

It is this second element that has exercised such a marked influence on the subsequent Tertiary and existing floras of temperate North America, and which is largely responsible for the parallelism between the existing floras of North America and Asia, which was first emphasized by Asa Gray so many years ago.

THE METASTABLE $2p_3$ -STATE OF MERCURY ATOMS

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1. Let us consider a mixture of mercury vapor, thallium vapor and nitrogen in a closed quartz tube under well defined conditions of pressure and temperature, illuminated by $\lambda 2537\text{\AA}$ of constant intensity.

Due to the absorption of the illuminating radiation a constant number N of mercury atoms will be activated in unit time. Those activated atoms persist in the $2p_2$ -state for a finite time t which is known to be of the order of magnitude of 10^{-7} sec.¹ If they escape collision during this period they return to their normal state in the ordinary way—emitting radiation (resonance). They may, however, while activated, collide with nitrogen molecules, normal mercury atoms or normal thallium atoms. We shall assume, for the present, that the amount of nitrogen and thallium sufficiently exceeds the amount of mercury, so that we may disregard totally the collisions between activated and normal mercury atoms.

We assume furthermore that all collisions between activated mercury atoms and thallium atoms result in the activation of the latter, producing the fluorescence radiation of thallium with a constant energy distribution between its different lines.

As to the collisions between activated mercury atoms and nitrogen molecules two possibilities have to be taken into account:

The total amount of energy stored up in activated mercury atoms may be used in the collision and converted into kinetic energy of the colliding particles. The activation energy is then divided between them according to the principle of conservation of momentum; the activated mercury atom returns to its normal state without emitting radiation (collisions of the second kind).

It is, however, also conceivable that the result of such a collision does not consist in a direct return of an activated atom to its normal state. The main part of the activation energy may be retained in the metastable $2p_3$ -state of the mercury atom, the difference only being converted into

the kinetic form. Such a "partially" activated mercury atom, in the $2p_3$ -state, would retain its energy indefinitely in vacuo (selection principle), it will actually retain it during a time t_m sec., determined by the pressure and the nature of the surrounding gas.

The enhancing effect of nitrogen and argon on the indirectly excited fluorescence of thallium vapor *in sealed off tubes under well defined conditions of pressure and temperature*² shows conclusively that some of the activated mercury atoms actually persist longer than 10^{-7} sec. in the metastable $2p_3$ -state, and while enduring many collisions with nitrogen and argon, lose their energy only in collisions with thallium and with normal mercury atoms. The question arises whether it will be possible to estimate the order of magnitude of the time t_m of the metastable atoms in the $2p_3$ -state *from the measurable ratio of the increase of intensity for a given line in the fluorescence spectrum of thallium?*

2. We call N the number of activated atoms produced in unit time by the effective radiation. If t is their life-time in the $2p_2$ -state and T the time between two collisions of mercury atoms and nitrogen molecules,³ then

$$\frac{t}{T + t}$$

measures the fraction of mercury atoms which collide while activated. We know from Stuart's⁴ measurements that when activated mercury atoms collide with nitrogen molecules, only 1,3% of the collisions are "collisions of the second kind." If we assume *that all of them result in throwing the colliding mercury atom into the metastable $2p_3$ -state*, we obtain for the number of metastable atoms produced in unit time:

$$N_m = \frac{1,3}{100} \frac{t}{T + t} N. \quad (1)$$

After a stationary state has been reached there will exist at every moment in our mixture \mathfrak{N} activated mercury atoms (in $2p_2$ -state) and \mathfrak{N}_m "partially" activated metastable mercury atoms (in $2p_3$ -state). The ratio of those numbers is evidently:

$$\frac{\mathfrak{N}_m}{\mathfrak{N}} = \frac{N_m}{N} \cdot \frac{t_m}{t} = \frac{1,3}{100} \cdot \frac{t_m}{T + t}. \quad (2)$$

The intensity of the indirectly excited fluorescence spectrum of thallium depends under constant conditions of temperature and partial pressures of the vapors only on the *total* number of activated mercury atoms. This number was \mathfrak{N} as long as no nitrogen was present in the tube; it is $\mathfrak{N} + \mathfrak{N}_m$ when nitrogen is added to the mixture. Due to its presence

the intensity of a given line say $\lambda 5350\text{\AA}$ increases α times. The increase of intensity in the ratio α is then equal to the ratio:

$$\frac{\mathfrak{N} + \mathfrak{N}_m}{\mathfrak{N}} = 1 + \frac{1,3}{100} \cdot \frac{t_m}{T + t} = \alpha. \quad (3)$$

3. An estimate of the order of magnitude of t_m may be obtained from a comparison of the blackening of the photographic plate by a given line, f.i., $\lambda 5350\text{\AA}$ of the fluorescence spectrum of thallium, excited without any, or with some, nitrogen present in the tube.

