NOMENCLATURE

P = total pressure, mm. of Hg
P_i = vapor pressure of component i, mm. of Hg
R = gas constant, 1.987 cal. per gram mole-° K.
T = temperature, ° K
V_{iL} = liquid molar volume of component i, cm.^{3} per gram mole
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase

Greek Letters

γ_i = liquid phase activity coefficient of component i
$(\lambda_{ij} - \lambda_{ii})$ = Wilson parameters for interaction of ij-pair relative to ii-pair
Λ_{ij} = parameter of Wilson equation, defined in Equation 4
Σ = summation of

Subscripts

1 = 2,3-dimethylbutane
2 = methanol
3 = acetone
4 = chloroform
e = experimental
p = predicted

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Heat Capacity of Alcohol Vapors at Atmospheric Pressure

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Vapor-phase heat capacity was measured in a flow calorimeter at atmospheric pressure in the temperature range from saturation to approximately 330° C. for the following aliphatic alcohols: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, *n*-pentyl, isopentyl-, and *tert*-pentyl. Equation 9 was derived as a suitable model for all the alcohols investigated and may be used for extrapolation to higher alcohols.

THE CHEMICAL engineering laboratories at the Technical University of Norway have for some time been investigating the tempeeature and pressure dependence of vapor-phase enthalpy. The pressure effect is measured by isothermal expansion in an apparatus described by Stri- is determined by measuring the heat capacity at atmospheric pressure in a flow calorimeter (*9*).

These measurements, carried out with a homologous series, may give a more accurate basis for estimation of the vapor-phase enthalpy. The first part of the investigation is concerned with 11 aliphatic alcohols. Their heat capacity at atmospheric pressure was measured from the normal boiling point to approximately 330° C. The measurement results and their mathematical correlation models are reported here.

EXPERIMENTAL

The heat capacity measurements were carried out as described by Lydersen and Rönne (*9*) in the flow calorimeter described by them.

The performance of the equipment was examined by measuring the heat capacity of steam. Figure 1 gives the results and the values from the VDI-steam table (*11*). The average deviation is 0.002 kcal./kg., ° C. (0.4%).

The alcohols used in the experiments were of the following origins:

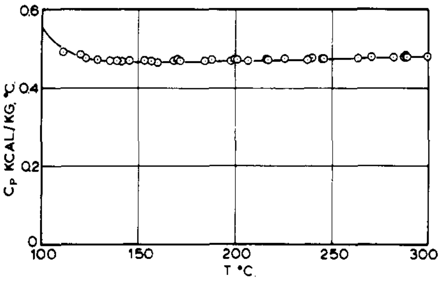

Figure 1. Heat capacity for steam measured at atmospheric pressure

Curve corresponds to steam table (*11*)
○ This work

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Methyl alcohol	Pro analysi, E. Merck, Darmstadt
Ethyl alcohol	Absolute ethyl alcohol from Vinmonopolet A/S
Propyl and butyl alcohols	Puriss, E. Merck, Darmstadt
Pentyl alcohols	F.d. Chromatographie, Schuchardt, München

The methyl, ethyl, propyl, and butyl alcohols were further purified by boiling with CaO powder and total refluxing for 12 hours, followed by simple distillation. The resulting samples for the experiments were a minimum of 99.8 vol. % pure, as determined in a gas chromatograph.

RESULTS

The vapor heat capacity measurements of 11 alcohols at atmospheric pressure and between their boiling points and 330° C. are presented in Tables I and II. Figures 2, 3, 4, and 5 are plots of the experimental heat capacity data. The curves correspond to Equation 9.

The accuracy uncertainty of the experimental heat capacities is estimated as less than ±0.3%. Literature data plotted in the graphs coincide well with the present measurements. The previously published measurements are limited to the temperature range from saturation to 132° to 168° C. The present investigation checks the previous measurements and extends the temperature range up to 330° C. Only three experimental values have been reported before for *n*-pentyl and *tert*-pentyl alcohol and none for isopentyl alcohol.

