TABLE L.—BOILING POINTS OF MIXTURES OF CHLOROFORM AND TOLUENE. BAR. PRESSURE, 743.7 ± 2 mm.

Molar % $CHCl_3$.	Boiling point.
0	108.92°
7.86	103.58
15.96	98.72
25.46	93.38
34.64	88.30
43.33	83.94
54.44	78.17
64.66	73.65
74.70	69.67
86.54	65.35
100	61.33

TABLE LI.—BOILING POINTS OF MIXTURES OF ACETONE AND TOLUENE. BAR. PRESSURE, 751.3 ± 0.2 mm.

Molar % $(CH_3)_2O$.	Boiling point.
0	109.43°
14.99	88.28
34.63	74.93
51.42	68.77
65.98	64.37
78.71	61.22
89.99	58.71
100	56.50

Summary.

A method and apparatus are described for determining the composition of vapors in equilibrium with liquid mixtures; the method is rapid and requires no special experience on the part of the manipulator. Also, results of measurements are given for the following four cases: Carbon disulfide—carbon tetrachloride, chloroform—toluene, acetone—toluene, and ethyl iodide—ethyl acetate. These data were needed here in connection with a study of fractional distillation, and the measurements were therefore carried out isopiestically, under ordinary atmospheric pressure.

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WORCESTER, MASS.

[CONTRIBUTION FROM THE W. GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE FREEZING POINT OF BENZENE AS A FIXED POINT IN THERMOMETRY.

BY THEODORE W. RICHARDS AND JOHN W. SHIPLEY.

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The transition temperatures of hydrated crystalline salts probably afford the most convenient and exact means of fixing points on the thermometric scale between 0° and 100° C. A number of these have been determined in this laboratory, chief among which are the transition temperature for sodium sulfate,[1] the dekahydrate of sodium chromate into hexahydrate and into tetrahydrate,[2] the dihydrate of sodium bromide into the anhydrous salt,[3] the transition of manganese chloride from the tetra-

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[1] Richards, *Am. J. Sci.* (1898); Richards and Wells, *Proc. Am. Acad.*, **38**, 431 (1902).

[2] Richards and Kelley, *Ibid.*, **47**, 171 (1911); THIS JOURNAL, **33**, 847 (1911).

[3] Richards and Wells, *Proc. Am. Acad.*, **41**, 435 (1906).

hydrate into the dihydrate,[1] and the transition of dekahydrated sodium carbonate into the heptahydrate.[2] These points are perfectly definite, subject to no appreciable change by ordinary changes in atmospheric pressure, and usually involve considerable latent heat of transition. Most of them are easily reproducible. For these reasons they are very useful in calibrating thermometers.

The use of the freezing points of liquids for determining fixed points on the thermometric scale probably comes next to transition temperatures in regard to convenience. Freezing points, like transition temperatures, are more constant than boiling points, because the influence of change in atmospheric pressure is usually negligible. On the other hand, however, the purity of the substance chosen becomes a very important issue.[3] Most liquids (except water and mercury) are very difficult to prepare in a pure state; and volatile impurities which scarcely affect the boiling point may very seriously change the freezing point. For this reason, the transition temperatures of pure salts are often preferable; such a substance as sodium sulfate is very easily purified by crystallization.

In other respects the errors to which the two types of equilibrium are subject are very similar. Both are liable to supercooling or superheating in the hands of the incautious experimenter; but in both, these sources of error are easily and completely eliminated by the use of plenty of each phase concerned, by proper protection of the system from gain or loss of heat with the help of an air-jacket and a like surrounding temperature, and by adequate but not too violent stirring. In both, the point is sharper and more accurate the greater the latent heat of melting. This is not only because outside heating or cooling is more quickly taken up, when this is large, but also because the influence of foreign substances on the freezing point is inversely proportional to the latent heat of fusion, provided that the crystals are uncontaminated by solute. This is expressed by a transposition of the well-known equation of van't Hoff, $\Delta T = RT^2/Mwl$, which gives the depression produced by 1 gram of dissolved substance of molecular weight M dissolved in w grams of solvent having a latent heat of fusion l per gram. The following table, therefore, shows that, whereas benzene is a good substance for this purpose, such substances as cyclohexane and cyclohexanol (especially the latter) are very unsuitable.

LATENT HEAT OF FUSION OF FOUR SUBSTANCES.

Water	79.8	cal. per gram
Benzene	30.1	cal. per gram
Cyclohexane	8.8	cal. per gram
Cyclohexanol	2.94	cal. per gram

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[1] Richards and Wrede, *Ibid.*, 43, 343 (1907) (Univ. of Berlin).

[2] Richards and Fiske, THIS JOURNAL, 36, 486 (1914).

