Printed at
Rajasthan Printing Works,
JAIPUR.

UNIVERSITY OF RAJPUTANA
STUDIES

PHYSICAL SCIENCES
(including Mathematics & Engineering)

1947

JAIPUR.
1951

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CONTENTS

A THEOREM ON THE GENERALISED LAPLACE'S TRANSFORM.

By

S. P. Kaushik, Ph. D, Bikaner.

On the Laplace's Transform introduced by Dr. R. S. Verma at the Indian Science Congress, 1945, I gave in my paper (Proc., Benares Math. Soc. Vol. VIII Part I, June, 1946) a theorem valid under certain conditions, givings $\psi\ (p)$, the Laplace Transform of $\phi_{k\,m}(x)$ in the form of an integral, involving $f(x)$ where $\phi_{k\cdot m}(p)$ is a Whittaker Transform of $f(x)$.

The object of this paper is to give the Hankel transform of $\phi_{k,m}(p)$ where $\phi_{k,m}(p)$ is the Whittaker Transform of $f(x)$, i. e. when

$$\phi_{k,m}(p) = p\int_{0}^{\infty} (2xp)^{-\frac{1}{4}}\, \mathrm{W}_{k,m}(2xp)\, f(x)\, dx \qquad (1)$$

The Hankel transform of $\phi_{k,m}(p)$ is obviously

$$\mathrm{I} = \int_{0}^{\infty} \phi_{k,m}(p)\ \sqrt{yp}\ \mathrm{J}_{r},(yp)\, dp$$

It follows from (1) that the required Hankel transform is

$$\mathrm{I} = \int_{0}^{\infty} p\ \sqrt{yp}\ \mathrm{J}_{r}(yp)\, dp \int_{0}^{\infty} (2rp)^{-\frac{1}{4}}\, \mathrm{W}_{k,m}(2xp)\, f(x)\, dx \qquad (2')$$

$$= \frac{\sqrt{y}}{2^{\frac{1}{4}}}\int_{0}^{\infty} x^{-\frac{1}{4}}\, f(x)\, dx \int_{0}^{\infty} p^{\frac{5}{4}}\, \mathrm{W}_{k,m}(2xp)\, \mathrm{J}_{r}(yp)\, dp \qquad (2)$$

on changing the order of integration.

Evaluating the last integral with the help of Goldstein's result[2]

$$\int_0^\infty x^{l-1} e^{-(a^2, + \frac{1}{2})x} W_{k,m}(x)\, dx$$

$$= \frac{\Gamma(l+m+\frac{1}{2})\,\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)}\; {}_2F_1\left[\begin{matrix} l+m+\frac{1}{2},\; l-m+\frac{1}{2}; \\ l-k+1 \end{matrix} -a^2\right]$$

$$R(l \pm m+\tfrac{1}{2}) > 0 \qquad a \mid I(a) \mid \angle 1$$

we get the Hankel transform of $\phi_{k,m}(p)$ as the function

$$\frac{Y^{v+\frac{1}{2}}}{2^{2v}+\frac{5}{2}} \int_0^\infty \frac{1}{x^v+\frac{5}{2}} f(x) \sum_{\gamma=0}^{\infty} \frac{\Gamma(v+2\gamma+m+\frac{11}{4}).\,\Gamma(v+2\gamma-m+\frac{11}{4})}{\Gamma(v+2\gamma-k+\frac{13}{4})}$$

$$\times\; {}_2f_1\left[\begin{matrix} v+2\gamma+m+\frac{11}{4},\; v+2\gamma-m+\frac{11}{4} \\ ;\,\frac{1}{2} \\ v+2\gamma+\frac{13}{4}-k \end{matrix}\right] \times \frac{(-1)^r \quad (\frac{1}{2}y)^{2r}}{\gamma!\,\Gamma(v+\gamma+1)(2x)^{2r}}\, dx \tag{3}$$

If we use the integral representation[3]

$$\frac{\Gamma(b)\;\Gamma(c-b)}{\Gamma(c)}\; {}_2F_1\left[a, b; c; z\right] = \int_0^1 t^{b-1}(1-t)^{c-b-1}(1-zt)^{-a}\, dt$$

to abbreviate the infinite series in (3) above, we get after some reduction, the Hankel transform of $f(x)$ to be a double integral,

$$\frac{y^{v+\frac{1}{2}}\;\Gamma\left(v+m+\frac{11}{4}\right)\Gamma\left(\frac{v}{2}+\frac{m}{2}+\frac{11}{8}\right)\Gamma\left(\frac{v}{2}+\frac{m}{2}+\frac{15}{8}\right)}{2^{2v+\frac{5}{2}}\;\Gamma(m-k+\frac{1}{2})\;\;\Gamma(v+1)}$$

$$\times \int_0^\infty \int_0^1 \frac{f(x)}{x^{v+\frac{5}{2}}}\; {}_2F_1\left[\begin{matrix}\frac{v}{2}+\frac{m}{2}+\frac{11}{8}, \frac{v}{2}+\frac{m}{2}+\frac{15}{8}; -\frac{y^2\,t^2}{4x^2}(1-\frac{1}{2}t)^{-2} \\ v+1 \end{matrix}\right]$$

$$\times \left\{ t^{v-m+\frac{7}{4}}\; (1-t)^{m-k-\frac{1}{2}} \left(1-\frac{1}{2}t\right)^{-(v+m+\frac{11}{4})} \right\} dx.\, dt \ldots\ldots\ldots\ldots\ldots \text{(iv)}$$

Next we have to justify the change in the order of integration.

Assume that

$$\theta(x) = \frac{\sqrt{y}}{2^{\frac{1}{4}}}\, x^{-\frac{1}{4}} f(x) \int_0^\infty p^{\frac{5}{4}}\, W_{k,m}(2xp)\, J_v(yp)\, dp,$$

If we take

$$f(x)=O(x^{\mu}), \qquad x \to 0 \tag{7}$$

then since[4]

$$W_{k,m}(x) = O(x^{\pm m+\frac{1}{2}}) \quad \text{as} \quad x \to 0 \tag{8}$$

and $\quad J_v(z) = O(z^{-\frac{1}{2}}) \quad$ and $\quad W_{k,m}(z) = O(e^{-\frac{1}{2}z} z^k)$

as $|z| \to \infty$

$\theta(x)$ convergse uniformly for $x \geqslant 0$ when

$$R(\mu \pm m+\tfrac{1}{4}) > 0 \text{ and } \quad R(v \pm m+\tfrac{11}{4}) > 0.$$

Again consider

$$\phi(p)=\frac{\sqrt{y}}{2^{\frac{1}{4}}} p^{\frac{5}{4}} J_v(yp) \int_0^{\beta} x^{-\frac{1}{4}} f(x) \quad W_{k,m}(2xp)dx.$$

where β is small.

On account of (7) and (8), $\phi(p)$ converges uniformly for $p \geqslant 0$ when $R(v \pm m+\frac{7}{4})>0$, adn $R(\mu \pm m+\frac{5}{4})>0$.

Lastly the integral

$$\frac{\sqrt{y}}{2^{\frac{1}{4}}} \int_T^{\infty} \left| x^{-\frac{1}{4}} f(x) \right| dx \int_{T'}^{\infty} \left| p^{\frac{5}{4}} W_{k,m}(2xp) J_v(yp) \right| dp$$

where T' and T'' are large, does not exceed a constant multiple of

$$\frac{\sqrt{y}}{2^{\frac{1}{4}}} \int_T^{\infty} \left| x^{k-\frac{1}{4}} f(x) \right| dx \int_{T'}^{\infty} \left| p^{\frac{5}{4}} e^{-xp} J_v(py) \right| dp$$

The last expression certainly tends to zero when T' and T'' both tend to infinity, provided that $f(x) = O(1)$ for large x.

It follows that our result is true when $R(\mu \pm m+\frac{1}{4})>o$, $R(v \pm m+\frac{7}{4})>0$ and $f(x)=O(1)$ for large x and $f(x)=O(x^{\mu})$ for small x.

REFERENCES

1. S. P. Kaushik: A theorem on the generalised Laplace's transform.—Proc., Benares Math. Soc. Vol. VIII Part I, June, 1946.

2. S. Goldstein: Operational representation of Whittaker's Confluent hypergeometric function and Weber's parabolic cylinder function, Proc. Lond. Math. Soc. (2). Vol. 34 (1932), 103—25.

3. Whittaker and Watson: Modern Analysis (1935) p. 293.

4. Ibid, p. 343 and p. 368.

DIAMAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE IN BICARBONATES AND NITRATES

By

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Abstract—The principal susceptibilities of bicarbonates of potassium and ammonium and nitrates of silver and ammonium have been measured and correlated with the known fine sturcture studies on them.

Introduction

In an important paper Krishnan and Raman (1927) pointed out that the magnetic anisotropy of crystals could be attributed to the intrinsic anisotropy of the molecules of which the crystals were built up. When these constituent molecules are all oriented parallel to each other the crystal anisotropy will be the same as the individual molecules, otherwise crystal anisotropy will be less than the individual molecules, In other words the magnitude of the anisotropy of the crystal will depend on the anisotropy of the individual molecules and their orientations relative to one another. It was indicated by Krishnan (1929) that if by some means the molecular anisotropy was known it should be possible to obtain very valuable information about molecular orientations in crystals by a comparison with the observed anisotropy of the crystal. In subsequent papers Krishnan and Banerji (1935) and Banerji (1938) studied the magnetic properties of a large number of aromatic compounds viewed in the light of their structures.

The present communication reports the magnetic measurements on some inorganic ions in crystals, for which X-ray studies are available and discussed in relation to their known crystal structure.

Experimental

Crystal were grown out of aqueous solution. Chemicals used were of analytical variety.

Magnetic measurements involve (1) the determination of the direction of principal magnetic axes (2) the measurements of the differences between principal susceptibilities and (3) the measurement of absolute susceptibility along any one convenient direction.

The determination of the axial directions and the magnetic anisotropy were carried out by the method of Krishnan and Banerji (1935).

Absolute susceptibilities were determined by the method as developed by Datta (1944). These values combined with anisotropy values gave the principal susceptibilities.

Results

Results of measurements are collected in tables I and II and expressed in the usual units i. e. 10^{-6} of c. g. s. e. m. u. For a rhombic crystal x_a, x_b and x_c denote the gram molecular susceptibilities along the three crystallographic axes a, b, and c respectively; for a monoclinic crystal x_3 is the gram molecular susceptibility along 'b' axis, while greater of the two in the symmetry plane (010) is denoted by x_1, and the smallar by x_2. θ is the angle which χ_2 makes with 'a' axis and ϕ that between χ_1 and 'c' axis; $\bar{\chi}$ denotes the mean of the three principal susceptibilities and is given by

$$\frac{\chi_a+\chi_b+\chi_c}{3} \quad \text{or} \quad \frac{\chi_1+\chi_2+\chi_3}{3}$$

as the case may be. Pascal's additive law values were from Stoner's book 'Magnetism and Matter (1934).'

TABLE I

Anisotropy

The unit adopted for χ is 10^{-6} of a c. g. s. E. M. U.

Crystal	Crystallo-graphic data	Mode of suspension	Orientation in the field	$\Delta\chi$ x10^6	Magnetic anisotropy x 10^6
NH_4HCO_3	Ortho-rhombic V_p^{10} z=8 a=7·29 A b=10·79 A c=8·76 A	'a' axis vertical	'b' axis along field	0·52	$\chi_b-\chi_a=5·00$
		'c' axis vertical	'b' axis along field	5·00	$\chi_b-\chi_c=0·52$
		'b' axis vertical	'c' axis along field	4·50	cal $\Delta\chi=4·50$
$KHCO_3$	Monocl. C_{2h}^5 z=4 a=15·01 A b=5·69 A c=3·68 A $\beta=104·8$	'b' axis vertical	$\theta=-42·2$	2·90	$\chi_1-\chi_2=2·9$
		'a' axis vertical	'b' axis along field	·70	$\chi_1-\chi_3=0·6$ $\phi=+56·7°$
		(001) plane horizontal	'b' axis along field	1·00	Cal $\Delta\chi=1·0$
NH_4NO_3	ortho-rhombic V_h^{13} z=2 a=5·75 A b=5·545 A c=4·96 A	'a' axis vertical	'c' axis along field	5·45	$\chi_c-\chi_b=5·45$
		'b' axis vertical	'c' axis along field	0·39	$\chi_c-\chi_a=0·39$
		'c' axis vertical	'a' axis along field	5·05	Cal $\Delta\chi=5·06$
$AgNO_3$	rhombic z=8 a=6·97 A b=7·34 A c=10·14 A	'a' axis vertical	'c' axis along field	3·41	$\chi_c-\chi_b=3·41$
		'c' axis vertical	'a' axis along field	1·07	$\chi_a-\chi_b=1·07$
		'b' axis vertical	'c' axis along field	2·34	Cal $\Delta\chi=2·34$

TABLE II

Absolute susceptibility.

No.	Crystal	direction along which sus. was mesured	Density of the crystal	Volume suscep- tibility.	Corresponding gm. mol susceptibility.	Principal susceptibilites.	MEAN SUSCEP ($\bar{x}$)	
							Our value.	Pascal's value.
1	NH_4HCO_3	along b-axis	1·512	-0·731	-38·2	$x_a = -43\cdot2$ $x_b = -38\ 2$ $x_c = -38\cdot7$	-40·0	-40·6
2	$KHCO_3$	along x_1-axis	2·168	-0·962	-44·4	$x_1 = -44\cdot4$ $x_2 = -47\cdot3$ $x_3 = -45\cdot0$	-45·6	-44·7
3	NH_4NO_3	along c-axis	1·721	-0·603	-28·1	$x_a = -\ 28\cdot5$ $x_b = -33\ 5$ $x_c = -28\cdot1$	-30·1	-28·6
4	$AgNO_3$	along c-axis	4·352	-1·098	-42·9	$x_a = -45\cdot2$ $x_b = -46\ 3$ $x_c = -42\cdot9$	-44·88	-45·2

Discussion

We now proceed to discuss the results in the previous sections in relation to x-ray data concerning the structure of the crystals.

Ammonium-bi-carbonate (NH_4HCO_3)–It crystallises in the orthorhombic system. Its structure has been analysed by Mooney (1932) by x-ray methods. He finds that there are eight molecules in the unit cell; the dimensions of the CO_3 groups are the same as in the normal carbonates ie., CO_3 group has the shape of an equilateral triangle with three oxygens at the three vertices and carbon atom at the geometric centre of the triangle, and that all the CO_3 groups are oriented with their planes parallel to the crystallographic plane a (100).

Let $K_{\|}$ denote the principal susceptibility of the CO_3 group along directions normal to the plane of the triangle and $K_{\perp}$ that along directions in the plane of the triangle. Evidently $K_{\|}$ is greater than $K_{\perp}$ algebraically. From the proposed structure since the CO_3 groups are oriented parallel to a (100) plane, x_a should be equal to $K_{\|}$ and $x_b = x_c = K_{\perp}$. Thus $x_b - x_a = K_{\perp} - K_{\|}$ and x_b should be almost equal to x_c. On referring to table I we find that $K_{\perp} - K_{\|} = x_b - x_a = 5.0$ which is practically the value obtained by Krishnan, Guha and Banerji (1933) for CO_3 groups in crystals of calcite, aragonite etc. , where CO_3 groups are all oriented parallel to each other. Further we find that $x_c - x_b = 0.5$ which is small as demanded by the structure. Thus magnetic data confirm x-ray findings.

Potassium-bicarbonate ($KHCO_3$)--It crystallises in the monoclinic system. X-ray studies of its space group by Dhar (1937) show that there are four molecules in the unit cell and that the molecular planes containing CO_3 groups lie very close to the plane (400).

From the results of magnetic measurement as given in tables I and II we find that $(\chi_1-\chi_2)+(\chi_1-\chi_3)=3\cdot5$, which is smaller than $5\cdot0=K\perp-K\|$ for CO_3 group. This means that the planes of all the four molecules in the unit cell of the crystal do not intersect the symmetry plane (010) in the same direction. Further the principal susceptibilities χ_1 and χ_3 are nearly equal $(\chi_1-\chi_3=0\cdot6)$ hence χ_2-axis may be taken as an axis of approximate magnetic symmetry. This symmetry axis is inclined to 'c' axis at an angle of 34°.2 and to 'a' axis at an angle of 45°·3.

