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X-RAY STUDY OF SELENIUM IN THE LIQUID AND COLLOIDAL STATE *

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Plate X

ABSTRACT. Liquid selenium at various temperatures, *viz.*, from 220° to 430°C, has been studied by the X-ray diffraction method with a specially designed camera. A single broad band with a band-spacing much bigger than that of amorphous varieties was obtained. The density of liquid selenium at various temperatures was also accurately determined. It is found that with the rise of temperature the band-spacing of liquid selenium also increases. By plotting the band-spacing of liquid selenium against the corresponding temperature and the cube-root of the reciprocal of density against the temperature, two smooth curves of similar nature were obtained.

Selenium, in its colloidal state, has been studied by the X-ray diffraction method. Colloidal solution prepared was fairly stable and coagulation occurs on addition of HNO_3. The solution is stable even when heated at 100°C for several hours. Both heated and unheated solutions, when allowed to evaporate at the room temperature form a sticky mass. Coagulum obtained with unheated solutions gives sharp monoclinic pattern if the coagulation is effected at a very slow rate. On rapid coagulation, however, the precipitate gives on X-ray analysis broad bands. Similar results are also obtained with previously heated solution, the difference being that the coagulated specimen now gives pure hexagonal pattern.

The gummy mass both from the heated and unheated sol gives only one single broad band. The spacing of the band (4.07 A.U.) is the same as that obtained in the case of liquid selenium, near its melting point, but it does not correspond with that of amorphous varieties of selenium (3.5 A.U.). This essential similarity in the nature of the diffraction pattern of liquid selenium and colloidal selenium suggests that the arrangement of atoms in each colloidal particle of selenium is the same as that in the groups present in the liquid selenium.

INTRODUCTION

The property of a substance in the colloidal state is peculiarly different from the same in the ordinary solid state. In the colloidal state, the substance is in a highly dispersed condition and each colloidal particle consists of several atoms or molecules of the substance closely packed to each other. The peculiarity of the property of the substance in their colloidal state can be attributed to the smallness of their particle-size and the mode in which the atoms are arranged in space, relative to each other in the small colloidal particle. Colloidal metal

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sols[1] in general give the diffraction pattern characteristic of the massive material, except that the sharp Debye ring is broadened in proportion as the particle size is smaller. It has also been noticed that the same substance giving crystalline pattern in the ordinary solid state gives band pattern in the colloidal state.

Substances in their liquid state also give on X-ray analysis broad bands which can be ascribed to the presence of some groups of (cybotactic) atoms on molecules in the liquid state. The groups are always being formed and destroyed due to thermal disturbances.

Substances in the amorphous state also characterise themselves by band pattern which has been attributed to the presence of groups or crystallites in which atoms or molecules are arranged in some particular fashion. Now, substances (*a*) in the colloidal state, (*b*) liquid state, and (*c*) amorphous state show bands on X-ray analysis and the nature of the band pattern is characteristic of the size of the group and the mode of arrangement of atoms in the groups.

An attempt has been made here to establish some relation which might exist among the different states mentioned above of the element selenium.

Liquid selenium :—Selenium melts at 217°C and diffraction photographs were taken at different temperatures lying between 220°C and 430°C. The camera essentially consists of a collimating system and a plane plate holder. The cell containing the liquid selenium consists of very thin walled glass capillary closed at both ends. The empty glass capillary was put before the X-ray and the wall of the tube was so thin that no diffraction pattern due to glass was obtained. One such capillary containing selenium closed at both ends was put before the slit cap. The slit cap being surrounded with an electric heater wound with nichrome wire resistance. The temperature of the liquid selenium was measured by introducing a thermocouple of Cu-Constantan at the position of the cell containing the liquid. The intensity of the band to be obtained in the case of liquid selenium being too weak, the film holder is to be kept very near the cell containing the liquid. The X-ray film is to be protected from the heat radiation coming out of the electrical heater surrounding the liquid cell. A water cooling jacket, in the form of a circular disc, with a 2 mm bore at the centre, was placed vertically, in between the film holder and the slit cap, so that the major part of the heat radiation from the heater was cut off, but only the scattered cone of X-rays from the specimens to be analysed can pass unobstructed through the central hole of the water-cooling jacket. The water was being continually circulated through the jacket during the exposure. This arrangement was quite successful up to 315°C. But at higher temperatures it was necessary to cool the X-ray film. The lid of the film holder pressing the film was replaced by a double walled metallic jacket through which water was constantly being circulated. This modification enabled us to take photographs of liquid selenium even upto 430°C [Plate X(1)]. Diffraction photographs were taken at 220°, 261°,

