the observed temperature for heat leak was calculated by integration by the trapezoidal rule of the heat leak as a function of time from measurements taken at half-minute intervals. The calculation was simplified by the linear relationship of heat leak to temperature over the temperature range of the measurements.

Enthalpies of Solution. The standard enthalpy of formation of $PO(NH_2)_3$ at 25°C was determined from the published enthalpies of formation of H_3PO_4, $NH_4H_2PO_4$, and H_2O, the enthalpy of dilution of H_3PO_4; and the enthalpy at 25°C of the reaction

$$2(H_3PO_4\cdot 1.5H_2O) + PO(NH_2)_3 = 3NH_4H_2PO_4 \qquad (3)$$

Temperature changes during dissolution were arbitrarily limited to 1°C, which determined the size of the sample of phosphoryl triamide and thus the amounts of the other materials in Equation 3.

In a preliminary test, in which 0.44 gram of $PO(NH_2)_3$ was dissolved in 84 ml 4*m* HCl at 25°C, hydrolysis to orthophosphate was complete in 5 min.

The enthalpy of reaction of Equation 3 was determined by the scheme

$$\begin{array}{rl} \text{ampul } H_3PO_4\cdot 1.5H_2O + \text{solvent} = \text{solution A} & \Delta H_1 \\ \text{ampul } PO(NH_2)_3 + \text{solution A} = \text{solution B} & \Delta H_2 \\ \text{ampul } NH_4H_2PO_4 + \text{solvent} = \text{solution B} & \Delta H_3 \end{array}$$

Results of determinations of ΔH_1, ΔH_2, ΔH_3 and their average values and double standard deviations are shown in Tables I–III. The sum of $2\ \Delta H_1 + \Delta H_2 - 3\ \Delta H_3$ is $-77{,}440 \pm 74$ cal (double standard deviation) for the enthalpy of reaction of Equation 3.

From the standard enthalpies of formation at 25°C (*5*) of H_3PO_4(l), −302.8 kcal; and $H_3PO_4\cdot 1.5H_2O$ (soln), −305.26 kcal (*5*); the enthalpy at 25°C of the reaction

$$H_3PO_4(l) + 1.5H_2O(l) = H_3PO_4\cdot 1.5H_2O(soln) \qquad (4)$$

was calculated to be −2.46 kcal. Addition of twice this value to the enthalpy of reaction of Equation 3 shows the enthalpy at 25°C of the reaction

$$PO(NH_2)_3(c) + 2H_3PO_4(l) + 3H_2O(l) = 3NH_4H_2PO_4(c) \qquad (5)$$

to be −82.36 kcal. Substitution of the standard enthalpies of formation from the elements at 25°C (*5*) of $NH_4H_2PO_4$(c), −345.38 kcal/mol; and H_2O(l), −68.315 kcal/mol; and the standard enthalpy of formation at 25°C of H_3PO_4(l); and the enthalpy of reaction of Equation 5 in the equation

$$\Delta H_f°PO(NH_2)_3(c) = 3[\Delta H_f°NH_4H_2PO_4(c)] - 2[\Delta H_f°H_3PO_4(l)] - 3[\Delta H_f°H_2O(l)] - \Delta H_R \qquad (6)$$

gave −143.2 kcal/mol for the standard enthalpy of formation of $PO(NH_2)_3$(c) at 25°C. An estimate of the uncertainty is not given because it is largely dependent upon the uncertainty of the auxiliary enthalpies of formation taken from ref. *5*.

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Densities, Viscosities, and Vapor Pressures of Copper(II) Chloride Solutions in Hydrochloric Acid

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Densities and viscosities of 1.5*M* copper(II) chloride solutions in 4.0, 5.0, 6.0, and 7.0*M* hydrochloric acid as well as 0.5 and 1.0*M* copper(II) chloride solutions in 5.0*M* hydrochloric acid have been determined for a temperature range from 30–90°C. Equations for calculating densities and viscosities as a function of copper(II) chloride and hydrochloric acid concentration, as well as temperature derived by multiple regression analysis, are supplied. Vapor pressures of water and hydrogen chloride of the mentioned solutions are reported for a temperature range from 60–90°C.

