TABLE II (Concluded)

Com-pound	Thorium, % Calcd.	Found	Bromine, % Calcd.	Found	Nitrogen, % Calcd.	Found	Calcd.	Found	CH₃COOC₂H₅, % Calcd.	Found	Atomic ratios Th:Br	H:C
6	31.89	31.92	43.92	43.79					24.18	24.36	1 : 3.98	
		32.12		43.12						24.34	1 : 3.99	
									C₆H₅COOC₂H₅, %			
7	23.17	23.00	31.91	32.48					44.92	44.19	1 : 4.10	
		23.74		32.48						44.54	1 : 3.97	
									C₆H₅CHO, %			
8	36.49	36.64	25.06	25.48	2.19	2.26	26.33	26.82	33.23	27.51ᵃ	1 : 2.02	1 : 0.99
		36.13		25.86		2.35		26.15		27.21	1 : 2.07	1 : 0.94
9	23.79	25.22ᵇ	32.76	34.05					43.45	39.25	1 : 3.84	
		25.60		33.83						39.75	1 : 3.93	
									C₆H₅NH₂, %			
10	25.12	25.05	34.61	35.55					40.27	40.15	1 : 4.12	
		25.61		35.58						39.70	1 : 4.03	
									C₆H₅N, %			
11	29.42	28.47	40.52	41.15					30.04	28.59	1 : 4.19	
		28.32		41.07						28.86	1 : 4.21	

ᵃ The low percentage of benzaldehyde found is likely due to its conversion into benzoic acid.

ᵇ The analyses of (9) indicate that the bromine was being displaced slowly at room temperature.

Summary

With certain organic liquids, anhydrous thorium tetrabromide reacts only to form molecular compounds up to temperatures as high as the boiling points of the respective solutions. The following compounds were formed with this class of liquids: $ThBr_4 \cdot 4C_2H_5OH$, $ThBr_4 \cdot 2CH_3COOC_2H_5$, $ThBr_4 \cdot 4CH_3CN$ and $ThBr_4 \cdot 3C_5H_5N$.

Anhydrous thorium tetrabromide reacts with other organic liquids to form molecular compounds at room temperature, but at the boiling point of the solutions other reactions ensue and in several cases hydrated thoryl bromide organic complexes were formed. The formulas of such substances are: $ThBr_4 \cdot 4C_6H_5CHO$, $2ThBr_4 \cdot 7C_6H_5COCH_3$, $ThBr_4 \cdot 4C_6H_5NH_2$, $ThOBr_2 \cdot 2C_6H_5CHO \cdot H_2O$, $ThOBr_2 \cdot 0.5C_6H_5COCH_3 \cdot H_2O$ and $ThOBr_2 \cdot 0.5C_6H_5COC_2H_5 \cdot 2H_2O$.

Ethyl benzoate and thorium tetrabromide form the molecular compound $ThBr_4 \cdot 3C_6H_5COOC_2H_5$ at room temperature but at the boiling point of the solution a reaction takes place: $ThBr_4 + 4C_6H_5COOC_2H_5 = (C_6H_5COO)_4Th + 4C_2H_5Br$.

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The Transition Point of Carbon Tetrachloride as a Fixed Point in Thermometry. The Melting Point. Heats of Transition and of Fusion

BY HERRICK L. JOHNSTON AND EARL A. LONG

The existence of an allotropic change in solid carbon tetrachloride, under atmospheric pressure, was first observed by Goldschmidt[1] who reported a change from "doubly refracting" to "optically isotropic" crystals at about 45° below zero centigrade. Latimer[2] set the temperature of transition at approximately −48.5°. More recently, McCullough and Phipps,[3] who describe the transition as a change from monoclinic crystals (low temperature) to cubic crystals (high temperature) reported the transition point at −48.54 ± 0.02°. They claimed that this point was constant and reproducible and recommended its use as a fixed point in thermometry. However, Skau and Meier,[4] who criticize the temperature scale of McCullough and Phipps, were unable to confirm the results of these earlier authors. Skau and Meier obtained a mean value of −47.55 ± 0.12° for the transition and reported variations between successive determinations of as much as 0.2°. Both McCullough and Phipps and Skau and

(1) V. M. Goldschmidt, Z. Krist., 51, 26 (1913).
(2) Latimer, THIS JOURNAL, 44, 90 (1922).
(3) McCullough and Phipps, ibid., 50, 2213 (1928).
(4) Skau and Meier, ibid., 51, 3517 (1929).

