with considerable accuracy. The zinc atoms are surrounded tetrahedrally by chlorine atoms at an average distance of 2.25 Å., and an extra chlorine atom not coördinated with the zinc is present to give the required stoichiometry. These extra chlorine atoms are octahedrally surrounded by ammonium ions at the average distance, 3.41 Å. One kind of ammonium ion is surrounded by a trigonal prism grouping of chlorine atoms at an average distance of 3.44 Å., while the other ammonium groups are surrounded by an irregular polygon of eight chlorine atoms at the average distance of 3.32 Å. The Zn–Cl bonds in the $ZnCl_4^=$ tetrahedra are essentially covalent, while all other bonds in the structure (except N–H) are essentially ionic in nature. The structure is a packing of NH_4^+, $ZnCl_4^=$, and Cl^- ions, and the formula of the compound would best be represented by $(NH_4)_2ZnCl_4 \cdot NH_4Cl$.

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The Heat Capacity of Carbon Tetrachloride from 15 to 300°K. The Heats of Transition and of Fusion. The Entropy from Thermal Measurements Compared with the Entropy from Molecular Data

By J. F. G. Hicks, J. G. Hooley[1a] and C. C. Stephenson

The calculation of the thermodynamic functions of carbon tetrachloride from molecular data has been the subject of a number of papers.[1b–5] The entropy of carbon tetrachloride calculated from the existing thermal data[6–9] agrees quite well with the theoretical entropy value,[2] but this agreement is somewhat fortuitous because the thermal entropy may be in error by as much as one entropy unit. The thermal data of this paper reduce the uncertainty of the third law entropy value and give an answer which is more reliable than that calculated from molecular data.

Material.—Two samples of carbon tetrachloride were used for the measurements. Both samples were prepared from Merck c. p. material which was distilled three times in a vacuum-jacketed column, the first and last quarter being rejected each time. The second sample was protected from light at all times. Melting-point determinations indicate that both samples contained about 0.02 mole per cent. of liquid-soluble solid-insoluble impurity, although the absence of any marked premelting effect on the heat capacity measurements in the region below the melting point gives a much smaller figure.

The measurements below 265°K. were made with Sample I which weighed 136.86 g. in vacuum. Sample II, which weighed 134.06 g. in vacuum, was used for the other series. The molecular weight of carbon tetrachloride was taken as 153.84.

Method.—The apparatus, method of measurement, and calorimeter have been described in an earlier paper.[10] At the conclusion of the measurements, the thermometer was checked at the melting points of ice and mercury and found to agree with the original calibration to within 0.01°.

The calorie used in this work is defined equal to 4.1833 int. joules. The absolute temperature of the ice-point is taken as 273.19°K.

Melting Point.—The melting point was observed with various percentages of the carbon tetrachloride melted. The results are summarized in Table I. The amount of impurity was calculated from the change observed in the melting point, and the accepted value, 250.3 ± 0.1°K., has been corrected for the effect of this impurity.

Table I

Melting Point of Carbon Tetrachloride

	% Melted	Time, hr.	T, °K.
Sample I	12	2	250.111
	12	3	250.094
	25	4.5	250.153
	25	5	250.149
	50	7.5	250.235
	50	8.5	250.234
Sample II	15	3	250.084
	30	4.5	250.148
	30	5.5	250.144
	50	7.5	250.206
		Accepted value	250.3 ± 0.1

Transition Temperature.—Determinations of the transition temperature are summarized in Table II.

Table II

Transition Temperature at 225.35°K.

Trial	% Transformed	Time	T, °K.
I	50	9	225.355
II	30	5	225.356
	50	9	225.346
	50	11	225.353
III	15	5	225.347
	25	13	225.394
		Accepted value	225.35 ± 0.03°K.

Melting points and transition temperatures observed by other experimenters are given in Table

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[1a] Royal Society of Canada Fellow.

[1b] D. P. Stevenson and J. Y. Beach, *J. Chem. Phys.*, **6**, 25, 108 (1938).

[2] R. C. Lord, Jr., and E. R. Blanchard, *ibid.*, **4**, 707 (1936).

