eq. (4) can now be simplified to

$$e^J = Bi\frac{1}{1+(b/p_{\mathrm{Hg}})}. \tag{5}$$

This equation fits the experimental points exceedingly well for all mercury transitions, and for the various pressures of argon or helium in the experimental discharge tube. Fig. 3 shows the experimental points and theoretical curves for typical transitions. Similar results were obtained for mixtures of helium and mercury vapor.

Tables IV and V give a typical set of values for the constants B, b, λ_{1A} and λ_{1He}. From the constant, b, the value of λ_{1A} or λ_{1He} may be computed from the known value of the pressure of argon or helium in the tube, and the value or λ_{1E} given in Table II. λ_{1A} and λ_{1He} are the probabilities of an electron exciting the argon or the helium atom and their values should be approximately constant. Data given in Tables IV and V show this to be true. The values of λ_{1A} and λ_{1He} agree within the right order of magnitude with kinetic theory values. The discrepancy may again be attributed, as before, to the fact that the value of d is not known accurately. The constant, b, should increase proportionally with the pressure of argon or helium in the discharge tube. This has been only qualitatively verified.

For large values of the mercury pressure, the discharge equation (2), which is valid for the gas mixtures, reduces to the same form as Eq. (1). A mixture of mercury and a foreign gas should exhibit accordingly the same characteristics as found for mercury alone in the discharge tube. In Table VI is given a set of data similar to Table III for the case of mercury admixed with argon. The difference in intensities for any two transi-

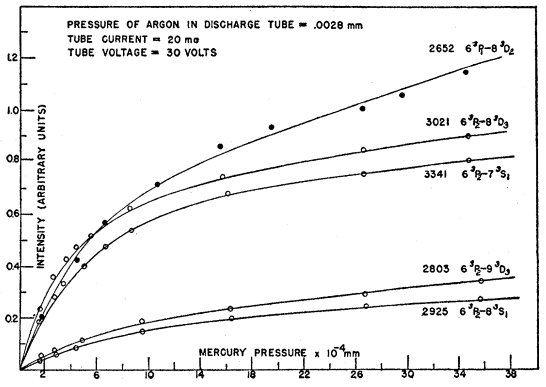

FIG. 3. Variation of intensity with abundance. Mercury vapor and argon.

tions gives approximately a constant as was found for mercury alone in the discharge. Likewise any two transitions starting from quantum levels having approximately the same energy value and ending on the same level have roughly the same intensity. A similar table for mixtures of mercury vapor and helium would show analogous results.

A direct comparison of the constant differences of intensities of various mercury transitions for mercury alone and for mercury admixed with a foreign gas can be made.

According to the simplified equation $I_{vj}=AiP_j$ the same constant difference in intensities taken for two different transitions at the same pressure of mercury should occur regardless of the amount and type of foreign gas contained in the discharge tube. Unfortunately, as was mentioned before, a direct comparison in this manner is not altogether valid. The position of the spectrograph and of the helium lamp was changed for each set of measurements. Their positions were approximately the same, however, and a rough check on the constancy of the intensity differences should be permissible.

Table VII gives a set of data taken for one pressure (34×10^{-4} mm) of mercury in the discharge tube. The intensities of various mercury transitions are given for mercury alone, mercury admixed with argon, and mercury admixed with helium. For example 3021A–2803A gives 0.68, 0.55, 0.41, and 0.46; also 2655A–3341A gives 0.13, 0.32, 0.13, 0.29, and 0.18. The transition 2655A seems to be in error in all cases. It is believed that the discrepancies are due mainly to the change in the positions of the apparatus.

Equation (5) represents a family of hyperbolae considering b as a parameter. The larger the value of b, the more quickly this curve approaches a straight line. The value of the multiplicative constant, B, was different for various pressures of argon and helium. Consequently, a family of hyperbolae for different values of b cannot be shown. Fig. 4 represents an experiment in which the constant $B\cdot i$ was identical for two cases; Eq. (3) is applicable to the curves marked "mercury," whereas Eq. (5) is applicable to the curves marked "mercury-helium." From the Eqs. (3) and (5) both curves should approach the same value of intensity asymptotically for large values of the pressure. At the origin the slope of Eq. (3) should be greater than the slope of Eq. (5). At very large values of the pressure, Eq. (3) should approach the asymptotic value sooner than Eq. (5). Hence, if the two curves cross at all after leaving the origin, they must do so an even number of times.

