BOILING-POINT AND MOLECULAR WEIGHT DETERMINATIONS WITH A NEW TYPE OF APPARATUS

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I

Introduction

The object of this research was to determine the reliability of boiling-point and molecular weight determinations with a new type of apparatus which was designed by Dr. J. H. Robertson of the Department of Chemistry of the University of Tennessee and presented by title to the American Chemical Society at its fall meeting in Pittsburgh in 1926. Classes in physical chemistry at the University of Tennessee have used the apparatus for molecular weight determinations regularly for five years and they have obtained satisfactory results but no systematic series of experiments which covered adequately the merits and limitations of the apparatus have heretofore been made. Certain difficulties to be overcome in any boiling-point method, a brief survey of the methods of overcoming these difficulties, and a description of the apparatus used in the present investigation are quoted here from the original paper referred to above.

"The importance of reliable methods for the determination of the boiling-points of pure liquids and of solutions has long been recognized, and many devices have been proposed for the purpose of overcoming certain theoretical or experimental difficulties in such measurements, their making the methods more accurate or more convenient. A discussion of the chief sources of error in boiling-point measurements has been given by Cottrell.[1]

"Especially difficult has been the problem of accurately determining the boiling-points of solutions, such as are required in molecular weight determinations. As a result of the rather large sources of error

1. Cottrell, J. Am. Chem. Soc., 41, 721, (1919).

in these measurements and of the consequent uncertainty of the results obtained, the organic chemist has been inclined to adopt cryoscopic methods almost to the exclusion of ebullioscopic methods for determining the molecular weights of non-volatile substances, whereas in many instances the latter would be distinctly to his advantage.

"Until the introduction of the 'percolator' principle of the measurements of boiling-points of solutions,[1] the most serious obstacle lay in the difficulty of obtaining equilibrium between the liquid and vapor phases, although the errors of super-heating have been minimized in various ways. In the method of Beckmann

(Beckmann, Z., Physik. Chem., 3,603 (1889); 8,223 (1891); 44,169 (1903))

and its modifications, super-heating is practically avoided by the use of glass beads or fragments of other inert materials placed in the boiling liquid. In the method of Sakurai[2] and its congeners, the objective is attained by causing vapor from the solvent to pass into the solution. The result is more conveniently achieved by the method of electrical heating, first introduced by Bigelow.[3]

"It is important to note, however, that even if the errors of super-heating are entirely avoided, the results obtained by any method in which the thermometer is immersed in the liquid will represent a mean of the graduation temperature from the surface of the boiling liquid to the depth to which the thermometer is immersed, rather than the true boiling temperature."[4]

Through the adaptations of the percolator principle to the measurements of boiling points as introduced by Cottrell[4] a closer

1. Ibid, 41, 721, (1919).
2. Sakurai, J. Chem. Soc., 61, 989 (1892).
3. Bigelow, Am. Chem. J., 19, 581, (1897).
4. Cottrell, loc. cit.

approach to ideal conditions for the measurement of boiling-points of solutions is achieved than by any other methods heretofore available. To obtain equilibrium between solution and vapor a mixture of the solution and its vapor is thrown against the thermometer suspended above the boiling liquid by means of a pump operating on the principle of the coffee percolator. The intermittent nature of the process necessitates rapid percolation to obtain a constant reading of the thermometer. The adjustment of the apparatus to give rapid and uniform percolation may be a very simple matter, but it is not always so. This is especially important because of the existence of hot air currents from the heating source, and frequently of cold drafts from windows in the room. A convenient design of apparatus of this type is that of Washburn and Read[1].

"An objection inherent in this form of apparatus is that the composition of the solution is never uniform, owing to the fact that the condensed vapors are run back into it. There is a possibility that the composition of the solution analyzed may not represent precisely the composition of the solution in equilibrium with the vapor surrounding the thermometer."

Apparatus

"As a result of attempts to overcome these difficulties, the apparatus herein described was devised. The construction of the apparatus is shown in Figures 1 and 2, and its operation is as follows:

"The pure solvent is placed in the outer tube "A" and the solution (or solvent), the boiling-point of which is to be determined, is placed in the inner tube "C" sealed into the outer tube at the top. The inlet

