

(4th row of Table I). Besides such a reversal of intensities, it may be noted that the low frequency lines exhibit polarisation features which may be regarded as reciprocal in character to those exhibited by the total symmetric oscillation. The figures given in Table I clearly support these conclusions.

The author has not been able to record the other weaker lines due to internal oscillations in the case of calcite but a few remarks about these will not be out of place here. A detailed analysis of the normal oscillations² shows that these are degenerate and come under the same category as the low frequency lines. Their behaviour should accordingly be akin to the low frequency lines rather than to the total symmetric oscillation. Contrary to this expectation, Nedungadi concludes that all the internal oscillations behave in a like manner. His pictures however show that while this is true in the matter of polarisation, it is not so if we consider the aggregate intensities. It is clear from Figs. 3a and c of his paper, which are intended to show this effect, that only the total symmetric oscillation becomes weak whereas the degenerate oscillation at 1385 as well as the low frequency lines remain quite intense. Figs. 6c and d of Nedungadi taken together also show the similarity between the low frequency lines and the degenerate internal oscillations in the matter of aggregate intensities. A detailed account of the results along with a fuller discussion of the same will appear elsewhere in due course.

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¹ *Proc. Ind. Acad. Sci.*, 1939, 10, 197.

² *Ibid.*, 1939, 9, 224.

Interaction of Atomic Energy Levels

THE mutual influence of different elements on their spectra due to mixture has not yet been studied in a systematic way, although there are a large number of papers dealing with the

influence of the rare gases on the spectra of several elements. The effect of introducing gases like hydrogen and nitrogen has also been studied to a certain extent. With the object of securing more extensive data regarding the changes produced in the spectra of elements by mixing them, we have first of all studied the effect of mixing zinc and mercury. The discharge from a 3 KVA, 2000 volt transformer was passed through a Pyrex tube containing mercury and zinc in two side limbs provided with tungsten electrodes and kept continuously evacuated by a Hyvac pump. The tube had a quartz window through which the discharge could be viewed end on. The light from the discharge was focussed on the slit of a concave grating of 10-foot focus in a Rowland mounting by means of quartz lenses. To distinguish between first and second order lines a thin glass plate was fixed across half the slit so that in the spectrogram the second order lines were shorter than the first order ones. Zinc of analytical reagent class was used as also another variety from De Haen which showed a slightly larger quantity of mercury as an impurity. Spectrograms were obtained with pure zinc and with a mixture of zinc and mercury so as to exhibit the same intensity in the case of the visible zinc triplet, and conclusions were based on a comparison of the intensities of other lines relative to these in the two spectrograms. A vacuum arc was produced in the same tube by connecting the two side limbs to 110 volts D.C. and having a third electrode which served to start the arc in the zinc vapour by means of a small induction coil connected to it and to one of the other electrodes. The spectrum of the arc was found to be almost identical with that of the discharge, except that the arc was much brighter. The spectra were photographed on Ilford hypersensitive panchromatic films and second order lines in the case of the discharge appeared with sufficient intensity after exposures of about an hour. A discharge through HgCl₂ vapour had previously been studied and the relative intensities of the mercury lines in the mixture were compared with the relative

intensities of the same lines in the HgCl_2 film. The following are the main results obtained:

1. The lines 3072 ($4\ ^3\text{P}_2 - 6\ ^3\text{S}_1$), 3036 ($4\ ^3\text{P}_1 - 6\ ^3\text{S}_1$) and 3018 ($4\ ^3\text{P}_0 - 6\ ^3\text{S}_1$) of zinc were very weak in both the arc and the discharge as compared with the resonance line

occurs in the case of 2568 ($4\ ^3\text{P}_2 - 8\ ^3\text{S}_1$), 2570 ($4\ ^3\text{P}_0 - 6\ ^3\text{D}_1$), 2583 ($4\ ^3\text{P}_1 - 6\ ^3\text{D}_2$), 2684 ($4\ ^3\text{P}_1 - 7\ ^3\text{S}_1$) and 2712 ($4\ ^3\text{P}_2 - 7\ ^3\text{S}_1$). 5182 ($4\ ^1\text{P}_1 - 6\ ^1\text{S}_0$) remains unaffected.

