

should be negligibly small as long as the concentration of the water is not great enough to affect the properties of the solvent appreciably. From a large number of experiments, a few examples of which are listed in Table IV, it is seen that the presence of 1% water in a buffer solution hardly affects the indicator-buffer equilibrium.

In Table V is given a summary of the values of the negative logarithms of the ionization constants of indicators, pK_1 , at an ionic strength of zero. The values, naturally, are no more reliable than the pK_A values from which they were calculated. The pK_1 of Tropeoline 00 has been obtained from experiments in dilute hydrochloric acid solutions in methanol, which will be reported in a subsequent publication.

In Table VI is given a list of the pK_A values of various acids at $\mu = 0$, which were calculated from the extrapolated pK' values and the pK_1 values of Table V.

Summary

1. Thermodynamic ionization constants of a number of indicators and of acids have been determined in methanol, and the effect of ionic strength studied.

2. The behavior of the sulfonphthaleins and thymolbenzein is in agreement with modern views of their structures.

3. In agreement with Baggesgaard-Rasmussen and Reimers, it was found that the behavior of methyl red is best explained on the basis of the existence of the free amino acid form, and not of the hybrid form, although the salt effect is not entirely accounted for by this interpretation.

4. The behavior of other indicators is in agreement with present concepts. At very small ionic strengths, the salt effect can be accounted for quantitatively by the limiting Debye-Hückel expression.

MINNEAPOLIS, MINN.

RECEIVED AUGUST 5, 1938

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

Specific Heats and Heat of Fusion of Tellurium Tetrachloride

BY K. J. FREDERICK AND J. H. HILDEBRAND

A calculation of the internal pressure of tellurium tetrachloride by the senior author¹ shows that this tetrachloride differs from all others in the magnitude of its molecular field, which is near to that of iodine. It is to be expected, therefore, that solutions of these two substances with each other should be nearly ideal, provided that they do not react and that the former does not have a more or less ionic field, which may prove to be the case. The freezing point diagram for this system is now being constructed in this Laboratory. In order to evaluate the data, however, it is necessary to have reliable figures for the specific heats and heats of fusion. Data for iodine recently have been reported by us² and this paper presents similar results for tellurium tetrachloride, for which no determinations of the quantities are to be found in the literature.

Preparation and Purification of Sample.—The material used was purified by fractional distillation, the final fraction distilling at a mean temperature of 390° under atmospheric pressure. Its

melting point was 224.1°. The purified material was enclosed in small Pyrex glass capsules, evacuated before sealing. The capsules had an external diameter of 12 mm., an internal diameter of 10 mm., and a length of approximately 6 cm. The ratio of weight of tellurium tetrachloride to weight of glass was about 1.4. Two different capsules were prepared and each one was used in a considerable number of the runs. The average free space in the capsules was 1.7 cc. Calculations indicate that the tellurium tetrachloride 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. The higher melting point of the tellurium tetrachloride necessitated further calibration of the thermocouple in the furnace and the melting point of tin was used for this purpose.

Results and Discussion.—The value of the heat capacity of the calorimeter was 11.3 ± 0.4 cal. per degree. Runs on the Pyrex glass used in making the capsules showed that its specific heat for the interval 25–250° could be

(1) J. H. Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936.

(2) Frederick and Hildebrand, *THIS JOURNAL*, **60**, 1436 (1938).

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 and liquid tellurium tetrachloride are given in Table I. The column headed $H-H_{298.1}$ represents the number of calories evolved in cooling one mole from the temperature in the other column down to 25° . The data listed in the tables are plotted in Fig. 1.

The two values obtained for the solid just below the melting point are abnormally high due to some pre-melting. If these two are neglected, the rest of the results for the solid range follow a linear relationship within experimental error. The slope of this line is the molal heat capacity of solid tellurium tetrachloride in the interval $25-224.1^\circ$ and is 33.1 ± 0.3 cal. per mole. A straight line was also found to fit the data for liquid tellurium tetrachloride within experimental error. This gives a molal heat capacity of liquid

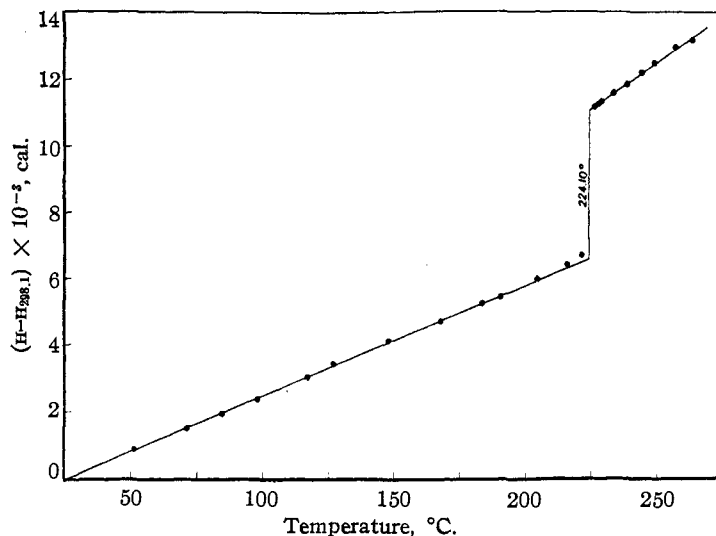


Fig. 1.

tellurium tetrachloride of 55.0 ± 0.5 cal. per mole for the interval $224.1-265^\circ$.

The heat of fusion of tellurium tetrachloride at the melting point is 4510 ± 30 cal. per mole. The entropy of fusion is 9.07 cal. per degree. This agrees excellently with the entropies of fusion of silicon tetrachloride, 9.08 ; titanium tetrachloride, 9.00 ; tin tetrachloride, 9.11 ; obtained by Latimer.³

TABLE I

Temp., °C.	$H-H_{298.1}$, cal./mole Solid	Temp., °C.	$H-H_{298.1}$, cal./mole Liquid
51.06	847.3	226.20	11,204.7
71.10	1491.3	227.80	11,312.9
84.32	1920.6	229.03	11,366.3
97.91	2331.3	233.28	11,604.4
116.94	3010.3	238.63	11,879.1
126.72	3399.8	244.40	12,224.1
148.36	4110.5	249.36	12,510.4
168.10	4705.5	256.85	12,964.7
184.63	5263.8	263.10	13,169.2
190.65	5466.3		
204.82	5980.5		
216.10	6410.3		
221.60	6720.0		

Summary

Employing the method of mixtures, the heat of fusion of tellurium tetrachloride at the melting point was found to be 4510 ± 30 cal. per mole, the molal heat capacity of solid tellurium tetrachloride in the interval $25-224.1^\circ$, 33.1 ± 0.3 cal. per mole, and the molal heat capacity of liquid tellurium tetrachloride in the interval $224.1-265^\circ$, 55.0 ± 0.5 cal. per mole.

BERKELEY, CALIF.

RECEIVED MAY 31, 1938

(3) W. M. Latimer, THIS JOURNAL, 44, 90 (1922).