in the purity of the alcohols which were used. Because of the sensitivity of GC analysis, the method was suitable for concentrations of 0.1% or less. Tables I-XIX summarize experimental measurements for systems studied. There are two interesting conclusions from studying the data. First, solubility of water in the alcohol remains quite high, even for C_7 and C_8 alcohols where solubility of alcohol in water becomes small. Second, solubility of alcohol in the water layer first decreases with temperature, goes through a minimum at about 60 °C, and then increases with temperature. Thus, any solubility equation which assumes increasing solubility with temperature will be in error, at least over the temperature range studied here.

Registry No. 1-Pentanol, 71-41-0; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 2-methyl-1-butanol, 137-32-6; 2-methyl-2-butanol, 75-85-4; 3-methyl-1-butanol, 123-51-3; 3-methyl-2-butanol, 598-75-4; 2,2-dimethyl-1-propanol, 75-84-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 2-methyl-1-pentanol, 105-30-6; 3-methyl-3-pentanol, 77-74-7; 4-methyl-2-pentanol, 108-11-2; 1-heptanol, 111-70-6; 2-heptanol, 543-49-7; 2,4-dimethyl-3-pentanol, 600-36-2; 1-octanol, 111-87-5; 2-ethyl-1-hexanol, 104-76-7.

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Effect of Concentration on Hydrolysis Rate of Tripolyphosphate at 25 °C

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The effect of concentration on the rate of hydrolysis of tripolyphosphate at 25 °C was determined at pH 5-7 in solutions that ranged from 4.76% to 32.3% in P_2O_5 content. The hydrolysis rate constants were found to increase with increasing total P_2O_5 content and decreasing pH. A general linear equation was developed for calculating rate constants and half-lives when the pH and the P_2O_5 content of tripolyphosphate solutions are known.

The hydrolytic degradation of tripolyphosphate has been studied previously (*1-11*). In a previous paper (*11*) it was indicated that concentration had little effect on the first-order rate constants for the hydrolysis of tripolyphosphate. This finding was contrary to that of previous investigators (*12*). However, later work (*13*) showed that there is an effect of concentration upon the specific rate of tripolyphosphate hydrolysis. To quantify this relationship, the rate of hydrolysis of ammonium tripolyphosphate was studied at five P_2O_5 concentrations and three pH levels.

Experimental Section

The solutions to be studied were prepared by making three stock solutions that were almost saturated with $(NH_4)_4HP_3O_{10}$ at pH 5, 6, or 7. Portions of each stock solution were diluted with distilled water in the following proportions of stock solution:water: 3:1, 1:1, 1:3, and 1:7. These diluted solutions were adjusted to the desired pH level with gaseous ammonia or cation-exchange resin in the hydrogen form. The diluted solutions, along with the stock solutions, were placed in a water bath at 25 ± 0.2 °C and agitated at 4 rpm. The solutions were sampled at various times (up to 1227 days) to determine the extent of tripolyphosphate (P_3O_{10}) hydrolysis, phosphate distribution, and pH.

Total P_2O_5 was determined gravimetrically (*14*) and the ammoniacal nitrogen determined by distillation into standard acid followed by back-titration with NaOH. The pH was measured with a glass electrode. One-dimensional paper chromatography (*15*) was used to determine the phosphate distribution as a function of reaction time.

Results and Discussion

The hydrolytic degradation of the tripolyphosphate ion proceeds according to the following model:

$$P_3O_{10} \xrightarrow[H_2O]{k_3} P_2O_7 + PO_4 \xrightarrow[H_2O]{k_2} PO_4 + PO_4 \tag{1}$$

where P_3O_{10} represents the tripolyphosphate anionic species, and P_2O_7 and PO_4 are the corresponding pyro- and orthophosphates, respectively. The hydrolysis of tripolyphosphate follows first-order kinetics (*16*) in the pH and P_2O_5 concentration ranges studied, as shown by the plots of log % P (as P_3O_{10}) vs. time in Figures 1-3.

