

close to the base ; on the other tower it should be near the constriction. The inner diameter of the constriction should in each case be smaller than the inner diameter of the neck in order to permit the introduction of the rubber stoppers and glass tubes. In setting up the apparatus for ordinary use an iron ring-stand with three clamps holding the apparatus at D, A and F, respectively, may be employed.

CORNELL UNIVERSITY,  
March, 1907.

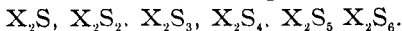
## THE SELENIDES OF SODIUM.

BY C. H. MATHEWSON.

Received March 21, 1907.

The existence of selenides of the general formula  $\text{Na}_2\text{Se}_x$  has long been known but no systematic attempt to prepare and study the series by crystallization from solutions corresponding in composition to various possible formulas or by physical chemical methods has been undertaken. Uelsmann<sup>1</sup> in 1860 observed that selenium and sodium combine very readily at moderately low temperatures, with evolution of heat and light. He prepared a compound which he assumed to be  $\text{Na}_2\text{Se}$  by passing hydrogen selenide into strong sodium hydroxide solutions. No analysis was given to support this conclusion. Hugot<sup>2</sup> prepared the monoselenide by action of sodammonium in excess on selenium and described it as a white amorphous substance soluble in water free from air producing a colorless solution. Air causes the immediate separation of red selenium. Fabre<sup>3</sup> obtained several crystalline monoselenides by treating sodium hydroxide solutions with hydrogen selenide. Ignition in nitrogen expels water of crystallization without further decomposition. Jackson<sup>4</sup> reduced sodium selenide with carbon, a method used by Wohler and Dean<sup>5</sup> for preparing the potassium compound. The resulting selenide gave a dibenzyl diselenide when treated with benzylchloride which characterized the alkali selenide as  $\text{Na}_2\text{Se}_2$  and not  $\text{Na}_2\text{Se}$ . Rathke<sup>6</sup> explained this formation of diselenide by the unavoidable presence of water in the carbon used for reduction, with consequent oxidation of the monoselenide. Sodium tetraselenide,  $\text{Na}_2\text{Se}_4$ , was prepared by Hugot<sup>7</sup> by the action of sodammonium on an excess of selenium.

Alkali sulphides of the following six types are known :—



Rigid experimental proof of the existence of this unbroken series of sul-

<sup>1</sup> Ann. Chem. Pharm., 116, 122 (1860).

<sup>2</sup> Compt. rend., 129, 299 (1899).

<sup>3</sup> Ann. chim. phys., (6), 10, 500 (1887).

<sup>4</sup> Ber., 7, 1277 (1874).

<sup>5</sup> Ann. Chem. Pharm., 97, 5 (1856).

<sup>6</sup> Ann., 152, 181 (1869).

<sup>7</sup> loc. cit., page 1.

phides of rubidium and cesium has been obtained by Biltz and Wilke-Dörfurt<sup>1</sup>. Their conclusions were based mainly upon freezing point determinations. A similar systematic investigation of the sodium and potassium sulphides has not been published but most of the formula types (at least for potassium) have been realized in purely preparative experiments.

The close analogy existing between sulphides and selenides would suggest a closely similar series of alkali selenides. Three representatives,  $X_2Se$ ,  $X_2Se_2$  and  $X_2Se_4$ , corresponding to above mentioned sulphides have been isolated for sodium and potassium. This thermo-analytical study of the selenides of sodium was undertaken with the purpose of describing all compounds of sodium with selenium which result from direct combination of the elements and are stable in contact with the liquid phase. For a detailed exposition of the application of the principles of heterogeneous equilibrium to the determination and interpretation of cooling curves reference may be made to three papers by Tammann<sup>2</sup>. Freezing point curves have often been compiled from cooling curves taken after successive additions of one component, thereby regularly increasing its concentration in the sample and simultaneously increasing the total weight. To obtain the actual limiting concentrations at which an eutectic begins to appear requires by this method an unusually large expenditure of experimental effort and results are generally obtained only in approximation. The practice of referring all cooling curves to the same weight of sample and the same rate of cooling permits a comparison of the results obtained in neighboring concentrations and a graphical determination of limiting concentrations as well as those representing maximum times of crystallization. By careful application of these principles the formulas of chemical compounds crystallizing in the melt can usually be determined with great accuracy.

### Experimental Procedure

Essentially the same method of experimentation was adopted as has been previously used and described by the author in the investigation of sodium-tin alloys<sup>3</sup>. It may be said in addition that the heat evolved by the reaction of sodium with selenium is greater than has been observed in the study of sodium alloys of tin, lead, zinc, cadmium, bismuth and antimony<sup>4</sup>, all of which form definite compounds. Bismuth and antimony alone enter into this combination with a somewhat comparable manifestation of free energy. Small pieces of amorphous selenium (a few milligrams) were added at intervals to molten sodium in a tube of Jena glass

<sup>1</sup> Z. anorg. Chem., 48, 297 (1905).

