Hydrolysis of Ammonium Pyro-, Tripoly-, and Tetrapolyphosphate at 25° and 50°C

Joseph W. Williard,[1] Thad D. Farr, and John D. Hatfield
Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

In 0.2*M* solution, ammonium pyro-, tripoly-, and tetrapolyphosphate hydrolyze by first-order reactions. The rate constants are determined as functions of pH in solutions of ammonium pyro- and tripolyphosphate at 25° and 50°C and in solutions of ammonium tetrapolyphosphate at 50°C.

Studies of the hydrolytic degradation of linear polyphosphates at various concentrations and with various cations are reported in the literature (*2, 3, 5–13, 16, 19, 22, 23, 25*). The present work with all the known crystalline ammonium polyphosphates was carried out at a constant molarity, 0.2*M*, as it has been shown (*10*) that the effect of the concentration of phosphate is minimal. Measurements were made at two temperatures, 25°C for ammonium pyro- and tripolyphosphates and 50°C for ammonium pyro-, tripoly-, and tetrapolyphosphates. The ammonium cation is most common in fertilizer solutions. The effect of different cations has been studied by others (*22, 25*).

Tetraammonium pyrophosphate and pentaammonium tripolyphosphate were crystallized from liquid fertilizers produced by ammoniation of electric-furnace superphosphoric acid containing 80% P_2O_5 (*18*), and hexaammonium tetrapolyphosphate was prepared by a modification (*10*) of published procedures (*12, 17*); each salt was dissolved in conductivity water to form 0.2*M* stock solutions of the single phosphate species. Portions of each stock solution were treated with the hydrogen form of Amberlite IR-120 resin or with anhydrous ammonia to adjust the pH to predetermined values. The solutions in screw-capped culture tubes were placed in a constant temperature water bath at 25.00° or 50.00°, each ±0.05°C, and sampled periodically for determination of pH, composition, and distribution of phosphate species. The distribution of phosphate species was determined by one- and two-dimensional paper chromatography (*4, 15*). Use of two-dimensional paper chromatography was necessary to determine the trimetaphosphate formed (*20, 21, 25*) when the ammonium tetrapolyphosphate hydrolyzed at 50°C. The amounts of trimetaphosphate formed at 50°C during the hydrolysis of ammonium tetrapolyphosphate were considerably less than those found by Wieker (*25*) in his study of guanidinium tetrapolyphosphate at 60°C.

Hydrolysis of Ammonium Pyrophosphate at 25° and 50°C

The disappearance of pyrophosphate follows a first-order reaction in the pH range studied, as shown in Figures 1 and 2. The pyrophosphate hydrolyzes by the reaction

$$P_2O_7 \xrightarrow{k_2} PO_4 + PO_4$$

The differential equation for this first-order hydrolysis reaction is

$$-d(P_2O_7)/dt = k_2(P_2O_7) \qquad (1)$$

in which P_2O_7 represents the fraction of the total phosphorus present as pyrophosphate.

The integrated form of Equation 1 is

$$P_2O_7 = (P_2O_7)_0 \exp(-k_2t) \qquad (2)$$

where $(P_2O_7)_0$ is the fraction of phosphorus as pyrophosphate at zero time. Nonlinear least-square regression of the

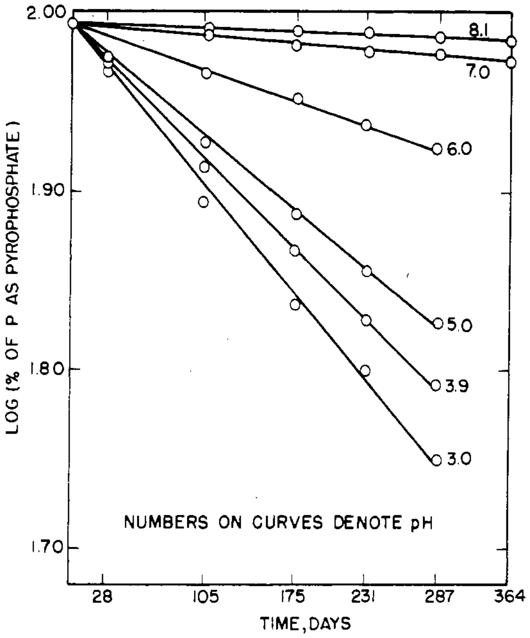


Figure 1. Rate of hydrolysis of ammonium pyrophosphate at 25°C

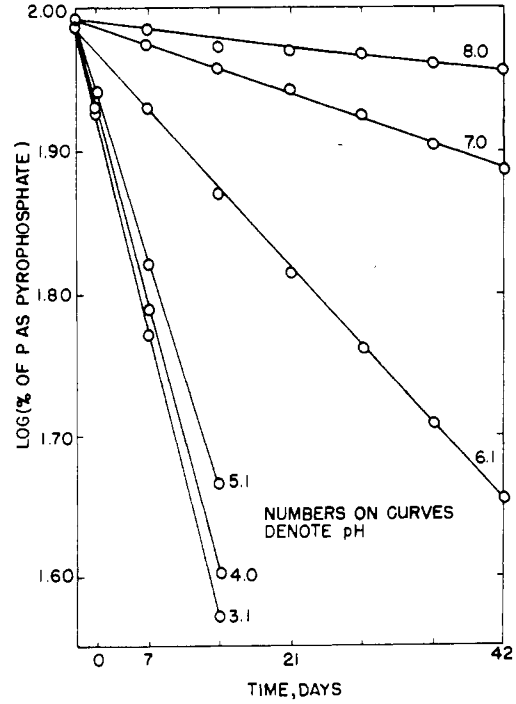


Figure 2. Rate of hydrolysis of ammonium pyrophosphate at 50°C

---

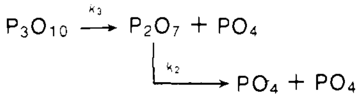
[1] To whom correspondence should be addressed.

experimental results was used to determine the best fit for the equation. The measured and calculated values of pyro- and orthophosphate at three pH levels and four sampling times are listed in Table I (complete tables have been deposited with the ACS Microfilm Depository Service).

