

walled Pyrex tubing. In connection with fragility, it may be added that no "setting" of the thermometer for different temperatures is required, for its zero reading for uniform temperature automatically adjusts itself near the bottom of the stem, thus leaving the major portion of the scale available throughout its whole length.

In certain respects, therefore, it would appear that this type of differential thermometer has advantages over the Walferdin metastatic type as elaborated by Beckmann; and the question arises as to whether such other factors as are peculiar to a given application are favorable to its use. In studying its application in ebullioscopy, for example, as outlined in the article following, one finds that the important disturbing factor, peculiar to ebullioscopy in its incidence, of barometric fluctuation does not measurably affect the readings of the newer type, while such pressure fluctuations are among the chief outstanding sources of error when the metastatic type is used. Another application in a different field may be described in the near future.

Summary.

A very simple form of differential thermometer has been described whose indications depend on the registration by a column of manometric liquid in a U-tube of differences of vapor pressure of this liquid in opposite limbs. A table is given for use when the filling liquid is water; and mention is made of certain advantages of this type over the metastatic type of thermometer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY.]

THE APPLICATION OF A DIFFERENTIAL THERMOMETER IN EBULLIOSCOPY.

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For purposes of molecular weight determination of dissolved substances, the ebullioscopic procedure has certain advantages over the method of cryoscopy. Since, to use the latter, one must for convenience employ solvents whose freezing points lie at easily accessible temperatures, it comes about that water, benzene and acetic acid have been commonly preferred. To obtain satisfactory values for the molecular weight of a solute, it is best to choose a solvent so like it chemically that compound formation shall be at a minimum. To be so closely restricted in the choice of solvents is therefore a disadvantage. Boiling temperatures are, in general, preferable to freezing temperatures as unfavorable to the formation of exothermic compounds. A majority of organic compounds boil normally below 300°. If, as is true, the solvent should differ by at least 150 degrees in boiling point from the solute in order that the volatility of the latter may

not vitiate the results, then, for most practical purposes, the use is indicated of such solvents as boil rather below 100° than above it, and these solvents are in point of fact those most commonly used. The low solubility of certain solutes at the freezing points of the available solvents is a factor against cryoscopy. On the other hand, the precision attainable in cryoscopy has, in the past, been considerably greater than that realized in ebullioscopy, even with apparatus fortified against error by the superimposition of a multiplicity of paraphernalia.

For these and other reasons, a very great deal of work has been carried out by very many investigators with a view to improving the ebullioscopic technique. One may but mention the two dozen papers by Beckmann and his collaborators;¹ and the work of Hite,² Orndorff and Cameron,³ Jones,⁴ Ross Innes,⁵ Meyer and Desamari,⁶ Drucker,⁷ Sakurai,⁸ Landsberger,⁹ Walker and Lumsden,¹⁰ McCoy,¹¹ Smits,¹² Rijber,¹³ Ludlam,¹⁴ Erdmann and Unruh,¹⁵ Lehner,¹⁶ and Turner.¹⁷ Even a single publication by one writer, Hite, reports the trial of over 100 different forms of apparatus. In all these, and many other investigations, the bulb of a mercurial thermometer has been submerged beneath the surface of the boiling solution, and much of the work has been directed to the avoidance of the consequent irregular superheating. In our opinion, the two most successful improvements made since 1892 have originated in this country, the introduction, namely, by Bigelow¹⁸ of electric heating, and by Cottrell¹⁹ of a "lift-pump" which pumps the solution over the bulb of the thermometer, which no

¹ References to the numerous papers of Beckmann and his collaborators may be found in the work of Jellinek, "Lehrbuch der Physikalischen Chemie," 2, 783 *et seq.*, (1915); and also in Staehler's "Handbuch der Arbeitsmethoden in der Anorg. Chemie," 3, 3 (1913).

² Hite, *Am. Chem. J.*, 17, 514 (1895).

³ Orndorff and Cameron, *ibid.*, 17, 517 (1895).

⁴ Jones, "The Freezing-Point, Boiling-Point and Conductivity Methods," Chemical Publishing Co., Easton, Pa., 1912.

