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# Anhydrous Perchloric Acid: Heat Capacities and Thermodynamic Functions from 5 to 300°K.

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The thermal behavior of anhydrous perchloric acid was studied by adiabatic calorimetry and the data obtained were used as the basis for the evaluation of the thermodynamic functions. The triple point of perchloric acid occurs at 172.0°K. with an associated entropy of melting of 9.67 cal./(mole °K.). At 298.15°K. the values of the heat capacity at constant pressure ($C_p$), the practical entropy ($S°$), the enthalpy function $[(H° - H_0°)/T]$, and the Gibbs free energy function $[(F° - H_0°)/T]$ are 28.80, 45.02, 23.11, and −21.91 cal./(mole °K.). The fusion data conflict with the phase diagram reported by others and provide evidence that $HClO_4$ does exist as an independent species in the crystalline state. This conclusion is consistent with that obtained from recent infrared and Raman spectra of the solid which reveal bands similar to those of the liquid.

## Introduction

Although anhydrous perchloric acid is notorious primarily as a consequence of its marked instability, methods for its preparation were described as early as 1818,[2] and liquid nitrogen temperatures may be used to retard decomposition.[3] Several investigators[4-7] have examined its physical properties but few thermal and thermochemical data are available.[8] Interest in the properties of anhydrous perchloric acid evolved from consideration of the thermodynamics of the hydronium perchlorate (perchloric acid monohydrate) transition. This paper is the first in an endeavor to study the system chlorine heptaoxide–water.

## Experimental

*Anhydrous Perchloric Acid Sample.* The sample for calorimetric investigation was prepared by the method of Smith,[3] with rigorous observation of two precautions: complete exclusion of oxidizable materials including vapor as well as condensed phase contaminants, and adequate temperature control of the distillation reservoir and other portions of the apparatus where perchloric acid vapors are present. Even the pure va-

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(1) To whom correspondence concerning this work should be addressed.

(2) F. von Stadion, *Ann. chim. phys.*, **8**, 406 (1818).

(3) G. F. Smith, *J. Am. Chem. Soc.*, **75**, 184 (1953).

(4) M. Usanovich and T. Sumarokova, *Acta Physicochim. URSS*, **21**, 836 (1946).

(5) O. Redlich, E. K. Holt, and J. Bigeleisen, *J. Am. Chem. Soc.*, **66**, 13 (1944).

(6) R. C. Taylor and G. L. Vidale, *ibid.*, **78**, 5999 (1956).

(7) M. Usanovich, T. Sumarokova, and V. Udovenko, *Acta Physicochim. URSS*, **11**, 505 (1939).

(8) M. Berthelot, *Ann. chim. phys.*, **27**, 214 (1882).

por is apparently very sensitive to decomposition at slightly elevated temperatures, resulting in pollution of the product.[9] To meet these criteria the preparation was performed in a Pyrex vacuum line containing no stopcocks or valves. Approximately 1 l. of 20–23% fuming sulfuric acid (reagent grade) was added to a 3-l. distilling flask which contained 0.26 l. of twice-distilled 70% perchloric acid. The vacuum line was then sealed, the flask cooled to 5°, and the system evacuated. At 10° and a pressure of 0.05 mm., perchloric acid was rapidly evolved and was collected as a liquid in a trap cooled with Dry Ice–2-propanol slush. The temperature of the flask was increased gradually to 50° with a heating mantle. It was subsequently sealed from the line under vacuum. An intermediate liquid nitrogen trap prevented the decomposition products formed during seal-off from contaminating the sample. The approximately 100 cc. of product obtained was twice distilled prior to the ultimate distillation into the Pyrex calorimeter liner. Fractional fusion data indicate a maximum of 2.5 mole % impurity (presumably hydronium perchlorate) by the Mastrangelo and Dornte[10] method for impurities which are soluble in both the liquid and solid phases. After completion of the cryogenic investigation the sample was subjected to several chemical tests in an endeavor to determine the acid and perchlorate content. The results of conductometric titrations for both species indicated about 95 wt. % purity and substantiated visual evidence that the sample had further decomposed prior to removal from the calorimeter and that it was still spontaneously decomposing. An increasingly strong yellow sample coloration observed during the unloading deepened to dark orange as the sealed liner stood at 25° for approximately 6 hr. It is presumed that the color is probably occasioned by the presence of ozone as suggested by Smith,[11] or of chlorine, which is claimed to be a decomposition product of anhydrous perchloric acid by Zinov'ev and Tsentsiper.[12] Several attempts were made to identify the contaminate by infrared spectroscopy, but the impurity was too dilute to permit detection in a liquid sample and too soluble to isolate as a gas. In all probability the sample was significantly purer for the major portion of the temperature range of heat capacity studies than terminal analyses indicate.

