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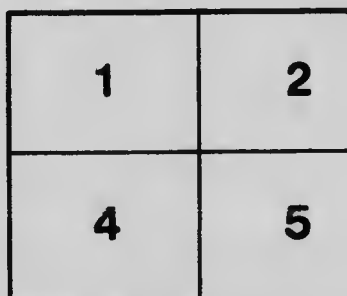
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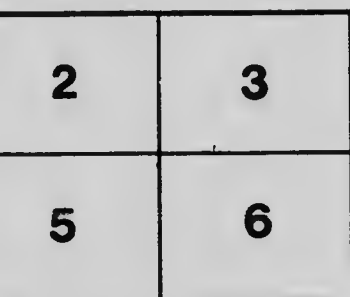
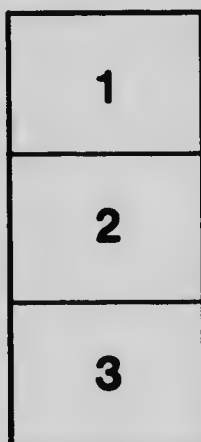
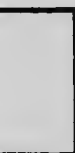
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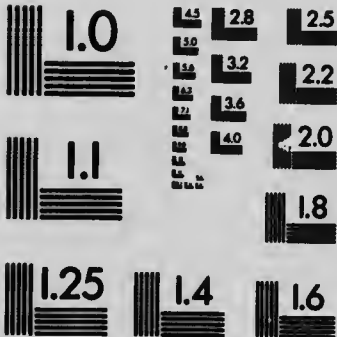
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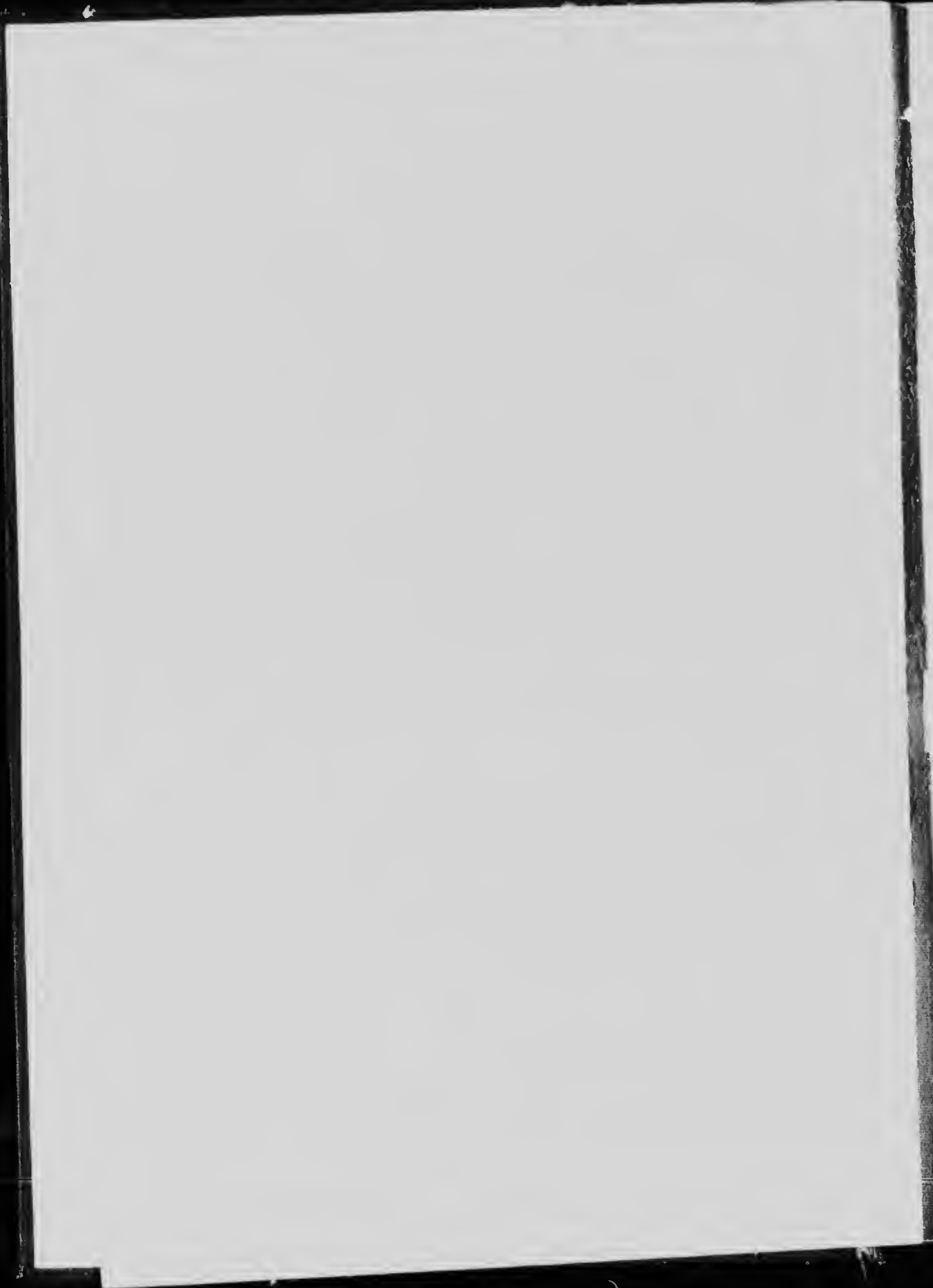
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No. 80: INDIRECT ANALYSIS BY MEANS OF THE DILATO-  
METER, BY W. LASH MILLER