CORRELATIONS

Previous investigators have suggested mathematical models correlating vapor heat capacity with temperature. Most common are the models in Equations 1 and 2.

$$C_p = a + bT + cT^2 + dT^3 + \cdots \quad (1)$$

$$C_p = a + b/T + c/T^2 + d/T^3 + \cdots \quad (2)$$

where

Table I. Heat Capacity of Alcohol Vapors at Atmospheric Pressure

Methyl Alcohol		Ethyl Alcohol		*n*-Propyl Alcohol		*n*-Butyl Alcohol		*n*-Pentyl Alcohol		*sec*-Butyl Alcohol	
t^a, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.
74.2	20.76	83.4	24.65	102.3	30.17	122.1	36.55	145.8	44.73	107.8	36.42
83.4	15.92	88.6	22.94	109.9	27.71	131.0	35.13	147.6	44.28	113.1	35.56
100.2	13.43	98.7	20.82	114.0	27.53	136.0	35.24	153.0	43.76	120.6	35.28
125.8	12.66	114.1	20.09	123.8	27.30	146.4	35.39	160.3	44.03	132.0	35.26
128.0	12.91	115.7	19.95	136.8	27.49	157.9	35.98	169.7	45.20	133.0	35.36
128.2	12.94	160.1	20.73	147.6	27.70	168.0	36.62	171.2	45.14	144.1	35.70
158.3	13.33	170.2	20.92	149.8	27.71	186.4	37.36	199.7	46.47	167.6	36.75
169.0	13.39	207.3	22.02	164.8	28.20	215.1	39.05	209.1	46.73	197.7	38.58
184.2	13.62	261.2	23.59	187.9	29.08	246.9	40.68	258.1	50.50	242.8	41.21
204.6	13.68	275.6	23.96	202.2	30.00	272.8	42.16	281.0	51.33	287.2	43.52
211.9	13.52	299.1	24.88	231.8	31.01	295.3	43.55	300.8	53.15	309.7	45.15
225.8	14.37	318.1	25.43	238.7	31.30	330.2	45.28	$\overline{\Delta C_p}$ =	0.34	$\overline{\Delta C_p}$ =	0.16
248.2	14.71	$\overline{\Delta C_p}$ =	0.26	259.2	32.27	$\overline{\Delta C_p}$ =	0.19				
282.8	15.28			286.9	33.42						
308.2	15.86			305.7	34.32						
312.2	15.97			330.1	35.24						
$\overline{\Delta C_p}^b$ =	0.28			$\overline{\Delta C_p}$ =	0.23						

[a] Mean temperature of measurement. Temperature differences used in experiments are all in region 4.9° to 17.4° C. and most often approximately 10° C. [b] Arithmetic mean deviation from Equation 9, kcal./kmole, ° C.

Table II. Heat Capacity of Alcohol Vapors at Atmospheric Pressure

Isopropyl Alcohol		Isobutyl Alcohol		Isopentyl Alcohol		*tert*-Butyl Alcohol		*tert*-Pentyl Alcohol	
t^a, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.	t, ° C.	C_p, kcal./kmole, ° C.
92.6	29.83	117.4	35.52	178.5	45.80	87.4	37.49	108.2	45.22
105.7	28.26	124.5	35.17	201.4	46.83	99.7	35.92	111.5	42.89
111.8	27.99	133.8	35.30	215.2	48.06	112.5	35.47	114.3	41.99
120.5	27.68	143.8	35.41	226.0	49.26	137.7	35.98	122.9	42.22
132.2	27.91	150.9	35.79			166.7	37.57	124.9	42.71
158.0	28.58	168.7	36.69	$\overline{\Delta C_p}$ =	0.26	168.3	37.64	152.8	44.94
180.0	29.46	178.1	37.40			197.6	39.41	202.1	48.14
193.6	29.95	201.2	38.79			226.1	40.71	247.7	50.98
207.4	30.51	204.6	38.91			255.6	42.56	302.9	57.16[b]
226.6	31.36	228.4	40.08			301.9	45.43	$\overline{\Delta C_p}$ =	0.99
240.8	31.87	252.7	41.64			318.4	46.64		
265.9	33.13	273.2	42.77			$\overline{\Delta C_p}$ =	0.27		
293.9	34.44	309.8	44.46						
324.1	35.54	329.4	45.81						
$\overline{\Delta C_p}^c$ =	0.38	$\overline{\Delta C_p}$ =	0.17						

[a] Mean temperature of measurement. Temperature differences used in experiments are all in region 4.9° to 17.4° C. and most often approximately 10° C. [b] Probably in error due to decomposition. [c] Arithmetic mean deviation from Equation 9, kcal./kmole, ° C.