Meier determined the transition point from cooling and heating curves and their temperature scales were established by calibration at a few fixed points.

In view of this wide disagreement it seemed to us worth while to repeat the measurements by a more accurate procedure and, at the same time, to devise a method for the practical utilization of the transition in thermometry.
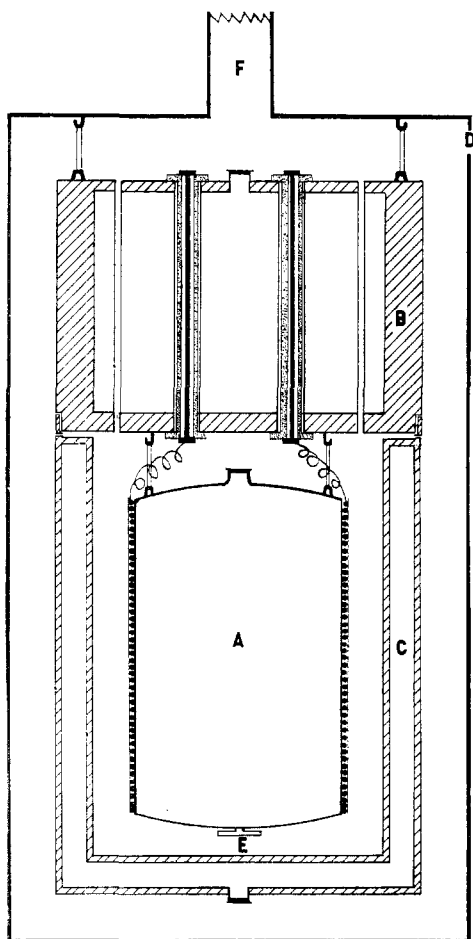

Fig. 1.—Diagram of apparatus: A, thin-walled copper calorimeter (64 cc. capacity) which contained the purified carbon tetrachloride (twelve thin radial copper vanes, not represented in the diagram, promoted rapid thermal equilibrium); B and C, hollow copper "blocks" filled with loose copper turnings and with commercial carbon tetrachloride; D, vacuum-tight outer container; E, thermocouple well; F, connection to high vacuum and tube for the introduction of electrical leads.

Apparatus and Procedure.—The apparatus used was a modified Nernst vacuum calorimeter which was similar, in its essential features, to

those developed by Giauque and co-workers.[5] Its principal features are shown diagrammatically in Fig. 1.

It was our practice to first cool the carbon tetrachloride in "A" to a temperature well below the transition[6] with the aid of a carbon dioxide–ether mixture which surrounded "D" and with hydrogen admitted to the vacuum spaces surrounding "A" and "B-C"; then to pump out the hydrogen (down to a pressure of 10^{-5} mm. or better) replace the carbon dioxide–ether mixture with a suitable cryostat bath and warm the calorimeter and blocks just to the transition. A further quantity of heat (sufficient to transform about half of the commercial carbon tetrachloride in "B" and "C") was then supplied to the blocks and a predetermined quantity of energy was likewise supplied to the pure carbon tetrachloride in "A." The entire system was then allowed to stand until temperature readings taken on "A" indicated that thermal equilibrium was fully attained. This ordinarily required several hours.[7]

Temperature Scale.—The temperature of the calorimeter, "A," and the final reported values for the transition point and melting point were determined by means of a sensitive copper resistance thermometer of No. 40 B. and S. gage copper wire wrapped tightly, and bakelited, on the outer surface of "A." The resistance thermometer, which also served as a heater during calorimetric measurements, was calibrated in place against a standard copper–constantan thermocouple whose junction was soldered into the copper well "E." Our standard thermocouple[8] was itself calibrated, indirectly, to the nearest 0.01°, as follows: (1) against the hydrogen scale of Giauque, Buffington and Schulze[9] using their method;[10] and (2) against

(5) In particular, cf. Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928), and Giauque and Johnston, ibid., **51**, 2300 (1929), where a fuller discussion is given of the treatment of the data.