⁵ Ross Innes, *J. Chem. Soc.*, 81, 682 (1902).

⁶ Meyer and Desamari, *Ber.*, 42, 797 (1909).

⁷ Drucker, *Z. physik. Chem.*, 74, 612 (1910).

⁸ Sakurai, *J. Chem. Soc.*, 61, 989 (1892).

⁹ Landsberger, *Ber.*, 31, 461 (1898).

¹⁰ Walker and Lumsden, *J. Chem. Soc.*, 73, 502 (1898).

¹¹ McCoy, *Am. Chem. J.*, 23, 502 (1900).

¹² Smits, *Proc. Acad. Sci. Amsterdam*, 3, 86 (1900).

¹³ Rijber, *Ber.*, 34, 1060 (1901).

¹⁴ Ludlam, *J. Chem. Soc.*, 81, 1193 (1902).

¹⁵ Erdmann and Unruh, *Z. anorg. Chem.*, 32, 413 (1902).

¹⁶ Lehner, *Ber.*, 36, 1104 (1903).

¹⁷ Turner, *J. Chem. Soc.*, 97, 1104 (1910).

¹⁸ Bigelow, *Am. Chem. J.*, 22, 280 (1899).

¹⁹ Cottrell, *THIS JOURNAL*, 41, 721 (1919).

longer need be submerged in the solution, but is located above the solution in the vapor phase. When Cottrell's device is employed, there remain outstanding, for non-volatile solutes, the errors inherent in the use of the Beckmann type of thermometer, the error due to uncertainty as to actual concentration of solute, and the very troublesome error due to change of boiling point caused by change of barometric pressure during the observations.²⁰ This last may, in part at least, be overcome by the employment of somewhat cumbersome "manostats,"²¹ by especially constructed aneroid barometers,²² or by the use of a second, duplicate, apparatus²³ operated simultaneously and containing another Beckmann thermometer immersed in the pure boiling solvent.

In 1910, Menzies²⁴ had described a simple apparatus, independent of barometric change, which, when properly constructed, gives molecular weights of solutes in solvents at their boiling points by direct measurement of lowering of vapor pressure, without the use of any thermometer. Continuing this effort at simplification, he found that the differential thermometer of the preceding article,²⁵ when applied to ebullioscopy with the Beckmann type of apparatus, served only to render more glaring the inevitable irregularities inseparable from that method of procedure. When however, Cottrell's paper appeared in 1919, opportunity was taken to work out the simplest possible apparatus and technique which should free ebullioscopy from all its most serious drawbacks.

The Apparatus.—The diagram, Fig. 1, shows a boiling tube, whose narrowed upper portion itself serves as condenser tube. A glass cylinder, open above and below and of diameter slightly less than the boiling tube, is located concentrically within the latter, and confers the advantages of a double jacket. Within this is supported the differential thermometer, on the lower bulb of which hangs the pump, loosely, as a hat on a peg.²⁶ The absence of rigid connection diminishes possibility of breakage, besides adding flexibility, literal and metaphorical.²⁷ The boiling tube is heated

²⁰ Cf. Meyer and Desamari, *Ber.*, **42**, 2809 (1909), who were misled by this error into obtaining only one-half the true value for the molecular weight of tribromo-resoquinone, and so to assigning to it an inaccurate formula. The practical text-books often recommend postponing ebullioscopy to a day when the barometer is steady.

²¹ Cf. Smits, *Z. physik. Chem.*, **39**, 415 (1902); Burt, *J. Chem. Soc.*, **85**, 339 (1904); Drucker, *Ref. 7.*; Beckmann, *Z. physik. Chem.*, **79**, 565 (1912); etc.

²² Meyer and Desamari, *Ber.*, **42**, 797 (1909).

²³ Cf. Beckmann, *Ref. 1.*; Washburn and Read, *THIS JOURNAL*, **41**, 729 (1919); Sluiter, *Proc. Acad. Sci. Amsterdam*, **17**, 1043 (1914).

²⁴ Menzies, *THIS JOURNAL*, **32**, 1615 (1910).