C_p = heat capacity at constant pressure, kcal./kmole, ° K.
T = absolute temperature, ° K.
a, b, c, d = empirical constants

More recently, Yuan and Mok (*15, 16*), have claimed the model in Equation 3 to be more accurate.

$$C_p = a + e \times \exp\,(-f/T^n) \tag{3}$$

where e, f, and n are empirical constants.

None of these models has the desired accuracy for polar associating compounds in the industrially important temperature range near saturation.

Alcohol vapors associate through hydrogen bonding, especially in the region near the saturation temperature. They form equilibrium mixtures of monomers, dimers, and most often assumed tetramers (*5, 7*) as can be concluded from spectroscopic studies and measurements of heat capacity.

Equation 4, derived from the present measurements, fits the experimental data well.

$$C_p = a + bT + e \times \exp\,(f_2/T) \tag{4}$$

This equation is, because of experimental conditions, valid at atmospheric pressure only.

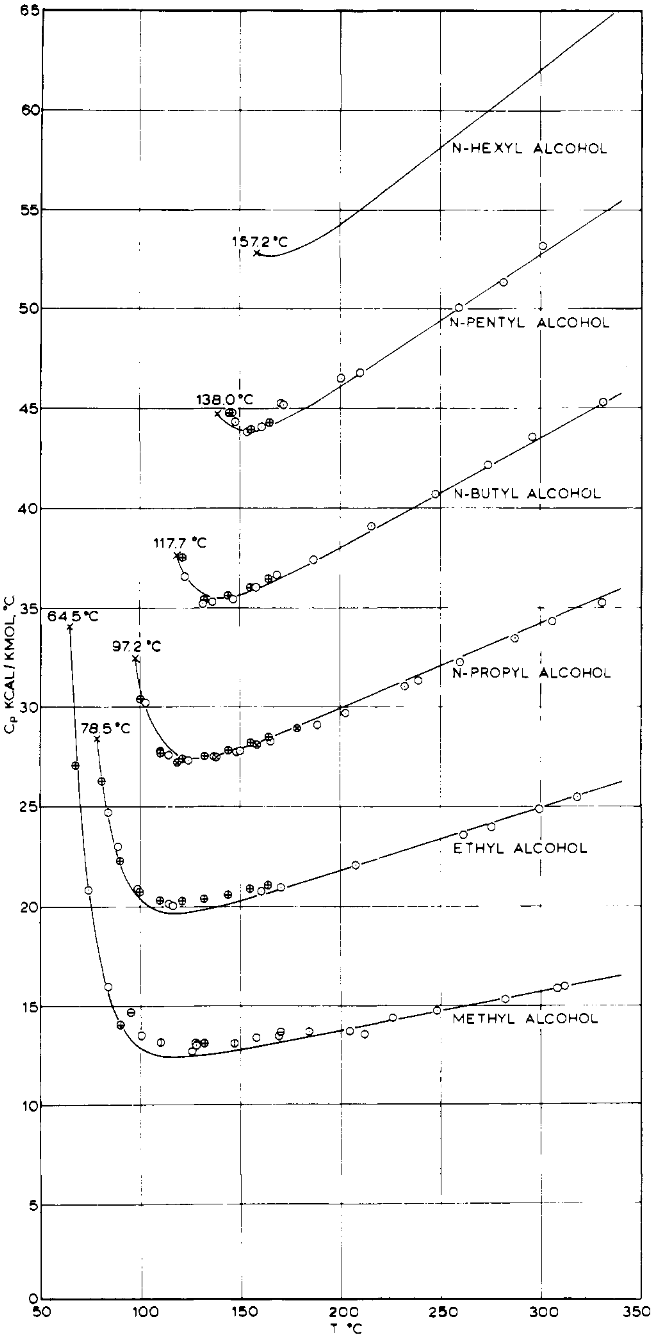

Figure 2. Heat capacity of normal alcohols at atmospheric pressure as a function of temperature

Curves correspond to Equation 9

⊙ This work
⊕ Sinke and deVries (*12*)
⊗ Mathews and McKetto (*10*)
⊖ deVries and Collins (*4*)
⦶ Jatkar (*8*)
× Normal boiling point

