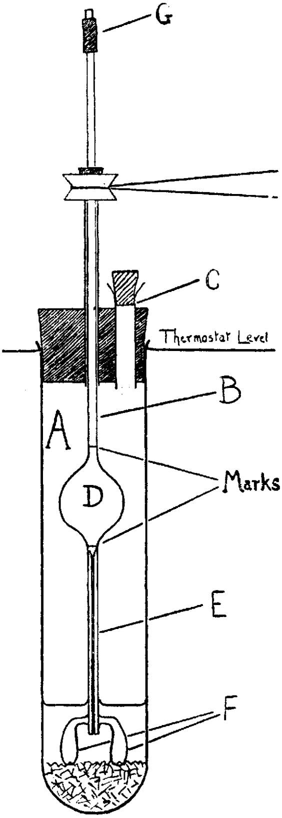
CCLXXIV.—*An Apparatus for the Viscosimetric Determination of Transition Points.*

By NORMAN HOLT HARTSHORNE.

DUNSTAN and LANGTON (J., 1912, **101**, 418) determined the transition points of a number of salts by preparing saturated solutions at different temperatures and measuring their times of flow in a viscosimeter of the Ostwald type. In the apparatus now described, successive solutions are prepared and their times of flow determined in one and the same vessel, thereby effecting a considerable saving of time.

The apparatus (Fig. 1) consists of a solubility tube, *A*, 25 cm. long and 5 to 6 cm. wide, fitted with a rubber bung carrying a combined viscosimeter and stirrer, *B*, and a wide tube, *C*, which normally is closed with a cork. The bulb, *D*, of the viscosimeter has a capacity of about 20 c.c. The capillary, *E*, is 10 cm. long, and its bore is varied to suit the nature of the substance to be examined; in the present work, about 0·75 mm. was found to be suitable, and this would probably be so for all salts of average solubility. Glass paddles, *F*, are sealed on the capillary about 0·5 cm. from the end.

FIG. 1.



To carry out a determination, about 80 c.c. of the saturated solution together with excess salt are placed in *A* and the apparatus is fitted together and immersed in a glass-sided thermostat (regulated to ± 0·02°). The viscosimeter, closed by a rubber cap, *G*, to exclude dust, is rotated until equilibrium is reached, the solid is allowed to settle completely, and *G* is replaced by a piece of rubber tubing by means of which solution is sucked up beyond the higher mark. The viscosimeter is raised clear of the remaining liquid, and its contents are allowed to drop back, the time of flow from the upper to the lower mark being noted. After a duplicate reading has been made in the same way, the viscosimeter is washed down with distilled water (2 c.c.), *G* is replaced, and the solution stirred again at another temperature. By means of additions or withdrawals through the tube *C*, the quantities of solid and solution can be adjusted when necessary. The time taken to reach equilibrium can readily be determined by taking readings at the same temperature until the results are constant. In the present work, 6 hours were usually found to be sufficient, but in most cases 12 to 24 hours were allowed.

The following transition points have been determined :—

$$Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4+10H_2O.$$
$$NiSO_4,7H_2O \rightleftharpoons NiSO_4,6H_2O(\text{blue})+H_2O.$$
$$Na_2HPO_4,12H_2O \rightleftharpoons Na_2HPO_4,7H_2O + 5H_2O.$$

The results are given below, the time of flow being recorded in seconds.

Sodium Sulphate.

$Na_2SO_4,10H_2O$. 20·0°, 133; 22·7°, 140; 23·0°, 142; 24·2°, 144; 26·5°, 156; 26·7°, 157; 29·6°, 174; 30·5°, 184; 32·5°, 219; 32·6°, 221; 32·7°, 225.

Na_2SO_4. 25·1°, 289; 26·1°, 277; 31·0°, 232; 32·0°, 225; 32·8°, 219; 33·2°, 215; 33·8°, 214; 34·8°, 205; 35·0°, 205; 35·9°, 198; 36·8°, 192; 38·4°, 183.

Nickel Sulphate.

$NiSO_4,7H_2O$. 21·4°, 355; 24·5°, 350; 27·0°, 347; 27·7°, 347; 28·1°, 347; 31·4°, 347; 34·3°, 347.