[3] Landolt, "Über die genaue Bestimmung des Schmelzpunktes organischer Substanzen," *Z. physik. Chem.*, 4, 349 (1889).

The presence of 0.001% of water lowers the freezing point of cyclohexanol by 0.02°,[1] whereas the same amount of this impurity affects the freezing point of benzene by less than 0.002°.[2]

Another property adds to the satisfactory nature of benzene for this purpose, namely, the possibility of freeing it from most of its impurities by fractional crystallization or freezing. Thiophene, it is true, cannot be separated in this way, but this impurity may easily be removed chemically. On the other hand, paraffin hydrocarbons, olefines, acetone, and most other impurities are quickly eliminated from the successive crops of crystals.

The fact that the melting point of these crystals is 5.5° above that of water—just the length of the usual Beckmann scale—makes it an especially useful fixed point, for, with the help of these two melting points, any such thermometer may be easily standardized, and then, with the help of the well-known correction factor, used with confidence at any other temperature—provided that due precautions be taken for correcting the result for the temperature of the exposed thread.

For these reasons it seemed to us worth while to make a careful study of this point, especially because the published work of others is conflicting with regard to it. Paterno[3] gives three values, 5.53°, 5.55°, and 5.48°, while Lachowicz[4] gives 5.42°, and Young,[5] 5.58°. The discord among these and other values is probably due to inaccurate thermometry.

As many of the observers were principally concerned with the purity of their benzene rather than with its absolute freezing point, the constancy of the melting temperature and not its exact value was all that was needed, but of course for other purposes the exact point must be known.

Dr. F. Barry, in 1910, and Dr. H. S. Davis, in 1913, under the direction of one of us, prepared benzene in a very pure state in order to determine its heat of combustion as a standard of comparison for other organic substances. Their final values, as determined by our best thermometers, were 5.484° and 5.486°, respectively. These results were entirely independent, as the necessary corrections had not been applied to the earlier thermometric readings when the later ones were made. Both experimenters determined the ice point on standard thermometers immediately after taking the melting point of the benzene. Neither of these investigations have as yet been published, but they will soon appear in print.

From this earlier work it was apparent that the true freezing point of

[1] Richards and Shipley, in a research as yet unpublished.

[2] Hertz, *Ber.*, **31**, 2669 (1898).

[3] Paterno, *Gazz. chim. ital.*, **27**, I, 481–536 (1897).

[4] Lachowicz, *Ber.*, **21**, 2206 (1888).

[5] Young, *Proc. Roy. Soc. Dublin*, **12**, 31, 385 (1910); *Trans. Chem. Soc.*, 40, 486 (1899). Professor Young, in private correspondence, has stated that not much pains had been spent upon thermometric precautions in his work. We are much obliged to him for the trouble he has taken in consulting his original records.

benzene probably lies between 5.48° and 5.50° with indication of the value 5.485°; yet more exhaustive work was needful in order to permit its use as a fixed point in thermometry. For this purpose we deemed it advisable to obtain benzene from two entirely different sources. Commercial "C. P." benzene procured from the distillation of a Pennsylvania coal-tar was the starting point for one preparation, and another specimen consisted of benzene prepared synthetically from benzoic acid by a well-known German firm. The two samples were carried through the same process of purification as follows:

(*a*) About 600 cc. of the benzene were shaken with clean mercury. No darkening of the surface of the mercury was observed.

(*b*) The benzene was next shaken on a shaking machine (about 2.5 hours each time) with six successive quantities of concentrated sulfuric acid. The acid was deeply blackened by the first four treatments, indicating the presence of substances charred by the action of strong acid, but the last two showed only a slight yellow coloration.

(*c*) The benzene was next washed with two quantities of water and then shaken out with a concentrated solution of sodium hydroxide, followed by two more washings with water.

(*d*) Following this came another shaking out with mercury for about four hours. A considerable blackening of the surface of the metal was observed.

(*e*) After washing several times with water, the benzene was dried over calcium chloride and sodium and distilled. Almost all of the product came over within 0.05°; that fraction distilling between 80.15° and 80.18° (uncorrected) was preserved for further purification.

(*f*) The benzene was next recrystallized in porcelain, the coal-tar product six times, the synthetic five, and the fractions were preserved over sodium in glass bottles kept in the dark. The sodium was freshly cut and allowed to stand for some time in the mother liquor of the second crystallization before being put through the sodium press.