The effect of pH on the hydrolysis of pyrophosphate at 25° and 50°C is shown in Figure 3 which demonstrates the effect of rise in temperature and fall in pH. Raising the temperature from 25° to 50°C increased the value of k_2 from 2.2×10^{-5} to 8.1×10^{-4} at pH 6. The change in the rate of hydrolysis is less per unit pH below pH 5 than that above this value. The constants a and b of the equation $pk_2 = a + b\text{pH}$, where k_2 is in units of hr^{-1}, are shown in Table II. At pH 6, 10% of the pyrophosphate is hydrolyzed in 29 weeks (4870 hr) at 25°C or in only 129 hr at 50°C. Raising the temperature at pH 6 from 25° to 50°C increases the rate of hydrolysis by a factor of 38; an equivalent rate change is obtained by lowering the pH from 8 to 3 at 50°C.

Hydrolysis of Ammonium Tripolyphosphate at 25° and 50°C

The hydrolytic degradation of ammonium tripolyphosphate follows a first-order reaction in the pH range studied, as is shown by Figures 4 and 5. The tripolyphosphate hydrolyzes by the reaction



$$\begin{tikzcd} P_3O_{10} \arrow[r, "k_3"] & P_2O_7 \arrow[d, "k_2"] + PO_4 \\ & PO_4 + PO_4 \end{tikzcd}$$

The differential equations for these consecutive and simultaneous first-order reactions are

$$-d(P_3O_{10})/dt = k_3(P_3O_{10}) \quad (3)$$

$$d(P_2O_7)/dt = (2/3)k_3(P_3O_{10}) - k_2(P_2O_7) \quad (4)$$

$$d(PO_4)/dt = (1/3)k_3(P_3O_{10}) + k_2(P_2O_7) \quad (5)$$

in which the chemical formulas denote fractions of the total phosphorus present as the indicated species.

The integrated forms of the equations are

$$P_3O_{10} = (P_3O_{10})_0 \exp(-k_3 t) \quad (6)$$

$$P_2O_7 = \{2/3\, k_3(P_3O_{10})_0 \exp[(k_2 - k_3)t]/(k_2 - k_3) + C\} \exp(-k_2 t) \quad (7)$$

where

$$C = (P_2O_7)_0 - 2/3\, k_3(P_3O_{10})_0\, 1/(k_2 - k_3)$$

$$PO_4 = 1 - (P_3O_{10} + P_2O_7) \quad (8)$$

where the subscript "0" indicates species fractions at zero time.

The experimental results were treated by nonlinear least-square regression to determine the best values of k_3 and $(P_3O_{10})_0$ from Equation 6 and of k_2 and $(P_2O_7)_0$ from Equation 7. The measured and calculated concentrations of tripoly-, pyro-, and orthophosphates at three pH levels and four sampling times are listed in Table III (complete tables have been deposited with the ACS Microfilm Depository Service). The standard deviation of k_3 ranged from 1.7 to 4.7%, average 2.9%, at 25°C and from 1.0 to 6.1%, average 2.2%, at 50°C. The values calculated for k_2 from the experimental results were random for pH values above 6 at 25°C and for pH values above 7 at 50°C. The plot of pk_2 vs. pH at 50°C will be shown in a later figure and discussed then.

The effects of pH and temperature on the hydrolysis of tripolyphosphate at 25° and 50°C are shown in Figure 6. The rate of hydrolysis at 25°C at pH 4 is 13 times that at pH 7, and the rate at 50°C at pH 4 is 11 times that at pH 7. At pH 6 the rate at 50°C is 31 times that at 25°C. The rate of hydrolysis of tripolyphosphate is higher at pH values below about

Table I. Hydrolysis of Ammonium Pyrophosphate

Hydrolysis at 25°C				Hydrolysis at 50°C			
Time, hr		Distribution, %, of phosphate		Time, hr		Distribution, %, of phosphate	
		Pyro	Ortho			Pyro	Ortho
	Results at pH 8.05				Results at pH 8.00		
0	Obs	98.20	1.80	0	Obs	98.60	1.40
	Calc	98.16	1.84		Calc	97.97	2.03
2520	Obs	97.60	2.40	336	Obs	94.00	6.00
	Calc	97.75	2.25		Calc	95.34	4.66
5544	Obs	97.50	2.50	672	Obs	93.10	6.90
	Calc	97.26	2.74		Calc	92.78	7.22
8736	Obs	96.70	3.30	1008	Obs	90.70	9.30
	Calc	96.75	3.25		Calc	90.29	9.71
	Results at pH 6.03				Results at pH 6.09		
0	Obs	98.20	1.80	0	Obs	97.00	3.00
	Calc	98.10	1.90		Calc	96.76	3.24
2520	Obs	92.40	7.60	48	Obs	93.40	6.60
	Calc	92.66	7.34		Calc	93.27	6.73
4200	Obs	89.50	10.50	336	Obs	74.30	25.70
	Calc	89.21	10.79		Calc	74.84	25.16
6888	Obs	83.90	16.10	1008	Obs	45.20	54.80
	Calc	83.94	16.06		Calc	44.77	55.23
	Results at pH 3.00				Results at pH 3.12		
0	Obs	98.20	1.80	0	Obs	97.00	3.00
	Calc	97.65	2.35		Calc	97.06	2.94
672	Obs	92.30	7.70	48	Obs	84.80	15.20
	Calc	92.46	7.54		Calc	84.64	15.36
4200	Obs	68.80	31.20	168	Obs	59.90	40.10
	Calc	69.42	30.58		Calc	60.09	39.91
6888	Obs	56.20	43.80	336	Obs	37.30	62.70
	Calc	55.80	44.20		Calc	37.20	62.80

4.5 than at higher values. The rate of hydrolysis of pyrophosphate at 50°C follows a similar pattern except that the change appears at about pH 5.5. The constants of the linear relationship,

$$pk_i = a + b\text{pH}$$

where k_i is in units of hr^{-1}, are shown in Table II. At pH 6, 10% of the tripolyphosphate is hydrolyzed in 71 days at 25°C or in 2.3 days at 50°C. At 25°C, 50% of the tripolyphosphate is hydrolyzed in 67 weeks at pH 6 or in more than 9 years (470 weeks) at pH 8.