Let the normal to the plane of CO_3 group make an angle δ with χ_2-axis ;—the magnetic symmetry axis. Hence

$$\frac{\chi_1-\chi_2}{K\perp-K\|}=1-\tfrac{3}{2}\sin^2\delta$$

using the values of $(\chi_1-\chi_2)$ from table I and for $(K\perp-K\|)=5\cdot0$ as is found in NH_4HCO_3, δ comes out as 31·9 degrees. Dhar obtains strong reflections from (400) planes ; hence all the molecular planes should be oriented parallel to 'b' axis and 'c' axis, and so δ should be equal to 33·3 degrees, which compares favourably with 31·9 degrees as found from magnetic measurements.

Ammonium nitrate (NH_4NO_3)—It crystallises in the orthorhombic system at room temperature. Its structure has been investigated. by West (1932). He finds that there are two molecules in the unit cell of the crystal and that the planes of CO_3 groups are normal to 'b' axis. Thus from the proposed structure, using the same notation as in bicarbonates, we have

$K\|=\chi_b$ and $K\perp=\chi_a=\chi_c$

Thus $\chi_a-\chi_b=K\perp-K\|$

$(K\perp-K\|)$ for NO_3 group should have practically same value as found by Krishnan, Guha and Banerji (1933) for the nitrates of sodium, potassium, where NO_3 groups are all oriented parallel to each other. Further the principal susceptibilities x_a and x_c should be almost equal. On referring to table I we find

$$x_a - x_b = K\perp - K_{\parallel} = 5{\cdot}4$$

$$\text{and } x_c - x_a = 0{\cdot}39$$

Thus $(K\perp - K_{\parallel})$ for NO_3 group in NH_4NO_3 has practically the same value as in other nitrates studied by Krishnan Guha and Banerji (1933); also x_c is nearly equal to x_a in agreement with the proposed structure.

Silver Nitrate ($AgNO_3$) It crystallises in the orthorbombic system. X-ray studies by Zachariasen (1928) about its space group gave 8 molecules in the unit cell of the crystal. If l, m and n are the direction cosines of the normal to the plane of the NO_3 triangle then we have

$$l^2 - m^2 = \frac{x_b - x_a}{K\perp - K_{\parallel}}$$

$$l^2 - n^2 = \frac{x_c - x_a}{K\perp - K_{\parallel}}$$

$$\text{and } l^2 + m^2 + n^2 = 1$$

using the value of $(x_b - x_a)$ and $(x_c = x_a)$ from table I and adopting $(K\perp - K_{\parallel})$ to be equal to 5·45 as found in NH_4NO_3, we find that normal to ($K_{\parallel}$ – axis) the NO_3 group makes an angle 50·1 degrees with 'a'. a is 38°·7 with 'b' axis and 98°.7 with 'c' axis. Thus x_c axis is almost normal to $K_{\parallel}$ axis which explains why x_c becomes a minimum diamagnetically and x_b the maximum. X-ray data available at present cannot verify the orientations as deduced magnetically.

Acknowledgement

The work was carried out at the laboratories of the Indian Association for the Cultivation of Science, Calcutta. The author wishes to express his thanks to its committee of management for affording all facilities and to Mr. R. K. Sen for valuable discussions.

References

Banerji's. (1928) Zeits. fur. Kristallo. **100**, 316.
Datta, A. K (1944) Ind. Jour. Phys. **18**, 249.
Dhar J. (1937) Ind. Jour. Phys. **11**, 187.
Krishnan, K. S. (1929) Proc. Ind Sc. congress January.
Krishnan K. S., Guha B. C., Banerji S. (1933) Philos-trans. Roy. Soc. London A. **231** 235
Krishnan K. S., Banerji S. (1935) Philos. Trans. Roy. Soc. A. **234**, 265
Krishnan K. S. and Raman C. V. (1927) Proc. Roy. Soc. A **115**, 549
Mooney R. C. L. (1932) Phys. Rev. **39**, 861
Stoner E. C. (1934) Magnetism and Matter (Methuen) p. 470
West C. D (1932) J. Am. Chem. Soc. **54**, 2256
Zachariasen (1928, Skrif Norske Videnes Akad Oslo I Mat Naturw KI 4.

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INVESTIGATION IN CAPILLARITY

By

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A. A Curious Observation

Lord Rayleigh (1902) records one of his omissions in a previous publication while discussing the size of drops and other associated phenomena under the heading '**A Curious Observation.**' He finds that while experimenting upon a shallow layer of mercury contained in a glass vessel with a flat bottom, a piece of iron gauze pressed under the mercury upon the bottom of the vessel unexpectedly remains down. He assures himself that there is no sticky substance present to which the effect can be referred, and on inspection from below it is seen that the mercury is out of contact with the bottom at places where the gauze is closest. He quite naturally comes to the conclusion that the phenomenon is plainly of a capillary nature and suggests that because of this the mercury refuses to fill up the narrowest chinks, even though the alternative is a vacuum. He also remarks that the experiment may be repeated in a simpler form by substituting for the wire gauze a piece of plate glass a few centimeters square.

B. Some Reflections

There is no doubt that the phenomenon is due to capillary action. The point is why should Rayleigh consider it curious ? It may be the phenomenon has caught him quite unawares. It is likely that he is making use of an iron gauze to 'ladle out' the scum on the mercury surface. While pressing the gauze and releasing, the gauze will ordinarily be expected to be buoyed up due to the greater upthrust of the displaced mercury. So it is quite an unexpected thing when it has refused to come up. That is the reason why he makes sure that there is no sticky substance present.

C. Experiments

A glass crystallising-dish with a flat bottom and having large diameter and height (8cm. and 5 cm.) has been taken so that any effects due to the small radius may be avoided and the depth of the mercury also may be varied at will. The mercury layer need not be shallow. On the other hand, to exhibit the full effects of buoyancy as well, it is better that the layer is such that it covers completely the object to be immersed. The mercury used is of ordinary commercial variety purified once with dilute nitric acid and dried. The following observations have been made.

(a) A rectangular piece of iron wire gauze (2 cm x 4cm) is taken and placed on the surface. It floats. It is then pressed to the bottom and released. Generally it will not come up. Anyway, the adhesion is affected easily by tilting the vessel so that the bottom of the glass vessel is seen and then placing the gauze there. On making the vessel horizontal, the gauze adheres to the surface. Seen from below, it will be observed that the mercury has collected in fine drops in the clear spacings of the gauze while the wires are in contact with the glass bottom.

(b) A microscope cover-slip is taken. When this is pressed to the bottom it readily remains in contact with it and does not come up.

(c) A piece of paper on pressing with hand readily adheres to the bottom surface.

(d) A concave watch glass is pressed with its convex side upwards so that it touches the bottom along its circumference alone. The procedure is simplified by placing the watch glass on the bottom first and then slowly allowing the mercury to cover it. It is seen that it remains in contact with the bottom. On viewing from below it is possible to observe a pellet of mercury inside. The presence of air also is easily demonstrated by lifting the watch glass slowly and observing the bubble which comes from within.

(e) Brass weights from a weight box float on the mercury surface. But on pressing them to the bottom, the flat surface of the weight adheres and the 'weight' does not come up. If the 'weight' is inverted and then pressed so that a smaller surface area is in contact with the bottom, it readily comes up and floats on the mercury surface.

(f) A small square piece of a preparation material floats on the surface. It is difficult to make it adhere to the bottom. The same material done into U--shape readily remains down on the bottom.

(g) A large piece of cork can never remain attached to the bottom. Care is taken to take such a quantity of mercury that the cork is completely immersed. But a small piece of cork with its flat surface readily attaches itself to the bottom on being pressed. By taking a large cylindrical piece of cork with a circular section and slowly reducing its length by grinding, it is found that though at first the cork does not adhere, when the cylinder is of a definite length it just begins to adhere. For all lengths smaller than this, the cork readily adheres itselt to the bottom.

(h) A big block of teak wood with a rectangular section is taken and pressed down to the bottom. It suddenly comes up. Then its thickness is slowly filed and it is found that when a critical thinkness is reached, the block just begins to adhere to the bottom and remains there provided the liquid is not disturbed. For all thicknesses smaller than this, the block readily attaches itself to the bottom on being pressed.

D. Discussion

All the above results of the experiments can be readily explained simply by saying that due to the capillary forces the substance is pulled downwards. Due to the lesser density of the substance there is a force of buyoncy which is opposite in direction to that of capillary forces and acts upwards. If the mercury displaced is little, the latter force will be small and the capillary forces can keep the substance down. This condition is readily satisfied in the experiments (a), (b), (c) and (d). In (e) the condition is satisfied when the area of the contact is large. In (f) when the shape is of U the conditions are very favourable to keep it pressed down to the bottom, not only because the area of contact is a bit increased but mainly due to an increase in the length of edges. In (g) and (h) to realise this condition the length or the thickness is filed off. This reduces the volume of the substance and hence the volume of the displaced mercury. Consequently the upthrust is slowly reduced. At the critical length the volume of the substance is such that the resultant of the capillary forces just counterbalances the upthrust and the substance remains down. Moreover, from the experiment (e). the presence or otherwise of air in between the bottom and the surface of the substance in contact with it affects the result little. What is of importance is the length or area of the substance that is actually in contact with the bottom.

In the case of experiments (g) and (h) the volume and mass of the solid for the critical length and thickness are determined. The density of the solid is then obtained. It is found that the calculated upthrust is considerably less than the force due to capillarity. One set of observations for a piece of cork is given below.

Mass of the cork = 0.55 gm
Diameter of the upper section = 1.8 cm
Diameter of the lower section = 2.0 cm
Approximate volume of the cork = 3.69 cc
Density of the cork = 0.15 gm per cc
Approximate upthrust = 49.52 gm. wt.
Force due fo capillarity calculated from the approximate formula $F = 2A\sqrt{gps}$ = 160 gm. wt.

E. Conclusion

It is seen that the resultant for the capillary forces acting downwards is considerably greater than the upthrust in all cases where the substance adheres to the bottom of the vessel containing mercury. The depth of the mercury layer is immaterial. The method offers a value for the surface tension of mercury if one can find the critical volume of the body immersed and the difficulties attending this determination are successfully overcome.

Thus the phenomenon is no more curious than the problem of a floating needle. It is a common experience that a razor blade can be made to float on the surface of water on successful manipulation. It this case the weight acting downwards is counterbalanced by the capillary forces whereas in the curious observation made by Lord Rayleigh, it is the resultant upthrust that is counterbalanced by the capillary forces. One does not know who has first noted the phenomenon of 'floating needle', but it is evident that Lord Rayleigh is the first to observe the phenomenon of what we may rightly term 'sticking iron gauze' and to reoord it so lucidly.

REFERENCE.

J. W. Strutt, *Scientific Papers*, vol IV (1892–1901)

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30th Dec. '50.

SATURATION EFFECT IN ATOMIC NUCLEI

By

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Recently much attention has been directed to the uniqueness of atomic nuclei containing a certain marked number of neutrons or protons. These numbers are particularly 28, 50, 82 and 126, to which may be added 2, 8, and 20. These nuclei show an amount of saturation as evidenced by several facts, among which may be mentioned the quadrupole moments, relative isotopic abndance, spin, beta decay, isomerism, delayed neutron emmission, and the neutron absorption cross-section. The evident suggestion is that nucleons are added to successive nuclei by stages which mark the filling up of successive shells, just as we have in the electrons round the nucleus as a result of the effectiveness of the Pauli exclusion principle.[1]

The explanation of the completion of the shells is provided by various theories. Perhaps, the most interesting of these is the one by Max Born and Yang, in which the nucleus is considered to be a degenerate system of nucleons.[1] An expression is derived for the density in terms of the angular momentum. By adjusting the constants involved, the number of neutrons for the angular momenta from zero to six units is seen to be quite close to the numbers 2, 8, 20, 28, 50, 82, and 126.

The existence of such a saturation effect also presupposes an unsaturation effect. The conclusion has been drawn from some previous investigations that the nuclei of the rare gas atoms possess such an unsaturation, and hence they readily combine among themselves to form saturated nuclei.[8] There is no doubt about the role assigned to the lightest of the rare gases, helium, as a nuclear component, as so abundantly evidenced by the alpha particle emission both in natural and artificial radioactivity. The process of the fission of nuclei also leaves little doubt that krypton and xenon are among the products of such disruptions; and, probably, they are also of the primary products of fission. Without going into the details of the mechanism of the synthesis of two such rare gas nuclei which would be at the most tentative in our present state of knowledge of the forces involved, we can well see that the elements fall into certain well defined and natural groups on the assumtion of such a combination of two rare gas nuclei to form a compound nucleus. These groups are, the halogens, the alkalis, the alkaline earths, the rare earths, the ferromagnetic metals, the group containing Sn, Cd, Sb, Te and In, and the radioactive elements.

The shape of the nucleus, as far as can be judged from the hyperfine structure of the spectral lines, is not spherical. The necessity of the introduction of quadrupole moments and potentials leads us to this conclusion. Such also would be the conclusion arrived at on the above hypothesis of the formation of nuclei. It also suggests that if the nucleus is not exactly represented by two constituents the dimensions of which may be considered to be small in comparison with the distance between them, they may be two interpenetrating or overlapping groups each behaving as an equivalent point.

Nuclei with neutron or proton numbers equal to 2, 8, 20, 28, 52 and 126 are set out below in groups of isotones, or nuclei with the same neutron number. N denotes the neutron number, Z the proton number, and A the isotopic mass number.

Table I

	He	O	Ca	Cl	K	Ca	Ti	Sr	Kr	Rb	Y	Zr	Mo	Sn
N	2	8	20	20	20	28	28	50	50	50	50	50	50	74
Z	2	8	29	17	19	20	22	38	36	37	39	40	42	50
A	4	16	40	37	39	48	50	88	86	87	89	90	92	124

	Xe	Ba	La	Ce	Pr	Nb	Sm	Pb	Bi	Na	Mg
N	82	82	82	82	82	82	82	126	126	(9–18)	(10–19)
Z	54	56	57	58	59	60	62	82	83	11	12
A	136	138	139	140	141	142	144	208	209	(20–29)	(22–31)

Here we have such elements as Ca, Sn, and Pb rich in isotopes. We notice in this the occurrence of the same elements that go to form the groups mentioned above as resulting from the combination of the rare gas nuclei, all of which are represented. This indicates that in addition to the explanation offered by the hypothesis of successive nuclear shells, we also have an alternative explanation offered by the hypothesis of successive nuclear shells, we also have an alternative explanation offered by the hypothesis of the formation of saturated nuclei by the combination of the rare gas nuclei which themselves are unsaturated. It just happens to be a coincidence that these nuclei belong to elements whose electronic shells are complete and saturated.

By considering the saturated nuclei as simple structures with the unsaturated nuclei as their components, it is interesting to find it possible to calculate the values of nuclear levels. Thus, one such calculation gives for the energy levels of Be^8 nucleus the values 17.6,10.0,3.3,1.8,0-9, and 0.1 Mev, which can be compared with the experimentally obtained values 19.2, 18.I,17.6,9.8,7.0, and 3.3 Mev.[3],[4]

References

1. Mayer, M. G.: Phy. Rev., **74**,235, (1948)
   Meitner, L: Nature, **165**, 561, (1950)
   Max Born & Yang, L. N. Nature, **166**,399,(1950)
2. Soonawala, M.F.: Ind. Jour. Phy., **3**, 489(1929); ibid, **16**, 291, (1942) ibid, **19**, 185, (19545); ibid, **21**, 137, (1947)
3. Soonawala, M.F.:Ind. Jour.Phy.,**24**, 315,(1950)
4. Hornyak, W.F. & Lauritsen, T.: Rev. Mod. Phy., **20**, 191, (1948)

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INFLUENCE OF AGEING IN CHLORINE.