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## INDIRECT ANALYSIS BY MEANS OF THE DILATOMETER: THE "LOWER HYDRATE" OF SODIUM ACETATE

BY W. LASH MILLER

In order to avoid the difficulties which sometimes attend the removal of mother-liquor from the solid products of a reaction,<sup>1</sup> various "indirect" methods of analysis have been devised for determining the composition of the latter.<sup>2</sup>

The method employed in the present paper is different in principle from those hitherto suggested; while less general in its application than some of them, it is perhaps the most convenient in the large group of cases to which it is applicable.

The behavior of crystallized sodium acetate,  $C_2H_3O_2Na \cdot 3H_2O$ , on heating, was first described by Jeannel<sup>3</sup>, who found that it begins to melt at  $58^\circ C$ , becomes completely liquid at  $75^\circ$ , and boils at  $123^\circ$ .

When he let the melted salt cool gradually in the air, it crystallized at  $58^\circ$  in prismatic needles, the temperature keeping constant at that point during the crystallization;<sup>4</sup> but if the solution was protected from "germs" it solidified to a white translucent mass of large shiny leaflets covered with a little liquid.

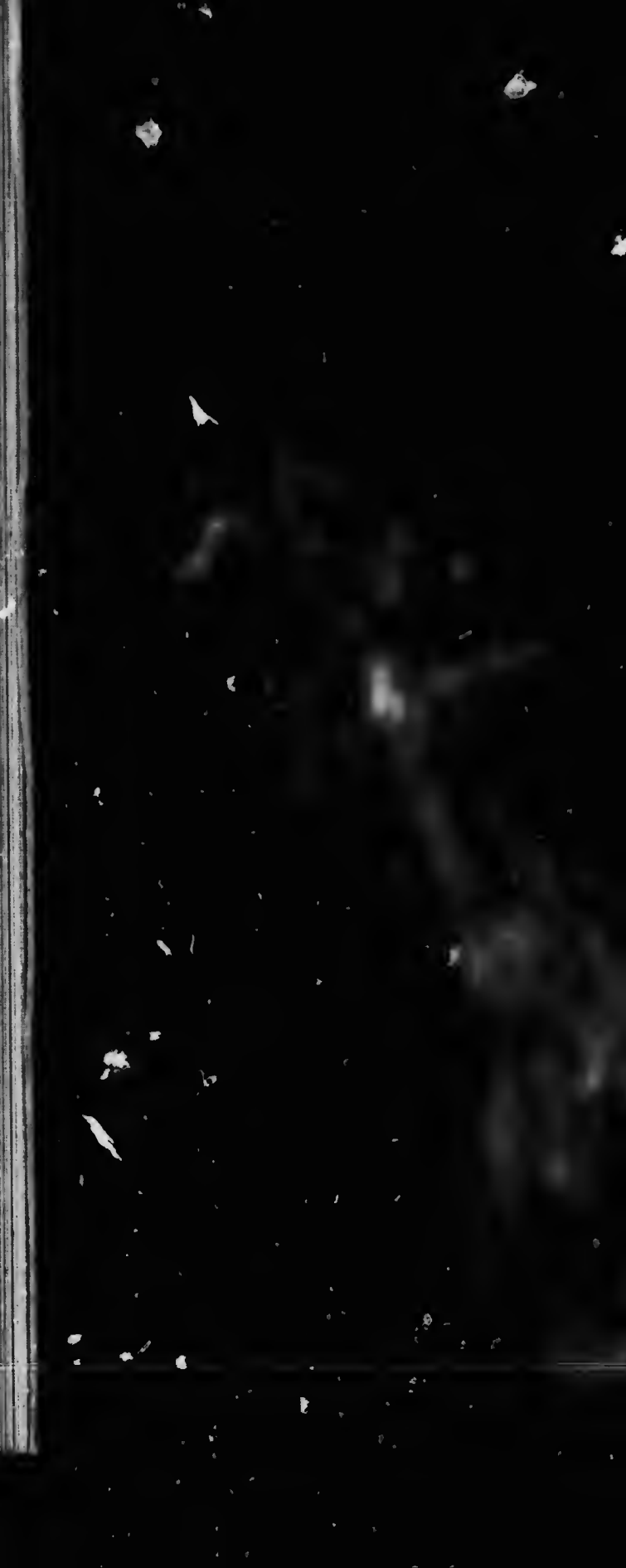
These leaflets were deliquescent in air in which the prismatic salt dried out, and were easily converted into the latter by bringing into dry air, or by touching with a glass rod,

<sup>1</sup> Bancroft: *Jour. Phys. Chem.*, **6**, 178 (1902); Lash Miller and Kenrick: *Ibid.*, **7**, 259 (1903).

<sup>2</sup> v. Bijlert: *Zeit. phys. Chem.*, **8**, 343 (1891); Schreinemakers: *Ibid.*, **11**, 81 (1893); Kentner: *Ibid.*, **39**, 658 (1902); Bancroft: *Jour. Phys. Chem.*, **6**, 178 (1902); **9**, 558 (1905); Browne: *Ibid.*, **6**, 287 (1902).