315°, and 430°C. The time of exposure varied between 30-40 hours, Voltage : 40 K.V., current 5-10 M.A.

EXPERIMENTAL RESULTS

The pattern obtained in the case of liquid selenium consisted of one diffuse band. Table I gives the values of the band spacings at different temperatures.

TABLE I

Band spacings of liquid selenium at different temperatures

Temp. of liquid selenium	Bragg angle θ	Spacings in A.U.
220°C	10 59′	4.04
261°C	10 51′	4.09
315°C	10 41′	4.15
430°C	10 18′	4.30

From the table it will be seen that with the increase of the temperature the values of the spacings also increase.

In fig. 1(*a*) spacings have been plotted against corresponding temperatures and the smooth curve AB has been obtained. The curve AB evidently suggests that the variation of spacing with temperature is almost linear and there is no sudden change in the spacing at any temperature in the region covered by our experiment. The density of liquid selenium at different temperatures were measured very accurately.

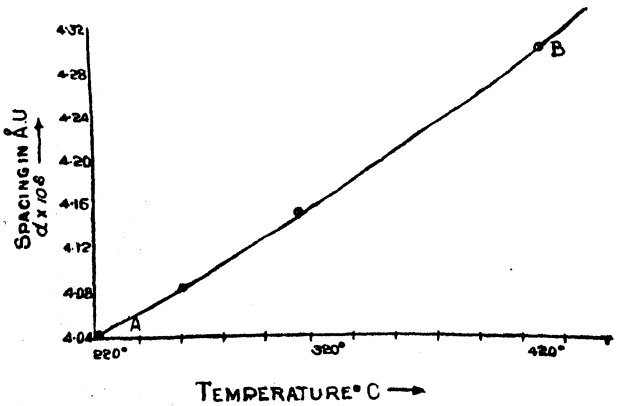

FIG. 1(*a*)

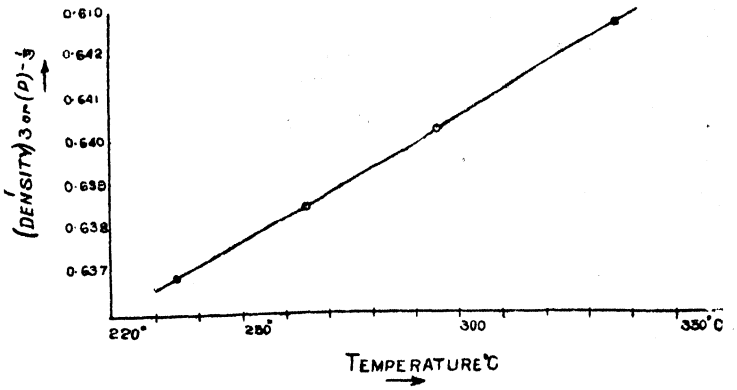

FIG. 1(*b*)

The density of liquid selenium at different temperatures were determined by using a glass tube with a narrow mouth. The tube containing the liquid selenium could be maintained at any temperature up to 400°C or more by inserting it into closely fitting holes of an electric heater the current through which could be regulated. The temperature of the bath was noted by a mercury thermometer. Two such tubes were taken and maintained at the desired temperature above the melting point of selenium and small pieces of selenium were gradually introduced which soon melted and thus the tubes were filled up with liquid selenium without any air bubble lying within it. To determine the density at some other higher temperature the current is regulated. Liquid selenium overflows through the capillary mouth. The tubes were taken out, cooled and weighed after carefully cleaning the surface of the tubes. The tubes were first filled up with distilled water and weighed, the density of water at that temperature was taken from the Physical Table. The value of the density calculated from the two tubes differed by less than one per cent. The density of liquid selenium at different temperatures are given in Table II.