Hydrolysis of Ammonium Tetrapolyphosphate at 50°C

In previous work at 25°C (*10*), the hydrolysis of tetrapolyphosphate was shown to be a straightforward hydrolytic degradation of P_4O_{13} to P_3O_{10} to P_2O_7 to PO_4. This work at 50°C shows that, as others have found (*20, 21, 25*), at this temperature the hydrolytic mechanism is different and the formation of cyclic trimetaphosphate is a significant part of the sequence of hydrolysis of linear phosphates with chain lengths of 4 or more. This mechanism at 50°C is illustrated in Figure 7 which shows the route for the formation of trimetaphos-

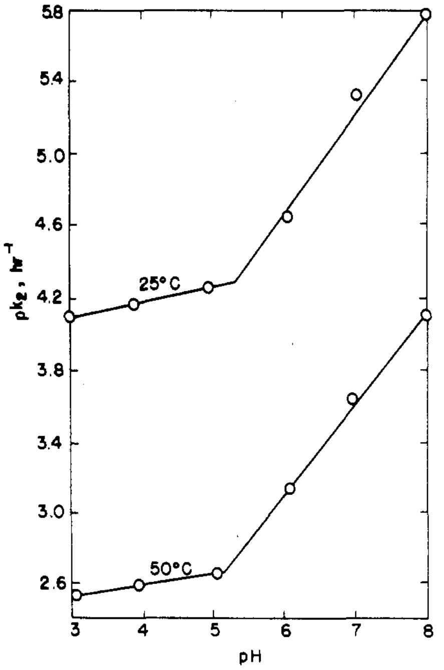


Figure 3. Effect of pH on rate of hydrolysis of ammonium pyrophosphate at 25° and 50°C

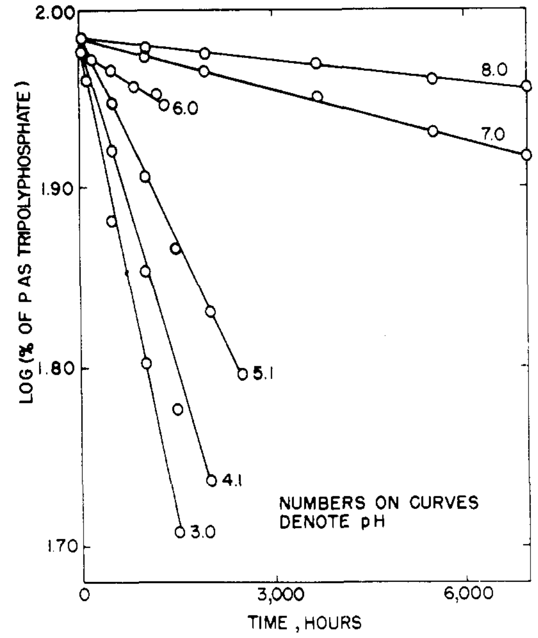


Figure 4. Rate of hydrolysis of ammonium tripolyphosphate at 25°C

Table II. Hydrolysis Constants of Condensed Phosphates
Expressed as $pk_i = a + b\text{pH}$

Constant[a]	Temp, °C	pH range	*a*	*b*
		Measured in ammonium pyrophosphate solutions		
k_2	25	3.0–5.3	3.8523	0.0797
		5.3–8.0	1.2748	0.5650
k_2	50	3.0–5.3	2.3692	0.0544
		5.3–8.0	0.0327	0.5094
		Measured in ammonium tripolyphosphate solutions		
k_2	50	3.0–5.5	2.3445	0.0881
		5.5–7.0	0.7700	0.6414
k_3	25	3.0–4.5	2.9476	0.1418
		4.5–8.0	1.6256	0.4305
k_3	50	3.0–4.5	1.7299	0.0817
		4.5–8.0	0.3364	0.3959
		Measured in ammonium tetrapolyphosphate solutions		
k_3	50	2.6–4.6	1.5288	0.1268
		4.6–8.0	0.1592	0.4124
k_s[b]	50	2.2–2.7	0.3871	0.5687
		2.7–5.7	1.8464	0.03865
		5.7–8.0	1.0139	0.1919

[a] All k's are in units of hr^{-1}. [b] $k_s = k_{40} + k_{41} + k_{42}$; see Figure 9.

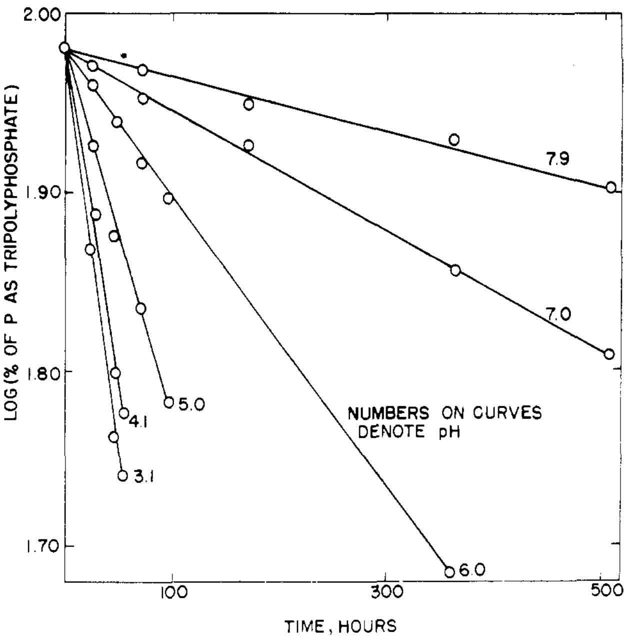


Figure 5. Rate of hydrolysis of ammonium tripolyphosphate at 50°C

phate and its subsequent hydrolysis to tripolyphosphate, in addition to the other steps in the overall reaction. The amounts of trimetaphosphate found in this work were not as large as those reported by Wieker (*25*) at 60°C, but this difference probably is due to the difference in temperature.

The disappearance of tetrapolyphosphate follows a first-order reaction in the pH range studied, as shown in Figure 8. The results support the hypothesis that the principal initial reaction is the splitting off of an end PO_4 group with the formation of tripolyphosphate and of much smaller amounts of trimetaphosphate. The trimetaphosphate ring splits to form tripolyphosphate; the combined tripolyphosphate hydrolyzes to pyro- and orthophosphate, and the pyrophosphate then hydrolyzes to orthophosphate.

