a six-membered ring similar to that postulated for the normal acids.

Summary

The effect of the character of an alkyl side chain on the processes of esterification and saponification, on acid dissociation constants, and on optical activity has been discussed. It has been shown that ring formation similar to that already postulated to explain the effect of the alkyl chain length of normal aliphatic acids on their velocity of esterification in methanol gives a satisfactory explanation of these phenomena.

The same structure may be used to explain other reactions. It is pointed out that the ortho effect is unquestionably due to the same type of structure.

BETHLEHEM, PENNA.   RECEIVED MARCH 2, 1939

Chlorine. The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization, and Entropy

BY W. F. GIAUQUE AND T. M. POWELL

This paper presents the results of a low temperature calorimetric investigation of chlorine. The entropy of chlorine has been calculated previously[1] from band spectrum data and the principal purpose of the present work is to compare the value obtained by means of the third law of thermodynamics with the accurately known spectroscopic value. No difficulty with false equilibrium at low temperatures, such as has been found with a few other substances, was anticipated in the case of a molecule like chlorine. Thus it was expected and has been found that the two methods of obtaining the entropy are in excellent agreement.

The measurements were made in a calorimeter which has been described as Gold Calorimeter II.[2] A detailed description of a similar calorimeter has been given previously.[3]

Chlorine reacts slowly with gold at ordinary temperatures and before the gold calorimeter was used for chlorine the reactivity was investigated by immersing a sheet of gold in liquid chlorine at its boiling point. The sheet had an area of 58.5 cm.[2] and was boiled in nitric acid, washed in alcohol and heated before weighing after each removal from the chlorine. During the first twenty-four hours the gold lost 0.0140 g. but subsequent immersion for four days caused an additional decrease of only 0.0087 g. Since the calorimetric investigation required that the liquid chlorine be at temperatures near the boiling point for a comparatively short period, the reaction could not occur to any appreciable extent. Moreover, the data on the rate of solution of gold were obtained with undried commercial liquid chlorine whereas the chlorine used to fill the gold calorimeter was carefully dried and purified. Presumably the reaction between gold and very dry chlorine would be much slower than that recorded above. When measurements were not in progress, the chlorine was solidified and kept near the temperature of liquid air.

The resistance thermometer was calibrated during the measurements against a copper-constantan thermocouple with the laboratory designation W.[4] Small corrections to this standard thermocouple were recently determined by Stephenson and Giauque.[5] Following the present research the standard thermocouple was compared with the vapor pressures of hydrogen and agreement with the corrections of Stephenson and Giauque was found.

Preparation of the Chlorine.—The chlorine was prepared by dropping 3 M HCl on manganese dioxide. The small amount of hydrogen chloride in the gas was removed by water and the chlorine was dried with concentrated sulfuric acid and finally with phosphorus pentoxide.

Chlorine prepared as above was placed in the calorimeter and measurements of the heat effect associated with premelting in the solid showed it to contain an impurity of about 5 parts in 10,000 on a molal basis. The material was removed from the calorimeter and fractionated in a vacuum jacketed column. Subsequent premelting

(1) Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

(2) (a) Giauque and Wiebe, *ibid.*, **50**, 101 (1928); (b) Blue and Giauque, *ibid.*, **57**, 991 (1935).

(3) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

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

(5) Stephenson and Giauque. *J. Chem. Phys.*, **5**, 149 (1937).

measurements in the temperature range a few degrees below the melting point showed that the liquid-soluble solid-insoluble impurity had been reduced to about 3 moles in 100,000.

The Vapor Pressure of Chlorine.—The vapor pressure of chlorine was measured with a mercury manometer using carbon dioxide as a buffer in the manner described previously[6] for nitrogen tetroxide. The measurements were made with the calorimetric apparatus since it permitted excellent temperature control. A system of capillaries and mixing bulbs was so arranged that the less dense carbon dioxide could not enter the calorimeter or the connecting lines adjacent to it. To guard against slow diffusion a small amount of chlorine was pumped from the calorimeter before each vapor pressure observation. Heat was then added until the desired temperature was reached. The results of two series of observations on the triple point are given in Table I.

TABLE I

TRIPLE POINT DATA FOR CHLORINE (0°C. = 273.10°K.)