Experimentally, the curves show; first, that the slope of Eq. (3) is greater than the slope of Eq. (5) at the origin; second, the curves may or

TABLE IV. *A mixture of argon and mercury in the discharge tube. Kinetic theory value for* λ_1 *argon* $=29.3\times10^{-3}$ *centimeter. Pressure of argon* $=0.0028$ *mm. Tube voltage* $=30$ *volts. Tube current* $=20$ *ma.*

WAVE-LENGTH	CLASSIFICATION	B	b	λ_{1A} (CM)
3021A	$6^3P_2-8^3D_3$	0.98	4.3×10^{-4}	8.8×10^{-3}
2803A	$6^3P_2-9^3D_3$	0.39	12.9×10^{-4}	5.43×10^{-3}
2652A	$6^3P_2-8^3D_2$	1.47	12.2×10^{-4}	3.44×10^{-3}
2482A	$6^3P_2-9^3D_2$	0.54	15.5×10^{-4}	5.1×10^{-3}
3341A	$6^3P_2-7^3S_1$	0.93	5.9×10^{-4}	7.9×10^{-3}
2925A	$6^3P_2-8^3S_1$	0.37	15.8×10^{-4}	3.4×10^{-3}
2655A	$6^3P_2-8^3D_2$	1.20	8.0×10^{-4}	4.4×10^{-3}
2483A	$6^3P_2-9^3D_2$	0.27	5.9×10^{-4}	7.9×10^{-3}

TABLE V. *A mixture of helium and mercury in the discharge tube. Kinetic theory value for helium* $=77\times10^{-3}$ *centimeter. Pressure of helium* $=0.025$ *mm. Tube voltage* $=30$ *volts. Tube current* $=20$ *ma.*

WAVE-LENGTH	CLASSIFICATION	B	b	λ_1He
3021A	$6^3P_2-8^3D_3$	0.99	10.4×10^{-4}	36×10^{-3}
2803A	$6^3P_2-9^3D_3$	0.48	22.4×10^{-4}	28.0×10^{-3}
2652A	$6^3P_2-8^3D_2$	1.41	20.2×10^{-4}	18.6×10^{-3}
2482A	$6^3P_2-9^3D_2$	0.33	12.65×10^{-4}	59.0×10^{-3}
3341A	$6^3P_2-7^3S_1$	0.79	9.77×10^{-4}	42.5×10^{-3}
2655A	$6^3P_2-8^3D_2$	0.96	12.0×10^{-4}	26.0×10^{-3}
2483A	$6^3P_2-9^3D_2$	0.22	10.7×10^{-4}	38.8×10^{-3}

TABLE VI. *Intensity of mercury transitions for various pressures of mercury in a discharge containing argon. Pressure of argon = 0.0028 mm. Tube voltage = 30 volts. Tube current = 20 ma. Differences of intensities are also shown.*

Mercury Pressure × 10^{-4} mm	Intensity 2652A		3341A		2482A		2925A	2655A		3021A		2803A		2483A	
6	0.49	0.05	0.44	0.29	0.15	0.05	0.10	0.44	0.54	−0.01	0.55	0.41	0.13	0.01	0.12
10	.67	.10	.57	.36	.21	.07	.14	.54	.68	.02	.66	.48	.18	.01	.17
14	.74	.12	.66	.42	.24	.06	.18	.58	.76	.04	.72	.51	.21	.02	.19
18	.87	.17	.70	.42	.28	.08	.20	.63	.83	.06	.77	.54	.23	.01	.22
22	.94	.21	.73	.42	.31	.09	.22	.66	.88	.08	.80	.54	.26	.03	.23
26	1.0	.24	.76	.43	.33	.09	.24	.69	.93	.10	.83	.55	.28	.05	.23
30	1.06	.24	.78	.43	.35	.10	.25	.74	.99	.14	.85	.55	.30	.06	.24
34	1.12	.28	.80	.42	.38	.11	.27	.77	1.04	.16	.88	.55	.33	.09	.24

may not cross; third, the curves begin to approach approximately the same saturation value. The latter point could not be further investigated due to the fact that cumulative ionization sets in at higher pressures. In the case of cumulative ionization, the abundance *versus* intensity plot does not remain constant as the pressure is increased, but shows a break in the curve at a definite value of the pressure. For higher pressures than this critical value, the intensity *versus* abundance plots increase again with approximately the same slope as for very low values of the pressure. That is, the curve seems to be starting to duplicate itself.

Equation (4) was verified for different current values. Two intensity curves were taken for tube currents of 40 and 60 ma, respectively. The plots of log (ratio of intensity of Hg line to the intensity of a He line) *versus* log (pressure of mercury) differed by exactly one logarithm unit (base 1.5). Thus,

$$e^{-0.810}/e^{-0.405}=0.67.$$

No experimental verification of Eq. (3) was carried out. However, since, as shown, the intensity varies accurately with the current as predicted by Eq. (4), one would expect Eq. (3) to hold likewise.