The differential equations for the hydrolysis reactions are

$$\frac{-dP_4O_{13}}{dt} = (k_{40} + k_{41} + k_{42})P_4O_{13} = (k_{\text{total}})P_4O_{13} = k_sP_4O_{13} \quad (9)$$

$$\frac{d[(PO_3)_3]}{dt} = (3/4)k_{41}(P_4O_{13}) - k_{43}\,[(PO_3)_3] \quad (10)$$

$$\frac{dP_3O_{10}}{dt} = (3/4)k_{40}(P_4O_{13}) + k_{43}[(PO_3)_3] - k_{30}(P_3O_{10}) \quad (11)$$

$$\frac{dP_2O_7}{dt} = k_{42}(P_4O_{13}) + (2/3)k_{30}(P_3O_{10}) - k_{20}(P_2O_7) \quad (12)$$

$$\frac{dPO_4}{dt} = \left(\frac{k_{40} + k_{41}}{4}\right)(P_4O_{13}) + (1/3)k_{30}(P_3O_{10}) + k_{20}(P_2O_7) \quad (13)$$

The solutions of these five rate equations are

$$P_4O_{13} = (P_4O_{13})_0 \exp\,[(-k_{40} - k_{41} - k_{42})t] = (P_4O_{13})_0 \exp\,(-k_st) \quad (14)$$

$$(PO_3)_3 = C_1[\exp\,(-k_st) - \exp\,(k_{43}t)] \quad (15)$$

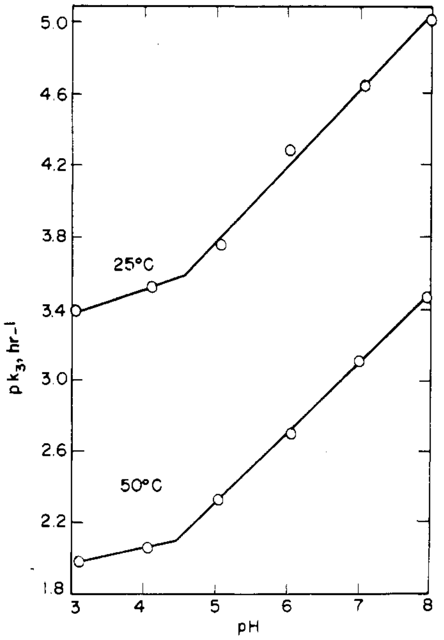


Figure 6. Effect of pH on rate of hydrolysis of ammonium tripolyphosphate at 25° and 50°C

Table III. Hydrolysis of Ammonium Tripolyphosphate

Hydrolysis at 25°C					Hydrolysis at 50°C				
Time, hr		Distribution, %, of phosphate: Tripoly	Pyro	Ortho	Time, hr		Distribution, %, of phosphate: Tripoly	Pyro	Ortho
		Results at pH 7.98					Results at pH 7.93		
0	Obs	96.60	2.40	1.00	0	Obs	95.60	2.60	1.80
	Calc	96.43	2.16	1.41		Calc	95.29	3.08	1.62
2016	Obs	94.70	3.20	2.10	72	Obs	93.10	4.70	2.20
	Calc	94.64	3.36	2.00		Calc	93.00	4.62	2.38
3696	Obs	93.40	4.20	2.40	360	Obs	85.10	9.90	5.00
	Calc	93.17	4.34	2.49		Calc	84.35	10.43	5.22
6888	Obs	90.50	6.20	3.30	504	Obs	80.10	13.30	6.60
	Calc	90.44	6.17	3.38		Calc	80.33	13.14	6.52
		Results at pH 6.01					Results at pH 6.02		
0	Obs	95.00	3.00	2.00	0	Obs	95.60	2.60	1.80
	Calc	94.80	3.29	1.91		Calc	95.27	3.43	1.30
504	Obs	92.60	4.90	2.50	48	Obs	87.00	8.60	4.40
	Calc	92.38	5.04	2.58		Calc	86.95	8.73	4.32
840	Obs	90.50	6.60	2.90	96	Obs	78.90	14.20	6.90
	Calc	90.80	6.21	2.98		Calc	79.36	13.36	7.28
1344	Obs	88.50	7.80	3.60	360	Obs	48.30	29.30	22.40
	Calc	88.49	7.99	3.53		Calc	48.01	29.43	22.56
		Results at pH 3.03					Results at pH 3.09		
0	Obs	96.60	2.40	1.00	0	Obs	95.60	2.60	1.80
	Calc	95.99	2.12	1.89		Calc	95.37	3.15	1.49
504	Obs	76.30	14.20	9.40	6	Obs	90.00	6.70	3.30
	Calc	77.72	14.02	8.27		Calc	89.59	6.93	3.48
1008	Obs	63.60	23.20	13.20	24	Obs	74.10	16.70	9.20
	Calc	62.92	23.24	13.84		Calc	74.28	16.61	9.11
1512	Obs	51.10	30.30	18.60	54	Obs	54.70	27.90	17.40
	Calc	50.94	30.30	18.76		Calc	54.35	28.24	17.42

where

$$C_1 = (3/4)k_{41}(P_4O_{13})_0/(k_{43} - k_s)$$

$$P_3O_{10} = C_2 \exp(-k_s t) + C_3 \exp(-k_{43} t) + [(P_3O_{10})_0 - C_2 - C_3] \exp(-k_{30} t) \quad (16)$$

where

$$C_2 = (3/4)k_{40}(P_4O_{13})_0 + k_{43}C_1/(k_{30} - k_s)$$

and

$$C_3 = -k_{43}C_1/(k_{30} - k_{43})$$

$$P_2O_7 = C_4 \exp(-k_s t) + C_5 \exp(-k_{43} t) + C_6 \exp(-k_{30} t) + [(P_2O_7)_0 - C_4 - C_5 - C_6] \exp(-k_{20} t) \quad (17)$$