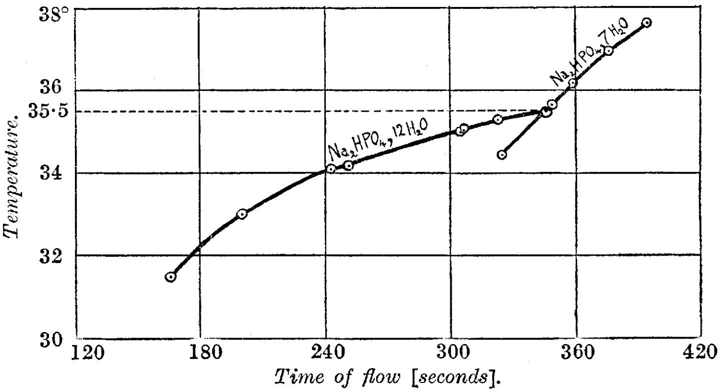
$NiSO_4,6H_2O$ (blue). 25·1°, 367; 25·8°, 361; 27·0°, 356; 29·1°, 349; 29·8°, 345; 30·1°, 343; 30·6°, 342; 32·1°, 336; 33·7°, 331; 34·5°, 329.

Disodium hydrogen phosphate.

$Na_2HPO_4,12H_2O$. 31·5°, 166; 33·0°, 200; 34·1°, 243; 34·2°, 252; 35·0°, 305; 35·05°, 306; 35·3°, 323; 35·5°, 346.

$Na_2HPO_4,7H_2O$. 34·45°, 325; 35·65°, 349; 36·2°, 359; 36·95°, 377; 37·65°, 395.

FIG. 2.



In the experiments with sodium sulphate and nickel sulphate the temperature regulation was not so sensitive as is desirable and the results when plotted show small irregularities. The transition points deduced from them are 32·55° for sodium sulphate (Richards and Wells, *Z. physikal. Chem.*, 1903, **43**, 471, found 32·383° on the hydrogen scale, whilst Berkeley, *Phil. Trans.*, 1904, **203**, [*A*], 209, and Gay-Lussac, *Ann. chim. phys.*, 1819, **11**, 312, found 32·5°) and 29·3° for nickel sulphate (Steele and Johnson, J., 1904, **85**, 113, found 31·5°). The low result in the case of nickel sulphate is attributed to impurity.

In the case of disodium hydrogen phosphate, the temperature was regulated to within ± 0·02° and the curve (Fig. 2) is markedly more regular. The transition point obtained is 35·5°. Values given by previous workers are 36·4° (Person, *Ann. chim. phys.*, 1849, [iii], **27**, 253), 35·0° (Tilden, J., 1884, **45**, 268), *ca.* 36·6° (Baur, *Z. physikal. Chem.*, 1895, **18**, 180), and 35·4° (D'Ans and Schreiner, *ibid.*, 1911, **75**, 99). The value obtained is thus in good agreement with the latest work. The salt used was B.D.H. ordinary reagent and was twice recrystallised, the crystals being washed with ice-water.

The reproducibility of the curves was shown by repeating portions of them; the figures so obtained are included in those given above. Duplicate readings were taken at all temperatures and never varied by more than 1 second, the agreement being usually within 0·5 second. Failure to reach this points to an obstruction in the capillary tube, which sometimes occurs when the viscosimeter has not been washed. A less frequent cause is the presence of dust in the solution, which should therefore be filtered before being poured into the apparatus. For a similar reason, it is better not to dry the solids with filter-paper after recrystallisation. In all cases except one, in which the solution contained a considerable quantity of filter-paper dust, it was found quite easy to clear the tube *in situ* with a little distilled water. The close agreement between duplicate readings shows that this plan of washing with water has no appreciable effect on the accuracy of the method.

The apparatus in its present form is not suitable for salts giving volatile products of hydrolysis, *e.g.*, sodium carbonate, which lost carbon dioxide on prolonged stirring, but could probably be made so by the addition of a mercury seal.

In conclusion, I desire to express my thanks to Dr. J. F. Spencer for his helpful interest in this work.

BEDFORD COLLEGE FOR WOMEN,
UNIVERSITY OF LONDON.

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