<sup>2</sup> Ibid., 37, 303 (1903); 45, 24 (1905); 47, 289 (1905).

<sup>3</sup> Ibid., 46, 94 (1905).

<sup>4</sup> Ibid., 48, 191 and 50, 171 (1906).

kept at a temperature slightly in excess of the melting point of sodium by a surrounding bath of paraffin oil. A slow current of dry hydrogen circulated in the apparatus. Notwithstanding the utmost precaution the glass tubes were not infrequently ruined by the violence of the combination. The addition of selenium to an excess of sodium occasions violent exothermic formation of the white monoselenide, addition of selenium to the monoselenide results in polyselenide formation without considerable heat evolution. Preparation of the pure monoselenide might be suggested as an advisable preliminary to the subsequent thermic work, but this itself presents difficulty. Passing hydrogen selenide into strong sodium hydroxide solutions furnishes a good product, but the irritating effect of this gas even in small quantities on the mucous membranes of the throat, nose and eyes renders the operation on a moderately large scale objectionable. The tube containing a mixture of monoselenide and selenium was transferred to a cylindrical iron sand bath surrounded by an asbestos mantle to prevent rapid heat radiation and the contents melted. Cooling was conducted at a nearly uniform rate of  $4.75^\circ$  in ten seconds, at or near  $500^\circ$ ,  $2.5^\circ$  at or near  $300^\circ$ ,  $1.8^\circ$  at or near  $200^\circ$  and  $0.6^\circ$  at or near  $100^\circ$ . Temperatures were measured by a thermo-electric couple of platinum, platinum rhodium (10 per cent.) which was calibrated from the following four fixed points on the air thermometer scale:

Boiling point water  $100^\circ$ , melting point zinc  $419^{01}$ , melting point tin  $232^{02}$ , melting point antimony  $630.6^2$ .

The cold junction of the thermo-couple was surrounded with water at  $18 \pm 2^\circ$  for these calibrations and during actual measurements the variation in the temperature of this bath was kept within these limits. Temperature readings were accurate throughout the whole range to about  $2^\circ$ . A sample of 10 g. total weight was used in each experiment. Weighings were carried to the nearest centigram. Some slight spattering during the preparation of the melt was unavoidable; analyses of several representative samples established the change in concentration due to this and other details of the manipulation at  $\pm 0.2$  wt. percent sodium. The melt was regularly stirred during cooling as long as its consistency would permit. Previous experience has shown the importance of thorough mechanical mixing in obtaining the normal time of crystallization at a temperature corresponding to nonvariant equilibrium between (a) primary crystals which have separated from the melt at higher temperatures along the freezing point curve, (b) crystals forming at this temperature during reaction between (a) crystals and melt and (c) melt (d) vapor). The stirring should secure thorough mixing rather than an artificial segregation of material, a condition somewhat difficult of attainment

<sup>1</sup> Holborn and Day, *Ann. Physik.*, 2, 545 (1900).

<sup>2</sup> Heycock and Neville, *J. Chem. Soc.*, 57, 380 (1890).

owing to the pasty consistency of the reaction mixture common at this point. It may be stated in anticipation that several instances of this type of equilibrium were discovered in the study of these compounds. Soft iron wire was used in stirring at temperatures below  $400^{\circ}$ , at higher temperatures this dissolved appreciably in the fusion and use was made of small rods of Jena glass. At these higher temperatures the Jena glass used throughout the work as receptacle for the fused mixtures, protective covering for the thermo-electric junction, and for stirring, was considerably blackened; below  $350^{\circ}$  very slightly. Changes of concentration due to this cause were found by analysis to be negligible.

The data from which cooling curves for 20 separate concentrations were constructed was obtained by observations taken every ten (10) seconds on the falling temperature in the molten mixtures. The temperatures were plotted as ordinates, time intervals as abscissae. Table I, gives a complete summary of these thermic results.

TABLE I.  
Summary of results from cooling curves.

