value 0.493. The entropy of monatomic magnesium vapor at atmospheric pressure and 25° has been determined empirically at 35.29 units, while the theoretical value is 35.5_1.

BRESLAU, GERMANY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE INFLUENCE OF THE PERIOD OF HEATING UPON THE BOILING POINT OF CERTAIN LIQUIDS USED IN EBULLIOSCOPY, WITH A NOTE ON TESTING THE PURITY OF VOLATILE LIQUIDS BY ISOTHERMAL DISTILLATION[1]

BY SYDNEY L. WRIGHT, JR., AND ALAN W. C. MENZIES

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This paper describes a series of experiments designed to determine as accurately as possible whether the boiling point of a liquid is dependent upon the liquid's previous thermal history, *i. e.*, whether a liquid which has been boiling for several hours, boils at exactly the same temperature as one recently elevated from a lower temperature. It is obvious, as pointed out by Smits and others, that in associated liquids there might be a delay in attaining the degree of association appropriate to the higher temperature. This would usually result in a slightly higher boiling point at the beginning of ebullition than would be observed several hours later. For purposes of investigation two associated liquids, bromine and acetic acid, and two supposedly non-associated liquids, benzene and carbon tetrachloride, were used.

We also briefly refer to a method of testing the purity of volatile liquids, far more sensitive than the ordinary methods of boiling point and distillation range.

This study was prompted by experiments reported by H. B. Baker,[2] who believed that they demonstrate a delay in the attainment of internal equilibrium in the case of bromine and acetic acid. These observations, if confirmed, might serve to explain several difficulties previously encountered in ebullioscopic work, such as (1) the frequently mentioned necessity of allowing an astonishingly long period of time for the pure solvent to attain a constant boiling point in Beckmann's ebullioscopic method of determining molecular weights,[3] (2) the classical controversy[4]

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[1] From the thesis of Sydney L. Wright, Jr., presented in partial fulfilment of the requirement of the degree of Doctor of Philosophy, 1928.

[2] Baker, *J. Chem. Soc.*, **129**, 949 (1927).

[3] Beckmann, *Z. physik. Chem.*, **6**, 473 (1890); **8**, 225 (1891). Biltz, translated by Jones and King, "Practical Methods for Determining Molecular Weights," 1912, p. 155; Jones, "The Elements of Physical Chemistry," 4th ed., 1915, p. 133; Walker, "Introduction to Physical Chemistry," 9th ed., 1922, p. 200; Findlay, "Practical Physical Chemistry," 4th ed., 1923, p. 264.

[4] Reference to the extensive literature on this subject may be found in Ostwald's "Lehrbuch der Allgemeinen Chemie," Vol. I, p. 308.

as to the equivalence of the static and dynamic methods of vapor pressure determination, (3) the frequency with which it is found that the most satisfactory vapor pressure curve of a liquid shows a temperature at 760 mm. pressure not identical with the best observed boiling point determinations. Raikes and Bowen[5] pertinently remark that this discloses a "situation which can be cleared up only by further research."

Experimental Method

The method in brief consisted of a differential reading between two isoteniscopes,[6] one containing a portion of the liquid which had been held near the boiling point for several hours, the other containing a portion recently rapidly elevated to the same temperature by insertion in the bath. Isoteniscopes, being compact in form, can be used in a bath designed for more adequate stirring than can be supplied for long barometer tubes. This, with the fact that the liquid under consideration is used as a manometric fluid instead of the denser mercury, and that the readings are differential and not absolute in nature, allows a far greater sensitivity[7] than that attained by Baker. The observations were continued until the liquids were more similar in thermal history. A difference in vapor pressure observed at first and not disappearing within a reasonable time must be due not to difference in thermal history but to some of the other factors discussed later.

Apparatus.—The isoteniscopes were constructed of pyrex glass, the bulb of 35-cc. capacity, being sealed to thick-walled tubing of 2 mm. bore which formed the left side of the manometer. The right side was of 10-mm. tubing in which, above the level of the bath, were blown four elongated bulbs to serve as the inner tube of a condenser 27 cm. long. Near the end it was bent at a slightly acute angle to prevent possible contamination from the rubber connections. Each isoteniscope was connected through a short piece of rubber tubing to a tube containing calcium chloride, thence through a long flexible tubing to a 1-liter flask which served as a reservoir to stabilize the pressure and facilitate delicate adjustment. Mercury manometers connected with these flasks were a convenience in manipulation. By means of glass and rubber tubing fitted with suitable clamps, it was possible to establish pressure equality between them, and to adjust both or either of them to any desired pressure not greater than atmospheric. The arrangement is shown diagrammatically in Fig. 1.

