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The Accurate Determination of Condensation Point Differences on Small Samples

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In search for a convenient method for the determination of boiling point (b. p.) differences on small samples, the method of Siwoloboff[1] has proved of value[2]. In this paper an improved differential Siwoloboff-method is described by which it is possible to obtain condensation point (c. p.) differences with an accuracy of 0.001 °C or less.

METHOD

In the original method of Siwoloboff a capillary tube (1 mm diameter), sealed at one end, is placed with the sealed end uppermost in a 4 to 5 mm tube containing the liquid to be tested. The tube is attached to at thermometer and immersed in a heating bath. When the temperature of the bath is gradually raised to the b. p. of the liquid, bubbles emerge slowly from the capillary and, due to the expansion of the enclosed air, are replaced by a rapid and continuous stream of gas bubbles. When the temperature falls to the condensation point, the bubbling ceases and the liquid is sucked back into the capillary. The latter procedure gives more reproducible results and has been the only one used here.

In an endeavour to increase the accuracy of the method the following changes were made:

1. The rate of cooling was carefully controlled. This was done by using an unsilvered Dewar-flask containing glycerol as the heating medium. The flask was inserted in an empty beaker, 20 mm wider then the Dewar-flask (see Fig. 1). The bath contained an electric nichrome wire heater, freely mounted around a thin-walled glass tube. The heater was fed from a variable transformer and with a constant voltage input. A constant temperature gradient of 0.0005 to 0.001 °C per second was found satisfactory. A propeller stirrer provided rapid agitation throughout the liquid.

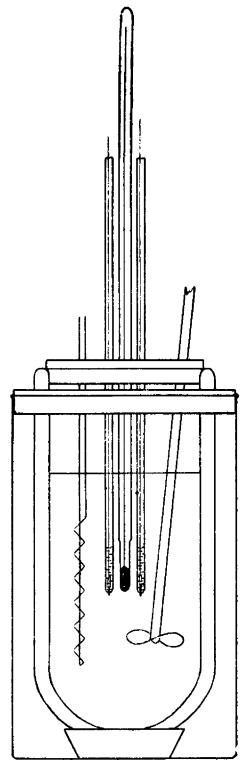

Fig. 1. Apparatus for determination of condensation point differences.

An Anschütz thermometer with graduation of 0.1 °C was placed in the bath and read under the microscope (magnification × 20). The cooling rate in seconds per 0.1 °C was measured with a stop watch by observing the times, necessary for the meniscus of the mercury stem to pass from one to another of the graduations.

2. The method of comparative measurement was strictly followed. Two boiling point tubes with an inner diameter of 3—4 mm were used. They were placed equally close to the thermometer bulb. The identical two cups made in the following way were inserted into the tubes. A thin-walled glass tube 3—4 mm in diameter was drawn out to an outer diameter of 0.8—1.0 mm. On this capillary three sharp marks, 2.00 mm apart, were ground on a lathe (see Fig. 2). The central mark was ground as deep as possible without breaking the capillary. The tube was sealed outside of the two outer marks. In this way a completely closed tube (12—14 mm in length) was obtained. At either end a long thin glass rod was fastened and the small tube was carefully broken

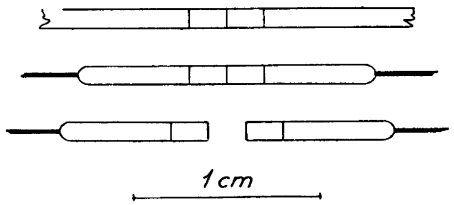

Fig. 2. Different stages in the making of cups.

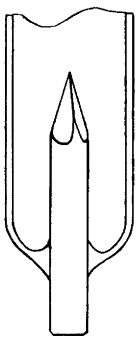

Fig. 3. Bottom part of boiling point tube.

along the central mark. Care was taken to keep the edge clean and even. The two cups were then tested for equivalence as outlined below.