Before determining the freezing point of the purified samples of benzene, the excellent Beckmann thermometer to be used was carefully compared with a standard instrument, Baudin No. 15200, which had been standardized by the Bureau International des Poids et Mesures in Paris, and frequently used for the most accurate thermometric work in this laboratory.[1] The Beckmann thermometer (P. T. R. 31827) was graduated in hundredths and covered a scale of six degrees, the length of a degree being 3.8 cm. It had been calibrated by the Physikalisch-Technische Reichsanstalt, Berlin, in 1907. The comparison of the instruments was carried out in collaboration with Dr. T. Thorvaldson, to whom we wish to express our gratitude for his kind assistance. The thermometers were compared at

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[1] See *Proc. Am. Acad.*, **38**, 434 (1902); *Z. physik. Chem.*, **443**, 467 (1903).

two points: the ice point of benzene and the ice point of water. The benzene used was commercial C. P. benzene distilled and dried over sodium. Since the determinations were for comparative purposes only, the purity of the benzene was not yet in question, but the ice point of water was, of course, carefully determined immediately afterwards under precisely parallel conditions.

The readings were taken immediately after vigorous stirring of the mixture and the two thermometers were read practically simultaneously. The measurement of the temperatures was carried out in accordance with the precautions pointed out by one of us in a recent publication.[1]

In this way it was found that a range of 5.125° on the Beckmann corresponds to 5.104° as read on the corrected standard Baudin; or 1.000° as read on the former over this range of temperature corresponds to 0.9958° on the hydrogen scale. This was essentially the value given by the Reichsanstalt for this thermometer under these conditions.

The Beckmann apparatus was used in the freezing point determinations, about 30 g. of substance being employed. The apparatus was swept with a current of air dried with sulfuric acid and the benzene was distilled directly into the apparatus through the side tube, the thermometer and stirrer being already in place. The first third of the distillate was rejected. During the distillation, as well as during the determination, a slow current of dry air was allowed to pass in through the side tube, thus preventing the access of moisture from the atmosphere. Such contamination was especially liable to happen during the operation of stirring. The benzene-ice was present in varying quantities and conditions. The most satisfactory mixture was obtained by subcooling the liquid several degrees, and then, by vigorous agitation, producing a large crop of finely divided crystals. It was found, however, that so long as plenty of crystals were present, the outside bath was not too cold, and adequate stirring was employed, the same constant freezing point was obtained with both finely divided and large crystals. The purity of the benzene was indicated by the constancy of the freezing point with diminishing proportion of mother-liquor, as the freezing progressed. Great constancy was observed in the fifth and sixth crystallizations of the coal-tar product, and in the fourth and fifth of the synthetic benzene.

Immediately after determining the freezing point of benzene, the ice point of water was taken in the same apparatus. Freshly distilled water was boiled and frozen under a variety of conditions; constant results were obtained with the same precautions as in the case of benzene; and this outcome was confirmed by the immersion of the instrument in a large bath of pure ice and water.

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[1] Richards, "The Measurement of Temperature in the Operations of Analytical Chemistry," *Orig. Comm. 8th Congress of Applied Chem.*, 1912.

The ice points of water and benzene were thus observed in the same apparatus in the same way and with the same depth of immersion of the bulb and the same length of mercury column exposed to room temperature. The only stem correction necessary was that for the difference between the room temperature and the temperature of the freezing point of benzene, applied to the number of degrees between the ice point of water and of benzene.

The samples used in each trial were as follows:

A. Coal-tar benzene, 5th recrystallization
B. Coal-tar benzene, 6th recrystallization
C. Synthetic benzene, 4th recrystallization
D. Synthetic benzene, 5th recrystallization
E. Coal-tar benzene, 5th recrystallization

Table I summarizes the results with the Beckmann thermometer P. T. R. No. 31827.

TABLE I.

Sample.	Constant Beckmann reading.	Ice point.	Difference.	Total correction.[1]	True temp.
A............	5.822	0.300°	5.522	—0.038	5.484°
B............	5.821	0.300°	5.521	—0.038	5.483°
C............	5.772	0.249°	5.523	—0.038	5.485°
D............	5.772	0.249°	5.523	—0.038	5.485°
E............	5.760	0.237°	5.523	—0.038	5.485°
				Average =	5.484°

Trials A and B were made on the same day; C and D were made about four weeks afterward; and E was made yet three weeks later. These tests show: first, that the coal-tar material (A, B and E) was essentially identical (at least as regards melting point) with the synthetic material; and secondly, that further recrystallization caused no change in the value. Hence, the presumption is that these results give the true value corresponding to the pure substance.