The hydrolysis rate constants were calculated as described previously (*16*). The rate constants for P_3O_{10}, k_3, at each pH and P_2O_5 concentration were determined by a nonlinear regression (NLIN) of the data fitted to the equation

$$P_3O_{10} = (P_3O_{10})_0 \exp(-k_3 t) \tag{2}$$

where P_3O_{10} = percent phosphorus present as P_3O_{10} at time t, days; $(P_3O_{10})_0$ = a constant (% P as P_3O_{10} initially present in solution); k_3 = first-order rate constant for P_3O_{10} hydrolysis, day^{-1}.

The rate constants for P_2O_7 hydrolysis, k_2, at each pH and total P_2O_5 concentration were determined by a NLIN computation method in which the data were fitted to the consecutive

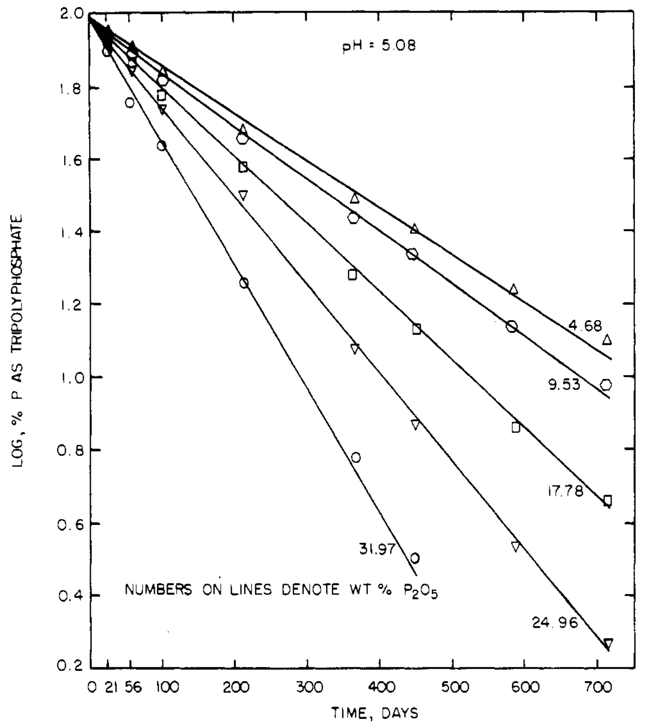

Figure 1. Rate of hydrolysis of ammonium tripolyphosphate at 25 °C and pH 5.08.

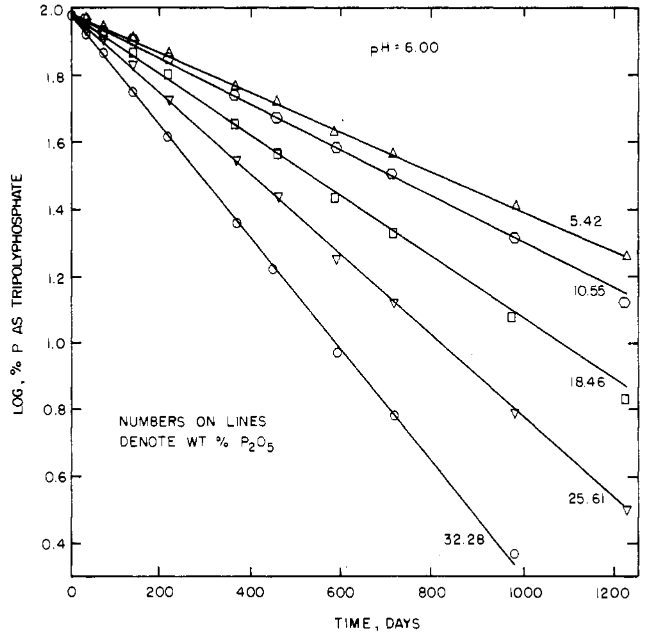

Figure 2. Rate of hydrolysis of ammonium tripolyphosphate at 25 °C and pH 6.00.

first-order reaction model using the previously evaluated k_3 and $(P_3O_{10})_0$ values:

$$P_2O_7 = (2/3)k_3(P_3O_{10})_0 \exp[(-k_3t)/(k_2 - k_3)] + [(P_2O_7)_0 - (2/3)k_3(P_3O_{10})_0/(k_2 - k_3)] \exp(-k_2t) \quad (3)$$

where P_2O_7 = percent phosphorus present as P_2O_7 at time t, days; $(P_2O_7)_0$ = a constant (% P as P_2O_7 initially present in solution); k_2 = first-order rate constant for P_2O_7 hydrolysis, day^{-1}.