No.	Weight per cent. Sodium	Atomic per cent. Sodium	Temp. of Primary cryst.	Secondary Crystallization.			
				Temp.	Time in sec.	Temp.	Time in sec.
			Pure Sodium—Melting Point $97.5^{\circ}$				
1		89.9	$343^{\circ}$	$97^{\circ}$	290		
2	72.3		$680^{\circ}$	$97^{\circ}$	165		
3	53.7	79.9		Sodium monoselenide (66.6 at % Na) melts above $875^{\circ}$ .			
4	30.4	60.0	?	$500^{\circ}$	45		
5	27.8	56.9	$745^{\circ}$	$480^{\circ}$	70		
6	24.0	52.0	$593^{\circ}$	$492^{\circ}$	110		
7	22.5	50.0		Sodium diselenide (50.0 at % Na) melts with decomposition at $495^{\circ}$ . Time of cryst. 160 sec.			
8	20.8	47.5	$469^{\circ}$	$314^{\circ}$	25		
9	19.2	44.9	$488^{\circ}$	$309^{\circ}$	70		
10	16.3	40.0	$368^{\circ}$	Sodium triselenide (40.0 at % Na) melts with decomposition at $313^{\circ}$ . Time of cryst. 135 sec.			
11	14.8	37.4	$333^{\circ}$	$308^{\circ}$	40	$285^{\circ}$	90
12	13.0	34.0	$306^{\circ}$			$290^{\circ}$	210
				Sodium tetraselenide (33.3 at % Na) melts with decomposition at $290^{\circ}$ . Time of cryst. 250 sec.			
13	12.0	32.0	$300^{\circ}$	$258^{\circ}$	25	$292^{\circ}$	185
14	11.1	30.0	$286^{\circ}$	$258^{\circ}$	70		
15	10.0	27.6	$280^{\circ}$	$258^{\circ}$	120		
16	8.8	25.0	$276^{\circ}$	Sodium hexaselenide (25.0 at % Na) melts with decomposition at $258^{\circ}$ . Time of cryst. 200 sec.			
17	6.8	20.0	$272^{\circ}$	$258^{\circ}$	120	$207^{\circ}$	30
18	4.9	15.1	$253^{\circ}$			$210^{\circ}$	140
19	2.5	8.1	$248^{\circ}$			$215^{\circ}$	210
20	1.2	4.0	$226^{\circ}$			$217^{\circ}$	230
21	0.6	2.0	$223^{\circ}$			$217^{\circ}$	250
22				Pure selenium (grey-metallic) melting point $217^{\circ}$ .			

In the table, column (2) contains the weight percents of sodium in the

mixtures; column (3) the corresponding atomic percents sodium<sup>1</sup>; column (4) the temperature at which initial retardation in the rate of cooling was observed. This is evinced by a more or less plainly marked break in the curve; columns (5) and (6) the temperature and time of secondary crystallization in the system, rendered nonvariant by the pressure of a second solid phase; columns (7) and (8) similar data relating to a second temperature of nonvariant equilibrium on the cooling curve.

These tabulated results are to be found in diagramatic form on page 872, Fig. I.

The curve Na - - - - B C D E Se joining the points of primary separation of a solid phase from the fusion of the twenty concentrations is the freezing point curve and consists of at least (5) branches; Na...B, BC, CD, DE and ESe. The six horizontal lines of the diagram (Bb, etc.) represent nonvariant crystallization at the temperatures for which they are drawn and within the concentration limits over which they are prolonged. The vertical lines (es. etc.) are proportional to the time during which the temperature remained constant on the cooling curves of the respective concentrations. The end points of the horizontals (representing minimum crystallization) were found by drawing the verticals to a larger scale and constructing curves joining the ends and intersecting the horizontals; these points of intersection are the required end concentrations. The actual concentrations corresponding to maximum crystallization were similarly obtained by construction on an enlarged scale.

Table 2, page 874, summarizes the figures obtained by these methods and presents the thermo-analytical conclusions.

The five (5) sodium-selenium compounds given in column 7 of this table may be further characterized as follows:

(a) *Sodium-monoselenide*, Na<sub>2</sub>Se, melts at some temperature above 875° which was not realized experimentally owing to the lack of a suitable containing vessel for the fusion. Iron, in which sodium may be distilled unchanged<sup>2</sup>, is unsuitable owing to ready reaction with selenium at these temperatures. Glass and porcelain are attacked by sodium. This compound has been described by Hugot<sup>3</sup>. Its color is white, rapidly changing to red in moist air owing to oxidation with separation of selenium. The water solution is colorless when kept in a non-oxidizing atmosphere, undergoing a similar change, however, in the air. Selenium dissolves readily in the solution of the monoselenide producing a wine color which

$$^1 \text{ Atomic percent sodium} = \frac{\text{Weight percent sodium}}{\frac{\text{Weight percent sodium}}{23.05} + \frac{\text{Weight percent selenium}}{79.2}}$$

<sup>2</sup> Ruff and Johannsen. Ber., 14, 3601 (1905).

<sup>3</sup> loc. cit., page 1.