By

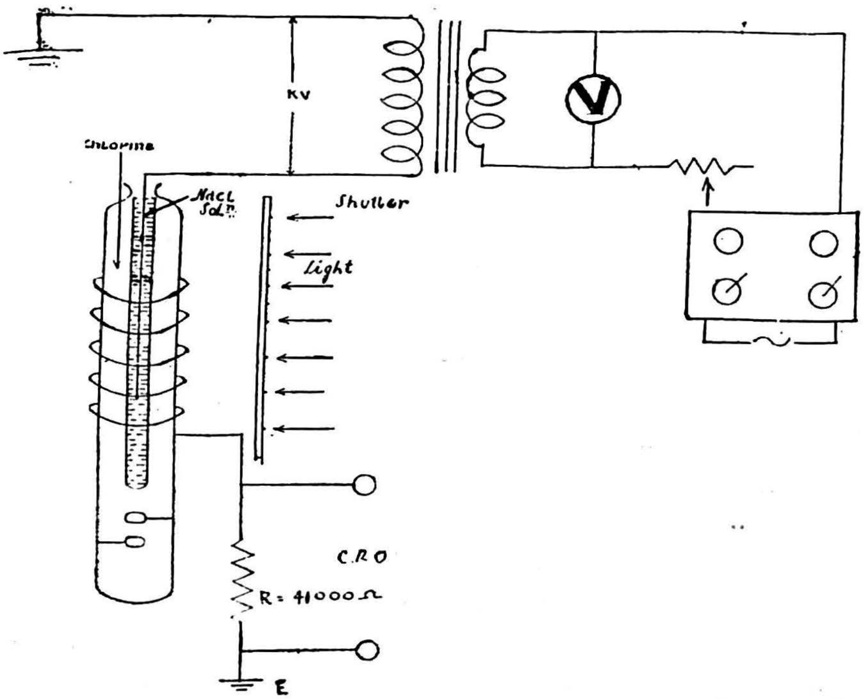
G. V. BAKORE. M. Sc.

(*Abstract*—The influence of ageing has been investigated with oscillograph. The results obtained are discussed in the light of Prof. Joshi's theory (1943) for the above phenomenon.)

The significance of the time–variation in electrical quantities for the analysis of the corresponding discharge reaction has been emphasised by Joshi (1929, 1939), Whilst this time variation in conductivity at sensibly constant electrial conditions has been attributed to the progress of the chemical change of the reactant material, no such simple mechanism can, in the first instance, be postulated in case of elementary gases. The observation, therefore, that the Joshi–Effect, $\triangle i$, is subject to the so called 'ageing' appears to be of interest. According to Joshi (1944) the high frequency components of the discharge current are the main seat of the effect $\triangle i$. It is, therefore, of interest to investigate the time variation of the h. f. components of the discharge current with cathode ray oscillograph.

The general arrangement of the apparatus is shown in the figure. Chlorine gas at a pressure of 150 mms., purified carefully over liquid air was contained in the annular space of a Siemen's type ozoniser with two copper ring electrodes separated by 5 mms. kept at the bottom in the annular space. The ozoniser was excited by A. C. potentials of 50 cycles frequency at 1. 5 kV. The low tension electrode of the tube was earthed through a non-inductive resistance R = 41000 ohms; and the voltage across the resistance was fed to the vertical plate of the oscillograph. The patterns were observed at different intervals of time when the ozoniser was (1) in dark and (2) irradiated with 220-volt, 200 watt incandescent glass lamp.

INFUENCE OF AGEING UNDER DISCHARGE IN CHLORINE,



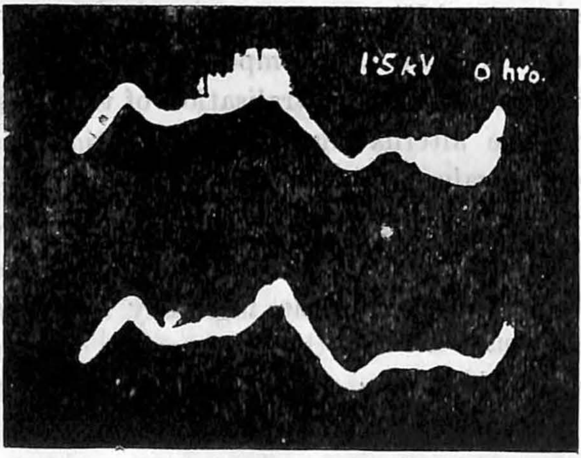
Wellish (1909) in a general interpretation of the phenomenon attributed"ageing"to a viscuous retardation of the motion of the electrons during a free path by the attraction exerted by the surrounding gas molecules. The above action is of a general type and further the loss in mobility occurs within a very short period of the order of a fraction of a second. Deo (1945) has shown that this period is of a different order of magnitude compared with that of "ageing". According to him the possible contribution to this "ageing" effect by changes in the ionic mobility due to cluster formation etc. is negligible. The results obtained have been attributed, in part, to a slow interaction between the (electrode) wall material and the activated gas under the discharge.

The explanation advanced by Joshi (1943) for the phenomenon is that of a formation and stabilisation of an adsorbed layer derived, in part, from excited molecules and ions, which according to him is also the chief seat of the photo–suppression of the discharge current. The process of adsorption alters the capacitance associated with the container walls and the gas phase; consequently the conductivity is altered. Associated with the instability of the formation of an adsorbed layer there is an intermittent sorption and desorption or / and the production at the surface of the walls, of unstable intermittent products of the discharge recation,–all leading to a synchronous time ratio in the conductivity.

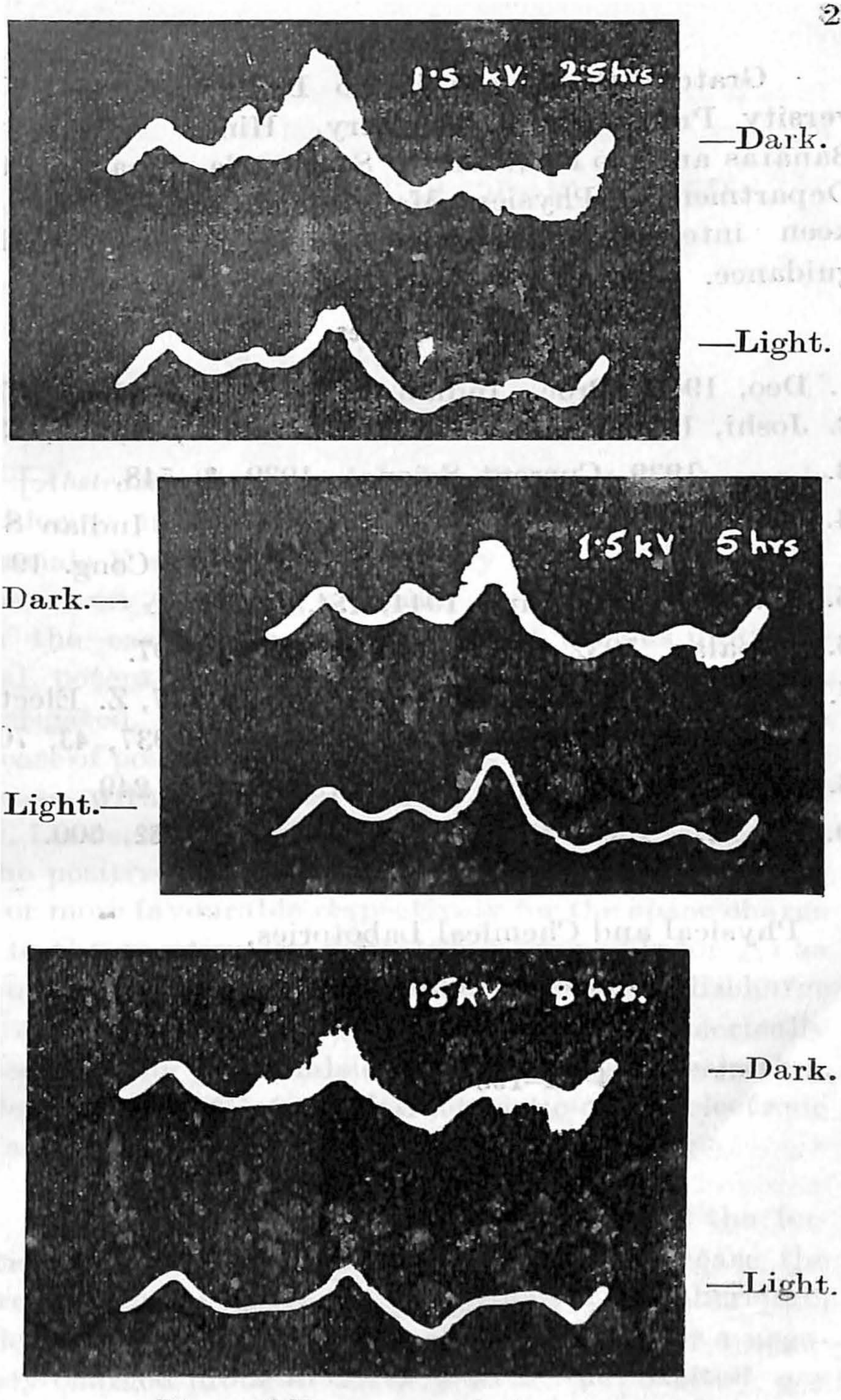
Experiments of Klemenc, Hinterberger and Hoffer (1937) show that the h. f. components of discharge current originate from the neutralisation of the surface charges when the alternating exciting potential passes through its zero value. The adsorbed layer profoundly influences the character of the discharge phenomenon. Kapalan (1932) for instance has been able to produce spectra resembling those of the night sky and aurora by specially "conditioning" the walls of the discharge tube by prolonged running. It is therefore postulated that the surface charges are associated with the adsorbed layer as suggested by Joshi.

Since the surface charges are associated with the adsorbed layer it follows that a change in the adsorbed layer during ageing should bring about a corresponding change in the proportion of the h. f. components of the discharge current. A change in the proportion of the h. f. components indicates a corresponding change in the adsorbed layer formed during the discharge. A change in the adsorbed layer during the discharge alters the capacitance associated with the container walls and the gas phase. Alteration in the capacity causes a phase shift with a consequent change in the wave pattern.

The photographs presented show a change in the wave pattern as well as in the proportion of the h. f. components, thus suggesting a time variation of the adsorbed layer during the discharge. The results are thus in confirmity with those expected from Joshi's explanation. The time variation of conductivity follows from the time variation of the adsorbed layer with a corrosponding time variation of the capacitance associated with the container walls and the gas phase.



Time of exposure = 1 sec.



Time of Exposure=1 Sec.

Grateful thanks are due to Dr. S. S. Joshi, University Professor of Chemistry, Hindu University, Banaras and to Prof. M. F. Soonawala, Head of the Department of Physics, Maharaja's College, for their keen interest, kind encouragement and valuable guidance.

References

1. Deo, 1945, Proc. Indian Acad. Sci. 1945, **214**, 79.
2. Joshi, 1929, Trans. Farad. Soc. 1929, **25**, 121, 139.
3.......... 1939, Current Science. 1939, **8**, 548.
4.......... 1943, Presi. Address Chem Sec. Indian Sci. Cong. 1943.
5.......... 1944, Nature, 1944, **154**, 147.
6. Kapalan, 1932, Phys. Rev., 1932, **42**, 807.
7. Klemenc, Hinterberger, and Hoffer, 1937, Z. Electro Chem, 1937, **43**, 708.
8. Wellish, 1909, Phil. Trans. 1909, **A209**, 249.
9. .... 1909, Proc. Roy. Soc, 1909, **A82**, 500.

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JOSHI-EFFECT IN CHLORINE UNDER MIXED DISCHARGE.

By

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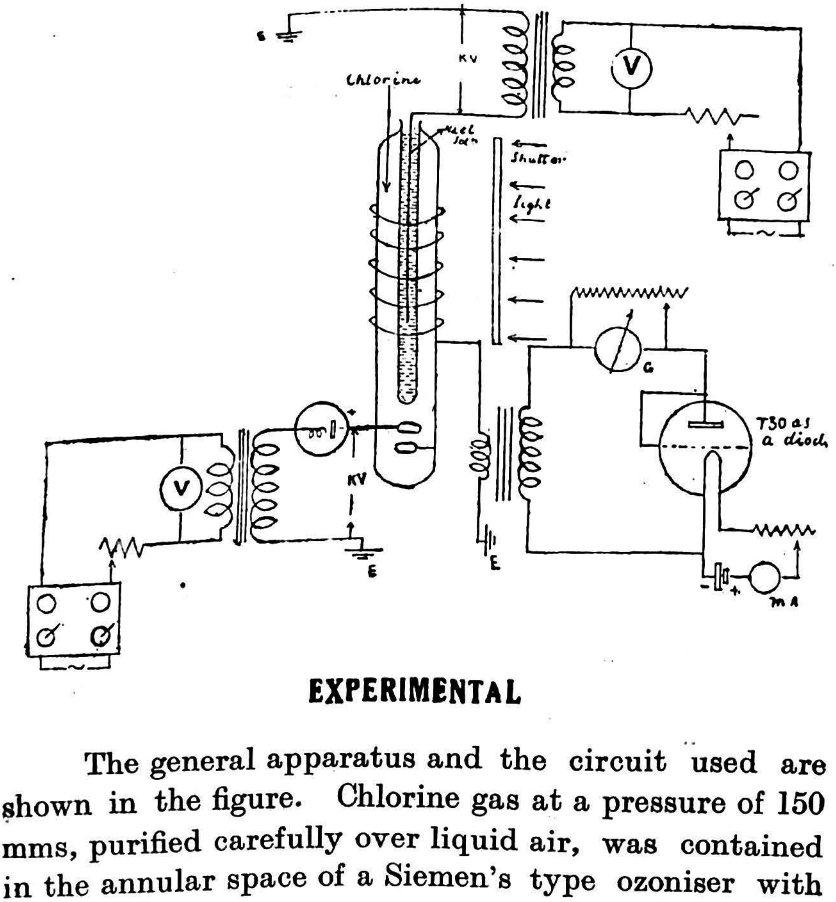
[*Abstract*—Studies of Joshi—Effect, Δi, were made in chlorine in a Siemen's ozoniser excited by A. C. potentials V of 50 cycles frequency over 1 to 2 kV. The influence on Δi of ring metallic electrodes in contact with the excited gas maintained at various unidirectional potentials in the range -2.3 to $+2.3$ kV was investigated. Δi and $\% \Delta i$ at a fixed V decrease with increase of positive ring electrode potentials and slightly increase with a numerical rise in the negative potentials, between $+1.7$ kV. and -1.7 kV. This is attributed to the positive or negative electrode potentials being less or more favourable respectively for the space charge due to the negative ion formation responsible for Δi as postulated by Prof. Joshi. Under the mixed discharge at a constant V, Δi and $\% \Delta i$ increase with numerically increasing ring potentials (positive or negative); thus indecating that Δi is a characteristic of the electrode surface and not of the conductivities.]

Joshi (1946, 1947, 1947a) has postulated the formation of negative ions under light which decrease the current as in the space charge effect. It is, therefore, anticipated that the presence of a positively or a negatively charged probe in contact with the excited gas should have a marked influence on the Joshi-Effect, Δi.

It is therefore, of interest to investigate this effect in Chlorine which gives maximum light effect under optimum conditions.

JOSHI EFFECT IN CHLORINE UNDER MIXED DISCHARGE



EXPERIMENTAL

The general apparatus and the circuit used are shown in the figure. Chlorine gas at a pressure of 150 mms, purified carefully over liquid air, was contained in the annular space of a Siemen's type ozoniser with two copper ring electrodes separated by 5 mms, kept at the bottom in the annular space. The ozoniser was excited by A. C. potentials of 50 cycles frequency over 1 to 2 kV. The ring electrode in contact with the excited gas was maintained at various unidirectional potentials obtained from a point to plate rectifier energised by a H. T. transfromer. The low tension electrode of the tube was earthed through a Bell type iron core step up transfromer (1:3); its secondaries were connected to the plate (and grid) of Triode 30 used as a diode, and the cathode through a reflection galvanometer with an appropriate shunt. The discharge current 1 was measured in dark and under irradiation from a 220 volt 200 watt incascendent (glass) lamp by manipulation of the shutter.

INFLUENCE OF THE RECTIFED POSITIVE POTENTIALS ON THE RING ELECTRODE.

TABLE 1.