Considerable data on the physical properties of hydrochloric acid are available, but no such data on copper(II) chloride solutions in hydrochloric acid have been published. Some properties of such solutions were determined and are reported.

EXPERIMENTAL

All temperature measurements were made by means of Princo thermometers graduated from −1.0–101.0°C in steps of 0.1°C. They were calibrated by immersing the thermometers into a silicone oil bath together with a standard platinum resistance thermometer (L&N 1119552) previously calibrated by the National Bureau of Standards.

Density measurements at different temperatures were made by measuring the volume expansion of a known amount of solution. A glass bulb was sealed to a precision buret so that 100 ml at room temperature would extend into the lower part of the buret. A stopcock at the upper end of the buret allowed us to keep the apparatus closed while bringing the system to temperature. Distilled water was employed to calibrate the graduation on the buret and to establish its linearity. Mea-

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surements at elevated temperatures allowed the computation of a correction factor for the expansion of glass.

One hundred milliliters of solution were introduced into this device through thin Teflon tubing to avoid droplets in the empty portion of the buret. The device was weighed and the weight of the solution obtained was corrected for the buoyancy of air. The device was then immersed in an ethylene glycol bath to avoid condensation on the wall of the buret. The end of the buret was closed with a stopcock and opened only while taking a reading. The temperature was maintained constant to ±0.05°C.

Viscosities were measured with an Ostwald viscometer modified according to Cannon Fenske. The viscometer was carefully cleaned before each measurement with a hot solution of potassium dichromate in sulfuric acid and extensively rinsed with distilled water and methanol. Air was sucked through cotton wool and then through the viscometer by means of an aspirator to complete dryness. Precisely 5 ml of solution were transferred into the viscometer and two stopcocks were connected to the ends of the viscometer by rubber tubing that had been boiled in distilled water. The stopcocks were closed and the viscometer was submerged into an ethylene glycol bath so that only $^{1}/_{2}$ in. of the viscometer extended above bath level.

The viscometer with the stopcocks closed was left in the bath for 3 hr to thoroughly equilibrate the temperature in the system, then the stopcocks were opened, and the liquid was pressed above the top mark by means of a squeeze bulb to minimize any composition changes due to evaporation. Five determinations of the efflux time were made. The deviation was found to be not greater than 0.1 sec for any of the sets of data measured. An average value was used for calculating the viscosity.

Water served as a standard, the density and viscosity of which was obtained from the literature (*1*, *2*). The viscosity data are based on the currently accepted value of 1.002 cP for the viscosity of water at 20°C. The absolute viscosity was obtained from the following equation:

$$\eta_s = \frac{\eta_w \times d_s \times t_s}{d_w \times t_w}$$

t represents the average efflux time, d the density, η the viscosity, the subscript s refers to solution and w to water. The bath temperature was kept constant at ±0.05°C.

Vapor pressure measurements were made by the "air saturation method." The apparatus employed consisted of an air cylinder, a drying tube loosely filled with glass wool and phosphorus pentoxide, a flowmeter, a 10-ft $^{1}/_{4}$-in. copper tubing, two saturator vessels, a glass tubing wrapped with heating tape, two cold traps in a Dry Ice–acetone bath, another drying tube with glass wool, and a wet test meter. The pieces were connected in the above order by thick gum rubber tubing that had been cleaned by boiling it with distilled water for a short time. The arrangements allowed the incorporation of thermometers into the gas stream after the copper coil, between the two saturator vessels, and before the wet test meter as well as an open end manometer after the second cold trap. The open end manometer was filled with a paraffin oil of known density to allow calculation of the pressure of the system in reference to the atmospheric pressure. The difference between the system pressure and the atmospheric pressure was less than 1 mm Hg in all cases.

