Sedimentation occurs normally within soap curd, confirming that the curd fibers enmesh the continuous aqueous mother liquor.

STANFORD UNIV., CALIF. RECEIVED JUNE 16, 1937

[CONTRIBUTION FROM THE INSTITUTE OF INORGANIC CHEMISTRY TECHNICAL UNIVERSITY OF NORWAY]

Fusion Point, Vapor Pressure and Heat of Evaporation of Vanadium Oxytrichloride

BY H. FLOOD, J. GØRRISSEN AND R. VEIMO

In connection with investigations relating to the formation of vanadium oxytrichloride during chloridizing roasting, the authors attempted to determine the fusion point, vapor pressure and heat of evaporation of this compound.

Vanadium oxytrichloride was prepared by conducting chlorine over vanadium pentoxide and cleaning the product in a current of nitrogen followed by a fractional distillation.

Fusion Point.—The fusion point of vanadium oxytrichloride has not been determined previously. H. E. Roscoe[1] (1870) states that the compound does not solidify when cooled down to −15°, while F. E. Brown and F. A. Griffitts[2] (1934) only verify that it is still liquid at −77°.

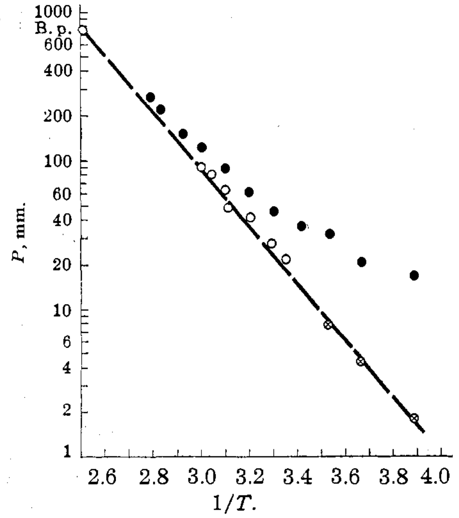

Fig. 1.—●, F. E. Brown, F. A. Griffitts; ○, ⊗, H. Flood, J. Gørrissen and K. Veimo.

By cooling our preparation with liquid air in a vessel surrounded by ethyl alcohol, a well-defined freezing point was recorded at −79.5° by means of a calibrated pentane thermometer.

Vapor Pressure.—The vapor pressure was determined by two methods, *viz.*, by comparative measurements based on saturated water vapor in the temperature range of 20–60° and for the range of −15 to +15° by conducting dry nitrogen gas over the preparation and determining by analysis the content of vanadium oxytrichloride per liter of gas. The analysis was made by reduction with hydrogen sulfide and titration by potassium permanganate.

The weakness of the first method is due to the ease with which the mercury of the manometer is attacked by the vanadium oxytrichloride, which produces errors on account of capillary depression and also possibly by the formation of volatile products of reaction.

In Fig. 1 are the observed vapor pressures plotted in a logarithmic scale in relation to the reciprocal of the absolute temperature ($1/T$), the open circles representing the values obtained by comparative measurements against saturated water vapor, while the crossed circles were established from tests in the nitrogen current.

After the authors had commenced their investigations, their attention was called to a communication from F. E. Brown and F. A. Griffitts[2] where data on vapor pressure of vanadium oxytrichloride are given for the temperature range of −77 to +80°. These data also have been included in Fig. 1 and are represented with full circles.

As will be seen from the plotting on Fig. 1 there is a considerable discrepancy between the latter data and those of the authors.

As the tensions determined by Brown and Griffitts show an abnormal variation with temperature (the heat of evaporation *decreases* rapidly with falling temperature) it is likely that their measurements are obscured with errors due to attack of manometer mercury by vanadium oxytrichloride.

Heat of Evaporation.—If a straight line is drawn through the plotted tension–temperature

---

[1] H. E. Roscoe, from J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green & Co., New York, N. Y., 1929, p. 807.

