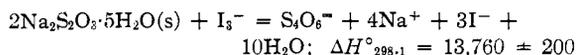


0.5Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> tends to give a lower result. Again we find from Bichowsky and Rossini

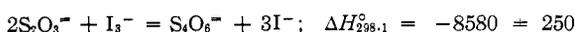
$$\begin{array}{r} \text{NaI} \cdot \infty \text{H}_2\text{O} \quad \Delta H_{291} = -70,849 \\ \text{NaI} \cdot 1500\text{H}_2\text{O} \quad \quad \quad -70,805 \end{array}$$

$$\Delta H_{\infty \text{H}_2\text{O}} - \Delta H_{1500\text{H}_2\text{O}} = -44 \times 0.0324/0.0103 = -160 \text{ cal./mole}$$

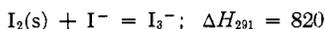
Applying these corrections to our experimental result and then doubling we find for the reaction



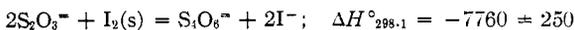
and combining this with the heat of solution



The heat of formation of I<sub>3</sub><sup>-</sup> (aq) listed by Bichowsky and Rossini, ΔH<sub>291</sub> = -12,140, does not agree with the experimental data given in the second section of their book. ΔH = -12,550 seems a more probable value for this quantity. Using this figure we find



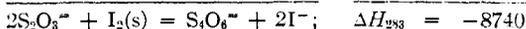
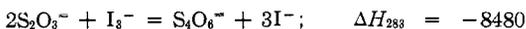
and, neglecting the small temperature difference



Thomsen found for this reaction

$$\Delta H_{291} = -7954$$

Berthelot reported

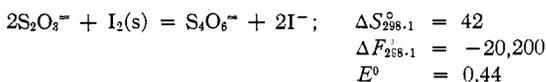


Obviously he made a mistake in sign in the second reaction and his result should read

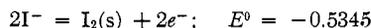
$$\Delta H_{293} = -8220$$

**Potential of the Thiosulfate-Tetrathionate Couple.**—The entropies of S<sub>2</sub>O<sub>3</sub><sup>=</sup> and S<sub>4</sub>O<sub>6</sub><sup>=</sup> are probably about 8 and 35, respectively. These estimates seem reasonable in comparison with the entropies of SO<sub>3</sub><sup>=</sup>, SO<sub>4</sub><sup>=</sup>, and HSO<sub>3</sub><sup>-</sup>, *i. e.*, 3, 4.4, and 32.6, respectively, as given by Latimer.<sup>6</sup>

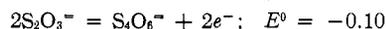
Taking the entropies of I<sub>2</sub>(s), 27.9, and of I<sup>-</sup>, 25.3, also from Latimer, we find



Combining with the potential of the I<sup>-</sup> - I<sub>2</sub> couple



we find



### Summary

The heat of oxidation of thiosulfate by triiodide has been measured. This determination, with the estimated entropies of thiosulfate and tetrathionate, leads to an approximate value for the potential of the thiosulfate-tetrathionate couple.

(5) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

BERKELEY, CALIFORNIA

RECEIVED MARCH 20, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## Specific Heats and Heats of Fusion and Transition of Carbon Tetrabromide

By K. J. FREDERICK AND J. H. HILDEBRAND

The subject of intermolecular forces and solubility has directed our attention particularly to a detailed study of the tetrahalides, for these substances are fine examples of molecules having widely differing volumes and intermolecular fields but with a common highly symmetrical structure. However, in many cases the evaluation of solubility data has been unsatisfactory on account of lack of accurate knowledge of specific heats and heats of fusion. This paper presents the results of determinations of the specific heats and heat of fusion of carbon tetrabromide, whose polymorphic nature, like that of carbon tetrachloride, makes it particularly interesting. The method of mixtures employed in this work

enabled us to determine the heat of the solid transition.

