

Table I. Solubilities and Henry's Law Constants

System	Temp., ° C.	Solubility, G. Moles/ Liter	Henry's Law Constant <sup>a</sup> , Atm.-Liter/ G. Mole
Cl <sub>2</sub> -C <sub>6</sub> H <sub>6</sub>	10.0	3.97	0.252
	20.0	2.86	0.350
	30.0	2.14	0.468
	40.0	1.65	0.607
	50.0	1.20	0.834
Cl <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> Cl	30.0	1.56	0.641
	45.0	1.10	0.909
	60.0	0.78	1.282
HCl-C <sub>2</sub> H <sub>5</sub> OH	57.0	2.93	0.341
	72.0	2.61	0.383
	86.0	2.18	0.459
	93.5	1.97	0.508
	101.0	1.79	0.559
	111.0	1.41	0.710
	121.0	1.19	0.841
HCl-C <sub>12</sub> H <sub>25</sub> OH	65.0	3.06	0.327
	78.0	2.73	0.366
	90.1	2.39	0.418
	100.5	2.09	0.478
	111.0	1.71	0.585
	121.0	1.47	0.680
	132.0	1.13	0.885

<sup>a</sup>Henry's law constant defined as  $H \equiv P/C$ , where  $P$  is partial pressure of solute in atmospheres and  $C$  is corresponding equilibrium solubility.

solubility values. Complete experimental details are given by Silberstein (5) and Daté (2).

## RESULTS

The solubilities measured for the three systems are given in Figure 1 as a function of temperature, together with the data of Krivonos (3) for chlorine in benzene as a reference for the chlorine-monochlorobenzene system. Krivonos showed that semilogarithmic plots of solubility *vs.* temperature are linear for a number of chlorine systems and the present data for monochlorobenzene are in accord with this, so relatively reliable temperature extrapolation is possible. The strong temperature-dependence in this case is probably due to the influence of molecular association complexes (1) between chlorine and these solvents. Solubilities of hydrogen chloride in the two alcohols are essentially linear in temperature over the range investigated, and extrapolation to higher temperatures is certainly possible. Numerical values for the measured solubilities and the corresponding Henry's law constants are reported in Table I.

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# Thermal Conductivity of Phosphoric Acid

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The thermal conductivity of phosphoric acid was measured in glass cells calibrated with water and with aqueous solutions of glycerol and of sulfuric acid. The results were expressed with an average deviation of 1.7% by the equation:  $K \times 10^4 = 11.727 + 0.01864T - 0.02169C - 0.0000338CT$ , in which  $K$  is thermal conductivity, cal./cm.(sec.)(° C.);  $T$  is temperature, ° C., 25° to 150°; and  $C$  is concentration, weight % H<sub>3</sub>PO<sub>4</sub>, 84 to 115% (61 to 83% P<sub>2</sub>O<sub>5</sub>).

THE GROWING use of concentrated phosphoric acid, especially in the manufacture of ammonium polyphosphate fertilizers, has increased the need for information on its properties. Turnbull (9) recently reported thermal conductivity data on phosphoric acid but did not cover the desired high temperatures and concentrations. This report covers measurements of the thermal conductivity of phosphoric acid over the concentration range 84 to 115% H<sub>3</sub>PO<sub>4</sub> (61 to 83% P<sub>2</sub>O<sub>5</sub>) and the temperature range 25° to 150° C. The results are expressed in a single equation.

## MATERIALS AND APPARATUS

Thermal conductivity measurements were made on acid produced in the TVA demonstration plant (1) that con-

tained 114% H<sub>3</sub>PO<sub>4</sub> and on its solutions diluted to 111, 97, 91, and 84% H<sub>3</sub>PO<sub>4</sub>. Each diluted solution was heated sufficiently to equilibrate the phosphate species. Three other solutions containing 115, 101, and 86% H<sub>3</sub>PO<sub>4</sub> were prepared by dissolving reagent P<sub>4</sub>O<sub>10</sub> in reagent (85%) H<sub>3</sub>PO<sub>4</sub>. The concentrations of the phosphoric acid solutions were determined by the gravimetric quinoline molybdate method for phosphorus (2) with an accuracy of about 0.1% at the highest concentrations. The glycerol and sulfuric acid were reagent grade, and the concentrations of their solutions were determined by Karl Fischer and alkalimetric titrations, respectively.

