

representative straight lines. These deviations were of the same order of magnitude as those on the best Boltzmann plots. The latter plots are based on the assumption that relatively few downward transitions are radiative and that the probabilities of radiative transition are proportional to $w_{AB}/[\lambda^2(n_A^*+n_B^*)(n_A^*-n_B^*)^2]$ where w_{AB} is the Kronig *a priori* probability, n_A^* and n_B^* are the effective quantum numbers of the upper and lower levels, and λ is the wave-length of the emitted radiation.

7. Representative straight lines drawn among the points on the Boltzmann plots described above gave electron temperatures of 7160 and 7880°K for mercury vapor pressures of 450 and 500 mm, respectively. Similar lines on the corresponding "excitation" plots gave electron temperatures of 5435 and 5460°K, respectively. Line breadth measurements and theoretical calcula-

tions set forth in the paper immediately following this one indicate that the electron temperature is at least 6000°K at these two pressures. The electron temperatures indicated by the "excitation" plots agree with this computed minimum value within the limits of uncertainty set by the scatter of the points on these plots. The electron temperatures indicated by the Boltzmann plots are not impossible, but are much higher than is required by the measured line breadths and the electrical characteristics of the arc. This conclusion is contingent on the formula chosen for transition probabilities.

8. Since neither excitation probabilities nor the probabilities of downward transitions are known, no quantitative basis is available for choosing between the hypothesis of a Boltzmann equilibrium and the hypothesis of an excitation-radiation balance.

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The Mechanism of the Positive Column in Mercury Vapor at Intermediate Pressures

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Calculations based on the radiant intensity for the principal spectral lines of 4-ampere mercury arcs at 450 mm and 500 mm (Hg) pressure, indicate for low quantum states a dynamic equilibrium with electrons at approximately 6000°K, the temperature indicated by the absolute spectral intensity for three reversed lines. For high quantum states differing only in total quantum number, there appears to be a tendency toward Boltzmann equilibrium due to collision with normal atoms at approximately the temperature (2500°K) calculated from the heat balance by Langmuir's theory of conduction and convection in gases. This agrees with predictions from the principle of *spectroscopic stability*.

THE electric discharge¹ in the inert gases or in mercury vapor offers the advantage of a relatively simple system: a single molecular species² with no rotational energy, and incapable of any other dissociation than that into electrons

¹ The discharge in mercury at atmospheric pressure is customarily referred to as a mercury arc. By Ornstein and Brinkman's definition (*Physica* **1**, 797 (1934)) it is a high pressure glow discharge, if, as we now believe, the electron temperature is significantly higher than the gas temperature.

² Mercury molecules and molecule ions are present in the discharge and may play an essential role, but in concentrations which will not affect significantly the mechanical and thermal properties of the vapor. Energy of electron excitation or spin is not ordinarily called "rotational energy."

and positive ions. Yet even this simple system is effectively a system of three components, atoms, ions, and electrons, present in different concentrations, and obeying different laws of motion.

The fact that some of the atoms are excited will have no material influence on the mechanical behavior of the gas, since the mass of the atom is not altered appreciably, and since collision of the second kind, whether between atoms or between an atom and a positive ion, will rarely have any other effect than an exchange of roles.³ Collisions

³ See, however, section on "Collision with Normal Atoms."

of the second kind between positive ions are improbable both because of the low ion concentration and because of electrostatic repulsion.

"Elastic" collisions of ions and electrons with atoms will not be numerous or violent enough to disturb the Maxwellian distribution of atomic velocities, but will transfer energy and momentum, raising the gas temperature and causing electrophoretic effects. Since most of the current is carried by electrons, these will furnish most of the energy; since the volume charge in the tube is predominantly positive, the electrophoretic effects at higher pressures will be produced chiefly by the positive ions—while at low pressures the greater transfer of axial momentum to the walls by the ions will more than compensate for the effect of the excess positive charge.⁴

ENERGY BALANCE

The dissipation of energy in the positive column involves three main processes: radiation, recombination of ions and electrons, and conduction and convection of heat. The laws of the conduction and convection of heat from a heated cylinder to a cooler surrounding gas have been worked out by Langmuir.⁵ On the basis that almost all the temperature fall is concentrated in a quasi-stationary film of gas between the solid cylinder (of diameter a) and a concentric cylinder of diameter b , and by the use of the integrated form of the differential equation for the flow of heat between isothermal surfaces one obtains

$$W = s(\varphi_1 - \varphi_0) = s \int_{T_0}^{T_1} k dT. \quad (1)$$

In this W is the power lost by thermal conduction per cm of length, s is the "shape factor,"⁶ likewise per cm of length, (for concentric cylinders $s = 2\pi/(\ln(b/a))$), and φ_1 , as indicated, is the integral of the thermal conductivity k from some

reference temperature, e.g., 0°C, to the temperature T_1 . φ_0 is the same integral for the lower temperature, T_0 .