Series	% melted	T, °K. Thermo-couple	T, °K. Resistance Ther.	$P_{inter.}$ cm. Hg
I	25	172.13	172.111	1.044
I	50	172.12	172.109	1.046
II	7	172.13	172.109	1.052[a]
II	30	172.14	172.120	1.046
II	80	172.11	172.115	1.042
Values accepted		172.12		1.044

[a] This value deviates by more than the error of measurement and is given no weight.

The results starting at the triple point are represented by the equation

Triple point 172.12 to 240.05°K.

$$\log_{10} P_{(inter. cm.)} = \frac{-1414.8}{T} - 0.01206\,T + 1.34 \times 10^{-5}\,T^2 + 9.91635 \quad (1)$$

The observed values of the vapor pressure are given in Table II where they are compared with Equation 1. The temperatures are given to thousandths of degrees in order that the high relative accuracy may be used in obtaining temperature coefficients. Near the triple point an error in pressure of 0.001 cm. corresponds to 0.01° and since the accuracy of the pressure measurements is about 0.002 cm. deviations of the order of 0.02° are within the limit of error. At the higher temperatures the larger dP/dT makes temperature measurement the limiting factor. The standard acceleration of gravity was taken as 980.665 cm. sec.$^{-2}$ and for this location $g = 979.973$ cm. sec.$^{-2}$.

(6) Giauque and Kemp, *J. Chem. Phys.*, **6**, 40 (1938).

TABLE II

VAPOR PRESSURE OF CHLORINE (0°C. = 273.10°K.)

T, °K.	$P_{obsd.}$ inter. cm. Hg	$P_{obsd.} - P_{calcd.}$	$T_{obsd.} - T_{calcd.}$
172.12	1.044	+0.002	−0.02
175.44	1.407	− .001	+ .01
180.38	2.158	+ .002	− .01
185.464	3.250	− .002	+ .008
190.513	4.774	+ .000	− .000
195.513	6.831	+ .002	− .004
200.413	9.507	− .003	+ .005
205.242	12.949	− .001	+ .001
210.000	17.274	− .006	+ .010
215.179	23.251	− .016	+ .013
219.909	30.124	+ .015	− .010
225.104	39.396	− .004	+ .002
229.958	50.042	+ .013	− .005
234.975	63.273	− .018	+ .006
240.050	79.385	+ .002	− .000

$dP/dT = 3.3425$ cm. deg.$^{-1}$ at 76.000 cm.

From Equation 1 the boiling point was found to be 239.05°K. The values for the melting and boiling points of chlorine are compared with those of previous observers in Table III.

TABLE III

MELTING AND BOILING POINTS OF CHLORINE

M. p., T, °K.	B. p., T, °K.	Observer
....	239.5	Regnault[7] (1863)
171	....	Olszewski[8] (1884)
171.6	239.4	Johnson and McIntosh[9] (1909)
172.2	....	Van der Goot[10] (1911)
....	238.6	Pellaton[11] (1915)
....	238.4	Trautz and Gerwig[12] (1923)
170.8	....	Eucken and Karwat[13] (1924)
172.6	239.15	Harteck[14] (1928)
172.12	239.05	This research

The Calorimetric Data.—The heat capacity results are presented in Table IV and results taken from a smooth curve through the observations are given in Table V. A small pressure of helium gas was used to assist thermal equilibrium in the solid at low temperatures. A correction was applied for vaporization into the small gas space due to changing vapor pressure in the liquid range. This correction was made with the assistance of density measurements on liquid chlorine by Pellaton,[11] who gives the equation

$$D = 1.468 - 2.89 \times 10^{-3} t - 5.3 \times 10^{-6} t^2 \quad (2)$$

(7) Regnault: Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag von Julius Springer, Berlin, 1923.
(8) Olszewski, *Monatsh.*, **5**, 124 (1884).
(9) Johnson and McIntosh, THIS JOURNAL, **31**, 1138 (1909).
(10) Van der Goot, *Tab. Ann.*, 67 (1911).
(11) Pellaton, *J. chim. phys.*, **13**, 426 (1915).
(12) Trautz and Gerwig, *Z. anorg. allgem. Chem.*, **134**, 417 (1923).
(13) Eucken and Karwat, *Z. physik. Chem.*, **112**, 474 (1924).
(14) Harteck, *ibid.*, **134**, 21 (1928).