3. The next step was to eliminate another disadvantage of the method. There is always a last vapor bubble (before condensation takes place) "hanging" at the opening of the cup. This bubble either leaves the orifice just before the beginning of the condensation, or the bubble tacks the opening and must be completely condensed before the liquid begins to rise into the cup. In the latter case the "sucking in" lags behind that in the first case even if all other conditions are equal. This difficulty was eliminated as is shown in Fig. 3. In the bottom of the boiling point tube a platinum wire, 1.0 mm diameter, was introduced. The end of the wire had been conically lathed (top angle 40°) and then three symmetrical planes had been chafed on the cone, the angle between the axis of the wire and the planes being 18°. The cup was placed on the triangular point thus obtained. The point extends about 0.5 mm into the cup. The exit area is thus reduced and the small bubbles will leave the orifice instantaneously.

EXPERIMENTAL PROCEDURE

The b. p. tubes and the cups were carefully cleaned and dried. They had been stored over phosphorous pentoxide. First of all the equivalence of the two cups was checked. The b. p. tubes were filled with the aid of a micro-pipette up to a height of about 20 mm with the same pure liquid (ether, acetone, ethanol, water or toluene). The marked cups (a and b) were inserted into the tubes (l and r) and the tubes were placed in the heating bath.

The heating bath was pre-heated to the boiling point of the liquid 30 minutes before the tubes were inserted, in order to establish equilibrium

between the apparatus and the surroundings. The b. p. tubes were then slowly inserted in the bath at a temperature just below the b. p. The bath was gradually heated to about 0.5 °C above the b. p. of the liquid. A rapid stream of bubbles emerged from the cups and the air inside the cups was slowly replaced by the vapor of the liquid. It is most important, that the gas phase is totally free from air, a step requiring 5 to 10 minutes. Now, the current through the heater was changed to a previously determined value in order to assure a rate of cooling of about 0.001 °C per second. The cooling rate was determined starting from 0.4 °C above the b. p.

In the vicinity of the condensation point the bubbling slowed down and then ceased; during a short time the meniscus was seen at the opening between the platinum pin and the cup wall. The meniscus ascended into the cup and when it passed the mark 2 mm above the orifice, another stop watch was started. When the liquid in the second b. p. tube passed the mark of the cup, the watch was stopped, thus giving the time difference between the passage of the menisci. When the determination was repeated immediately, the heating current was switched on before the cups were completely filled with liquid, which occured, if the temperature was allowed to decrease to much. Within a few seconds the b. p. was reached and then the measurement was

Table 1.

Time for meniscus passage in capillary in sec.		Time diff. reduced to 0.001 °C/sec.	Condensation point (uncorr.)	Actual cooling rate sec./0.1°
a	*b*			
(in l)	(in r)			
0	1.2	1.1	77.94	110
0	0.8	0.7	77.94	120
0	1.0	0.9	77.95	115
0	3.5	2.2	77.95	160
(in r)	(in l)			
0	0	0	77.95	150
0	1.1	0.6	77.95	185
0	2.7	1.4	77.95	190
0	3.4	1.8	77.95	190
(in l)	(in r)			
0	2.2	2.0	77.92	110
0	2.1	1.3	77.92	160
0	1.1	0.6	—	180

Mean value = 1.3 sec.
Standard deviation = 0.7 sec.
Standard deviation of the mean = 0.2 sec.

carried out again. A new series of determinations was done after cleaning the tubes and cups, but this time with the cups interchanged (in the first series *a* in r and *b* in l, in the second *b* in r and *a* in l).

Table 1 gives the values for one set of determinations.

In the first and second column the times observed for the menisci to pass the respective mark are given at the actual cooling rate shown in the last column. The time differences are reduced to a constant cooling rate of 0.001 °C per sec. (column 3). The actual temperature of the c. p., as read on the Anschütz-thermometer, is given in column 4.

If the reduced time difference exceeds 3 sec. it is advisable to correct the volumes of the cups with the aid of a small micro flame and repeat the measurement.

The liquid levels must be controlled after each determination. Different heights of liquid in the two tubes give different pressures inside the cups and thus the c. p. difference found will be incorrect. It is useful to engrave a scale on the b. p. tubes, beginning at the Pt-point. A difference in height is read directly on these scales and the pressure dependence of the b. p. is easily found from an additional experiment. Low boiling liquid will evaporate more or less even if the b. p.tubes are as long as shown in Fig. 2. Furthermore a slight fractionation is inevitable even at total reflux, due to the formation of vapor inside the tubes. This phenomenon, however, seems to be of less importance.