For a convex cylinder, the diameter of the virtual limit of thermal conduction, b , is related to the diameter of the solid cylinder, a , by the equation of Adams⁵

$$b \ln b/a = 2B, \quad (2)$$

where B is the film thickness for an infinite plane surface. The assumptions used in deriving this formula do not hold for the present case of a concave cylinder cooler than the enclosed gas, but the qualitative statement may be made that the film thickness in a discharge tube at atmospheric pressure will be somewhat greater than for an infinite plane surface, i.e., $>B$.

For mercury vapor at atmospheric pressure, Langmuir found $B = 0.0784$ cm, from which a round figure of 0.08 cm may be taken as the film thickness in Elenbaas' tube of 2.0 cm internal diameter with mercury vapor at atmospheric pressure.⁷ As the precision of the data does not justify interpolation in Langmuir's table of integrated heat conductivity of gases ($\varphi = \int k dT$), 2500°K, 900°K, and 300°K will be taken as the respective temperatures of the mercury vapor, tube, and surroundings; the thickness of the tube walls will be assumed to be 0.1 cm, and the film thickness of air outside the tube 0.4 cm.

The rate of flow of heat from the mercury vapor to the tube is

$$W = s\varphi = \pi(1.96/0.08)(0.481 - 0.062) = 32.2 \text{ watt cm}^{-1}. \quad (3)$$

The rate of flow of heat from the tube to the surrounding is

$$W = s\varphi + A\sigma(T^4 - T_0^4) = \pi(2.6/0.4)(0.297 - 0.039) + \pi \times 2.2 \times 3.70 = 5.3 + 25.6 = 30.9 \text{ watt cm}^{-1}. \quad (4)$$

Elenbaas estimated the heat flux lost by conduction and convection as 70 percent of 43.8 w cm^{-1} , the input per cm of positive column.

$$W = 0.70 \times 43.8 = 30.7 \text{ watt cm}^{-1}. \quad (5)$$

Whereas Elenbaas⁷ found discrepancies as great as a factor of four by assuming that convection could be neglected, the calculation above,

⁷ W. Elenbaas, *Physica* **1**, 211-24 (1934) esp. p. 222.

⁴ I. Langmuir, *J. Frank. Inst.* **196**, 751-62 (1923).

⁵ I. Langmuir, *Phys. Rev.* **34**, 401-22 (1912). Langmuir's value of φ , the temperature integral of thermal conductivity of mercury vapor, was calculated from an assumed value of the Sutherland viscosity constant and may be considerably in error. Since we are using the value of B (film thickness for a plane surface) computed from this value of φ and Langmuir's data taken at atmospheric pressure, to calculate convection at atmospheric pressure, only a second-order error will be introduced by any uncertainty in φ .

⁶ I. Langmuir, E. Q. Adams, and G. S. Meikle, *Trans. Am. Electrochem. Soc.* **24**, 53-84 (1913).

based on measured⁸ convection losses agrees well within the precision of the data used in the calculation.

DISTRIBUTION OVER THE CROSS SECTION

It follows that (at atmospheric pressure) up to within a millimeter of the wall of the tube the mercury vapor temperature is substantially constant and approximately 2500°K. The electron temperature (as judged from the relative intensity of the various lines of mercury) cannot be less than 3500°K, and therefore the vapor and the electrons are *not* in thermal equilibrium with one another. Since the electrons in all parts of the tube cross section are moving in an equal electromotive gradient through vapor of constant temperature and pressure, the electron temperature, mean free path (as concerns collision with mercury atoms) and drift velocity must likewise be uniform, and the relative spectral distribution should be uniform over the cross section, as has been found to be the case.⁸