Each of the two saturator vessels contained a 60-mm coarse sintered disc (Corning Glass Works) through which the air was introduced. Each vessel contained 250 ml of solution. A ground glass joint on top of the vessel was filled loosely with glass wool in order to catch droplets without increasing the pressure drop of the system. A thermometer well allowed measurement of the temperature of the solution. The copper coil and the two saturator vessels were completely submerged in an ethylene glycol bath. The $^{1}/_{2}$-in. glass tubing, connecting the second saturator vessel and the first cold trap, was heated well above the bath temperature to avoid composition changes due to condensation. At least $^{1}/_{2}$-in. glass tubing was used for all the lines from the second saturator vessel to the open end manometer to avoid a pressure drop in this section.

The proper flow rate and operation of this apparatus were established by using 5*M* hydrochloric acid as a test substance. The air flow rate was decreased until agreement with data reported in the literature (*3*) was obtained. Half of this flow rate was used in our experiments to assure saturation of the gas stream during the experiments. The apparatus was carefully cleaned, dried, filled with the copper chloride solution and placed in the bath. Upon reaching thermal equilibrium at the desired temperature, the air flow was started and 10–30 grams of condensate were collected in the cold trap in 60–240 min, depending on the temperature and the composition of the solution. The temperature remained constant to ±0.05°C during the time of the measurement. All condensate was collected in the first of the two cold traps. Since the amount condensed was small compared to the roughly 600 grams of solution in the saturator vessels, the change in composition of the copper chloride solution during the measurements was small enough to be disregarded in computing the vapor pressure data. No crystallization in the saturator vessels was observed.

When the cold traps reached room temperature, they were carefully dried on the outside, vented to the atmosphere, and weighed. The total condensate was then washed with distilled water into a 250-ml volumetric flask and aliquots of 10 or 25 ml were titrated with 0.1*N* sodium hydroxide solution to obtain the HCl content.

The vapor pressure was calculated from the following equation:

$$p = \frac{g}{M \cdot V} \cdot \mathrm{R} \cdot T$$

where

p = vapor pressure of the component
g = weight of the component
M = molecular weight of the component
V = total volume of both components and air
R = gas constant
T = absolute temperature

The volume contributions of HCl and H_2O to the total volume, V, were computed by using the above equation, only this time we solved for the volume of the particular component. The pressure observed on the open end manometer was added to the atmospheric pressure to obtain the pressure in the system. The air volume had to be corrected since the temperature of the air entering the wet test meter differed from the air temperature in the saturator.

RESULTS

The densities of solutions of copper(II) chloride at different temperatures are listed in Table I. The experimental error

Table I. Densities of Copper(II) Chloride Solutions in Hydrochloric Acid

Concn of $CuCl_2$, *M*	Concn of HCl, *M*	Density, g/ml 30°C	50°C	70°C	90°C
1.496	7.08	1.2585	1.2462	1.2298	1.2152
1.524	6.00	1.2486	1.2337	1.2203	1.2050
1.492	5.06	1.2341	1.2199	1.2058	1.1924
1.500	4.08	1.2220	1.2095	1.1960	1.1802
0.992	4.94	1.1810	1.1675	1.1571	1.1425
0.502	5.00	1.1296	1.1170	1.1073	1.0951