where t is the centigrade temperature. Since the vapor pressure and heat of vaporization were known accurately, there was no appreciable error involved in the small vaporization correction.
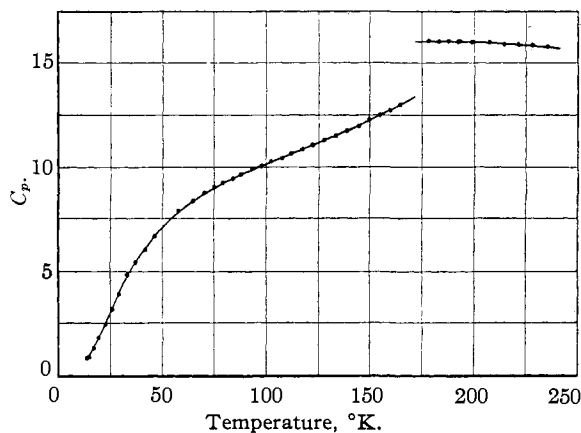

Fig. 1.—Heat capacity in calories per degree per mole of chlorine.

It is estimated that a smooth curve through the data represents the heat capacity to 0.1–0.2% at all temperatures above 35°K. The percentage accuracy decreases near the boiling point of hydrogen due to the rapidly decreasing heat capacity and the rapid decrease in the temperature coefficient of the resistance thermometer in this region.

TABLE IV

THE HEAT CAPACITY OF CHLORINE

0°C. = 273.10°K. Molecular weight, 70.914. 2.3385 moles were in the calorimeter.

T, °K.	ΔT approx.	C_p cal. deg.$^{-1}$ mole^{-1}	T, °K.	ΔT approx.	C_p cal. deg.$^{-1}$ mole^{-1}
14.05	1.1	0.810	118.15	5.4	10.81
15.21	1.0	0.916	123.53	5.2	11.00
17.40	2.7	1.331	128.67	5.0	11.24
19.81	2.0	1.842	134.06	5.7	11.47
22.93	3.9	2.467	139.67	5.4	11.72
26.37	3.0	3.192	145.19	5.2	11.92
29.88	4.0	3.946	150.39	5.0	12.24
33.94	3.2	4.804	155.45	4.8	12.41
37.68	4.2	5.421	160.31	4.6	12.69
42.37	5.1	6.018	164.99	4.5	12.93
47.14	4.4	6.675	172.12		Melting point
58.59	6.0	7.879	178.98	4.6	16.01
65.42	5.3	8.382	183.75	4.5	16.02
70.50	4.9	8.720	188.40	4.4	15.99
75.25	4.6	8.973	193.21	4.4	15.99
79.71	4.3	9.201	194.08	7.1	15.95
84.06	4.3	9.427	201.50	6.9	15.94
88.66	4.9	9.626	208.63	6.7	15.92
93.47	4.6	9.827	215.90	6.5	15.85
98.06	4.4	10.03	222.82	6.4	15.81
102.92	5.2	10.22	229.73	6.2	15.79
108.06	5.0	10.38	236.77	6.1	15.73
112.99	4.7	10.57	239.05		Boiling point

TABLE V

THE HEAT CAPACITY OF CHLORINE

Values from curve through observations. 0°C. = 273.10°K. Molecular weight, 70.914,

T, °K.	C_p cal. deg.$^{-1}$ mole^{-1}	Devn., % E. and K. —This research	T, °K.	C_p cal. deg.$^{-1}$ mole^{-1}	Devn., % E. and K. —This research
15	0.89		130	11.29	3.4
20	1.85	1.6	140	11.73	4.3
25	2.89		150	12.20	4.9
30	3.99	4.3	160	12.68	5.5
35	4.97		170	13.17	
40	5.73	8.2	Melting point		
45	6.39		172.12	13.27	
50	6.99	9.0	172.12	16.03	1.4
60	8.00	6.5	180	16.02	1.4
70	8.68	4.8	190	15.99	1.6
80	9.23	3.5	200	15.95	1.9
90	9.71	2.5	210	15.89	2.3
100	10.10	1.5	220	15.84	2.6
110	10.47	2.7	230	15.77	3.0
120	10.87	2.8	240	15.70	3.5

The inaccuracy is estimated to be within 1% at 20°K. but the error may easily be several per cent. at 15°K. In calculating energy 1 calorie (15°) was taken as 4.1832 international joules.

The heat capacity of chlorine has been measured by Eucken and Karwat[13] and their results have been compared with the present work in Table V. The weight of the chlorine used for the heat capacity measurements was found by condensing the material in a steel container with a valve and weighing the liquid at room temperature. 165.829 g. or 2.3385 moles of chlorine were used for the measurements.