where

$$C_4 = k_{42}(P_4O_{13})_0 + (2/3)k_{30}C_2/(k_{20} - k_s)$$

$$C_5 = (2/3)k_{30}C_3/(k_{20} - k_{43})$$

and

$$C_6 = (2/3)k_{30}[(P_3O_{10})_0 - C_2 - C_3]/(k_{20} - k_{30})$$

$$PO_4 = 1 - [P_4O_{13} + (PO_3)_3 + P_3O_{10} + P_2O_7] \quad (18)$$

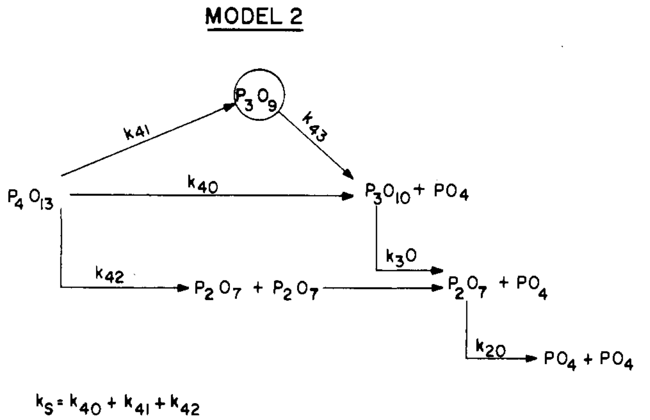


Figure 7. Hydrolytic mechanism of tetrapolyphosphates at 50°C

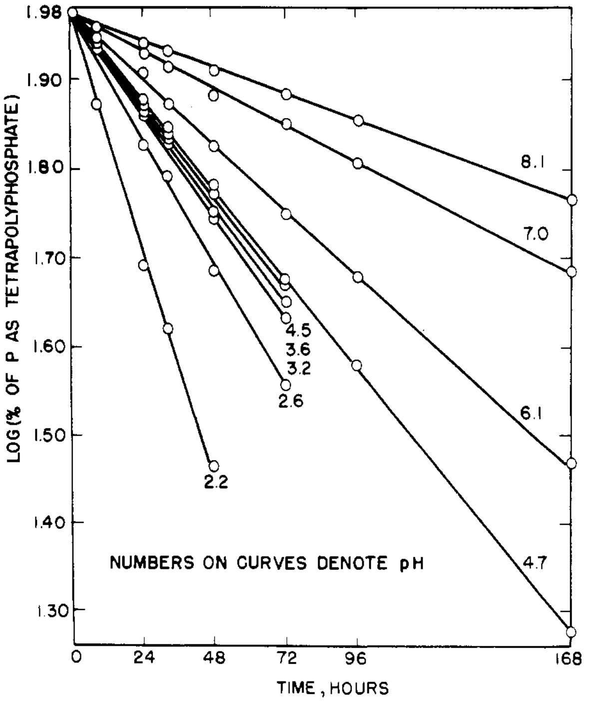


Figure 8. Rate of hydrolysis of ammonium tetrapolyphosphate at 50°C

The parameters of these equations that gave the best fit to the experimental results were determined by nonlinear least-square regression for Equations 14 through 17. Examination of a solution at pH 8.13 showed no detectable trimetaphosphate in the degradation products; the values of p*k* then were calculated by the method used in a previous study (*10*).

Table IV shows the measured and calculated concentrations of tetrapoly-, tripoly-, trimeta-, pyro-, and orthophosphates at three pH levels and four sampling times (tables of all the experimental data have been deposited with the ACS Microfilm Depository Service).

The set of constants that reproduces the experimental data for the hydrolysis of ammonium tetrapolyphosphate according to the mechanism of Figure 7 is listed in Table V. The standard errors of pk_s, pk_{43}, and pk_{30} indicate average errors of about 1% in k_s, 8.5% in k_{30}, and 20% in k_{43}. The hydrolysis constants for pyrophosphate, k_{20}, could not be determined precisely because of the relatively small change in pyrophosphate during the hydrolysis. The ratios $k_{40}:k_s$, $k_{41}:k_s$, and $k_{42}:k_s$ in Table V show the fractions of tetrapolyphosphate that are hydrolyzed by the three different routes indicated in Figure 7. At pH above 6 at 50°C, all the tetrapolyphosphate is hydrolyzed to tripolyphosphate and orthophosphate; when the pH is 2.5, about 15% of the tetrapolyphosphate initially forms the cyclic trimetaphosphate, which then splits to form tripolyphosphate; the amount of tetrapolyphosphate that hydrolyzes to pyro, k_{42}, is very small at all pH values at 50°C.

The effect of pH on the simultaneous hydrolysis of tetrapoly-, tripoly-, and pyrophosphates is shown in Figure 9. As was observed in previous studies, the relationship between p*k* and pH is linear for each polyphosphate species, and the constants of the relationship

$$pk_i = a + b\text{pH}$$

Table IV. Hydrolysis of Ammonium Tetrapolyphosphate at 50°C

		Distribution, %, of phosphate				
Time, hr		Tetra-poly	Tri-poly	Pyro	Ortho	Tri-meta
		Results at pH 7.02				
0	Obs	93.90	1.74	2.43	1.93	0.00
	Calc	93.47	1.74	2.43	2.36	0.00
24	Obs	84.68	8.57	2.57	4.08	0.10
	Calc	85.03	8.15	2.41	4.31	0.10
48	Obs	76.33	14.14	2.90	6.42	0.21
	Calc	77.36	13.79	2.50	6.15	0.21
108	Obs	48.19	32.96	4.20	13.72	0.93
	Calc	48.20	32.80	4.16	13.91	0.93
		Results at pH 4.73				
0	Obs	94.11	1.65	2.46	1.78	0.00
	Calc	94.41	1.65	2.46	1.48	0.00
8	Obs	87.09	6.63	2.58	3.42	0.28
	Calc	87.56	6.36	2.65	3.15	0.28
32	Obs	70.51	16.51	3.83	8.28	0.88
	Calc	69.84	17.19	4.02	8.05	0.90
96	Obs	38.04	29.53	10.11	20.88	1.44
	Calc	38.21	29.46	10.41	20.46	1.47
		Results at pH 3.22				
0	Obs	93.87	1.66	2.39	2.08	0.00
	Calc	94.02	1.66	2.39	1.93	0.00
8	Obs	86.23	6.98	2.58	3.69	0.52
	Calc	86.27	6.77	2.64	3.79	0.54
24	Obs	72.51	14.50	4.00	7.62	1.37
	Calc	72.63	14.56	3.87	7.60	1.33
72	Obs	43.00	24.68	10.33	19.74	2.24
	Calc	43.34	24.71	10.15	19.54	2.27

Table V. Hydrolysis Constants[a] for Assumed Mechanism (Figure 9) of Hydrolysis of Tetrapolyphosphate at 50°C

	pk_s		pk_{43}		pk_{30}		Ratios		
Av pH	Value	Std error	Value	Std error	Value	Std error	k_{40}: k_s	k_{41}: k_s	k_{42}: k_s
2.16	1.6154	0.0100	1.504	0.098	1.561	0.020	0.82	0.16	0.02
2.61	1.8713	0.0060	1.703	0.622	1.866	0.018	0.84	0.14	0.02
3.22	1.9683	0.0043	1.891	0.059	1.932	0.015	0.92	0.07	0.01
3.57	1.9870	0.0030	1.709	0.139	1.976	0.034	0.90	0.08	0.02
4.48	2.0230	0.0037	1.543	0.074	2.101	0.047	0.91	0.07	0.02
4.73	2.0258	0.0043	2.012	0.047	2.149	0.020	0.94	0.04	0.01
6.06	2.1540	0.0060	2.529	0.041	2.645	0.038	1.00	0.00	0.00
7.07	2.4042	0.0065	...	...	2.960	0.095	1.00	0.00	0.00

[a] All k's are in units of hr^{-1}.