²⁵ Menzies, *ibid.*, **43**, 2309 (1921).

²⁶ The complete apparatus, with both boiling tube and water-filled thermometer of Pyrex glass, is furnished by Messrs Eimer and Amend, 205 Third Avenue, New York, N. Y.

²⁷ We have on no occasion yet broken any part of the apparatus.

by direct contact with the low flame of a common Bunsen burner, protected by the customary draughtshield of metal, best in an inverted position. When boiling begins, portions of the liquid in the bulb are carried by the vapor in fragments up the pump and discharged to form a thin film over the lower bulb of the thermometer, which thus attains the temperature at which this liquid, or solution, is in equilibrium with the vapor. The upper bulb acquires the temperature of the pure boiling solvent. The thermometer registers the difference between these two temperatures. Equilibrium is reached so rapidly, except in cases of slow solubility, that fresh additions of solute may be made as fast as they can be weighed out. Contrary to all ebullioscopic tradition, the apparatus will give good results in a room that is not free from draughts. Unlike every other ebullioscopic apparatus, this form is entirely free from all corks, ground glass joints or stoppers.

The sources of error, including that due to barometric change, eliminated by the use of the new type of differential thermometer have been briefly referred to in the preceding article. The advantages gained by removing the lower bulb from immersion in the boiling liquid have been well explained by Cottrell,¹⁹ and confirmed by Washburn and Read²³ and by Spencer,²⁸ to whose interesting papers the reader is referred for consideration of many matters that cannot be dealt with here. To their remarks may, perhaps, be added that the error due to change of bubble size caused by the marked change of surface tension on addition of certain solutes; that due to change of head of liquid above the thermometer bulb; and the errors caused by fractionation of the solvent and by slow removal by distillation of somewhat volatile solutes, incident to the Sakurai-Landsberger method, are also alike avoided. The chief residual source of error lies in the uncertainty as to the true concentration of the boiling solution as deduced, not by subsequent analysis, but simply from the weights of solvent and solute used. Part of the solvent is absent from the solution in the form of condensate on the walls, and part is absent in the form of vapor. This source of error, ever present in the Beckmann type of apparatus, has often failed of due consideration. To minimize it, we constrict the boiling tube above the lower bulb, mark cc. graduations on the cylindrical neck so developed, and read off the actual working volume of the solvent an instant after ebullition has been caused to cease, while the tube is still wet with condensate and filled with vapor.

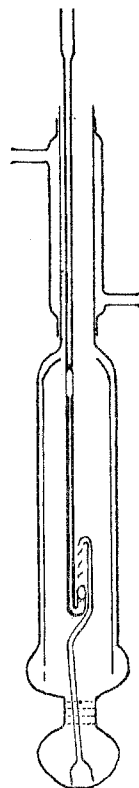


Fig. 1.

²⁸ Spencer, *THIS JOURNAL*, 43, 301 (1921).

A simple water-filled differential thermometer suffices for the range of temperature from the boiling point of water to that of ether, thus embracing the use of such solvents as carbon disulfide, acetone, chloroform, methyl, ethyl and propyl alcohols, methyl acetate and iodide, ethyl formate, acetate, bromide and iodide; carbon tetrachloride, and benzene, and allowing a choice adequate for ordinary purposes. No "setting" of the thermometer is required for the use of different liquids.

