INTERACTION OF ATOMIC ENERGY LEVELS—VI

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Introduction and Summary

THE present work is a continuation of the investigations which have already been briefly described in *Current Science*[1] undertaken with the object of finding out the mutual influence of the atoms of two elements on their spectra. The method adopted is a straightforward one: the spectra of the two elements and of their mixture are produced under similar conditions and the relative intensities of the lines of each element in the spectrum of the mixture are compared with the relative intensities of the same lines in the spectra of the individual elements. It is found that some lines are strengthened and others are weakened. Since conditions of temperature, pressure, current, etc., are kept unchanged as far as possible, the alterations in intensity can safely be ascribed to the mutual influence of the two atoms, especially through the medium of impacts of the second kind. Though detailed theoretical knowledge of these phenomena is not available, there are some general principles which are explained, for example, in Mott and Massey's *Theory of Atomic Collisions*, Chap. XIII, 3.3. A good deal of experimental work has been done on the subject of collisions of the second kind; our method has however, the advantage that information can be obtained regarding highly excited levels and a large dispersion can be employed. Here we shall deal with the mutual effect of mercury and lead.

Experimental

In order to produce the spectra required under identical conditions and at the same time be sure that the atoms of the two elements are present in sufficiently large numbers to produce a noticeable effect we have employed a vacuum discharge tube as the source in all our work. The design by one of us (T. S. S.) employed in the present work has proved flexible and adapted to work with various elements. It is illustrated in Fig. 1.

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[1] *Current Science*, 1939, **8**, 508; 1940, **9**, 14; **1940**, **9**, 173; 1941, **10**, 71.

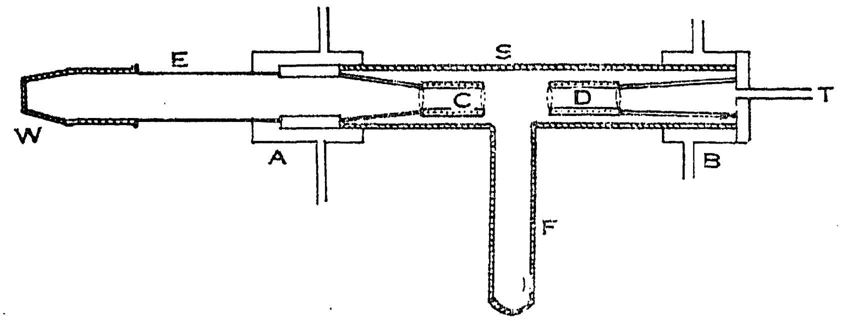

FIG. 1

S is a silica tube with a T-piece F in which the element can be placed. The silica tube has two cylindrical electrodes A and B provided with concentric jackets for water-cooling. The electrodes are fixed to S by means of shellac. Hollow carbon cylinders C and D are attached to the electrodes by means of copper wires. The cylinder B has a side-tube T which is connected to a Cenco Hyvac Pump. The cylinder A has another tube E fixed to it and this tube carries a quartz window W connected to it by a ground joint. This enables the window to be strongly heated now and then to drive off any deposit that may form on it, and thus to be kept transparent. In the case of elements like lead and tin whose boiling point is very high, the metal is also packed into the cylinder D so that the heat of the discharge vaporises it and its lines are strongly excited. Easily vaporised metals like mercury are kept in the side tube F which is heated if necessary. A and B are connected to the secondary of a 3 K.V.A. 4000 volt transformer whose primary is connected to 220-volt mains through suitable rheostats. A concave grating of 10 ft. radius in a Rowland mounting was used to photograph the spectra. Usually exposures of one hour were given when employing hypersensitive panchromatic films. The grating has a dispersion of 5·5 Å per mm. in the first order.

Results

A comparison of the relative intensities of the lines of mercury and lead as they appear in the spectra of the pure metals and in that of their mixture shows that some lines are strengthened and others are weakened as set forth in the table below. The spectra reproduced herewith show some of these alterations in intensity quite clearly but some others can only be clearly perceived in the negatives. Square brackets indicate that the change of intensity is not pronounced.