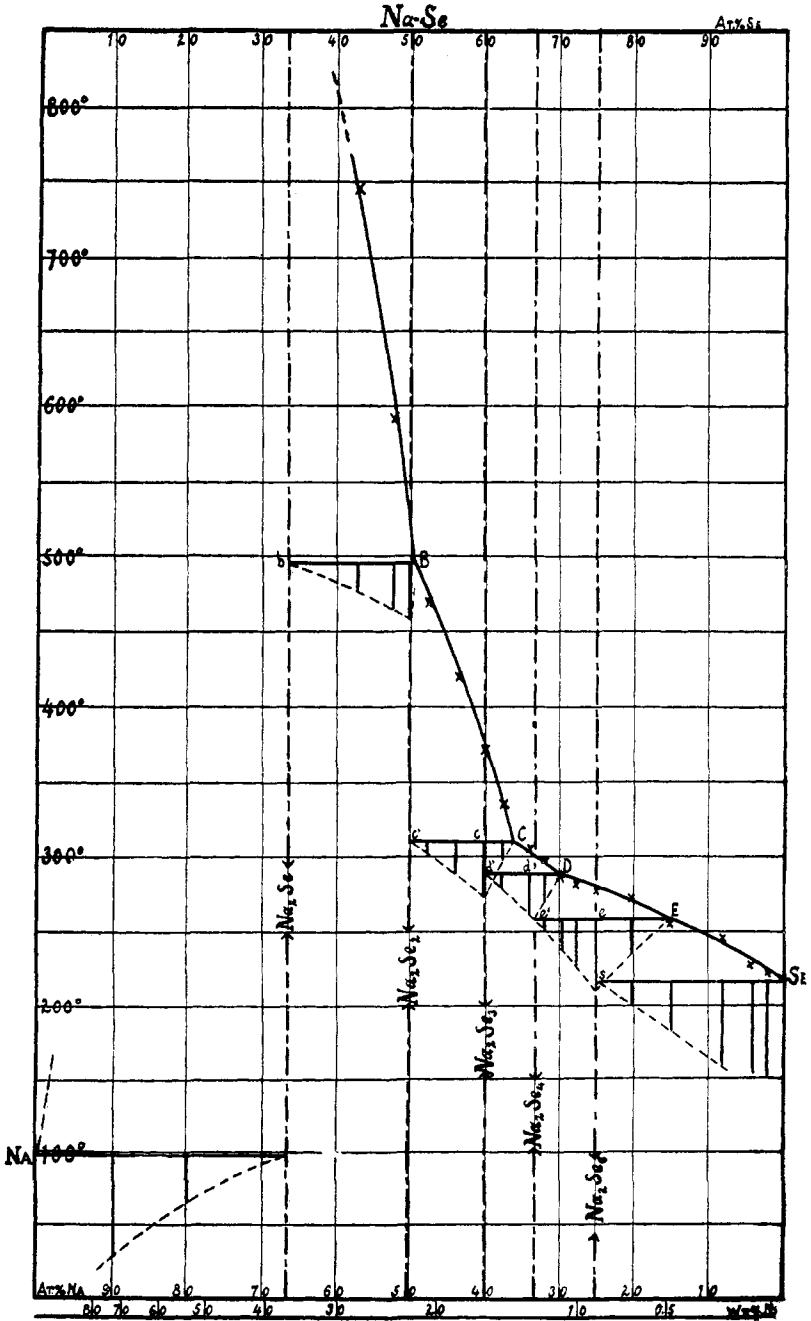


FIG. 1

deepens with increasing addition of the element, finally becoming dark and opaque. Such solutions may be concentrated in hydrogen without separation of selenium.

(b) *Sodium diselenide*,  $\text{Na}_2\text{Se}_2$ , is in equilibrium with the melt along the branch, BC, of the melting point curve (Fig. 1). The break at B in the curve is represented as nearly coincident with the concentration to which the maximum time of crystallization along the horizontal Bb corresponds. Experiments have not been sufficiently detailed to conclusively establish this construction. Owing to the appreciable reactivity of the melts towards glass at temperatures in the vicinity of B ( $495^\circ$ ) a somewhat greater error limit must be conceded to these points than to those between C and Se. It is, nevertheless, most probable that the concentration of the pure compound lies somewhat to the left of the point B, as shown in the diagram, in which case the following reversible reaction takes place at  $495^\circ$  :

$1 \text{ Na}_2\text{Se}_2 \rightleftharpoons a \text{ Na}_2\text{Se} + \text{melt of conc. B.}$ , the coefficient  $a$  being a small fractional number. Other possibilities are, (I) the point B represents exactly the concentration of the pure compound which then melts without decomposition and dissolves no monoselenide at its melting point. (II). The pure compound melts without decomposition and dissolves monoselenide sparingly with a proportionately slight lowering of the melting point<sup>1</sup>.