If the radiant flux resulting from the collisions of a single electron is the same in all parts of the cross section of the tube, any variation in steradiancy,⁹ beyond the cosine effect of the cylindrical cross section, must be attributed to a change in electron concentration. This in turn is due to the radial electromotive gradient due to the excess of positive ions over electrons. The experimentally determined variation in steradiancy (\mathfrak{B}) indicates a nearly Gaussian distribution of electron concentration. (For this special case it may be shown that the radial and pinacoidal¹⁰ variations of electron concentration follow the same law.)

$$\begin{aligned} dJ/dV &= (dJ/dV)_0 e^{-r^2/a^2} \\ &\equiv (dJ/dV)_0 e^{-x^2/a^2} e^{-y^2/a^2}, \quad (6) \end{aligned}$$

where J is radiant intensity, V is volume, and x and y are the components, across and along the line of sight, of the distance r from the axis. a is a parameter defining the radial distribution and subscript 0 indicates the axial value of the derivative dJ/dV .

⁸ See preceding article.

⁹ Cf. W. E. Forsythe, *et al*, *The Measurement of Radiant Energy* (McGraw-Hill Book Co., Ltd., New York and London, 1937), especially p. 3. See also *Rev. Sci. Inst.* **7**, 322 (1936).

¹⁰ From the Greek, pinax = slab.

$$\begin{aligned} \mathfrak{B} &= \int (dJ/dV) dy \\ &= a(dJ/dV)_0 e^{-x^2/a^2} \int e^{-y^2/a^2} d(y/a), \quad (7) \end{aligned}$$

where \mathfrak{B} is steradiancy (surface density of radiant intensity).

If the value of dJ/dV at the wall is negligibly small with respect to $(dJ/dV)_0$, the integral becomes the complete integral

$$\int_{-\infty}^{+\infty} e^{-t^2} dt = \pi^{1/2}, \quad (8)$$

$$\mathfrak{B} = a\pi^{1/2}(dJ/dV)_0 e^{-x^2/a^2}. \quad (9)$$

While this equation accounts almost quantitatively for the distribution of steradiancy near the axial plane of the discharge, it cannot be expected to apply to the entire cross section of the tube, for a Gaussian distribution of electron concentration implies a parabolic distribution of electric potential, which in turn requires a uniform volume concentration of (net) positive charge. Near the axis of the tube the radial electric potential gradient is small and the convective stirring of the mercury vapor will be sufficient to keep the concentration of positive ions practically uniform. Where the potential gradient is greater and the stirring less vigorous, a radial concentration gradient of positive ions can be maintained and it is improbable that the net positive charge will remain unchanged.

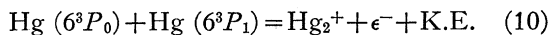
The electron distribution at a distance from the axis cannot be determined precisely from the distribution of steradiancy, for the strongest lines in the discharge are all due to transitions whose lower level is 6^3P_0 , 6^3P_1 , or 6^3P_2 . Absorption and re-emission should increase the peripheral intensity of these lines relative to those due to transitions to higher levels, as is found to be the case.⁸

FORMATION AND NEUTRALIZATION OF MERCURY MOLECULE IONS

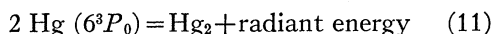
Calculations indicate that the net positive volume charge is a small fraction ($\cong 10^{-3}$) of the concentration of positive ions, hence the rapid decrease in the concentrations of positive ions and electrons with increasing radius cannot be

accounted for by recombination at the walls. The direct recombination of atomic positive ions and electrons is a rather improbable process; hence the possible intervention of mercury molecules and molecule ions must be considered.

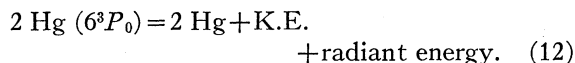
Mercurous salts have been shown¹¹ to be derived from the doubly-charged molecule ion, Hg_2^{++} . The stability of such a grouping in aqueous solution and in solid compounds,¹² proves the possibility of a strong bonding between mercury atoms. The absorption spectrum of unexcited mercury shows a strong band, which is to be attributed to molecules of two atoms of mercury,¹³ on the long wave side of $\lambda 2537\text{A}$. Foote¹⁴ and Houtermans¹⁴ found ionization produced by irradiation with $\lambda 2537$ in mixtures of mercury vapor and argon, which they assigned to a reaction of mercury atoms in the 6^3P_0 and 6^3P_1 states:



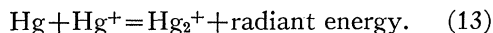
and Foote, Ruark and Chenault¹⁵ observed under similar conditions a blue-green band emission which they attributed to the interaction of two 6^3P_0 mercury atoms



or



The existence of the molecule ion makes possible the reaction



Since the concentration of atomic mercury is

¹¹ Cf. G. A. Linhart, J. Am. Chem. Soc. **38**, 2356-61 (1916). G. A. Linhart and E. Q. Adams, J. Am. Chem. Soc. **39**, 948-50 (1917).