The measured and calculated concentrations of tripolyphosphate for the 31.97% P_2O_5 solution at pH 5 are listed in Table I (complete table is included in the supplementary material; see paragraph at end of text regarding supplementary material). The calculated rate constants, k_3 and k_2, are

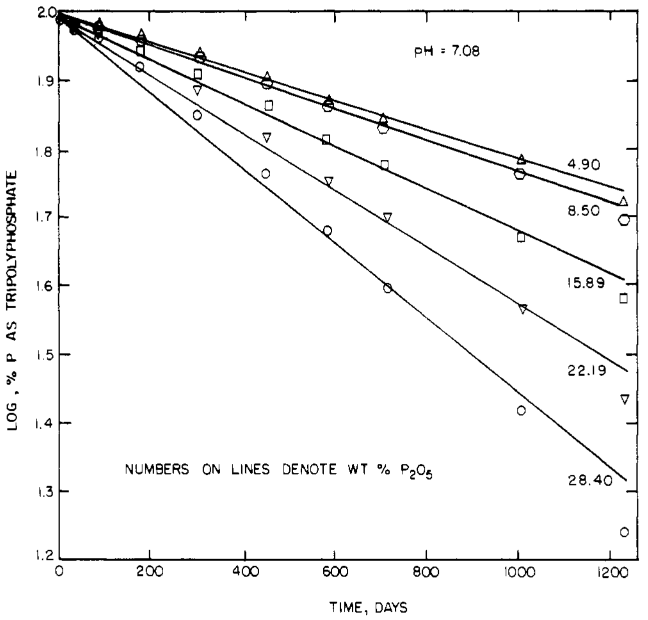

Figure 3. Rate of hydrolysis of ammonium tripolyphosphate at 25 °C and pH 7.08.

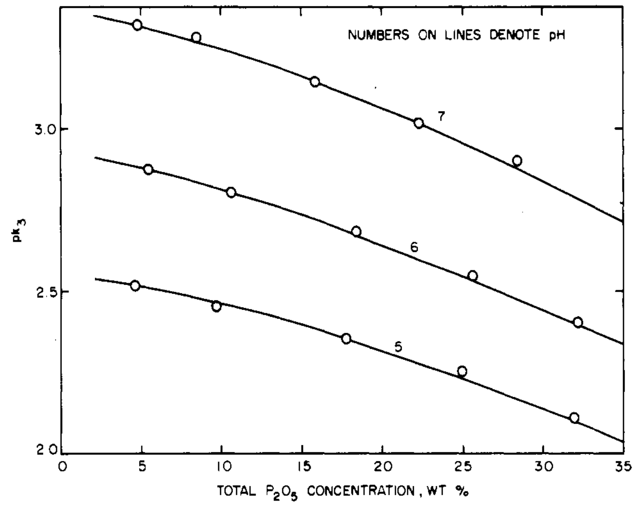

Figure 4. Relationship of hydrolysis rate constant of tripolyphosphate to P_2O_5 concentration and pH at 25 °C (lines are predicted values from eq 4).

Table I. Distribution Changes of P_2O_5 Species at 25 °C Starting from Tripolyphosphate[a]

time, days	pH	% P as P_3O_{10} obsd	% P as P_3O_{10} calcd	% P as P_2O_7 obsd	% P as PO_4 obsd
0	5.08	95.4	94.6	3.0	1.6
1	5.07	94.9	93.9	3.7	1.4
2	5.05	94.3	93.1	4.3	1.4
21	5.08	79.9	80.3	14.3	5.8
22	5.07	78.4	79.6	15.5	6.1
23	5.08	78.3	79.0	15.4	6.3
56	5.06	60.3	61.0	25.8	13.9
57	5.06	58.6	60.5	27.4	14.0
100	5.07	43.7	43.2	34.7	23.6
101	5.10	42.8	42.9	35.7	21.5
210	4.99	18.4	18.2	47.0	34.6
211	5.00	19.8	18.1	44.9	35.3
365	5.05	6.0	5.4	47.2	46.8
366	5.04	5.8	5.4	47.2	47.0
449	4.98	3.2	2.8	45.1	51.7
449	5.00	3.3	2.8	45.0	51.7

[a] Solution 1: 8.20% N; 31.97% P_2O_5.