(c) *Sodium triselenide*,  $\text{Na}_2\text{Se}_3$ , separates as the primary crystalline phase along the short branch CD. At  $313^\circ$  the triselenide is in equilibrium with diselenide and melt of the concentration C. The quantitative relations are as follows :

$1 \text{ Na}_2\text{Se}_3 \rightleftharpoons 0.32 \text{ Na}_2\text{Se}_2 + \text{melt (1.35 mol. Na} + 2.35 \text{ mol. Se) concentration C.}$

(d) *Sodium tetraselenide*,  $\text{Na}_2\text{Se}_4$ , crystallizes primarily along the flat branch DE.

The reversible reaction at  $290^\circ$  is expressed by the equation :

$1 \text{ Na}_2\text{Se}_4 \rightleftharpoons 0.40 \text{ Na}_2\text{Se}_3 + \text{melt (1.20 mol. Na} + 2.80 \text{ mol. Se) concentration D.}$

(e) *Sodium hexaselenide*,  $\text{Na}_2\text{Se}_6$ , is the primary crystalline phase separating along the branch E Se. By falling temperature the following reaction proceeds at  $258^\circ$  to the left ; by rising temperature in the reverse direction :

$1 \text{ Na}_2\text{Se}_6 \rightleftharpoons 0.73 \text{ Na}_2\text{Se}_4 + \text{melt (0.54 mol. Na} + 3.08 \text{ mol. Se) concentration E.}$

The polyselenides of sodium are all readily soluble in water, producing

<sup>1</sup> For a more extended discussion of a similar case compare Vogel, Z. anorg. Chem., 48, 333 (1906).

TABLE II.  
Thermic Analysis of the Selenides of Sodium.  
*See Diagram 1, Fig. 1.*

Solid phases crystallizing at the same temperature in a successive series of concentrations.	Atomic per cent. Na corresponding to maximum time of cryst.	Limiting concentrations expressed in atomic per cent Na.		Average of concentrations determining formulas of compounds.		Formulas	Calculated composition		Thermo-analytical error.	
		Na richest	Se richest	Atomic per cent Na	Weight per cent Na		Atomic per cent Na	Weight per cent Na	At per cent. Na	Wt per cent. Na
Sodium crystallizing at 97° [Na—.]	Approx 100.	Approx 100.	67.3	66.3	36.4	Comp'd. No. 1 Na <sub>2</sub> Se	66.66	36.79	0.4	0.4
Compound No. 2 crystallizing at 495° from mixtures of compound No. 1 and melt. [Horizontal Bb]	50.2	65.3								
Compound No. 3 crystallizing at 313° from mixtures of compound No. 2 and melt. [Horizontal Ccc']	40.3	48.8	.....	49.5	22.0	Comp'd. No. 2 Na <sub>2</sub> Se <sub>2</sub>	50.00	22.54	0.5	0.5
Compound No. 4 crystallizing at 290° from mixtures of compound No. 3 and melt. [Horizontal Ddd']	32.7	40.1	.....	40.2	16.36	Comp'd. No. 3 Na <sub>2</sub> Se <sub>3</sub>	40.00	16.25	0.2	0.1
Compound No. 5 crystallizing at 258° from mixtures of compound No. 4 and melt. [Horizontal Eec']	24.6	33.1	.....	32.9	12.5	Comp'd. No. 4 Na <sub>2</sub> Se <sub>4</sub>	33.33	12.70	0.4	0.2
Selenium crystallizing at 217°. [Se—s]	Approx. 0.	24.9	..... Approx. 0.	24.75	8.7	Comp'd. No. 5 Na <sub>2</sub> Se <sub>6</sub>	25.00	8.84	0.25	0.1



red solutions, the depth of color being approximately proportional to the amount of selenium in the solution.

The reguli are somewhat darker than pure grey selenium. In the air they redden and slowly disintegrate in consequence of separation of selenium. Excepting those containing sodium as a structure element the reguli are brittle.

Addition of selenium to sodium does not produce an appreciable lowering of its melting point. Although the temperatures, electrically measured, were accurate only to  $\pm 2^\circ$ , supplementary measurements with a mercury thermometer proved conclusively that this hypothetical lowering can not exceed  $0.2^\circ$ .

The extreme reactivity of mixtures of sodium monoselenide and sodium at the high temperatures necessary for fusion prevented satisfactory completion of this part of the curve. No thoroughly suitable containing vessel was available. A mixture containing 80 atomic per cent. sodium appeared to soften considerably below the melting point of pure sodium monoselenide but the actual initial temperature of primary crystallization was not determined. It is doubtful if a true state of fusion was attained.

