[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE IDENTIFICATION OF SOLIDS BY MEANS OF THE BOILING POINT ELEVATION IN SATURATED SOLUTIONS

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Compounds which decompose before melting, or immediately after melting, are frequently encountered. These compounds cannot be tested and identified, with certainty, by the familiar measurements of melting points and mixed melting points. In such cases a procedure based on solubilities may be substituted. Suppose, for example, that we wish to compare samples of two materials which are suspected of being identical. If we measure first the individual solubilities, then that of a sample made by mixing the two, we have the required information. If the two materials are identical, all three solubilities must be equal, but, if they are different, that of the mixture will be greater than that of either individual. This is a procedure which has not been employed as frequently as its usefulness would warrant. Recent examples are found in the work of Montgomery and Hudson,[2] and that of Austin,[3] who have identified sugar derivatives in this way.

The tests which will be described here may be looked upon as applications of the solubility procedure in which the concentrations of the solutes are evaluated by boiling point measurements, and are based on the fact that the addition of a pure non-volatile solid to a solution can cause an increase of the boiling point only when the solution is not yet saturated with that solid. The substitution of boiling point determinations for analytical measurements, wherever feasible, should effect a saving of time and apparatus. In fact, in some cases, our procedure is as expeditious as the melting point method. Its principal disadvantage is that the best combination of solvent and apparatus for a given measurement is not always evident.

We are not in a position to state exactly which form of ebullioscope will be most useful for our purpose. Probably a small boiling tube of the Beckmann type, fitted with a side-arm condenser, internal heater and a small Beckmann thermometer, will cover the widest range of situations. Our tests have been carried out mainly with the ebullioscope described by Menzies and Wright.[4] This gives satisfactory results, but is perhaps too limited in temperature range to be suitable for general use. However, the high sensitivity of this apparatus is an advantage, for our present purpose, for we have considered it worth while to try out the procedure under

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[2] Montgomery and Hudson, THIS JOURNAL, **52**, 2105 (1930).

[3] Austin, *ibid.*, **52**, 2111 (1930).

[4] Menzies and Wright, *ibid.*, **43**, 2314 (1921).

conditions near the limit of its applicability, and have found it desirable to be able to measure small temperature differences.

The principal application of our method is in the comparison of materials which may be identical. However, it may also be used to test the purity of individual samples of material.

Comparison Tests

The procedure employed in the test for identity, analogous to the mixed melting point, follows that of the determination of molecular weight, with the simplification that the sample need not be weighed and is preferably added in the form of powder, rather than pellets. After the first addition of solid, the temperature increases slowly and reaches a constant value, indicating saturation, in fifteen to twenty minutes. If the addition of a second portion produces no further temperature increase, the substance may be considered pure and the material to be compared is added. If the two samples are identical, the temperature will not rise, but if they are different, the second substance being soluble, a decided increase of boiling point follows in a few minutes. A second measurement should be made with fresh solvent, reversing the order of addition of the substances. Identical materials, when tested individually, will produce saturated solutions of the same boiling point, and the addition of one to the boiling saturated solution will cause no additional boiling point elevation.

We have tested this procedure with several amino acids, using methyl and ethyl alcohols as solvents. Although the boiling points of individual saturated solutions were somewhat variable, there was no doubt in any case of the identity of two samples of the same material, or the non-identity of samples of different materials.

The first comparison attempted, that of *dl*-alanine and *dl*-valine, is typical of the results. The addition of *dl*-valine to boiling ethyl alcohol produced a temperature elevation of 0.0217°, which was increased to 0.0449° by the addition of *dl*-alanine. Starting with *dl*-alanine the initial rise was 0.0211°, increased to 0.0493° by the introduction of *dl*-valine.

In Table I, the results of similar tests with several amino acids in ethyl alcohol are summarized. Table II is similar for the methyl alcohol solutions. The names above and to the left of any figure show the substances

TABLE I

ELEVATION OF THE BOILING POINT OF ETHYL ALCOHOL IN SATURATED SOLUTIONS OF SEVERAL AMINO ACIDS AND THEIR MIXTURES

	Glycine	*dl*-Alanine	*dl*-Valine	*l*-Tryptophane	*d*-Glutamic Acid
d-Glutamic acid					0.0023
l-Tryptophane	0.0318	0.0392	0.0472	0.0180	
dl-Valine	.0424	.0493	.0292		
dl-Alanine	.0265	.0191			
Glycine	.0143				