1. Washburn and Read, J. Am. Chem. Soc., 41, 729, (1919).

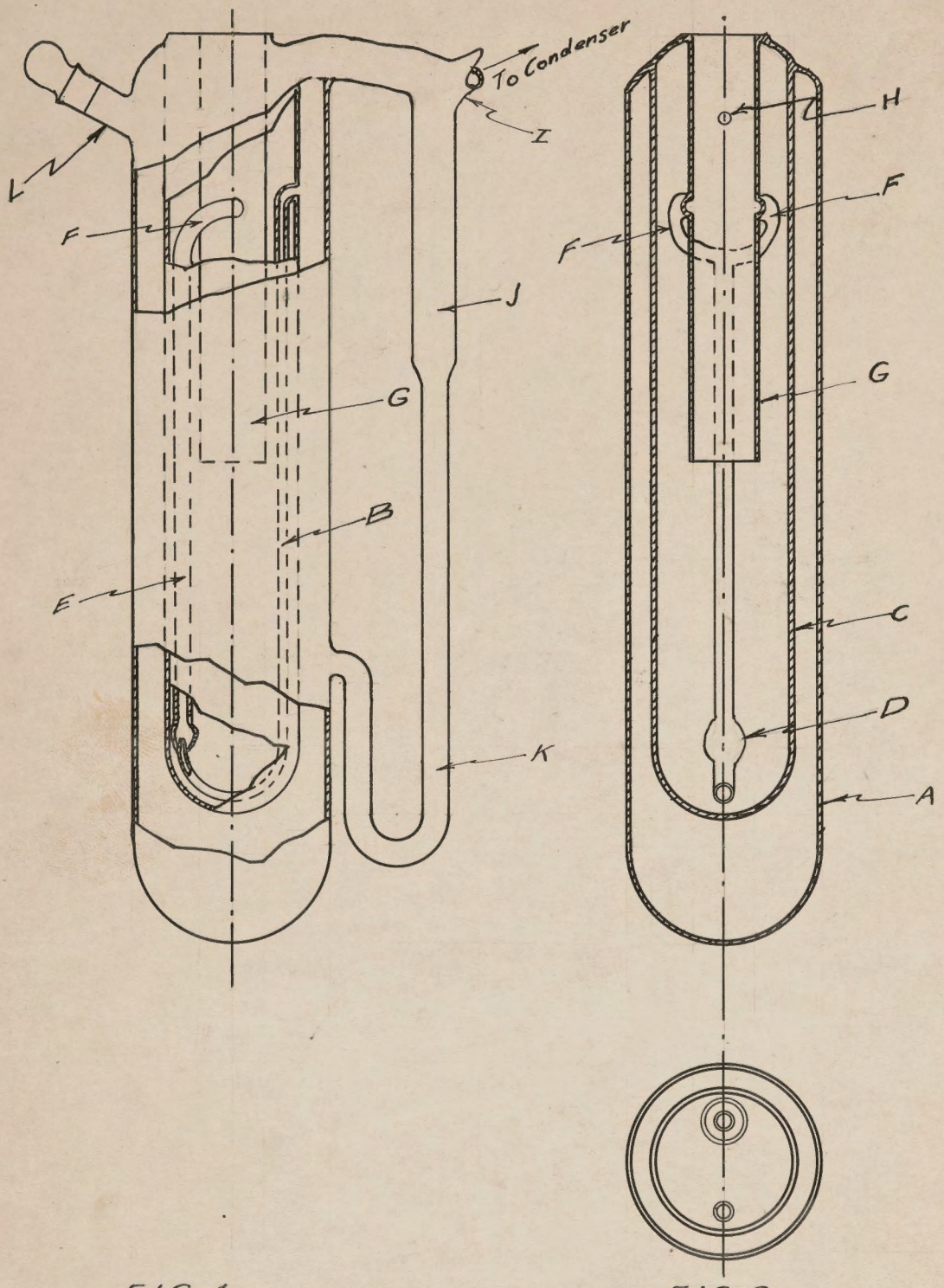

FIG. 1 FIG. 2

BOILING POINT APPARATUS

"L" is closed and the liquid in "A" boiled. Vapor passes around "C" heating the liquid it contains, and out through the side tube "KJI" to the condenser. As the vapor is condensed, it runs back into the tube "IJK" forming a seal and accumulates until its back pressure reaches a value such that the vapor in "A" passes through the tube "B" into the liquid in the vessel "C". In practice it may be desirable to pour a little of the cold solvent through the condenser into the tube "IJK" to form the seal after the liquid in the vessel "C" has been heated to near its boiling-point. The seal should not be made before this, because it would result in excessive condensation of vapor in the solution in "C". The vapor now passes into the "vapor-injector" "D" and pumps the solution (or solvent) up the tube "E" into the tubes "FF" which convey the mixture of vapor and liquid through opposite sides of the cylinder "G" surrounding the thermometer. The tubes "FF" project about 1 mm. into the cylinder. The mixture of vapor and liquid is thrown uniformly against the thermometer. A small hole in the cylinder at the point "H" permits part of the vapor to escape into the outlet tube "I", which leads to the condenser. From the condenser the liquid flows down the tube "I" and back through "JK" into the outer jacket "A". The substance whose molecular weight is to be determined is inserted in the cylinder "C".