*Cryogenic Technique.* The Mark III cryostat employed for these low temperature measurements resembles one reported earlier[13] which has been more fully described by Carlson.[14] Oxidizing power of the sample is such as to preclude even the use of noble metals in contact with the anhydrous perchloric acid. Silver, nickel, copper, and gold specimens subjected to the anhydrous acid at 300°K. were readily oxidized as

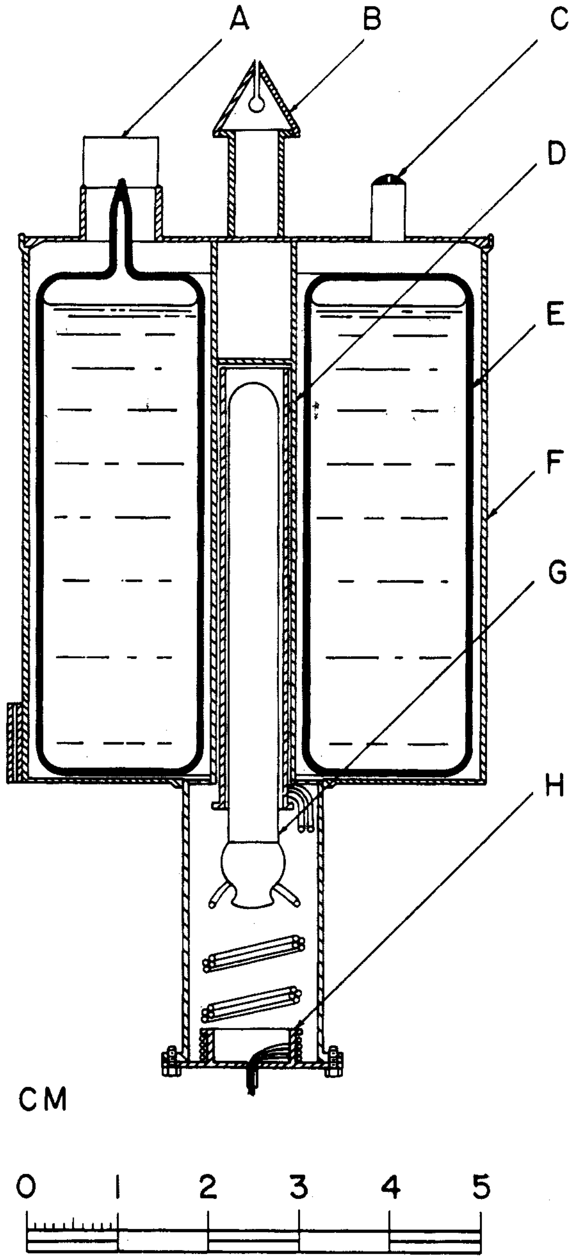

Figure 1. Schematic diagram of calorimeter W-33: A, cap over liner filling tube; B, thermal conductivity cone; C, helium filling tube; D, heater–thermometer well assembly; E, glass liner; F, calorimeter shell; G, thermocouple well; H, spool to equilibrate leads.

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(9) A. A. Zinov'ev, *Zh. Neorgan. Khim.*, **3**, 1205 (1958).

(10) S. V. R. Mastrangelo and R. W. Dornte, *J. Am. Chem. Soc.*, **77**, 6200 (1955).

(11) G. F. Smith, personal communication.

(12) A. A. Zinov'ev and A. B. Tsentsiper, *Zh. Neorgan. Khim.*, **4**, 724 (1959).

(13) E. F. Westrum, Jr., *J. Chem. Educ.*, **39**, 443 (1962).

(14) H. G. Carlson," Thermodynamic Properties of Methyl Alcohol, 2-Methyl- and 2,5-Dimethylthiophene and 2-Methylfuran," Doctoral Dissertation, University of Michigan, 1963; USAEC Report TID-15153 (1962).

shown by a loss in weight. Under the same conditions platinum did not lose weight but its presence resulted in rapid decomposition of the acid. Consequently, a Pyrex liner to contain the sample was used within a modified calorimeter (laboratory designation W-33) of the type shown in Fig. 1 conventionally used in this Laboratory. The copper calorimeter vessel's 0.2 mm. thick cylindrical shell is 5.3 cm. long, 4.4 cm. in diameter, and weighs about 44.3 g. This shell houses an annularly cylindrical Pyrex liner, E, with an internal volume of about 45 cc. and a weight of 36.5 g. Because of the necessity of avoiding even radiation heating of the perchloric acid sample, the liner is first soldered within its gold-plated copper shell and the small diameter Pyrex filling tube is then fused to the vacuum line used for the preparation of the sample. After loading the sample, 72.7128 g. *in vacuo*, and adding 14.4 mm. of purified helium gas to facilitate thermal conduction, the liner filling tube is sealed off and a small Monel cap, A, is soldered in place with low-melting Cerroseal (50% Sn–50% In) solder. This soldering operation is done while the sample is still at liquid nitrogen temperature. The sample in the sealed liner was brought into good thermal equilibrium with the surrounding copper vessel by admitting 17.8 cm. of helium gas pressure to the intervening space at 300°K. and sealing over a small aperture in the Monel tube, C, by fusing Cerroseal solder. The axial entrant well, D, accommodates the heater–thermometer assembly. The temperature-sensing element is a Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-3) within a cylindrical copper heater sleeve bifilarly wound with Fiberglas-insulated Advance wire having a resistance of 150 ohms. Apiezon-T grease is used to provide thermal contact between thermometer, heater, and calorimeter.