[3] R. D. Vold, This Journal, **57**, 1192 (1935).

[4] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy, IX. The Entropies of Inorganic Substances, Revision (1940) of Data and Methods of Calculation. Bull. 434, Bureau of Mines, 1941.

[5] D. M. Yost and C. Blair, This Journal, **55**, 2610 (1933).

[6] W. M. Latimer, *ibid.*, **44**, 90 (1922).

[7] H. L. Johnston and E. A. Long, *ibid.*, **56**, 31 (1934).

[8] D. R. Stull, *ibid.*, **59**, 2726 (1937).

[9] J. H. Mathews, *ibid.*, **48**, 562 (1926).

[10] J. F. G. Hicks, *ibid.*, **60**, 1000 (1938).

III. For comparison, all of the temperatures have been converted to the Kelvin scale with an ice-point of 273.19°K., with the exception of the values by Turkevich and Smyth, who give no ice-point comparison.

TABLE III

MELTING AND TRANSITION TEMPERATURES OF CARBON TETRACHLORIDE

Melting point, °K.	Transition temperature, °K.	Observer
250.4	225.1 (cooling)	A. Turkevich and C. P. Smyth[11]
250.31	225.56 (warming)	D. R. Stull[8]
250.36 ±0.01	225.73 (warming)	H. E. Phipps and J. H. Reedy[12]
	225.32 (cooling)	H. E. Phipps and J. H. Reedy[12]
250.32 ±0.05	225.53 ±0.05 (warming)	H. L. Johnston and E. A. Long[7]
250.33	225.76 (warming)	E. V. Skau and H. F. Meier[13]
	225.52 (cooling)	E. V. Skau and H. F. Meier[13]
250.3 ±0.10	225.35 ±0.03 (warming)	This research

Johnston and Long have proposed that this transition temperature be used as a fixed point for low temperature thermometry, but the deviations shown in Table III do not warrant the acceptance of their suggestion. These deviations may be due to three causes: the temperature scales may be different, the samples may have different amounts of impurities which could affect the transition temperature, or a true state of equilibrium may not be reached in a reasonable period of time. The good agreement of the melting-point temperatures indicates a satisfactory agreement of the temperature scales. The differences observed between the temperature obtained when the equilibrium is approached from the low temperature phase and the temperature obtained by cooling from the high temperature phase indicate that equilibrium cannot be reached in a reasonable period of time in spite of the fact that the results here given and the results of Johnston and Long are self-consistent. Supercooling and superheating as well as hysteresis occur frequently in solid–solid transitions, and, in order to establish a transition temperature, it is necessary to approach the equilibrium from both high and low temperatures.

TABLE IV

HEAT CAPACITY OF CARBON TETRACHLORIDE (MOLECULAR WEIGHT, 153.84) (0°C. = 273.19°K.)

T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$	T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$	T, °K.	C_p, cal. mole^{-1} deg.$^{-1}$
17.09	3.71	101.62	16.13	228.21	27.97
18.64	4.33	107.12	16.64	231.27	28.12
20.11	5.12	113.16	17.21	234.81	28.33
21.81	5.93	118.80	17.73	235.08	28.24
24.40	6.65	126.51	18.40	238.13	28.77
27.49	7.44	132.67	18.90	239.38	28.76
30.98	8.27	137.81	19.25	240.07	28.67
34.67	9.00	142.76	19.66	241.30	29.14
38.16	9.51	147.74	19.97	243.66	29.16
41.78	10.03	156.22	20.83	244.44	29.21
45.56	10.48	161.19	21.23	244.94	29.28
49.17	10.96	166.05	21.72	247.20	29.48
52.91	11.38	174.38	22.34	250.3	Melting point
56.75	11.71	179.58	22.76	253.82	31.16
57.66	11.79	185.04	23.24	254.01	30.95
60.34	12.07	188.22	23.53	258.08	31.02
60.57	12.04	193.38	24.09	258.72	31.02
63.91	12.37	199.09	24.57	263.08	31.06
64.23	12.51	203.64	24.99	263.08	31.39
67.18	12.80	209.01	25.91	263.82	31.24
69.93	13.04	213.63	26.25	269.00	31.35
72.73	13.34	214.91	26.68	274.84	31.10
76.28	13.70	215.84	26.14	280.49	31.51
81.45	14.12	218.94	26.98	286.34	31.55
86.35	14.59	220.76	27.69	292.40	31.46
91.11	15.19	221.41	27.54	298.49	31.37
96.09	15.56	225.35	Transition		