Method of Procedure.—The boiling tube is clamped in a vertical position by means of a large single clamp located just under the upper side-tube of the condenser jacket. Beneath it is clamped a Bunsen burner at such a height that when the top of its tube is in position about 1 cm. below the bottom of the boiling tube, the base of the burner is a few centimeters above the sole of the supporting ring-stand. The boiling tube is filled with solvent to the level of the lower graduations on the constricted neck, the condenser water turned on, and the flame lighted and suitably adjusted by means of the customary screw-clip. The boiling point of the solvent is now taken to the nearest tenth of a degree by means of a good ordinary thermometer, in which operation the avoidance of exposed thread is usually easy. While the thermometer used for this purpose is reaching thermal equilibrium, the barometer may conveniently be read, and information thus obtained as to the purity of the solvent. The actual working volume of the solvent is next found by lowering the burner (not its gas supply) so that it is ready to be swung clear, quickly swinging it aside, and causing instant cessation of bubble formation by immersing the bottom of the boiling tube in cold water raised by hand from below in a small beaker. The reading of volume—best against a white card in the background—should be made immediately ebullition is caused to cease, before the access of solvent that drains from the walls. The burner is then replaced in position. For purposes of molecular-weight determination, one may employ as ebullioscopic constant the boiling-point rise in degree produced by one mole of solute per 100 cc. of solvent at its boiling point (K_2 in Table I p. 2320). The mercurial thermometer is now withdrawn, the pump introduced and lowered to the bottom of the boiling tube by means of a deep hook on the end of a wire, and the differential thermometer inserted, engaged on the pump, and clamped in suitable position by the end of its handle which is made wide so as to be more easily gripped by the clamp. While temperature equilibrium is being reached, which may occupy 15 minutes, it is convenient to prepare pastilles of the solute and to make the first weighing of the bottle containing them.

In making readings of the differential thermometer, the error of parallax may be simply avoided by fixing a white card, of the size of a postal card, with bold graduations in centimeters across it corresponding to those on the thermometer, at a suitable distance behind the latter at the same level,

and placing the eye so that the readings on card and thermometer correspond. The zero reading is given by the difference between the readings on the stem and on the lower bulb, and its value obviously serves as a most useful index of the purity of the solvent. Unsteadiness of reading is caused by too slow boiling.

A pastille of solute is now dropped, from forceps, down the condenser. If it be easy of solution, the reading will at once rise and become constant the moment solution is complete. The ebullioscopic rise is obtained by subtraction of the zero reading from the difference of level now observed. This is later translated into temperature at leisure by the help of a conversion factor extracted from such a table as that given in another communication.²⁵ It is to be noted that, for fine work, in order to obtain the true conversion factor, one must use as argument the average temperature of the two ends of the thermometer, which is higher than the boiling point previously found by the mercurial thermometer by an increment of temperature corresponding to half the observed ebullioscopic rise. If half the ebullioscopic rise multiplied by the factor selected by a first inspection does not, when added to the boiling point of the solvent, yield a temperature that agrees with the chosen factor, then the factor may be reselected accordingly.

Case of Volatile Solutes.—It is generally agreed²⁹ that, for purposes of straightforward molecular weight determination, the boiling point of an ebullioscopic solvent should lie at least 150° below that of the solute. For this reason, benzil (b. p. 347°) has found favor as a standardizing solute because it may be assumed to be virtually absent from the vapors escaping from its solution in the common ebullioscopic solvents. If, however, the solute be as volatile as naphthalene (b. p. 218°) in boiling carbon tetrachloride or benzene, then one would anticipate that the mixed vapors, on partial condensation, would tend to yield a liquid of the concentration with which they are in equilibrium, namely the concentration of the solution from which they have just escaped. The upper bulb of the differential thermometer might thus be expected to acquire precisely the same temperature as the lower bulb; and, if precaution be taken to minimize condensation on the thermometer, this condition can indeed be approximated. The gross composition of the vapor phase, however, is close to that of the pure solvent, so that if this vapor is completely condensed and caused to lave the upper portion of the differential thermometer, the temperature it acquires in contact with the surrounding vapor is very close to the boiling point of the pure solvent, which is the temperature here desired. In order to provide an adequate laving of this kind, a very simple plan is to embrace the handle of the thermometer, at a point a few centimeters above the upper bulb, with a pair of wires of

²⁹ Cf. Staehler, Ref. 1.

perhaps 24 S. W. G. twisted together where they meet on opposite sides of the handle, and to direct the two twisted tags so formed upwards in such a way that, by resting against the inner walls of the condenser tube, they may uniformly divert a modicum of the condensate on to themselves and thence to the thermometer. The diagram, Fig. 2, shows these wires, which are prevented from slipping either up or down by reason of the slight constriction in the handle where they are applied. In practice