A thorough examination of the literature reveals only meager information concerning carbon tetrabromide. The phase diagram has been studied carefully by Roozeboom and others<sup>1</sup> and they have established definitely the fact that there are two solid forms of carbon tetrabromide with a temperature of transition within the range of 46.6 to 46.9°. There exists also a high pressure modification which need not concern us here. The heat of decomposition of carbon tetrabromide into bromine, hexabromoethane,

(1) B. Roozeboom, "Heterogene Gleichgewichte," Vol. I, 1901, p. 127; W. Wahl, *Proc. Roy. Soc. (London)*, **A87**, 152 (1913); *Phil. Trans.*, **A212**, 117 (1913).

and tetrabromoethylene was first reported by Merz and Weith.<sup>2</sup> Taylor<sup>3</sup> studied the rate of decomposition in the temperature interval 300–330° and gives a value for the heat of activation for the first order reaction. No reference can be found pertaining to any direct calorimetric measurements with carbon tetrabromide. Kelley<sup>4</sup> in his survey of the heats of fusion of inorganic compounds gives certain values for the heat of fusion of carbon tetrabromide obtained from its solubility in solutions which are approximately ideal. These are 930 cal. for solutions in bromine, 1070 cal. in carbon disulfide, and 1060 cal. in aluminum bromide.

**Preparation and Purification of Sample.**—The material used was obtained from Eastman Kodak Co. and was purified by repeated recrystallizations from absolute alcohol. The purified material had a melting point of 90.1° and a transition point of 46.9°. It was enclosed in Pyrex glass capsules, evacuated before sealing. The capsules had an external diameter of 12 mm., an internal diameter of 10 mm., and varied in length, averaging around 11 cm. Four different capsules were prepared and each one was used for a number of runs. The ratio of the weights of carbon tetrabromide to glass varied from 0.76 to 1.15. The average free space in the capsules was 2.5 cc. Calculations indicate that the carbon tetrabromide vapor in the capsules was a negligible factor.

**Method.**—The apparatus and method used in these determinations were the same as described in the account of the work with iodine.<sup>5</sup> In order to determine the effect resulting from the small decomposition of carbon tetrabromide a method was devised whereby the percentage decomposition for a given heat treatment could be determined. For this purpose weighed amounts of carbon tetrabromide were enclosed in small glass capsules. Each capsule in turn was heated for five hours in a furnace regulated to within  $\pm 1.0^\circ$ . Four different temperatures in the interval 90.1–155° were employed. We had already observed from the runs made on the heat content of the solid that the heat decomposition below the melting point (90.1°) was negligible. After heating, the capsule was placed below the surface of a water-carbon disulfide mixture and smashed. The unchanged carbon tetrabromide and the bromine and other products formed from the decomposition all dissolved completely in the bottom layer of carbon disulfide. The solution was then made slightly acidic with acetic acid and an excess of potassium iodide was added. The liberated iodine was titrated immediately with standard thiosulfate, using the disappearance of the violet color of the carbon disulfide layer as the end-point. This titration with thiosulfate gives a measure of the amount of bromine formed. Assuming that the tetrabromoethylene is the other principal product of decomposition, the percentage decomposition

of the carbon tetrabromide at each temperature can then be calculated. The effect of time upon the decomposition was also determined by extending the time of heating to twenty-four hours.

**Results and Discussion.**—The value of the heat capacity of the calorimeter was  $16.9 \pm 0.4$  cal./deg. Runs on the Pyrex glass used in making the capsules showed that its specific heat for the interval 25–150° could be expressed within  $\pm 0.3\%$  by the equation

$$C_p = 0.186 + 5.5 \times 10^{-5}(t - 25) + 1.15 \times 10^{-6}(t - 25)^2$$

The results of the runs made on solid carbon tetrabromide are given in Table I, while the runs on liquid carbon tetrabromide are listed in Table II. The columns headed  $H - H_{298.1}$  represent the number of calories (1 cal. = 4.1833 int. joules) required to raise one mole of carbon tetrabromide from 25° up to the final temperature of the run.