The heat of fusion was measured in the usual manner; heat input was started at a temperature somewhat below the melting point and ended several degrees above. The known heat capacity of each phase permitted accurate correction. The results are presented in Table VI.

TABLE VI

HEAT OF FUSION OF CHLORINE

Melting point, 172.12°K. Molecular weight, 70.914

Run	ΔH cal. mole^{-1}
1	1530.5
2	1529.8
3	1531.1
4	1530.7
Average	1531 ± 1
Eucken and Karwat[13]	1615

The heat of vaporization was measured by attaching an absorption bulb, filled with a solution which contained 2 M sodium hydroxide and 1.7 M potassium iodide, to the calorimeter. In order to prevent the solution from being sucked back,

the entrance tube was immersed in a small amount of mercury at the bottom of the absorption bulb. The iodide was added to prevent clogging of the opening when a small portion of the chlorine reacted with the mercury. Heat was introduced so slowly that vaporization could proceed quietly from the surface. The results for the heat of vaporization at the boiling point are given in Table VII.

TABLE VII
HEAT OF VAPORIZATION OF CHLORINE
Boiling point, 239.05°K. Molecular weight, 70.914

Moles evapd.	Time of energy input, min.	ΔH cal. mole^{-1} at 760 mm.
0.16916	40	4881
.17280	40	4884
.17289	40	4876
.17148	40	4874
	Average	4878 ± 4

From vapor pressure equation, $\Delta H = 4851$

The value for the heat of vaporization calculated from the vapor pressure measurements, 4851 cal. mole^{-1}, agrees within the limit of accuracy of the data but is given no weight compared to the reliable calorimetric value. In calculating the heat of vaporization from dP/dT we made use of data of state observations on chlorine gas. Measurements have been made near the boiling point by Eucken and Hoffmann,[15] who also summarize the measurements of other observers. They represent the volume of chlorine gas by the equation

$$V = \frac{RT}{P} + 39 - \frac{8.5 \times 10^8}{T^{2.6}} \text{ cm.}^3/\text{mole} \quad (3)$$

In many previous researches in this Laboratory the gas volume at the boiling point has been estimated by means of Berthelot's equation of state in order to calculate the heat of vaporization from the vapor pressure. It is of interest to note that in the case of chlorine Berthelot's equation gives a gas volume and therefore heat of vaporization only 0.1% less than Equation (2) at the boiling point. The volume of liquid chlorine at the boiling point was obtained from the density equation of Pellaton[11] mentioned above.

The Entropy of Chlorine.—The calculation of the entropy of chlorine from the calorimetric data is summarized in Table VIII. The correction of the entropy to the ideal gas state was made by means of the thermodynamic equation

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P$$

and Berthelot's equation of state. The critical

(15) Eucken and Hoffmann, *Z. physik. Chem.*, **B5**, 442 (1929).

constants were taken as $P_c = 76.1$ atm.,[11] $T_c = 417°K.$[11]

$$\Delta S = S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$$
$$= 0.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ at the boiling point.}$$

We have used Berthelot's equation in preference to Equation (3) in making the above calculation because the data used in obtaining Equation (3) are not sufficiently complete to determine temperature coefficients at the boiling point.

TABLE VIII
THE ENTROPY OF CHLORINE

0–15°K., Debye function $hc\nu/k = 115$	0.331
15–172.12°K., graphical	16.573
Fusion 1531/172.12	8.895
172.12–239.05°K., graphical	5.231
Vaporization 4878/239.05	20.406
Entropy of actual gas at boiling point	51.44
Correction for gas imperfection	0.12
Entropy of ideal gas at boiling point	51.56 cal. deg.$^{-1}$ mole^{-1}

The calculation of the entropy of chlorine from spectroscopic data has been carried out by Giauque and Overstreet,[1] who have considered the effect of the three isotopic molecular species in considerable detail. We have used their equations and constants to calculate the entropy at the boiling point, 239.05°K. The value for the entropy of the ideal gas at this temperature and 1 atmosphere is found to be 51.55 cal. deg.$^{-1}$ mole^{-1}.

The calorimetric and spectroscopic values of the entropy are compared in Table IX.