TABLE II

Temperature of the liquid selenium	Density in gms/c.c.
235°C	3.8719
265°C	3.8393
295°C	3.8094
335°C	3.7741

The smooth curve A′B′ in fig. I(*b*) is obtained by plotting the reciprocal of the cube-root of density against the temperature. The similarity between the

curve AB (Fig. I*a*) and curve A′B′ (fig. I*b*) evidently suggests that the mode of variation of the cube-root of specific volume with temperature and that of the spacings with the temperature are similar. The observed change in spacing is merely a natural consequence of the thermal expansion of the liquid which is also responsible for the change in density.

DISCUSSION

The band-spacing of the liquid selenium at 220°C, *i.e.*, near about the melting point is 4.04 A.U. Now the largest value of the spacings obtained in the case of amorphous varieties, is with colloidal selenium coagulated by electrolytes or coagulated on ageing, and the value is found to be 3.8 A.U.

It has been observed that the colloidal selenium left to atmosphere at the room temperature forms a gummy mass which on X-ray analysis gives one broad band and peculiarly enough the nature of the band is similar to that obtained in the case of liquid selenium.

The points of similarity lie in the fact that (1) both liquid selenium and the gummy colloidal selenium on X-ray analysis give one single broad band, whereas in the case of amorphous varieties of selenium, *viz.*, vitreous selenium, red amorphous selenium and colloidal selenium coagulated by means of electrolyte we always get three broad bands. (2) The value of the band-spacings in the case of gummy colloidal selenium is 4.07 A.U. which agrees well with the value of the spacing, 4.09 A.U., in the case of liquid selenium at 261°C. This interesting point of similarity between colloidal selenium will be dealt later on.

Colloidal selenium : preparation[2] *and properties* :—Equimolecular quantities of SeO_2 and extra pure dextrose were taken in a small basin with a little quantity of distilled water and kept over a water bath. The solution becomes reddish and syrupy. On addition of a few drops of liquor ammonia to this syrupy liquid, frothing begins. This process is continued till the solution turns deep red. The syrupy condition being always maintained by adding drops of water at intervals and finally the whole thing is stirred up with cold water and red colloidal solution of selenium is obtained. The solution containing excess of any electrolyte is dialysed by means of a cellophane paper membrane.

Colloidal solution thus prepared is fairly stable. Spontaneous coagulation occurs just after the preparation of the solution ; but the rate of such coagulation becomes imperceptible after 2 or 3 days. The colour of this natural coagulum is red. The colloidal sol was boiled at 100°C for 36 hours, but the sol was stable even after boiling. Coagulation does not take place when colloidal sol is exposed to X-rays. On addition of few drops of dilute HNO_3 coagulation takes place in the case of both heated and unheated colloidal sol. The rate of coagulation depends very much on the amount of electrolyte (HNO_3) added and also on the amount of shaking. Colloidal selenium sol when allowed to evaporate

at the room temperature forms a gummy mass. This gummy mass when shaken with water, the original colloidal sol is obtained. Thus, we have the following types of samples to be examined by the X-ray diffraction method :—

(A) Coagulum formed during ageing.

(B) Precipitate obtained by *rapid coagulation* of unheated sol by addition of HNO_3.

(C) Precipitate obtained by *slow coagulation* of aged unheated sol by addition of HNO_3.

(D) Precipitate obtained by *rapid coagulation* of colloidal sol, heated at 100°C for different periods by the addition of HNO_3.

(E) Precipitate obtained by *slow coagulation* of colloidal sol heated at 100°C for different hours by the addition of HNO_3.