TABLE I		TABLE II			
Temp., °C.	$H - H_{298.1}$ cal./mole	Temp., °C.	$H - H_{298.1}$ cal./mole		
Solid II	32.65	280.6	Liquid	91.45	5055.2
	35.50	315.6		94.65	5163.0
	38.20	473.3		99.00	5269.1
	40.90	548.2		101.20	5414.0
	43.08	627.8		105.50	5567.6
	46.63	777.4		107.70	5643.2
Solid I	50.35	2338.9	113.30	5847.5	
	58.20	2659.2	119.60	6035.2	
	57.60	2670.5	127.30	6361.6	
	64.38	2958.4	135.80	6640.2	
	70.20	3191.9	144.70	7013.0	
	76.80	3474.5			
	83.60	3769.6			
	88.06	3953.1			

The following results were obtained in the heat decomposition analyses. A heating of five hours produced a 0.04% decomposition at 102°, 0.18% at 115°, 0.99% at 127°, and 1.39% at 139°. When the time of heating was extended to twenty-four hours, the percentage decomposition increased to 0.25% at 104°, 0.75% at 115°, 1.06% at 135°, and 4.34% at 156°. The question of the effect of the decomposition upon the results listed in the tables now can be seen to be insignificant, for in the regular heat content run the time of heating never exceeded one and a half hours and hence the maximum heating endured by any one capsule was never greater than five to six hours. Consequently, for at least a major portion of the runs made on liquid carbon tetrabromide, we can safely say that less than 0.30% decomposition took place, corresponding to a

(2) V. Merz and W. Weith, *Ber.*, **11**, 2235 (1878).

(3) H. A. Taylor, *J. Phys. Chem.*, **35**, 1795 (1931).

(4) K. K. Kelley, *U. S. Bur. Mines*, 393 (1936).

(5) K. J. Frederick and J. H. Hildebrand, *THIS JOURNAL*, **60**, 1438 (1938).

maximum error of 0.20% in the value calculated for the heat content.

The results listed in Tables I and II have been plotted in Fig. 1. The points for both solid forms follow a linear relationship within experimental error. The slope of the line for the heat content is the molal heat capacity. For solid II in the interval 25–46.9° this is  $35.0 \pm 0.5$  cal./mole, and for solid I in the interval 46.9–90.1° it is  $42.9 \pm 0.3$  cal./mole. The heat of transition of solid carbon tetrabromide at the transition point is  $1420 \pm 15$  cal./mole. The entropy of transition is 4.44 e. u.

The results in the liquid range likewise follow a linear relationship within experimental error, leading to a value of  $36.7 \pm 0.5$  cal./mole for the molal heat capacity of liquid carbon tetrabromide in the interval 90.1–150°. The heat of fusion at the melting point is  $945 \pm 25$  cal./mole. The entropy of fusion of carbon tetrabromide is 2.61 e. u. It would seem then that the value of 1050 cal./mole for the heat of fusion of carbon tetrabromide selected by Kelley<sup>4</sup> in his study of solubility data is much too high, due, in all probability, to the use of non-ideal solutions.

There will be found in Table III a summary of directly measured heats of fusion and transition of the tetrahalides.

TABLE III

Substance	$T_m, \text{°K.}$	$\Delta S_f$	$M, \text{°K.}$	$\Delta S_f$	$\Delta S_f + \Delta S_f$
$\text{CBr}_4$	320.0	4.44	363.2	2.61	7.05
$\text{CCl}_4^6$	225.44	4.79	250.23	2.31	7.10
$\text{TiCl}_4^7$	....	..	250.0	9.00	9.00
$\text{TeCl}_4^8$	....	..	497.2	9.07	9.07
$\text{SiCl}_4^7$	....	..	205.5	9.08	9.08
$\text{SnCl}_4^7$	....	..	239.9	9.11	9.11
$\text{SnI}_4^9$	....	..	417.6	11.01	11.01

The statement has often been made that the sum of the entropy of fusion and entropy of transition is equal to a constant for structurally similar molecules<sup>10</sup> and this seems to be the case for carbon tetrachloride and bromide. It will be seen that the tetrachlorides of titanium, tellurium, silicon, and tin all have approximately the same entropy of fusion, while the tetraiodide of tin has a much higher entropy of fusion. The comparison between the tetrahalides of carbon and the others

(6) H. L. Johnston and E. A. Long, *THIS JOURNAL*, **56**, 31 (1934).

(7) W. M. Latimer, *ibid.*, **44**, 90 (1922).

(8) K. J. Frederick and J. H. Hildebrand, *ibid.*, **60**, 2522 (1938).