Photographs of this kind were recently published by the author in the *Physical Review*.⁵ Some of the original negatives were used for a microphotometric comparison carried out by Miss L. Ware from the staff of the Carnegie Mount Wilson Observatory in Pasadena. The originals were made: (1) on the same plate, one below another, (2) under the same conditions of uniform temperature, (3) with the same time of exposure.

Figure 1 shows the "intensity curves" obtained by means of the registering microphotometer of Koch-Babcock, Pettit and Nicholson.⁶ Since the original was a negative the lines are represented by depressions in the curves. Due to reflection and scattering of light from the illuminating arc, all mercury lines appear also on the plate. The thallium lines are indicated by arrows. Each plate contains sections of a curve corresponding to a run through "clear glass" as well as to runs corresponding to "total blackness." These curves help to eliminate the errors due to non-uniformity of the plate itself. The steadiness of the records was tested independently and proved to be trustworthy. Special runs, made through clear glass over the whole length of the plate, coincide exactly with the corresponding sections on the plates used for the measurements. With regard to the approximate character of our estimate of the order of magnitude of t_m no attempt was made to correlate precisely the actual density curve of the negative to the true intensity curve of the spectrum. It is sufficient to regard the ratio α as numerically equal to the ratio of the depressions of the curve corresponding to a given thallium line. The assumptions involved in the derivation of formula (1) allow at any rate only an estimate of the *lower* limit of t_m . The correction, brought in eventually by a precise determination of the relation between the density curve and the intensity distribution (monochromatic intensity marks printed on the same plate!), could evidently affect the result only in one direction, i.e., it would at most increase the value of α .

The curve *A* gives the density curve of the spectrum excited in a tube containing mercury at 0,5 mm. Hg and thallium at saturation pressure.⁷

The curve *B* corresponds to the spectrum excited in a tube which con-

tains mercury at 0,16 mm. Hg, thallium at saturation pressure and nitrogen at 5 mm. pressure.

The time of exposure was in both cases 30 minutes. The constant and uniform temperature of the tubes was 590°C. The comparison shows that the depression of the curve at the point corresponding to $\lambda = 5350\text{\AA}$, is about 9 times deeper in the case when nitrogen is present in the tube. Putting then

$$\alpha = 9; T = 6, 2 \cdot 10^{-7} \text{ sec.}; t = 10^{-7} \text{ sec.}$$

we get

$$t_m > 3,8 \cdot 10^{-4} \text{ sec.}$$

4. It must be remembered, however, that the time t_m is not a "life-time" of the atom in the same sense as the t in $2p_2$ -state is. The time of existence of an atom in the metastable $2p_3$ -state will depend on the number of its collisions with other atoms. These collisions are "effective" not only when the second colliding atom is a normal thallium atom but also in the case when it is a normal mercury atom. We must expect therefore that, since the increase of intensity (α) of thallium fluorescence due to the presence of nitrogen appears relatively weaker when the pressure of the mercury vapor in the illuminated tube is very much higher than that of thallium,⁸ also the time t_m , computed from the result of a comparison of corresponding spectra will come out smaller. Comparing, for instance, the curve *A* with a similar curve registering the spectrum excited in a tube containing mercury at 0,5 mm., nitrogen at 8 mm. and thallium at saturation pressure at the same temperature as before, we find

$$\alpha = 2,6; T = 3,8 \cdot 10^{-7} \text{ sec.}$$

and therefore

$$t_m > 0, 66 \cdot 10^{-4} \text{ sec.}$$

The time t_m being not an atomic constant but a quantity determined by the number of "effective" collisions, it may be expected to change with increasing pressure of thallium. The saturation pressure of thallium increases rapidly with increasing temperature. From less than 0,056 mm. at 590°C. it comes up to 0,45 mm. at 680°C. An analogous comparison of the intensity of the green thallium line excited indirectly in the same tubes at a temperature of 680°C. should lead therefore to smaller values of t_m . Corresponding to a ten-fold number of available thallium atoms the "life-time" of the metastable $2p_3$ -mercury atoms should come out to be about 10 times shorter, and a computation carried through precisely as above checked this conclusion, i.e., it came out of the order $5 \cdot 10^{-5}$ seconds. It must be born in mind, however, that this value is probably too low on

account of the circumstance that the assumption as to the ratio α being an approximate measure of the ratio of intensities will probably not be justified any more under conditions existing at the temperature 680°C .