(6) Like Skau and Meier (Ref. 4) we observed the presence of supercooling. Under the conditions pertaining to our own cooling process the carbon tetrachloride normally supercooled to a temperature about 3° below the transition without any noticeable break in the cooling curve; then, quite abruptly, the temperature would cease falling and would rise, within a few seconds, to the transition point, where it would remain during the several minutes necessary to remove the heat of the transformation.

(7) Early measurements demonstrated that equilibrium (to within 0.01 or 0.02°) was not attained within the first two or three hours.

(8) In the course of the investigation two thermocouples were employed. The first thermocouple which we used gave reproducible values of the melting and transition temperatures throughout the entire period of its use and gave consistent comparisons against the resistance thermometer but it was subsequently discovered that it had experienced a permanent injury—apparently at the time that it was introduced into the apparatus—which produced a definite, although fixed, variation in its readings. For this reason a second thermocouple was installed and was employed as the basis for the resistance thermometer calibration during the final runs. However, the consistent intercomparisons of the resistance thermometer with the injured thermocouple during the period that the latter was in use, and the reproducibility of the thermocouple at the transition and at the melting points permitted us to give full weight to the data taken with the resistance thermometer during the several months prior to its correct calibration.

(9) Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

(10) Our standard couple, identified by our laboratory designation as "couple A," was compared in our laboratory, at 5° intervals, with a standard couple calibrated in Berkeley by Greensfelder and Milner [cf. Greensfelder and Latimer, THIS JOURNAL, **50**, 2205 (1928)] directly in terms of the University of California scale.

the temperature scale of the United States Bureau of Standards.[11] The freezing point of mercury as determined by this couple was within 0.03° of that reported by the "International Critical Tables." The values here reported are, we believe, probably correct to within 0.03° but the accuracy claimed, in view of the indirectness of the calibrations, is 0.05°.

Purification of the Carbon Tetrachloride.—As starting material we employed Mallinckrodt "reagent quality" carbon tetrachloride whose label showed 0.02 of 1% of carbon disulfide by analysis. This was subjected to fractional distillation through a Loveless column.[12] The middle portion of the distillate was collected and redistilled in three successive fractionations. The middle fraction from the last distillation boiled within a range[13] of 0.001°.

This final middle portion was then twice fractionally recrystallized in an atmosphere of nitrogen, the product of the first recrystallization being centrifuged. The final sample was preserved in a sealed tube of Pyrex glass.

The Transition Point.—Table I is the record of a typical run.[14]

TABLE I

SAMPLE DATA IN THE DETERMINATION OF THE TRANSITION POINT OF CARBON TETRACHLORIDE

(Run IX, 25% of the carbon tetrachloride transformed to the high temperature form.)

Date and hour	T, by Couple A, °C.	T, by res. therm., °C.
4/4/33 9:30 A. M.	(Heated into transition)	
11:00 A. M.	−47.65	−47.655
1:00 P. M.	−47.65	−47.662
2:00 P. M.	−47.66	−47.662
3:30 P. M.	−47.66	−47.662
4:45 P. M.	−47.66	−47.667
8:30 P. M.	−47.66	−47.665
Equilibrium value = −47.665°		

In all, seven successful determinations of the transition point were made over an interval of thirteen months. The amounts transformed varied between 15 and 75%, and each equilibrium was observed for nine to thirty-four hours. The mean transition temperature, as measured on the sensitive resistance thermometer,[15] was −47.661°,

(11) By comparison with our "Couple K" which itself was calibrated at 10° intervals, in terms of the Bureau of Standards scale, through the kindness of Dr. Brickwedde.