(9) G. R. Negishi, *ibid.*, **58**, 2293 (1936).

(10) J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

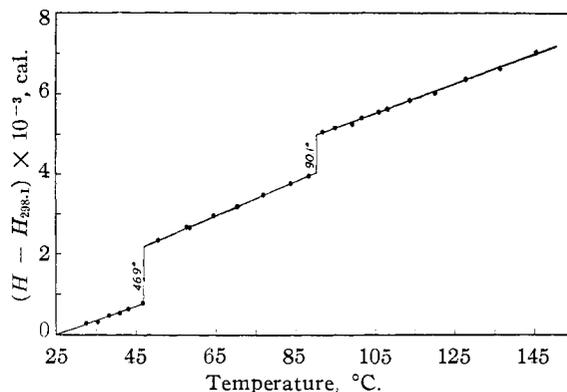


Fig. 1.

listed in Table III may be made in another manner. The addition of the entropies of fusion and transition fails to take account of the fact that the heat capacity of the solid I form is much larger than either that of solid II or that of the liquid. If solid II were superheated to 90.1° it would have a heat content of 2280 cal./mole, (extrapolated); its heat of fusion would be 2745 cal./mole and the entropy of fusion 7.56 e. u. Even this larger value is still far from the entropies of fusion observed for most tetrahalides. An explanation of these differences in entropy undoubtedly is connected with the crystal structure, but very little is known, unfortunately, concerning the crystal structure of most of the tetrahalides for which there can be found reliable calorimetric measurements. According to Mark<sup>11</sup> carbon tetrabromide solid II is monoclinic with a unit cell of 2 molecules and solid I is cubic with tetrahedral symmetry. Dickinson<sup>12</sup> has carefully studied stannic tetraiodide and reports a cubic unit of 8 molecules with pyritohedral symmetry. This represents the complete stock of information available on the crystal structure of the tetrahalides in Table II, hence, the theoretical treatment of the entropy of fusion of the tetrahalides must await further studies of their crystal structure.

### Summary

Employing the method of mixtures, the heat of fusion of carbon tetrabromide was found to be  $945 \pm 25$  cal./mole at the melting point, the heat of transition of the solid,  $1420 \pm 15$  cal./mole at the transition point, the molal heat capacity of solid II in the interval 25–46.9°,  $35.0 \pm 0.5$  cal./mole, the molal heat capacity of solid I in the

(11) H. Mark, *Ber.*, **57B**, 1820 (1924).

(12) R. G. Dickinson, *THIS JOURNAL*, **45**, 958 (1923).

interval 46.9–90.1°, 42.9 ± 0.3 cal./mole, and the molal heat capacity of liquid carbon tetrabromide

in the interval 90.1–150°, 36.7 ± 0.5 cal./mole. BERKELEY, CALIFORNIA RECEIVED APRIL 3, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## The Coefficient of Expansibility of Aqueous Solutions of Urea at 27.5° Calculated from the Densities at 25 and 30°

BY FRANK T. GUCKER, JR., AND CHARLES E. MOSER

Several years ago, it was shown<sup>1</sup> that the apparent molal expansibility of electrolytes, like the apparent molal volume and several other properties, is a linear function of the square root of the volume concentration (molarity) and therefore that the coefficient of thermal expansibility can be expressed by an equation of the type suggested by Root.<sup>2</sup> In the course of the investigation of the properties of non-electrolytes, we published recently a precise determination of the densities of aqueous solutions of urea at 25 and 30°.<sup>3</sup> Up to a concentration of about 3 molar, the apparent molal volume of this solute is a linear function of the *first power* of the molarity, within a few parts per million in the density. These data suffice to determine the apparent molal expansibility of urea, although the calculations are complicated by the fact that the molarity, as well as the density, is a function of the temperature. The method described below is an extension of our previous treatment of partial molal solute quantities which are functions of the molarity.<sup>4</sup>