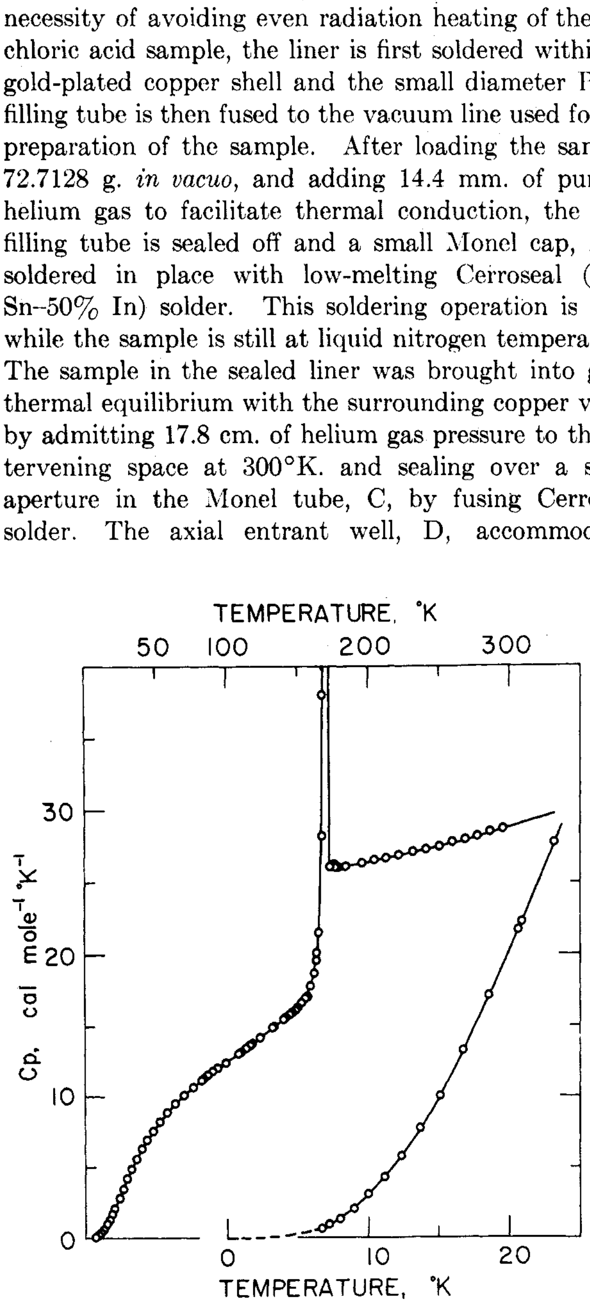

Figure 2. Heat capacity of perchloric acid.

In the Mark III cryostat, the calorimeter is surrounded by a cylindrical adiabatic shield, the three portions of which are individually controlled by separate channels of automatically regulated a.c. power to the heaters. This recording electronic circuitry provided with proportional, rate, and reset control action is used in preference to manual shield control above 50°K. and follows the temperature of the calorimeter to within approximately a millidegree, thereby reducing the energy exchange between the calorimeter and surroundings so that it is negligible compared with other sources of error. Copper–Constantan thermocouples monitor the temperature difference between calorimeter and shield and between shield and the ring used to temper the gradient in the bundle of leads. All measurements of temperature, time, potential, resistance, and mass are referred to calibrations or standards of the National Bureau of Standards.

The heat capacity of the heater–thermometer–liner–calorimeter assembly was determined in a separate set of experiments with the amounts of glass, Apiezon-T grease, and Cerroseal solder carefully adjusted to match those used during the measurements made on the loaded calorimeter or appropriate adjustments applied for the small differences.

## Results and Discussion

*Heat Capacity.* The experimental heat capacity values are listed in chronological sequence in Table I and presented graphically in Fig. 2. These data are presented in terms of the defined thermochemical calorie of 4.184 abs. j., the ice point of 273.15°K., and the 100.465 g. molecular weight of perchloric acid. The approximate temperature increments used can usually be inferred from the differences in the mean temperatures of the adjacent runs in Table I. Adjustment of the observed $\Delta H/\Delta T$ values for curvature was done by the method of Osborne, *et al.*,[15] and had a maximum value of 0.2% below 15°K. and decreased rapidly to less than 0.01% at higher temperatures. No correction for vaporization of the sample was found necessary since the vapor space was minimized and because a

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[15] N. S. Osborne, H. F. Stimson, T. S. Sligh, Jr., and C. S. Cragoe, Department of Commerce, Bureau of Standards, Scientific Paper No. 501 (1925), p. 65.

trial calculation showed that the correction would be less than 0.01% at the highest temperature studied. Smoothed heat capacities obtained by a digital computer least-squares fit presented in Table II are essentially identical with those obtained from a large-scale plot.