G. A Brief Statement of the Physical Meaning of the Phenomena Observed

Mercury alone in the discharge tube

The intensity of any particular transition of an atom is proportional to the number of inelastic impacts that occur. When the gas pressure is low, the number of elastic collisions and likewise the number of inelastic collisions is small, and the observed intensity of the transition is weak. As the pressure increases, more and more inelastic impacts occur due to the greater number of times the electron comes in contact with the atoms. Correspondingly, the observed intensity of the transition increases. This continues until finally practically all of the electrons have an inelastic impact before reaching the anode, and any further increase in pressure does not yield any more inelastic impacts. In this state, the intensity of the different lines *versus* abundance plot shows saturation.

Mercury in a mixture of gases

Each high velocity electron can have one and only one inelastic impact and this may be with a

TABLE VII. *Intensity of various mercury transitions at a pressure of mercury equal to 34×10^{-4} mm in discharge tube. Tube voltage = 30 volts. Tube current = 20 ma.*

Wave-length	Hg Alone	P_A = 0.0028 mm	P_A = 0.0038 mm	P_{He} = 0.025 mm	P_{He} = 0.046 mm
2655A	1.16	1.04	0.82	0.68	0.59
3021A	1.04	0.88	0.77	0.72	0.80
2803A	0.36	0.33		0.32	0.34
2483A	0.35	0.24	0.21	0.71	0.13
2655A	1.22	1.12	0.91	0.88	0.68
3341A	1.09	0.80	0.78	0.59	0.50
2482A	0.47	0.37		0.24	0.24
2925A	0.18	0.27			

foreign or a mercury atom. The fraction of high energy electrons having exciting collisions with mercury will be the ratio of the excitation cross section of the mercury atoms to the total excitation cross section. As the pressure of the mercury is increased the fraction slowly approaches a constant value. The rate of approach depends upon the amount of foreign gas present. Thus, the intensity *versus* abundance plots show saturation.

H. Results of This Investigation as Applied to Practical Quantitative Spectrochemical Analysis

A plot of J, $\log (I_{Hg}/I_{He})$, *versus* $\log X$, (log percent Hg) is a straight line. The straight lines are the standard analytical curves used in practice.

When the concentration of the test element, i.e. mercury, is high Eq. (5) is no longer valid. In this case the exact Eq. (4) applies. For high concentrations of the test element, $b \ll p$, the multiplicative factor simply reduces to $B \cdot i$. The plot of the resulting equation shows saturation for large values of the pressure. Under these conditions the spectral line is said to be insensitive.

This insensitiveness is the reason why quantitative spectrographic analysis fails for high percentages of the test element.

The answer to more practical and important problems can now be given; namely, what can be done if one desires to analyze a substance containing a high percentage of the test element and what spectral lines are most suitable? From Eq. (4) the spectral lines of an element become insensitive when $b \ll p$ and p itself becomes large.

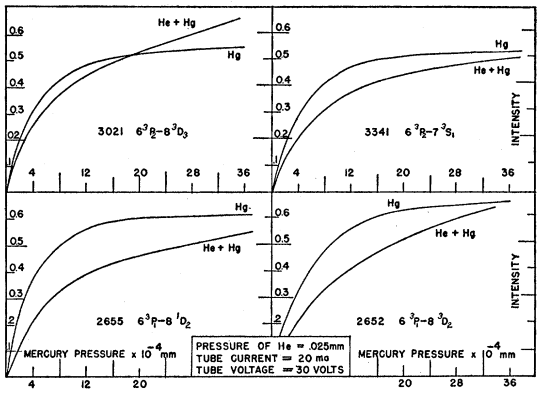

FIG. 4. Comparison of variations of intensity of mercury lines with abundance in mercury alone and mercury-helium mixtures.

To regain sensitivity the specimen must be diluted with foreign atoms, i.e., make b greater. Higher term members will be more sensitive than lower term members because b is proportional to the average mean free path of the electron for excitation of the test element. As may be seen from Table II, λ_{1E} is greater for higher term members.

In this discussion it has been tacitly assumed that the mechanism for excitation in practice is the same as the excitation condition of this investigation. Actually the mechanism is far more complicated as the sources used in spectrochemical analysis do not provide such simple excitation conditions as the sources used in this investigation. Nevertheless, the analytical curves for most sources used in practice are straight lines for a given range of abundance and the departures from these straight lines are as one would expect from the reasoning given above.