<sup>3</sup> *Comptes rendus*, **62**, 834 (1866).

<sup>4</sup> Jeannel suggested the use of melted sodium acetate for testing and standardizing thermometers; a note on the suitability of the salt for this purpose will shortly be published.



or with a crystal of "ordinary" sodium acetate—dehydrated sodium acetate had no effect.<sup>1</sup>

Although the supersaturated solutions of sodium acetate have been studied by a large number of authors, among them Reischauer,<sup>2</sup> Gernez,<sup>3</sup> Böttger,<sup>4</sup> Thomson,<sup>5</sup> and Baumhauer,<sup>6</sup> the composition of the leaflets described by Jeannel has not yet been ascertained with certainty. They are commonly referred to in the literature as "a lower hydrate,"<sup>7</sup> and Gernez,<sup>8</sup> though without quoting his authority, gives them the formula  $2C_2H_3O_2Na \cdot 3H_2O$ ; but the only analyses of which I have been able to find any account are due to Zettnow.<sup>9</sup>

This chemist melted the commercial acetate in a flask, boiled the liquid, closed the mouth of the flask with cotton wool, and drained the crystals deposited on cooling, by tilting the flask. When the cotton was removed, the (supersaturated) mother-liquor solidified, breaking the flask; the upper layer of crystals was then removed and analyzed, with the following results (in Expts. 3 and 4 the melting was repeated):

TABLE I

Expt.	Water Percent	Formula
1	35.66	$C_2H_3O_2Na \cdot 2.52 H_2O$
—	35.33	" 2.49 "
2	21.33	" 1.24 "
3	18.14	" 1.03 "
—	21.05	" 1.20 "
4	20.04	" 1.14 "
5	32.6	" 2.20 "
6	33.3	" 2.27 "

<sup>1</sup> Berthelot: Comptes rendus, 77, 975 (1873).