*Melting Behavior.* The earliest reported melting temperature of anhydrous perchloric acid, −112° (160°K.), is that of Van Wyk,[16] who used a pentane thermometer calibrated by comparison with a toluene thermometer from 0 to −70°. Hence he had extrapolated his scale more than 40° and indeed measured the eutectic temperature and assumed the maximum melting point for the pure anhydrous acid was only slightly higher. From the data of this research, the

**Table I:** Heat Capacity of Anhydrous Perchloric Acid[a]

| $\overline{T}$ | $C_p$ | $\overline{T}$ | $C_p$ | $\overline{T}$ | $C_p$ |
|---|---|---|---|---|---|
| Series I | | Series IV | | Series IX | |
| 6.64 | 0.065 | 144.80 | 15.83 | Fusion run F | |
| 7.18 | 0.092 | 150.55 | 16.39 | | |
| 7.97 | 0.129 | 156.16 | 16.96 | Series X | |
| 8.92 | 0.203 | 161.13 | 18.57 | | |
| 9.98 | 0.306 | 164.99 | 21.43 | 173.27 | 26.05 |
| 11.14 | 0.427 | 167.63 | 37.97 | 176.40 | 26.16 |
| 12.37 | 0.576 | | | | |
| 13.65 | 0.776 | Series V | | Series XI | |
| 15.06 | 1.016 | | | | |
| 16.68 | 1.329 | Fusion run A | | Fusion run G | |
| 18.52 | 1.712 | | | 177.77 | 26.06 |
| 20.59 | 2.170 | Series VI | | | |
| | | | | Series XII | |
| Series II | | 86.55 | 11.54 | | |
| | | 93.60 | 12.05 | 113.88 | 13.51 |
| 20.82 | 2.226 | 100.90 | 12.56 | 123.32 | 14.21 |
| 23.18 | 2.775 | 108.51 | 13.11 | 132.08 | 14.87 |
| 25.99 | 3.437 | 116.24 | 13.67 | 140.40 | 15.55 |
| 29.01 | 4.131 | 124.39 | 14.30 | 148.36 | 16.18 |
| 32.24 | 4.852 | 132.61 | 14.94 | 155.88 | 16.94 |
| 35.75 | 5.583 | 139.72 | 15.50 | 162.66 | 19.68 |
| 39.26 | 6.250 | 146.54 | 16.05 | 167.43 | 46.42 |
| 42.93 | 6.869 | 153.23 | 16.65 | | |
| 47.10 | 7.531 | 158.78 | 17.71 | Series XIII | |
| 51.99 | 8.201 | 163.55 | 20.08 | | |
| 57.33 | 8.853 | 167.03 | 28.21 | Fusion run H | |
| 63.01 | 9.474 | Fusion runs B | | 186.82 | 26.19 |
| 69.14 | 10.05 | 176.10 | 26.05 | 195.30 | 26.34 |
| 75.93 | 10.64 | 178.64 | 26.07 | 204.02 | 26.52 |
| 83.38 | 11.28 | 181.78 | 26.10 | 212.90 | 26.68 |
| | | | | 221.90 | 26.84 |
| Series III | | Series VII | | 231.31 | 27.08 |
| | | | | 240.97 | 27.28 |
| 82.11 | 11.18 | Fusion run C | | 250.53 | 27.49 |
| 90.40 | 11.83 | 178.44 | 26.05 | 259.78 | 27.78 |
| 99.25 | 12.44 | | | 268.60 | 27.95 |
| 108.11 | 13.08 | Series VIII | | 277.54 | 28.19 |
| | | | | 286.41 | 28.47 |
| Heated to 181°K. | | Enthalpy run D | | 295.14 | 28.86 |
| | | Fusion run E | | | |
| | | 178.83 | 26.10 | | |
| | | 184.49 | 26.16 | | |

[a] Units: cal., mole, °K.