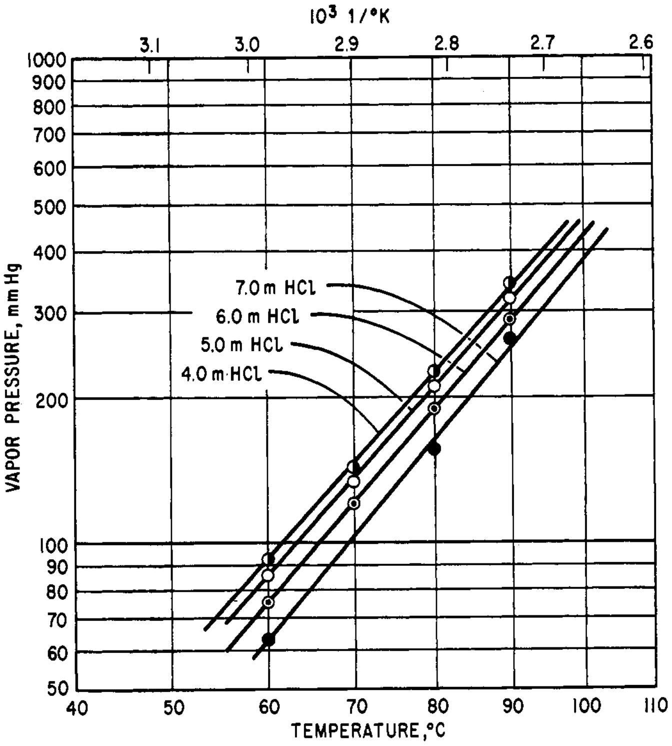

Figure 1. Vapor pressures of water over 1.5*M* $CuCl_2$ in 4.0–7.0*M* hydrochloric acid

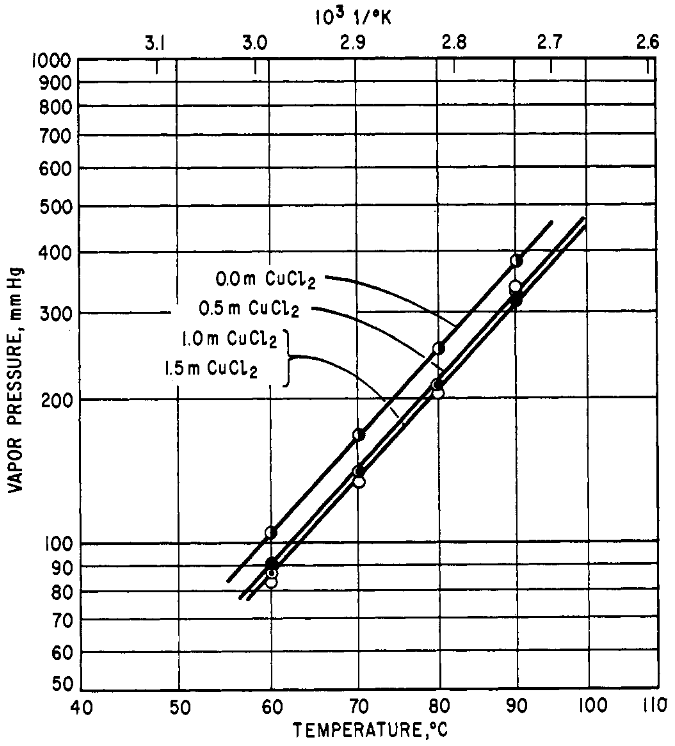

Figure 3. Vapor pressures of water over 5.0*M* hydrochloric acid containing 0.0–1.5*M* $CuCl_2$