The Heat Capacity of Carbon Tetrachloride.—The observed heat capacities are summarized in Table IV. The data are shown in Fig. 1. Table V gives values of the heat capacities taken from a smooth curve through the observations. These values are compared with the unpublished measurements of R. W. Blue and E. R. Blanchard from 20 to 80°K., as cited by Lord and Blanchard,[2] and the measurements of Stull[8] from 90 to 300°K. The preliminary values of the heat capacity

TABLE V

HEAT CAPACITY OF CARBON TETRACHLORIDE (MOLECULAR WEIGHT, 153.84) (0°C. = 273.19°K.)

Values taken from a smooth curve through the data

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Deviations, % Blue and Blanchard — This research	Stull — This research
20	5.05	−1.4	
25	6.81	−0.4	
30	8.05	+ .5	
35	9.06		
40	9.78	+3.0	
50	11.07	+2.2	
60	12.05	+3.3	
70	13.08	+4.5	
80	14.08	+4.9	
90	15.06		+2.7
100	16.00		+1.3
110	16.92		−0.6
120	17.80		−1.3
130	18.65		−1.8
140	19.48		−1.5
150	20.29		−1.2
160	21.11		−0.6
170	21.95		− .5
180	22.80		− .2
190	23.70		− .3
200	24.70		− .6
210	25.80		−1.3
220	27.04		−2.3
225.35	Transition		
230	27.98		−2.2
240	28.84		−0.1
250	29.74		+2.2
250.3	Melting point		
260	31.15		−1.1
270	31.24		−0.2
280	31.33		+ .2
290	31.41		+ .6
300	31.49		+ .8

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(11) A. Turkevich and C.P. Smyth, THIS JOURNAL, 62, 2468 (1940).

(12) H. E. Phipps and J. H. Reedy, *J. Phys. Chem.*, 40, 89 (1936).

(13) E. V. Skau and H. F. Meier, THIS JOURNAL, 51, 3517 (1929).

measurements made by Stull, quoted by Lord and Blanchard, are considerably higher than his final values, which he estimates to be accurate to 1.25%. The apparatus and technique employed by Blue and Blanchard were similar to those of this work.

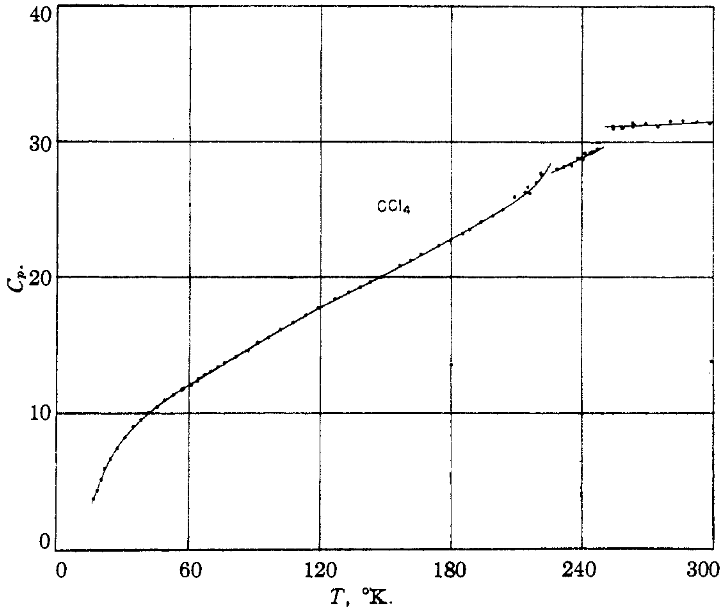

Fig. 1.

Since this calorimeter has been shown to give reliable results for the heat capacity of naphthalene,[10] the large differences between the results of Blue and Blanchard and of this work are attributed to some undiscovered source of error in their measurements.