Table II. First-Order Rate Parameters for Hydrolysis of Tripolyphosphate at 25 °C

soln no.	composn, %		pH	tripolyphosphate				pyrophosphate			
	N	P_2O_5		$10^{-4}k_3$, day^{-1}	$10^{-4}\cdot[SE(k_3)]$,[a] day^{-1}	pk_3	$t_{0.5}$, day	$10^{-4}k_2$, day^{-1}	$10^{-4}\cdot[SE(k_2)]$,[a] day^{-1}	pk_2	$t_{0.5}$, day
1	8.20	31.97	5.08	78.3779	1.0	2.1058	88.4	10.7878	0.26	2.9671	643
2	6.50	24.96	5.08	55.8381	1.1	2.2531	124	9.7729	0.32	3.0100	709
3	4.60	17.78	5.05	43.0602	0.65	2.3659	161	9.3901	0.35	3.0273	738
4	2.30	9.53	5.01	33.8378	0.34	2.4706	205	9.7557	0.17	3.0107	711
5	1.10	4.68	5.02	30.2020	0.41	2.5200	230	10.8669	0.29	2.9639	638
6	9.55	32.28	6.00	38.8253	0.12	2.4109	179	4.8923	0.04	3.3105	1417
7	7.47	25.61	6.01	27.7222	0.21	2.5572	250	4.2913	0.08	3.3674	1615
8	5.37	18.46	6.02	20.9600	0.21	2.6782	331	4.0438	0.12	3.3932	1714
9	2.95	10.55	6.02	15.6739	0.17	2.8048	442	4.0080	0.12	3.3971	1729
10	1.46	5.42	6.00	13.6083	0.17	2.8662	509	4.6471	0.22	3.3328	1492
11	9.22	28.40	7.08	12.6498	0.35	2.8979	548	1.3017	0.25	3.8855	5325
12	7.13	22.19	7.01	9.6298	0.24	3.0164	720	1.1985	0.26	3.9214	5783
13	5.07	15.89	7.02	7.2250	0.17	3.1412	959	1.0281	0.26	3.9880	6742
14	2.55	8.50	7.03	5.2360	0.12	3.2810	1324	0.7623	0.30	4.1179	9093
15	1.50	4.90	7.02	4.8144	0.11	3.3175	1440	0.6952	0.30	4.1579	9970

[a] SE = standard error.

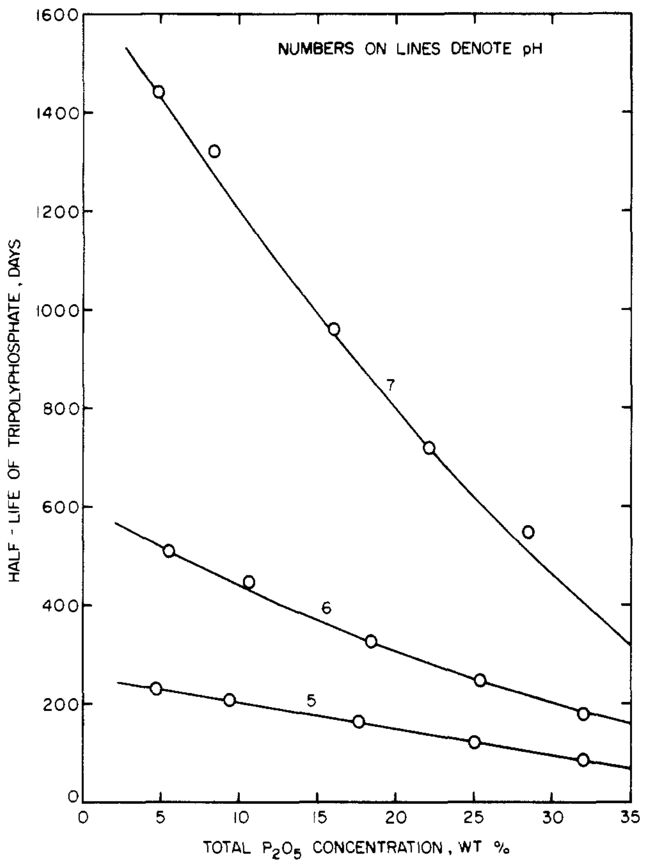

Figure 5. Effect of P_2O_5 concentration and pH on half-life of tripolyphosphate at 25 °C (lines are predicted values from eq 4).

