

force constants decrease regularly from boron trifluoride to boron triiodide (2). Thus, one correctly predicts that B-triiodoborazine prepared by Nöth (16) is thermally unstable around room temperature (15).

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#### LITERATURE CITED

- (1) Bauer, S.H., Beach, J.Y., Simons, J.H., *J. Am. Chem. Soc.* **61**, 19 (1939).
- (2) Beckman, L., Gutjahr, L., Mecke, R., *Spectrochim. Acta* **21**, 141 (1965).
- (3) Booth, H.S., Halbedel, H.S., *J. Am. Chem. Soc.* **68**, 2652 (1946).
- (4) Brown, C.A., Laubengayer, A.W., *Ibid.*, **77**, 3699 (1955).
- (5) Cornell Computing Center Write-Up for Multiple Regression Analysis (MUREG), Cornell University, Ithaca, N. Y., March 1965.

- (6) Emeleus, H.J., Videla, G.J., *J. Chem. Soc.* **1959**, p. 1306.
- (7) Finger, G.C., Reed, F.H., *U. S. Air Force Tech. Rept. No.* 54-148.
- (8) Heilbron, I., Bunbury, H.M., "Dictionary of Organic Compounds," Vol. IV, p. 545, Oxford University Press, New York, 1953.
- (9) Hutto, F.B., M. S. dissertation, Cornell University, Ithaca, N. Y., 1950.
- (10) International Critical Tables, Vol. III, p. 206, McGraw-Hill, New York, 1928.
- (11) Laubengayer, A.W., Watterson, K., Bidinosti, D.R., Porter, R.F., *Inorg. Chem.* **2**, 519 (1963).
- (12) Massey, A.G., Park, A.J., *J. Organometal. Chem.* **2**, 461 (1964).
- (13) Niedenzu, K., *Inorg. Chem.* **1**, 943 (1962).
- (14) Niedenzu, K., Beyer, H., Jenne, H., *Chem. Ber.* **96**, 2649 (1963).
- (15) Niedenzu, K., Dawson, J.W., "Boron-Nitrogen Compounds," p. 103, Springer-Verlag, Berlin, Germany, 1965.
- (16) Nöth, H., *Z. Naturforsch.* **16b**, 618 (1961).
- (17) Stull, D.R., *Ind. Eng. Chem.* **39**, 517 (1947).
- (18) Thompson, P.G., Ph.D. dissertation, Cornell University, Ithaca, N. Y., 1959.

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## Electrical Conductivity of Concentrated Phosphoric Acid from 25° to 60° C.

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**The electrical conductivity for concentrated phosphoric acid in the range 62.14 to 85.58% P<sub>2</sub>O<sub>10</sub> has been measured at 25°, 30°, 40°, 50°, and 60° C. The results differ from several previous conductivity measurements in the concentrated phosphoric acid region.**

PHOSPHORIC ACID is an effective absorbent-electrolyte in water-vapor electrolysis cells (2). To carry out voltage analysis studies on such cells, reliable electrical conductivity data is needed.

Several reports on the electrical conductivity of concentrated phosphoric acid have appeared in the literature (5, 6, 7). However, in view of the variability of reported values, the electrical conductivity of concentrated phosphoric acid has been redetermined over a wide range of concentration at intervals from 25° to 60° C.

#### EXPERIMENTAL

Acid samples in the range 64.08 to 73.61 weight % phosphorus pentoxide were prepared by the thermal dehydration of analytical reagent grade "85%" phosphoric acid (62.14% phosphorus pentoxide by analysis in this laboratory) at about 150° C. Samples more concentrated than 73.61% P<sub>2</sub>O<sub>10</sub> were prepared by the slow addition of reagent grade P<sub>2</sub>O<sub>10</sub> to a thermally dehydrated acid sample containing approximately 70% P<sub>2</sub>O<sub>10</sub>. Since concentrated phosphoric acid attacks glass above 200° C., the sample vessel was placed in an ice bath during the addition of P<sub>2</sub>O<sub>10</sub> to prevent a large temperature rise. Samples prepared by the addition of P<sub>2</sub>O<sub>10</sub> were finally heated to 180° C. to hasten dissolution of the oxide. Samples ranged from a transparent, colorless liquid at the lower concentrations, to a straw yellow color at the higher concentrations.