II

Recent studies of boiling point methods

In the studies of colligative properties of solutions, the most reliable determination is usually the freezing point. The boiling-point is the property next in favir but, because of the danger of super-heating, and the relative small molecular elevation of the boiling-point by solutes, the use of the boiling-point method has been limited. The data that are available do not cover the very concentrated solutions or the very dilute ones or even show the changes over the entire range of moderate concentration.

Recent experiments on the various types of boiling-point apparatus by W. D. Bancroft and Herbert Davis[1] showed considerable difficulty with super-heating. The first apparatus used consisted of a Dewar flask of about 250 cc. capacity fitted with a rubber stopper with five holes. The Beckman thermometer, the reflux condenser tube, a small stoppered tube for the introduction of the solute, and two mercury-filled glass tubes sealed to the platinum heating spiral and the supporting were passed through these. Just above the spiral there was a pyrex tube with vigreux tips to break the bubbles as they rose and to pump solution around the bulb of the thermometer and out over the tube. The temperature readings in the apparatus were found to be influenced by the volume of the liquid and the depth to which the thermometer was inserted. It was also found that there was considerable super-heating and that the amount of super-heating decreased as the amount of solute was increased. It was found that this question of super-heating is the one that requires more attention than any other in the determination of boiling-points of aqueous

1. Bancroft, S. D. and Davis, H. L., J. of Physical Chem. 33, 591 (1929).

solutions. Super-heating was found to rise from two principle causes. The first of these was the inherent reluctance of the liquid in contact with the heating surface to form bubbles of vapor. A second cause is the fact that bubbles formed 3.5 cm. under the surface of water will be about .1° hotter than if formed at the surface. The use of large roughened surfaces eliminate the first to a large degree.

The Washburn-Read[1] modification of the Cottrell apparatus was found to be much better in reducing this. This was tested by stoppering the pump tube of the Cottrell apparatus. If there were no super-heating, the thermometer should read the same whether pure water or steam is being pumped over the apparatus. It was found that the thermometer read from .03° to .04° lower when the tube was closed. A modification of the Cottrell apparatus was designed which showed a super-heating of about .008°. In this apparatus the position of the pump tube was changed so as to reduce the hydrostatic head on the small bubbles before they entered it.

1. J. Am. Chem. Soc., 41, 729, (1919).

III

Experimental

The molecular weight determinations with the new type of apparatus used in this investigation were carried on in the following manner. The apparatus, after being thoroughly cleansed with the solvent to be used, is suspended over a wire gauze by several clamps attached to an iron stand. The clamps must not be adjusted too tightly or the apparatus will break upon heating due to expansion. A condenser is connected to the tube "I" and a sufficient flow of water supplied to keep the condenser temperature around 22° C. A small piece of asbestos is placed under the arm of the tube "K" to prevent boiling of the liquid in the trap. This has occasionally happened when using benzene without sufficient insulation resulting in a wide fluctuation in the thermometer reading. The Beckman thermometer, which has been set for the boiling-point of the solvent to be used, is inserted through a drilled stopper in the tube "G". The apparatus is so designed that the flare in the Beckman causes a snug fit and at the same time allows the thermometer to protrude to the desired depth. Approximately 150 cc. of the solvent are then poured into the outer shell "A" through the inlet "C". The apparatus is then heated with a small Fisher burner until the solvent in "A" reaches the boiling temperature. While this is being done, it is best to heat, separately, a 75 cc. portion of the solvent and then place it in inner tube "C" through the entrance in "G". This saves an appreciable amount of time. The apparatus is then sealed tightly by the stopper in "L" and the cork in "G". The boiling should be regular and the rate of pumping uniform. If the liquid is boiled too rapidly, the vapor will be unable to escape as rapidly as it is formed causing a back pressure which forces the liquid in the trap up through the tube "KJI" and