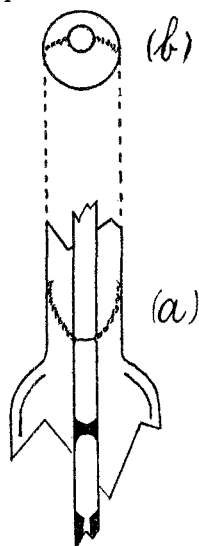


Fig. 2.

it is useful to employ these wires in all cases, not only because of possible prejudicial volatility of the solute, but to meet the contingency of spattering of the upper portion of the thermometer by minute droplets from a frothing solution. The wires may also very conveniently be bent so that the handle of the thermometer is stationed sufficiently eccentrically within the condenser tube as to allow a very clear passage for the introduction of pastilles. This is indicated in Fig. 2 (b).

Collected Useful Data.—In Table I are collected, from diverse sources, certain useful data for a few of the commoner solvents: their normal boiling points; the barometric change, dp/dt , in mm. of mercury that produces a change of 1° in the boiling point; the density, D , of the liquid at the boiling point; its change, dD/dt , per degree of temperature; the ebullioscopic constant, K_1 , for one mole of solute in 100 g. of solvent; the ebullioscopic constant, K_2 , for one mole of solute in 100 cc. of solvent at its boiling point.

TABLE I.
CONSTANTS USEFUL IN EBULLIOSCOPY.

Solvent.	B. p.	dp/dt .	D.	dD/dt .	K_1 .	K_2 .
Acetone.....	57.0	26.4	0.7522	0.0011	17.2	22.9
Benzene.....	80.1	23.4	0.8149	0.0010	26.1	32.0
Carbon disulfide.....	46.3	24.7	1.2223	0.0016	23.7	19.4
Carbon tetrachloride..	76.8	23.3	1.4801	0.0021	48.0	32.4
Chloroform.....	61.2	25.2	1.4101	0.0018	39.0	27.7
Ethyl acetate.....	77.2	25.1	0.8302	0.0010	27.9	33.6
Ethyl alcohol.....	78.4	30.3	0.7389	0.0011	11.7	15.8
Ethyl ether.....	34.6	26.9	0.6968	0.0011	21.6	31.1
Methyl acetate.....	57.1	26.8	0.8802	0.0014	20.6	23.4
Methyl alcohol.....	64.7	29.6	0.7468	0.0010	8.8	11.8

The values for K_1 are taken chiefly from Staehler's *Handbuch*¹ as an impartial source. We doubt the accuracy of some of these values. It must be remembered that the values determined and adopted by even a single investigator such as Beckmann, for example, have varied from time to time. The matter will be reverted to on another occasion. The change

of the ebullioscopic constants with barometric pressure is of the order of 0.3% per 10 mm. near 760 mm.

Examples of Results.—We shall here limit ourselves to a very few typical cases to illustrate merely the consistency of the results obtainable by the use of this apparatus, and their general agreement with the results of others. For a later redetermination of certain ebullioscopic constants, especial purification of materials and other precautions will be required; but for the present purpose the ordinary materials of the laboratory supply-room have proved sufficient. In order to conform to the practice of Beckmann and most others, we have employed in computing our results the well-known simple, if inadequate, relationship $K_1 = \text{temp. rise} \times \text{mol. wt. of solute} \times \text{wt. of solvent} \div 100 \times \text{wt. of solute}$.

(a). **Benzil in Benzene.**—Values of the ebullioscopic constant K_1 used by Beckmann³⁰ were 26.7 (1890), 26.1 (1895), 24.2 (1905), 25.7 (1907, 1914). Drucker⁷ found 26.7, Innes⁸ 24.1, etc. Beckmann's present accepted value, 25.7, is the mean of two sets of each three measurements with benzil in benzene, as follows: (1) rise, 0.180°, 0.354°, 0.568°, corresponding respectively to $K_1 = 25.7, 25.6, 25.2$: (2) rise, 0.205°, 0.450°, 0.688°, yielding $K_1 = 25.6, 26.2, 25.7$. We made two sets of