Lead Lines

Strengthened.	*Weakened*
6059·4 (6p7s $^3P_1^\circ$ — 6p8p 2_0)	[4168·04 (6p^2 $^1D_2$ — 6p6d 1_2°)]
3683·47 (6p^2 $^3P_1$ — 6p7s $^3P_0^\circ$)	4019·64 (6p^2 $^1D_2$ — 6p6d 4_3°)
2833·07 (6p^2 $^3P_0$ — 6p7s $^3P_0^\circ$)	3671·50 (6p^2 $^1D_2$ — 6p8s $^3P_1^\circ$)
[2802·01 (6p^2 $^3P_2$ — 6p6d 4_3°)]	2657·1 (6p^2 $^3P_1$ — 6p6d 1_2°)
2663·17 (6p^2 $^3P_2$ — 6p7s $^3P_2^\circ$)	[2476·38 (6p^2 $^3P_1$ — 6p7s $^3P_2^\circ$)]
2613·66 (6p^2 $^3P_1$ — 6p6d 3_1°)	2446·18 (6p^2 $^3P_1$ — 6p8s $^3P_1^\circ$)
2614·18 (6p^2 $^3P_1$ — 6p6d 2_2°)	2411·75 (6p^2 $^3P_2$ — 6p7d 4_3°)
2577·27 (6p^2 $^3P_2$ — 6p7s $^1P_1^\circ$)	2388·8 (6p^2 $^3P_2$ — 6p7d 3_1°)
	2332·47 (6p^2 $^3P_2$ — 6p9s $^3P_1^\circ$)
	2246·90 (6p^2 $^3P_1$ — 6p7d 1_2°)
	4386·6 Pb II
	4245·0 Pb II

Mercury Lines

Strengthened	*Weakened*
4916·04 (6 $^1P_1$ — 8^1S_0)	
2752·78 (6 $^3P_0$ — 8^3S_1)	5675·86 (7 $^3S_1$ — 9^1P_1)
2464·06 (6 $^3P_0$ — 9^3S_1)	[5460·74 (6 $^3P_2$ — 7^3S_1)]
	[4358·34 (6 $^3P_1$ — 7^3S_1)]
	4046·56 (6 $^3P_0$ — 7^3S_1)
	[2893·60 (6 $^3P_1$ — 8^3S_1)]
	2699·50 (6 $^3P_2$ — 9^3D_2)
	2698·85 (6 $^3P_2$ — 9^3D_3)
	2639·93 (6 $^3P_2$ — 10^3D_1)
	2603·15 (6 $^3P_2$ — 11^3D_1)
	2378·34 (6 $^3P_0$ — 8^3D_1)

Discussion

In order to arrive at an explanation of the observed changes of intensity we have to take into consideration the various possible impacts between lead and mercury atoms in different states and also the probability of transference of excitation energy from one atom to another. Since mercury and lead are both heavy atoms and their size is also large, the result indicated by the theory is that exchange of energy is most probable when there is resonance, *i.e.*, the sum of the internal energies of the lead and mercury atoms before impact is equal to that after impact. We must first consider impacts in which one atom is in the normal and the other in a metastable state and then impacts between two atoms both of which are in metastable states; next in importance will be the impacts between one atom in a metastable state and another in an excited state, the impacts between two excited atoms not in metastable states coming last. Mercury has two metastable levels at 37642 (6 $^3P_0$) and 44040 (6 $^3P_2$) cm.$^{-1}$ respectively and lead has four at 7817, 10648, 21456 and 29456 cm.$^{-1}$ respectively above the ground state. Taking impacts between one normal and one metastable atom, we should expect only two of these to lead to any observable change. One of these is that between a normal lead atom and a metastable mercury atom in the 6 $^3P_2$ state resulting in bringing the lead atom to one of the excited states 6p7p 1_1 (42915), 6p7p 2_0 (44397), 6p7p 3_1(44672), 6p7p 4_2 (44807) or even 6p7d 1_2°(45441), 6p6d 2_2°(46059) and 6p6d 3_1°(46067). The other is an impact between a normal lead atom and a metastable mercury atom in the 6 $^3P_0$ state leading to the lead atom being raised to the 6p7s 3P_1 (35285) or 6p7S 3P_0 (34958) state. These interactions may be put in the form of equations, thus:

$$\text{Pb}\,(^3P_0) + \text{Hg}'\,(^3P_2) \rightarrow \text{Pb}'\,(\cdots) + \text{Hg}\,(^1S_0) \qquad \text{(I)}$$

$$\text{Pb}\,(^3P_0) + \text{Hg}'\,(^3P_0) \rightarrow \text{Pb}'\,(\cdots) + \text{Hg}\,(^1S_0). \qquad \text{(II)}$$