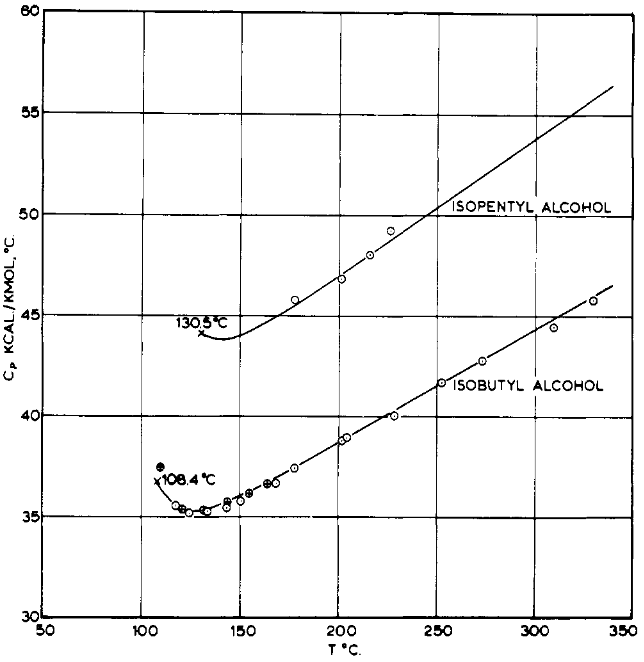

Figure 3. Heat capacity of iso alcohols at atmospheric pressure as a function of temperature

Curves correspond to Equation 9

⊙ This work
⊕ Sinke and deVries (*12*)
× Normal boiling point

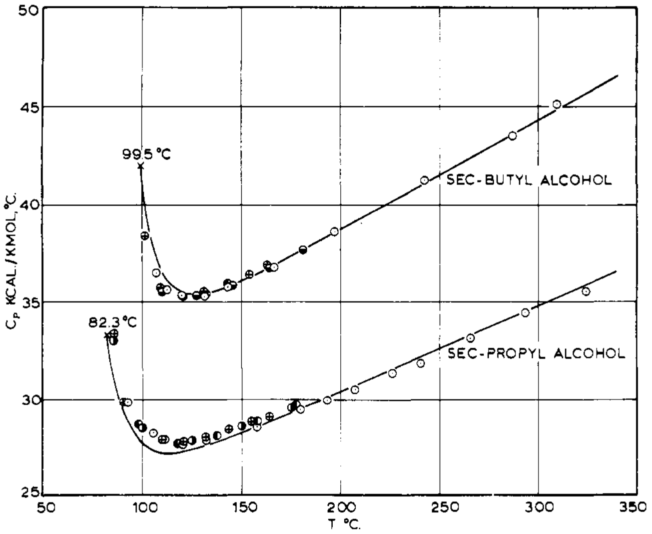

Figure 4. Heat capacity of secondary alcohols at atmospheric pressure as a function of temperature

Curves correspond to Equation 9

⊙ This work
⊕ Sinke and deVries (*12*)
◒ Bermon and McKetta (*2*)
◐ Berman, Larkam, and McKetta (*1*)
◑ Hales, Cox, and Lees (*6*)
× Normal boiling point

Weltner and Pitzer (*14*) proposed Equation 5 to give the temperature and pressure-dependency of the heat capacity of methyl alcohol.

$$C_p = C_p^\circ + AP + CP^3 \tag{5}$$

where

C_p° = heat capacity of the ideal gas, often given in the polynomial form of Equation 1
P = pressure, atm.
A = exponential function of energy change in dimerization reaction, and of temperature
C = exponential function of energy change in tetramerization reaction, and of temperature

At atmospheric pressure and with C_p° approximated to only the first two terms of Equation 1, Equation 5 reduces to

$$C_p = a + bT + A(T) + C(T) \tag{6}$$

If the sum of the exponential functions, $A(T) + C(T)$, that takes into account the energy change in association, is approximated by one exponential function, $e \times \exp(f/T)$, Equation 6 simplifies to

$$C_p = a + bT + e \times \exp(f/T) \tag{7}$$

Equation 7 is identical to Equation 4—i.e., the heat capacity model proposed here can be regarded as a simplified form of the Weltner-Pitzer equation.

For the normal alcohols investigated at atmospheric pressure and constant temperature above 175° C. (the region of negligible association), the increase in heat capacity from one alcohol to the next higher one is constant. This gives for 1 atm.

$$C_p^\circ = f_1 \times (a + bT) \tag{8}$$

where f_1 for the normal alcohols is a linear function of the number of carbon atoms in the molecule.

