EBULLIOSCOPIC DETERMINATIONS WITH A COMMON THERMOMETER.

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The present high cost and fragile character of the Beckmann thermometer has raised a doubt as to the advisability of placing so valuable an instrument in the hands of the ordinary student. Even the experienced instructor has come to handle it gingerly and with no little foreboding.

Herewith described is an arrangement whereby an ordinary stock thermometer graduated in degrees may be read to hundredths of a degree with an error of not more than 1%. Molecular weights determined by the boiling-point method with this device compare favorably in accuracy with those obtained by the usual method.

The so-called "error of parallax" has long been a source of concern to the reader of scale divisions. It occurred to the writer that this same "error" or apparent shift might well be turned to account in the estimation of fractions of a division. As a test of this idea a common thermometer possessing a solid stem, measured 24 cm. from 0 to 100°, was chosen out of stock. A meter rod graduated in millimeters was attached to a stand and equipped with a sliding peep-sight made from a strip of thin sheet metal. When this rod was set parallel with the thermometer, with the hole of the peep-sight at a distance of 6 inches from the thermometer scale, an apparent shift of the mercury amounting to 1° necessitated a corresponding movement of the sliding sight over 20 cm.

Repeated sets of the sight gave readings that corresponded within one mm., which is equivalent to 0.005°. These readings were facilitated greatly by projecting light on the mercury with a hand mirror and noting the exact position in which the brilliant gleam from the thread of quicksilver just disappeared behind a scale mark on the thermometer. Indeed this procedure is absolutely essential to the success of the method.

However, several difficulties were encountered at this stage. First of all, no method could be devised by which the scale could be calibrated with the requisite degree of accuracy. It was practically impossible to get more than an approximate measurement of the distance from the reference mark on the thermometer stem to the capillary. Moreover, the value of the degree interval selected on the thermometer could readily be in error by 0.1° or even more. The approximation obtained above, 20 cm. per degree, was therefore used until it became clear that the average error of a series of molecular weights was negligible. whence the foregoing value was adopted.

The second difficulty was caused by the refraction due to the glass stem. Having assumed the index of the glass to be 1.5, calculations showed all angular readings up to about 30° to be proportional to movements along the capillary within an error of 1% if such readings lay either all above or all below a perpendicular from the meniscus to the scale. Under these conditions the light rays are all bent in the same direction. However, if the angle read includes the perpendicular, the rays are bent in opposite directions, and tangent 20° differs from 4 times tangent 5° by 8%. The foregoing angles are external, while the above 8% is of course calculated for the corresponding angles in the glass.

In spite of the above objections, it was found that fairly good results could be obtained when the temperature elevations were relatively slight and the angles correspondingly small. The following are representative figures obtained under varying conditions and on the above assumptions. Carbon tetrachloride is especially valuable as a solvent owing to its non-inflammability, high constant 48, and low boiling point.

TABLE I.—ANALYSES.

Borneol, mol. wt. 154, in carbon tetrachloride.

Expt. No.	Rise, degrees.	Mol. wt.	Error. %.
1	0.48°	142	—8
2	0.54°	157	+2
3	0.53°	163	+6
	Average,	154	
Fructose, mol. wt. 180, in water;	0.09°	175	—2

Experiments also were performed to determine whether a change of 0.01° could be detected by this method. The amount of borneol calculated to produce the above rise, 0.0096 g. in 30 g. carbon tetrachloride, was added to the latter amount of this solvent and the rise measured. Three trials gave the following readings in terms of millimeters on the peep-sight scale: 1.2, 2.0, 1.5. The barometric pressure was somewhat variable during these tests. The experiment was repeated, using fructose in water, 0.069 g. in 20 g. water. This gave a rise of 1.5 mm. Hence a movement of 0.01° can be detected with certainty.

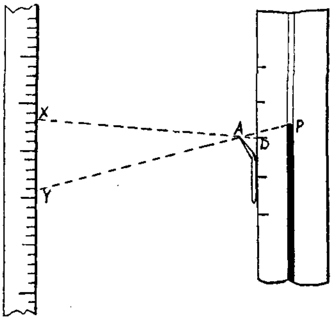

Fig. 1.