<sup>2</sup> Liebig's Ann., 115, 116 (1860).

<sup>3</sup> Jahresbericht, 1865, 75.

<sup>4</sup> Jahresbericht, 1867, 390.

<sup>5</sup> Jour. Chem. Soc., 35, 196 (1870).

<sup>6</sup> Jour. prakt. Chem., 104, 449 (1868).

<sup>7</sup> Ostwald: Lehrbuch II, (2) page 770 (1902).

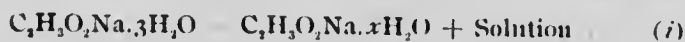
<sup>8</sup> Comptes rendus, 84, 1389 (1877).

<sup>9</sup> Pogg. Ann., 142, 306 (1871).

The author regards his experiments as establishing the existence of the hydrates  $C_2H_3O_2Na \cdot H_2O$ ,  $2C_2H_3O_2Na \cdot 5H_2O$ , and  $2C_2H_3O_2Na \cdot 9H_2O$ ; in the absence of proof that his crystals were free from mother-liquor, however, much weight cannot be attached to these results. The formate and valerate of sodium crystallize with one mol of water, but Thomson's<sup>1</sup> observations that these salts cause no formation of crystals in supersaturated solutions of sodium acetate speaks against the existence of a hydrate  $C_2H_3O_2Na \cdot H_2O$ .

On repeating Jeannel's experiments it was at once apparent that the "partial melting" at  $58^\circ C$  consists in the complete disappearance of the crystals of trihydrate, and the formation of a solution and of crystals of a new salt (leaflets); a few more experiments, carried out after the manner of Zettnov's, showed that both solution and leaflets, like the trihydrate from which they were formed, were slightly alkaline to litmus. From this observation (which was subsequently confirmed with the crystals separated by the centrifugal apparatus described by Mr. Green)<sup>2</sup> it follows that the leaflets consist of a neutral acetate of sodium, hydrated or anhydrous; as, if they had been formed of an acid or basic acetate, either the crystals themselves or the mother-liquor must have had an acid reaction.

The "partial melting point" of the trihydrate, then, must be considered as the temperature at which the reaction



is in equilibrium; in other words, it is a transition point in a two-component system, and the following

#### Considerations based on the phase rule

lead to a method of determining the composition of the crystals in question without removing them from the mother-liquor.

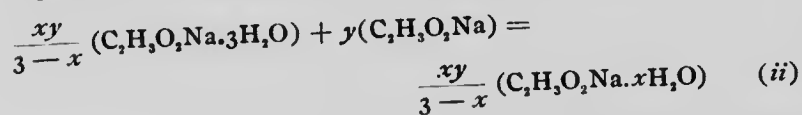
As the existence of equilibrium in heterogeneous sys-

<sup>1</sup> Loc. cit., page 203.

<sup>2</sup> Jour. Phys. Chem., 12, 655 (1908).

tems is not dependent on the quantities of the various phases present, addition of  $C_2H_3O_2Na \cdot xH_2O$  in any quantity would cause no change in the temperature of "melting," in the composition of the solution, or in the amount of trihydrate present. Addition of a third hydrate, however, or of the anhydride (supposing  $x$  different from 0) renders a new reaction possible, *viz.*, reaction (ii), between trihydrate,  $x$ -hydrate, and third hydrate (or anhydride); and, as it is very unlikely that both reactions *i* and *ii* will be in equilibrium at the same temperature,<sup>1</sup> it is fair to assume that reaction *ii* will proceed until either the new hydrate or the trihydrate is completely used up.