The bath consisted of a 3-liter beaker filled with glycerin and stirred by a six-bladed glass stirrer electrically propelled. Adjacent were two heating units and the expansion bulb of the thermostat. Near the front of the bath was a bakelite millimeter scale supported vertically. The scale was 120 mm. long and the markings were about 5 cm. wide, so that when the isoteniscopes were in position, the bulbs hung over the top of the scale near the center of the bath, while the manometers, side by side in front of the scale, could be read almost simultaneously. Except for windows at the front and back.

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[5] Raikes and Bowen, "International Critical Tables," Vol. III, 1928, p. 215.

[6] Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

[7] The sensitivity is illustrated in the last column of Table I, which shows the temperature change corresponding to a pressure change of 1 mm.

the beaker was insulated with cotton wool. A lamp behind the bath furnished illumination. The heating units and the thermostatic control were so connected with rheostats that the difference between the current intensities during the "on" and the "off" periods could be reduced to a minimum at the time of reading, thus diminishing the "pumping" effect referred to later.

Procedure.—Except in the case of bromine (*q. v.*) the liquid was taken up in a dried pipet and 5 cc. placed in each of the thoroughly cleaned and dried isoteniscopes, which were immediately connected to the vacuum system. The permanent gases were removed as far as possible by repeatedly boiling out near room temperature. With water running through the condensers, the isoteniscope was evacuated to a pressure corresponding to the vapor pressure a few degrees above room temperature. A small flame was then applied intermittently to the bottom of the bulb. The vapor passed through the manometric portion of the isoteniscope carrying the dissolved gases with it and, condensing, formed a trap which prevented their readmission. By allowing the bulb to cool, the greater part of the liquid was returned to it, leaving sufficient in the manometer to form a trap. When this had been repeated several times with each isoteniscope, comparison in the bath at room temperature showed that their vapor pressures agreed within the experimental error and further boiling out caused no change. After the final comparison, isoteniscope A was removed from the bath and by closing clamp 1 was cut off from the rest of the system. The heat was then turned on and the pressure over the liquid in B allowed to increase as the vapor pressure rose. When the pressure had increased to within a few centimeters of 76, the thermostat was set to hold the bath at the corresponding temperature. The isoteniscopes were allowed to stand thus, A at room temperature, B near the boiling point, for about four hours. The position of the manometric liquid was watched during that time and any necessary adjustments made to prevent the entrance of air into the bulbs. Near the end of this period the pressure on B was reduced slightly so that bubbles of vapor passed through the confining liquid and condensed, thus eventually evaporating all the liquid from the bulb. Meanwhile, by slightly warming A, the liquid in that isoteniscope also was condensed in the wide arm of the manometer. At this point clamp 2 was closed, the connecting tubes evacuated and clamp 1 opened, allowing the pressure on A to be altered without affecting B. Isoteniscope A was then placed in the hot bath and by means of clamp 3 the pressure was increased as rapidly as possible without forcing any liquid into the bulb. When the behavior of the liquid in A indicated that temperature equilibrium was near attainment, clamp 2 was opened, thus assuring the identity of the external pressure on the two isoteniscopes. As rapidly as possible the greater part of the liquid in both isoteniscopes was returned to the bulbs and comparative vapor pressure readings taken. Agitation of the liquid in the bulbs hastened temperature equilibrium. When A was inserted without the precautions noted above, the sudden inflow of heat from the large surface of the

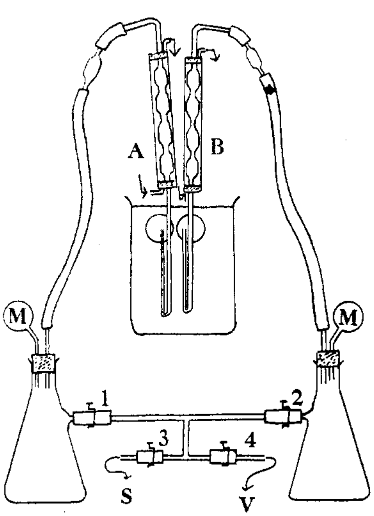

Fig. 1.—Diagram showing apparatus with isoteniscopes in position for reading. A, B, isoteniscopes; 1, 2, 3, 4, clamps; M, mercury manometers used for convenience in adjustment. S, to air; V, to vacuum.

bulb caused instant and complete evaporation, with considerable loss of liquid. This procedure, by reducing the heating surface, allowed the increase of pressure to keep pace with the speed of heating.