(12) Loveless, *Ind. Eng. Chem.*, **18**, 826 (1926).

(13) Measured by means of a five-junction copper–constantan thermocouple.

(14) The equilibrium value for this run is taken as the average of the last three readings by the resistance thermometer since during the last five hours of the run the readings were constant at this value to within the normal reproducibility of the resistance thermometer (± approximately 0.002° for this thermometer). The records of other runs, which were purposely extended to much longer periods than necessary, also indicated that no further change was likely.

(15) The thermocouple readings show normal fluctuations of ±0.01° due to thermoelectric effects, inhomogeneities in portions of the wire situated in temperature gradients, etc. But the *averages* of a large number of thermocouple readings at a fixed point when compared with the averages of the readings on the more constant, though more sensitive, resistance thermometer provide an excellent calibration of the latter.

with a maximum deviation of 0.006° and an average deviation of 0.003°.

As these results show, the transition in carbon tetrachloride is sharp and, with proper experimental procedure, may be used reliably for thermometric calibration. The attainment of thermal equilibrium in carbon tetrachloride is only a little less rapid than in other substances for which careful transition measurements have been made (for example, oxygen).[5]

The Melting Point.—The melting point was determined by a procedure entirely analogous to that described in the measurement of the transition. In order to avoid the presence of traces of supercooled liquid the carbon tetrachloride was always cooled below the transition and warmed back up before measurements of melting point (or of heat of fusion) were begun. One of us had previously found this procedure both necessary and effective in analogous measurements with solid oxygen.[5]

Six determinations in an interval of ten months with observations, in each instance, extended over five to twenty-two hour periods, yielded a mean value of −22.870° with a maximum deviation of 0.010° and an average deviation of 0.005°. The fraction of material in the liquid phase, in these six measurements, was likewise purposely varied between the limits of 15 and 75% but no systematic differences in the melting point were observed. A special additional determination was made with approximately 5% of the material melted, in order to have an estimate of the impurity present (it is, however, less accurate than the heat capacity method) and will be discussed in a later paragraph.

Table II compares our values for the transition and melting points with the principal values in the literature.[16]

Heats of Transition and of Fusion.—Heats of transition and of fusion were determined calorimetrically by the usual procedure of making a heat capacity determination from a temperature a little below the transformation point to a temperature a little above. In order to have accurate values for the important $\int C_p dT$ corrections we also measured total heat capacities (calorimeter +

(16) All values in the table, including our own, are based indirectly on gas thermometer scales with the assumed value for the ice point placed at or near 273.10. If conversion be made to a temperature scale based on an ice-point value of 273.20, which is preferred in the more recent publications, the freezing point temperatures should each be lowered by 0.008° and the transition temperatures by 0.017°.

TABLE II

TRANSITION AND MELTING POINTS OF CARBON TETRA-
CHLORIDE

Observer	Transition point, °C.	Melting point, °C.
This research	−47.66 (±0.05)	−22.87 (±0.05)
McCullough and Phipps	−48.54 (±0.02)	
Skau and Meier	−47.55 (±0.12)	
Timmermans, Onnes and van der Horst		−22.89 (±0.05)
Keyes, Townshend and Young[17]		−22.87
Timmermans[18]		−22.82
Skau[19]		−22.86

CCl₄, in calories per ohm) at approximately
3 to 4° intervals from about −70 to about 0°.

The values we obtained[20] are given in Table III,
which also includes the values found by Latimer.[2]

TABLE III

HEATS OF TRANSITION AND OF FUSION OF CARBON TETRA-
CHLORIDE

Transition at 225.44 °K.			Fusion at 250.23 °K.	
Temperature interval	Corr. total heat input		ΔH transition	ΔH fusion
224.52–228.66	806.09	100.76	1083.8	. . .
225.33–231.10	844.09	140.38	1081.3	. . .
225.34–226.87	737.58	36.55	1077.2	. . .
249.72–252.16	441.71	66.31	. . . .	576.8
250.16–252.82	444.89	69.98	. . . .	576.1
249.77–250.51	393.96	18.58	. . . .	576.8
249.67–252.48	451.99	75.12	. . . .	579.1
Mean values of molal ΔH			1080.8 (±3)	577.2(±1)
Latimer			1100	644

All runs were carried out with 0.6508 mole of
carbon tetrachloride in the calorimeter. Column
two gives the actual heat input corrected for all
experimental factors but not including a correc-
tion for $\int C_p dT$, given in the third column.
A small correction for premelting is also included
in the $\int C_p dT$ figures for the heat of fusion runs.
The last two columns are *molal* values.

