Thermal Conductivity of Phosphoric Acid

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Thermal conductivities of 87 wt. % aqueous orthophosphoric acid and of the pure acid have been measured over the range 20° to 130° C., and the form of the conductivity-concentration relation has been derived. The relatively high conductivities and positive temperature coefficients of orthophosphoric and other inorganic acids are attributed to hydrogen bonding.

THERMAL CONDUCTIVITY data (*4, 11*) for the orthophosphoric acid-water system are incomplete and somewhat contradictory. No data exist for the pure acid to permit an investigation of the deviation from the ideal mixing rule, and no temperature coefficients of conductivity are available. For such an extensively hydrogen-bonded liquid, positive temperature coefficients like those of water might be predicted.

In industry, the thermal conductivity may be used to predict heat transfer during manufacture and distillation of phosphoric acid and in its possible use as a heat transfer medium (*5*). Owing to the high viscosity, thermal conductivity is an important factor controlling heat transfer in the concentrated acid.

The transient hot-wire method (*13*) has been used to measure thermal conductivities of a typical commercial composition, 87 wt. % H_3PO_4, and of the pure acid, over the range 20° to 130° C.

EXPERIMENTAL

Materials. The sample of chemically pure aqueous orthophosphoric acid contained 87.0 wt. % H_3PO_4 and was reported to contain negligible impurities (*5*). The anhydrous H_3PO_4 was obtained from it by careful evaporation at 150° as described by Mellor (*6*). Compositions were checked before and after use by pycnometric density measurements at 20°, giving 1.715 grams per cc. (87%) and 1.865 grams per cc. (100%). The pure acid easily supercooled to room temperature, below the reported (*5*) freezing point of 42.4° C.

Apparatus. The transient hot-wire method has been previously described (*13*). Samples were held in a borosilicate glass cell, closed to prevent evaporation or water absorption from the air (*14*), and no corrosion was observed. Owing to the high viscosity of these liquids, the plots of temperature rise of the heated wire *vs.* log time were linear for periods of 30 to 60 seconds before convection became appreciable. The thermal conductivities derived from the slope of such plots are given in Table I, each being the mean of three measurements having an average range of ±1.5%. As discussed previously (*14*), tests with known liquids indicated an absolute accuracy within ±3%. Temperatures were measured with an accuracy of ±0.5°, using the hot wire as a resistance thermometer.

Table I. Thermal Conductivity of Phosphoric Acid

Concentration, Wt. % H_3PO_4	Temperature, ° C.	$10^4 K$, Cal./Cm. Sec. ° C.	$10^7 dK/dt$, Cal./Cm. Sec. ° C.^{2}
87	23	10.63	
	63	11.48	
	103	12.35	22
	128	12.95	
100	23	10.38	
	63	11.30	21
	98	12.00	

RESULTS

Both the 87% and 100% acids show a linear increase of thermal conductivity with temperature of 21 to 22 x 10^{-7} cal./cm. sec. deg.^{2} They give no evidence of a limit of conductivity even at 120° where water reaches its maximum conductivity (*2*). By interpolation, these results may be compared with those of other workers at 20° and 29° on a conductivity *vs.* concentration plot (Figure 1). Riedel (*11*) reported his results for 5 to 50 wt. % H_3PO_4 at 20°, and those of Braune for 50 to 90 wt. % H_3PO_4 at 29°. Both were probably measured with a steady state concentric cylinder apparatus. These results join smoothly with present data for 87% and 100% H_3PO_4 at 20° and 29° and the accurate values for water (*2*) at 20° and 29°. In particular, the results of Braune (*11*) for 80% and 90% H_3PO_4 at 29° and the present results for 87% H_3PO_4 at 23° and 63° may each

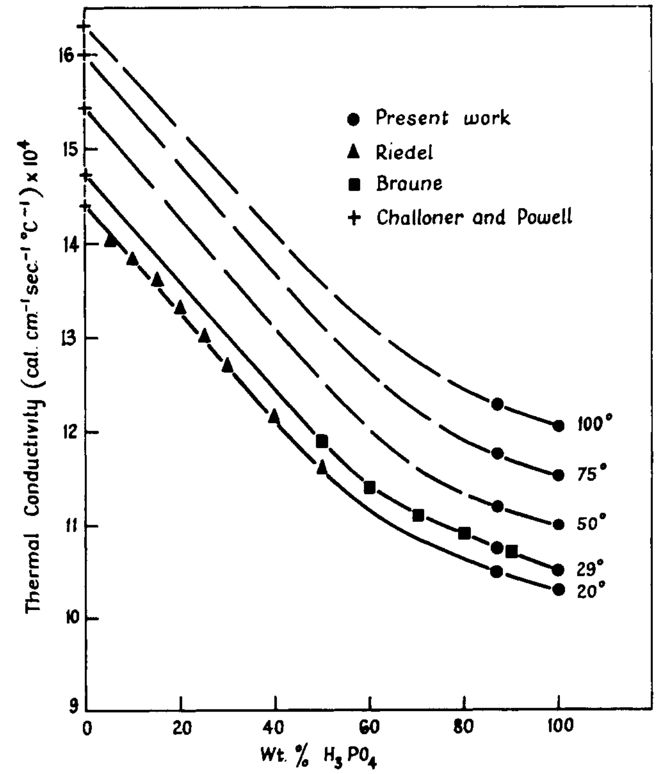

Figure 1. Thermal conductivity *vs.* composition for $H_2O - H_3PO_4$

be interpolated to give the same conductivity, 10.75 cal./cm. sec. deg. for 87% H_3PO_4 at 29°.