4. The mercury lines 2753 ($6\ ^3\text{P}_0 - 8\ ^3\text{S}_1$), 2894 ($6\ ^3\text{P}_1 - 8\ ^3\text{S}_1$) and 3342 ($6\ ^3\text{P}_2 - 8\ ^3\text{S}_1$) showed a definite increase in intensity as compared with the same lines produced by the discharge through HgCl_2 , while 3663 ($6\ ^3\text{P}_2 - 6\ ^1\text{D}_2$ and $6\ ^3\text{P}_2 - 6\ ^3\text{D}_1$), 3655 ($6\ ^3\text{P}_2 - 6\ ^3\text{D}_2$) and 3650 ($6\ ^3\text{P}_2 - 6\ ^3\text{D}_3$) showed only a slight increase. 3132 ($6\ ^3\text{P}_1 - 6\ ^1\text{D}_2$ and $6\ ^3\text{P}_1 - 6\ ^3\text{D}_1$) and 3126 ($6\ ^3\text{P}_1 - 6\ ^3\text{D}_2$) seemed to be unaffected.

5. The only spark line of zinc, 2558 ($4\ ^2\text{P}_{3/2} - 5\ ^2\text{S}_{1/2}$), and of mercury, 3984 ($5\text{d}^96\text{s}^2\ ^2\text{D}_{3/2} - 5\text{d}^{10}6\text{p}\ ^2\text{P}^0_{3/2}$) occurring in the discharge used, disappeared in the mixture.

The brightening of 3076 must be due to collisions of the second kind between mercury atoms in the $6\ ^3\text{P}_1$ state (energy 4.86 volts) and normal zinc atoms. According to Larché² the optimum excitation potential of 3076 is 4.9 volts. This explanation is also in accord with the fact that the spectrum of zinc given by Lord

3076 ($4\ ^1\text{S}_0 - 4\ ^3\text{P}_1$), whereas in the spectrogram given in Fowler's Report 3072 is brighter than 3076. This was true both in pure zinc and in the mixture. The intensities of these lines given by Hetzler, Boreman and Burns¹ show that this peculiarity is characteristic of the vacuum arc itself.

2. In the discharge through pure zinc 3076 was weaker than 3345 ($4\ ^3\text{P}_2 - 4\ ^3\text{D}_{2,3}$) and 3302 ($4\ ^3\text{P}_1 - 4\ ^3\text{D}_2$), but in the mixture it was stronger. Hetzler, Boreman and Burns who used an arc in vacuum between brass electrodes find 3076 weaker than 3345 and 3302. We find

that 3076 brightens considerably with even small amounts of mercury, and possibly also with other impurities.

3. The zinc lines 2464 ($4\ ^3\text{P}_2 - 8\ ^3\text{D}_3$), 2480 ($4\ ^3\text{P}_0 - 7\ ^3\text{D}_1$), 2492 ($4\ ^3\text{P}_1 - 7\ ^3\text{D}_2$) and 2516 ($4\ ^3\text{P}_2 - 7\ ^3\text{D}_3$) decrease considerably in intensity in the mixture as compared with pure zinc. 2609 ($4\ ^3\text{P}_2 - 6\ ^3\text{D}_3$) and 2671 ($4\ ^3\text{P}_0 - 7\ ^3\text{S}_1$) also decrease in brightness to about a similar extent. A smaller decrease in intensity

Rayleigh,³ who distilled zinc vapour into a cadmium arc, shows 3076 weaker than 3072 itself. The energy of the $5\ ^3\text{P}_1$ state in cadmium is only 3.78 volts.

The weakening of 2464, 2480, 2492 and 2516 must be due to the impoverishment of the $8\ ^3\text{D}$ and $7\ ^3\text{D}$ zinc atoms (energy 9.06 and 8.96 volts by interaction with mercury atoms in the $8\ ^3\text{S}_1$ state (energy 9.12 volts) since 2753, 2894 and 3342 of mercury show