Turnbull (9) measured thermal conductivities of phosphoric acid solutions in a hot-wire apparatus, but attempts to repeat his work were unsuccessful. Although Turnbull

reported no such difficulty, our measurements apparently were impaired by polarization of the electrolyte which made it impossible to obtain the true value of either the temperature of the wire or the quantity of heat liberated by the wire. Our results with the hot-wire apparatus were in good agreement with published values for water and glycerol solutions, but not for phosphoric and sulfuric acid solutions.

The polarization effect was avoided by use of all-glass thermal conductivity cells similar to one described by van der Held and van Drunen (5). Each cell was 41 mm. in diameter and 20 cm. long. A 1.5-mm. thin-walled capillary tube on the longitudinal axis of the cell was sealed at each end to 5-mm. tubes that contained the electrical connections. The test liquids were introduced and removed through 10-mm. tubes connected to the top and bottom of the cell. The capillary tube contained a 40-gage cotton-covered manganin heater wire and a copper-constantan thermocouple centered vertically in the capillary. The thermocouple leads were of 38-gage copper in a 5-mm. connection tube. The constantan thermocouple lead was soldered to a copper lead at the ice-bath reference junction. The thermocouple voltage was measured with a High Wenner potentiometer and a photocell amplifier galvanometer; the galvanometer displacement was related linearly to the thermocouple voltage. A digital voltmeter across a standard resistor served as a check on the constancy of the heating current, which varied less than 0.02% for all the runs reported.

A chronograph was assembled by connecting the pen circuit of a high-chart-speed recorder and a microswitch in series across a battery. Just before each thermal conductivity run (duration of run, 50 seconds to 2 minutes), the current was stabilized by passage through a dummy heater. The chart-drive motor on the recorder then was started, and a battery voltage was applied to the potentiometer that slightly overbalanced the thermocouple voltage and displaced the galvanometer to near one end of the 25-cm. scale. Time was measured on the chronograph by jogging the recorder pen manually through closing the microswitch at the instant the run was started and at successive instants at which the galvanometer displacement reached preselected values. This arrangement permitted accurate and rapid measurements of the thermocouple voltage at several definite times during each run.

The cells were mounted in a glycerol bath in which the temperature was held constant to  $\pm 0.01^\circ\text{C}$ . and monitored with a quartz thermometer.

#### CALIBRATION

Gillam *et al.* (4) listed a basic equation for the determination of thermal conductivity by the transient hot-wire method as:

$$K = \frac{Q}{4\pi} \frac{d \ln t}{dT}$$

where

$$\begin{aligned} K &= \text{thermal conductivity, cal. cm.}^{-1} \text{sec.}^{-1} \text{ } ^\circ\text{C.}^{-1} \\ Q &= \text{heat flux from hot wire, cal. cm.}^{-2} \text{sec.}^{-1} \\ t &= \text{time, sec.} \\ T &= \text{temperature, } ^\circ\text{C.} \end{aligned}$$

Since the current was constant within 0.02% in each run and there was negligible change in the resistance of the manganin heater wire,  $Q$  remained constant and

$$K \propto d \ln t/dT$$

The cells were calibrated with liquids with established values for thermal conductivity—water (3, 6), glycerol solutions (6), and sulfuric acid solutions (8). The values for water of Challoner and Powell (3) and for water and glycerol of Riedel (6) agree to within 2% with the consensus values selected by Touloukian (7) from his comprehensive evaluation of published data. Tsederberg's values for sulfuric acid solutions (8) fall smoothly on the calibration curve and so are assumed to be of about the same reliability as those for water and glycerol solutions. The combined calibration points are shown in Figure 1.

Each value of  $d \ln t/dT$  in Table I is an average of five or six determinations with a constant heating current of 100 ma. Plots of  $\ln t$  against thermocouple voltage for each run showed an initial curved portion for the time required for the temperature difference between the outside surface of the capillary tube and the thermocouple to become constant, the useful straight-line portion, and the curved terminal portion that indicated the onset of convection. The value of  $d \ln t/dT$  was determined from the straight-line portion, which ranged from 30 seconds for solutions with high conductivity to 90 seconds for solutions with low conductivity.