The results of van der Held and van Drunen (*4*) at 19.5°, using a transient hot-wire method for 32, 64.5, and 86 wt. % H_3PO_4, are 0.4 to 1.0 cal./cm. sec. deg. higher than the above results at 20°. This is probably due to an inadequate allowance for the thickness of their glass-enclosed hot wire.

DISCUSSION

A useful correlation formula given by Filippov (*3*) claims to predict the thermal conductivity of a binary mixture, K_m, from those of the components, K_1 and K_2, with 1 to 2% accuracy:

$$K_m = K_1w_1 + K_2w_2 - \alpha w_1w_2|K_2 - K_1| \qquad (1)$$

where w_1 and w_2 are the weight fractions of the components. The constant, α, has an average value of 0.72 for five pairs of normal liquids and 0.75 for nine pairs of associated liquids (*3*).

This equation may be tested for the water-phosphoric acid system at 20° and 29° with the data collected in Table II. If the thermal conductivities of water and 100% phosphoric acid are taken to be correct, a value of $\alpha = 0.73$ gives the best over-all agreement of predicted and observed results at intermediate concentrations. The present results for 87% H_3PO_4 fall close to the predicted curve at both 20° and 29°. The results of Riedel at 20° fall slightly above the predicted curve, while those of Braune at 29° fall slightly below, the maximum deviation being 1% in both cases. This is considered to be well within the combined accuracy of the three sets of data. Thus the water-phosphoric acid system shows a deviation from the ideal mixing rule which is closely analogous to those of organic mixtures.

Thermal conductivity data for other inorganic acids are insufficient to test the Filippov relation further, but it is of interest to compare their conductivities and temperature coefficients at 30° (Table III). Higher conductivities appear to be associated with more positive temperature coefficients, and both these trends appear to be related to increase of the degree of molecular association owing to hydrogen bonding. Although other factors, such as molecular size, also influence K and dK/dT, almost all nonassociated liquids have values in the ranges 2 to 5 × 10^{-4} cal./cm. sec. deg. and −1 to −10 × 10^{-7} cal./cm. sec. deg.^{2}, respectively (*12*). Hence, the much higher values in Table III are probably related to an extra conducting mechanism such as the making and breaking of hydrogen bonds suggested by Palmer (*9*). An analogous mechanism of proton jumps through a hydrogen-bonded structure has also been postulated (*7*) for the electrical conductivity of phosphoric acid.

Table II. Thermal Conductivity of Phosphoric Acid

Concentration, Wt. % H_3PO_4	10^4 K, Cal./Cm. Sec. °C. Calcd. Eqn. 1	10^4 K, Cal./Cm. Sec. °C. Obs.	Reference
	Temperature, 20° C.		
0	...	14.42	(*2*)
5	14.07	14.0	(*11*)
10	13.74	13.85	(*11*)
15	13.43	13.6	(*11*)
20	13.13	13.3	(*11*)
25	12.85	13.0	(*11*)
30	12.58	12.7	(*11*)
40	12.09	12.15	(*11*)
50	11.64	11.6	(*11*)
87	10.54	10.55	This work
100	...	10.35	This work
	Temperature, 29° C.		
0	...	14.73	(*2*)
50	11.89	11.85	(*11*)[a]
60	11.50	11.4	(*11*)[a]
70	11.17	11.1	(*11*)[a]
80	10.90	10.9	(*11*)[a]
87	10.76	10.75	This work
90	10.70	10.7	(*11*)[a]
100	...	10.55	This work

[a] Braune's data as reported by Riedel (*11*).

Table III. Thermal Conductivity of Pure Liquids

Liquid	10^4 K at 30°, Cal./Cm. Sec. °C.	10^7 dK/dt at 30° Cal./Cm. Sec. °C.^{2}	Association (*10*)
H_2O (2)	14.8	+33	Extensive H-bond network
H_3PO_4	10.5	+21	Extensive H-bonding of PO_4 ions
H_2SO_4 (*1*)	7.25	+13	Probably dimers
HNO_3 (*1*)	6.8	+12	Slight association expected
HCl (*8*)	6	−5	Slight association

Probably the least associated inorganic oxy-acid is perchloric acid. From the single thermal conductivity value available (*4*), 4.1 × 10^{-4} cal./cm. sec. deg. for 66 wt. % $HClO_4$ at 25°, the Filippov relation has been used to estimate a value of 2 × 10^{-4} cal./cm. sec. deg. for pure perchloric acid. Although of lower accuracy than the data in Table III, this value falls within the range of nonassociated liquids as expected.

Similar behavior has been shown in organic alcohols and amines where abnormally high conductivities and positive or small negative temperature coefficients have been attributed to hydrogen bonding (*10*). At present, knowledge of both the mechanism of conductivity and the degree of association is inadequate for a quantitative theory.

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