TABLE IX
COMPARISON OF CALORIMETRIC AND SPECTROSCOPIC VALUES FOR THE ENTROPY OF CHLORINE
Entropy in cal. deg.$^{-1}$ mole^{-1}

T, °K.	Calorimetric data		Spectroscopic
	Actual gas	Ideal gas	
239.05	51.44	51.56	51.55
298.10	...	53.32	53.31

The entropy calculated from spectroscopic data does not include the entropy of isotopic mixing or that due to the nuclear spin of Cl^{35} and Cl^{37} since both of these effects cancel in chemical reactions with a high degree of accuracy. The molecular constants for each of the three isotopic molecular forms of chlorine were of course considered in the calculation. The symmetry number was taken as two in calculating the values given in the last column of Table IX. The value given for the ideal gas at 298.1 was obtained by using the band spectrum data for the gas above the boiling point.

The excellent agreement of the entropies calculated from calorimetric and from molecular data supports the third law of thermodynamics and also adds to the substantial evidence that only protons or deuterons may cause molecular rotation in the solid state at the temperatures of liquid hydrogen.

We thank Dr. R. A. Ruehrwein for assisting with the measurements.

Summary

The heat capacity of solid and liquid chlorine has been measured from 14°K. to the boiling point.

The melting and boiling points were found to be 172.12 and 239.05°K., respectively (0°C. = 273.10°K.).

The heat of fusion is 1531 cal. mole^{-1} and the heat of vaporization at the boiling point is 4878 cal. mole^{-1}.

The vapor pressure of liquid chlorine has been measured and the results represented by the equation: triple point 172.12 − 240°K., $\log_{10} P$ (int. cm. Hg) $= -(1414.8/T) - 0.01206\,T + 1.34 \times 10^{-5}\,T^2 + 9.91635$.

The observed triple point pressure was found to be 1.044 cm.

The entropy of chlorine was found to be 51.56 and 53.32 cal. deg.$^{-1}$ mole^{-1} at 239.05 and 298.10° K., respectively, for the ideal gas by means of the third law of thermodynamics.

The data are in excellent agreement with a calculation based on band spectrum data giving 51.55 and 53.31 cal. deg.$^{-1}$ mole^{-1} at the two temperatures.

The Ternary Systems KBrO₃–KClO₃–H₂O at 25° and NaBrO₃–NaClO₃–H₂O at 25 and 50°[1]

BY THEODORE SWENSON AND JOHN E. RICCI

These systems have been investigated for the purpose of finding and studying other examples of the type of solid solution previously suggested[2] as a possible addition to the types in the usual Roozeboom classification, namely, the formation of a single incomplete or limited series of solid solutions between two salts without any experimentally measurable degree of mutual solubility for one of the components. Such solid solutions were noted between potassium chlorate and potassium nitrate[3] and between sodium bromate and sodium sulfate.[2] The combinations of potassium bromate and chlorate, and of sodium bromate and chlorate, were therefore studied, as ternary systems with water, using the usual phase rule methods for the investigation of the solubility relationships.

Experimental

High grade (99.9%) potassium bromate was used without recrystallization, while sodium bromate was purified by recrystallization. The chlorates both contained small

amounts of the corresponding bromates; this bromate content was in each case determined, by the method described below, and the necessary corrections were then made when the dry chlorates were weighed out for the preparation of the ternary complexes.

The solubility determinations were made according to the usual procedure described in similar investigations, insofar as method of stirring, sampling, filtering, density determination and temperature control are concerned. Starting with complexes of known composition, and analyzing the saturated solutions at equilibrium, the solid phases were then determined by the usual methods of graphical or algebraic extrapolation, besides occasional analyses of wet and centrifuged residues.

The analytical method for the saturated solutions depended on the determination of the combined percentage of the two salts concerned, by evaporation, and iodometric titration of the bromate with thiosulfate, thus allowing the calculation of the percentage of the second salt by difference. This simple scheme involves the difficulty of titrating small quantities of bromate in the presence of large and varying amounts of chlorate. A preliminary investigation of this analytical problem was therefore necessary.

Iodometric Titration of Bromate in Presence of Chlorate.—The determination of bromate by iodometry, in the presence of chlorate, depends on the proper regulation of the acidity, the concentration of iodide, and the time allowed for reaction and titration. Conditions for the differential titration were first given by Junck,[4] chiefly

(1) The material of this paper is taken from the thesis of Mr. T. Swenson presented to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Master of Science.

(2) Ricci, THIS JOURNAL, 57, 805 (1935).

(3) Toda, J. Chem. Soc. (Japan), 43, 320 (1922).

(4) Junck, Z. Ges. Schiess Sprengstoffwesen, 8, 412 (1913).