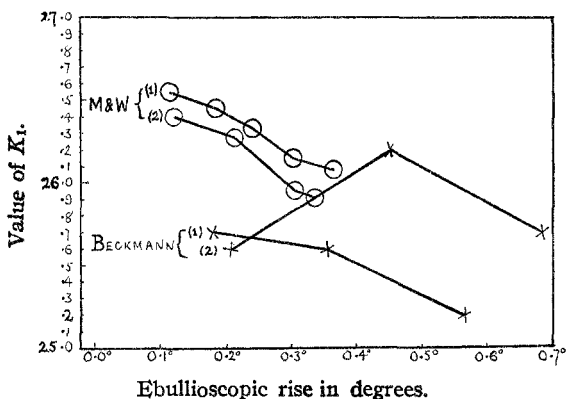


Fig. 3.

measurements, on different days, as follows: (1) rise, 0.1142°, 0.1820°, 0.2440°, 0.3016°, 0.3661°, corresponding respectively to $K_1 = 26.6, 26.5, 26.3, 26.2, 26.1$: (2) rise, 0.1218°, 0.2126°, 0.3052°, 0.3355°, yielding $K_1 = 26.4, 26.3, 26.0, 25.9$. The fourth significant figure has some meaning for our higher readings. From these data, which are shown plotted in Fig. 3, it would appear that the values in each of our sets are rather more self-consistent than those of Beckmann, although obtained with much simpler apparatus; and that 0.1 mm. on the scale of the differential thermometer may be estimated successfully. Our two sets differ from each other, on the average by 0.6%, an error that would be caused by an error of 0.2 cc. in reading 30.0 cc., the approximate volume of benzene employed. As we have learned from many other results, this is the largest value to which this error ever attains; more often the error from this cause is 0.1 or 0.0 cc., averaging well under 0.5% in the result. Aside from possible systematic error, it is the chief single source of error entering into our determi-

³⁰ Cf. Beckmann, *Z. physik. Chem.*, **88**, 23 (1914); **58**, 555 (1907).

nations. The details of the observations of Set 1 follow, serving to illustrate the use of conversion factor and to indicate the time consumed.

TABLE II.
OBSERVATIONS OF SET 1.

Volume of benzene at the boiling point, 31.6 cc. Boiling temperature, corrected, 79.7°. Barometric reading, corrected, 755.2 mm. Solute, benzil, 210.1.

Obs. No.	Time. h. m.	Wt. of benzil. G.	Diff. therm. reading. Mm.	Conversion factor.	Rise. °C.	K_1 .
0	1.26	0.0	10.5 (zero)	0.0	...
1	1.32	0.2326	22.8 (above zero)	0.005011	0.1142	26.56
2	1.36	0.3726	36.4 (above zero)	0.005005	0.1820	26.46
3	1.41	0.5011	48.8 (above zero)	0.004999	0.2440	26.33
4	1.46	0.6238	60.4 (above zero)	0.004994	0.3016	26.16
5	1.52	0.7595	73.4 (above zero)	0.004988	0.3661	26.08

(b). **Anthracene in Chloroform.**—Benzol, alcohol and chloroform are perhaps the three best-studied ebullioscopic solvents, and we chose this example because, in particular, the Sakurai-Landsberger method has been critically studied by Turner¹⁷ who used it to redetermine the constant for chloroform. Of Turner's solutes, anthracene was most readily available to us in reasonably pure form.²¹ Because of its ease of decomposition, we do not regard chloroform as so suitable an ebullioscopic solvent as carbon tetrachloride, which covers a similar field of solutes.