The constant "pumping" movement of the manometric liquid due to small fluctuations of bath temperature was reduced as much as possible by proper rheostat adjustment. To minimize the error from this source the reading was made as far as possible at the time of momentary rest between rise and fall of temperature, the pressure being so adjusted that at that instant the menisci in A were level. The pressure difference was then read on the manometer of B. When the liquid in the wide arm of B was higher than in the capillary, it indicated that the vapor pressure of A was less than that of B. Such readings were recorded as negative. Readings were made at frequent intervals until they became constant, and then occasionally for a longer period.

Isothermal Distillation.—When the readings were completed, it was found advisable to test the purity of the liquids by isothermal distillation. The deficiency of this method as a means of measuring or even detecting impurities has recently been discussed by Washburn.[8] The data forming the basis of his discussion are, however, limited to the difference between the vapor pressure of the liquid with an infinitely large and an infinitely small vapor phase. The method here described, in that it furnishes a few intermediate points, is more promising and was found useful in testing at least the *relative* purity of the two samples.

The fractionation was generally carried out immediately after the completion of the main experiment, when both samples of liquid were already at the boiling point and supposedly free of permanent gas. By closing clamp 1, and reducing the pressure, bubbles of vapor could be made to pass through the manometer of B and, condensing, increase the volume of the manometric fluid. The speed of this evaporation could be controlled by the amount of change of pressure. By continuous agitation of the liquid in the bulb, and slow rate of evaporation, the condition is approached where the condensing vapor is of the composition in equilibrium with the liquid. At any point the distillation could be interrupted, temperature equilibrium reëstablished and the change of vapor pressure in B observed by comparison with A. At the same time, the volume of the liquid in the manometer (previously calibrated against the millimeter scale) was read. Thus, by a series of observations, there could be plotted against the percentage of the original amount of liquid in the bulb, the corresponding reduction in vapor pressure. The points obtained are shown in Fig. 2, in which the lowering is expressed as percentage of saturation vapor pressure which in all cases was close to 760 mm. The points for a sample of acetic acid less pure than that used are included for comparison, as is also a line showing the points to be expected by a liquid containing one mole of a non-volatile solute in 9999 moles of solvent. Where the impurity is volatile, the theoretical curve will vary with each pair of substances according to the behavior of their partial vapor pressures. It may be seen

[8] Washburn, *Z. physik. Chem.* (Cohen Festband), 592 (1927).

at a glance, however, that the benzene and bromine used in these experiments are of a higher order of purity than the acetic acid.

The most striking feature of this method of isothermal distillation is its sensitivity. Constancy of boiling point, a generally accepted criterion of purity, is crude in comparison, for the acetic acid used, which distilled completely within a range of 0.02°, was found, on isothermal distillation, to show vapor pressure changes up to 58 mm. of acetic acid (used as manometric liquid) in the course of the fractionation.[9] This acid had been subjected to fractional crystallization twelve times, until the melting point became constant within 0.02°, and was then distilled twice, all but a negligible residue coming over within a range of 0.02°, m. p. 16.6°, b. p. 117.8°.[10] These figures are in agreement with the best observations in the literature. In this case, therefore, fractionation as here carried out furnished the only evidence of the impurity undoubtedly present.[11] Im-