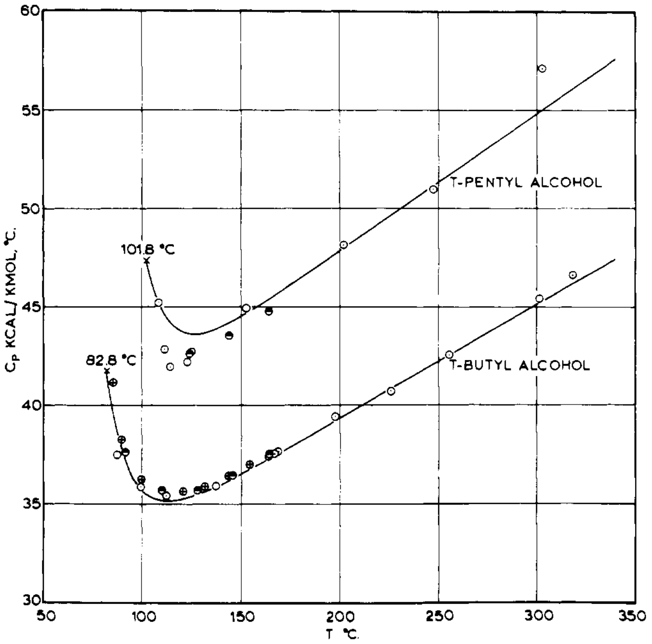

Figure 5. Heat capacity of tertiary alcohols at atmospheric pressure as a function of temperature

Curves correspond to Equation 9. Point at 302.9° C. for *tert*-pentyl alcohol believed to be in error due to decomposition

⊙ This work
◒ Beynon (3)
⊕ Sinke and deVries (12)
× Normal boiling point

The actual figures for the normal alcohols show that f_2 in Equation 4 is also a linear function of the number of carbon atoms in the molecule with methyl alcohol the only one showing a slight deviation. Hence, a general equation for the heat capacity of alcohols at atmospheric pressure is

$$C_p = f_1 \times (a + bT) + e \times \exp(f_2/T) \tag{9}$$

where f_1 and f_2 are linear functions of the number of carbon atoms for the normal alcohols. The constants and functions of Equation 9 are empirically determined to be:

a = $1.73, b = 8.20 \times 10^{-3}, e = 1.774 \times 10^{-13}$
f_1 = $(1.0 + 1.444 \times N \times G)$
f_2 = $(10220 + 454 \times (N - H) \times G^2)$ for $N > 1$
f_2 = 10977 for $N = 1$ (methyl alcohol)
N = number of carbon atoms in molecule
H = "degree of branching" = number of —CH_3 groups in molecule − 1—i.e., $H = 0$ for normal alcohols
G = "configuration factor" = $(1.000 + 0.0022 \times H)$
T = absolute temperature (° K.) ≧ saturation temperature

The configuration factor, G, and the degree of branching, H, are introduced in functions f_1 and f_2 in order to make Equation 9 valid also for branched alcohol molecules.

The average deviation from the experimental data for all the alcohols investigated is ±0.32 kcal./mole ° C.

Equation 9 might seem complex, but becomes simple when the actual figures are inserted. It is suitable for use in a computer program, and there is no indication that it should not be valid for engineering calculations on even higher alcohols.

CONCLUSIONS

The lack of a suitable model for the temperature dependence of the heat capacity of homologous series of associating vapors led to Equation 9, derived from the experimental values presented here. This expression is a simplified form of the Weltner-Pitzer equation, which is based on theoretical considerations, and it is simple enough to be useful in engineering calculations. It fits well for the whole temperature range for the 11 alcohols investigated.

ACKNOWLEDGMENT

The measurements of the heat capacity of methyl and ethyl alcohol were made by Rolf Strömmen.