Ring Potns. (kV):		0.0	0.7	1.1	1.2	1.3	1.5	1.6	1.7	2.0*	2.3*
Exciting Potentials(kV): 1.2 kV.	i_d	13.8	13 8	13.8	14.0	14.0	14.1	14.1	14.1	18.5	20 5
	i_l	4.8	4.8	4.8	5.2	5.4	5.6	5.7	6.1	9.4	12.3
	Δi	9.0	9.0	9.0	8.8	8.6	8.5	8.4	8.0	9.1	8.2
	% Δi	65.2	65.2	65.2	62.9	61.4	60.3	59.7	56.8	49.2	40.0
1.3 kV.	i_d	16.5	16.5	17.1	17.0	17.0	17.0	17.0	17.0	19.5	23.0
	i_l	7.5	7.5	8.0	8.0	8.3	8.3	8.3	8.8	11.0	14.5
	Δi	9.0	9.0	9.1	9.0	8.7	8.7	8.7	8.2	8.5	8.5
	%Δi	54.5	54.5	53.2	52.9	51.2	51.2	51.2	48.2	43.6	37.0
1.5 kV.	i_d	19.0	19.0	19.5	19.5	19.5	19.5	19.6	19.5	21.7	25.7
	i_l	10 0	10.0	10 5	10.8	10.8	10.8	11.0	11.5	13.2	16.7
	Δi	9.0	9.0	9.0	8.7	8.7	8.7	8.6	8.0	8.5	9.0
	% Δi	47.4	47.4	46.2	44.4	44.4	44.4	43 9	39.5	39.2	35.0
1.6 kV.	i_d	21.9	21.9	22.0	22.0	22.0	22 0	22.0	22 0	23.8	28.4
	i_l	13.0	13.0	13.3	13.6	13.7	13.8	13.8	14.4	16.0	19.4
	Δi	8 9	8.9	8.7	8.4	8.3	8.2	8.2	7.6	7.8	9.0
	% Δi	40.6	40.6	39.6	38.4	37.7	37.3	37.3	34.5	32.8	31.7

1.7 kV.	i_d	24.0	24.0	24.4	24.4	24.4	24.4	24.4	24.5	26.3	31.6
	i_1	15.5	15.6	16.0	16.1	16.2	16.3	16.4	17.5	19.0	22.1
	Δi	8.4	8.4	8.4	8.3	8.2	8.1	8.0	7.0	7.3	9.5
	% Δi	35.0	35.0	34.4	34.0	33.6	33.2	32.8	28.6	27.8	30.1
1.9 kV.	i_d	26.4	26.4	26.4	26.5	26.5	26.5	26.7	27.2	29.7	34.5
	i_1	18.0	18.0	18.3	18.6	18.8	19.0	19.2	20.7	22.0	24.7
	Δi	8.4	8.4	8.1	7.9	7.7	7.5	7.5	6.5	7.7	9.8
	% Δi	31.3	31.3	30.7	29.8	29.1	28.3	28.1	23 9	25.9	28.4

* Glow sets in between the ring electrode and the L. T. of the ozoniser; (that is mixed discharge.)

INFLUENCE OF THE RECTIFIED NEGATIVE POTENTIALS ON THE RING ELECTRODE.

TABLE 2.

Ring Potns. (kV):		0.0	0.7	1.1	1.2	1.3	1.5	1.6	1.7	2.0*	2.3*
Exciting 1.2kV.	i_d	11.8	12.0	12.0	12.0	11.8	11.8	11.6	11.7	16.9	15.2
Potentials (kV).	i_1	5.4	5.4	5.4	5.3	5.3	5.4	5.3	5.4	12.0	9.7
	Δi	6.4	6.6	6.6	6.7	6 5	6.4	6 3	6.3	4.9	5.5
	% Δi	54.2	55.0	55.0	55.1	55.1	54.2	54.3	53.8	29 0	42.8
1.3 kV.	i_d	13 0	13.0	13.0	13.0	13.0	13.2	13.0	13.0	18.1	16.4
	i_1	7.4	7.4	7.4	7.4	7.3	7.3	7.4	7.4	14.2	12.7
	Δi	5.6	5.6	5.6	5.6	5.7	5.9	5.6	5.6	3.9	3.7
	% Δi	43.1	43.1	43.1	43.1	43.8	44.7	43.1	43.1	21.6	22.6
1.5 kV.	i_d	14.5	14.5	14.5	14.7	14.5	14.5	14.5	14.7	19.7	18.3
	i_1	10.0	10.0	10.1	10.1	10.0	10.0	10.0	10.0	16.4	15.0
	Δi	4.5	4.5	4.4	4.6	4 5	4.5	4.5	4.7	3.3	3.3
	% Δi	31.0	31.0	30.4	31.3	31.0	31.0	31.0	32.0	16.6	17.9
1.6 kV.	i_d	16.4	16.4	16.4	16.8	16.4	16.4	16.4	16.4	21.8	20.4
	i_1	12.8	12.8	12.7	13.0	12.7	12.7	12.7	12.7	19.0	17.4
	Δi	3.6	3.6	3.7	3.8	3.7	3.7	3.7	3.7	2.8	3.0
	% Δi	22.0	22.0	22.6	22.6	22.6	22.6	22.6	22.6	12.8	14.7

1.7 kV.	i_d	18.2	18.2	18.3	18.3	18.3	18.3	18.3	18.3	23.9	22.7
	i_1	15.1	15.1	15.1	15.1	15.1	15.1	15.1	15.1	21.7	20.0
	Δi	3.1	3.1	3.2	3.2	3.2	3.2	3.2	3.2	2.2	2.7
%	Δi	17.0	17.0	17.5	17.5	17.5	17.5	17.5	17.5	9.2	11.9
1.9 kV.	i_d	20.4	20.4	20.4	20.4	20.5	20.5	20.5	20.5	26.3	25.0
	i_1	18.1	18.1	18.1	18.1	18.1	18.1	18.1	18.0	24.9	22.6
	Δi	2.3	2.3	2.3	2.3	2.4	2.4	2.4	2.5	1.4	2.4
%	Δi	11.3	11.3	11.3	11.3	11.7	11.7	11.7	12.2	5.3	9.6

*Glow sets in between the ring electrode and the L. T. of the ozoniser; (that is mixed discharge.)

DISCUSSION

Joshi (1929, 1931, 1939, 1945) has emphasised the fundamental importance of the minimum threshold potential Vm as a determinent of the rate and nature of a chemical or quasi-chemical change in the gaseous systems under electric dischange. This Vm may be related simply to the corrosponding Paschen potential especially in elementary gases. It is marked by a sudden increase in the current through and the wattage dissipated in, the system. This Vm was found to be 1.07 kV. for A. C. discharges and glow passes between the ring electrode and the L. T. of the ozoniser at + or − 1.7 kV.

Well below Vm, Δi, dose not occour. Furthermore Δi and % Δi is maximum at Vm and decrease thereafter. This is true at all fixed electrode potentials thus at the fixed electrode potential + 0.7 kV, Δi and % Δi is 9.0 and 65.2 respectively at 1.2 kV. and 8.4 and 31.3 respectively at 1.9 kV. The results are in agreement with the general findings of Joshi (1945) that well below Vm, when the conduction is mainly capacitative, $\triangle i$, does not occur despite the use of intense and even short-wave radiations and large displace-ment currents obtained with high frequencies input to the system (Joshi and 1945).

At a constant A. C. potential, i_D, under dark slightly increases when the ring electrode potential is varied upto $+1.7$ kV.; while the dark current is practically unaltered when the ring electrode potential is varied upto -1.7 kV. Thus at the constant A. C. potential 1.5 kV, the dark current increase from 19.0 to 19.5 when the ring electrode potential is varied from 0.0 kV. to $+1.7$ kV.; and changes from 14.5 to 14.7 when the ring electrode potential is varid from 0.0 kV to -1.7 kV. Under the mixed discharge, however, the dark current increases with positive ring electrode potentials and decreases with a numerical increases in the negative ring electrode potentials. Thus, under the mixed discharge, at a constant A. C. potential 1.7 kV, the dark current increases from 26.3 to 31.6 when the ring electrode potentials are varied from $+2.0$ to $+2.3$ kV.; while the dark current decreases from 23.9 to 22.7 when the ring electrode potentials are varied from -2.0 to 2.3 kV.

$\triangle i$ and $\%\triangle i$ at a fixed A. C. potential decrease with a numerical increase of positive ring electrode potentials and are practically unaltered with a numerical rise in negative ring electrode potentials between $+1.7$ kV. and -1.7 kV. Thus, $\triangle i$, and $\%\triangle i$ at the fixed A. C. potential 1.5 kV, varies from 9.0 to 8.0 and 47.5 to 39.5 repectively when the ring electrode potentials are vrried from $+0.0$ to $+1.7$ kV.; and from 4.5 to 4.7 and 31.0 to 32.0 when the ring electrode potentials are varied from -0.0 to -1.7 kV. These results are to be anticipated from Prof. Joshi's theory of the light effect, Δi (1946, 1947, 1947 a)

According to Prof. Joshi (1946, 1947, 1947 a) : (1) under electric discharge an adsorption like ionic and molecular layer in dynamic equlibrium with the gas phase is formed ; (2) as a primary step photo-electric emission occurs from the above layer and the photo-electrons thus emitted are converted into slow moving negative ions due to the electron affinity of the excited medium and these reduce the current as in the space-charge effect.

The magnitude of the light-effect, thus, depends on the negative ion space-charge formed under light. When the ring electrode potentials are positive the negative ion space-charge decreases due to the drift velocity of these towards the ring electrode. Thus more and more of the negative ions will move out from the discharge space with increasing positive ring electrode potentials ; thus decreasing the light-effect with increasing positive ring electrode potentials as observed. When the ring electrode potentials are negative the negative ions are not removed from the discharge space and the proportion of these would increase due to the removal of positive ions by the negatively charged electrode. The increase in the proportion of the negative ions will be, however, small on account of the low mobility of the positive ions and will only be appreciable at large negative ring electrode potentials. The light-effect should, therefore, either be unaltered or slightly increased when the ring electrode potentials are negative. This is actually observed.

Under the mixed discharge, at a constant A. C. potentials, Δi and $\%\Delta i$ increase with numerically increasing ring potentials (positive or negative). Thus, at the fixed A. C. potential 1.7 kV, $\triangle i$ and $\% \triangle i$ varies from 7.3 to 9.5 and 27.8 to 30.1 respectively when the ring electrode potentials are varied from + 2.0 to + 2.3 kV.; and from 2.2 to 2.7 and 9.2 to 11.9 respectively when the ring electrode potentials are varied from—2.0 to—2.3 kV. These results indicate that $\triangle i$ is a characteristic of the electrode surface and not of the conductivities.

Grateful thanks are due to Prof. S. S. Joshi, University Professor of Chemistry, Hindu University, Banaras; and to Prof. M. F. Soonawala, Head of the Department of Physics, Maharaja's College, Jaipur, for their keen interest, kind encouragement and valuable guidance.

REFERENCES.

1. Joshi, 1929, Trans. Faraday Soc. 1929, 25, 118, 137.
2. ... ..., 1931, Proc. Indian Sci. Cong. 1931, Part III, Chem. Sec. Abst. No. 26
3. ... ..., 1939, Current Science, 1939, 8, 548.
4. ... ..., 1945, Proc. Indian Acad. Sci. 1945, A 22, 389.
5. Joshi and Lad, 1945, ibid. 1945, A 22, 293.
6. Joshi, 1946, Proc, Indian Sci. Cong. 1946, Part III, Phys. Sec. Abst. No. 26.
7. ... ..., 1947, ibid, Part III, Phys. Sec. Abst. No. 27.
8. ... ..., 1947a, Current Science, 1947, 16, 19.

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A STUDY IN ELECTROLYTIC DEPSOITION OF SODIUM ON GLASS

By

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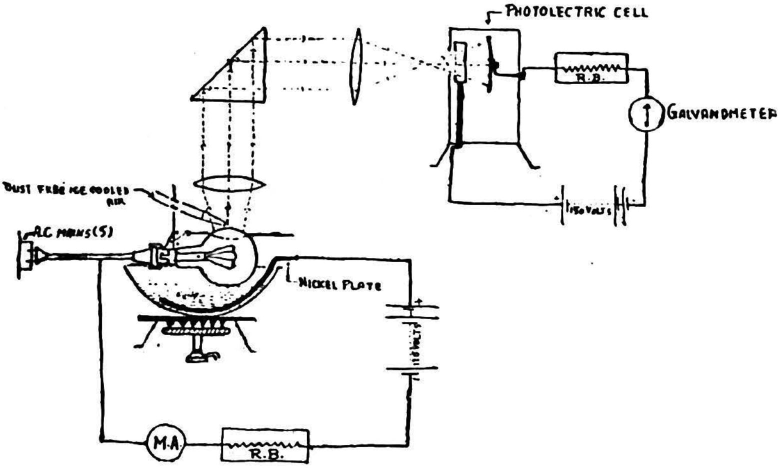
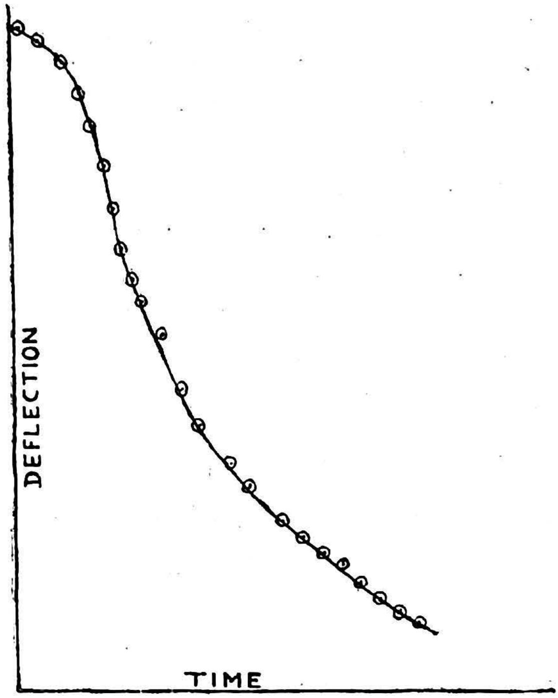
(*Abstract:*—Sodium is deposited gradually on the cooled part of a vacuum electric lamp by the electrolysis of sodium nitrate. The absorption of the light emitted by the lamp on its passage through the sodium film was studied, and the rate of deposition of sodium on glass determined.)

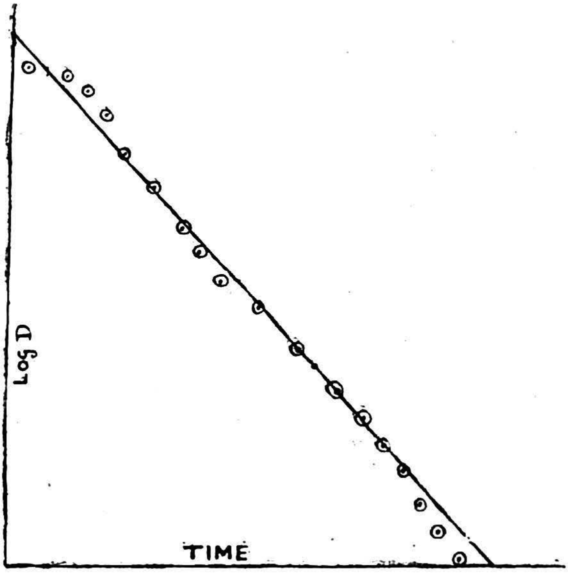


The experiment followed the lines shown by Burt. An evacuated electric lamp of soda glass of 40 watts at 220 volts was partially immersed in a mixture of sodium nitrate and sodium chloride in a porcelain dish. The function of the sodium chloride was to lower the melting point of the mixture. A bent nickel plate was also placed in the mixture. The lamp was painted black all over except over a small area at which it was in contact with the sodium mixture, and at another small area near the top.

A pressure of about 120 volts d. c. was maintained between the lamp filament as the cathode and the nickel plate as the anode. On heating the mixture a current of the order of 3 mamps. began to flow soon after the melting of the mixture. This current remained independent of the area of contact between the mixture and the lamp, and was simply dependent on the potential applied and the lamp used. Due care was taken to keep the current constant by manual control. The sodium migrates into the vacuum of the lamp throught its walls as positive ions, which are then neutralized by the electrons emitted from tha filament which is made incandescent by connecting to the electric mains. The sodium vapour thus formed deposits itself on the cooled surface of the glass envelope of the lamp. The cooling is done by projecting a blast of dust–free ice cooled air on the wall of the lamp where it is kept clear for the purpose. Under these circumstances, any possibility of contamination or oxidation of the freshly formed sodium surface is automatically avoided in the evacuated interior of the lamp the light of the lamp which passes through the sodium deposit is concentrated on to a photoelectric cell in series with a galvanometer and a suitable source of electric potential This latter was supplied by a rectifier employing the '80 valve and was maintained constant by one or more voltage regulating tubes of the type The photoelectric current was noted at intervals of half a minute by a lamp and scale. The experiment was carried out under conditions of as constant a pressure of electric supply as could be had during the day. The observations are contained in Table I. The graphs between the galvanometer deflection and time is given in Fig. 1.