(F) Gummy colloidal selenium obtained by evaporating both heated and unheated colloidal sol, at the room temperature.

The samples mentioned above were all pressed against the slit cap on a thin zig-zag paper and photographs taken in a hemicylindrical camera.

EXPERIMENTAL RESULTS

(A) Three broad bands similar to those obtained in the case of red amorphous selenium and black vitreous selenium were obtained [Plate X(2)]. The band spacing of the first intense band is 3.8 A.U. which is greater than the value 3.55 A.U. in the case of black vitreous selenium. The values of the band spacings obtained in the case of colloidal selenium (A) are given in Table III.

TABLE III

Coagulum formed during Ageing

Intensity	Bragg angle θ	Band Spacing in A.U.
S	11 41′	3.80
W	24 54′	1.83

This increase in the band-spacing is attributed as due to the smallness of the particle size of colloidal selenium.

(B) Coagulum obtained by rapid coagulation of sol by addition of HNO_3 gives also three broad bands similar to (A).

(C) Slow coagulum obtained by addition of HNO_3 from aged, unheated sol showed purely crystalline pattern [Plate X(3)]. The interplanar spacings correspond to that of the monoclinic selenium but the intensity distribution of the lines are peculiarly different as can be seen from [Plate X(3)]. The table IV below shows the values of the spacings against the corresponding spacings obtained with monoclinic selenium prepared in the Laboratory.

TABLE IV

Precipitate obtained by Slow Coagulation of Aged Unheated Sol by addition of HNO_3

Intensity	Bragg angle θ	Spacing in A.U.	Monoclinic prepared in the Lab.	
			Intensity	Spacings in A.U.
W	10 18′	4.29	W	4.26
W	11 24′	3.90	W	3.84
W	12 30′	3.55	S	3.56
S	13 34′	3.28	W	3.28
W	14 29′	3.09	S	3.07
V.W.	15 55′	2.82	S	2.87
M.S.	20 9′	2.23	V.W.	2.24
W	21 27′	2.10	V.W.	2.11
S	22 31′	2.00	W	1.99
W	23 56′	1.90	W	1.90
W	25 5′	1.81	V W.	1.77

(D) Precipitate obtained by rapid coagulation of colloidal sol heated previously for 36 hours at 100°C by HNO_3 gives on X-ray analysis three broad bands similar to those obtained in the case of amorphous varieties of selenium.

(E) Precipitate obtained by slow coagulation of colloidal sol heated previously at 100°C for 36 hours by the addition of HNO_3 gives on X-ray analysis purely crystalline pattern. Table V shows that the interplanar spacings correspond to the hexagonal form of selenium [Plate X(4)].

TABLE V

Intensity	Bragg angle θ	Spacings in A.U.	Spacings of the hexagonal Se prepared in the Lab. in A.U.
W	10 25′	3.84 (β)	3.781
S	11 89′	3.81	3.77
W	13 23′	2.99 (β)	2.99
S	14 53′	2.99	2.99
W	20 49′	2.16	2.17
V.W.	21 49′	2.07	2.07
V.W.	26 15′	1.74	1.75
V W.	28 8′	1.63	1.63

(F) Gummy colloidal solution both from heated and unheated solution give on X-ray analysis one single broad band the spacing of which is 4.07 A.U. [Plate X(5)].

From these experiments it is clear that if colloidal soi (either heated or unheated) is precipitated slowly the particles give crystalline pattern. Whereas the sample (heated or unheated) if precipitated rapidly produces so-called broad amorphous bands. But it is evident from the experiments that heated sample precipitated slowly produces hexagonal pattern whereas the unheated sample treated in the same way produces only monoclinic pattern.