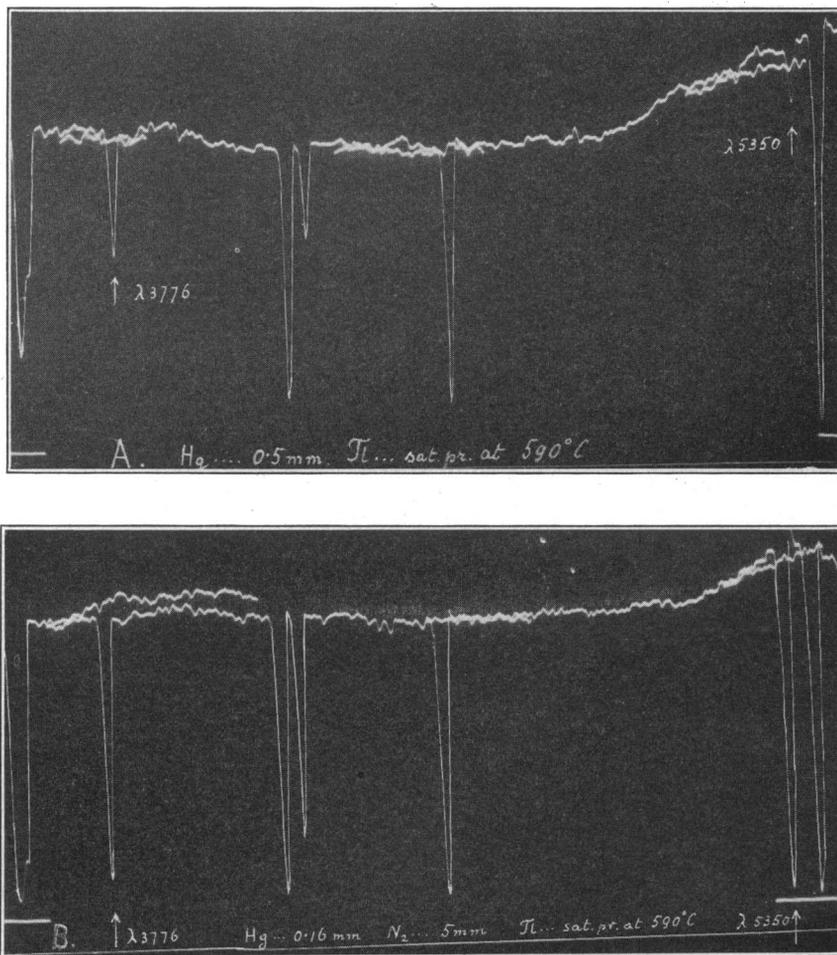


FIGURE 1.

Intensity curves obtained from the negatives by means of a registering microphotometer. A. No gas present in the tube. B. Nitrogen at 5 mm. pressure enhances the intensity of Tl-lines.

5. It is interesting to notice that the order of magnitude of 10^{-4} sec. we obtained above agrees well with the conclusions drawn by H. W. Webb⁹ from experiments of an entirely different nature. He produced the metastable state of mercury atoms at low pressures by electron impacts

of 4,9 volts and measured the persistence of the radiation by means of a photo-electric device. The interpretation of his results is based on the assumption "that the excited atoms remain in a metastable state, carry the energy of excitation to the photo-electric surface and there give it up." The lapse of time between the excitation and the arrival at the plate was about from $1,3 \cdot 10^{-4}$ to $2,8 \cdot 10^{-4}$ sec.

Webb finds it difficult to assign the functions of the carriers of the stored-up energy to the atoms in the $2p_3$ -state and is inclined to regard rather the atoms in the $2p_2$ -state as responsible for the energy transfer. That would mean that also atoms in $2p_2$ -state ought to be regarded as metastable under his experimental conditions—a conclusion hard to reconcile with Bohr's theory and with the results of all indirect measurements of t .