Of the seven possibilities mentioned above in connection with reaction (I) we find only two occurring, *viz.*, those in which the lead atom is raised to the 6p6d 2_2° (46059) and 6p6d 3_1° (46067) states resulting in the strengthening of 2614·18 and 2613·66. Here resonance is not good and there is a large energy discrepancy (2000 cm.$^{-1}$ = 0·25 electron volt) while the other possibilities involving much less discrepancy have not been realised. Here therefore we have an example of the state of affairs which is expected to exist when the interaction between the atoms is strong (*e.g.*, see Mott and Massey, p. 244), but the theory does not seem to be adequate to explain why only this particular possibility should occur. Apart from this, an alternative explanation for the strengthening of 2614 and 2613·7 is possible as shown a little later on. In the case of equation (II), we find both of the possibilities realized, *viz.*,

$$\begin{array}{ccccccc} \text{Pb}\,(^3P_0) & + & \text{Hg}'\,(^3P_0) & \rightarrow & \text{Pb}'\,(6p7s\ ^3P_1^\circ) & + & \text{Hg}\,(^1S_0) \\ 0 & + & 37642 & & 35285 & + & 0 \end{array} \qquad (1)$$

and

$$\begin{array}{ccccccc} \text{Pb}\,(^3P_0) & + & \text{Hg}'\,(^3P_0) & \rightarrow & \text{Pb}'\,(6p7s\ ^3P_0^\circ) & + & \text{Hg}\,(^1S_0) \\ 0 & + & 37642 & & 34958 & + & 0 \end{array} \qquad (2)$$

The first is evidenced by the strengthening of λ 2833 and the second by λ 3683 becoming somewhat stronger. The better resonance represented by (1) is possibly the reason for the greater change of intensity observed in λ 2833.

Now considering impacts between a metastable mercury atom and a metastable lead atom we find that Hg′ ($^3P_0$) + Pb′ ($^3P_1$) = 37642 + 7817 = 45459. This is quite near to 6p6d 1_2° (45441) but somewhat further removed from 6p7p 1_1, 2_0, 3_1, 4_2 and 6p6d $2_2°$, $3_1°$ and $4_3°$, which are at 42915, 44397, 44672, 44807 and 46059, 46067 and 46327 cm.$^{-1}$ respectively. The strengthening of λ 2614 shows, however, that even here the process

$$\text{Hg}'(^3P_0) + \text{Pb}'(^3P_1) \rightarrow \text{Pb}'(6p6d\ 2_2° \text{ or } 3_1°) + \text{Hg}(^1S_0)$$
$$37642 + 7817 \qquad 46059 \text{ or } 46067 + 0$$

which represents a less sharp resonance is the one that probably takes place. The strengthening of λ 2614 may occur by this process as well as by the one already considered in connection with equation (I). The less pronounced strengthening of λ 2802 shows that the process Hg$'(^3P_0)$+ Pb$'(^3P_1)$ = Hg $(^1S_0)$+ Pb$'$(6p6d $4_3°$) also occurs but less frequently. Then we have Hg$'$ $(^3P_0)$+ Pb$'$ $(^3P_2)$ = 37642 + 10648 = 48290. Levels of Pb near this value are 6p8s $^3P_0°$, $^3P_1°$, and 6p7s $^3P_2°$ and $^1P_1°$, whose energies are 48725, 48685, 48187 and 49438 respectively. The strengthening of λ 2663 and λ 2577 shows that of these four possibilities two, *viz.*,

$$\text{Hg}'(^3P_0) + \text{Pb}'(^3P_2) \rightarrow \text{Hg}(^1S_0) + \text{Pb}'(6p7s\ ^3P_2°)$$
$$37642 + 10648 \qquad 0 + 48187$$

and $$\text{Hg}'(^3P_0) + \text{Pb}'(^3P_2) \rightarrow \text{Hg}(^1S_0) + \text{Pb}'(6p7s\ ^1P_1°)$$
$$37642 + 10648 \qquad 0 + 49438$$

are realised. The first of these represents very close resonance, but why the second should occur in preference to the other two possibilities mentioned is not clear.

Next we have Hg$'$ $(^3P_0)$+Pb$'$ $(^1D_2)$ = 37642 + 21456 = 59098 and this is near the ionization energy of Pb, *viz.*, 59821. The weakening of the Pb II lines λ 4387 and λ 4245 shows that ionization of Pb does not occur with greater frequency, but that the process probably takes place in the reverse direction.

The addition of the energies of Hg$'$ $(^3P_0)$ and Pb$'$ $(^1S_0)$ gives 37642 + 29456 = 67098 which is 7277 cm.$^{-1}$ above the ionization energy of Pb.