In the two sets of experiments for which he gives data, Turner obtained the following results: (1) rise, 0.646°, 0.527°, 0.436°, 0.363°, corresponding respectively to $K_1 = 40.5, 40.4, 40.5, 40.3$; (2) rise, 0.559°, 0.455°, 0.376°, yielding $K_1 = 38.3, 38.0, 38.5$. In two sets of experiments we obtained, (1) rise, 0.2672°, 0.3981°, 0.5045°, 0.6213°, yielding $K_1 = 39.58, 39.42, 39.09, 38.66$; (2) rise, 0.3166°, 0.4042°, 0.4792°, 0.5565°, 0.6515°, yielding $K_1 = 39.90, 39.25, 38.56, 38.59, 38.09$. Turner averages his two sets at 40.4 and 38.3 respectively,—results discrepant by 5.4%, or 2.7% from their mean. Our results, when plotted, diverge from a straight line drawn through them by 0.56% on the average. It may be said that the impure chloroform used does not show our method to advantage. The unsatisfactory character of chloroform as an ebullioscopic solvent is further indicated by the rather wide variation of the values for the constant employed by Beckmann from time to time, ranging from 35.9 (1895) to 39.0 (1908).

(c). **Naphthalene in Ether and in Carbon Tetrachloride.**—It is necessary to add these further examples to illustrate the use of an appreciably volatile solute. In a single run in which we added 8 successive quantities of naphthalene to ether of normal boiling point, 34.1°, with consequent elevations of temperature ranging from 0.27° to 2.04°, we obtained values for K_1 of 21.47, 21.43, 21.11, 20.68, 20.39, 20.31, 19.82, 19.77, results which diverge on the average by about 0.33% from a straight line drawn through their plot. If, however, the twisted wires described above were omitted in this case, the results obtained were low and unsatisfactory. It should, perhaps, be added that one does not expect strict rectilinearity in the graph obtained as above; and that, in the case of ether, which has a considerable vapor pressure at the temperature of the condenser, a small correction, under 1% per hour, might be made for progressive loss of solvent by diffusion into the air. A straight line, however, is undeniably a smooth curve, for purposes of reference.

Carbon tetrachloride boils only 141° below naphthalene, thus falling within the forbidden range of 150° referred to above. To secure more copious lavage of the upper

²¹ Through the courtesy of the Chemical Department of the Barrett Co.

portion of the thermometer by the condensate in this case, we employed twisted double wires instead of single wires in constructing the drainage mechanism, and opened the ends in contact with the condenser tube so as to form forks, thus withdrawing the condensate from the walls at four points each served by a pair of wires twisted together. This had the effect of raising the zero reading by a few millimeters. Using a solvent of normal boiling point, 76.2° , we obtained, from elevations of 0.1888° , 0.2822° and 0.3990° , values for K_1 of 47.23, 47.89, and 48.46. For computation merely the simple relationship mentioned above was utilized, without correction for volatility of the naphthalene. Benzene as solvent for naphthalene gave results of similar quality, thus demonstrating that usable results may still be obtained even in these somewhat adverse cases.

Summary.

A simple apparatus for ebullioscopy has been described and illustrated in which is employed a new type of differential thermometer. Most of the sources of experimental error that have influenced the very many earlier forms of ebullioscopic apparatus have here been avoided or so minimized that results consistent to within 0.5% are readily obtained.

PRINCETON, NEW JERSEY.

[CONTRIBUTION FROM THE SYNTHETIC PRODUCTS LABORATORY, DRUG DIVISION, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

DISTRIBUTION OF CERTAIN DRUGS BETWEEN IMMISCIBLE SOLVENTS.

By W. O. EMERY AND C. D. WRIGHT.

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Of the many medicinal preparations examined by this laboratory, those containing analgesic and antipyretic agents have been fruitful fields for various lines of investigation. In the isolation of these substances preliminary to their quantitative determination, recourse was frequently had to the use of immiscible solvents, such as aqueous solutions and chloroform, the latter preferably on account of its physical properties and consequent ease of separation and recovery. During the earlier stages of the work, the relative volumes of the solvents, as well as the number of extractions deemed necessary or expedient for complete isolation of the substance sought, were governed largely by empirical considerations, care, being taken, however, that any error of commission should involve an excess rather than a deficiency in organic solvent. In operations with caffeine and antipyrine, for example, substances possessing about equal solubility in chloroform but differing widely in this respect toward water (1 g. of caffeine is soluble in 46 mils, 1 g. of antipyrine on the other hand in less than 1 mil of water), it was assumed that, given like volumes, antipyrine would require a greater number of extractions than caffeine. From preliminary experiments on controls, carried out in the usual way with the