DUNSTAN AND LANGTON: THE VISCOMETRIC

LI.—The Viscometric Determination of Transition Points.*

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IN connexion with an investigation which the authors are conducting on the existence of double salt molecules in the dissolved state, a simple method has been developed for the determination of transition points.

In brief, this method consists in measuring and plotting the viscosities of saturated solutions of the various compounds at different temperatures, when a curve is obtained on which singular points are exhibited at the transition temperatures.



The solution to be examined was stirred at constant temperature for a prolonged time, varying from two to seven hours in the cases examined in this investigation. A viscometer was designed to allow of the saturated solution being filtered directly into the instrument, and incidentally to carry out a density determination to check the course of the saturation. To this end the measuring bulb A of the modified Ostwald viscometer described by one of the present authors (Trans., 1907, 91, 1730) was ground into the receiving limb instead of being fused on (Fig. 1). To the tap could be attached a filtering tube of the usual type. When filled with the clear solution, this measuring bulb was supported in the thermostat, and the level of the liquid adjusted to the mark. Before filling, the bulb was warmed in the bath. On being dried and cooled, a density determination could be made, since the bulb was previously cali-Any solid that separated was soon rebrated. dissolved when the bulb was immersed in warm water. It was then connected with the visco-

meter, the tap opened, and after a sufficient time for temperature equilibrium the liquid was sucked up above the mark in the A rapid method for the determination of the delivery bulb B. transition point is thus possible, the rapidity being only conditioned by the time required for saturation to be set up. In each of the series of experiments described below, analyses were made of the



^{*} For abstract, see Proc., 1912, 28, 14.

solid phase in equilibrium with the solution, and each experimental point is the mean of several determinations of times of flow. It will be seen from the curves that points on the metastable curves have been recorded on several occasions.

Astrakanite.

This salt was prepared by dissolving molecular proportions of sodium and magnesium sulphates in as little water as possible, and evaporating the solution on the water-bath until on stirring a



copious precipitate of the double salt occurred. This was collected, and dried on porous earthenware. Several analyses were made to find the percentage of water of crystallisation, which was found to be 21.53 (calculated for $Na_2SO_4,MgSO_4,4H_2O=21.60$). Some difficulty was met with in obtaining equilibrium, and prolonged stirring was needed. The transition temperature is 21.7°. The metastable curve for the mixed sulphates is well shown.

	Time of flow [Time of flow
Temperature.	(seconds).	Temperature.	(seconds).
32.4	283.5	21.5	518.0
30.7	291.0	20.9	506.0
25.0	528.0	20.02	486.5
24.9	365 0	17.95	474.0
23.0	419.0	16.78	467.3
21.9	480.0		

F1G. 2. Astrakanite.

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Starting with the mixed sulphates at 25°, it was possible by varying the period of stirring to obtain values for the time of flow ranging between 540 and 360 seconds, depending on the degree of persistence of the metastable condition.

Sodium Sulphate, Na₂SO₄,10H₂O.

Recrystallised from Schuchardt's purest preparation. The anhydrous salt, Na_2SO_4 , was prepared from this.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
27.0	98.3	33.0	141.2
30.0	116.0	36.0	124.0
32.42	141.4	45.2	95.0





The transition point from the intersection of the curves for the anhydrous and decahydrated salts is 32.6°. Richards and Wells (Zeitsch. physikal. Chem., 1903, 43, 471) find 32.4°.

Sodium Carbonate.

The crystallised decahydrate used was Schuchardt's purest pre-The monohydrate was obtained from the effloresced paration. decahydrate.

DETERMINATION OF TRANSITION POINTS.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
24.8	183.5	35.0	374.0
26.1	197.0	35.5	374.0
30.6	287.0	36-2	386-0
31.5	343.0	36.4	352.0
32.4	346.0	38.2	324.0
32.5	338·0	39.7	298.0
34.1	362.0	42.35	270.5
34.5	365.0		





The transition point for $Na_2CO_3, 10H_2O$ — $Na_2CO_3, 7H_2O$ is $32^{.}5^{\circ}$, and for $Na_2CO_3, 7H_2O$ — Na_2CO_3, H_2O is $35^{.}4^{\circ}$. Ketner (Annalen, 1872, **25**, 546) gives $31^{.}85^{\circ}$ and $35^{.}1^{\circ}$ respectively.

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Sodium Bromide.

Recrystallised from Kahlbaum's purest dihydrated salt. The anhydrous phase was prepared from the crystalline dihydrate.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
41.0	66.4	50.3	61.6
43 [.] 9	65·0	51.3	60.2
45·7	63.6	53·8	58.0
48-4	62.3	56·7	54.9
49.0	62·2		





FIG.	6
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The transition point for NaBr,2H₂O-NaBr is at 50^{.5°}. Richards and Churchill (*Zeitsch. physikal. Chem.*, 1899, **28**, 314) found 50^{.7°}.

Barium Acetate.

The hydrate was crystallised from Schuchardt's preparation. The monohydrate was prepared by efflorescence of the trihydrate, and the anhydrous phase by heating the monohydrate in a steam-oven.

Temperature.	Time of flow (seconds).	Temperature.	Time of flow (seconds).
19.5	252.0	30.2	201.0
20.6	249.2	33.2	182.0
21.75	244.2	39.2	155.0
23.25	243.0	43.9	136.8
25.3	238.3	45.5	134.0
26.4	235.0	48.2	120.7
28.1	212.7	54.0	104.0

The transition points are: $Ba(C_2H_3O_2)_2, 3H_2O$ — $Ba(C_2H_3O_2)_2, H_2O$, 25.2°; $Ba(C_2H_3O_2)_2, H_2O$ — $Ba(C_2H_3O_2)_2, 42.2°$. Walker and Fyffe (Trans., 1903, 83, 173) find 24.7° and 41° respectively.

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