Purity of the Carbon Tetrachloride.—The
extent of impurity present in the carbon tetra-
chloride was determined by the sensitive pro-
cedure of measuring heat capacities just below
the melting point.[21] Three special, very short,

(17) Keyes, Townshend and Young. *J. Math. Phys. Mass. Inst. Tech.,* **1**. 243 (1922).

(18) Quoted by Skau (Ref. 19) who gives the reference. *Communications Phys. Lab. Univ. Leiden,* Suppl. No. **84**, 3 (1928). However, there is apparently some error in this reference since we have been unable to locate a Supplement **84** and a Communication by Timmermans on page 3 of Supplement **64** does not give this value.

(19) Skau, *J. Phys. Chem.,* **37**, 609 (1933).

(20) In our experimental procedure, treatment of data, corrections, etc., both for the heats of transition and fusion and for the accompanying heat capacity measurements, we employed the accurate methods of Giauque and co-workers (Ref. 5).

(21) For method and symbols used *cf.* Johnston and Giauque. THIS JOURNAL, **51**, 3206 (1929); see also Clayton and Giauque, *ibid.,* **54**, 2614 (1932).

runs were made for this purpose. The accurate
heat capacity data which were taken in connection
with the corrections, and our determinations of
the melting point and of the heat of fusion, pro-
vided the other data necessary for the calculations.

The results of this analysis are given in Table
IV which also includes a value obtained from the
less sensitive method of freezing point depression.
The agreement is within the limits of error of the
latter determination, especially since the estimate
of 5% fusion is, in this case, rather rough. We
conclude that the amount of impurity present in
our sample of carbon tetrachloride did not exceed
0.001 of 1% in molar percentage.

TABLE IV

MOLE PERCENTAGE OF IMPURITY IN THE CARBON TETRA-
CHLORIDE[21]

T'	T''	Heat of pre-melting (calories)	N_1'	N_c^o	Impurity, mole per cent.
248.58	249.27	0.584	0.99237	0.99553	0.00048
247.80	248.67	.385	.98875	.99276	.00065
247.99	248.45	.138	.98964	.99176	.00046
From melting point depression (*cf.* p. 33, Col. 2)					.0017

**The Transition Point in a Carbon Tetra-
chloride–Methyl Alcohol Mixture.**—The chief
disadvantage in the use of a solid–solid transition
for thermometric calibration arises from the
difficulty in attaining good thermal contact
between the thermometer and the solid phases,
or even within the latter. This is particularly
true in non-metallic systems, where the thermal
conductivity is low. The use of a suitable liquid
in which the solid phases may be suspended at the
transition point naturally suggests itself.[22]

We were led, from consideration of relative
internal pressures,[23] to select methyl alcohol as a
suitable liquid in which to make a trial of this
procedure, with carbon tetrachloride. The re-
sults amply justified the selection.

Coleman and Bell "c. p." methyl alcohol and
Baker and Adamson "reagent quality" carbon
tetrachloride were employed for the tests, which

(22) We find that this procedure has already been suggested by Wyatt [*Trans. Faraday Soc.,* **25**, 48 (1929)], who measured the transition of CCl₄ suspended in various organic solvents. However. Wyatt's accuracy was not sufficient to preclude small variations in the temperature of transition and it seems probable that solid solution occurred in some cases [*cf.* Timmermans, *Bull. soc. chim. Belg.,* **37**, 409 (1928)].