Heat of Transition and of Fusion.—The heats of transition and of fusion were determined by the usual procedure of starting heat input at a temperature slightly below the transition temperature and heating to a temperature slightly above. Appropriate $\int C_p \, dT$ corrections were applied.

The value obtained for the molal heat of fusion for Sample I was 602.0 ± 2 calories, and for Sample II, 600.3 ± 2 calories

Two measurements of the molal heat of transition at 225.35°K. were made. The value for Sample I was 1094.9 ± 3 calories and for Sample II, 1095.8 ± 3 calories.

The results of recent measurements of the heats of fusion and of transition are summarized in Table VI.

Table VI

Heats of Fusion and of Transition of Carbon Tetrachloride

Heat of transition	Heat of fusion	Observer
1098 ±7	644	Latimer
1080.8 ±3	577.2 ±1	Johnston aud Long
1100	581	Stull
1095 ±3	601 ±2	This research

There is no apparent reason for the differences in these observations which are well outside the limits of error claimed. For the entropy calculation, the results of this research are preferred because they are consistent with our own interpretation of the $\int C_p \, dT$ correction.

The Entropy from Calorimetric Data.—The entropy of liquid carbon tetrachloride at 298.19°K. was calculated in the usual way by integrating $\int C_p \, d \ln T$ for the solid and liquid and adding to this the entropy of transition and of fusion. The entropy contribution for 0 to 18°K. was obtained from a Debye function with θ = 148. An itemized account of the calculation is given in Table VII.

Lord and Blanchard,[2] who have made a similar calculation, obtained 52.17 cal. deg.$^{-1}$ mole^{-1} as the entropy of the liquid. Their result is too high mainly because they used the preliminary heat capacity values of Stull which are much higher than his final published values. On the other hand, Stull,[8] who also calculated the entropy of the liquid, gives a still higher value of 52.4 cal. deg.$^{-1}$ mole^{-1}, but he made a dubious extrapolation from 0 to 91°K., rather than use the experimental values quoted by Lord and Blanchard. He has also apparently made a mistake in calculating the entropy from 91°K. to the transition; a recalculation from his measurements gives 18.29 rather than his 18.86 entropy units. His total entropy, when corrected, agrees with the results of this paper to a few hundredths of an entropy unit from 91 to 298.19°K.

Table VII

The Entropy of Liquid Carbon Tetrachloride

0–18°K., Debye function $h\nu/k$ = 148	1.39
18–225.35°K., graphical	34.118
Transition, 1095/225.35	4.859
225.35–250.3°K., graphical	3.009
Fusion, 601/250.3	2.401
250.3–298.19°K., graphical	5.478
	51.25 ± 0.15

Comparison of Thermal and Statistical Entropies.—In order to compare the thermal entropy and the statistically calculated entropy, the entropy change from the liquid to a perfect gas at one atmosphere pressure must be added to the entropy of the liquid found above. The heat of vaporization, according to J. H. Mathews,[9] is 7160 cal. per mole at 348.5°K. K. S. Pitzer,[14] who also showed that the heat capacity of the gas agrees with the calculated heat capacities given by R. D. Vold,[3] gives $\Delta H_{349.8}$ = 7170 ± 20 cal. per mole. The extrapolated heat capacities of the liquid and the calculated heat capacities of

(14) K. S. Pitzer, This Journal, 63, 2413 (1941).

the gas were used to calculate the entropy changes of the liquid and perfect gas. A Berthelot correction to a perfect gas and the entropy of compression to one atmosphere were combined with the entropy of vaporization to give $\Delta S_{298.19} = 22.4 \pm 0.1$ cal. deg.$^{-1}$ mole^{-1}. The entropy of carbon tetrachloride (gas) is then 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K.