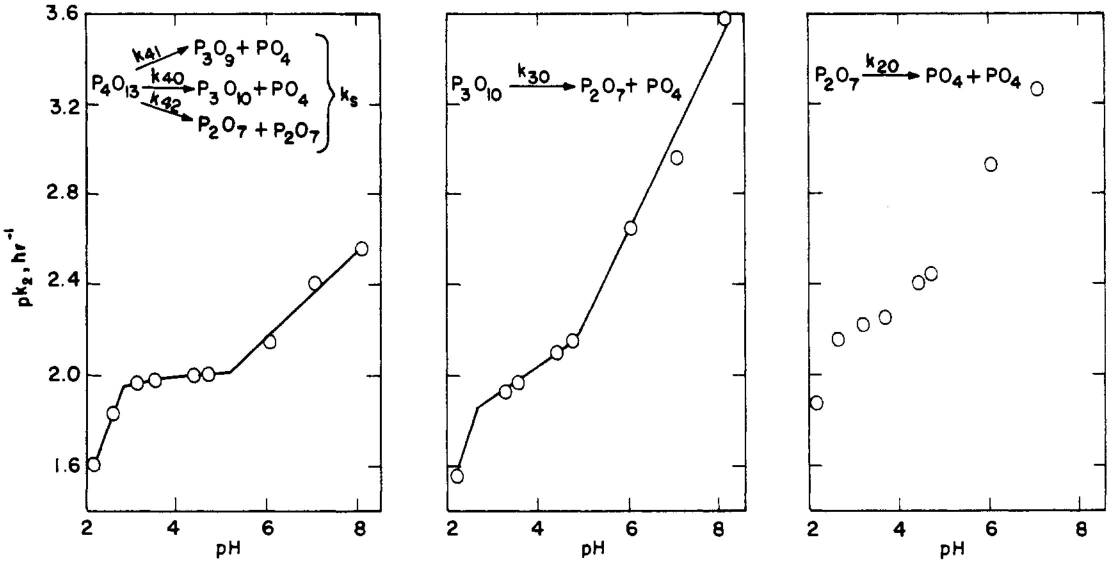


Figure 9. Effect of pH on rate of hydrolysis of ammonium tetrapolyphosphate at 50°C

are shown in Table II. All three polyphosphates have the same pattern of hydrolysis over the pH range studied, with breaks at about the same pH values. There are two breaks in the relationship of pk_i vs. pH over the pH range studied, and these occur in all three species. Similar breaks at the higher pH were observed in the previous study of tripoly- and pyrophosphate.

The half-life of the tetrapolyphosphate at 50°C is 174 hr at pH 7 and 69 hr at pH 4. The time required to hydrolyze 10% of the tetrapolyphosphate is 26 hr at pH 7 and 10.5 hr at pH 4. At pH 6 the half-life is 2550 hr at 25°C (*10*), whereas at 50°C the half-life is 94 hr. The half-life periods calculated from the rate constants obtained in the present study and from those reported in the literature are compared in Table VI.

Comparison of Hydrolysis Rates of Pyro- and Tripolyphosphates from Different Systems

The P_2O_7 formed at 50°C from the hydrolysis of solutions of the P_3O_{10} ion hydrolyzed at about the same rate as that in solutions of only P_2O_7 ions. In the pH range 6–8, the hydrolysis constant, k_2, in pyrophosphate solutions is proportional to the 0.5 power of the H^+ ion activity, whereas in tripolyphosphate solutions k_2 is proportional to the 0.6 power of the H^+ ion activity. In the pH range 3–5, k_2 for pyrophosphate solutions is proportional to the 0.05 power of the H^+ ion activity, and in the tripolyphosphate system it is proportional to the 0.09 power of the H^+ ion activity.

Table VI. Hydrolytic Degradation of Tetrapolyphosphates

Temp, °C	pH	k_4, hr^{-1} × 10^4	Half-life, hr	Ref
65.5	2.55	1080	6.42	(*3*)
	5.35	498	13.9	(*3*)
	5	398	17.3	(*19*)
60	3	282	24.5	(*25*)
	4	276	25.2	(*13*)
	4.5	144	48.2	(*25*)
	7	120	57.8	(*13*)
	8	64.2	108	(*25*)
50[a]	2	299	23.2	...
	2.5	155	44.6	...
	3	109	63.6	...
	4	99.8	69.5	...
	5	91.2	76.0	...
	6	73.4	94.4	...
	7	39.9	174	...
25	2.55	3.56	1950	(*10*)
	3	3.39	2050	(*10*)
	4	3.04	2280	(*10*)
	4.5	2.87	2410	(*10*)
	5	2.72	2550	(*10*)
	7	1.16	5980	(*10*)

[a] All data at 50°C from present work; value of k_4 calculated from equations in Table II.