Although these results are very concordant and indicate that the freezing temperature of benzene affords an accurate point for thermometric work, it was deemed advisable to take a series of observations directly on a Baudin standard instrument, in order to verify the absolute value of the above series of results. A shorter wide test tube was substituted for the inside tube of the Beckmann apparatus, and through the cork of this test tube passed the Baudin thermometer, No. 15200, and a narrower tube for the stirrer. This latter had a side arm, through which a current of dry air passed during the determination. The tube was submerged in the cool outside bath to within 0.5 cm. of the bottom of the cork, and the

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[1] This correction was in each case —0.023 for the fundamental interval (1.000° on the thermometer = 0.9958 true degrees) and —0.015 for the 5.50 stem exposed to the constant room temperature 23° or —0.038 in all.

reading of the Baudin was made through the glass almost at the surface of this bath. By this means the necessity for any stem correction was obviated. The ice point of water was taken immediately afterwards in the same apparatus with the same precautions. Four determinations were made on three successive days, the last two being made on the same day. The readings were verified in each case by Dr. Thorvaldson. In Table II, each observed reading listed is the average of a number of independent observations not varying between the extremes by more than 0.003°. The barometer readings for three days varied by only 3 mm., the readings being 763 mm., 762 mm., and 765 mm., respectively. Since the bulb of the thermometer was immersed to the same depth in each determination, the effect of the exterior pressure was identical in all four cases. The conditions of the experiments were so chosen that all other corrections were necessarily invariable.

TABLE II.

Corrections to be Applied.

	At ice point benzene.	At ice point water.
Calibration	+0.023	+0.002
Interior pressure	+0.015	+0.009
Exterior pressure	—0.001	—0.001
Fundamental interval	+0.004	±0.000
Stem	±0.000	±0.000
Total correction	+0.041°	+0.010

Final Readings, Observed and Corrected.

	Benzene.			Water.		
Determination.	Observed melting point.	Corr.	Corr. reading.	Observed ice point.	Corr.	Corr. reading.
F	+5.688°	+0.041°	5.729°	0.208°	0.010	0.218°
G	5.686°	+0.041°	5.727°	0.207°	0.010	0.217°
H	5.688°	+0.041°	5.729°	0.207°	0.010	0.217°
I	5.689°	+0.041°	5.730°	0.207°	0.010	0.217°

Determination.	Benzene melting point corr. reading.	Water ice point corr. reading.	F. pt. benzene.	Hyd. scale corr.	F. pt. benzene hyd. scale.
F	5.729°	0.218°	5.511°	—0.030	5.481°
G	5.727°	0.217°	5.510°	—0.030	5.480°
H	5.729°	0.217°	5.513°	—0.030	5.482°
I	5.730°	0.217°	5.513°	—0.030	5.483°
				Averages	5.482°

This compares very satisfactorily with the values previously found, as follows:

	Average values.	Variation from mean.	Maximum variation between extremes.
Beckmann	5.484°	0.001	0.002
Baudin	5.482°	0.002	0.003

The true freezing point of benzene may then be safely taken as 5.483°. This is only 0.001° different from the result of Barry, and 0.003° different from the latest and best trials of Davis.

The wide deviations of others are probably to be referred chiefly to doubtful thermometry, for benzene is evidently not very difficult to obtain in a pure state.

These experiments show that the freezing point of pure benzene, 5.483°, is attained so easily that it may be used as a very satisfactory fixed point in thermometry; and taken in connection with the freezing point of water, about 5.5° below, may afford an excellent means of fixing two points on a Beckmann thermometer.

The authors are glad to express indebtedness to the Carnegie Institution of Washington for generous support in this investigation.

Summary.

The results of this research may be summed up as follows:

(1) Benzene pure enough for the purpose in hand is not difficult to prepare.

(2) With due precautions in the thermometric measurements a very definite freezing point is given by benzene. The true value is determined by constancy after repeated fractional crystallization.

(3) The freezing point of benzene is 5.483° ± 0.002° on the international hydrogen scale.

(4) This fixed temperature may be advantageously used, in connection with the ice point of water, for calibrating Beckmann thermometers. Especial attention must be paid to the temperature of the exposed column in correcting this interval for use at other temperatures.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

ON THE ABSORPTION OF GLUCOSE BY BONE-BLACK.

[PRELIMINARY COMMUNICATION.]

BY HAROLD A. MORTON.

In connection with a study of the mutarotation and specific rotatory power of the sugars, I have been obliged to purify a considerable quantity of glucose. Using bone-black as a decolorizer, I observed that a surprisingly large quantity of the sugar was extracted by the bone-black from the aqueous solution. It appeared interesting to investigate the phenomenon systematically, the question being whether the partition of the sugar does not follow some simple principle, like the distribution law.

Preliminary experiments soon indicated that at ordinary temperatures the process of absorption is exceedingly slow, and that, to obtain results within a reasonable time, it would be best to employ a temperature of about 80°. In the experiments described below, a Freas constant tem-