TABLE II

ELEVATION OF THE BOILING POINT OF METHYL ALCOHOL IN SATURATED SOLUTIONS OF SEVERAL AMINO ACIDS AND THEIR MIXTURES

	Glycine	*dl*-Alanine	*dl*-Valine	*l*-Tryptophane	*d*-Glutamic acid
d-Glutamic acid					0.0052
l-Tryptophane	0.0500	0.0626	0.0757	0.0356	
dl-Valine	.0644	.0635	.0392		
dl-Alanine	.0479	.0278			
Glycine	.0244				

compared in the individual test. Where these names are different, the reading recorded was obtained in a single test. The values given for the individual substances are averages of two or three determinations made in starting different comparisons. The values with *d*-glutamic acid have been included, not because of faith in their accuracy, but to illustrate a case in which comparison by mixing is unnecessary, where the solubilities of the individual substances suffice to distinguish between them.

The results of similar tests with three isomeric leucines are given in Table III.

TABLE III

BOILING POINT ELEVATIONS OF METHYL AND ETHYL ALCOHOLS IN SATURATED SOLUTIONS OF ISOMERIC AMINO ACIDS AND THEIR MIXTURES

Alcohol	*l*-Leucine	*dl*-Leucine	*dl*-Isoleucine	*l*-Leucine + *dl*-Leucine	*dl*-Leucine + *dl*-Isoleucine	*dl*-Isoleucine + *l*-Leucine
Methyl	0.033	0.031	0.040	0.043	0.050	0.063
Ethyl	.019	.013	.025	.025	.037	.037

The combination of *dl*-leucine with *dl*-isoleucine showed a value in methyl alcohol much lower than the sum of the individual elevations. However, the result in ethyl alcohol brings out the difference. The mixture of *dl*-leucine with *l*-leucine is interesting, showing a sufficient elevation after the addition of the second substance to indicate that the two are not identical. The fact that *l*-leucine alone produces a greater elevation than *dl*-leucine is sufficient to establish the latter as a racemic compound, for a racemic mixture should produce approximately twice the effect of one of the isomers.

We have also run comparison tests on sulfanilic acid and two isomeric disodium naphthol-*di*-sulfonates in aqueous solutions. The apparatus consisted of a test-tube with side arm condenser and a mercury thermometer graduated in tenth degrees. The thermometer was first tested in the vapor phase over boiling water, and thereafter the boiling point of water was determined for any one experiment from the barometer, since it is almost impossible to obtain a constant reading with a thermometer immersed in pure water. However, in the presence of excess of the solid materials, readings consistent to 0.1° were obtained. The results are summarized below

Sulfanilic acid	0.25°	Mixture 1.9°
Disodium 2-naphthol 6,8-disulfonate	1.7°	
Disodium 1-naphthol 3,8-disulfonate	..	Mixture > 4°

As a further example, we have compared triphenylmethyl peroxide and 9-phenylfluorenyl peroxide in benzene, using the Menzies apparatus. The two samples melted with decomposition, respectively, at 179–181° and 193–194°. The mixed melting point with the lower melting substance in excess was 178–180°. The results with the ebullioscope were more satisfactory, although not as definite for the individual substances as those with the amino acids. With triphenylmethyl peroxide, the temperature elevation lay between 0.10 and 0.13°, and was a function of the amount of solid added, giving 0.13° as the maximum value for the true elevation. With 9-phenylfluorenyl peroxide a constant value of 0.166° was recorded, and when the former was added to the boiling saturated solution of the latter, the reading increased rapidly to 0.246°, which represents a minimum for the mixture and definitely brings out the difference.

Tests for Purity

The measurement of boiling points of saturated solutions is not sufficiently sensitive to permit the accurate determination of small amounts of impurities. However, when the percentage of impurity is high enough, useful information may be obtained.

In testing for purity, three procedures are available. The first of these we have not tried out, considering it sufficiently evident. It is analogous to the comparison of melting points after successive recrystallizations, and consists of a similar comparison of boiling points. The samples of material added to the apparatus in successive tests should have approximately the same weight, and should be introduced in considerable excess if the procedure is to be sensitive, since a sufficiently high concentration of the impurity must be obtained.

The second test for purity is a variation of the first. A relatively large sample of the substance is boiled with successive portions of the solvent, and the boiling point (or, more frequently, the boiling point elevation relative to the pure solvent) recorded after each change of solvent. In this way the extraction of the impurity by the solvent may be observed. Removal of the hot liquid is effected by a combination of decantation and filtration, and the residue from filtration is returned to the apparatus. A decrease of the boiling point between any two successive measurements indicates the presence of impurity. Erroneous results may be obtained when testing a mixture of two or more similar materials in approximately equal amounts, where it is impossible to extract any one of the substances without dissolving the entire sample.