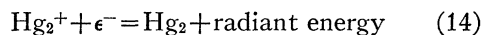
¹² Ch. Mauguin, Comptes rendus **178**, 1913-6 (1924). E. Hylleraas, Physik Zeits. **26**, 811-4 (1925). R. J. Havighurst, Am. J. Sci. **10**, 15-28 (1925); J. Am. Chem. Soc. **48** 2113-25 (1926). H. Mark and J. Steinbach, Zeits. f. Krist. **64**, 79-112 (1926).

¹³ J. Franck and W. Grotrian, Zeits. f. tech. Physik **3**, 194-7 (1922). The fact that the intensity of this band, at constant concentration of mercury, decreases with rising temperature, indicates that the band is due to an actual Hg_2 molecule, and not to a "virtual" molecule existing only during collisions.

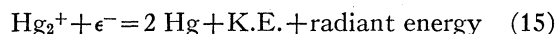
¹⁴ P. D. Foote, Phys. Rev. **29**, 609 (1927). F. G. Houtermans, Zeits. f. Physik **41**, 140-54 (1927). Cf. A. L. Hughes, Wash. Univ. Studies, N.S., Sci. Tech. **2**, 25-30 (1929). It should be emphasized that the energy of two excited 6^3P_1 atoms is insufficient to ionize an atom of mercury.

¹⁵ P. D. Foote, A. E. Ruark and R. L. Chenault, Phys. Rev. **37**, 1685 (1931).

high and constant, this reaction would be apparently unimolecular in (Hg^+) . The neutralization reaction:



or



would be much more probable than the direct neutralization of the atomic ion, since many more degrees of freedom are available to store energy and prevent the reionization of the molecule. Let it be assumed that it is enough more rapid than (13) to make (13) the rate-determining step, and the disappearance of positive ions effectively unimolecular.

Such a reaction sequence in a region of the tube in which ions are not being produced would give a concentration of positive ions (and hence of electrons)

$$C = ar^{-\frac{1}{2}}e^{-br}, \quad (16)$$

where (b) and (a) are constants dependent, respectively, on the rate of destruction of ions in the outer parts of the tube and on the rate of production of ions near the axis of the tube.

A production of ions proportional to the first power of the current density will be equivalent to a reduction in the rate of neutralization of ions, since both processes are proportional to the ion concentration. The maintenance of the discharge then requires some process of ionization proportional to a higher power of the current density. Cumulative ionization by electrons is most likely to occur where the concentrations of electrons and of excited atoms are the greatest, namely near the axis of the tube. The electron temperature of approximately 6000°K estimated from the kinetics of radiation, is high enough to account for a reasonable amount of ionization of mercury atoms in this region of the tube.

A Priori Probabilities

In the estimation of electronic (or atomic) temperatures from relative line intensities, allowance needs to be made for the *a priori* probabilities of the states and processes involved.

It should be noted that the "strength"¹⁶ of

¹⁶ E. U. Condon and Shortley, *Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 98: $S(A, B) = \text{line strength} = \text{sum of the squared matrix components for the transition } A \rightarrow B$.

Condon and Shortley, S , is not the same as the "strength"¹⁷ of Ladenburg, f .

Following Dirac,¹⁸ Condon and Shortley identify the matrix components with the components of the electric amplitude, ϵ (ϵ =electron charge, \mathbf{r} =displacement from point of rest of the equivalent oscillator.) The "oscillator strengths" of Ladenburg, being abstract numbers, and shown by Thomas¹⁹ and by Kuhn²⁰ to obey a sum rule first suggested by Van Vleck²¹ seem to the authors more likely, *a priori*, to be given by formulas involving only quantum numbers. For the special case of an $S \rightleftharpoons P$ resonance transition, e.g., sodium, where $f_{BA} \cong \frac{1}{3}$, Ladenburg and Minkowski²² have shown that the resonance life is approximately equal to that of the classical oscillator of equal $h\nu$.