If  $y$  be taken to represent the number of mols of anhydride mixed with  $A$  mols of trihydrate, reaction *ii* may be represented by the following chemical equation:



which shows that  $xy/(3-x)$  mols of the trihydrate would disappear, leaving only  $A - xy/(3-x)$  mols to enter into reaction *i*.

A determination of the residual trihydrate, therefore, together with the known values of  $A$  and  $y$ , is sufficient to determine  $x$ , that is, the composition of the crystals formed by melting the trihydrate at  $58^\circ C$ .

The easiest way to determine the amount of trihydrate in a mixture of trihydrate and  $x$ -hydrate is to heat to  $58^\circ$  and measure the change of volume which accompanies the "melting." This is obviously proportional to the amount of trihydrate present; by means of a blank experiment, in which the dilatometer is filled with a known quantity of the pure trihydrate, the weight of that salt corresponding to one division of the dilatometer scale may be ascertained.

<sup>1</sup> The statement of the phase rule, that in a two-component system at arbitrary pressure not more than three phases can exist in equilibrium, is only another way of putting this.

Dilatometer measurements

To facilitate the introduction of weighed amounts of salt into the dilatometer, the bulb of the latter was replaced by a cylindrical vessel closed by a perforated cork with capillary through which the (dried and air-free) coal oil was sucked into the instrument; contrary to expectation, there was no trouble due to swelling of the cork when the whole was immersed in the water bath.

Two sets of measurements were carried out: the first with 4.040 grams of the pure trihydrate, and the second with 3.350 grams of a mixture prepared by grinding trihydrate and anhydride together, heating for some time above 60°, cooling, and powdering again. The amount of water in this mixture was determined by heating to 120° until the weight was constant:

Weight before heating 1.7156 g.  
 Weight after heating 1.4460

TABLE II

4.040 g. trihydrate			3.350 g. mixture		
Interval Hrs. min.	Temp.	Dilat. div'ns	Interval Hrs. min.	Temp.	Dilat. div'ns
— 30	56.6° C	47.0	— 7	57.0° C	123.0
— 27	57.0	48.0	— 7	57.5	126.0
— 11	57.5	51.0	— 5	58.0	131.5
— 8	58.0	53.0		58.5	143.0
3 12	58.5	56.8		Heated to 75°	
17 0	59.0	227.0	I 4	59.5	188.0
I 10	59.35	229.0		58.8	187.5
I 5	58.7	228.0		(Interp) 58.0	187.0 melted
	56.3	220.0		58.0	131.5 solid
(Interp)	58.0	224.5 melted		Expansion	55.5
	58.0	53.0 solid			
Expansion		171.5			

Assuming that the melting takes place at 58° on the thermometer employed, the first experiment shows that

the expansion per gram of trihydrate melted is 42.44 divisions of the dilatometer scale. The expansion of the mixture, 55.5 divisions, corresponds to 1.308 grams of trihydrate or 0.009616 mols.

Thus  $A - xy/(3-x) = 0.009616$ . The values of  $A$  and  $y$ , calculated from the weight and composition of the mixture, are 0.009750 and 0.02346, respectively; from which it follows that  $x = 0.017$ , or that the composition of the "x-hydrate" is  $C_2H_3O_2Na \cdot 0.017H_2O$ .

The reliability of this result obviously depends on the accuracy of the dilatometer measurements. The error of each of the expansions measured is probably at least one scale division, but certainly less than five divisions; while even if 5 divisions be added to the expansion of the trihydrate and 5 be subtracted from that of the mixture—the most unfavorable combination—the value of  $x$  rises only to 0.16.

The measurements therefore prove conclusively that the crystals deposited by the trihydrate on "melting" consist of anhydrous sodium acetate.

*The University of Toronto,  
June 1903.<sup>1</sup>*

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<sup>1</sup> Read before the American Chemical Society at the Buffalo Meeting September 1905, under the title "A new use for the Dilatometer."