Graph 1.



Graph No. 2

and that between the logarithm of the deflection and time in Fig. 2.

The latter is seen to be a straight line except at the beginning and the end. These slight variations can be due to variations in the intensity of the lamp light. The exponential decay in the intensity of the transmitted light is well represented by an expression of the form $I=I_0 \exp(-kx)$, where I_0 is the initial intensity, and I the intensity at any instant when the thickness of the sodium deposit is x. This demonstrates that the rate of deposition has been very fairly uniform..

It is known that

$$I=I_0 \exp(-4\pi kx/\lambda)$$

where k is the coefficient of extinction and the wavelength of the transmitted light can be taken to correspond to the wavelehgth of yellow light at 6000 A.U. as the most intense part in the light of the lamp employed. K, the coefficient of absorption is related to k, the coefficient of extinction of (   ) by

$$k=K\lambda/4\pi.$$

The value of K is taken as 55 for the wavemlength employed. The value of x then comes out to be equal to 5.5×10^{-4} cm/minute. Similar results are obtained with other lamps.

It would be more instructive to deduce values of the absorption coefficient from these experiments if suitable alternative methods can be developed for the estimation of the rate of deposition of sodium. As this rate would also obviously depend upon the thermal conductivity of the glass of the lamp, further studies in this direction are being continued.

I am much indebted to professor M. F. Soonawala for advice and guidance.

TABLE 1

Time min.	Deflection cms.	Time min.	Deflection cms.	Time min.	Deflection cms.
0·5	28·5	8·5	15·5	16·0	7·0
1-5	28·0	9·0	14·8	16·5	6·7
2·0	28·0	9·5	13·2	17·0	6·3
2.5	27·8	10·0	12·4	17·5	6·0
3·0	27·5	10·5	11·7	18·0	5·8
3·5	27·3	11·0	10·8	18·5	5·6
4·0	26·8	11·5	10·2	19·0	—
4·5	25·5	12·0	10·0	19·5	5·2
5·0	24·2	12·5	9·5	20·0	4·8
5·5	22·7	13·0	9·2	20·5	4·6
6·0	21·0	13·5	8·8	21·0	4·3
6·5	19·2	14·0	8·2	21·5	4·1
7.0	18·0	14·5	7·9	22·0	3·7
7.5	17·0	15·0	7·6	22·5	3·5
8.0	16·2	15·5	7·4	23·0	3.2

References.

1, Burt, R. C. : J. Opt. Soc. Am., 11, 87, (1925)
2. R. W. Wood : Physical Optics, (1934), p. 102.
3. International Critical Tables, (193),Vol. ,p.

ENERGY IN LIQUID STATE

By

M. G. Bhatawdekar, M. Sc.

[*Abstract:*—The surface of a liquid can be treated as a potential barrier and the probability of transition across it of a molecule calculated. By comparision with experimental results, the potential energy of the molecule and the change in the free energy and internal energy ealculated.]

The surface of a liquid is assumed to offer a potential barrier to the passages of a molecule from the liquid to the vapour state. The probability of transition of a molecule across the surface is, then,

$$F = \left(\frac{km}{\pi}\right)^{\frac{1}{2}} \left\{ \int_{u_0}^{\infty} q_1 \, e^{-kmu^2} \, du + \int_{-\infty}^{u_0} q_2 \, e^{-kmu^2} \, du \right\}$$

$$= f_1 + f_2$$

(Soonawala[1] equ. VII)
2

when q_1 and q_2 are given on wave-machanical theory by

$$q_1 = \frac{16 a_0 a_2}{(a_0 + a_2)^2 \cos^2 a_1 a + \frac{1}{a_1^2}(a_1^2 + a_0 a_2) \sin^2 a_1 a}$$

and
$$q_2 = \frac{4 a_0 a_2}{(a_0 + a_2)^2 \cosh^2 \beta_1 a + \left(\beta_1 - \frac{a_0 a_2}{\beta_1}\right)^2 \sinh \beta_1 a}$$

when $a_0 = \frac{8\pi^2 m}{h^2}(W - U_0)$, $a_1^2 = \frac{8\pi^2 m}{h^2}(W - U_1)$, $a_2^2 = \frac{8\pi^2 m}{h^2}(W - U_2)$,

and $a_1 = i\beta_1$

f_1 provides the principle contribution to F, in comparison with which f_2 was found to be negligibly small in the case of water. We come to the same conclusion for other liquids here treated, and hence only f_1 is calculated at the different temperatures shown. The simplified value of f_1 is

$$f_1 = 4p\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmb} \int_0^{\infty} \frac{e^{-kmx^2}\, x^3\, dx}{px^2\sqrt{x^2+b}\,\cos^2 gx + \sqrt{x^2+b} + x^2/\sqrt{x^2+b}}$$

where $p = \frac{16\pi^2 m^2}{h^2}$, $b = \frac{2U_1}{m} = \frac{2+2mL}{m} = 4\,L$, $u^2 - b = x^2$ and

$$g = \frac{a}{2}\sqrt{p}$$

(Soonawala[1] equ. XIII)

L is the latent heat of vaporisation and a is the thicknees of the potential barrier.

The previous procedure was adopted for these calculations also. The value of $\pi A/BC$, where

$$A = e^{-km} x^{2}_{m}\, x^{3}_{m},$$

$$B^2 = p^2 x^{2}_{m} \frac{a^2}{4} \sqrt{x^{2}_{m} + b},$$

$$C^2 = \sqrt{x^{2}_{m} + b} + \frac{x^2 m}{\sqrt{x^{2}_{m} + b}},$$

and $g\, x_m = (2n+1)\frac{\pi}{2}$.

(Soonawala[1] equs. XV, XVI, and XVII)

was calculated for various values of n, the number of the maximum. The total area of the curve between $\pi A/BC$ and n gives the value of the integral I.

As before, the value of a is taken to satisfy the relation $\frac{a}{2}\sqrt{p} = \frac{\pi}{1000}$

as the exact value of a has no effect upon the value of the integral. The results of such calculations for ammonia, carbon tetrachloride, and ethyl alcohol are given here in Tables I, II and III. I is not smooth function of log km, and hence it becomes necessary to calculate it in detail.

At any temperature, the value of F should be equal to the ratio of the number of molecules per c.c. in the vapour state to the similar number in the liquid state in equilibrium. Thus,

$$F = d/D$$

where d and D are the densities of the vapour and liquid in equilibrium. To make the calculated value of F agree with the experimental value of d/D, it becomes necessary to express F in the form

$$F = \frac{d}{D} = 4\,p\,e^{-km(b+\beta)} \sqrt{\frac{k\,m}{\pi}}\,I.$$

Hence, in the distribution law

$$dP = \left(\frac{k\,m}{\pi}\right)^{\frac{3}{2}} e^{-k\,m\,(u^2+v^2+\omega^2)}\,du\,dv\,dw$$

we have

$$dP = \left(\frac{k\,m}{\pi}\right)^{\frac{3}{2}} e^{-k\,m\,(n^2+v^2+\omega^2-\beta)}\,du\,dv\,dw,$$

$$= \left(\frac{k\,m}{\pi}\right)^{\frac{3}{2}} e^{-2k\left\{\frac{1}{2}m(u^2+v^2+\omega^2)-\frac{m\beta}{2}\right\}}\,du\,dv\,dw$$

Evidently, $m\beta = \phi/k$. Here $\phi/2k$ comes in as the potential energy of the molecule. The free energy is taken as $H = \frac{1}{2}(b+\beta)$, where $b = 4L$. The internal energy E and the free energy would be connected by Thomson's equation

$$H = E + T.\,dH/dT$$

$$\text{or, } (H-E)/T = dH/dT$$

As in the case of water, the values of dH/dT and

$(\dot{H} - E)/T$ agree fairly well. The results are set out in the tables below.

REFERENCES.

1. Soonawala, M.F.: Ind. Jour. Phy., **10**, 5,353, (1936).
2. Frenkel, J.: Wave Machanics, elementary; eqn. 80(b)
3. Ibid Eqn. 80
4. Soonawala, M.F.: Ind. Jou. Phy., **18**, 4, (1944)

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TABLE I (AMMONIA)

Temperature. °C	Log *km.*	Number of Maxima.	I	F	$r=\frac{d}{D}$
—45	$\overline{10}.6558$	130	3378	4.6×10^{-3}	7.2×10^{-4}
—20	$\overline{10}.6106$	135	4050	$2\ 1\times10^{-1}$	2.4×10^{-3}
0	$\overline{10}.5775$	140	4575	3.0×10^{0}	5.4×10^{-3}
20	$\overline{10}.5468$	145	5337	3.6×10^{1}	1.1×10^{-2}
50	$\overline{10}.5045$	150	6130	1.1×10^{3}	2.8×10^{-2}
132.5	$\overline{10}.4057$	180	25510	$2\ 7\times10^{9}$	1.0×10^{0}

TABLE II (CARBON-TETRACHLORIDE)

80	$\overline{9}.4247$	35	72	2.7×10^{0}	4.1×10^{-3}
140	$\overline{9}.3535$	40	95	6.6×10^{2}	1.9×10^{-2}
200	$\overline{9}.2946$	45	126	6.2×10^{4}	6.2×10^{-2}
240	$\overline{9}.2594$	50	158	1.5×10^{6}	1.4×10^{-1}
283.1	$\overline{9}.2243$	60	438	9.7×10^{9}	1.0×10^{0}

TABLE III (ETHYL ALCOHOL)

80	$\overline{10}.8981$	80	695	2.0×10^{-3}	2.4×10^{-3}
120	$\overline{10}.8515$	85	848	8.1×10^{-1}	9.5×10^{-3}
160	$\overline{10}\ 8094$	90	1036	6.7×10^{1}	3.0×10^{-2}
200	$\overline{10}.7710$	100	1527	3.7×10^{5}	9.1×10^{-2}
243	$\overline{10}.7333$	110	4325	1.2×10^{9}	1.0×10^{0}

TABLE IV (AMMONIA)

Temperature; O°C	$\beta \times 10^{-10}$ ergs per gm.	$H \times 10^{-10}$ ergs.	$P(v_2-v_1) \times 10^{-9}$ ergs.	$(H-E) \times 10^{-10}$ ergs.	$\left(\frac{H-E}{T}\right) \times 10^{-7}$ ergs per deg.	dH/dT from graph.	$\frac{\phi}{K} \times 10^{13}$ ergs.	$2\phi R \times 10^{15}$ ergs per deg.
—45	0·41	3·01	1·09	1·72	7·70		1·16	0·52
—20	1·09	3·20	1·82	2·00	7·88		3·09	1·21
0	1·68	3·36	1·24	2·22	8·15	8.04×10^{7}	4·74	1·74
20	2·30	3·53	1·27	2·47	8·41	lying between $7·7 \times 10^{7}$ and	6·52	2·22
50	3·31	3·75	1·25	2·83	8·76	$8·8 \times 10^{7}$	9·36	2·90
132·5	8·52	4·26	0·00	4·26	10·50		24·11	5·95

TABLE V (CARBON-TETRA CHLORIDE)

80	0·25	0·51	0·18	0·34	0·95		6·31	1·79
140	0·46	0·57	0·20	0·42	1·01	$9·6 \times 10^{6}$	11·85	2·87
200	0·70	0·63	0·18	0·51	1·07	lying between	17·91	3·79
240	0·89	0·66	0·15	0·57	1·11	$9·5 \times 10^{6}$ and	22·77	4·44
283·1	1·37	0·69	0·00	0·69	1·23	$1·1 \times 10^{6}$	35·09	6·31

TABLE VI (ETHYEL-ALCOHOL)

80	—0·02	1·69	0·62	0·90	2·55		—0·02	—0·05
120	0·54	1·79	0·65	1·10	2·79	$2·65 \times 10^{7}$	4·17	1·07
160	1·20	1·90	0·64	1·31	3·04	lying between	9·16	2·13
200	2·58	2·01	0·53	1.70	3·60	$2·5 \times 10^{7}$ and	19·75	4·18
243	4·23	2·12	0·00	2·12	4·10	$3·6 \times 10^{7}$	32·39	6·25

A POSSIBLE EXPLANATION OF THE ETHER DRIFT EXERIMENTS AND THE LAW OF REFRACTION OF LIGHT.

By

M. L. GUPTA M. Sc.

[*Abstract* :—The ether drift experiments being regarded as experiments to decide between the wave and corpuscular aspects of the velocity of light, an explanation of them has been attempted on the new corpuscular view, that of light consisting of a stream of photons each consisting of an energy quantum E and apparent mass E/c^2 where c is the velocity with which it moves. The apparent mass of a photon inside a refracting meduim has been considered to be μ^2 times its mass in vacuum where μ is the refractive index of the meduim. The law of refraction has also been proved according to the same concept. Thus lending further support to the view of an apparent change of mass of the photon inside the refracting medium.]

The calebrated series of experiments performed with a view to measure the relative velocity between ether and matter and known as ether drift experiments are ultimately experiments to find out the effect of the velocity of the meduim upon the velocity of light, whather the change in the velocity of light observed is due to a drift of the ether permeating material media or is due to the reactions of the medium upon the stream of light depends upon the particular theory of light propagation, we adopt. Since at the time when these experiments were carried out, the wave-theory of light reigned supreme and since these experiments themselves were made in quest of a physical proof of the existence of the ether and its motion, it was natural to interpret the change in the velocity of light with the motion of the medium as due to a drift of the ether with the material medium and to call all such experiments as ether drift experiments. But once we give up the idea of the wave in ether, it is no longer necessary to call them experiments on ether drift. The inconsistencies in the explanations of these experiments on the basis of an ether drift is sufficient proof against the supposition of the dependence of the velocity of light upon the ether, if not against the existence of the ether itself, and it theretore appears to be more correct to regard these experiments as deciding between the two opposing views for the velocity of light, one that of a wave-velocity and the other that of a particle velocity, considering light as something which partakes of the characteristics of both wave and particles ; in one case the velocity of light depending purely on the propertion of the ether and its motion and in the other case being influenced by the velocity of the source.

As has already been pointed out, during the days when these experiments were carried out, the wave-theory was regarded as being established beyond all possibility of doubt. There was therefore no question of interpreting the results of these experiments in terms of anythingelse but an ether drift. The very fact that even hypotheses such as the Fitzerald contraction and the time dilatation were brought forward to explain the negative result of the Michelson Morley experiment, shows the firmness with which the idea of light being a wave in ether was implanted in the minds of the physicists of those days. But now that the quantum hypothesis has brought about a resurrection of the corpuscular aspect of light, it is high time that we should reconsider these experiments and see whether they can be consistently explained according to the particle concept. There is no doubt that these experiments have since been explained by the theory of Relativity, but it has been again by introducing ideas that are contrary to all classical ideas about the nature of space and time, the Fitzerald contraction and the time dilatation being logical consequences of the fundamental hypotheses of the theory of relativity.

In what follows an attempt has been made to explain the results of the ether drift experiments in a simple way, making use of the new quantum conception, that of light consisting of particles of energy i. e. photons, each having mass equal to E/c^2 where E is the energy carried by each photon and C the velocity with which it moves. The eqution of the mass of energy $E=mc^2$ can of course be derived theoretically.

The key results of these experiments are the Fresnel convection co-efficient and the negative result of the Michelson Morley experiment and it will saffice for the purposes of this article to consider these two alone.

The Michelson Morley experiment:—it will be remembered that the result of this famous experiment was that the relative velocity of the ether with respect to the earth was zero i. e. that the ether was drifted with the whole velocity of the earth when the latter moved through space and that the velocity of light in the direction of the earth's motion was therefore $(c+v)$

where c is the velocity of light and v that of the earth with respect to a fixed frame of reference. It is clear that this precisely will be the result if the photon is regarded as partaking of the velocity of the source, which also being carried away in the direction of the earth's motion. The velocities in other directions will also be altered in such a manner that the velocity of light as measured by an observer on the earth in every direction will be only c. The velocity of light in any direction will be increased by an amount equal to the component of the velocity of the earth in that direction so that the velocity of ether drift in any direction (according to the ether drift interpretation of the change of velocity) will be equal to the velocity component of the earth in that direction and therefore the relative velocity of the ether with respect to the earth in every direction will be zero. The velocity of the earth will thus not make any alteration in optical phenomena observed with terrestrial sources of light and it will be impossible to detect the motion of the earth with optical experiments confined to the earth.