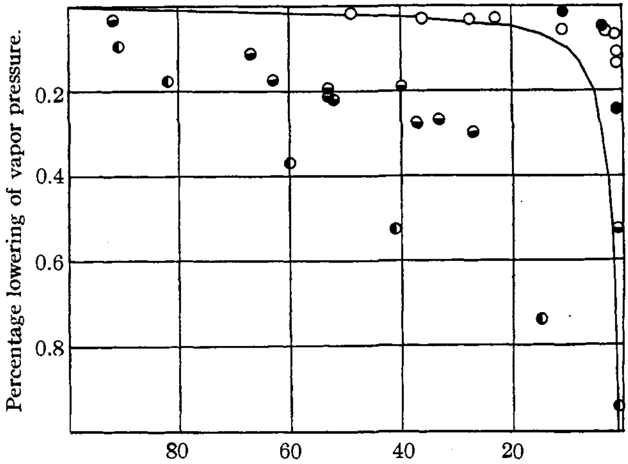

Fig. 2.—Graph showing the fall in vapor pressure resulting in progressive evaporation of liquid by slow isothermal distillation. Fall in vapor pressure is expressed as per cent. of saturation pressure (near 76 cm.). The line represents the theoretical curve for a non-volatile solute. ○, Benzene; ●, bromine; ⊖, acetic acid, m. p. 16.6°; ◐, acetic acid, m. p. 16.4°.

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[9] Fifty-eight mm. acetic acid; density 0.94 ≡ 4.0-mm. mercury, density 13.6 ≡ 0.53% of 760 (Fig. 2).

[10] The thermometers used for testing the purity of liquids were compared with a standard thermometer, whose certified accuracy was 0.1°. The constancy of the readings could be estimated more closely as the thermometers were graduated in 0.2°. Unless otherwise stated, boiling point observations are corrected to 760 mm. pressure.

[11] Lack of this evidence was undoubtedly the cause of the difficulties encountered by Meyer and Jaeger, *Ber.*, **36**, 1555 (1903), and Kahlbaum, *ibid.*, **16**, 2479 (1883), in working with acetic acid.

purities, therefore, too small in amount to be detected by ordinary means are capable of causing appreciable error in vapor pressure measurements where the circumstances are favorable to fractionation.

Errors.—Fractionation as a source of error in our results is eliminated by the expedient of evaporating all the liquid from the bulbs of both isoteniscopes immediately before the comparison is made. The liquid on condensing is thoroughly and automatically mixed by bubbles of vapor passing upward through it. On returning the liquid to the bulbs, one is then certain that the vapor pressures observed are those of the whole mixed portions of liquid. Error from parallax was negligible, because it was suffered alike by each limb of the confining liquid within the isoteniscopes; this was tested also by the very close agreement of two isoteniscopes in the bath under like conditions.

The most important single source of error remaining was the constant movement of the manometric liquid in the isoteniscopes. In Table I, Col. 5, is shown the amount of movement that would be caused by a variation of 1° in the bath temperature.

TABLE I

COLLECTED USEFUL DATA

Liquid	Temp. expt., °C.	Density at the b. p., g. per cc.	Factor, mm. liquid to mm. Hg	At normal boiling point p in mm. liquid	
				dp/dt, mm. liq.	dt/dp liq., °C.
Acetic acid	117.5	0.94	0.069	346	0.0029
Bromine	58.8	2.98	.219	115	.0087
Carbon tetrachloride	75.0	1.48	.109	213	.0047
Benzene	79.4	0.81	.060	392	.0026

Actually, by adjustment of the rheostat and making the reading in the manner described, the error of reading the pressure difference at the boiling points was probably not greater than ±1 mm. At room temperature these fluctuations were entirely absent. Temperature variation was significant only on account of this "pumping" effect. The actual temperature of the bath was of importance secondary to that of its constancy of temperature. Traces of impurity, if present in both samples in the same amount, produce no appreciable effect on the differential vapor pressure readings. Minute differences in the amount of impurity in the samples contained in the two isoteniscopes, however, produce considerable effect. Except in the case of bromine there was a possibility of absorption of moisture in transferring the liquids to the isoteniscopes. A greater source of error was the possible presence of permanent gases, even after boiling out and comparing the isoteniscopes at room temperature. Any traces of gas dissolved in the liquid or adsorbed on the inner walls of the isoteniscopes would tend to enter the vapor phase during the heating. Any such accumulation in B would be removed when it was boiled out just before the insertion of A, but in A the heating was of necessity deferred until the readings were to be made and the accumulating gas would cause a gradual increase in the apparent vapor pressure of A as compared to B. This was an error of the second order in all experiments but benzene (a), which was continued for ten hours. In this case a gradual increase of pressure amounting to 0.1 mm. of mercury was noted. Though nearly within the experimental error from other sources, it appeared to be quite definite, and could be accounted for by the liberation of only 0.004 cc. of permanent gas.