A Washburn conductivity cell with platinized platinum electrodes, maintained at a constant temperature ( $\pm 0.05^\circ\text{C}$ .), was used in measuring the conductivity. The cell constant,

0.759 cm.<sup>-1</sup>, was determined at 25° C. by measuring the resistance of a 0.01N KCl solution. The conductivity values for 0.01N KCl used to calculate the cell constant were obtained from the data of Jones and Bradshaw (4). Resistance was measured with a General Radio 1650A impedance bridge at a frequency of 1000 c.p.s. No fewer than five measurements of the resistance were made, over varying time intervals, at each temperature for any given concentration. Bridge balance was determined by either an oscilloscope or the impedance bridge null detector. No difference in resistance, within experimental error, could be detected by using either the oscilloscope or the null detector. (The manufacturers estimate for the accuracy of the resistance reading is  $\pm 1\%$ ). The accuracy of the measurements was further checked by measuring the conductivity of 0.1N KCl at 0° and 25° C., and of 0.01N KCl at 0° C. These data were then compared with values found in the literature (4). The mean standard deviation between this work and the reported values for the conductivity of potassium chloride is  $\pm 0.4\%$ .

Following the conductivity measurements, three samples of acid were taken for analysis. Samples were transferred with a glass syringe from the conductivity cell to glass stoppered weighing bottles and weighed immediately. The acid concentration was determined by titration with sodium hydroxide using an expanded scale pH meter to detect the first equivalence point.

#### RESULTS AND DISCUSSION

In Table I values for the specific conductivity of phosphoric acid (62.14 to 85.58 weight % phosphorus pentoxide)

Table I. Specific Conductivity of Concentrated Phosphoric Acid

Concn., Weight % P <sub>4</sub> O <sub>10</sub>	Specific Conductivity, Ohm <sup>-1</sup> Cm. <sup>-1</sup>				
	25.0° C.	30.0° C.	40.0° C.	50.0° C.	60.0° C.
62.14 ± 0.08	0.0888	0.102	0.134	0.167	0.202
64.08 ± 0.04	0.0801	0.0928	0.122	0.154	0.189
65.58 ± 0.06	0.0734	0.0858	0.114	0.146	0.180
67.89 ± 0.16	0.0641	0.0756	0.102	0.131	0.165
70.31 ± 0.11	0.0535	0.0639	0.0870	0.115	0.145
72.25 ± 0.13	0.0447	0.0534	0.0740	0.0975	0.124
73.61 ± 0.08	0.0355	0.0432	0.0606	0.0814	0.106
75.64 ± 0.17	0.0210	0.0262	0.0389	0.0550	0.0744
77.33 ± 0.11	0.0115	0.0148	0.0234	0.0346	0.0490
80.03 ± 0.04	0.00336	0.00471	0.00855	0.0141	0.0220
81.54 ± 0.06	0.00175	0.00256	0.00495	0.00855	0.0137
83.77 ± 0.14	0.000860	0.00125	0.00245	0.00429	0.00699
85.58 ± 0.09	0.000183	0.000282	0.000597	0.00108	0.00183

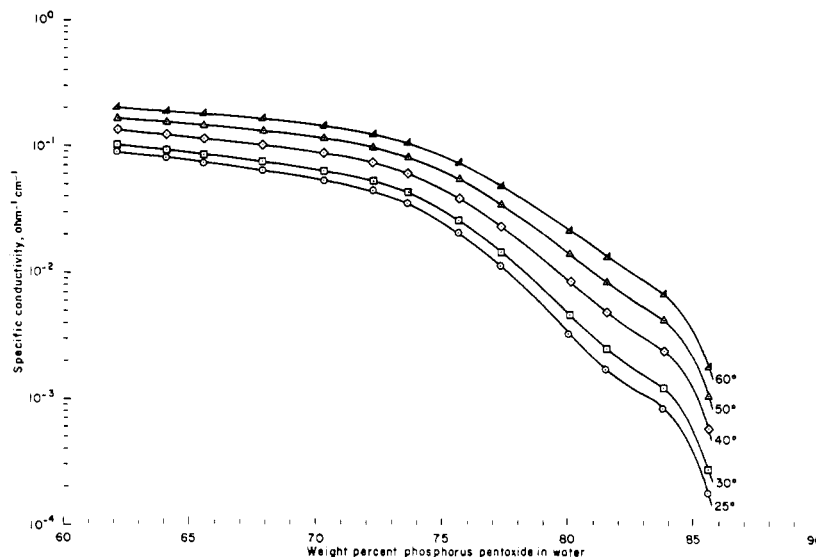


Figure 1. Specific conductivity vs. weight % phosphorus pentoxide

from 25° to 60° C. are shown. The uncertainty in the concentration is expressed as the standard deviation. The mean standard deviation of the specific conductivity is  $\pm 0.2\%$ . The standard deviations ranged from  $\pm 0.1$  to  $\pm 0.5\%$ . Specific conductivity isotherms vs. weight % phosphorus pentoxide in water are shown in Figure 1.