The question is one of normalization. Since the most satisfactory tests of intensity formulas have been with close multiplets and the Zeeman and Stark effects, the question as to the power to which the frequency enters has not greatly concerned the experimental workers. Thus Frerichs²³ wrote, "Es spielt da die wichtige, experimentell noch unentschiedene frage hinein, ob die Summenregeln für die Intensitäten J oder die 'Sprungzahlen' J/ν gelten (vgl. u.)" [!] while earlier in the same year Schrödinger had given²⁴ two formulas for the dipole moment, in the sec-

ond of which the frequency as a factor was eliminated in the process of normalization, without any proof that the method of normalization used is correct, other than a reference to Heisenberg. Now Heisenberg²⁵ has stated the quantum condition in the form:

$$2\pi m \{ b^2(n, n-1; m, m-1) \omega(n, n-1) - b^2(n, n-1; m-1, m) \omega(n, n-1) \} = (m + \text{const.}) h$$

for the special case of the Zeeman effect of a quantized rotator, where the first m is electronic mass. Elsewhere n is a rotational and m a magnetic quantum number. The b 's are the amplitudes of the perturbed circular orbits, ω is angular velocity, and h the Planck constant. For a multiply-periodic system there would be a summation in which the ω 's would not all be equal. Taking account of the known relation of Einstein's coefficient B to the squared amplitude, a^2 ,

$$B = (8\pi^3 \epsilon^2 / 3h^2) a^2$$

(and $\omega = 2\pi\nu$) it can be seen that the total-summation rule of Van Vleck, Thomas, Reiche and Kuhn, is just such a summation.

This summation, it should be emphasized, is an algebraic one. If it is to be applied to individual electrons, account must be taken of transitions which cannot occur because both the upper and lower levels are filled. As stated by Kronig and Kramers²⁶ "Solange die Koppelung der Elektronen gegen die sonstigen vorhandenen Kräfte sehr Klein ist, bewirkt das Pauliverbot einfach ein Wegfallen der Oszillatoren der einzelnen Elektronen, die Übergängen nach schon besetzten Zuständen entsprechen, und zwar in Paaren von positiven und negativen Oszillatoren gleicher Frequenz und Stärke, während die übrigen Oszillatoren unbeeinflusst bleiben." It is thus possible, e.g., for the first term of a principal series to have an aggregate f value of unity, in spite of the existence of other permitted upward transitions.

For comparison with the *a priori* multiplet-transition probabilities of Kronig,²⁷ w_{AB} , it is

¹⁷ R. Ladenburg, Rev. Mod. Phys. 5, 243 (1933):

f_{kj} = oscillator strength (Condon and Shortley, reference 16, p. 108)
= number of dispersion electrons, per atom in the state j , associated with the transition $j \rightarrow k$.

¹⁸ P. A. M. Dirac, Proc. Roy. Soc. A111, 281-305, 405-23 (1926). On p. 302 Dirac states, "We cannot actually determine the amplitudes at present because we do not know the action and angle variables corresponding to the r 's and P_r 's. If, however, we assume that the Fourier expansion of r does not involve p, j, ϕ , or ψ , then when $x/r, y/r, z/r$ are expanded as Fourier series in $e^{i\phi}, e^{i\psi}$, the ratios of the coefficients will give the ratios of the corresponding amplitudes. We can thus determine the relative intensities of the lines of a multiplet and of the components into which these lines are split in a weak magnetic field.

¹⁹ W. Thomas, Naturwiss. 13, 627 (1925); F. Reiche and W. Thomas, Zeits. f. Physik 34, 510-25 (1925).

²⁰ W. Kuhn, Zeits. f. Physik 33, 408-12 (1925).

²¹ J. H. Van Vleck, Phys. Rev. 24, 359-60 (1924); Bull. Nat. Res. Council 10, (54) 152 (1926).

²² R. Ladenburg and R. Minkowski, Zeits. f. Physik 6, 163 (1921). At that time the *a priori* probabilities of the 3S and 3P levels of sodium were not known, but an expression was given explicitly relating the radiational decay time to the *a priori* probabilities " $g_{1,5s}, g_{2p_1}, g_{2p_2}$ " and the classical decay time, τ .

²³ R. Frerichs, Ann. d. Physik 81, 840 (1926).

²⁴ E. Schrödinger, Ann. d. Physik 79, 755; 80, 464 (1926).

²⁵ W. Heisenberg, Zeits. f. Physik 33, 892 (1925).