Table II

Experimental Details for Acetic Acid

Temp., 117.5°; period of heating B, 4 hrs., 50 min.

Time elapsed since insertion of A		Vapor pressure diff. obs.		Diff. in b. p. indicated, °C.
Hrs.	Min.	Mm. liq.	Mm. Hg	
	9	−6	−0.41	+0.017
	12	−4	− .28	+ .012
	8	−2.5	− .17	+ .007
	21	−2.5	− .17	+ .007
	33	−2.5	− .17	+ .007
2	42	−2.0	− .14	+ .006
4	10	−2.5	− .17	+ .007

Results

Detailed experimental data are reported in only one instance for purpose of illustration. The results for all liquids are summarized in Table III. Information not readily tabulated is given under the heading of each liquid. The observations of pressure difference are given to the nearest 0.5 mm., as in some cases, notably those of bromine and carbon tetrachloride, this refinement of measurement has probably some significance, due to a diminished amount of pumping. The time required to heat the bath to the boiling point of the liquid varied from fifteen minutes in the case of bromine to eighty minutes in the case of acetic acid. The period of heating was not considered to have started until the boiling point was attained.

Acetic Acid.—The purity of this material has been discussed. Experimental details are shown in Table II. The pressure difference observed indicated that the more recently heated portion possessed a vapor pressure 0.17 mm. of mercury lower than that heated for about five hours. This is in the direction suggested by Baker's results, but there was no change in this difference over a period of four hours, at which time the thermal history of the two samples was more nearly similar.

Bromine.—This was prepared from recrystallized potassium bromide and purified by the method of Robinson and Briscoe.[12] It was then dried in contact with fused calcium bromide prepared from a portion of the pure bromine. The isoteniscopes were in this case sealed to the drying tube,

[12] Robinson and Briscoe, *J. Chem. Soc.*, **127**, 142 (1925).

after which the system was evacuated and allowed to stand for a week. Finally 5 cc. of bromine was distilled into each isoteniscope, which was then sealed off, the tip being later broken after connection to the vacuum system. The desirability of this method of treatment is reflected in the results. The bromine used had not been elevated above room temperature for three months previous to the experiment; vapor pressure 760.5 mm. at 58.8°. Isothermal distillation indicated a very high order of purity. There was no difference observed between the pressures of the two samples and no change in this condition over a period of four hours.

Carbon Tetrachloride.—The original liquid boiled at 76.6° within a range of 0.05°. The middle portion was retained and kept for eighteen months in contact with metallic calcium. This was an early experiment, completed before the disturbing effect of fractionation had been observed. In this case, instead of evaporating all the liquid from both bulbs immediately before making the comparison, B was not allowed to boil out, while A of necessity boiled out completely on immersion. No test of purity by isothermal distillation was made.

Benzene.—A high quality commercial product was shaken successively with sulfuric acid, sodium hydroxide and water, and dried over fused calcium chloride. On distillation it boiled at 80.1°. It then stood for twenty-two months at room temperature, for twenty months in contact with metallic calcium and for two months with sodium. Experiment (a) showed a higher vapor pressure in the more recently heated portion, amounting approximately to 0.3 mm. of mercury. The experiment was

TABLE III

SUMMARY OF EXPERIMENTAL WORK

1 Liquid	Acetic acid	Bromine	CCl_4	Benzene	
				(a)	(b)
2 Time liquid in A had remained at room temp., months	2.5	3	18	22	22
3 Time liquid had been held at the boiling point, hours	4.8	4.0	4.5	4.5	19.1
4 Time required for A to attain temp. equilibrium with bath, minutes	12–18	5	6	5	5
5 Duration of expt. after insertion of A, hours	4.2	3.4	0.5	10.0	0.3
6 Av. press. diff. for 15 minutes, mm. liquid first	−2.5	0.0	−1.0	+4.1	+0.8
7 Av. press. diff. for later observations, mm. liquid	−2.3	+0.1	−1.0	+5.8	+0.5
8 Change of press. diff. between 6 and 7, mm. Hg	+0.014	+0.022	0.000	+0.102	−0.018
9 Change in b. p. indicated by 8 in °C	0.0006	0.0009	0.0000	0.0043	0.0008

