LVI.—*Volume Changes which Accompany Transformations in the System $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$.*

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IN the course of some experiments on the lowering of the temperature at which sodium thiosulphate pentahydrate is transformed into the dihydrate, certain observations were made relative to the crystallisation of supercooled solutions which appeared to warrant a closer examination of the possible changes in the system $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$.

A paper by S. W. Young and J. P. Mitchell on supercooled fusions and solutions of sodium thiosulphate (*J. Amer. Chem. Soc.*, 1904, **26**, 1389) escaped our notice until a considerable amount of experimental work had been done, and the publication of numerous solubility data has been rendered unnecessary by the appearance of the above-mentioned and by a later paper by Young and W. E. Burke (*ibid.*, 1906, **28**, 315) on the hydrates of sodium thiosulphate.

On this account the present communication deals almost entirely with the observations made in the study of the volume changes which accompany transformations in the system containing 5 mols. of water per mol. of sodium thiosulphate.

In this investigation a number of dilatometers have been subjected to a succession of temperature changes extending over many months. The dilatometers containing known quantities of recrystallised sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and of heavy petroleum to serve as index fluid were heated in a thermostat, the temperature of which could be maintained constant within the limits $\pm 0.05^\circ$. The volume of the contained system, which is read off on the graduated capillary stem of the dilatometer, varies with the nature of the component phases, and it has been found that by suitable thermal treatment the volume may at one and the same temperature assume several different, but yet perfectly defined, values.

The volume differences are most readily seen, and the conditions under which the various forms of the system have been obtained can be most easily described by reference to the appended diagram.

In this, temperatures are represented on the abscissa and dilatometer readings, the differences between which measure the changes in volume investigated, are plotted as ordinates.

In discussing the volume relationships, the very convenient nomenclature introduced by Young and Burke (*loc. cit.*) for the purpose of grouping the various hydrates of sodium thiosulphate will be used. Curve (1) in the diagram represents the volume at a series of temperatures when

the system $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$ is in the form of ordinary sodium thiosulphate—primary pentahydrate. When maintained for a sufficiently long time at a constant temperature above 48° , the primary pentahydrate is transformed, and either partial or complete liquefaction takes place. Which of these changes will occur under given conditions cannot be predicted. It is not entirely a question of temperature, for whereas complete liquefaction took place when the primary pentahydrate was heated at 49° , 50° , and 52° , yet at 51° the liquefaction was only partial and a small quantity of a new solid phase appeared. Furthermore, in a series of tubes containing pentahydrate which were slowly heated

Volume-temperature curves for the system $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$.

in a large water-bath under exactly similar conditions, superheating, resulting in complete liquefaction, was observed in about 60 per cent. of cases, partial liquefaction in the remaining 40.

On cooling the dilatometer containing the system $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$ in the liquid condition, the volume temperature curve (6) was obtained.

The composition of the crystals, which appear on partial liquefaction of the primary pentahydrate, was determined by slowly evaporating a concentrated solution of sodium thiosulphate in a jacketed thermostat at a temperature of 50 – 55° . When crystallisation had commenced, the solution was allowed to cool slowly out of contact with

the air, when large, well-formed crystals separated out. In order to remove these in a pure condition, the temperature was raised to about 55° , the mother liquor poured off, and the crystals washed with a mixture containing 80 per cent. of methyl alcohol and 20 per cent. of water which had been also heated to the same temperature. Analysis of the crystals gave numbers corresponding almost exactly with the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

On cooling the dilatometer in which crystals of this dihydrate—primary dihydrate—had formed, and shaking the contents so as to ensure the attainment of equilibrium between the solid and liquid phases at each observation temperature, the volume temperature curve (4) was obtained. Along this curve the system is represented by an equilibrium mixture of primary dihydrate and its saturated solution. The temperature of disappearance of the dihydrate, at which curve (4) intersects curve (6) was determined, in a more exact manner than is possible in the dilatometer itself, by rotating sealed tubes containing the system $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in the form of primary dihydrate and saturated solution in a water-bath with glass sides, the temperature of this being slowly raised. In this way the two curves were found to intersect at 54° .

When the dilatometer containing supercooled liquid of the composition $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is subjected to a temperature between -10° and -20° , complete solidification takes place and secondary pentahydrate separates in the form of long needle-shaped crystals (Parmentier and Amat, *Compt. rend.*, 1884, 98, 735). With the system in this form the volume temperature curve (2) was obtained. There is an upper limit to this curve, for, at about 30° , partial liquefaction accompanied by increase in volume occurs and a new system, characterised by its own volume temperature curve, is formed. The composition of the hydrate resulting from the transformation of secondary pentahydrate was determined by operating in a manner similar to that employed in the separation of primary dihydrate, and the analytical data correspond with the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. The new system formed at 30° is thus represented by a mixture of the tetrahydrate (secondary tetrahydrate) and its saturated solution. By raising and lowering the temperature and agitating the contents of the dilatometer to obtain equilibrium between the solid and liquid phases, the volume temperature curve (3) was realised. At 39.5° the solid phase disappears and this is the temperature at which curve (3) intersects curve (6). The portion of curve (3) below 30° corresponds with a supercooled condition. Young and Barke (*loc. cit.*) express the opinion that the system, secondary tetrahydrate and saturated solution, cannot be cooled below the temperature of formation of secondary tetrahydrate from pentahydrate, but we have on two

occasions succeeded in cooling the system to 25° , thereby obtaining a perfectly definite dilatometer reading corresponding to a volume which is considerably greater than the volume of the system in the form of secondary pentahydrate.