The use of hydrogen to prevent oxidation of sodium occasions some loss of selenium owing to direct union of the elements to form hydrogen selenide. This loss was greatest between  $300^\circ$  and  $400^\circ$ , in extreme cases amounting to 0.4 percent of the total selenium used. Very careful corrections by analysis<sup>1</sup> were made in concentrations corresponding to the possible formulas  $\text{Na}_2\text{Se}_5$  and  $\text{Na}_2\text{Se}_6$ . Cooling curves of these concentrations were repeated several times both in hydrogen and carbon dioxide, with fresh samples and very satisfactory agreement was attained. That the solid phase in question possesses the formula  $\text{Na}_2\text{Se}_6$  and not  $\text{Na}_2\text{Se}_5$  is rendered apparent by the graphical representations (I) and (II) in Fig. 2.

These melts were cooled in carbon dioxide. The accompanying figures refer to initial weighed percentages of sodium and are subject to correction not exceeding  $\pm 0.2$  percent sodium.

<sup>1</sup> Results from two analyses of a regulus made up to contain 8.6 % Na were as follows:

	I	II
Sodium	8.30	8.47
Selenium	90.99	91.02
Silicon	0.38	0.42
	<hr/>	<hr/>
	99.67	99.91

Samples weighing about 2.g were taken for analysis. These were dissolved in a moderately large amount of water (about 500 cc.) and decomposed by a slow current of air. Towards the end of the operation which requires several hours the solutions were acidified with sulphuric acid and boiled. The separated selenium was filtered, washed and weighed in a porcelain Gooch crucible, after drying at  $100^\circ$ . The filtrates were concentrated, silica removed in the usual manner, and sodium determined as sulphate.

The compound  $\text{Na}_2\text{Se}_6$ , which constitutes the primary crystalline phase in these concentrations reacts quantitatively [maximum time of crystallization, 200 sec.] with the melt in some concentration closely approximated by No. II, Fig. 2, containing 8.6 percent sodium, to form a secondary solid phase. The composition of these secondary crystals is therefore defined by the formula  $\text{Na}_2\text{Se}_6$ , which requires 8.8 percent sodium. That a lesser amount of this solid phase is furnished by the same reaction in concentration No. I with 10.2 percent sodium is established by the more limited heat evolution [shorter time of crystallization, 110 sec.]. The cooled melt of this concentration is accordingly a mixture of tetraselenide and hexaselenide crystals and not a homogeneous crystalline regulus corresponding to the formula  $\text{Na}_2\text{Se}_6$ , requiring 10.4 percent sodium.

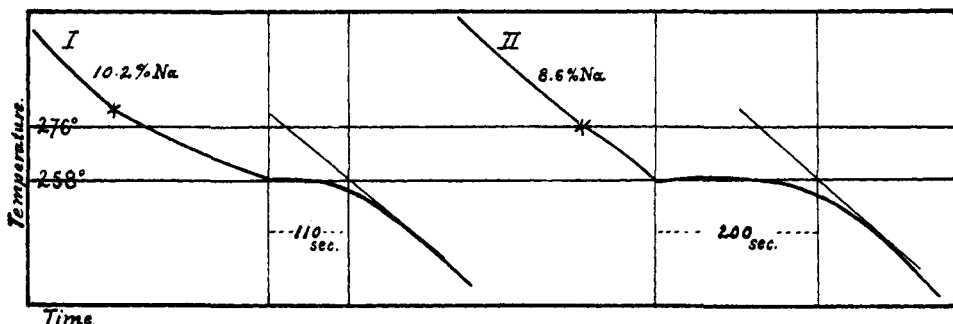


FIG. 2

The addition of sodium in small amounts to melted selenium sufficiently modifies its normal behavior on cooling to render a somewhat detailed discussion pertinent. Grey metallic selenium is the variety stable at higher temperatures in the vicinity of its melting point  $217^\circ$ . Saunders<sup>1</sup> concluded from dilatometric measurements that this is the only stable form at all temperatures below the melting point. Marc<sup>2</sup> has more recently published heating curves of amorphous selenium exhibiting two separate accelerations in the rate of rise of temperature (heat evolution by rising temperature). The temperatures at which these heat effects occurred were variable with the rate of heating and must correspond to two monotropic changes, the first heat evolution accompanying transition of amorphous selenium into a crystalline variety, I, and the second heat evolution corresponding to the monotropic relation between this and another form II. Monotropic substances frequently fail to crystallize the variety with the highest melting point on cooling from the liquid state<sup>3</sup>. This is notably true of selenium. Fig. 3, 1a (p 878) shows a cooling curve of 20 g. selenium.