Comparing different fractions from a fractional distillation, one fraction has to be taken as a reference standard. First, the equivalence of the cups is checked with the reference fraction in both tubes and then the b. p. differences between the reference standard and the fractions are determined. It is necessary to replace the reference liquid for each determination. Extreme cleanliness is very important as even the smallest contamination may cause misleading results.

The maximum c. p. difference for which the method outlined above is useful, is less than 1 °C and it is somewhat dependent on the boiling point of the sample. At a cooling rate of 0.001 °C per sec. a c. p. difference of 1 °C corresponds to a time difference of about 17 minutes. The lower boiling sample will be more superheated than the higher boiling sample and, furthermore, it has to boil for a longer time. For low boiling substances the loss of substance due to evaporation is appreciable and consequently the results will be unreliable. By inceasing the rate of cooling the time of boiling is cut down and the evaporation diminished.

The method has been used for temperatures between 35 and 140 °C. Above this temperature the glycerol soon becomes dark and good observations are

thereby prevented. With silicone oil as a heating medium it will probably be possible to use the method at higher temperatures.

Tables 2 and 3 give the results from two successive distillations of *n*-amyl chloride *. In the first series the cooling rates were varied within wide limits, in the second they were kept as constant as possible. The last column in the tables gives the difference between the read (mean) temperatures of the fractions during the distillation. Fraction F4 from the first distillation, which was believed to be rather pure, gave on second distillation a first fraction boiling 0.04 °C below the main fraction. This was probably due to the presence of a small quantity of water, driven off as an azeotrop (*cf.* Swietoslawski [3, p. 84]).

Table 2.

Fractions	Rate of cooling sec. per 0.1 °C	C.p.diff. °C	Temperature diff. (mean) from distillation
F4-A10	84	0.640	0.64
	333	0.635	
F4-C8	108	0.255	0.26
	80	0.252	
F4-C9	273	0.160	0.16
	221	0.158	
F4-F1	167	0.097	0.10
	292	0.097	
	94	0.096	
F4-F2	227	0.017	0.01
	460	0.017	
	166	0.018	
	88	0.019	
F4-F3	260	0.003	—
	172	0.003	
	160	0.003	
	207	0.003	
	162	0.003	

The order of fractions: Al-C3 (5 fractions) together 80 g, A 10 6.0 g; C8 7.1 g; C9 6.5 g; Fl 9.4 g; F2 15.2 g; F3 14.8 g; F4 29.9 g.

* We are indebted to Prof. L. Smith for permission to study the fractions in question. The distillations were done by Mr. L. Bjellerup.

Table 3.

Fractions	Rate of cooling sec. per 0.1 °C.	C.p.diff. °C.	Temperature diff. from distillation
B9-C6	159	0.040	0.04
	160	0.040	
	161	0.040	
B9-B6	160	0.002_5	
	161	0.002_5	
	152	0.003_0	
	154	0.003_0	
B9-B8	162	0.001_0	
	164	0.001_5	
	165	0.001_0	
	165	0.001_0	
B9-E2	164	$-\ 0.004_5$	
	164	$-\ 0.006_0$	
	167	$-\ 0.005_0$	

Fraction F4 from Table 2 distilled. Order of fractions: C6 5.6 g.; B6 5.7 g.; B8 5.3 g.; B9 4.7 g. and E2 residue 5.1 g.

The method outlined above was worked out mainly as an aid in estimating the purity of substances for combustion calorimetry where the available amounts are often rather limited and the requirements on the purity of the substances burned are very high.

SUMMARY

A description is given of a differential Siwoloboff-method allowing the determination of condensation point differences with an accuracy of 0.001 °C on samples as small as 0.1 ml. The maximum c. p. difference hitherto determinable with this accuracy is about 0.5 °C. The method is useful for the estimation of the purity of fractions in fractional distillation of small samples.

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