The Fresnel convection co-efficient :—it means that when a material medium moves with velocity v, the ether permeating the medium drifts only with a velocity $v\left(1-\frac{1}{\mu^2}\right)$, where μ is the refractive index of the medium and therefore the additional velocity imparted to a beam of light passing through the moving medium is only $v\left(1-\frac{1}{\mu^2}\right)$. To understand this result on the photon theory, we observe that the apparent mass of the photon inside the refracting medium is μ^2 times its mass outside : for let the velocities and masses of the photon outside and inside the refracting medium be c, c' and m, m' respectively. If E be the energy carried by each photon, then,

$m = \frac{E}{c^2}$ and $m' = \frac{E}{c'^2}$ (Tho energy remaining intact when the photon enters the medium).

$\therefore m' = \frac{E}{c^2} \cdot \frac{c^2}{c'^2} = \mu^2 m$ where $\mu = c/c'$ the refractive index of the medium-

The influence of the medium on the photon is thus merely to change its mass from m to μ^2 m. This change may well be thought of as due to the reactions of the particles of the meidum which decrease the velocity of the photon and consequently attract with it an apparent extra mass equal to $(\mu^2 - 1)$ m. When the medium is at rest, the extra mass (μ^2-1) m does not possess any velocity of its own ; but when the medium is in motion with velocity v, this fictitious extra-mass having its origin in the reactions of the particles of the medium is also moving with an inherent velocity v and its motion must be shared by the photon also. The momentum of the extra-mass on account of its velocity $=(\mu^2-1)$ m. v.

Since the photon shares the motion of the extra-mass, this momentum will also be the extra-momentum of the whole mass (photon + extra mass) i. e. μ^2m. Thus if v′ is the common velocity of the two masses inside the medium on account of the velocity v of the extra-mass (μ^2-1) m, we have on applying the law of conservation of momentum.

$$(\mu^2-1)\, m\, v = \mu^2 m\, v'$$

$$\text{or} \quad v' = v\left(\frac{\mu^2-1}{\mu^2}\right) = v\left(1-\frac{1}{\mu^2}\right)$$

Thus the additional velocity of the photon inside the moving medium on account of the velocity v of the latter is merely $v\left(1-\frac{1}{\mu^2}\right)$.

That a change in mass of the photon inside the medium actually takes place becomes clear when this very concept is applied to explain other important phenomena in optics. For example let us apply this to the explanation of the law of refraction of light. The momentum of the photon before and after entering the refracting medium are respectively mc and $m' c'$ or $\mu^2 mc'$.

Then as in Newton's Corpuscular theory, equating the components of momenta of the photon parallel to the surface, (for any forces acting on the photon can only be perpendicular to the surface of the medium) before and after refraction, we have,

$$m\,c \operatorname{Sin} i = m'\,c' \operatorname{Sin} r$$

$$\text{or } m\,c \operatorname{Sin} i = \mu^2 m\,c' \operatorname{Sin} r$$

$$\text{or } \frac{\operatorname{Sin} i}{\operatorname{Sin} r} = \frac{c^2}{c'^2} \cdot \frac{c'}{c} = \frac{c}{c'} = \mu$$

It is clear that for $\mu > 1$ i.e. for glass etc. the velocity of the photon inside the medium is less than that in vaccum a fact which could not be explained by the corpuscular theory of Newton and which led ultimately to its downfall.

It thus appears that the idea of the change of mass of the photon inside the refracting medium rests on foundations of truth.

PARACHOR OF SEMI-POLAR BOND FROM THE STUDY OF THE PARACHORS OF HYDRATED SALTS

By

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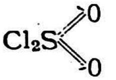
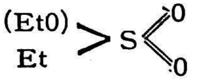
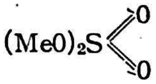
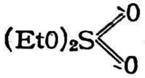
M. Sc.

W. V. BHAGWAT
D. Sc., F. A. Sc.

Sugden[1] in deducing atomic parachors has made a fundamental assumption that the contribution to the parachor of a shared pair of electron is zero. He has tried to justify his hypothesis by analysing parachors not in terms of atoms and linkages but in terms of electrons and cores. It has been shown that the atomic parachors can only be regarded as true measure of the volume of the atom, if the contribution of shared and unshared electrons are equal. He has examined mercury and thallus compounds and has verified the statement that the effect of sharing an electron is zero.

Sugden has also calculated the value of a semi-polar bond (He calls it semi-polar double bond) from the study of a number of compounds containing this bond. His results are reproduced below :—

Substance.	Formulae.	P. Obs.	ΣP	P. Semi-Polar.
Phosphorus-Oxy-Chloride	$Cl_3P \Rightarrow O$	217.6	220.6	−3.0
Ethyl Phosphate	$(EtO)_3P \Rightarrow O$	399 1	403.0	−3.9
Phenyl Phosphate	$(PhO)_3P \Rightarrow O$	686.5	687.7	−1.2
Thionyl Chloride	$Cl_2S \Rightarrow O$	174.5	176.8	−2.3
Sulphuryl Chloride	 $Cl_2S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$	193.3	196.8	−1.75
Ethyl Sulphite	$(EtO)_2S \Rightarrow O$	299.7	298.4	+1.3
Ethyl Ethane Sulphonate	 $\begin{smallmatrix} (EtO) \\ Et \end{smallmatrix} > S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$	295.8	298.4	−1.3
Methyl Sulphate	 $(MeO)_2S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$	238.9	240.4	−0.75
Ethyl Sulphate	 $(EtO)_2S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$	313.8	318.4	−2.3

Mean = −1.6

Here ΣP is the sum of the atomic and structural parachors except that of the linkage studied, namely the semi-polar bond. Sugden thus fixes a value of −1.6 for the parachor of a semi-polar bond.

In our opinion the determination of the contribution of a semi-polar bond to parachor needs revision. The above table clearly shows that there is no justification for assuming −1.6 as the mean value for a semi-polar bond. The values are so widely different from one another that we cannot take their mean. In one case the value is actully positive. Further Sugden himself admits that in his method of determining parachor there is a possibility of an error of 0.5%. In majority of cases the value of P.Obs. is about 300, or there is a possibility of an error of 1.5 units, a value which is attributed to a semi-polar bond. The simple inference therefore, is that the method of determining the parachor of a semi-polar bond adopted by Sugden is hardly accurate. If the value of a semi-polar bond is of the order of 1.6 it will not be possible to differentiate it from the experimental error, unless the compound contains a large number of semi-polar bonds. The proper method, therefore, would be to select such compounds, determine their parachors and then calculate the contribution due to a semi-polar bond by subtracting ΣP as defined above. The most suitable compounds in our opinion are the hydrates which contain large amount of water of crystallization or Werner's compounds. We have selected the following hydrates for this purpose :—

$CuSO_4.5H_2O$, $Na_2SO_4 10H_2O$, $Na_2CO_3.10H_2O$, & $MgSO_4.7H_2O$

The value of the semi-polar bond, in our case, will then be calculated as :—

P.Obs. $(CuSO_4.5H_2O) = \Sigma P + 5 \times P$. Semi polar, etc.

The difference will, therefore, be many times greater than the experimental error which is likely to occur and hence the true value for the parachor contribution of a semi-polar bond can be calculated accurately.

PARACHORS OF SALTS CALCULATED WITHOUT WATER OF CRYSTALLIZATION.

In calculating the parachors of the salt without water molecules the procedure adopted is as follows:—

A known weight of the hydrated salt was dissolved in a known weight of water. The amount of the salt without water of crystallization was calculated. The weight of this combined water was then added to the water actully taken. Thus the total weight of water was obtained. The molar fraction of each was then calculated as usual. One example will clear the point :—

Weight of $CuSO_4.5H_2O$	= 2.065 gms.
Hence weight of $CuSO_4$	= 1.321 gms.
Weight of water of crystallization	= 0.7432 gms.
Weight of water taken	= 12.64 gms.
Hence the total weight of water	= 13.38 gms.

Parachor of the solute has been found out by the method of solution viz. by the application sf Hammick and Andrews[3] equation.

$$Pm = X\,Px + (1 - X)\,Ps.$$

where :—

Pm = Parachor of the mixture.
Px = Parachor of the solute.
P_s = Parachor of the solvent.
X = Molar fraction of the solute.
$(1 - X)$ = Molar. fraction of the solvent.

Other symbols used in this paper are as follows :—

d = Density of the solution.
r = Surface tension of the solution

Onr experimental observations and the values of the parachors of anhydrous substances obtained are given in the following tables.

Parachor of $CuSO_4$

Temp.	Wt. of $CuSO_4$	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	1.321	13.38	0.0110	1.094	72.31	52.13	33.40
	2.745	11.98	0.0161	1.138	73.13	52.12	39.30
	3.243	19.88	0.0182	1.157	73.55	52.02	34 70
	4.386	22.14	0.0220	1.188	73.98	52.06	39.60
	2.051	9.943	0.0228	1.192	72.55	52.13	40.10
	2.383	10.21	0.0256	1.219	74.27	52.10	42.50

Parachor of Na_2SO_4

Temp.	Wt. of Na_2SO_4	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	4.183	17.40	0.0295	1.185	75.73	55.93	106.3
	4.623	20.82	0.0287	1.179	75.30	53.68	105.0
	3.167	16.95	0.0231	1.149	74.73	53.45	99.50

Parachor of Na_2CO_3

Temp.	Wt. of Na_2CO_3	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	5.778	24.86	0.0380	1.193	73.92	52.46	55.50
	5.033	19.92	0.0410	1.212	75.93	52.66	60.10
	6.020	20.05	0.0486	1.243	76.68	53.03	56.50

Parachor of $MgSO_4$

Temp.	Wt. of $MgSO_4$	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	2.687	11.79	0.0329	1.199	74.75	52.06	44.30
	3.754	12.34	0.0435	1 262	75.45	52.30	51.03
	4.432	12.77	0 0492	1.288	74.05	52.50	55.40

PARACHORS OF HYDRATES.

In this case a known weight of the hydrated salt is dissolved in a known weight of water. Thus the number of gm. moles. of the hydrated salt dissolved in known moles. of water are known and hence the molar fraction of each can be calculated as shown below :—

Weight of $Cu50_4.5H_20$ = 2.071 gms.
Weight of H_2O = 13.29 gms.

Hence the number of gm. moles. of $CuSO_4.5H_20$ dissolved
= 0.0083

and the number of moles. of water used
= 0.7386

Hence the molar fraction of $CuSO_4.5H_2O$ (i. e. X)
= 0.0110

Parachor of $CuSO_4.5H_2O$

Temp.	Wt. of $CuS0_4.5H_2O$	Total-Wt. of H_2O	X	d	r	Pm	Px
25c	2.071	13.29	0.0110	1.092	71.78	54.84	279.6
	2.733	11.98	0.0161	1.124	70.47	56.07	284.0
	5·249	19.90	0.0182	1.147	73.33	56.67	285.2
	6.870	22.16	0.0220	1.170	73.02	57.59	290.0
	3.213	9.992	0.0228	1.174	72.13	57.71	288.8
	3.731	10.21	0.0256	1.193	73.02	58.65	298.7

Parachor of $Na_2SO_4.10H_2O$

Temp.	Wt. of $Na_2SO_4.10H_2O$	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	7.305	16.96	0.0231	1.220	72.09	65.33	607.4
	10.48	19.85	0.0287	1.137	72.65	68.55	608.1
	9.496	17.49	0.0295	1.410	71.93	68.79	611.8

Parachor of $Na_2CO_3.10H_2O$

Temp.	Wt. of Na_2CO_3 $10H_2O$	Total Wt. of H_2O	X	d	r	Pm	Px
25°c	7.829	12.45	0.0380	1.147	72.76	71.80	564.4
	6.778	9.950	0.0410	1.155	74.30	73.78	573.9
	16.39	20 18	0.0486	1.171	74.75	77 75	575.1

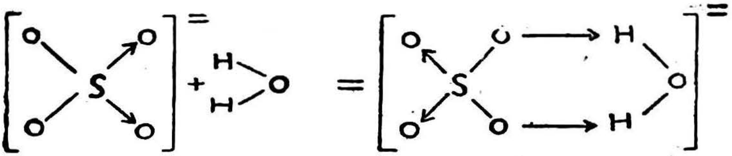
Parachor of $MgSO_4.7H_2O$

Temp.	Wt. of $MgSO_4 10H_2O$	Total Wt. of H_2O	x	d	r	Pm	Px
25°c	5.508	11.79	0.0329	1 169	73.35	63 95	405.7
	7.710	12.39	0.0435	1.206	73 31	67.79	409.2
	9.112	12.79	0.0492	1.223	74.64	70.37	413.3

Classical theory originally assumed that the valency of an element is a constant quantity. This assumption however failed to explain the structure of such compounds as $ZnSO_4.7H_2O$; $COC1_2.6NH_3$; K_2SO_4 (Al_2SO_4).24H_2O ; KF HF etc. In 1891 Werner showed that in addition to the 'principal' valency, some atoms possess the power of uniting between themselves, atoms, groups, or even apparently saturated molecules by 'subsidiary' valency. Werner's theory had, however one serious drawback. It was necessary to postulate two kinds of valencies ; 'principal' and 'subsidary', but no satisfactory reason was assigned to this distinction.

The electronic theory of valency has enabled us to solve these problems successfully. Sidgwick (1923)[3], for the first time, accounted for the structures of coordinated complexs where combination is taking place between apparently saturated molecules and ions or between saturated molecules as in hydrates.

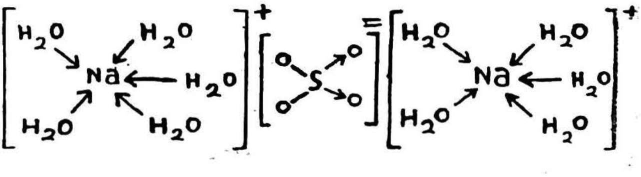
The hydration of salts which occurs in solution or in solid state (so called water of crystallization) is easily understood, since water molecule contains unshared electrons which it is ready to donate. This explains the hydration of many salts assuming the hydration of cation only. There are many hydrates however, with one more molecule of water of crystallization beyond the number allowable to the cation by co-valency rule, e. g. $ZnSO_4.7H_2O$ and other 'vitriols'. It is possible therefore, that the anion is also hydrated here, since water can take part in dative co-valency either by donation on the part of oxygen atom or by acceptance on the part hydrogen. The former occurs when a cation is hydrated ; the latter may produce hydration of a suitable anion as SO_4.



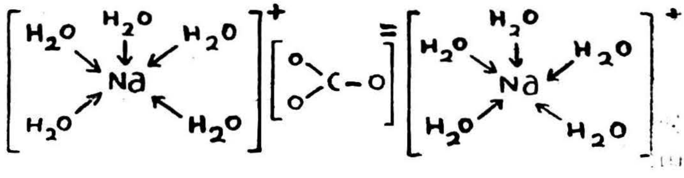
On the above lines the structures of the hydrates investigated by us are follows :—

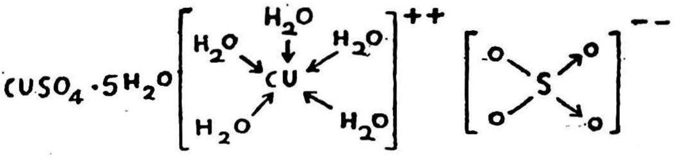
(the maximum co-ordination number of Cu, Na and Mg atoms is six.)

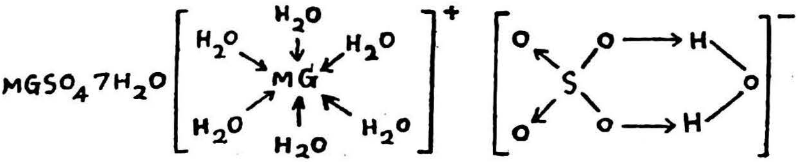
$Na_2SO_4.10H_2O$



$Na_2CO_3.10H_2O$







Thus there are twelve semipolar bonds in $Na_2SO_4.10H_2O$; ten in $Na_2CO_3.$ $10H_2O$; ten in $MgSO_4.77H_2O$ and seven in $CuSO_4.5H_2O$. Hence these compounds can be advantageously used for determining the parachor contribution by a semipolar bond, as the experimental error will be negligible in comparison to the total contribution to parachor by these large number of semipolar bonds in these hydrates.