NOMENCLATURE

a, b, c, d, e, n = empirical constants In Equation 9 $a = 1.73$, $b = 8.20 \times 10^{-3}, e = 1.774 \times 10^{-13}$
A, C = exponential functions of temperature and enthalpy and entropy change in polymerization reactions as described by Weltner and Pitzer (*14*)
C_p = vapor heat capacity at constant pressure, kcal./kmole, ° C.
C_p° = heat capacity at constant pressure of ideal gas, kcal./kmole, ° C.
f, f_1, f_2 = empirical functions In Equation 9 $f_1 = (1.00 + 1.444 \times N \times G)$, $f_2 = (10220 + 454 \times (N - H) \times G^2$ for $N > 1$, $f_2 = 10977$ for $N = 1$
G = configuration factor = $(1.000 + 0.0022 \times H)$
H = degree of branching = number of —CH_3 groups in molecule − 1—i.e., $H = 0$ for normal alcohols
N = number of carbon atoms in molecule
P = pressure, atm.
T = absolute temperature, ° K.
t = temperature, ° C.

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Effect of Impurities on Density and Viscosity of Simulated Wet-Process Phosphoric Acid

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Each of the common metallic impurities—Al, Fe, K, Ca, and Mg—increased the density and viscosity at 25° C. of simulated wet-process phosphoric acids containing 50, 75, and 104.4% H_3PO_4. Common anionic impurities—Cl, F, SO_4, and SiO_2—had little effect on either viscosity or density. When two or more impurities were present, their effects were roughly additive, but no general relationship of the effects of the different impurities could be established.

THE BEGINNINGS of the manufacture of wet-process phosphoric acid from phosphate rock and sulfuric acid are difficult to date precisely, but the method attained its prominence in 1917 to 1932 (*18*). Only in the last few years, however, the impurities in the wet-process acid have increased sufficiently to interfere seriously with the processing of the acid into fertilizers (*1, 5*). The increase in the amounts of these impurities, largely iron and aluminum, dissolved from the rock in the acidulation step results from the use of lower-grade rock in the manufacture of the acid because of the depletion of the reserves of high-grade rock. The impurities increase the viscosity of the acid as long as they remain in solution; as the acid is concentrated they precipitate as sludges that interfere with the mechanical handling of the acid. The sludge compounds, largely complex iron and aluminum phosphates, have been identified and characterized by Lehr *et al.* (*9*).

Dahlgren (*4*) studied the effects of the common impurities on the density and viscosity of acids containing 30, 43, and 54% P_2O_5 (41, 59, and 75% H_3PO_4). Burkert and Nickerson (*2*) studied the effects of iron, aluminum, magnesium, and sulfate on the properties of acids in the range 65 to 78% P_2O_5 (90 to 108% H_3PO_4) in an attempt to determine the amounts of impurities that could be tolerated in phosphoric acids that were to be concentrated to superphosphoric acid (usually 70 to 75% P_2O_5, or 97 to 104% H_3PO_4).

Results are reported here of a study of the effects of the common impurities on the density and viscosity at 25° C. of acids containing 36.2, 54.3, and 75.6% P_2O_5 (50, 75, and 104.4% H_3PO_4). Some of the mixtures were prepared to be initially supersaturated with respect to the impurities; the salts that precipitated were identified and the compositions of the acids were determined when precipitation was complete and the acids presumably were saturated with the impurities.

MATERIALS AND METHODS

To control the initial amounts and proportions of the impurities, the study was made with simulated wet-process acids. Acids containing 50 and 75% H_3PO_4 were prepared from reagent 85% H_3PO_4, and acid containing 104.4% H_3PO_4 was prepared from a superphosphoric acid produced in the TVA stainless steel demonstration plant. In the superphosphoric acid, 55.7% of the phosphorus was present as orthophosphate and 44.3% as condensed phosphates or polyphosphates.

In the simulated acids containing 50 or 75% H_3PO_4, almost all the cations were added as nearly saturated solutions of their phosphates in acid of the desired concentration. Solutions of the iron and aluminum phosphates were prepared by dissolving the pure metals in the phosphoric acid; the iron solutions were oxidized with hydrogen peroxide except when the ferrous salt was desired. Solutions of other phosphates and of the anion impurities, which were usually added as acids, were prepared from reagent chemicals.

In the simulated acids containing 50 or 75% H_3PO_4, the $H_2O:H_3PO_4$ ratio was maintained at its value in the initial acid. The phosphate added with a cation impurity was assumed to be present in the final mixture as H_3PO_4 and to require the proper amount of water to maintain the desired concentration. The cation impurities and the anhydrous acid impurities were ignored in calculating the concentration of the phosphoric acid. When all the impurities had been added, the $H_2O:H_3PO_4$ ratio was

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[1] Deceased.