ment is quite satisfactory. Similar data for solutions up to 0.1 *M* have been discussed by Scatchard.[28]

The writer wishes to express his indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing mechanical aid in the calculations.

Summary

A report is made of the determination of the freezing points of aqueous solutions of hydrochloric acid up to a concentration of 1.0 molal, making use of a platinum thermometer as a temperature measuring device.

The activity coefficients are calculated and compared with those derived from electromotive force measurements.

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[CONTRIBUTION FROM THE LABORATORY OF THE LINDE AIR PRODUCTS COMPANY]

SOME PHYSICAL PROPERTIES OF VINYL CHLORIDE

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Although vinyl chloride (C_2H_3Cl) has been known as a chemical compound for a number of years, owing to the difficulties attending its preparation and purification, relatively little exact work has been done with it. Recent progress in chemical synthesis has made this material available in quantity commercially and therefore it has seemed worth while to review previous work on the subject in order to ascertain the present state of knowledge of the properties.

Beyond a few scattered values of the boiling point of vinyl chloride, very little has been published concerning its physical properties. Recently the desirability of utilizing vinyl chloride as a refrigerating fluid (boiling point —13.9°) has been suggested, and hence it has appeared desirable to conduct an experimental determination of its most important physical properties. In this investigation the measurements of the vapor-pressure curve, liquid densities and freezing point are reported; in addition a few of its other physical properties have been estimated from theory.

Description of Experiments

Vapor-Pressure Curve.—Commercial samples of vinyl chloride[1] were obtained in small steel cylinders. This liquid was purified by fractional distillation in a vacuum insulated, low-temperature Hempel column and was further subjected to a fractional distillation in a closed, low-

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[28] Scatchard, THIS JOURNAL, **47**, 641 (1925). See also LaMer, *Trans. Amer. Electrochem. Soc.*, **51**, (1927), preprint No. 58; and Van Laar, *Z. anorg. allgem. Chem.*, **139**, 108 (1924).

[1] Material obtained from the Carbide and Carbon Chemicals Corporation, New York City.

temperature fractionation apparatus, operated with a Langmuir pump in series for the purpose of removing the traces of moisture and all non-condensable gases. Finally, the samples were tested for boiling range and pressure drop in the vapor-pressure apparatus mentioned below. On distilling off over 95% of the sample at constant temperature, the pressure drop was found to be less than 2 mm. in 760 mm. of Hg, and on distilling off at constant pressure the temperature drop was less than 0.05°. It is probable that the purity was higher than 99.9%.

The vapor pressures were measured over the temperature range from —28 to 60°, corresponding to a pressure range of 40 to 760 cm. of Hg absolute or from 0.5 to 10 atm. absolute. Below and around one atmosphere a mercury manometer, with a vacuum over one arm, was employed for the pressure measurement. From one to five atmospheres a tall mercury manometer was used, while above this pressure a dead-weight piston gage served to measure the pressure. Various forms of containers for the sample were used. In general the experimental technique was similar to that used in the measurement of the vapor pressures of some paraffin hydrocarbons,[2] to which work reference is made for experimental details.

The boiling point at one atmosphere was determined a number of times and was found to be —13.9, ±0.1°. Biltz[3] gives the boiling range as —18 to —15°, which would seem to be much too low temperatures and too wide a range to correspond with the pure material tested in this investigation. In the following table are given the values of the pressures and corresponding temperatures observed for the vapor pressures.

TABLE I

VAPOR PRESSURES OF VINYL CHLORIDE

Temp., °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg	Temp., °C	Press., cm. Hg
−28.73	39.56	4.01	149.06	39.72	450.0
−23.02	51.30	5.53	158.2	46.80	543.4
−16.61	67.76	16.21	225.8	54.87	667.6
−13.61	76.75	25.72	302.7	60.34	758.6
− 8.32	94.90	33.53	378.9	60.34	760.3
− 1.57	122.48	39.72	449.2		

The experimental observations have been combined into the well-known Nernst[4] equation of the form

$$\log p = a + b/T + 1.75 \log T + cT$$

in which the pressure p is expressed in atmospheres absolute and the temperature T in degrees centigrade absolute. The values for the constants are as follows

$$a = 0.8420; \quad b = -1150.9; \quad c = -0.002415$$

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[2] Dana, Jenkins, Burdick and Timm, *Refrigerating Eng.*, **12**, 387 (1926).

[3] Biltz, *Ber.*, **35**, 3525 (1902).

[4] Nernst, "Theoretical Chemistry," Macmillan Co., New York, **1923**, p. 815.

On the average the agreement of the observed results with those computed by the formula is within the experimental error, 0.3%.