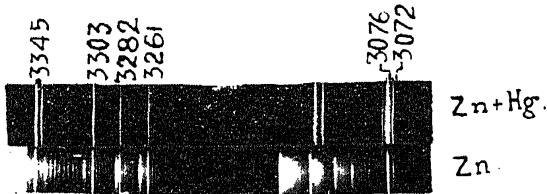


FIG. 1

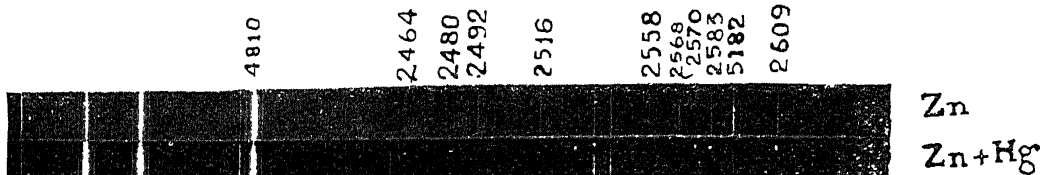


FIG. 2

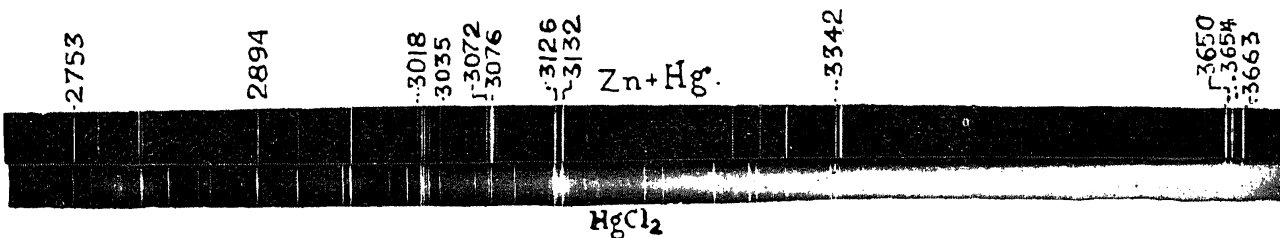


FIG. 3

an increase in intensity. The fact that the 6^3D states of mercury (energy 8.80 volts) do not show any marked enrichment at the expense of the 6^3D states of zinc (energy 8.79 volts) shows that such an interaction does not depend merely on the nearness of their energies. We may surmise that electrons first take up energy from the 8^3D and 7^3D zinc atoms and then enrich the 8^3S_1 mercury states.

The work is proceeding; further details will be published elsewhere.

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¹ *Phys. Rev.*, 1935, 48, 656.

² *Zeit. f. Phys.*, 1931, 67, 440.

³ *Proc. Roy. Soc.*, (A), 1926, 112, 14.

Sound Velocity and Inter-Molecular Forces

IN recent years the velocity of sound has been determined with precision in a large number of liquids using ultrasonic waves.¹ The velocity of sound in a liquid is determined by the molecular arrangement in the liquids and the nature of the inter-molecular forces. It is found that in general the velocity of sound decreases with rise in temperature. A study of these shows that the ratio of the relative temperature co-

efficient of sound velocity to the coefficient of molar volume expansion is constant for a number of non-associated liquids. The mean value for the constant is found to be -3.03 . Thus

$$\frac{\frac{1}{v} \frac{dv}{dt}}{\frac{1}{V} \frac{dV}{dt}} = -3.03,$$

where v is the velocity of sound in the liquid at temperature t and V the molar volume of the liquid. On integrating the above expression

$$vV^{3.03} = \text{constant}$$

$$v^{0.33}V = \text{constant}.$$

Table I gives the values of the velocity of sound and density at various temperatures. The molecular volume V multiplied by $v^{0.33}$ is found to be a constant over the entire temperature range for which values are available. In Table I values for only two liquids are given but the relation holds good for a number of other liquids like octane, heptane, chloroform and carbon tetrachloride.

Table II gives the values of the constant $R = v^{0.33}V$ for a number of liquids and also the molecular critical volume V_c . It is found that the ratio of the constant R to the molecular critical volume V_c of a given compound has an almost constant value of 3.53 for all substances.

Since the molecular volume is proportional to the cube of the inter-molecular distance it follows from $R = v^{0.33}V$ that the velocity of sound in a liquid varies inversely as the ninth

TABLE I

Benzene				Toluene			
Temperature	Velocity (m./s)	Density	$v^{0.33}V = R$	Temperature	Velocity (m./s)	Density	$v^{0.33}V = R$
10	1375	.8896	951	0	1414	.8848	1141
20	1324	.8790	951.5	10	1370.5	.8752	1140
30	1278	.8684	952.1	20	1327.5	.8657	1140
40	1231	.8576	953	30	1284.5	.8563	1141
50	1184	.8467	951.9	40	1242.0	.8470	1141
..	50	1199	.8378	1140