**Table II:** Thermodynamic Functions of Perchloric Acid[a]

| $T$ | $C_p$ | $S°$ | $H° - H_0°$ | $-(F° - H_0°)/T$ |
|---|---|---|---|---|
| | | Crystal | | |
| 5 | 0.034 | 0.011 | 0.042 | 0.003 |
| 10 | 0.300 | 0.088 | 0.672 | 0.021 |
| 15 | 1.005 | 0.330 | 3.770 | 0.079 |
| 20 | 2.037 | 0.755 | 11.28 | 0.191 |
| 25 | 3.204 | 1.334 | 24.36 | 0.359 |
| 30 | 4.369 | 2.021 | 43.30 | 0.578 |
| 35 | 5.449 | 2.777 | 67.90 | 0.838 |
| 40 | 6.389 | 3.568 | 97.55 | 1.129 |
| 45 | 7.199 | 4.369 | 131.57 | 1.445 |
| 50 | 7.907 | 5.164 | 169.37 | 1.777 |
| 60 | 9.125 | 6.717 | 254.70 | 2.472 |
| 70 | 10.18 | 8.205 | 351.36 | 3.185 |
| 80 | 11.11 | 9.627 | 457.96 | 3.902 |
| 90 | 11.91 | 10.983 | 573.16 | 4.614 |
| 100 | 12.60 | 12.273 | 695.73 | 5.316 |
| 110 | 13.26 | 13.505 | 825.00 | 6.005 |
| 120 | 13.95 | 14.688 | 960.99 | 6.680 |
| 130 | 14.70 | 15.834 | 1104.2 | 7.340 |
| 140 | 15.50 | 16.952 | 1255.2 | 7.897 |
| 150 | 16.36 | 18.050 | 1414.4 | 8.621 |
| 160 | (17.33) | 19.137 | 1582.8 | 9.244 |
| 171.13 | (18.25) | 20.323 | 1779.0 | 9.919 |
| | | Liquid | | |
| 171.13 | (26.06) | 29.999 | 3436.0 | 9.919 |
| 180 | 26.14 | 31.302 | 3664.7 | 10.942 |
| 190 | 26.25 | 32.718 | 3926.6 | 12.052 |
| 200 | 26.43 | 34.069 | 4190.0 | 13.119 |
| 210 | 26.62 | 35.364 | 4455.3 | 14.148 |
| 220 | 26.83 | 36.607 | 4722.5 | 15.141 |
| 230 | 27.04 | 37.804 | 4991.8 | 16.100 |
| 240 | 27.26 | 38.959 | 5263.3 | 17.029 |
| 250 | 27.49 | 40.077 | 5537.1 | 17.928 |
| 260 | 27.73 | 41.160 | 5813.2 | 18.801 |
| 270 | 27.98 | 42.210 | 6091.7 | 19.649 |
| 280 | 28.25 | 43.223 | 6372.9 | 20.472 |
| 290 | 28.55 | 44.229 | 6656.9 | 21.274 |
| 300 | 28.75 | 45.198 | 6943.8 | 22.059 |
| 273.15 | 28.07 | 42.54 | 6180 | 19.91 |
| 298.15 | 28.80 | 45.02 | 6891 | 21.91 |

[a] $HClO_4$; 1 mole = 100.465 g.; units: cal., mole, °K.

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(16) H. J. Van Wyk, *Z. anorg. allgem. Chem.*, **48**, 1 (1906).

triple point of the anhydrous stoichiometric acid is 172.0°K., suggesting that Van Wyk's calibration was seriously in error. Moreover, he determined his temperature from thermal arrests of less than 1 min. during heating rates of 1.5 to 6°/min. Zinov'ev and Rosolovskii[17] report from partial thermographic and visual-polythermal data on the system chlorine-heptaoxide-water from 25 to 100 mole % of the former that the eutectic occurs at 53 mole % of $Cl_2O_7$ and $-100 \pm 2°$ ($173 \pm 2°$K.) and in contradiction of their own phase diagram (*cf.* Fig. 3) describe this as the melting point of perchloric acid. Moreover, they indicated that no "crystallization line" exists for the composition $HClO_4$, considered the components of the eutectic to be hydronium perchlorate and either $Cl_2O_7$ or a metastable compound such as $Cl_2O_7{\cdot}2HClO_4$, and postulated the following equilibrium, to exist at the 1:1 composition

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4$$

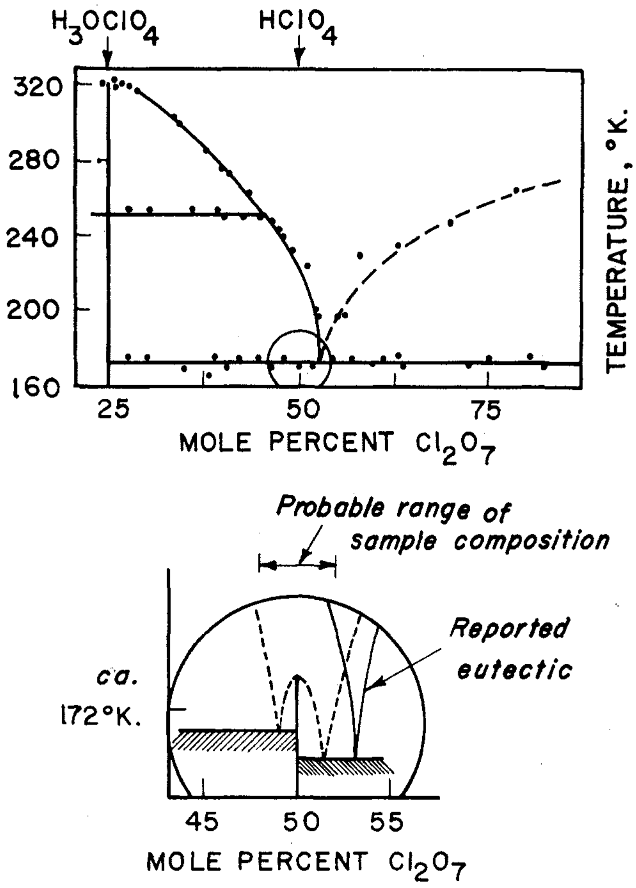

Figure 3. Phase diagram of the system chlorine heptaoxide-water from Zinov'ev and Rosolovskii[17]: circular inset: hypothetical congruent melting maximum for molecular perchloric acid species.

and to shift to the right with decreasing temperature. They report no evidence for either congruent melting or peritectic melting.