DISCUSSION

Colloidal selenium consists of groups of atoms of selenium packed together in the way as in the liquid selenium. This follows naturally, from the fact, that the band pattern obtained by X-ray analysis of liquid selenium and highly concentrated colloidal selenium (gummy colloidal selenium) are similar in every respect. The growth of size of the above-mentioned groups present in the colloidal selenium always takes place, both on ageing the solution and also on heating the samples; but generally this growth is not large enough so as to precipitate the selenium present in colloidal solution. Thus, in the case of both aged colloidal sol and heated colloidal sol, each colloidal particle although of dimension less than 10^{-5} cm is now a "colloidal crystal." On rapid coagulation the growth of size of these "colloidal crystals" takes place only by the capillary action and we get on X-ray analysis three broad bands as have been obtained in the case of so-called amorphous varieties of selenium. On slow coagulation however, the growth of size is effected not only by the capillary action but also

PLATE X.

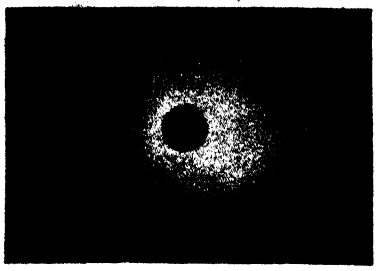

Fig. 1.

Fig. 2.

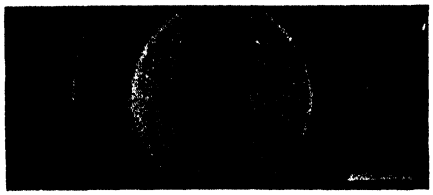

Fig. 3.

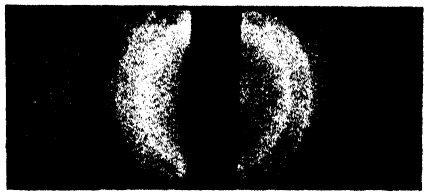

Fig. 4.

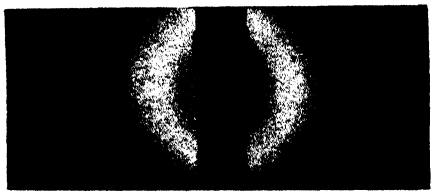

Fig. 5.

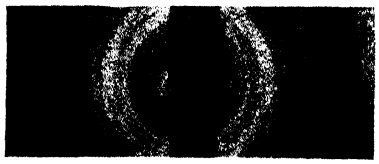

Fig. 6.

(1) Liquid selenium at 315°C.

(2) Coagulum formed during ageing.

(3) Precipitate obtained by slow coagulation of aged unheated Sol by addition of HNO_3

(4) Precipitate obtained by slow coagulation of colloidal Sol heated at 100°C for 16 hours, by the addition of HNO_3

(5) Gummy colloidal selenium.

(6) Presence of S_ω in colloidal Sulphur.

some orientating field is predominant which causes a regular lattice formation so that the precipitate on X-ray analysis gives a sharp crystalline pattern. From the experimental results we have found that with the previously heated colloidal solution, the precipitate obtained by slow coagulation gives always hexagonal crystals. But, unheated aged, colloidal sol on slow coagulation gives monoclinic crystals. The conditions in which the hexagonal or monoclinic crystals are formed from so-called amorphous selenium have been discussed in another paper.[3]

Thus the experimental results show that colloidal sol of selenium may contain both hexagonal and monoclinic crystals. To determine whether colloidal particles of sulphur can also exist both in S_α and S_ω form various samples of colloidal sol of sulphur prepared under different physical conditions were examined. The presence of S_α in colloidal sulphur sol has been previously shown in this Laboratory.[4]

THE PRESENCE OF S_ω IN COLLOIDAL SULPHUR

The colloidal sol of sulphur was prepared by passing pure H_2S gas through a concentrated solution of SO_2 in water. The solution was kept in a tall cylinder completely immersed in an ice-bath. The colloidal sol thus obtained is poured on a flat basin and was allowed to evaporate at about 25°C in a moist atmosphere. A thin gummy rubber like membrane was obtained, which could be torn to pieces. X-ray diffraction photograph of these pieces was taken, samples being changed every half an hour. A good crystalline pattern was obtained and the interplanar spacings of the rings were found to correspond accurately to those of insoluble white sulphur (S_ω) [Plate X(6)]

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