²⁶ R. de L. Kronig and H. A. Kramers, Zeits. f. Physik 48, 178 (1928).

²⁷ R. de L. Kronig, Zeits. f. Physik 33, 261-72 (1925). A common factor of 16 has been omitted in Table III of the preceding article.

more convenient to deal with the symmetrical function $(2j_A+1)f_{AB} = -(2j_B+1)f_{BA} \equiv \varphi_{AB}$, where²⁸ j_A is the inner quantum number of state A , and f_{AB} is the "oscillator strength" for the transition $A \rightarrow B$.

The "transition strength" φ_{AB} depends on the total quantum numbers as well as on the Kronig probability, w_{AB} . For purposes of computation, this last has been divided by $(n_A^*+n_B^*) \cdot (n_A^*-n_B^*)^2$ as a function which satisfies the correspondence principle both for series, and for transitions between nearly circular orbits. (n_A^* and n_B^* are the effective quantum numbers for states A and B .) This is to be regarded, however, as a makeshift, pending the evaluation of the appropriate radial quantum integrals.²⁹

Similarly, in default of an exact knowledge of the collision area for various processes as a function of electron velocity, it has been assumed that the rate of excitation by electron collision is proportional to the *a priori* probability $(2j_A+1)$ of the upper state and to the rate of collisions with electrons whose energy exceeds the energy of transition by not more than a constant energy. This assumption gives $\Sigma J\lambda / [(2j_A+1)\epsilon V]$ as the function which should vary exponentially with the energy, ϵV , of the upper level, A , in the event that the excitation by electron collision is the rate-determining step, and that practically all downward transitions are radiative.

²⁸ The transition strength φ_{AB} should not be confused with the heat-conductivity integral $\varphi = \int k dT$ of Langmuir.

²⁹ This function does not reproduce well the intensities of the first five lines of the principal series of sodium $nP_{3/2} - 3S_{3/2}$, but gives good agreement for larger values of n :

n	λ	$f_{AB}(n_A^*+n_B^*)(n_A^*-n_B^*)^2$
3	5893A	87.3
4	3303	5.3
5	2853	7.44
6	2680	5.26
7	2594	4.10
8	2544	3.57
9	2512	3.36
10	2491	3.26
11	2476	3.27
12	2464	3.28
13	2456	3.30
14	2449	3.38
15	2444	3.46
16	2440	3.55
17	2437	3.44
18	2434	3.41

For the principal series of lithium and of cesium on which less work has been done, the agreement of the formula with the experimental values of intensity is not as good as with sodium.

TEMPERATURE ESTIMATE FROM LINE INTENSITY

The principle that the spectral steradiance of the arc cannot exceed that of a black body at a temperature equal to the electron temperature permits the setting of a lower limit to the electron temperature. The ratio of the steradiance for a given emission line to the spectral steradiance of a black body at that wave-length sets a lower limit for the effective line width, for any assumed black-body temperature.

Line widths were measured on films taken on a 21-foot concave grating with 30,000 lines per inch, for a mercury arc at approximately 450 mm (Hg) pressure. We are indebted to our colleague, Mr. A. Poritsky, of the Cleveland Wire Works of the General Electric Company, for these spectrograms.

Table I compares the result of calculations for $\lambda 4047$, 4358 and 5461A, and assumed temperatures of 3000°, 4000°, 5000°, and 6000°K (using $c_1 = 1.177 \times 10^{-2}$ cm² w rad⁻² and $c_2 = 1.432$ cm °K in the Planck radiation formula) with the net widths of these three reversed³⁰ lines. It may be concluded that the electron temperature is at least 6000°K.

COLLISION WITH NORMAL ATOMS

It remains to take into account the possible influence of collisions with normal atoms upon

TABLE I. Width of reversed lines calculated for different temperatures and observed values.

WAVE-LENGTH	OBSERVED W RAD ⁻² CM ⁻²	LINE-WIDTH				OBSERVED
		3000°K	4000°K	5000°K	6000°K	
4047A	0.074	91A	4.7A	0.81A	0.25A	0.21A
4358	0.109	83	5.4	1.04	0.35	0.25
5461	0.114	29	3.3	0.89	0.37	0.33

³⁰ With an unreversed line there will be no assurance that the absorption is great enough to give black-body steradiance even at the central wave-length. It may be pointed out that this degree of absorption does not necessarily invalidate the assumption on which the excitation plot is based: that all downward transitions are radiative. Since that plot uses measurements of the radiation from the entire width of the arc, absorption followed by reemission of the same triplet will not affect the estimate of the rate of excitation to the common upper level, 7^3S_1 . The short wave-length wing, region of reversal, and long wave-length wing, respectively, of the three lines measured were: $\lambda 4047$: 0.095, 0.07, 0.115; $\lambda 4358$: 0.115, 0.12, 0.14; $\lambda 5461$: 0.15, 0.10, 0.175A. These figures are the averages of readings by four observers. We are indebted to P. D. Cargill, Miss M. A. Easley, and W. J. Karash for these comparator readings.