We have :—

P. obs. (Na_2SO_4.10 H_2O) – P. obs. Na_2SO_4. – 10 P.H_2O=
10 P. Semipolar bond

In a similar way the value of parachor contribution of a semipolar bond can be calculated from other hydrates.

The method used by us for calculationg P. Somipolar is somewhat different from that of Sugden. He employed the expression :—

$$X \text{ P. Semipolar} = \text{P obs.} - \Sigma \text{P}$$

Where Σ P is the sum of the atomic and structural parachors except that of the linkage studied. This method cannot be employed here since the parachor of electrolytes as observed in water is never given by summing up the parachors of the constituent atoms and linkage. It is necessary, therefore to determine the parachor of the salt without molecules of water to get P. obs. This was done by dissolving the hydrated salt in water and then calculating the amount of the salt and the total water as explained in the beginning. Further complications are introduced in these investigations by the fact that the parachor values of electrolytes change with dilution. No comparision will be accurate unless the parachor values are determined with the same molar concentration for the salt with and without water of crystallization. We have, therefore, determined the parachors at the same molar concentration. The results are recorded in the previous tables.

If a semipolar bond had no parachor value then the results obtained by two methods should only differ by the value corresponding to the parachor of molecules of water present in the hydrate. Actually it is not so.

The following values are obtained for the structural parachor of a semipolar bond from these results :—

Salt	X	P. with water of cryst.	P. Without water of cryst.	n P. of H_2O	P. Semi-polar
(Temp. 25°c)	0.0110	279.6	33.40	261.5	-3.10
$CuSO_4.5H_2O$	0.0161	284.0	39.30	261.5	-3.40
	0.0182	285 2	34.70	261.5	-2.20
	0.0220	290.9	39.60	261.5	2.20
	0.0228	288.8	40.10	261.5	-2.60
	0.0256	298.7	40.20	261.5	-3.10
	0.0231	607.4	99.50	523.0	-1.50
$Na_2SO_4.10H_2O$	0.0287	608.1	105.0	523,0	-2.00
	0.0293	611.8	106.3	523.0	-1.74

Salt	X	P. with water of cryst.	P. Without water of cryst.	n P. of H_2O	P. Semi-polar
$Na_2CO_3.10H_2O$	0.0380	564.4	55.50	523.0	-1.41
	0.0410	573.9	60.10	523.0	-0.92
	0.0486	575.1	66.30	523.0	-1.44
$MgSO_4.7H_2O$	0.0329	405.9	44.30	366.1	-0.55
	0.0432	409.2	51.03	366.1	-1.00
	0.0492	413.3	55.40	366.1	-1.00

The number of semipolar bonds left in the expression :—P.(Salt)—P.(Salt without water of cryst.) − n P. H_2O is = n in case of copper sulphate, sodium sulphate and sodium carbonate, (since in copper sulphate and sodium sulphate the semipolar bonds associated with SO_4 groups are cancelled in the subtraction they being common to hydrated as well as anhydrous salt.) In case of magnesium sulphate this difference, however, cannot bequal to 'n' but is n + 1, since when SO_4 ion is hydrated two more semipolar bonds come into existance. The results with magnessium sulphate are particularly low. This is because we have not taken into account the fact that in case of magnesium sulphate the hydration of SO_4 ion produces a ring of six. The value of the contribution of semipolar bond in this case will, therefore, be given by :—

P. Semipolar = P. (hydrate)—P. (Anhydrous) − n P.H_2O − P. ring of six Thus we have

Salt	X	P.(hyd.)-	P. (anhyd.)-	-P. ring of six	-n P. of H_2O	P. Semi polar
$MgSO_4$, $7H_2O$	0.0329	405.9	-44.30	-6.10	-366.1	-1.30
	0.0432	409.2	-51.03	-6.10	-366.1	-1.70
	0.0492	413.3	-55.40	-6.10	-366.1	-1.80

The above results clearly establish the fact that the parachor contribution of a semipolar bond is negative. This is in accordance with Sugden's observation, but in. our case no anamolous + ve result has been obtained. Further the results are more in line with one another and are more reliable. Sugden has determined his values from compounds which contained one or two semipolar bonds so that the experimental error of 1.5 units which is possible in his expriments is of the same order of magnitude as the value of the semipolar bond obtained by him. If very high and very low results are neglected in our case an avarage value of the parachor contribution by a semipolar bond comes out to be − 1 8. The value is not very different from that given by Sugden (− 1.6) but the value is based on reliable reasoning and is truely an average of the values which are not widely different from one another. Sugden's value being an arbitrary mean of the observed results involving the same amount of error as the result itself. Incidently the results with magnesium sulphate support the hydration of anion, by semipolar bond through hydrogen, so as to form a ring of six.

SUMMARY

The parachor value of a semipolar bond has been determined from compounds (hydrates) containing large number of semipolar bonds. It is shown that Sugden's method of calculation was not reliable. If semipolar bond had no parachor value the parachor calculated for a salt with and without water of crystallization would have differed by an amount equal to the parachor value of water molecules. It is observed that it is not so. A value equal to − 1.8

has been obtained for the parachor of a semipolar bond. Incidentaly the hydration of anion in case of $MgSO_4.7H_2O$ is established.

REFERENCES

1. Sugden The Parachor and valency page......116
2. Hammick and Andrews. J. Chem. Soc., 754, 1929
3. Sidgwick J. Chem. Soc., 123, 725, 1923

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ISOMERISATION OF α– NAPHTHYLAMINE THIOCYANATE AND m-NITRO-ANILINE THIOCYANATE.

By

RAMJI LAL MITAL R. D. GUPTA

The present investigation was under-taken, primarily, to (i) correlate alkalinity of bases with the speed of isomerisation of their thiocyanates to, substituted thiocarbamides, in presence of media and without them and (ii) ascertain conditions, including presence of functional groups, influencing setting up of equilibrium, in systems, referred to above, such as has been observed in case of ammonium cyanate $\rightleftarrows$ urea,[1] ammonium thiocyanate $\rightleftarrows$ thiourea.[2] Indications of attainment of equilibrium has also been met in the system aniline thiocyanate $\rightleftarrows$ mono - phenyl - thiocarbamide[3].

α – Naphthylamine thiocyanate, m. p. 130-131°C, a thiocyanate of a base, having the dissociation constant 9.9×10^{-11} at 25°C is prepared. Study of its isomerisation to substituted thiocarbamide is undertaken. Its insolubility in water and stability at room temperatures, are strikingly different from those of the thiocyanate of aniline – a base having the dissociation constant 4.6×10^{-10} at 25°C. A sample of α – Naphthylamine thiocyanate kept in air at room temperatures including summer temperatures for over two years, did not undergo any isomerisation to substituted thiocarbamide. The change could not be detected even qualitatively. Aniline thiocyanate, under similar conditions, was found to change completely to its isomer, in less than six months. The stability of α – Naphthylamine thiocyanate cannot be explained on the basis of dissociation of the base.

From the results of isomerisation, in aqueous alcoholic solution at 84-85°C and in solid state i. e. without medium, at 100°C/and 130°C, it may be concluded that the introduction of a negative radical, hastens isomerisation considerably. A similar study of m-Nitro. aniline thiocyanate, also confirms the above conclusion. Ammonium thiocyanate does not isomerise under similar conditions, and is found to isomerise only in the fused state at 149°C-150 C.

The establishment of a condition of dynamic equilibrium, in the system α - Naphthylaminethiocyanate $\rightleftarrows$ α – Naphthylthiocarbamide in aqueous alcoholic solution at 84-84°C, when the concentration of the reversible isomerides is 1:1, has been observed and confirmed. The change is monomolecular.

EXPERIMENTAL

Preparation of α — Naphthylamine thiocyanate :—

It was prepared by mixing ethereal solution of thiocyanic acid and α - Naphthylamine in equivalent proportions, when a white crystalline solid separated. This was crystallised from dry dioxane. The melting point was found to be 130–131°C.

Preparation of m—Nitroaniline thiocyanate.

This, also, was prepared by mixing ethereal solutions of thiocyanic acid and m–Nitroaniline, in equivalent proportions. A white crystalline solid separated out. This was crystallised from absolute alcohol. The melting point came out to be 139–140°C.

Study of isomerisation α—Naphthylamine thiocyanate in aqueous alcoholic solution (35 : 65) at 84–85°C.

Concentrations of aqueous alcoholic solution of Naphthylamine thiocyanate were N, N/2 and N/5.

Solutions of α—Naphthylamine thiocyanate were refluxed in a conical flask, attached to an efficient condenser, carrying an outlet, for taking out samples, at desired intervals of time. For cutting of loss of heat, due to radiation, the entire apparatus was shielded by means of a hollow wooden protector. After definite intervals of time, known volumes were withdrawn, cooled and analysed.

Study of isomerisation in aqueous alcoholic solution of m–Nitraniline thiocyanate at 84–85°C.

This also, was studied in the same way as α—Naphthylamine thiocyanate. The concentrations of solutions were N/2 & N/5. Normal solution could not be prepared in this case, due to its limited solubility, in aqueous alcohol.

Method of estimating thiocyanic acid in presence of substituted thiocarbamide and α—Naphthylaminc.

Naphthylamine gives a blue colour with a ferric salt, which is used as an indicator in such estimations. As such, blue colour would mask the end point.

Both thiocyanic acid and substituted thiocarbamides give insoluble precipitates with silver nitrate or mercuric nitrate, in presence of nitric acid[5]. Hence thiocyanic acid, in presence of substituted thiocarbamides, was estimated as follows.

The liquor, under examination, was treated with an excess of 10% sodium hydroxide solution, to precipitate α—Naphthylamine. Clear filtrate was desulphurised with ammoniacal silver nitrate. Excess of silver was removed by passing H_2S, excess of which (H_2S) was removed by adding cadmium carbonate. The mixture was left over night. The clear filtrate, after acidification with dilute nitric acid, was titrated against standard mercuric nitrate. Unchanged α—naphthylamine thiocyanate was then calculated. 1.c.c. of N/20 mercuric nitrate = 0.01 gm. of naphthylamine thiocyanate. The velocity constant was calculated with the help of the following formula.

$$K = \frac{1}{t} \log \frac{a}{a-x}$$

where t = time

a = initial concentration of thiocyanate of α—naphthylamine.

a — x = concentration of thiocyanate of the base, after time t,

Method of estimating thiocyanic acid in presence of m—nitroaniline and m-nitro-phenyl thiocarbamide.

This was estimated as in the case of α—naphthylamine thiocyanate, but the substituted thiocarbamide so formed was desulphurised by William's method i. e. by the addition of 10 c. c. of 10% cadmium sulphate and 10 c. c. of 10% sod. hydroxide solution. The cadmium sulphide, so precipitated, on heating, was filtered. The filtrate was titrated against standard solution of mercuric nitrate, using ferric alum as indicator. 1. c. c. of N/20 mercuric nitrate = 0.00985 gm. of m – nitrophenylamine thiocyanate.

Study is isomerisation in solid state i. e. without a medium at 98°C and 130°C

Several test tubes, having definite amounts of solid α – naphthylamine thiocyanate, arranged in a rack, were put in a bath maintained at a particular temperature. After definite intervals of time, known weight of the heated residue were estimated for thiocyanic acid contents as described above.

Study of isomerisation, in solid state i. e. without a medium, of m-nitroaniline thiocyanate at 98°C and 140°C

This was studied in the same way as α – naphthylamine thiocyanate.

TABLE I

Isomerisation of α – Napthylamine thiocyanate in aqueons alcoholic solution (35 : 65)
Concentration N/5 Temperature 85°c

Time in hours	Percentage of HCNS remaining behind	Velocity constant
2	95.57	.02228
4	90.60	.02672
6	85.63	.02809
8	81.21	.02647
10	77.07	.02626
11	71.82	.03535
12	69.06	.03914
13	66.3	.04077
14	62.93	.0520
15	62.93	...

Result:—Only 62.93% of HCNS remained behind after 15 hours heating.

TABLE II

Isomerisation of α—Naphthylamine thiocynate in aqueons alcoholic solution (35 : 65)

Concentration N/2 Temperature 85°c

Time in hours	Percentage of HCNS remaining behind	Velocity constant
2	75.73	.1389
4	71.69	.02752
6	68.02	.02629
8	64.46	.02683
9	62.5	.03086
10	60.60	.02973

Result :—After 10 hours heating only 60.60% of HCNS remained behind.

TABLE III

Isomerisation of α—Napthylamine-thiocyanate in aqueons alcoholic solution

Concentration N Temperature 85°c

Time in hours	Percentage of HCNS remaining behind.	Valocity constant
2	66.04	.2075
4	62.75	.02557
6	59.95	.02867
8	56.04	.02786
10	53.20	.02786
12	50.38	.02717
13	50.56	...
14	50.56	...
15	50.56	...

Result :—The conversion of normal solution of α—Napthylamine-thiocyanate into α—Napthyl-thiccarbamide in 12 hours is nearly 50%.

TABLE No. IV

Conversion of α—Napthylamine-thiocyanate into the corresponding Thiocarbamide when heated in the solid state at its melting point (130° c).

Time in minutes	Percentage of HCNS remaining behind
2	25.02
4	17.37
6	15.13
8	12.32
10	6.16
11	5.60
12	5.32
13	5.04
14	5.04
15	5.04

Result :— At 130-131°c in 13 minutes only 5.04% of HCNS remained behind.

TABLE No. V

To study the rate of the isomerisation of α—Napthyl-thiocarbamide in alcoholic solution into α—Napthylamine-thiocyanate.

$$C_{10}H_7NH.CS.NH_2 \rightleftarrows C_{10}H_7NH_2\ HCNS$$

Concentration 1.1732% Temperature 85°c

Time in hours	Percentage of HCNS formed	Velocity constant
20	3.82	.001946
30	6.68	.003017
40	9.53	.003109
50	12.89	.003800
70	18.62	.003396
90	20.87	.003339
100	26.26	.003399
110	28.64	.003289

Result :—In 110 hours only 28.94% of HCNS was formed. The reaction is very slow.

TABLE No. VI

The Rate of isomerisation of m. Nitroaniline-thiocyanate in aqueous alcoholic solution into corresponding thiocarbamide.

Concentration N/5 Temperature 85°c

Time in hours	Percentage of HCNS remaining behind.	Velocity constant
4	90.06	...
6	83.52	.03766
8	77.33	.03834
10	71.74	.03768
12	66.45	.03823
14	61.49	.03880

Result :—After 14 hours heating only 61.49% of HCNS remained behind.

TABLE No. VII

Rate of isomerisation of m. Nitroaniline-thiocyanate in aqueous alcoholic solution into corresponding thiocarbamide

Concentration $\frac{N}{2}$ = Temperature 85°c

Time in hours	Percentage of HCNS remaining behind.	Velocity constant
2	87.21	.06852
4	80.90	.03754
6	75.08	.03731
8	69.65	.03754
10	64.63	.03743
12	59.94	.03766
13	57.76	.03708
14	55.68	.03662

Result :—After 14 hours heating only 55.68% of HCNS remained behind.

TABLE No. VIII

Rate of isomerisation of m. Nitroaniline-thiocyanate into corresponding thiocarbamide when heated at m. point (139°–140°c), in solid state.

Time in minutes	Percentage of HCNS remaining behind
5	9.09
10	9.58
12	6.97
14	6.97
16	6.97
18	6.97
20	6.97

Result :—In about 12 minutes time at 139-140°c the change seems to attain equilibrium or the change is very slow and so could not be measured.

TABLE No. VIII (a)

Rate of isomerisation of m. Nitroaniline-thiocyanate into corresponding thiocarbamide when heated at 98°C in solid state.

Time in minutes	Percentage of HCNS remaining behind
10	66.66
20	63.64
30	62.12
40	30.30
50	28.78
60	26.67
70	24.24
80	19.69
90	16.66
100	15 55

Result :—In 100 minutes time only 15.55% at HCNS remained behind.

TABLE No. VIII (b)

Rate of isomerisation of α– Napthylamine-thiocyanate into coresponding thiocarbamide when heated at 98°C in solid.

Time in minutes	Percentage of HCNS remaining behind
10	88.52
20	64.42
30	63.30
40	56.08
50	55.46
60	54.24
70	53.22
80	44.82
90	42.52
100	41.46

Result :—In 100 minutes heating on 98° C only 41.46% of HCNS remained behind.