Table I. Calibration of Thermal Conductivity Cells

Liquid	Temp., °C.	$d \ln t / dT$	Thermal Conductivity, Cal./ (Cm.) (Sec.) (°C.), $\times 10^4$		
			Published	This work	% dev.
CELL 1					
96% glycerol	25	4.101	6.98 <sup>a</sup>	7.10	+1.7
	50	4.153	7.06	7.18	+1.7
	75	4.191	7.15	7.25	+1.4
	100	4.302	7.24	7.44	+2.8
56% glycerol	25	5.478	9.69	9.43	-2.7
	50	5.802	10.06	9.97	-0.9
	75	6.126	10.38	10.52	+1.3
30% glycerol	25	6.843	11.80	11.74	-0.5
	50	7.124	12.41	12.21	-1.6
	75	7.697	12.87	13.18	+2.4
75% H <sub>2</sub> SO <sub>4</sub>	25	5.540	9.68 <sup>b</sup>	9.53	-1.5
	50	5.726	10.25	9.85	-3.9
	75	6.172	10.74	10.60	-1.3
	100	6.685	11.03	11.47	+4.0
H <sub>2</sub> O	25	8.243	14.61 <sup>c</sup>	14.10	-3.5
	40	8.890	15.11	15.20	+0.6
	50	9.187	15.40	15.70	+1.9
CELL 2					
96% glycerol	25	3.942	6.98 <sup>a</sup>	6.81	-2.4
	50	3.995	7.06	6.90	-2.3
	75	4.125	7.15	7.12	-0.4
	100	4.301	7.24	7.41	+2.3
61% glycerol	25	5.489	9.26	9.40	+1.5
	50	5.784	9.59	9.89	+3.1
	75	5.972	9.87	10.21	+3.4
31% glycerol	25	6.767	11.72	11.53	-1.6
	50	7.280	12.32	12.39	+0.6
	75	7.787	12.78	13.24	+3.6
75% H <sub>2</sub> SO <sub>4</sub>	25	5.662	9.68 <sup>b</sup>	9.69	+0.1
	50	5.901	10.25	10.09	-1.6
	75	6.113	10.74	10.44	-2.8
	100	6.426	11.03	10.96	-0.6
H <sub>2</sub> O	25	8.422	14.61 <sup>c</sup>	14.30	-2.1
	40	8.756	15.11	14.86	-1.7
	50	9.168	15.40	15.55	+1.0

<sup>a</sup> Tsederberg (8). <sup>b</sup> Riedel (6). <sup>c</sup> Challoner and Powell (3).

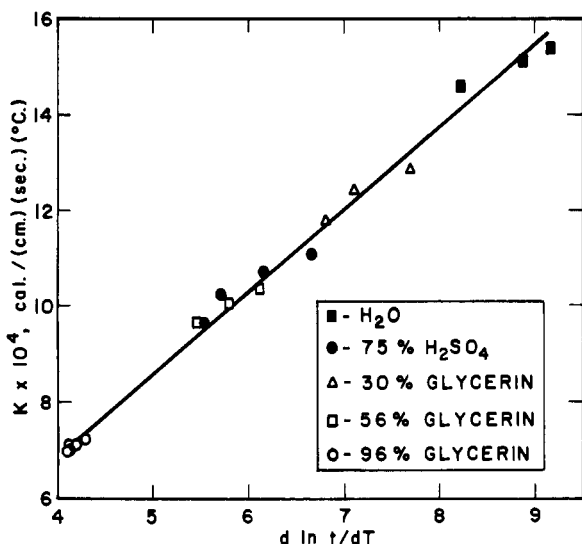


Figure 1. Calibration of cell 1

The published values for thermal conductivity of the reference liquids were fitted by the method of least squares to a linear equation in  $d \ln t/dT$  for each cell.

$$\text{Cell 1. } K \times 10^4 = 0.15694 + 1.69200 d \ln t/dT \quad (1)$$

$$\text{Cell 2. } K \times 10^4 = 0.22811 + 1.67072 d \ln t/dT \quad (2)$$

The thermal conductivities of the reference liquids calculated from Equations 1 and 2 are compared with the established values in Table I. The average deviation is  $\pm 2.0\%$  for cell 1 and  $\pm 1.8\%$  for cell 2.

## RESULTS

Values of  $d \ln t/dT$  for the phosphoric acid solutions were measured under the conditions used for the calibrations, and the thermal conductivities were calculated by Equation 1 or 2. There were no differences in thermal