The pronounced decrease in conductivity with increasing concentration in the region of 85% phosphorus pentoxide was also found by Keidel (6). A possible explanation for this decrease is that the formation and polymerization of metaphosphoric acid begins at about 83% P<sub>4</sub>O<sub>10</sub> and appears to reach a maximum concentration at 89% P<sub>4</sub>O<sub>10</sub> as determined by Bell (1).

There is good agreement between Munson's (8) value of  $4.596 \times 10^{-2}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 25° C. for the specific conductivity of an equilibrated sample of 100% phosphoric acid (72.43% phosphorus pentoxide) and the value  $4.60 \times 10^{-2}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at 25° C. taken from the curve in Figure 1. The good agreement between the two studies at 25° C., where an equilibrium concentration of acid species would be more difficult to attain than at the higher temperatures, suggests that the samples in this work were equilibrated (within experimental error) in the region of 100% phosphoric acid.

Studies were carried out to determine if the conductivity at high acid concentrations was changing with time owing to a slow approach to equilibrium. The conductivity of a sample containing 83.77% phosphorus pentoxide was monitored for 30 hours with the sample temperature maintained at  $60 \pm 0.05^\circ$  C. No change in resistance, within experimental error, was observed. The conductivity of the

same sample was then monitored for 2 weeks at  $25 \pm 0.05^\circ$  C. with no change observed.

The absence of any measurable change in resistance during the time periods studied suggests that a consistent set of conductivity data in the polyphosphoric acid region can be obtained if measurements are made over reasonable time periods. This consistency is borne out by the data shown in Figure 1. However, at very high acid concentrations, the time required to reach equilibrium may be much longer than the time allowed in this work. Greenwood and Thompson (3) found that 21 days at 40° C. were required to reach equilibrium in a freshly melted sample of stoichiometric orthophosphoric acid. The high viscosity and the many equilibria involved as the P<sub>4</sub>O<sub>10</sub> concentration is increased (in the polyphosphoric acid region) make meas-

Table II. Comparison of Specific Conductivity for Concentrated Phosphoric Acid

Concn., Weight % P <sub>4</sub> O <sub>10</sub>	Temp., ° C.	Specific Conductivity, Ohm <sup>-1</sup> Cm. <sup>-1</sup>			
		This work	Kakulin, <i>et al.</i> (5)	Ref. (7)	Keidel (6)
65	40	0.114	0.0979	0.104	...
70	40	0.0899	0.0792	0.078	...
75	40	0.0452	0.0216	0.035	...
75	50	0.0638	0.0308	...	0.071
80	50	0.0144	...	...	0.016
85	50	0.00202	...	...	0.0039

<sup>a</sup> No data reported for 40° C. <sup>b</sup> No data reported for 50° C. <sup>c</sup> Data reported for the concentration range 65.2 to 75.4 weight % P<sub>4</sub>O<sub>10</sub>.

urements of the conductivity increasingly more difficult. Therefore, the data in the polyphosphoric acid region would be expected to be less accurate than below 100%  $H_3PO_4$ .

Shown in Table II are some interpolated values for the conductivity of phosphoric acid which are representative of results obtained in this work and by others (5, 6, 7). The values found in this work are consistently higher than the values reported by Kakulin and Fedorchenko (5) and elsewhere (7). However, values found in this work are lower than those of Keidel (6). The limited amount of experimental detail regarding sample preparation, analysis, and thermal history in the three reports cited does not allow for a critical comparison with this work.