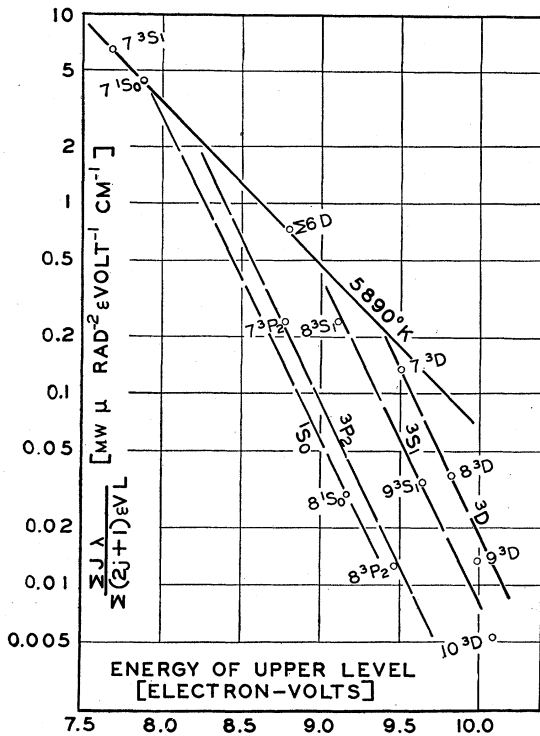


FIG. 1. Plots of $\Sigma J \lambda / [\Sigma (2j+1) \epsilon V L]$ for various types of upper state.

the relative concentrations of the higher excited states. It is well established that such collisions will not be inelastic for mercury in the ground state; but when the orbital radius becomes comparable³¹ with the mean distance between mercury atoms, and the energy differences between states become less than the thermal kinetic energy of the atoms, neither geometric nor energetic considerations forbid inelastic collisions. Since the colliding normal atom will suffer no change except in velocity, the principle of *spectroscopic stability*³² demands that the most

³¹ Since the radius of the first Bohr orbit of hydrogen is 0.528A, the classical radius of a circular orbit with $n=10$ should be 53A; the "maximum elongation" for an electron in the corresponding s -orbit, on account of quantum defect, will be less than this (about 30A). Since the number of molecules in a cubic centimeter of gas at 273°K and 1 atmosphere is 2.706×10^{19} , at 2500°K and 450 mm (Hg) pressure, the distance between molecules in cubic array would be 83A.

³² A collision between a normal and an excited mercury atom may be regarded from two alternative points of view: the temporary exposure of the excited atom to the perturbing field of the colliding normal atom, or the formation and subsequent dissociation of an Hg_2 molecule. For an inelastic collision, the collision must be close enough to relax to some extent the quantization of the excited atom

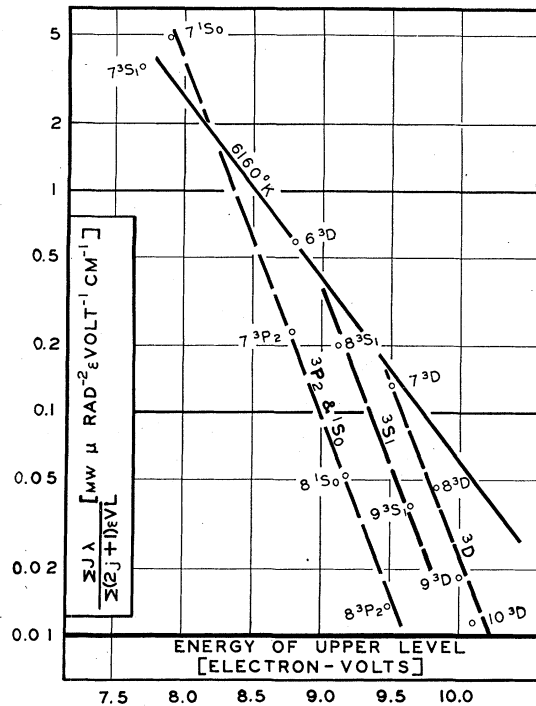


FIG. 2. Plots of $\Sigma J \lambda / [\Sigma (2j+1) \epsilon V L]$ for various types of upper state.

probable transitions be those in which neither j nor S changes, i.e., to states differing only in total quantum number from the initial state.