Taking the other metastable level of Hg we have Hg$'$ $(^3P_2)$ + Pb$'$ $(^3P_1$, $^3P_2$, $^1D_2$ and $^1S_0)$ = 51857, 54688, 65496 and 73496 respectively. The strengthening of λ 6059 shows that the first of these representing a close resonance leads to the production of Pb$'$ (6p8p 2_0) which is = 51784. Thus Hg$'$ $(^3P_2)$ + Pb$'$ $(^3P_1)$ = Hg $(^1S_0)$ + Pb$'$ (6p8p 2_0). There are two levels of Pb—6p8p 3_1 and 1_1—equal to 51915 and 51318 which have nearly the same energy but we find no evidence of these being excited by the above process. Although there are a number of levels of Pb near 54688 we have found no change in any lines involving them. The third process leads to ionization of Pb. The fourth process is probably concerned partly in the production of Hg′ (8^1S_0) and Hg′ (8^3S_1)—of energies 74402 and 73959—as evidenced by the strengthening of the Hg lines λ 4916 and 2753.

Having completed the consideration of impacts between two metastable atoms we may now take up impacts between one metastable atom and another excited atom. The number of different possibilities will here be very large. We will therefore confine ourselves only to such instances as can lead to the observed changes of intensity. We cannot at present explain why other interactions which seem equally probable do not occur. An exhaustive consideration of all the possibilities will be of use only when very slight changes of intensity can also be detected by means of microphotometer curves. Hence taking only those processes which seem to be involved in the observed changes of intensity we can write down the following equtions:

$$\begin{array}{ccccccc} Hg'\,(7^3S_1) & + & Pb'\,(^3P_2) & \rightarrow & Hg'\,(8^1S_0) & + & Pb\,(^3P_0) \\ 62348 & + & 10648 & & 74402 & + & 0 \end{array}$$

This process requires not only that Hg′ (8^1S_0) must be produced, as evidenced by the strengthening of 4916, but also that Hg′ (7^3S_1) must be destroyed which leads to the weakening of λ 5461, 4358 and 4047. All these changes, *viz.*, the weakening of 5461, 4358 and 4047 are observed.

Next take

$$\begin{array}{ccccccc} Hg'\,(7^3P_1) & + & Pb'\,(^3P_1) & \rightarrow & Hg'\,(9^3S_1) & + & Pb\,(^3P_0) \\ 69659 & + & 7817 & & 78214 & + & 0 \end{array}$$

$$\text{or}\quad \begin{array}{ccccccc} Hg'\,(7^3P_2) & & Pb'\,(^3P_1) & \rightarrow & Hg'\,(9^3S_1) & + & Pb\,(^3P_0) \\ 71205 & + & 7817 & & 78214 & + & 0 \end{array}$$

We cannot decide which of these two occurs. Either of these can explain the strengthening of Hg 2464.

Considering the interaction between an excited and a normal atom we find that the following reactions probably take place.

$$\begin{array}{ccccccc} Hg\,(^1S_0) & + & Pb'\,(6p6d\ 1_2{}^\circ) & \rightarrow & Hg'\,(^3P_2) & + & Pb\,(^3P_0) \\ 0 & + & 45441 & & 44040 & + & 0 \end{array}$$

This explains why λ 2657 and 4168 of Pb are weakened.

Partly also the reaction

$$\begin{array}{ccccccc} Hg\,(^1S_0) & + & Pb'\,(6p6d\ 4_3{}^\circ) & \rightarrow & Hg'\,(^3P_2) & + & Pb\,(^3P_0) \\ 0 & + & 46327 & & 44040 & + & 0 \end{array}$$

may occur since λ 4020 of Pb is weakened. Otherwise the weakening of these lines may be brought about according to the equations:—

$$Hg'(^3P_0) + Pb'(6p6d\ 1_2{}^\circ) \rightarrow Hg^+ + Pb\ (^3P_0)$$
$$37642 \ + \ 45441 \qquad 84179 + \ 0$$
and
$$Hg'(^3P_0) + Pb'(6p6d\ 4_3{}^\circ) \rightarrow Hg^+ + Pb\ (^3P_0)$$
$$37642 \ + \ 46327 \qquad 84179 + \ 0$$

leading to the ionization of the mercury atom. Exactly in the same way the energies of Pb 6p8s $^3P_1{}^\circ$ and 6p7s^3 $P_2{}^\circ$ may ionize the mercury atom starting from the 6^3P_0 state. This will explain the weakening of λ 3672, 2446 and 2476.