(23) *Cf.* Hildebrand, "Solubility." The Chemical Catalog Co., New York, 1924, p. 116. Two simple criteria which the suspending medium must satisfy are: (1), that it be not too good a solvent for the solid carbon tetrachloride and (2), that it does not form a solid solution with carbon tetrachloride. The latter requirement follows from simple phase rule considerations.

were carried out in an unsilvered Pyrex Dewar of about 250 cc. capacity, surrounded by an eutectic mixture of $CaCl_2$-H_2O. A rubber stopper covered with tin foil closed the neck of the Dewar. Through this stopper projected the thermocouple tube, a hand stirrer of glass and a tube for admitting nitrogen or dry air. It was found best to employ a mixture of about 3 parts of carbon tetrachloride to 1 part of methanol, by weight, since this gave a mixture which was about 50% solid and 50% liquid at the transition point. About 75 cc. of this mixture, previously cooled into the transition, was introduced into the Dewar and slowly stirred while readings were taken on the thermocouple. Three determinations gave -47.67, -47.68 and $-47.65°$, respectively, as compared with the accurate value of $-47.66°$. The deviations are barely greater than the limits of reproducibility of the thermocouple and are certainly within the limits of error with this simple apparatus. The melting point of the carbon tetrachloride employed in these determinations was also measured in a nearly similar piece of apparatus,[24] and found to be $-22.86°$, in good agreement with our previous more accurate determination.

The work described in the preceding pages was begun with the assistance of Mr. Sidney J. Simkins, who purified the carbon tetrachloride and assembled a portion of the apparatus. We also wish to acknowledge the able mechanical

(24) Kanolt, Scientific Papers, U. S. Bureau Standards, No. 520, p. 622 (1926).

assistance of Mr. John F. Betz, who constructed the vacuum calorimeter. In particular, we wish to thank Dr. F. G. Brickwedde of the Cryogenic Division of the United States Bureau of Standards who very kindly provided us with calibrations on our thermocouples C and K.

Summary

The transition and melting points of carbon tetrachloride have been measured by an accurate procedure and found to be -47.66 (± 0.05)° and -22.87 (± 0.05)°, respectively.

The transition has also been measured in a suspension of solid carbon tetrachloride in methyl alcohol and found to be in agreement with the value given above.

Heats of transition and of fusion of carbon tetrachloride have been measured, calorimetrically, and found to be 1080.8 (± 3) cal./mole and 577.2 (± 1), cal./mole, respectively.

The purity of the carbon tetrachloride employed in the above investigations was tested by the measurement of heat capacities just below the melting point. It was found that the impurity present did not exceed 1×10^{-3} mole per cent.

The transition in solid carbon tetrachloride was found to be both sharp and reproducible. It is concluded that the carbon tetrachloride transition provides a satisfactory secondary fixed point for the calibration of thermometric instruments and a simple procedure for employing it in practical laboratory standardizations is described.

The Adsorption of Nitrogen by Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND STEPHEN BRUNAUER

Experimental research carried on by various workers[1] to ascertain the mechanism by which ammonia is synthesized from hydrogen–nitrogen mixtures over iron catalysts has culminated in the idea that the nitrogen molecules enter into some sort of adsorptive or chemical combination with the iron atoms in the catalyst surface and are thereby made capable of reacting with gaseous or adsorbed hydrogen to form ammonia.[2]

(1) See Emmett. J. Chem. Ed., 7, 2571 (1930).
(2) Frankenburger. Ullmans "Enzyklopädie der Technischen Chemie," 1928.

As yet, however, no data have been published to indicate[3] whether or not the actual rate at which nitrogen is taken up by the catalyst surface is sufficiently fast to permit this adsorption to constitute an essential step in the actual synthesis. The present work has, accordingly, been undertaken to measure (1) the rate of adsorption of nitrogen at one atmosphere pressure on active as well as on rather inactive synthetic ammonia catalysts at 200 to 450°, (2) the variation of the vol-

(3) Emmett and Brunauer, THIS JOURNAL, 55, 1738 (1933).