<sup>1</sup> J. Physic. Chem., 4, 423 (1900).

<sup>2</sup> Z. anorg. Chem., 48, 408 (1905).

<sup>3</sup> See discussion by B. Roozeboom. Die heterogenen Gleichgewichte, I, p. 163.

No crystallization occurs at  $217^{\circ}$ , the melting point of grey, metallic selenium II and no other crystalline form separates on cooling, the substance gradually solidifying as vitreous amorphous selenium. This behavior is occasioned by unavoidable supercooling to such an extent that the higher forms are no longer stable and cannot appear.

Studies of Tammann<sup>1</sup> on the degree of supercooling have shown that of the two factors which determine crystallization; (1) the spontaneous appearance of crystalline nuclei in the liquid and (2) the rate of growth of these crystalline grains, the former increases very greatly as the temperature falls below the melting point, reaching a maximum and thereafter decreasing with falling temperature. The latter factor increases during a short temperature interval below the melting point, subsequently attaining a lower value. It is readily seen that supercooling beyond certain limits lessens the tendency to crystallization of the phase in question and brings the system within the stability limits of other solid phases. In the case of selenium these factors are at no time large enough for any crystalline modification to produce solidification.

The effect of sodium on the crystallization of selenium is rendered most apparent by reference to the melting point, (Diagram Fig. 1), and to Fig. 3 which shows a heating curve of 20 g. pure selenium (1b) which was previously maintained at  $175\text{--}205^{\circ}$  for 18 hours to cause complete transformation into the metallic variety, and the following cooling curves, all from 20 g. samples; I a—pure Se, II—0.1 per cent. Na, III—0.6 per cent. Na, IV—1.2 per cent. Na, and V—2.5 per cent. Na.

The addition of 0.1 per cent. Na (II) suffices to induce complete crystallization of the selenium. The regulus has the appearance of pure grey metallic selenium. The effect of smaller percentages of sodium on the crystallization was not studied.

Two solid phases, grey metallic selenium and sodium hexaselenide, appear in these concentrations. The eutectic horizontal Se — s (Diagram, Fig. 1) extends from pure selenium to the concentration of the pure compound,  $\text{Na}_2\text{Se}_6$ , allowing 0.25 per cent. Na experimental error. This establishes complete immiscibility, or extremely limited miscibility of these two substances in the solid phase. Moreover addition of sodium does not lower or raise the melting point of selenium to an appreciable extent. Although the accuracy of these pyrometric measurements was not greater than  $\pm 2^{\circ}$ , additional experiments with a mercury thermometer in which heating curves of pulverized metallic selenium and the pulverized regulus containing 0.1 per cent. sodium were taken, established agreement within  $\pm 0.2^{\circ}$ . The solubility of sodium hexaselenide in selenium at its melting point is, therefore, exceedingly limited. Notwithstanding these facts it is not impossible that the very limited misci-

<sup>1</sup> Z. physik. Chem., 25, 441 (1898).

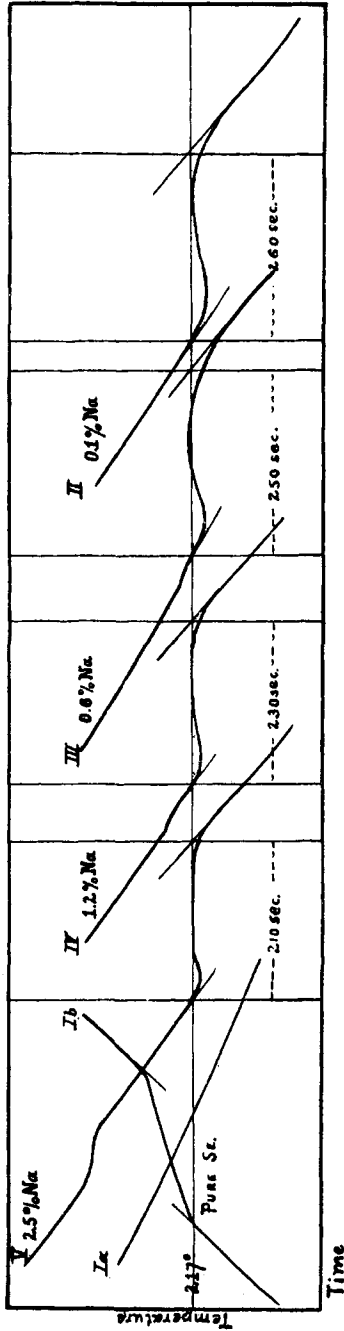


FIG. 5

bility not excluded by these experiments may play some important part in inducing crystallization. Exact laws governing the effect of foreign substances in small amount on a liquid in the metastable condition with relation to a solid phase have not been established. Tammann<sup>1</sup> has shown that an unlimited variety of soluble and insoluble substances exert an enormously modifying influence on the spontaneous formation of crystalline nuclei within the liquid, in some cases acting positively and in others negatively.<sup>2</sup>