In the case of the discharge at 450 mm (Hg) pressure, sufficient data are available to permit a search for such an effect of atomic collisions. Figs. 1 and 2, plots of $\Sigma J \lambda / [\Sigma (2j+1) \epsilon V L]$ show that for each type of upper state, 1S_0 , 3P_2 , 3S_1 and ΣD , for low total quantum number the rates of excitation as measured by the totality of radiative transitions from any state lie on a line whose slope indicates an electron temperature of 5890°K for 450 mm Hg pressure, and 6160°K for 500 mm Hg pressure, while for high total quantum number, they lie on a series of nearly parallel lines.

(from the former point of view) or to destroy the one-to-one correlation between atomic and molecular states with the result that an atom may leave in a configuration different from that in which it enters the molecule (from the second). Since one of the atoms is in a 1S_0 state, and S , L and j for the other are small, a change in S , L or j is unlikely, and the most probable change is in the largest quantum number, n , of the excited electron. This change may be either a promotion or a demotion, and since the energy difference is added to or taken from the atomic kinetic energy, the ratio of the rates of the two processes will depend on the atomic temperature.

As an indication of the atomic temperature, these pairs of points have been connected on the Boltzmann diagrams, Figs. 4 and 5 of the preceding paper, by dotted lines.

The slopes of these lines indicate temperatures of 4250°K, 4000°K, 3050°K, 5060°K, 4410°K, 4150°K, intermediate between the temperatures of the electrons and of the atoms.³³ Whether the higher members of the same series would give a closer approach to the atomic temperature is a question which cannot be answered experimentally as the line intensities become too weak to measure. It seems certain, however, that collisions of the second kind with unexcited atoms are a significant factor in determining the concentrations of higher states.

PERSISTENCE OF RADIATION

The continuance of radiation after the current has been interrupted cannot be accounted for

³³ It may be of interest to note that the calculated electron temperature is approximately that of the surface of the sun, and the atomic temperature that of the filament of a tungsten lamp. According to the theory of Elenbaas, reference 7, the electron temperature and the gas temperature are equal, and vary with the distance from the axis; according to the present theory, they are uniform, and unequal. The wall temperature, the maximum electron temperature and the mean gas temperature are substantially the same in both.

quantitatively by the kinetic energy of the electrons. The only apparently significant stores of energy are in the kinetic energy of the atoms and the excitation energy of the $6P$ states. Since the atomic-Boltzmann equilibrium has been shown to remove energy from the higher excited states, during the steady state, and since the radiation pattern does not change discontinuously when the current is interrupted³⁴ the atoms must be a sink rather than a source of energy, at least until the electron temperature has fallen nearly to that of the atoms. Rough calculations based on a Boltzmann equilibrium between the electron velocity and the excitation³⁵ to the 6^3P states, indicate that the stored energy is of the right order of magnitude. In making these calculations it must be remembered that only about 10 percent of the power input is radiated, and that nonradiative dissipative processes and binary collisions of excited atoms to yield molecules or molecule ions may be expected to fall off more rapidly than the atomic radiative processes.

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The Signs of the Nuclear Magnetic Moments of Li^6 and K^{41} *

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Nonadiabatic transitions between magnetic quantum states of atoms in an atomic beam were used to determine the signs of the nuclear magnetic moments of Li^6 and K^{41} . The nuclei of these isotopes were found to have positive magnetic moments.

SCHULER'S¹ determination of the sign of the nuclear magnetic moment of Li^6 was based upon intensity measurements of h.f.s. separations which were incompletely resolved. In view of the uncertainties which arose in connection with the spectroscopic determination of the sign of the

nuclear moment of K^{39} because of incomplete resolution of the h.f.s.,^{2,3} it was considered desirable to determine the sign of the nuclear moment of Li^6 by the method of atomic beams. In the case of K^{41} it was of interest to see if the addition of two neutrons changes the sign of the

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³ D. A. Jackson and H. Kuhn, *Nature* **140**, 276 (1937).