In order to avoid the above uncertainties, both of calibration and of reading, the method was so changed as to necessitate the use of but a single reference point on the thermometer. The principle of triangulation was utilized in establishing this point. For this purpose the stock thermometer was fitted with a pen-shaped metallic indicator tapered to a width at the point equal to the apparent width of the capillary. This was blackened, bent so that the tip stood at a distance of three millimeters from the scale, and attached to the thermometer with a screw clamp. This served to determine the angle between a degree mark and the meniscus, using the peep-sight as in the previous work. For example (see Fig. 1) the readings X and Y serve to establish accurately the position P on the capillary with reference to D. The distance between X and Y once known, the apparatus may be dismantled, set up again, and the position P as definitely fixed as before, providing the indicator has not been moved relative to the degree mark.

The manipulation is as follows and is as valuable when a Beckmann thermometer is used as it is important with this apparatus. Place about 30 g. of carbon tetrachloride in the weighed boiling tube with a known amount of purified borneol. Note the exact angle between the nearest degree mark and the meniscus when the latter has reached equilibrium at the true boiling point, reading this angle in terms of divisions on the peep-sight scale, thus establishing the point P. Read the barometer and weigh the tube and contents to determine the true weight of solvent. This accounts for the solvent lost during the boiling process. These weights should be correct to at least one cg.

Knowing the weight of solvent, weight of solute and the molecular weight of the latter, it is easy to calculate the rise in temperature over that of the pure solvent. The tube is now carefully cleaned, weighed, and a weighed amount of a substance of unknown molecular weight added with a few grams of the solvent. This is brought to the boiling point and small portions of the pure solvent added from time to time until the meniscus reaches the same point as in the borneol trial, as determined by the angle X A Y. In case too much solvent is added, the condenser may be detached for a few minutes to allow the excess to evaporate. However, this should be avoided, if possible, as any impurity in the solvent will change the boiling point appreciably, if the solvent is permitted to evaporate to any large extent. As soon as the mercury reaches equilibrium at the proper point, namely P, the flame is removed and the tube and contents weighed. The weight of the solvent is thus determined; the temperature rise has been calculated from the borneol trial; hence it is a simple matter to calculate the molecular weight of the unknown.

In both cases the same point on the thermometer has been used for reference, hence a calibrated instrument is unnecessary. Furthermore, the error due to pure solvent clinging to the tube has been largely eliminated. The error due to the index of refraction of glass is also obviated. The flame height must be kept constant throughout the work.

The following results are characteristic:

	Found.	Error.
Borneol, 154, was compared with borneol	158	2.6%
Camphor, 152, was compared with borneol	157	3%
Triphenyl methane, 244	250	2.5%

These results are satisfying in the light of the crude thermometer used.

In conclusion, the writer wishes to extend his thanks to the Editor for his kind and helpful criticisms.

Summary.

A method is suggested whereby it is possible to read small temperature intervals on a common thermometer by measurements of the parallax on an auxiliary scale.

It is possible to eliminate several heretofore troublesome errors in the boiling-point method of determining molecular weights by using but one reference point on the thermometer scale during a given determination, having established this point by the use of a known substance having a high degree of purity.

It follows from the above that the use of a calibrated thermometer is not essential to accurate work.

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A NEW TABLE OF THE PERIODIC SYSTEM.

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The progress of chemistry and the increase of our knowledge require a modification of the classical periodic table. The many proposed "new" tables indicate the interest and demand for a suitable table. Recent papers employ mainly spirals or curves in order to show the different length of the periods. But these graphical representations are cumbersome for practical use on account of their difficult reproduction. In the following a table will be described, which has been derived from a spiral, and thus embodies the advantages of the different models of the periodic system.

The principle involved in a tabular representation of the periodic system is illustrated by Fig. 1, which shows the structure of the system, that is the different length of the periods and the characteristic of the elements in the sub-periods. The terminals of a period are the noble gases, with zero valency and infinite electro-potential. Between each terminal the elements change from positive to negative and the transition point is an element of the carbon family. In the third and fourth period a sub-period (III′, IV′) appears with a change in the inverse direction as seen from Fig. 1. The corresponding sub-periods with analogous elements are clearly expressed in the periodicity of the valency and electromotive force as shown in Fig. 1.

This principle of sub-periods is expressed in the proposed table of the periodic system as reproduced in Table I. The framework of the table