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#### LITERATURE CITED

- (1) Bell, R.N., *Ind. Eng. Chem.* **40**, 1464 (1948).
- (2) Clifford, J.E., Beach, J.G., Gurklis, J.A., Kolic, E.S., Gates, J.T., Faust, C.L., Battelle Memorial Institute, NASA CR-60851, 1964.
- (3) Greenwood, N.N., Thompson, A., *J. Chem. Soc.* **1959**, p.3485.
- (4) Jones, G., Bradshaw, B.C., *J. Am. Chem. Soc.* **55**, 1780 (1933).
- (5) Kakulin, G.P., Fedorchenko, I.G., *Russ. J. Inorg. Chem. (Eng. Transl.)* **7**, 1289 (1962).
- (6) Keidel, F.A., *Anal. Chem.* **31**, 2043 (1959).
- (7) Monsanto Chemical Co., St. Louis, Mo., Tech. Bull. No. I-239.
- (8) Munson, R.A., *J. Phys. Chem.* **68**, 3374 (1964).

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## Heterogeneous Phase and Volumetric Equilibrium in the Methane-*n*-Nonane System

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Vapor-liquid compositions and molar volumes are presented for eight isotherms between  $-50^\circ$  and  $150^\circ$  C. The three-phase, vapor-liquid-solid behavior is presented at pressures up to 150 atm. Vapor-liquid critical temperatures are presented at five temperatures between  $-25^\circ$  and  $75^\circ$  C.

THE STUDY of Savvina (13) appears to be the only one in which experimental vapor-liquid behavior on the methane-*n*-nonane binary system is reported. Savvina presents vapor-liquid isotherms at  $40^\circ$ ,  $60^\circ$ ,  $80^\circ$ ,  $100^\circ$ ,  $120^\circ$ , and  $150^\circ$  C. at pressures up to the critical. Unfortunately, the data are presented only in graphical form on a scale which lacks the accuracy necessary for most scientific and engineering purposes.

The volumetric behavior of methane has been studied extensively (1, 3, 8-11). Matthews (9) and Canjar (1) have evaluated the thermodynamic properties of methane from the *P-V-T* data.

The volumetric behavior of *n*-nonane has been established by Carmichael (2) up to 680 atm. and above  $40^\circ$  C. Data on the liquid density, vapor pressures, critical constants, and heat of fusion were reported by Rossini (12).

#### EXPERIMENTAL

The equipment and experimental techniques were described by Kohn (7) and were the same as those used in other studies of binary hydrocarbon systems (4, 6, 7, 14). Temperatures were taken on a platinum resistance thermometer which was calibrated to indicate temperature within  $0.02^\circ$  C. of the International Platinum Scale. Pressures were taken on bourdon tube gages which were accurate to  $\pm 0.07$  atm. Each bourdon gage was checked at the start of an experimental run by use of an accurate dead weight gage. The only change was in the equilibrium cells used for the vapor-liquid study at pressures in excess of 100 atm. The

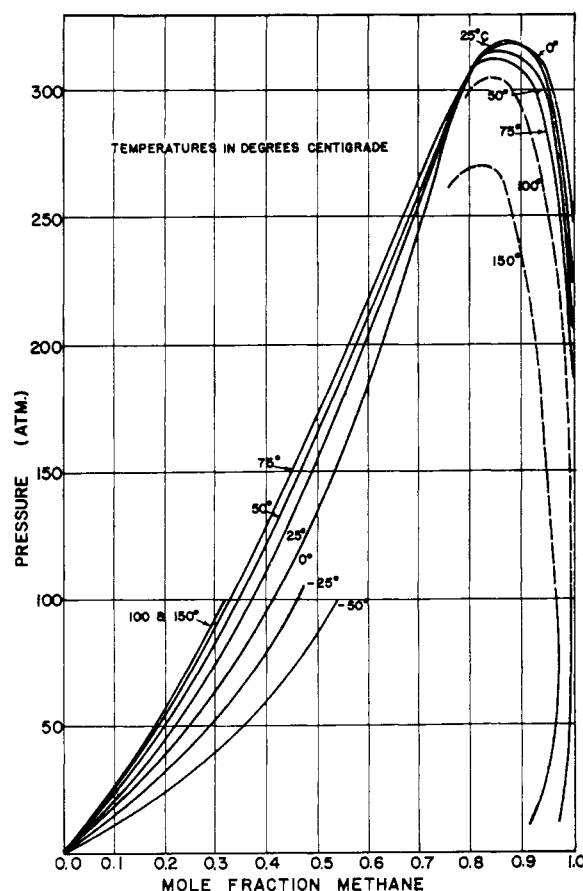


Figure 1. Smoothed pressure-temperature diagram

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