Table VII. Relations Among pH, Activation Energy for Hydrolysis, and Preexponential Factor for Polyphosphates

$\Delta E = c + d\text{pH}$; $\log s = e + f\text{pH}$; $\Delta E = g + h \log s$

pH range	c	d	e	f	g	h
			Pyrophosphate			
3.0–5.0	26.151	0.4461	15.318	0.2473	−1.481	1.804
5.5–8.0	21.902	0.9804	14.781	0.1536	−72.442	6.383
			Tripolyphosphate			
3.0–4.5	21.472	1.0597	12.792	0.6351	0.128	1.669
5.0–8.0	22.732	0.6101	15.039	0.0167	−526.687	36.533
			Tetrapolyphosphate			
3.0–5.5	26.090	0.1636	15.799	0.0720	−9.805	2.272
6.0–8.0	21.567	0.8958	13.573	0.4139	−7.809	2.164

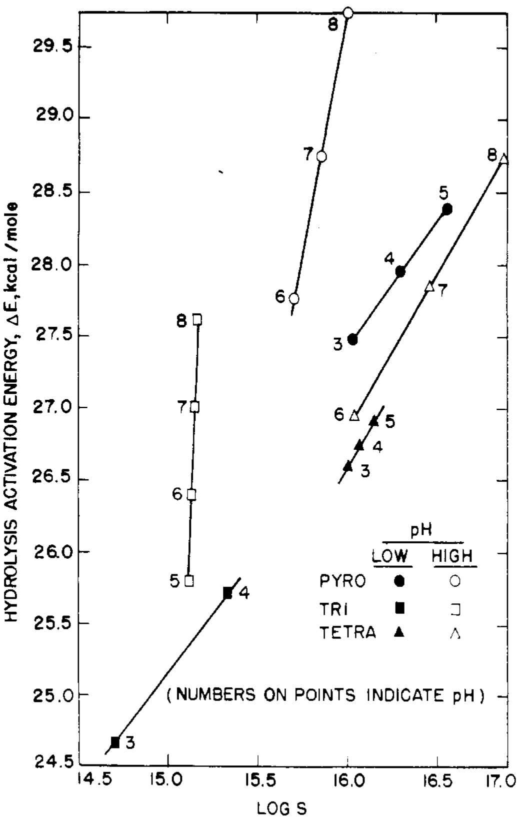


Figure 10. Compensation effect of Arrhenius parameters in hydrolysis of condensed phosphates

In comparing the rate of hydrolysis of P_3O_{10} at 50°C with that of the P_3O_{10} formed from P_4O_{13}, in the pH range 4.5–8, k_3 for the tripolyphosphate solutions is proportional to the 0.40 power of the H^+ ion activity, whereas k_3 for the tetrapolyphosphate solutions is proportional to the 0.36 power of the H^+ ion activity. In the pH range 3.0–4.5, k_3 for the tripolyphosphate solutions is proportional to the 0.08 power of the H^+ ion activity, whereas k_3 for the tetrapolyphosphate solutions is proportional to the 0.13 power of the H^+ ion activity. At 25°C in the pH range 4.5–8, the hydrolysis constant, k_3, for the tripolyphosphate solutions is proportional to the 0.43 power of the H^+ ion activity, and k_3 for the tetrapolyphosphate solutions (*10*) is proportional to the 0.39 power of the H^+ ion activity. In the pH range 3.0–4.5, k_3 for the tripolyphosphate solutions is proportional to the 0.14 power of the H^+ ion activity, whereas k_3 for the tetrapolyphosphate solution is proportional to the 0.23 power of the H^+ ion activity.

The hydrolysis constants calculated from the several systems are in fair agreement. However, the hydrolysis constants were measured with greater precision in the solutions initially containing a single phosphate species and in which the fraction of hydrolyzing species changed rapidly. Thus, the preferred hydrolysis constants for each species are those measured in solutions that initially contained only the ammonium salts of that species. Although the agreement was poorer, there was reasonable agreement of the values of hydrolysis constants of the shorter chains in the presence of large amounts of the longer-chain species with those determined in their absence.

Compensation Effect in Arrhenius Equation

In the Arrhenius equation

$$k = s \exp(-\Delta E/RT) \tag{19}$$

relating the rate constant to temperature, the parameter s is a frequency or collision factor that is often independent of the experimental conditions, and the parameter ΔE is the energy barrier that must be overcome for the reaction to proceed, so that the value of ΔE determines, in large measure, the temperature range in which the reaction rate is important. Many reactions are known (*1*), however, in which both s and ΔE vary with the experimental conditions and affect the temperature dependence of the reaction. The relationship between these parameters and pH for the hydrolysis of pyro-, tripoly-, and tetrapolyphosphates is worthy of exploration.

In logarithmic form, Equation 19 is

$$\log k = \log s - (\Delta E/2.303\,R)\,(1/T) \tag{20}$$

and substitution of the empirically determined relations (Table II) of pk with pH at 25° and 50°C yields for the Arrhenius parameters the following functions of pH

$$\Delta E = 17.633[(a_1 - a_2) + (b_1 - b_2)\text{pH}] \tag{21}$$

$$\log s = (1/0.08385)[(a_1 - 1.084\,a_2) + (b_1 - 1.084\,b_2)\text{pH}] \tag{22}$$

where a_1 and b_1 are the constants in the relation p$k = a + b$pH at 25°C, and a_2 and b_2 are those at 50°C. Equations 21 and 22 are linear relations between ΔE (or log s) and pH, and these relations are collected in Table VII. Elimination of the variable pH from Equations 21 and 22 yields the linear relation between ΔE and log s

$$\Delta E = g + h \log s \tag{23}$$

This relation is given in Table VII for the hydrolysis of the several condensed phosphates over specific pH ranges. A similar relation between the kinetic parameters for the calcination of naturally occurring limestones and dolomites was described recently (*14*).

The compensation effect of the Arrhenius parameters in the hydrolysis of the lower condensed phosphates is illustrated in Figure 10. The slopes of ΔE *vs.* log s for tetrapolyphosphate at all pH values and for tri- and pyrophosphate at low pH values are similar, indicating somewhat the same dependence of one parameter upon the other under these conditions. At high pH, however, tripolyphosphate, and to a lesser extent pyrophosphate, show a wider range in the values of the activation energy for hydrolysis ΔE and a smaller range in the magnitudes of the frequency factor s; the curves for these two species are quite steep. The interpretation of the hydrolysis of pyro- and tripolyphosphate at pH above 5 is that the change in the activation energy is sufficient to explain the temperature dependence of the reaction, as is true for many other reactions (*1*). At low pH values and for tetrapolyphosphate at high pH, it is necessary to change both the activation energy and the frequency factor to explain the temperature dependence of the hydrolysis. These results agree with a recent publication (*24*) that shows the interdependence of the Arrhenius parameters at pH values ≤ 2.5 for sodium pyro- and tripolyphosphate. The reasons for this anomalous behavior are not apparent.