**The Coefficient of Expansibility.**—This may be defined as

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,m} = - \frac{1}{d} \left( \frac{\partial d}{\partial T} \right)_{P,m} \quad (1)$$

where  $P$  is the pressure and  $m$  the molality. When the apparent molal volume is a linear function of the molarity in dilute solutions, the density may be expressed by means of a power series in  $c$

$$d = d_1 + A_1c + A_2c^2 + A_3c^3 + \dots \quad (2)$$

where  $d_1$  is the density of the pure solvent,  $c$  is the concentration of the solute in moles per liter, and  $A_1$ , etc., are constants characteristic of the solute and temperature. Equation (2) may be differentiated with respect to  $T$ , keeping  $P$  and  $m$  constant. Remembering that  $c$  is a function of  $T$  and that  $\partial c/\partial T = -\alpha c$ , the result is

$$\left( \frac{\partial d}{\partial T} \right)_{P,m} = \frac{\partial d_1}{\partial T} + \left[ \frac{\partial A_1}{\partial T} - A_1\alpha \right] c + \left[ \frac{\partial A_2}{\partial T} - 2A_2\alpha \right] c^2 + \left[ \frac{\partial A_3}{\partial T} - 3A_3\alpha \right] c^3 + \dots \quad (3)$$

If  $\alpha$ , like  $d$ , can be expressed as a power series

$$\alpha = \alpha_1 + B_1c + B_2c^2 + B_3c^3 + \dots \quad (4)$$

we can rearrange (3) into the form

$$\left( \frac{\partial d}{\partial T} \right)_{P,m} = \frac{\partial d_1}{\partial T} + \left[ \frac{\partial A_1}{\partial T} - A_1\alpha_1 \right] c + \left[ \frac{\partial A_2}{\partial T} - 2A_2\alpha_1 - A_1B_1 \right] c^2 + \left[ \frac{\partial A_3}{\partial T} - 3A_3\alpha_1 - 2A_2B_1 - A_1B_2 \right] c^3 \dots \quad (5)$$

Division of (5) by (2) gives at once the coefficient of expansibility as

$$\alpha = \alpha_1 - \frac{1}{d_1} \left( \frac{\partial A_1}{\partial T} \right) c - \frac{1}{d_1} \left[ \frac{\partial A_2}{\partial T} - A_2\alpha_1 \right] c^2 - \frac{1}{d_1} \left[ \frac{\partial A_3}{\partial T} - 2A_3\alpha_1 + 2 \frac{A_2}{d_1} \left( \frac{\partial A_1}{\partial T} \right) \right] c^3 + \dots \quad (6)$$

This equation now may be employed to calculate the coefficient of expansibility of aqueous solutions of urea at 27.5°.

The equations for the densities at 25 and 30° are<sup>3</sup>

$$d_{30} = 0.995673 + 0.015705c - 1.082 \times 10^{-4}c^2 \quad (7)$$

$$d_{25} = 0.997074 + 0.015964c - 1.315 \times 10^{-4}c^2 \quad (8)$$

Subtracting the coefficients of (8) from those of (7) and dividing by 5 gives

$$\Delta d_1/\Delta T = -280.2 \times 10^{-6}; \text{ whence } \alpha_1 = 281.2 \times 10^{-6}$$

$$\Delta A_1/\Delta T = -51.8 \times 10^{-6} \text{ and } \Delta A_2/\Delta T = 4.66 \times 10^{-6}$$

Taking the mean of the coefficients of (7) and (8) gives for the density of urea solutions at 27.5° the equation

$$d_{27.5} = 0.996374 + 0.015835c - 1.199 \times 10^{-4}c^2 \quad (9)$$

Hence,  $B_1 = 0.015835$  and  $B_2 = 1.199 \times 10^{-4}$ . Substituting these values into (5) gives for the mean coefficient of expansibility the equation

$$\alpha_{27.5} = (281.2 + 52.0c - 4.71c^2) \times 10^{-6} \quad (10)$$

Terms involving higher powers of  $c$  are negligible at the highest concentrations to which equations (7) and (8) are applicable. The estimated un-

(1) Gucker, *THIS JOURNAL*, **56**, 1017 (1934).

(2) Root, *ibid.*, **55**, 850 (1933).

(3) Gucker, Gage and Moser, *ibid.*, **60**, 2582 (1938).

(4) Gucker, *J. Phys. Chem.*, **38**, 307 (1934).