into the tube "C". If the liquid does not boil rapidly enough, there will not be enough pressure to cause the perculator to function. When the vapor does not condense rapidly enough to close the trap, a small amount of liquid may be poured into it by means of the condenser tube. The heating is continued until the thermometer readings are constant. This requires from one-half to three-quarters of an hour when the solution is preheated as described above or from one to one and one-half hours when it is not preheated. A sample of the substance whose molecular weight is to be determined is then accurately weighed and placed in a small beaker. This is dissolved in a small amount of warm solvent, the Beckman thermometer is replaced by a funnel, and the solution poured into the tube "C". The beaker and funnel are then carefully washed with warm solvent. The thermometer is again inserted and the heating continued. The burner is not removed during this operation. The sample may also be inserted by carefully brushing it into the tube with a fine brush, but this is usually unsuccessful because of the wetting of the sample by the vapor. After ten or fifteen minutes, readings are taken every two minutes until a constant temperature is reached. The flame is withdrawn, the plug in "L" is removed, and the apparatus allowed to cool. The solution is pipetted from the tube "C" and measured accurately. It was found that because of a slight increase in the volume of solution in "C" due to condensation before the solution reached its boiling-point, it is not best to measure the liquid originally. The maximum volume of solution that can be used without having the thermometer immersed, is 145 cc. For good pumping, a volume of 80 cc. is necessary. From the data obtained, the molecular weight of the substance is calculated as shown below.

Wt. of sample	2.0666 grams.
Last reading of thermometer=	1.184°
First reading of thermometer=	1.015°
Rise in temperature=	.169°
Weight of aqueous solution	103.

$$\text{Molecular wt} = \frac{1000 \times .518 \times \text{wt. sample}}{\text{weight of solution} \times \text{degrees rise}}$$

$$\text{Molecular wt} = \frac{1000 \times .518 \times 2.0666}{103 \times .169} = 61.4$$

The weight of solute should be large enough to cause a rise of at least .150°. This will reduce the error considerably, although many good results were obtained using a much smaller rise.

In order to determine whether or not there was any super-heating in the apparatus, the liquid was heated in "A" with none in the inner shell. After a constant temperature was reached, it was recorded, and some liquid was then placed in the inner shell and a like reading observed. The last reading was found to be from .002° to .004° higher showing practically no super-heating.

The boiling-point of water and benzene were compared with those obtained by a Cottrell type of apparatus and were found to be from .01° to .02° lower. There was therefore, considerably more super-heating in the Cottrell apparatus.

In order to determine whether the thermometer gives a constant reading over a long period of time the apparatus was heated until a constant temperature was reached and then continued for four hours with

readings taken every 15 minutes. The following readings resulted:

P. M.	Thermometer Readings
2:00	3.273
2:15	3.273
2:30	3.278
2:45	3.278
3:00	3.278
3:15	3.275
3:30	3.275
3:45	3.274
4:00	3.275
4:15	3.276
4:30	3.276
4:45	3.276
5:00	3.276
5:15	3.275
5:30	3.275
5:45	3.276
6:00	3.276

Any change in the atmospheric pressure would of course alter the boiling temperature. In order to determine the maximum difference in temperature that can be obtained with water and benzene the following calculations were made.

Average heighth of water in "KJI" = 3" = 76.2 mm. and that for benzene was 3.5 in. = 76.2 mm. of water.

76.2 mm. of H_2O = $\frac{76.2}{13.6}$ = 5.6 mm. of mercury

$$\frac{dp}{dt} = \frac{l\ m\ P}{R\ T^2}$$

where dp = difference in pressure

dt = difference in temperature

m = molecular weight

P = atmospheric pressure in mm. of mercury

T = absolute temperature

R = 2

For water

$$dt = \frac{5.6 \times 2 \times (373)^2}{538 \times 18 \times 760} = .211°C.$$

For Benzene

$$dt = \frac{5.6 \times 2 \times (373)^2}{92.9 \times 78 \times 760} = .284$$

This allows a rise of .211° for water and .284 for benzene. This is the average although at times the apparatus was used with greater pressures.