Liquid Densities.—The method employed for the determination of the liquid densities has been described in an earlier paper by the authors,[2] and is similar to that used by the Bureau of Standards on ammonia.[5] Preliminary experiments were first made in a Pyrex pycnometer in which only the coefficient of expansion of the liquid was measured, since the weight of liquid vinyl chloride in the pycnometer was not ascertained. The final measurements were made with the pycnometer, shown in Fig. 1, constructed of Jena 16^{III} glass. After calibrating the pycnometer carefully with mercury, the sample was condensed in and the pycnometer sealed off. Readings of the liquid in the stem were observed at various temperatures from —13 to 60° in a thermo-regulated bath and the temperatures were read by a platinum resistance thermometer. By weighing the pycnometer full and empty, the corrected weight of vinyl chloride was found to be 5.9716 g. Enough data were then available for computing the absolute density. The results for the coefficient of expansion agreed to 0.1% with those obtained with the Pyrex pycnometer.

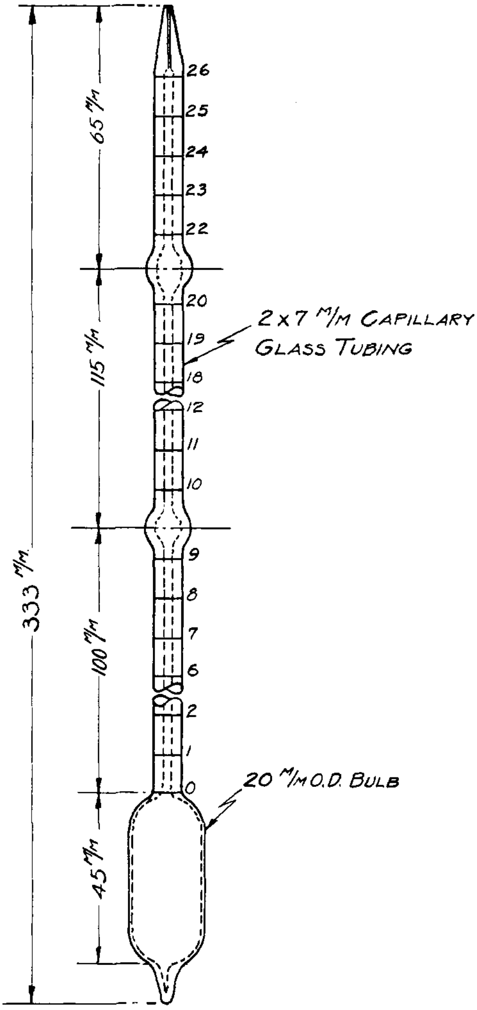

Fig. 1.—Piezometer for liquid densities.

Correction has to be applied for the quantity of vapor in the vapor space above the liquid in the pycnometer. No experimental values for the vapor densities are available, however, so that these values were computed theoretically. Since, however, the maximum value for this correction is about 0.15% and an accuracy

[5] Cragoe and Harper, Bureau of Standards, Scientific Paper, No. 420.

of 0.1% is claimed for the results, it is evident that an accuracy of 50% for the vapor density correction is sufficient. It is believed that the vapor density can be computed with much higher accuracy and as a matter of interest this has been done and the results are given later on.

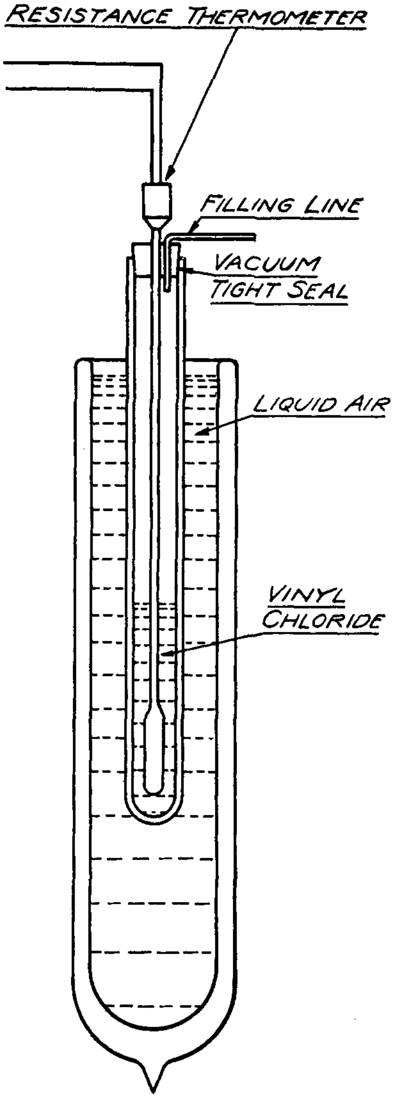

Fig. 2.—Freezing-point apparatus.

The liquid densities of vinyl chloride are shown in Table II.

It is believed that the results are good to 0.1%.

An empirical formula representing the results from —13 to 60° is as follows

$$d = 0.9471 - 0.001746t - 0.00000324t^2$$

in which d is the liquid density in grams per cc. and t is the temperature in degrees centigrade. The data agree with the formula to better than 0.1%.