The volume temperature curve (5) remains to be discussed. When the dilatometer containing supercooled liquid was allowed to stand at the room temperature for some days (in some cases weeks), well-formed crystals separated out slowly in small quantity. Crystals which separated under similar conditions from the same liquid contained in sealed tubes, gave on analysis numbers corresponding with the monohydrate $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The volume temperature curve for the system monohydrate and saturated solution is somewhat difficult to realise on account of the slowness with which equilibrium between the solid and liquid phases is attained. The comparatively large size of the crystals and the difficulty of agitating the contents of the dilatometer at constant temperature for long periods of time prevented the determination of the volume of the system at gradually increasing temperatures, but by cooling in ice for several days a constant reading of the dilatometer was obtained, and this gives a point on the curve (5) at 0° . By rotating sealed tubes containing the system

in the form of monohydrate and saturated solution, the temperature of disappearance of the solid phase was found to be 31.3° , which is therefore the temperature at which curve (5) cuts curve (6).

A special interest attaches to these observations with the dilatometer in that the different forms in which the system

can exist at a particular temperature are clearly indicated by different scale readings, each corresponding to a definite volume. At 25° , for example, the volume has been found to have at least six different values corresponding to the following forms: (1) primary pentahydrate; (2) secondary pentahydrate; (3) secondary tetrahydrate and saturated solution; (4) primary dihydrate and saturated solution; (5) secondary monohydrate and saturated solution; (6) liquid. Referred to the formula weight ($\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$) in grams, the volume of the system in these various forms is, 142.30, 146.38, 147.03, 148.34 (149.08), and 149.13 c.c. respectively.

According to the observations of Young and Burke (*loc. cit.*), all the possible forms of the system $\text{Na}_2\text{S}_2\text{O}_3 : 5\text{H}_2\text{O}$ at 25° have not been realised in our dilatometer experiments. Supercooled fusions of the pentahydrate, when cooled, are said to yield occasionally an opaque mass of crystals consisting of a mixture of hexahydrate (tertiary or quaternary) and anhydrous salt. At about 14° the hexahydrate is transformed into tertiary sesquihydrate, $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$,

or into a quaternary hydrate of the composition $3\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, and according to solubility data it should be possible to obtain the system $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in the form of each of these hydrates and the corresponding saturated solution. A further form of the system, quaternary dihydrate and saturated solution, is also possible according to solubility data (Young and Burke, *loc. cit.*). In our experiments the formation of hexahydrate from supercooled fusions of primary pentahydrate has not been observed and the conditions for the three last-mentioned forms of the system have in consequence not been attained.

The stable form of the system below 48° is that represented by the primary pentahydrate, and in the course of the investigations the transformation of the forms (2), (5), and (6) into (1) has been observed at the room temperature. It should, however, be stated that the possibility of inoculation by nuclei was not positively excluded under the conditions of the experiments, for the dilatometers were not hermetically sealed, although the contents were effectually prevented from contact with the atmosphere by a long column of petroleum in the capillary stem of the instrument.

The transformation of secondary pentahydrate into the stable primary form affords an interesting lecture experiment. A glass tube closed at one end, 30—40 cm. long and about 1 cm. in diameter, is almost filled with the liquid obtained by heating ordinary sodium thiosulphate at 70 — 80° , and after being closed with a well-fitting cork is cooled in a mixture of ice and salt. The liquid solidifies completely and the resulting secondary pentahydrate presents a more or less translucent appearance. If a crystal of the ordinary hydrate is dropped into the tube, transformation of secondary into primary pentahydrate begins at once, and a considerable quantity of heat is developed. On account of the opaque appearance of the transformed mass, the surface of separation, which moves steadily down the tube, can be readily seen from a considerable distance. The opacity of the resulting primary pentahydrate is probably connected with the contraction in volume which accompanies its formation from the secondary form. Experiments are now being made to determine the velocity with which this surface of transformation is propagated under varying conditions.

The readings obtained with carefully calibrated dilatometers containing known quantities of sodium thiosulphate permit of a very accurate determination of the specific gravity of the primary and secondary pentahydrates, for the volumes of these can be directly compared with the volume of the supercooled liquid, the specific gravity of which was determined by means of a pycnometer. For the specific gravity of the primary pentahydrate the following values

have been given : 1.734 (Schiff, *Annalen*, 1860, 113, 350) ; 1.736 at 10° (Kopp, *Annalen*, 1855, 93, 129) ; 1.729 at 17° (Dewar, *Chem. News*, 1902, 85, 289). By extrapolation, from measurements of the specific gravity of less concentrated solutions, Schiff (*Annalen*, 1860, 113, 188) obtained $D_4^{19^\circ} = 1.6659$ for a solution of the composition

These numbers all appear to be too small. The values which we have obtained for $D_4^{20^\circ}$ are (1) liquid $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 1.6730 ; (2) primary pentahydrate, 1.750 ; (3) secondary pentahydrate, 1.702.

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