(A) Water As Solvent

	I	II	III	IV
Grams of Urea	.4986	.4986	2.0666	2.66552
Weight of Solution	118	114	103	125
Last Reading of Thermometer	1.05	1.055	1.184	1.226
First Reading of Thermometer	1.015	1.020	1.015	1.045
Rise in Temperature	.035	.035	.169	.181
Apparent Molecular Weight	62.6	64.7	61.4	61.
Formula Weight	60.05	60.05	60.05	60.05

Grams of	I	II	III	IV
Hexamethylenetetramine	2.9974	2.8774	3.1314	2.872
Weight of Solution	108	107	113	120
Last Reading of Thermometer	1.042	1.039	1.060	1.043
First Reading of Thermometer	.945	.945	.962	.960
Rise in Temperature	.097	.094	.098	.083
Apparent Molecular Weight	145	148	145	148
Formula Weight	140.13	140.13	140.13	140.13

	I	II	III	IV
Grams of Acetamide	2.632	2.843	2.7366	2.5420
Weight of Solution	122	131	121	131
Last Reading of Thermometer	3.325	3.322	3.334	3.300
First Reading of Thermometer	3.140	3.138	3.148	3.140
Rise in Temperature	.185	.184	.186	.160
Apparent Molecular Weight	60.1	61.2	62.3	62.5
Formula Weight	59.05	59.05	59.05	59.05

	I	II	III	IV
Grams of Dextrose	2.3630	3.0482	2.4492	3.0558
Weight of Solution	98	114	98	97
Last Reading of Thermometer	1.022	1.335	1.0600	1.0780
First Reading of Thermometer	.968	1.267	.9900	1.0000
Rise in Temperature	.054	.070	.0700	.0780
Apparent Molecular Weight	230	197.8	185	209
Formula Weight	198.11	198.11	198.11	198.11

	I	II	III	IV
Grams of Galactose	3.6930	7.8088	7.8088	7.8088
Weight of Solution	139	144	135	137
Last Reading of Thermometer	2.998	3.100	3.106	3.106
First Reading of Thermometer	2.905	2.935	2.935	2.935
Rise in Temperature	.093	.165	.1710	.171
Apparent Molecular Weight	150	170	175	172
Formula Weight	180.1	180.1	180.1	180.1

	I	II	III	IV
Grams of Sucrose	7.5960	10.0000	10.000	10.000
Weight of Solution	120	144	140	138
Last Reading of Thermometer	1.125	3.105	3.110	3.109
First Reading of Thermometer	.984	2.968	2.965	2.965
Rise in Temperature	.141	.137	.145	.144
Apparent Molecular Weight	233	268	254	260
Formula Weight	342	342	342	342

(B) Benzene as Solvent

	I	II	III	IV
Grams of Napthalene	1.5300	1.5300	1.5300	1.5300
Weight of Benzene Solution	105	95.6	97.4	107
Last Reading of Thermometer	.93	.98	.936	.919
First Reading of Thermometer	.65	.65	.640	.640
Rise in Temperature	.28	.33	.296	.279
Apparent Molecular Weight	134	125	136	132
Formula Weight	128	128	128	128

	I	II	III	IV
Grams of Camphor	1.73	1.73	1.73	1.73
Weight of Solution	106	101	101	104
Last Reading of Thermometer	1.00	.855	.856	.845
First Reading of Thermometer	.68	.540	.55	.285
Rise in Temperature	.32	.315	.306	.285
Apparent Molecular Weight	132	140	145	150
Formula Weight	152	152	152	152

	I	II	III	IV
Grams of Benzoic Acid	1.73	1.73	1.73	1.73
Weight of Solution	103	101	100	104
Last Reading of Thermometer	.670	.655	.290	.66
First Reading of Thermometer	.430	.280	.430	.43
Rise in Temperature	.24	.23	.26	.23
Apparent Molecular Weight	180	192	172	186
Formula Weight	122	122	122	122

	I	II	III	IV
Grams of Anthracene	2.990	3.00	3.000	3.000
Weight of Solution	119	113	109	114
Last Reading of Thermometer	.95	.98	.985	.955
First Reading of Thermometer	.55	.55	.54	.55
Rise in Temperature	.40	.43	.455	.405
Apparent Molecular Weight	162	159	156	168
Formula Weight	178	178	178	178

IV

Discussion of Results

These results are very favorable as compared with those that are obtained with other types of apparatus when corresponding sample sizes are used. It is interesting to note, that in the case (A) using water as the solvent, with the exception of sucrose and galactose, the experimental results as compared to the formula weights, are in almost all cases higher.