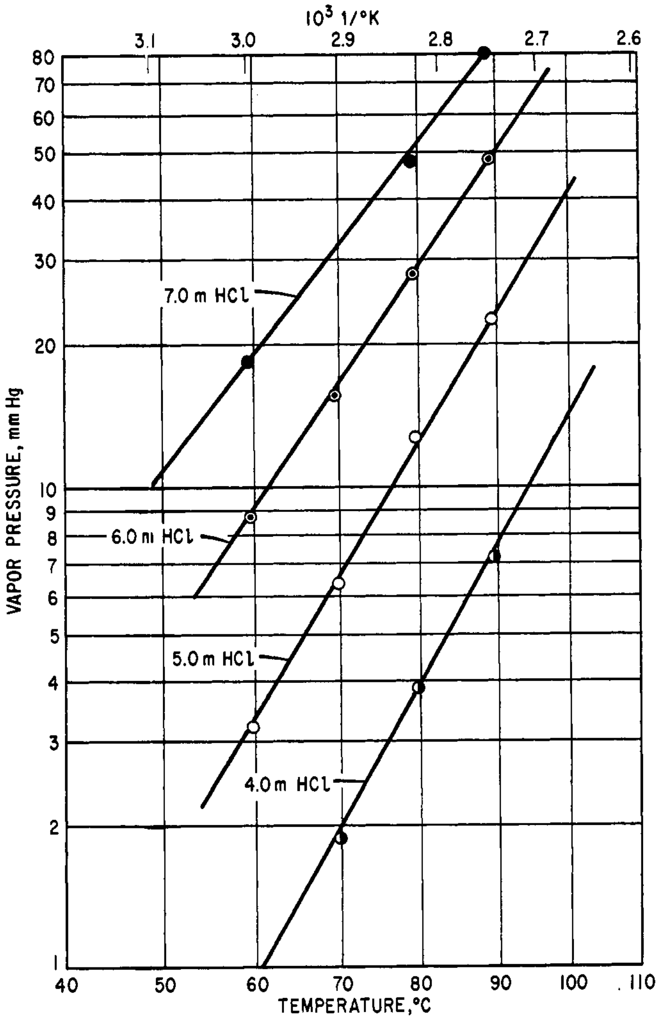

Figure 2. Vapor pressures of hydrogen chloride over 1.5*M* $CuCl_2$ in 4.0–7.0*M* hydrochloric acid

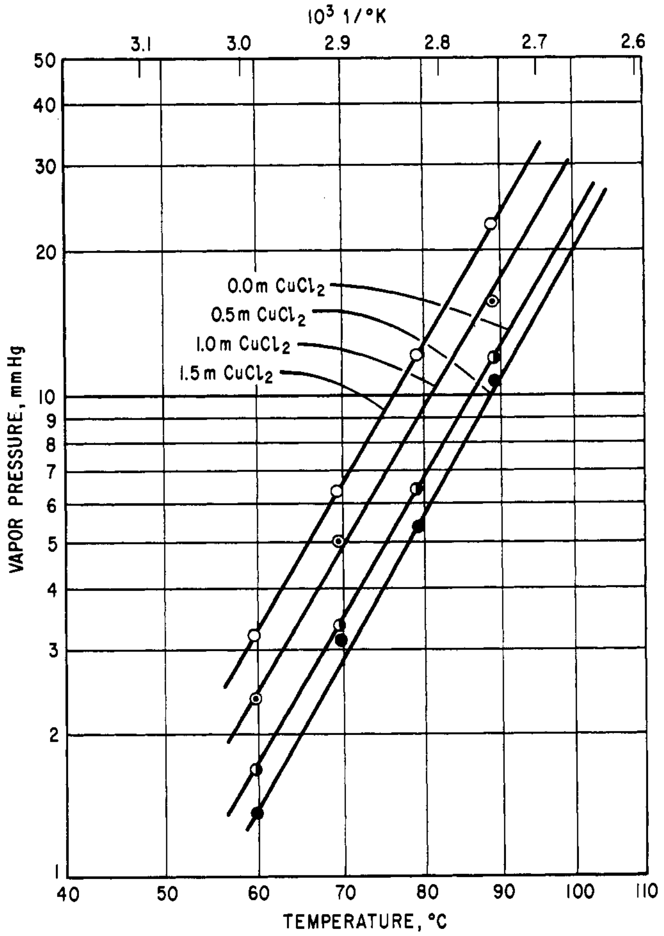

Figure 4. Vapor pressures of hydrogen chloride over 5.0*M* hydrochloric acid containing 0.0–1.5*M* $CuCl_2$

for these measurements was estimated to be ±0.0002 g/ml. The densities of a given solution were found to decrease linearly with increasing temperature.

Multiple linear regression analysis was employed to obtain the following mathematical relationship among the density, temperature, and concentration:

$$d = 1.0122 + 0.1220\,(\mathrm{CuCl_2}) + 0.1618 \times 10^{-1}\,(\mathrm{HCl}) - 0.5085 \times 10^{-3}\,(t) - 0.2770 \times 10^{-2}\,(\mathrm{CuCl_2})\,(\mathrm{HCl}) - 0.1320 \times 10^{-3}\,(\mathrm{CuCl_2})(t)$$

where

d = density, g/ml
t = temperature, °C
(HCl) = molar concentration of HCl
($CuCl_2$) = molar concentration of $CuCl_2$

The standard deviation of the equation is ±0.0011.