We also have the processes

$$Hg\ (^1S_0) + Pb'\ (6p7d\ 4_3{}^\circ,\ 3_1{}^\circ,\ 1_2{}^\circ \text{ or } 6p9s^3P_1) \rightarrow Hg'\ (^1P_1) + Pb\ (^3P_0)$$
$$0 \ + \ 52100, 52498, 52309 \text{ or } 53508 \qquad 54066 \ + \ 0$$

involving the weakening of the lines 2412, 2389, 2247 and 2332 of Pb.

Since the energies of the upper states of the weakened mercury lines are higher than the ionization energy of lead we must either assume that they excite some level of ionized lead or that in an impact with a lead atom the mercury atom is brought to some intermediate level, the excess of energy raising the lead atom to some excited level.

Since the levels nearest to $^2P_2$ of Pb II are at distances of 14081, 69740, 68964, 92514 and 92529 cm.$^{-1}$ from it, none of these can be resonantly excited by the upper states of the weakened Hg lines. Hence the second alternative seems to be the only one left. Here the intermediate state to which the Hg atom falls seems to be arbitrary. But in the following we have suggested processes which can explain the observed strengthening of some lead lines or which at least do not require any alteration of intensity which does not occur according to our observations.

$$Hg'\ (8^3S_1) + Pb\ (^3P_0) \rightarrow Hg'\ (6^3P_0) + Pb'\ (6p7s\ ^3P_1{}^\circ)$$
$$73959 \ + \ 0 \qquad 37642 \ + \ 35285$$
or
$$Hg'\ (8^3S_1) + Pb\ (^3P_0) \rightarrow Hg'\ (6^3P_1) + Pb'\ (6p7s\ ^3P_1{}^\circ) \text{ or } Pb'\ (6p7s\ ^3P_0{}^\circ)$$
$$73959 \ + \ 0 \qquad 39410 \ + \ 35285 \quad \text{or} \quad 34958$$

This explains the weakening of λ 2894 of Hg and the strengthening of 2833 or 3683 of Pb.

$$Hg'\ (8^3D_1) + Pb\ (^3P_0) \rightarrow Hg'\ (^3P_2) + Pb'\ (6p7s\ ^3P_1{}^\circ)$$
$$79676 \ + \ 0 \qquad 44040 \ + \ 35285$$

This explains the weakening of λ 2378 of Hg and the strengthening of λ 2833 of Pb. For the weakening of 5676, 2700, 2699 of Hg we have

$$Hg'(9^1P_1) + Pb(^3P_0) \rightarrow Hg'(^3P_2) + Pb'(6p7s\ ^3P_1^{\circ})$$
$$79961 + 0 \quad 44040 + 35285 \; ;$$
$$Hg'(9^3D_2) + Pb(^3P_0) \rightarrow Hg'(^3P_2) + Pb'(6p7s\ ^3P_1^{\circ})$$
$$81074 + 0 \quad 44040 + 35285 \; ;$$
and
$$Hg'(9^3D_3) + Pb(^3P_0) \rightarrow Hg'(^3P_2) + Pb'(6p7s\ ^3P_1^{\circ}) .$$
$$81082 + 0 \quad 44040 + 35285$$

For the weakening of 2640 and 2603 of Hg we may have either

$$Hg'(10^3D_1) + Pb(^3P_0) \rightarrow Hg'(^3P_0) + Pb'(6p6d\ 2_2^{\circ})$$
$$81899 + 0 \quad 37642 + 46059$$
and
$$Hg'(11^3D_1) + Pb(^3P_0) \rightarrow Hg'(^3P_0) + Pb'(6p6d\ 2_2^{\circ})$$
$$82439 + 0 \quad 37642 + 46059$$

involving an explanation of the strengthening of λ 2614 of Pb; or we may have

$$Hg'(10^3D_1, 11^3D_1) + Pb(^3P_0) \rightarrow Hg'(^1P_1) + Pb'(^1S_0)$$
$$81899, 82439 + 0 \quad 54066 + 29456,$$

which cannot be tested by alteration of intensity of any line within the region of our observation.

Concluding, we may say that the experiments prove the existence of an exchange of energy at impact which is subject to a law of resonance, but until quantitative intensity measurements are made, it is not possible to test all the processes suggested above as possible explanations of the observed changes of intensity.

Finally, we have great pleasure in thanking Prof. A. Venkat Rao Telang, for the many facilities placed at our disposal.

Plate VI will appear in a later issue of the *Proceedings*.