Literature Cited

(1) Boudart, Michel, "Kinetics of Chemical Processes," pp 179, 196, Prentice-Hall, Englewood Cliffs, N.J., 1968.
(2) Crowther, J. P., Westman, A. E. R., *Can. J. Chem.*, **32,** 42 (1954).
(3) Crowther, J. P., Westman, A. E. R., *ibid.*, **34,** 969 (1956).
(4) Ebel, J. P., *Mikrochim. Acta,* **1954,** p 679.
(5) Farr, T. D., Fleming, J. D., *J. Chem. Eng. Data,* **10,** 20 (1965).
(6) Farr, T. D., Fleming, J. D., Hatfield, J. D., *ibid.,* **12,** 141 (1967).
(7) Farr, T. D., Williard, J. W., *ibid.,* **14,** 367 (1969).
(8) Farr, T. D., Williard, J. W., *ibid.,* **16,** 67 (1971).
(9) Farr, T. D., Williard, J. W., *ibid.,* **17,** 317 (1972).
(10) Farr, T. D., Williard, J. W., Hatfield, J. D., *ibid.,* p 313.
(11) Green, Jerome, *Ind. Eng. Chem.,* **42,** 1542 (1950).
(12) Griffith, E. J., *J. Inorg. Nucl. Chem.,* **26,** 1381 (1964).
(13) Griffith, E. J., Buxton, R. L., *J. Am. Chem. Soc.,* **89,** 2884 (1967).
(14) Hatfield, J. D., Kim, Y. K., Mullins, R. C., McClellan, G. H., Investigation of the Reactivities of Limestone to Remove Sulfur Dioxide from Flue Gas, Figure 1, PB-202-907, 1971.
(15) Karl-Kroupa, E., *Anal. Chem.,* **28,** 1091 (1956).
(16) Mitra, R. P., Malhotra, H. C., Jain, D. V. S., *Trans. Faraday Soc.,* **62,** 173 (1966).
(17) Osterheld, R. K., Langguth, R. P., *J. Phys. Chem.,* **59,** 76 (1955).
(18) Scott, W. C., Wilbanks, J. A., *Chem. Eng. Progr.,* **63** (10), 58 (1967).
(19) Strauss, U. P., Day, J. W., *J. Polym. Sci., Part C,* **16,** 2161 (1967).
(20) Strauss, U. P., Krol, G. J., *ibid., p* 2171.
(21) Thilo, E., Wieker, W., *Z. Anorg. Allg. Chem.,* **291,** 164 (1957).
(22) Thilo, E., Wieker, W., *J. Polym. Sci.,* **53,** 55 (1961).
(23) Van Wazer, J. R., Griffith, E. J., McCullough, J. F., *J. Am. Chem. Soc.,* **77,** 287 (1955).
(24) Watanabe, M., *Bull. Chem. Soc. Jpn.,* **47** (8), 2048 (1974).
(25) Wieker, W., *Z. Anorg. Allg. Chem.,* **355** (1–2), 20 (1967).

Received for review September 9, 1974. Accepted March 10, 1975.

Supplementary Material Available. Complete data for Tables I, III, and IV will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JCED-75-276.

Salt Effects on Vapor-Liquid Equilibrium of Tetrahydrofuran-Water System

Eizo Sada,[1] **Tetsuo Morisue, and Kazuhisa Miyahara**[2]
Department of Chemical Engineering, Nagoya University, Nagoya, Japan

Vapor-liquid equilibrium data at atmospheric pressure for the systems tetrahydrofuran (THF)–water, THF–water–LiCl, THF–water–NaCl, and THF–water–$CaCl_2$ were obtained by use of a modified Othmer still. THF was salted out from the aqueous solution by addition of these salts, and the salting out of THF caused separation into two liquid phases. The order of the salting out effect was LiCl > $CaCl_2$ > NaCl.

The system tetrahydrofuran (THF) and water is of theoretical and industrial importance. A good deal of information on this system is already available. Matous et al. (*4*) found that this system has a closed loop region of limited miscibility (71.8° ~ 137.1°C). Cigna and Sebastiani (*1*) and Shnitko and Kogan (*9*) measured the isobaric vapor-liquid equilibrium at 760 mm Hg and found that THF forms a homogeneous positive azeotrope with water, boiling at 63.52°C and containing 18.28 mol % of water. Matous et al. (*5*) measured the isothermal vapor-liquid equilibria at 50° and 70°C, and Signa et al. (*10*) at 25°C. Fukala and Kopechy (*2*) and Yoshioka et al. (*11*) proposed methods for dehydration of THF solution by salting out, but no data for the vapor-liquid equilibrium are given.

In this paper, the effects of addition of LiCl, NaCl, or $CaCl_2$ on the vapor-liquid equilibrium of the THF-water solution are measured at fixed solvent composition and atmospheric pressure. Furthermore, the equilibrium data saturated with each salt are also obtained.

Experimental

All vapor-liquid equilibrium data were obtained by use of a modified Othmer still (Figure 1). The total volume of the still was about 500 cc, of which about 300 cc was occupied by liquid. The holdup in the condensate receiver was about 7 cc. To heat the boiling chamber of the still, an external electric heater regulated by a variable rheostat was used. The liquid in the boiling chamber was stirred by a magnetic stirrer. To avoid the partial condensation of vapor on the inside still wall, an electric heater was wound around the upper portion.

The boiling point temperature was measured within an accuracy of ±0.05°C by using a mercury-in-glass thermometer (0° ~ 100°C, 0.1°C divisions) calibrated against a standard thermometer certified by the National Research Laboratory. Atmospheric pressure was measured with a mercury column barometer. Equilibrium vapor condensate was analyzed by means of density measurement at 25.00° ± 0.02°C. An Ostwald pycnometer (capacity ca. 5 cc) was used. Liquid-phase composition was calculated by taking a material balance (*6*). The accuracies of both compositions were ±0.001 mole fraction.

In this work, since all measurements were made under atmospheric pressure, the boiling points should be corrected to those at 760 mm Hg. As all vapor-phase compositions were over 75 mol % of THF and boiling point temperatures were nearly equal to that of pure THF, we assumed that the value of (dt/dP) for the mixture is equal to that of THF at the normal boiling point, that is, 0.044°C/mm Hg (*7*). The correction of the vapor-phase composition with respect to the small change in pressure

---

[1] To whom correspondence should be addressed.

[2] Present address, Osaka Gas Co., Ltd., Osaka, Japan.