The entropy values of carbon tetrachloride calculated from Raman spectra and electron diffraction data range from 74.0 to 74.3 cal. deg.$^{-1}$ mole^{-1}. The error in this theoretical value is difficult to estimate, but Kelley[4] has adopted the value 74.2 ± 0.5 which is 0.5 cal. deg.$^{-1}$ mole^{-1} higher than the third law entropy value. This difference is undoubtedly within the limits of error of the two values. There is no reason to suspect any lack of equilibrium in solid carbon tetrachloride which would lead to a low thermal entropy value, nor does the extrapolation below 17°K. seem uncertain. On the other hand, there is a large vibrational contribution to the theoretical entropy which may be uncertain to several tenths of an entropy unit. The third law entropy value, 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K., is recommended for thermodynamic calculations at the present time.

Summary

The heat capacities of solid and liquid carbon tetrachloride have been measured over their respective ranges from 17 to 300°K. The heat of transition at 225.35°K. is 1095 ± 3 calories per mole. The heat of fusion is 601 ± 2 calories per mole and the melting point is 250.3°K.

The entropy of CCl_4 (liquid) is 51.25 ± 0.15 and of CCl_4 (gas) is 73.7 ± 0.3 cal. deg.$^{-1}$ mole^{-1} at 298.19°K. The third law entropy is in agreement with the value calculated from Raman and electron diffraction data, and is recommended for thermodynamic calculations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

The Polarographic Reduction of Rhodium Compounds

BY J. B. WILLIS

In view of the close similarity of the coördination chemistry of trivalent cobalt and trivalent rhodium, it is surprising that the bivalent state of the latter metal is almost unknown. The few compounds of Rh^{II} described in the literature are mostly either of doubtful identity or else only stable over a limited range of conditions at high temperatures (*e. g.*, rhodium monoxide and rhodium dichloride).[1]

Recently, however, Dwyer and Nyholm have systematically investigated the action of reducing agents on Rh^{III} compounds[2] and have prepared stable and well-defined coördination compounds of Rh^{II} with tertiary arsines[3] and with pyridine.[4] Simple inorganic complexes have not, however, been isolated.

It was considered that the polarographic reduction of trivalent rhodium compounds might throw some light on the valence states of rhodium in such cases and possibly enable the reduction potentials to be calculated.

Theory

Although rhodium is more noble than mercury, it is shown in the present work that a number of its complexes are stable toward mercury and yield well-defined polarographic steps. If reduction of Rh^{III} takes place through Rh^{II}, two steps should be obtained, whereas direct reduction of Rh^{III} to rhodium should give one step only. Two general methods were used in the identification of the steps obtained:

(*a*) Application of the Ilkovič equation to evaluate n.

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$$

where i_d is the diffusion current in microamperes, n the number of electrons involved in the reduction of one molecule of the reducible substance, D the diffusion coefficient of the latter, C its concentration in millimoles/liter, m the rate of flow of mercury in mg./sec., and t drop time in seconds. D is conveniently calculated for an ion from λ^0, the equivalent ionic conductance at infinite dilution, by Nernst's equation, which reduces to $D = 2.67 \times 10^{-7}\lambda^0/z$ cm.^{2} sec.$^{-1}$ at 25°[5a] where z is the valency of the ion. Conductivity data for rhodium compounds are scarce, but in the case of complex ions the values for the corresponding cobalt or other heavy metal complexes can be used without any serious error since the mobility of such ions depends almost entirely on the relatively large volume of the coördinated groups, and D occurs as a square root in the Ilkovič equation.

(*b*) By plotting the potential of the dropping mercury electrode $E_{d.e.}$ against $\log i/(i_d - i)$ where i is the current at any point on the wave, a straight line is obtained if the reduction is reversible. The slope of this log plot is $0.0591/n$ volts at 25°, *i. e.*, 60 mv. for a one-electron step,

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[1] Wöhler and Müller, *Z. anorg. allgem. Chem.*, **149**, 125 (1925).

[2] Dwyer and Nyholm, *J. Proc. Roy. Soc.*, N. S. W., **76**, 122 (1942).

[3] Dwyer and Nyholm, *ibid.*, **76**, 127 (1942).

[4] Dwyer and Nyholm, *ibid.*, **76**, 275 (1943).

[5] Kolthoff and Lingane, "Polarography," Interscience Publishers, N. Y., 1941; (a) p. 45, (b) pp. 163, 168, (c) p. 64, (d) p. 285.