If one assumes for discussion the correctness of their melting diagram, the phenomenon observed in these calorimetric studies corresponds to the situation at the eutectic composition (53 mole %) rather than to that indicated at 50 mole % on their diagram. For, were the latter situation correct, a continuing thermal effect should have been obtained over the entire region from the eutectic ($173 \pm 2°$K.) to complete melting of the sample at 222°K. About 90% of the total thermal effect would be expected to appear at the eutectic temperature (from tie line relations) and the remaining 10% over the region 173 to 222°K. with some tendency toward concentration in the upper part of the range if the melting curve slope is reliable. However, since the observed heat capacities at all temperatures above the eutectic appear to be nearly linear and certainly not 4 cal./(mole °K.) higher than normal over the range 173 to 222°K., the phase diagram reported may be assumed erroneous in one of two ways. Possibly either (1) the analyses of the samples used in the phase study are faulty, thereby shifting the limit of the saturation curve such that the eutectic is almost exactly at 50 mole % chlorine heptaoxide; or (2) "fine structure" in the vicinity of 50 mole % of the diagram (circled portion in Fig. 2) was not detected; or both.

In the conversion from the weight per cent results of the titrimetric method used by Zinov'ev and Rosolovskii, an error of 0.5% yields a 3% error in the mole per cent in the concentration range near 50 mole % chlorine heptaoxide. Recognition of this fact and realization of the difficulty in analysis of high perchloric acid concentrations make it seem not unlikely that an error in the reported eutectic composition sufficient to place it at 50 mole % could occur.

The presence of a congruent melting point for perchloric acid would suggest its stability and lack of disproportionation in the solid. The circled portion of the phase diagram in Fig. 3 is enlarged at the bottom of the figure showing a hypothetical congruent fusion in the saturation curve and the formation of crystalline perchloric acid. The shaded areas of the figure emphasize that neither eutectic temperature has been sharply defined experimentally except to establish the existence of transitions in this region. The two postulated eutectic temperatures, however, may differ by less than 1°. Moreover, the extent of the postulated solid solution region needs to be delimited. The melting point

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(17) A. A. Zinov'ev and V. Ya. Rosolovskii, *Zh. Neorgan. Khim.*, 3 2382 (1958).

is estimated to be about 1° above the eutectic since the temperature of the latter reported by Zinov'ev and Rosolovskii is close to the melting temperature found in the present study.

Recent infrared investigation of crystalline anhydrous perchloric acid by Giguère and Savoie[18] is also consistent with the suggestion of the persistence of the molecular compound into the crystalline region proposed herein and does not support the interpretation of Zinov'ev and Rosolovskii, although the possibility of such an equilibrium does not appear to have been considered in the infrared study. A Raman study at liquid nitrogen temperatures by Dahl, Trowbridge, and Taylor[19] on a portion of the same crystalline $HClO_4$ used for the calorimetric investigation yielded eight frequencies in good accord with Raman lines observed by Simon and Weist[20] on liquid perchloric acid and infrared spectral lines by Giguère and Savoie on the gaseous, liquid, and crystalline states of the acid. Moreover, neither the very intense 921 cm.$^{-1}$ vibration of $H_3OClO_4$[6] nor the 501 and 695 cm.$^{-1}$ Raman[21] and infrared[22] bands of $Cl_2O_7$ were observed. Interference with these bands in the Raman spectra is unlikely and their absence indicates that neither species is present in the crystalline $HClO_4$ in appreciable amounts. In conclusion, the thermal, infrared, and Raman data all accord with the existence of an $HClO_4$ species in the crystalline state and provide ample evidence that the phase diagram and its interpretation by Zinov'ev and Rosolovskii are in error. Further investigation of this system in the vicinity of $HClO_4$ appears desirable for clarification of the nature of the phase relationships.

Considerable apparent premelting is evidenced in the heat capacity data even though heat capacity values as high as 1820 cal./(mole °K.) were observed. Table III and Fig. 4 summarize the fractional melting data from two separate series of runs used to calculate purity and melting point. The method of Mastrangelo and Dornte[10] for solid solutions was employed for this calculation and revealed a maximum impurity content of 2.5 mole %. As discussed previously, this is presumed to be largely hydronium perchlorate. On this basis, the melting point of the sample is 171.13°K. and that of pure anhydrous perchloric acid extrapolates to 172.0°K.

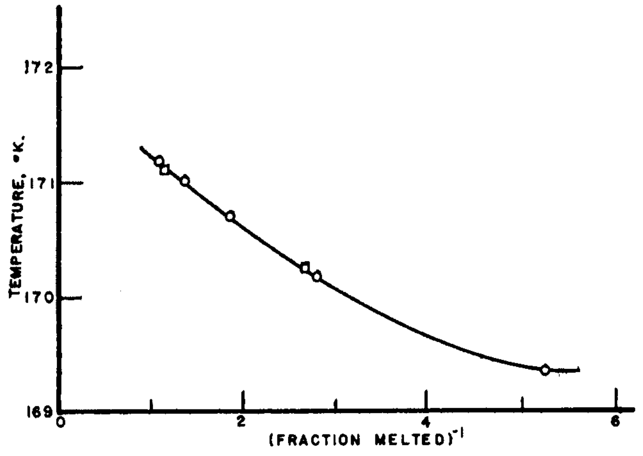

Figure 4. Fractional fusion for perchloric acid: fusion runs B, O; fusion runs G, □.