On the other hand, the sensitized fluorescence is always accompanied by a strong resonance of mercury vapor. The presence of this resonance shows conclusively that a relatively large number of activated atoms actually escapes collisions and returns undisturbed to the normal state. The time between collisions of mercury atoms with nitrogen molecules being in our cases $3,8 \cdot 10^{-7}$ sec. and $6,2 \cdot 10^{-7}$ sec., this return could have occurred in average after 10^{-7} sec. as we assumed.

The coincidence of the order of magnitude of our value for t_m with the values found by Webb seems therefore to support the view that also in his experiment rather the atoms in $2p_3$ -state than those in $2p_2$ -state have to be regarded as the metastable ones.

Another attempt to determine the time of existence of the mercury atom in the metastable $2p_3$ -state was made by M. Marshall.¹⁰ He used for this purpose the current potential curves for alternating and intermittent arc obtained by use of a Braun tube. The results lead to a value 10 times higher than the lower limit computed above, i.e., about $5 \cdot 10^{-8}$ sec. It must be pointed out, however, that recently serious objections have been raised¹¹ against the interpretation of the results obtained with the method used by Kannenstine and Marshall.

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¹ W. Wien, *Ann. d. Phys.*, **73**, 483 (1924); R. C. Tolman, *Phys. Rev.*, **23**, 693 (1924); L. A. Turner, *Ibid.*, **23**, 464 (1924); J. A. Eldridge, *Ibid.*, **24**, 234 (1924).

² S. Loria, *Physic Rev.* for November, 1925.

³ Computed by means of the well known formula: $\nu = 2666,6\sigma^2p \sqrt{\frac{2\pi N}{k\theta}} \sqrt{\frac{m+m'}{mm'}}$.

⁴ H. Stuart, *Zeit. f. Phys.*, **32**, 262 (1925).

⁵ S. Loria, *Physic. Rev.* for November, 1925.

⁶ E. Pettit and S. B. Nicholson, *Journ. Opt. Soc. Amer.*, **7**, 195 (1923).

⁷ Less than 0.056 mm. This value was obtained by Villiers (*Ann. d. Chem.*, **30**, 558 (1913)) for 634°C.

⁸ S. Loria, *Physic. Rev.* for November, 1925.

⁹ H. W. Webb, *Physic. Rev.*, **24**, 113 (1924).

¹⁰ M. Marshall, *Astroph. Journ.*, **60**, 243 (1924); F. M. Kannenstine, *Astroph. Journ.*, **55**, 345 (1922); **59**, 133 (1924); *Physic. Rev.*, **19**, 540 (1922); **20**, 115 (1922); **23**, 108 (1924).

¹¹ C. Eckart, *Science*, **61**, No. 1585, 517 (1925).

SOME EXPERIMENTS ON COLLISIONS OF THE SECOND KIND

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The idea of the conversion of kinetic energy into potential energy by a so-called inelastic collision between an electron and an atom had been current for a number of years before Klein and Rosseland¹ showed by thermodynamic reasoning that the reverse process must also occur. According to this principle as extended by Franck,² an excited atom, on return to the normal state, may give up its excess energy either as radiation or as kinetic energy shared with an electron or another atom with which it collides. This idea has already proved extraordinarily fruitful and is supported by a considerable amount of experimental evidence.^{3,4} The evidence is, however, of a rather indirect sort and it therefore occurred to the writer that an attack on the problem from a different angle might be of interest. Some efforts in this direction are described in the present paper.

The Electron Affinity of Iodine.—An iodine atom has an electron affinity of 3.5 volts. That is to say, an electron has a tendency to attach itself to an iodine atom, thereby forming a negative ion and once the ion is formed 3.5 volts work must be done to remove the electron. Thus, the system formed by an iodine atom and an electron at a great distance from it may be considered as having 3.5 volts of potential energy which must be dissipated in some way during the formation of the negative ion. The possibility of radiation arising from this process has been considered by other investigators;⁵ but may not the energy be lost equally well by a collision of the second kind? We know little or nothing of the process of binding of the extra electron, but it seems reasonable to consider it as analogous to the binding of an electron by an ionized atom. If, therefore, one electron comes within the field of a neutral iodine atom and another "collides" with the system so formed before the process of binding the first electron is completed, the second electron may be expected to proceed with increased kinetic energy gained by a collision of the second kind.