[2] F. E. Brown and F. A. Griffitts, *Iowa State Coll. J. Sci.*, **9**, 89 (1934).

values on Fig. 1 and the boiling point (b. p.) at 127° and 760 mm.,[3] the slope of this line will be proportional to the heat of evaporation according to the well-known formula $Q = R \, \mathrm{d} \ln p/\mathrm{d}(1/T)$.

From this the average heat of evaporation between −15 and +130° is computed to be $Q = 8.7 \pm 0.2$ kcal.

The following table shows the relation of vapor tension to temperature, column I indicating temperature in °C., column II the tension computed on basis of $Q = 8.7$ kcal. (*i. e.*, from the mean curve), and column III the measured tension values, all in mm.

I	II	III
−15	1.75	1.9
0	4.6	4.4
11.5	8.4	8.0
19.1	13	15.5
31.1	24	28.3
40	35	42
50	55	64
60	85	93
80	175	
100	340	
(127)	(760)	(760)

The authors gratefully acknowledge financial support from "Nansenfondet."

Summary

Determination of the vapor pressure of vanadium oxytrichloride against saturated water vapor and by lower temperatures in a nitrogen current has been made. By these methods the error due to attack of vanadium oxytrichloride on manometer mercury is avoided.

The heat of evaporation has been calculated based upon the results obtained in the investigation. The fusion point of vanadium oxytrichloride has been found to be −79.5°.

TRONDHEIM, NORWAY RECEIVED JULY 22, 1937

---

[3] A. Safarik and H. E. Roscoe from Mellor, ref. 1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY[1]

The Heat Capacity of Supercooled Liquid Glycerol[1]

BY A. G. OBLAD[2] AND ROY F. NEWTON

Introduction

The heat capacity of glycerol has been determined by F. Simon[3] and by G. E. Gibson and W. F. Giauque[4] as a part of a program of critically testing the third law of thermodynamics. The results of these investigations are nearly identical, although Simon used glycerol containing about 1.2% of water. The determinations were made by a modification of the Nernst method of electrical heating in which the time from the initial temperature to the last significant temperature of a determination usually was not more than thirty minutes. According to their data the specific heat of crystalline glycerol decreases almost uniformly with decreasing temperature, while that of the supercooled liquid is somewhat greater and remains so down to about 190°K. In the neighborhood of this temperature the specific heat of the liquid rapidly approaches that of the crystals, and at still lower temperatures the specific heats become practically coincident and remain so to the lowest temperatures reached by Gibson and Giauque. These results indicate a difference of about 5 e. u.[5] between the entropy of the supercooled liquid and the crystalline solid at the absolute zero, and have led to the rather common view that the third law of thermodynamics applies only to crystalline substances, and that supercooled glasses possess a positive entropy at the absolute zero.

Otto Stern, in an unpublished communication, and F. Simon[6] have criticized these determinations on the grounds that complete equilibrium with respect to all possible forms of thermal energy may fail to be reached at low temperatures in such a short time interval as that allowed in the Nernst method. Since the determination of the heat capacities of supercooled liquids has such an

---

[1] Based upon a thesis submitted by A. G. Oblad to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1937. Presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

[2] Present address: Standard Oil Company, Whiting, Indiana.

[3] F. Simon, *Ann. Physik*, **68**, 241 (1922).

[4] G. E. Gibson and W. F. Giauque, THIS JOURNAL, **45**, 93 (1923).

[5] Simon and Lange, *Z. Physik*, **38**, 227 (1926), and Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 539 (1937), have extended these results to 10 and 2.8°K., respectively, and have obtained a difference of 4.6 e. u. The latter authors also compared the heat capacities of two glycerol glasses which had been cooled through the congealing zone at very different rates, and found the differences to be about equal to the experimental error.

[6] F. Simon, *Z. anorg. allgem. Chem.*, **203**, 219 (1931).