continued for ten hours, the difference increasing to 0.4 mm. As it was suspected that the original vapor pressure difference was caused by an impurity, both portions of the benzene were subjected to isothermal distillation. The sample contained in isoteniscope B showed good agreement with the other results for benzene, while that in A showed distinctly greater impurity (probably permanent gas). In order to see if this difference disappeared with equally pure samples, experiment (b) was performed. In this experiment the difference in vapor pressure amounted to only 0.06 mm. of mercury, and isothermal distillation showed almost identical curves for the samples in the two isoteniscopes.

Discussion

The following four points (Table III) are most pertinent to the question of whether the phenomenon reported by Baker has any influence on ebullioscopic determinations.

(1) All liquids had been standing at room temperature for a considerable time before being used, thus assuring attainment of the equilibrium for that temperature.

(2) Except in the case of acetic acid, the isoteniscope which had been plunged into the hot bath gained the temperature of the bath in six minutes or less.

(3) The difference in pressure observed varies in direction, suggesting that it is fortuitous. In benzene (a) the difference was accounted for by an impurity found in one of the isoteniscopes. In acetic acid the difference would amount to only 0.007° difference in boiling point. The striking contrast of this result with Baker's is shown in Table IV.

TABLE IV

COMPARISON OF RESULTS WITH ACETIC ACID

Temp. of obsn., °C.	Pressure difference Mm.	In percentage of satn., press., %	Corresponding temp. diff., °C.	Observer
20	2	17	3	Baker
117.5	0.17	0.002	0.007	Wright and Menzies

(4) In all cases but benzene (a) there was no perceptible change in the pressure difference produced by continued comparison over a period of time. The case of benzene (a) has been accounted for by a gradual accumulation of permanent gas.

Summary

To determine whether the boiling point of a liquid is altered by prolonged heating at the boiling point, an apparatus was constructed which allows a direct differential vapor pressure measurement to be made upon two samples of a liquid, one sample having been kept at the boiling point for several hours, the other elevated to the boiling point from room tem-

perature immediately before making the observation. Isothermal distillation within the apparatus furnishes a very sensitive test for the purity of the liquid. As the result of observations made on acetic acid, bromine, benzene and carbon tetrachloride, it may be concluded that the vapor pressure of a sample of liquid rapidly elevated to the boiling point is identical with that which it exerts after remaining for several hours at the boiling point. Delay in attaining internal equilibrium is therefore not a factor of influence in the measurement of boiling point or vapor pressure of these liquids, and observations may be made as soon as temperature equilibrium is established.

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[CONTRIBUTION NO. 38 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

THE KINETICS OF THE POLYMERIZATION OF VINYL ACETATE

BY HOWARD W. STARKWEATHER AND GUY B. TAYLOR

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Vinyl acetate forms high polymers on heating alone or in solution, with or without a catalyst.[1] The present investigation indicates that the probable mechanism of the process from monomer to polymer is a type of chain reaction.

The rate of polymerization was observed by measuring the contraction in volume. A linear relation was established between percentage contraction on the original volume of the monomer and the degree of polymerization by density measurements and by evaporating mixtures of monomer and polymers to constant weight, the polymers being nonvolatile.

Apparatus

Dilatometers similar to those used in measuring the thermal expansion of liquids were constructed, consisting of bulbs of 18 mm. tubing and approximately 20 cc. capacity, sealed to straight tubes 4–7 mm. in diameter. The straight tubes were graduated in per cent. Those made from the smaller tubing could be read to 0.02% and the larger one to 0.05%. The thermostats for heating the dilatometers consisted of three large tubes equipped with condensers and filled with boiling benzene, water and toluene. The temperatures of the different baths at the position of the dilatometer bulbs as determined by calibrated thermometers were 82, 101 and 111°.

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[1] H. Staudinger, K. Frey and W. Starck, *Ber.*, **60**, 1782–92 (1927); Whitby, McNally and Galley, *Trans. Roy. Soc. Can.*, **22**, 27–32 (1928). There are also numerous patents on the subject.