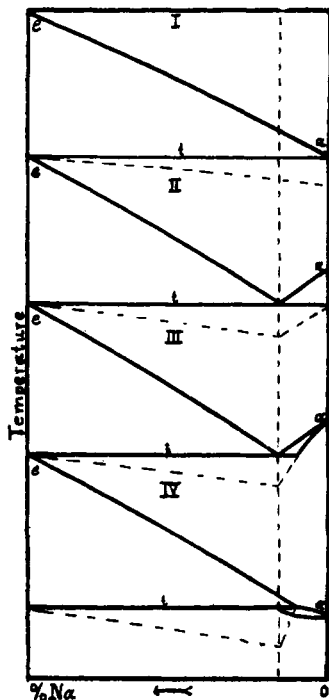


FIG. 4.

The possible nature of the solidification processes under discussion may be illustrated by the four diagrammatic representations in Fig. 4. The crystallization in question occurs invariably at the left of the dotted line, which represents a very inconsiderable sodium content (not exceeding 0.1 per cent.). The relations in (I) are those given in the melting point diagram, Fig. 1. Sodium hexaselenide crystallizes primarily and selenium separates secondarily at its true melting point ( $t$ ). A true eutectic is shown in (II), the hexaselenide crystallizing primarily, followed

<sup>1</sup> Z. physik. Chem., 25, 440, and 26, 314 (1898). Addition of 0.1 per cent. anisic acid to Betol multiplies the number of grains more than threefold.

<sup>2</sup> For effect of foreign substances on the rate of crystallization compare also Bogajulenski, Z. physik. Chem., 27, 585 (1898).

by the selenium rich eutectic at a temperature ( $t$ ) lower than the true melting point of selenium. In both these cases pure selenium must crystallize in the presence of primary crystals of the hexaselenide, which therefore constitute the dynamic factor of the crystallization. Case III represents primary crystallization of  $\text{Na}_2\text{Se}_6$  followed by secondary separation of the same solid phase and mixed crystals rich in selenium, simultaneously, at a temperature ( $t$ ) lower than the true melting point of pure selenium. According to case IV, primary crystals of  $\text{Na}_2\text{Se}_6$  react with the melt at a temperature ( $t$ ) higher than the true melting point of selenium and form selenium-rich mixed crystals.<sup>1</sup>

The well known effect of isomorphous substances in inducing crystallization<sup>2</sup> might suggest Cases III and IV characterized by formation of mixed crystals, as the most probable, but the fact that in all cases selenium crystallizes in the presence of crystals of the hexaselenide strongly indicates that this alone may be the determining factor and renders Case I, which is most forcibly suggested by the thermic results, a tenable conclusion.

Comparison of the five formula types constituted for the thermo-stable<sup>3</sup> selenides of sodium with those already mentioned for the alkali sulphides (Cs and Rb) reveals close conformity. The one exception to be noted is the non-existence of a sodium selenide of the type  $\text{X}_2\text{Se}_5$ . It is by no means improbable that rubidium and cesium furnish the complete series. The pentasulphides of these elements are characterized by great stability, both melting without decomposition while the hexasulphides show a lesser range of stability making it the more noteworthy that the latter type alone is represented in the sodium series of selenides. Bloxam<sup>4</sup> was able to crystallize only one polysulphide of sodium, to which he ascribes the formula  $\text{Na}_4\text{S}_3$ . Sodium and selenium do not combine directly to form a thermo-stable compound of this atomic ratio or any compound into which four atoms of sodium must of necessity enter.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.  
March, 1907.

<sup>1</sup> Actual examples of these four types of solidification may be consulted as follows:

- I. Na-Na<sub>4</sub>Sn, Mathewson, *Z. anorg. Chem.*, **46**, 94 (1905).
- II. Bi-NaBi, Mathewson, *Z. anorg. Chem.*, **50**, 171 (1906).
- III. Au-AuSn, Vogel, *Z. anorg. Chem.*, **46**, 60 (1905).
- IV. Zn-AuZn<sub>3</sub>, Vogel, *Z. anorg. Chem.*, **48**, 319 (1906).

<sup>2</sup> Ostwald, *Z. physik. Chem.*, **22**, 289 (1897).

<sup>3</sup> I use this term solely to indicate stability of the solid phase in the presence of liquid phase of same composition.

<sup>4</sup> *J. Chem. Soc.*, **77**, 753 (1900).