Table II summarizes viscosities of copper(II) chloride solutions at different temperatures. A linear relationship was observed between the reciprocal of the absolute temperature and the logarithm of the viscosity of a solution of given composition. The experimental error for the least precise data was estimated to be ±0.003 cP.

The following equation can be used to calculate viscosities for copper(II) chloride solutions in hydrochloric acid.

$$\log_{10} \eta = [740.08 + 39.907\,(\mathrm{CuCl_2}) - 9.1775\,(\mathrm{HCl})]\frac{1}{T} + 0.05835\,(\mathrm{HCl}) - 0.006224\,(\mathrm{HCl})(\mathrm{CuCl_2}) - 2.54564$$

η = viscosity, cP
T = absolute temperature, K
(HCl) = molar concentration of HCl
($CuCl_2$) = molar concentration of $CuCl_2$

The standard deviation for this equation is ±0.010.

The vapor pressure data for the solutions studied are presented in Figures 1–4. A linear relationship between the reciprocal of the absolute temperature and the vapor pressures of HCl and H_2O was observed for the temperature range studied. The accuracy of the data reported is 10% for vapor pressures above 10 mm Hg and 15% for smaller vapor pressure data.

Although some efforts were undertaken to obtain a mathematical relationship for the vapor pressures as a function of temperature and concentration of HCl and H_2O, none of the equations obtained by multiple linear regression analysis were acceptable. The main obstacles to a suitable equation seemed to be the complex formation of $CuCl_2$ in hydrochloric acid and, to a certain degree, the limited amount of data.

Table II. Viscosities of Copper(II) Chloride Solutions in Hydrochloric Acid

Concn of $CuCl_2$, M	Concn of HCl, M	Viscosity, cP			
		30°C	50°C	70°C	90°C
1.496	7.08	1.693	1.189	0.884	0.667
1.524	6.00	1.621	1.122	0.823	0.633
1.492	5.06	1.552	1.076	0.779	0.604
1.500	4.08	1.496	1.028	0.742	0.570
0.992	4.94	1.369	0.966	0.707	0.548
0.502	5.00	1.208	0.865	0.646	0.506

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Physical Properties in Reaction of Ethylene and Hydrogen Chloride in Liquid Media

Diffusivities and Solubilities

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Determinations of diffusion coefficients and solubilities of ethylene and hydrogen chloride in nitrobenzene and ethylene dichloride were made to enable a detailed analysis of the kinetics of the ethylation of hydrogen chloride to ethyl chloride in the two liquid media (nitrobenzene and ethylene dichloride). The solubility of ethyl chloride in nitrobenzene was also determined. With nitrobenzene as the solvent, the solubilities of hydrogen chloride and ethylene were also determined at various concentrations of aluminium chloride, which was used as the catalyst in the ethylation reaction.

DIFFUSIVITIES

Experimental. Several methods (and apparatus) for determining diffusivities have been reviewed by Himmelblau (*4*). In the present work, a modified version of the Ringbom's apparatus (*12*) was used (Figure 1). It consisted of two capillaries fused together and connected to two different reservoirs through three-way capillary stopcocks. The fine capillary was 40 cm and the other 10 cm in length. The area of cross section of the fine capillary was 1.42×10^{-2} cm^2 and that of the other 3.413×10^{-2} cm^2. The reservoir flasks were of 250-ml capacity each. The side arm of the left reservoir was connected to a Hg manometer, the other end of which was closed. The fine capillary was graduated in mm and was calibrated before fusing. One more capillary cell with fine and coarse capillary cross sections of 1.25×10^{-2} and 6.876×10^{-2} cm^2, respectively, was fabricated.

Nitrobenzene, ethylene dichloride, ethylene, and hydrogen chloride of purity more than 99% were used. The purity was tested in a gas chromatographic apparatus.

The procedure adopted was similar to that of Smith et al.

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