TABLE No. IX

Isomerisation of m. Nitrophenyl-thiourea into m. Nitroaniline-thiocyanate in aqueous alcoholic solution.

Concentration 1% Temperature 85°c

Time in hours	Percentage of HCNS formed	Velocity constant
10	No Thiocyanate was observed even qualitatively.	
20	2.98	.001509
30	5.88	.003038
40	8.72	.003064
50	11.45	.003040
60	14.14	.003086
70	16.68	.003017
80	19.22	.003088
90	21.64	.003039
100	24.07	.003155

Results :—The Conversion is very slow. After 100 hours heating at 85°c only 24.07% of HCNS was formed.

TABLE No. X

Comparative results of α - Napthylamine-thiocyanate & m. Nitroaniline thiocyanate in alcoholic solutions.

Pereentage of Thiocarbamide formed.

Tempr 85°c

Concentration	Interval of time	m. Nitrcaniline *$k=4.0\times10^{-12}$	α—Napthylamine $k=9.9\times10^{-11}$
N/5	4 hours	9.94%	9.40
	8 hours	22.67%	18.79
	12 hours	33.55%	30.94
	14 hours	38.51%	37.07

Result :—The Conversion is more rapid in the case of m. Nitroaniline —thiocyanate (thiocyanate of a base having the dissociation constant 4.0×10^{-12} at 25°c)

SUMMARY.

1. α— Napthylamine and m. nitroaniline thiocyanates were prepared for the first time.
2. Introduction of negative radical in thiocyanates of bases hastens isomerisation to substituted thiocarbamides.
3. Setting up of conditions of dyanamic equilibrium in the system of α Napthylamine-thiocyanate and corresponding substituted thiocarbamide when the concentration of reversible isomerides is 1 : 1, has been observed and confirmed.

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*k=the dissociation constant at 25°c.

REFERENCES.

1. Walker & Hambly, J. C. S., 1895, **67**, 7 48.
2. Reynolds & Werner, J. C. S., 1903, **83**, 1.
   Atkins & Werner, J.C.S., 1912, T, **99**, 1167 and 1982.
3. Gupta, R. D. & Gupta N. P., Proe. Raj. Acad of Sc. 1950, **1** (1), 9.
4. Atkins & Werner, J.C.S., 1912,(T) 99, 1167 and 1982.
5. Williams J. S. C. I. 1932, **58** 77-79 T.

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CONSIDERATIONS IN THE DESIGN OF GAS TUBES FOR LOW VOLTAGE INVERTER CIRCUITS.

By

Dr. A. K. CHATTERJEE.

Introduction :

The Commercial hot cathode gas tubes used for inverter circuits for the conversion of D. C. to A. C. have tube drops of the order of 10 to 20 Volts. The input D. C. Voltage in such circuits is usually 115 volts or higher and as such the tube drop forms only a small fraction of the available voltage and no difficulty is encountered in the conversion. But if the D. C. supply voltage happens to be low, for instance, of the order of 24 volts, the relative tube drop becomes a considerable part of the total available voltage and consequently the conventional inverter circuits give discouraging results. Such conversion is often required, as for example, in case of mobile transmitters operated from 24 volts battery. Present method is to use mechanical vibrator for the purpose which, though satisfactory under normal condition, are sometimes not reliable and trouble is experienced sometimes in the moving contacts. Replacement of this vibrater by an electronic device would therefore be highly welcome. Since the available D. C. voltage is low, it is apparant that if any of the conventional circuits is to be used a gas tube has to be developed which will have a tube drop not exceeding 2 or 3 volts.

A study of the behaviour of the gas tubes with regard to tube drop under various conditions of electrode spacing, gas pressure and temprature and type of gas used has been made in the present paper. Experiments have been made on commercial tubes, results of which indicate the possibility of a new approach towards developing a low voltage drop gas tube.

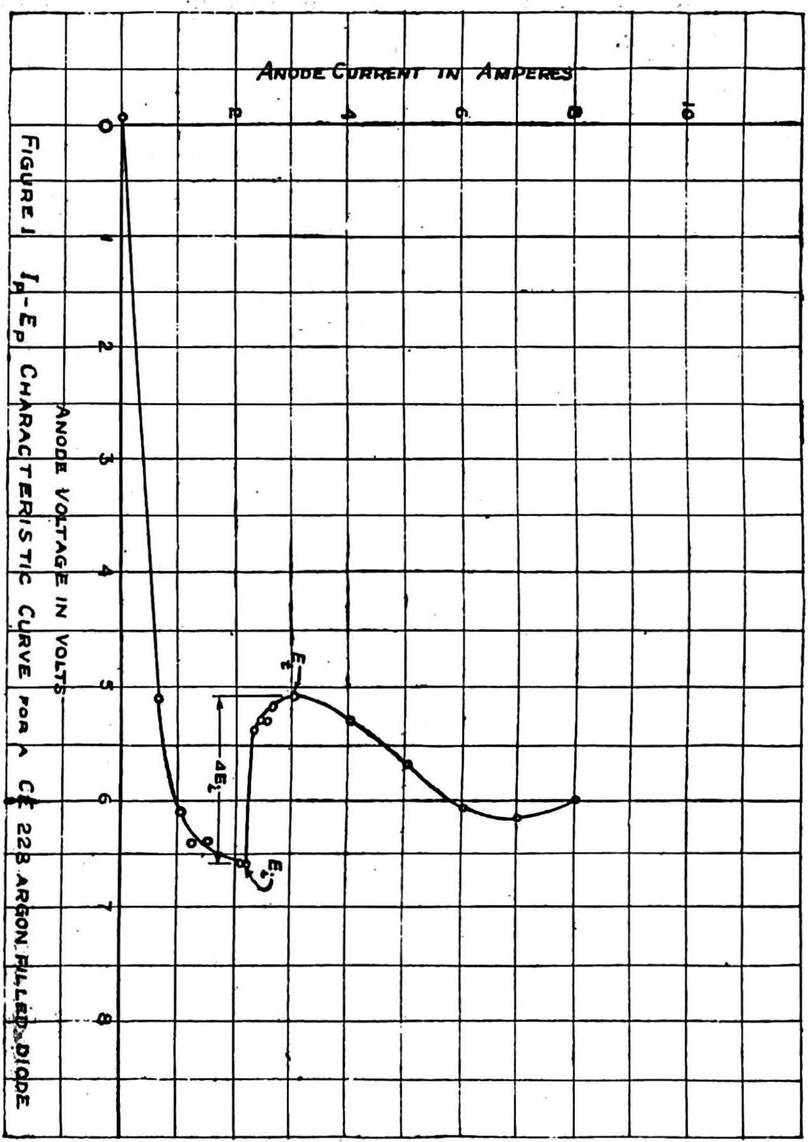
2. Characteristic of a gas Diode.

A study of the literature on gases and their behaviour revealed that, although much information is available, the theoretical considerations are not carried far enough to be of much help in making actual computations towards tube design. Some experimental results are recorded and these proved to be of limited help.

Since calculated results were either questionable or impossible to obtain, some simple experiments were then made on commercial gas tubes. Quantitative results were obtained where possible, and where actual measurments could not be made qualitative results were accepted.

Fig. 1. Shows the anode characteristic of the commercial gas tube CE 228 which is a argon filled diode. It will be seen that there is a negative resistance region between the ignition potential E_i and the start of the region of stable operation indicated by E_t. This region is designated as ΔE_i and will hereafter be referred to as the ignition drop.

If an arc tube is to function as a commutating device, the range of voltage in the negative resistance region should be as great as possible. In other words, the voltage required to start the arc (ignition voltage)



(Fig. 1)

should be large and the tube drop E_1 which is obtained after the arc is started should be as small as possible. In the case under consideration, an ignition voltage of the order of 20 volts or so and a tube drop of about 2 volts would be quite satisfactory.

3. Effect of variation of electrode spacing, gas density, temp., etc.

Theoretical considerations show that the tube drop in a gas tube is a function of electrode spacing, gas density, gas temperature and the ionizing potential of the gas. The following experiments were performed to verify the above statement and if possible to determine ways and means of extending the range of ignition drop.

(a) **Electrode Spacing :** A test to determine the effect of electrode spacing on tube drop and ignition drop was made on type FG57 mercury vapour thyratron. The ignition voltage and tube drop were measured with the tube operated as a diode, first using the anode and the cathode and then using the grid and cathode. The following results were obtained.

	E_t	E_i	$\triangle E_i$
Plate and Cathode	10 volts	11 volts	1 volt.
Grid & Cathode	4 volts	9 volts	5 volts.

The results of this test indicate that for the plate to cathode spacing, the tube drop is 2.5 times that for the grid to cathode spacing, and the ignition drop is increased 5 times when the spacing, is reduced. Although the experiment is rather crude it suggest the importance of electrode spacing as a factor in controlling the tube drop and ignition drop.

It may be remembered that the main consideration which limits the electrode spacing in commercial tubes is the peak inverse voltage when the tube is used as a rectifier. In the present case the peak inverse voltage will never exceed 48 volts and therefore closer spacing can be safely used if this materially improves the desired characteristic.

Effect of Temperature: Two tests were made, one on a type CE 228 argon filled tunger tube and the other on a type WE249C mercury vapour diode. The tube being tested was placed in an oven and readings of ignition potential, anode current and tube drop were taken as the temperature of the tube was increased. The results are recorded in Table I.

TABLE I.

Data for Argon filled Diode.

T	E_i	T_p	E_t	ΔE_i
Deg.C	volts	Amps.	volts	volts
50	11.5	3	6.1	5.4
60	11.5	3	6.2	5.3
80	12.0	3	6.4	5.6
100	12.2	3	6.6	5.6
120	12.3	3	6.1	6.2
140	12.0	3	6.1	5.9

Data for Mercury Vapour Diode.

50	10.0	3	7.0	3.0
60	10.1	3	7.4	2.7
80	10.0	3	6.8	3.2
100	9.6	3	5.8	3.8
120	9.4	3	5.5	3.9
140	12.5	3	5.1	7.4

Before attempting to compare and analyse the results, an important difference in the two tests must be recognised. The argon filled diode contained a given volume of gas and, except for minor expansion of the glass envelope, the volume, and hence the density of the gas remained constant as the temperature was increased. In the mercury vapour diode, however, the density of the vapour increased with the temperature because as the temperature was raised, more of the mercury in the tube was evaporated.

The data for the Tungar tube show that as the temperature is increased, there is a slight increase in the ignition Potential but very little change in the tube drop. Ignition drop, therefore increases very slightly with temperature. The mercury vapour diode, on the other hand, shows an increase in the ignition potential, a decrease in the tube drop and a considerable increase in ignition drop. From the results of this test, therefore, it appears that although the gas temperature has some effect on the firing characteristics of a gas tube, the gas density has a much greater effect than the temperature. It appears, therefore, that if argon is used at a higher pressure than is usually used, the gas density will increase and so the tube drop will be reduced and the ignition drop will be increased.

The test described so far seem to indicate that the tube drop can be lowered by reducing the electrode spacing, increasing the gas density, and increasing the gas temperature. The ignition drop is increased to some extent by these changes, but not sufficiently to provide the characteristic desired. In a typical thyratron, the ignition potential is satisfactorily controlled by a grid. In a tube using critical anode cathode spacing, needed to minimise tube drop, it may be impracticable to attempt to place a control grid in the tube. *The critical grid voltage is determined by the pressure, as well as electrode spacing and if the temperature and pressure are sufficiently high the grid may lose control entirely.

It is suggested that for such a gas tube with critical anode cathode spacing, the ignition potential may be controlled by a magnetic field. If a magnetic field is placed so that the lines of force are at right angles to a line between anode and cathode, the ignition potential is raised. An experiment was performed for the purpose of determining the effect of a magnetic field on the tube drop and ignition drop, and to determine how these voltages vary with filament voltage, The data are recorded in Table II.

TABLE II

E_f volts	I_f Amps.	I_p Amps	E_i volts	E_t volts	ΔE_i volts	Magnetic Field.
2.5	20.3	1.30	12.2	4.32	7.86	0
2.3	19.5	1.26	12.5	4.8	7.70	0
2.0	18.3	1.24	13.0	5.15	7.85	0
2.5	20.3	1.13	14.5	7.30	7.70	H°
2.3	19.5	1.13	14.8	7.50	7.30	H°
2.0	18.3	1.10	15.0	7.90	7.10	H°

Where E_f – filament voltage.
I_f – filament current.
I_p – Anode current.

H° indicates that a magnetic field was present, the exact magnitude of which was not determined since

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* Theory and applications of Electron Tubes H. J. Reich pp. 442 2nd Edition.

the experiment was performed merely for the purpose of comparison.

An analysis of the data in table 1 reveals several interesting facts which lead to certain conclusions. In the first place, it is apparant that a magnetic field raises the ignition potential. With rated filament voltage, an increase of 18.8% in the ignition potential was obtained by the application of a magnetic field. This is desirable because a higher ignition potential is being sought. The data further reveal, however, that the application of a magnetic field also raises the tube drop so that the ignition drop is actually less with a magnetic field than it is without. This is unfortunate because a large ignition drop is desired.

If the circuit could be operated so that the magnetic field was present when the tube fired and was then immediately removed, the ignition potential according to the above data, would be 14.5 volts, the tube drop (without field) would be 4.32 volts, and the ignition drop would be 10.18 volts. In this way a magnetic field could be used satisfactorily to obtain the desired characteristics.

The importance of proper filament voltage, which assures a copious supply of electrons emitted, is also shown by the above data. When the filament voltage is reduced, the ignition potential is increased but the tube drop also is increased so that the ignition drop actually decreased.

Tube Design Considerations:

The gas tube which will satisfactorily meet the requirements of this application should have the following characteristics :—

1. The tube drop should be of the order 2 volts.
2. Ignition must be controllable so that an ignition potential greater than 20 volts may be obtained.
3. In the final design, the tube must conduct currents of sufficient magnitude to give the desired output.
4. The cathode heating structure must be efficient.
5. Peak inverse voltage need not be greater than 48 volts.
6. A gas having a low ionization potential and not critical as to ambient temperature should be used.

A tube drop of 2 volts may be impossible to actually obtain but it is a value that is desired. In the tunger tube, a tube drop of less than the ionization potential of the gas is obtained. This is probably due, in part, to the pressure (about lmm of H_g). By proper selection of gas pressure and electrode spacing this may be reduced.

The selection of proper gas is also an important factor. Mercury vapour is used in the majority of the larger gas tubes but since the vapour pressure of mercury is a function of temperature, changes in ambient temperature results in changes of operating characteristics, so that mercury vapour would be unsuitable for this application. The inert gases are better in this respect although they have some disadvantages when compared with mercury. Xenon, which is the most desirable of the inert gases because of its low ionization potential, is very rare and, therefore, much more expensive than mercury. Furthermore, the inert gases are more difficult to introduce into the tube than mercury. Cesium has a very low ionization potential (about 3.9 volts) and so a tube could probably be developed using cesium vapour as the conducting gas and an atomic layer of cesium on a tungsten surface as an emitter. But cesium is very active and considerable practical difficulties are experienced in introducing it into the tube and it also effects the sealing meterial. Moreover the operating characteristics would depend on temperature more then those of mercury and so it may not be suitable for the purpose.

Recently Mr. A. W. Hull of the General Electric Co. U. S. A. claimed to have developed a cesium rectifier but so far it has not come out in the commercial field.

Although the power required to heat the cathode is essential to provide a copious supply of emitted electrons, it represents a loss which must be charged against the efficiency of the tube. It is important, therefore, that a well designed cathode heating structure be used. Probably the most efficient arrangement would be to have an indirectly heated cathode in which the heater operates on 24 volts. This would present some constructional problems, having 24 volts between the heater leads in a gas tube, but the tube designers claim that this can be done.

A few gas diodes were designed and constructed by the author in order to study the behaviour of the tube under different conditions of electrode spacing, gas pressure etc. Argon gas was used in all the tubes.

Proper shapes of electrodes were chosen which was not possible to get, in case of commercial tubes. Although decisive results could not be obtained, as it involves a long process of constructing a large number of tubes having different dimensions and operated under different conditions, nevertheless, the results obtained from the experimental tubes indicate that there is a critical gas pressure and a corresponding critical electrode spacing which will give the minimum tube drop.

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