**Table III:** Fractional Fusion Data for Anhydrous Perchloric Acid[a]

| $\bar{T}_{mean}$ | $\Delta T$ | Apparent $C_p$ | $\Delta H_{excess}$ | $1/F$[b] | $T_{final}$ |
|---|---|---|---|---|---|
| | | Fusion runs B | | | |
| 168.830 | 1.035 | 284.4 | 316.50 | 5.238 | 169.348 |
| 169.765 | 0.835 | 352.0 | 594.92 | 2.787 | 170.182 |
| 170.444 | 0.525 | 593.8 | 896.95 | 1.848 | 170.706 |
| 170.857 | 0.301 | 1108 | 1224.78 | 1.354 | 171.007 |
| 171.092 | 0.171 | 1826 | 1533.09 | 1.081 | 171.178 |
| 173.073 | 3.791 | 57.04 | 1651.43 | | 174.968 |
| | | Fusion runs G | | | |
| 159.672 | 21.148 | 46.78 | 625.38 | 2.651 | 170.247 |
| 170.684 | 0.872 | 980.3 | 1464.71 | 1.132 | 171.119 |
| 173.349 | 4.460 | 68.47 | 1655.18 | | 175.579 |
| | Melting point: this sample | | | (1.000) | 171.132 |
| | Melting point: pure compound | | | (0.000) | 172.008 |

[a] Units: cal., mole, °K. [b] $F$ is the fraction melted.

The resolution of the normal lattice vibrational (phonon) contributions from excess values was done by extrapolating the heat capacity of crystal and liquid to the transition temperature and resulted in an enthalpy of fusion of 1657 cal./mole and a corresponding entropy increment of 9.67 cal./(mole °K.).

*Thermodynamic Functions.* Molal thermodynamic functions obtained by computer integration of the data combined with a Debye $T^3$ heat capacity extrapolation below 5° are listed at selected temperatures in Table II. The entropy and free energy functions do not include contributions from nuclear spin or isotopic mixing and hence are practical values for chemical thermodynamic purposes.

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(18) P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

(19) A. J. Dahl, J. C. Trowbridge, and R. C. Taylor, *Inorg. Chem.*, **2**, 654 (1963).

(20) A. Simon and M. Weist, *Z. anorg. allgem. Chem.*, **268**, 301 (1952).

(21) R. Fonteyne, *Natuurw. Tijdschr.* (Ghent), **20**, 275 (1938).

(22) R. Savoie and P. A. Giguère, *Can. J. Chem.*, **40**, 991 (1962).

As a test of the precision of the calorimetry and the heat capacity-type runs in the transition region, several enthalpy increments, each covering the anomalous region, were made and compared with the integral of heat capacity determinations in Table IV. The agreement will be seen to be quite satisfactory.

**Table IV**: Enthalpy and Entropy Increments of Perchloric Acid[a]

| Designation | Energy increments | $T_{\text{final}}$ | $T_{\text{initial}}$ | $H_{180}° - H_{150}°$ | $S_{180}° - S_{150}°$ |
|---|---|---|---|---|---|
| | | | Fusion | | |
| Series VI[b] | 12 | 180.05 | 150.26 | (2244.8) | (13.218) |
| Series VII | 2 | 181.63 | 150.00 | 2250.6 | 13.252 |
| Series VIII | 2 | 181.61 | 151.72 | 2251.4 | 13.255 |
| Series XI | 4 | 179.96 | 149.10 | 2248.5 | 13.245 |
| Run A[c] | 1 | 183.55 | 147.21 | (2258.8) | (13.300) |
| Run F | 1 | 175.04 | 148.57 | 2250.8 | 13.252 |
| Run H | 1 | 183.20 | 149.71 | 2250.4 | 13.251 |
| | | | Average | 2250.3 | 13.251 |
| | | | | $H_{180}° - H_{114}°$ | |
| | | | Crystal | | |
| Series VI | 5 | 150.26 | 112.30 | 589.69 | |
| Series XII | 5 | 152.24 | 108.85 | 588.96 | |
| Run D | 1 | 151.72 | 110.67 | 588.16 | |
| | | | Average | 589.27 | |
| Numerical quadrature of smoothed curve: | | | | 589.42 | |

[a] Units: cal., mole, °K. [b] Rejected from average due to long time (4.5 days) necessary to attain desired drift. [c] Rejected from average by Chauvenet's criterion.

The experimental precision of the thermodynamic functions may be considered to be 0.1% above 100°K. and an estimate of the effect of the apparently impure nature of the sample on the thermodynamic functions can be made on the basis of the following assumptions: that the impurity is entirely perchloric acid monohydrate and that the heat capacities of water and perchloric acid are additive for this substance. Maximum deviations occasioned in the heat capacity, enthalpy, entropy, and free energy functions at 298.15°K. are 0.21 cal./(mole °K.), 46 cal./mole, 0.20 cal./(mole °K.), and 0.05 cal./(mole °K.), respectively.