Table II. Thermal Conductivity of Phosphoric Acid

H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	Cell	Thermal Conductivity, Cal./ (Cm.) (Sec.) (° C.), $\times 10^4$ of Acid at Indicated Temperature, ° C.						
		25	50	75	100	125	150	
84 P	1	Obsd.	10.4	10.8	10.8	12.0	12.2	
		Calcd. <sup>b</sup>	10.3	10.7	11.1	11.5	11.9	
86 R	1	Obsd.	10.4	10.7	11.0	11.2	12.0	
		Calcd.	10.2	10.6	11.0	11.4	11.8	
86 R	1	Obsd.	10.1	10.5	11.1	12.1	12.0	
		Calcd.	10.2	10.6	11.0	11.4	11.8	
86 R	1	Obsd.	10.0	10.6	10.9	11.3		
		Calcd.	10.2	10.6	11.0	11.4		
86 R	2	Obsd.	9.9	10.3	10.6	11.2	11.4	
		Calcd.	10.2	10.6	11.0	11.4	11.8	
91 P	1	Obsd.	10.1	10.5	10.9	11.1	11.4	
		Calcd.	10.1	10.5	10.9	11.3	11.7	
97 P	1	Obsd.	10.0	10.6	10.9	11.6	12.6 <sup>c</sup>	
		Calcd.	10.0	10.4	10.8	11.2	11.5	
101 R	2	Obsd.	9.8	10.0	10.4	10.8	11.3	11.7
		Calcd.	9.9	10.3	10.8	11.1	11.4	11.8
111 P	1	Obsd.	9.7	10.2	10.5	11.0	11.3	
		Calcd.	9.7	10.1	10.4	10.8	11.2	
114 P	1	Obsd.	9.8	10.2	10.6	11.1	11.5	
		Calcd.	9.6	10.0	10.4	10.7	11.1	
115 R	2	Obsd.	9.7	10.2	10.5	10.7	11.0	11.4
		Calcd.	9.6	10.0	10.3	10.7	11.1	11.4

<sup>a</sup> P denotes plant acid, R reagent acid. <sup>b</sup> Calculated by Equation 3. <sup>c</sup> Not used in determination of constants in Equation 3.

Table III. Smoothed Values of Thermal Conductivity of Phosphoric Acid

Temp., ° C.	Thermal Conductivity, Cal./ (Cm.) (Sec.) (° C.), $\times 10^4$ , at Indicated Concentration, % H <sub>3</sub> PO <sub>4</sub>						
	85	90	95	100	105	110	115
25	10.3	10.2	10.0	9.9	9.8	9.7	9.6
30	10.4	10.2	10.1	10.0	9.9	9.8	9.7
35	10.4	10.3	10.2	10.1	10.0	9.9	9.8
40	10.5	10.4	10.3	10.2	10.0	9.9	9.8
45	10.6	10.5	10.4	10.2	10.1	10.0	9.9
50	10.7	10.6	10.4	10.3	10.2	10.1	10.0
55	10.8	10.6	10.5	10.4	10.3	10.2	10.0
60	10.8	10.7	10.6	10.5	10.4	10.2	10.1
65	10.9	10.8	10.7	10.6	10.4	10.3	10.2
70	11.0	10.9	10.8	10.6	10.5	10.4	10.3
75	11.1	10.9	10.8	10.7	10.6	10.5	10.3
80	11.1	11.0	10.9	10.8	10.7	10.5	10.4
85	11.2	11.1	11.0	10.9	10.7	10.6	10.5
90	11.3	11.2	11.1	10.9	10.8	10.7	10.6
95	11.4	11.3	11.1	11.0	10.9	10.8	10.6
100	11.5	11.3	11.2	11.1	11.0	10.8	10.7
105	11.5	11.4	11.3	11.2	11.0	10.9	10.8
110	11.6	11.5	11.4	11.2	11.1	11.0	10.9
115	11.7	11.6	11.4	11.3	11.2	11.1	10.9
120	11.8	11.6	11.5	11.4	11.3	11.1	11.0
125	11.8	11.7	11.6	11.5	11.3	11.2	11.1
130	...	...	...	11.5	11.4	11.3	11.2
135	...	...	...	11.6	11.5	11.4	11.2
140	...	...	...	11.7	11.6	11.4	11.3
145	...	...	...	11.8	11.6	11.5	11.4
150	...	...	...	11.8	11.7	11.6	11.4

conductivity between reagent-grade acid and acid produced in the TVA stainless steel demonstration plant. An equation for thermal conductivity as a function of both concentration and temperature was derived from thermal conductivities measured on both types of acid.

$$K \times 10^4 = 11.727 + 0.01864T - 0.02169C - 0.0000338CT \quad (3)$$

where

$K$  = thermal conductivity, cal./ (cm.) (sec.) (° C.)

$T$  = temperature, ° C., 25° to 150°

$C$  = concentration, weight % H<sub>3</sub>PO<sub>4</sub>, 84 to 115%

The observed thermal conductivities and those calculated from Equation 3 are shown in Table II. The average deviation between the observed and calculated values is  $\pm 1.7\%$ . Calculated values of thermal conductivity at even intervals of temperature and concentration are listed in Table III.

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