Freezing Point.—Since relatively large quantities of vinyl choride, purified by fractional distillation for the vapor-pressure measurements, had been prepared, it was decided to determine the freezing point by direct immersion of the thermometer in a large sample. The apparatus is shown in Fig. 2. Throughout the measurements the sample was handled in a closed system to keep out moisture. Liquid air was employed as the cooling medium. With a single tube the rate of cooling was too rapid; hence a double-walled tube was used. This also had the effect of producing a uniform temperature gradient in the freezing-point sample. Preliminary determinations with a calibrated, propane filled, low temperature thermometer resulted in the value —159°. The final and most accurate determination was made with a platinum resistance thermometer which had previously been calibrated at the freezing point of mercury, the sublimation point of carbon dioxide and the boiling point of oxygen.[2] The period of freezing lasted about seven minutes and the freezing temperature was constant to within 0.1° at —159.7°. Considering the purity of the sample it is safe to claim an accuracy of 0.1° for this freezing point.

TABLE II

LIQUID DENSITIES OF VINYL CHLORIDE

Temp., °C.	Liquid density, g./cc.	Temp., °C.	Liquid density, g./cc.
−12.96	0.9692	39.57	0.8733
1.32	.9443	48.20	.8555
13.49	.9223	59.91	.8310
28.11	.8955		

Estimated Vapor Densities and Latent Heats

Since the vapor densities were required for correction terms to the liquid densities, it appeared worth while to estimate them as accurately as possible so that the values might be of use elsewhere. At the same time, since the vapor-pressure curve was measured, the latent heats could be estimated with the aid of Clapeyron's equation.

Unfortunately the critical constants of vinyl chloride are not known so that the law of corresponding states could not be employed directly; but van Laar[6] has described methods based on empirical relationships by means of which the critical constants may be computed, which in turn serve in other relationships from which the specific volumes can be ascertained. By these methods the estimated critical pressure is 52.2 atm. while the estimated critical temperature is 142°.

In the following table the estimated specific volumes of the saturated vapor, estimated by the method of van Laar, are given.

TABLE III

ESTIMATED SPECIFIC VOLUMES OF SATURATED VAPOR OF VINYL CHLORIDE

Temp., °C.	Spec. vol., cc./g.	Temp., °C.	Spec. vol., cc./g.
−30	635	20	105.4
−20	418	30	79.7
−10	284	40	60.3
0	199	50	46.3
+10	143.3	60	36.2

To compute the latent heats the above values for the specific volumes were used and the slopes of the vapor-pressure curve were determined graphically.

The latent heats were also computed by means of the law of corresponding states, comparing with the values given by Holst[7] for methyl chloride. At the boiling point the values by the two methods agree to 1%, while at 50° they agree to 5%.

[6] Van Laar, "Die Zustandsgleichung," Leopold Voss, Leipzig, **1924**, pp. 186, 21.

[7] Holst, *Comm. Phys. Lab. Univ. Leiden*, No. 144c.

TABLE IV

ESTIMATED LATENT HEATS OF VINYL CHLORIDE

Temp., °C.	Slope of vapor-pressure curve, cm. of Hg/°C.	Latent heat, cal./g. By Clapeyron's equation	Latent heat, cal./g. By corresponding states
−20	25.4	88.4	85.7
−10	35.4	84.1	84.1
0	47.1	81.2	83.0
+10	61.8	79.8	81.7
20	79.7	77.7	80.2
30	100.2	76.2	78.5
40	124	73.2	76.6
50	151	70.1	74.4

Summary

The vapor pressure of vinyl chloride was measured from —28 to 60°. The normal boiling point was found to be —13.9, ±0.1°.

The liquid densities were measured over the temperature range —13 to 60°.

The freezing point was found to be —159.7, ±0.1°.

Estimated values of the vapor densities and latent heats were computed from theoretical relationships.

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NOTE

Calculation of Heats of Combustion.—Kharasch and Sher[1] have applied the electronic conception of valence to the calculation of heats of combustion of organic compounds. They find that the energy change which accompanies the displacement of one valence electron from the position which it occupies in methane, a carbon chain or the benzene nucleus to the position after combustion in carbon dioxide is 26.05 kg. cal. per mole. Thus the heat of combustion of a hydrocarbon is given by the product $26.05 \times N$, where N is the number of electrons displaced.[2] Electrons associated with bonds other than C—C and C—H are accompanied by an additional energy change during combustion. To the term $26.05\ N$, Kharasch and Sher add 26 kg. cal. for each aliphatic ether group, 13 kg. cal. for each ethylenic linkage, primary alcohol, ester or aromatic ether group and 6.5 kg. cal. for each secondary alcohol or ketone group. No correction is added for tertiary alcohol, phenol or acid groups. In most cases this method gives good results, but for aromatic compounds the calculated values are uniformly higher than the experimental values and the

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[1] Kharasch and Sher, *J. Phys. Chem.*, **29**, 625 (1925).

[2] Each bond corresponds to two electrons. In oxygen compounds the two oxygen bonds are disregarded. Thus N is 8 for methane, 30 for benzene, 58 for phenyl benzoate, etc.