*Comparison with Spectroscopic Entropy.* The standard entropy of perchloric acid in the ideal gas state was reported as 70.7 cal./(mole °K.)[18] and subsequently corrected to 70.5 by Giguère[23] upon incorporating a recalculation of the rotational contribution based on recent electron diffraction data.[24] We deduced that a threefold potential energy barrier of 1.6 kcal. hinders internal rotation. Utilizing a recent development by Wulff[25] which permits evaluation of the barriers to internal rotation from thermal data on condensed phases only, we estimated the torsional frequency of the hydroxyl rotation to be 309 ± 14 cm.$^{-1}$ in good accord with the frequency $\nu_{12}$ = 307 cm.$^{-1}$ for the gaseous molecule.[18] This datum provides further evidence for the validity of the assumed magnitude of the barrier.

Comparison with the calorimetrically determined entropy (*cf.* Table V) involves evaluation of the entropy of vaporization, of compression, and of correction from the real to the ideal gaseous state. Unfortunately, definitive data are absent for all three terms. However, application of the Clausius–Clapeyron equation to two single vapor pressure data values (18 mm. at 16°[16] and 56 mm. at 39°[26]) of questionable reliability from different sources gives an entropy of vaporization of 29.7 cal./(mole °K.) and a vapor pressure of 28.7 mm. at 298.15°K. Compression from 28.7 to 760 mm. at this temperature would give an additional −6.5 cal./(mole °K.) entropy contribution if the gas is assumed to be ideal. As indicated in Table V, inclusion of these values gives a standard entropy of 68.2 ± 2.0 for gaseous perchloric acid monomer. Consideration of the gas imperfection occasioned by the estimated[18] 3 kcal./mole intermolecular hydrogen bonds (comparable to those in $HNO_3$ and notably weaker than in $H_2O$, $H_2O_2$, and in the alcohols) would tend to increase the entropy somewhat. At present the accord between spectro-

**Table V**: Entropy of Gaseous Perchloric Acid at 298.15°K.[a]

| | |
|---|---|
| 0–5°K. Debye extrapolation | 0.011 |
| 5–171.13°K., solid, numerical integration | 20.31 |
| Fusion, 1657.0/171.13 | 9.67 |
| 171.13–298.15°K., liquid, numerical integration | 15.02 |
| Vaporization at 28.7 mm , 8850/298.15 | 29.7 |
| Compression from 28.7 mm. to 760 mm., $-R \ln (760/28.7)$ | −6.5 |
| Total, $S°_{298.15}$ (ideal gas, 1 atm.) | 68.2 |
| Spectroscopic,[18] $S°_{298.15}$ (ideal gas, 1 atm.) | 70.5 |

[a] Units: cal., mole, °K.

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scopic and calorimetric entropy can only be said to be within experimental error and does not provide evience for or against the existence of residual entropy. Further studies on the vaporization and thermodynamics of the gaseous phase are obvious desiderata.

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# Triethanolamine Borate. The Heat Capacity and Thermodynamic Functions from 5 to 350°K.

by Peter Castle, Richard Stoesser, and Edgar F. Westrum, Jr.[1]

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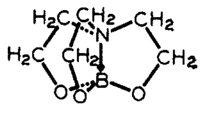
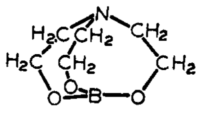
The heat capacity of $B(OCH_2CH_2)_3N$ has been determined by adiabatic calorimetry and its temperature dependence found to be sigmoid with no thermal anomalies over the range 5 to 350°K. Thermodynamic properties were derived by integration of the measured heat capacity data. The heat capacity at constant pressure ($C_p$), the practical entropy ($S°$), the enthalpy function ($[H° - H_0°]/T$), and the free energy function $-([G° - H_0°]/T)$ at 298.15°K. in cal./(g.f.w. °K.) are: 44.75, 43.78, 22.48, and 21.30.

## Introduction

Thermophysical properties of triethanolamine borate [2,2′,2″-nitrilotriethanol borate, $B(OCH_2CH_2)_3N$] are interesting, first because of the possibility of further elucidation of the general thermodynamic characteristics of globular molecules, and second due to the postulated existence of two spatial configurations[2-4] for the molecule. The "triptych" form



involves a postulated bond between boron and nitrogen, while the cage structure



has a nitrogen electron pair on the exterior of the cage. Kinetic studies of reactions involving attack on the nitrogen electron pair by alkyl iodides,[2] by mineral acids,[2] and by hydrolysis,[5] indicate that reactions at ambient temperatures involving the nitrogen electron pair in triethanolamine borate proceed much more slowly than identical reactions with ordinary tertiary amines. Infrared spectroscopic studies[3] indicate the possible formation of a boron–nitrogen bond which requires the triptych structure. In addition, the dipole moments of triethanolamine borate and its derivatives[5] show the nitrogen electron pair to be almost equally distributed between the boron and nitrogen, which indi-

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(1) To whom correspondence concerning this work should be addressed.

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