As an example of this procedure, 0.5 g. of a mixture containing 10% of glycine and 90% of *dl*-alanine was boiled with three successive 32-cc. portions of ethyl alcohol. The temperature elevations, relative to the boiling point of alcohol, were 0.027, 0.021 and 0.021°, showing that the amount of impurity was sufficient to produce a measurable concentration in 32 cc. of solvent, and that it was extracted almost entirely by the first portion. An estimate from the data indicates 5% of glycine. This could be made more reliable by using a larger sample.

The third test for purity depends upon the difference in concentration of the impurities produced by varying the amount of solid added to a single portion of the solvent. The substance is added to the boiling liquid in small weighed portions, and the boiling point is recorded as a function of the amount of material. This procedure is roughly quantitative, since the change of boiling point between successive additions is determined by the amount of material extracted from a weighed quantity of solid.

Two mixtures of *dl*-alanine and *dl*-valine, containing, respectively, 10 and 20% of the latter, were tested by this procedure. Each of the weighed portions contained more *dl*-alanine than was required to saturate the solution. The volume of boiling alcohol was 32 cc. The results are summarized in Table IV, in which the first row shows the total weight added, and the second and third rows give the temperatures with the 10 and 20% mixtures.

TABLE IV

TEST FOR PURITY APPLIED TO MIXTURES OF *dl*-ALANINE AND *dl*-VALINE

Weight added, g.	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70
Elevation (10% valine)	.019		.027		.032		.035	.038	.042	.045
Elevation (20% valine)	.024	.029	.035	.038	.041	.045				

The presence of impurity, greater in quantity in the second sample than in the first, is demonstrated by the fact that a given weight of the 20% mixture produces a larger elevation of the boiling point than the corresponding amount of the 10% mixture. The quantitative interpretation depends principally on an accurate knowledge of the boiling point of a solution saturated with *dl*-alanine. If the temperature is plotted as a function of the total weight added, and a straight line is drawn through the points to intersect the temperature axis at the value 0.0265, taken from Table I, for *dl*-alanine, the slope of the line gives a measure of the concentration of impurity built up from unit weight of the solid. If the volume is known, this may be converted to moles per unit weight. Since, in the above tests, the molecular weight of the impurity is known, it may be expressed as weight per cent. The results for the above mixtures were

9.8 and 19.0%. In the general case, of course, results are expressed as moles per unit weight.

The writer is indebted to Professor James B. Conant, who suggested carrying out the above tests.

Summary

The measurement of the boiling points of saturated solutions is suggested as an aid in identifying and testing the purity of compounds to which the familiar melting point procedure is not applicable because of decomposition. Examples of the method are given.

Negative results in the tests for impurities are not necessarily conclusive. Any of the procedures is subject to essentially the same limitations as the analogous test by the melting point method.

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NOTES

A Diaphragm Valve.—In connection with some experiments in which a greaseless device for regulating gas flows was needed, the diaphragm valve described in this note was developed. It consists of an aluminum diaphragm A, about 0.3 mm. in thickness, resting on the flange of a glass cup B, which has an outlet tube C, and a capillary inlet tube D, as shown in Fig. 1. The upper end of tube D and the flange are ground flat with fine carborundum powder. Around the edge of the diaphragm and the flange of the cup is a rubber gasket, E. These parts are held together by a brass frame F. The position of the diaphragm is adjusted by a differential screw G. The lower surface of the diaphragm is roughened with very fine emery paper, so as to have better contact with the ground end of the capillary tube for the regulation of the low flows.

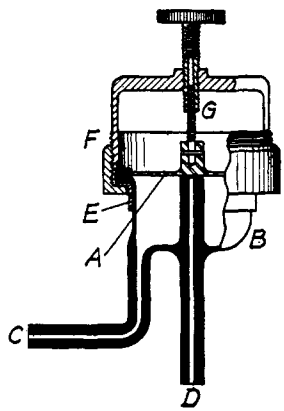

Fig. 1.

In cases where the gas used is likely to react with or corrode aluminum, a thin piece of mica is cemented with Duco Household Cement across the entire lower surface of the aluminum diaphragm. The mica surfaces should first be roughened with fine emery paper.

By varying the diameter of the inlet and outlet tubes, and the size and thickness of the diaphragm, this type of valve can be adapted to a wide range of gas flows. In connection with some experiments in this Laboratory, this type of valve was used successfully to regulate gas flows ranging from a few tenths of a cubic centimeter to several liters of gas per minute.