From the formula

$$\text{Molecular Weight} = \frac{1000 \times .518 \times \text{Wt. of Sample}}{\text{Wt. of Solvent} \times \text{Rise in Temperature}}$$

it is apparent that the error lies in the rise in temperature or the purity of the sample as the remaining members of the equation are either constants or can be measured with sufficient accuracy to prevent any notable error. This seems to point to the fact that there is again super-heating, and that it is, of course, present to a greater extent with the pure solvent than with the solution. This can hardly be true as the previous tests mentioned above showed no super-heating. The error could also be due to impurities in the solute. This would cause a high result. The fact that the results are regular seem to indicate that the error is due to some definite cause and not to carelessness in determining the results. For the most part the results are within 5% of the formula weight which is as close as can be expected with any apparatus of this type. There is always a chance of dissociation although nobody postulates any dissociation or change in dissociation with cane sugar and yet its apparent molecular weight changes abnormally as evidenced by the data above and by the results of Dr. W. D. Bancroft[1] which ranged from 212 to

1. Bancroft, W. D., J. Physical Chem., 33, (1929)

360 for the molecular weight of sugar. This is indeed an important matter to be investigated, and before the actual value of ebullioscopic methods of molecular weight can be determined, definite results and knowledge must be obtained on this subject.

It is more difficult to obtain accurate results when using benzene than when using water as the solvent. The specific heat being less adds to the difficulty of obtaining constant readings when the apparatus is subject to a draft or a variation in the heating flame due to change in gas pressure. The volume change in "C" is also apt to be greater than in the case of water owing to the smaller value of the heat of vaporization of benzene. With careful manipulation of the apparatus it is possible, however, to obtain very steady readings with benzene.

The results in two of the series are lower than the formula weight. This, in a large measure, dispells the above idea that there was any appreciable super-heating with the pure solvent. There is, however, a chance that in the cases of such volatile substances as Napthalene and Camphor, some of the solute has passed off and more than compensated the super-heating if any were present. The possibility of dissociation and of association should of course always be considered.

V

Improvements

A number of improvements on this apparatus are suggested by this series of experiments. The tube "KJI" is to be made larger so as to increase the inertia of the water column eliminating rapid fluctuations in pressure due to the variation of the heighth of the water column with slight irregularities in the boiling of the solution in "A". The entrance tube "L" is to be made more vertical to facilitate the pouring of the solution into "A". Instead of the single hole at "H", a number of similar outlets are to be made in the tube "G" to reduce the chance of having the liquid and vapor surrounding the thermometer at a greater pressure than one atmosphere when the liquid in "A" is rapidly boiled. A small protrusion on the upper wall of "I" would prevent any condensed vapors or liquids flowing down the condenser from entering the tube "C". A small depression in the bottom of the tube "C" would facilitate the withdrawing of the solution with a pipet in determining the volume of the solution. In order to reduce the capacity of the apparatus, the tube "B" may be replaced by a standpipe in "A" and sealed through the bottom of "C" to the injector "D". The tubes "FF" should project .25 cm. into the cylinder "G" in order that a maximum amount of solution be pumped on the thermometer instead of running down the sides of the tube.

VI

Conclusion

This series of experiments show many advantages of this type of apparatus. The remarkable constant temperatures that can be obtained as shown by the four-hour test, allows an accurate reading to be taken and it is not necessary to rely on a mean of several fluctuation values.

It was believed that the super-heating in the Cottrell apparatus was mostly due to the hydrostatic head under which the bubbles were formed and entered the pump tube. If this super-heating were in part relieved by causing the bubbles to pass freely through a mass of the solution before entering the pump, the rest of the super-heating might well be removed in that tube. In this apparatus the pump tube passes through the body of the apparatus in such a way that the vapor bubbles pass upward freely through the liquid and up the pump tube allowing the vapor and the solution to be in equilibrium and eliminating super-heating which is shown to be true by the tests made.

Great uniformity is obtained in the pumping of the solution and vapor over the thermometer. This is one of the chief causes for the steady reading obtained as just stated. No special care or precautions are necessary to produce the uniformity of pumping.

In the usual apparatus, a slight draft will cause considerable variation of temperature. This apparatus is so efficiently insulated forced drafts showed no temperature variation.

A special merit of the apparatus is the simple and automatic operation requiring no special manipulative skill. Any student can follow the simple procedure outlined under "Manipulative details", and obtain very good results.

The temperature of the solution is not affected by the return of cool condensed vapors these vapors, after condensing in the condenser, flow down into the tube "IJK" and finally into the outer jacket "A".

The apparatus is of rugged construction and made in one piece. This eliminates chances of the breaking and losing of small parts and simplifies operation.

This new apparatus appears to be one of the best yet designed for the determination of boiling-points.

Approval

The foregoing thesis is hereby approved as a creditable study on an engineering subject, carried out and presented in a manner sufficiently satisfactory to to warrant its acceptance as a prerequisite to the degree for for which it is submitted. It is to be understood that by the approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein but approves the thesis only for the purpose for which it is submitted.

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