Table III. Coefficients for Eq 4

	response			
	pk_3[a]	$(t_{0.5})_3$[b]	pk_2[a]	$(t_{0.5})_2$[b]
a_0	1.71649	9138.66	7.62269	109114.37
a_1	0	−215.01	−0.12632	−2159.11
a_2	0	−3553.67	−2.08174	−41227.24
a_{11}	−0.00019	−0.8911	−0.00154	−16.8703
a_{22}	0.03382	355.2111	0.22747	3892.7766
a_{12}	−0.00173	88.3977	0.05819	910.3549
a_{112}	0	0.1740	0.00022	2.9859
a_{122}	0	−9.2613	−0.00600	−92.9329
R^2[c]	0.999	0.999	0.999	0.998
SD[d]	0.008	12.69	0.016	200.61
CV[e]	0.30	2.53	0.45	6.23

[a] $pk_3 = -\log k_3$; $pk_2 = -\log k_2$. [b] $(t_{0.5})_3$ and $(t_{0.5})_2$ are half-lives for tripolyphosphate and pyrophosphate, respectively. [c] R^2 = multiple correlation coefficient. [d] SD = standard deviation of predicted response values. [e] CV = coefficient of variation.

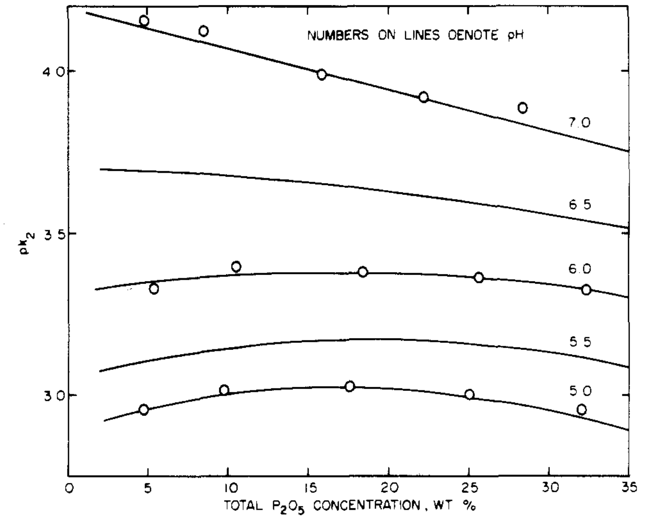

Figure 6. Relationship of hydrolysis rate constant of pyrophosphate to P_2O_5 concentration and pH at 25 °C (lines are predicted values from eq 4).

presented in Table II together with the standard error (SE), pk_3 and pk_2 (i.e., $-\log k_3$ and $-\log k_2$), and the half-life, $t_{0.5}$, of the tripolyphosphate and pyrophosphate ions, respectively.

The pk's and half-lives of tripolyphosphate and pyrophosphate hydrolysis at 25 °C may be expressed as functions of P_2O_5 concentration (P_T, %) and pH by the general linear equation

$$A = a_0 + a_1P_T + a_2\text{pH} + a_{11}P_T^2 + a_{22}\text{pH}^2 + a_{12}P_T\text{pH} + a_{112}P_T^2\text{pH} + a_{122}P_T\text{pH}^2 \quad (4)$$

where the response, A, represents either pk or half-life for the hydrolysis of tripolyphosphate or pyrophosphate, respectively. The data in Table III show the constants for eq 4 for the various responses (A), as well as the correlation coefficient, standard deviation, and coefficient of variation for each response. These relationships are shown in Figures 4–7. In each figure the plotted points are the observed values and the curves were calculated by using the constants from Table III.

As can be seen from Figure 4, the pk_3 values decrease when the P_2O_5 concentration in the solution increases at the same pH value or when pH decreases at the same P_2O_5 con-

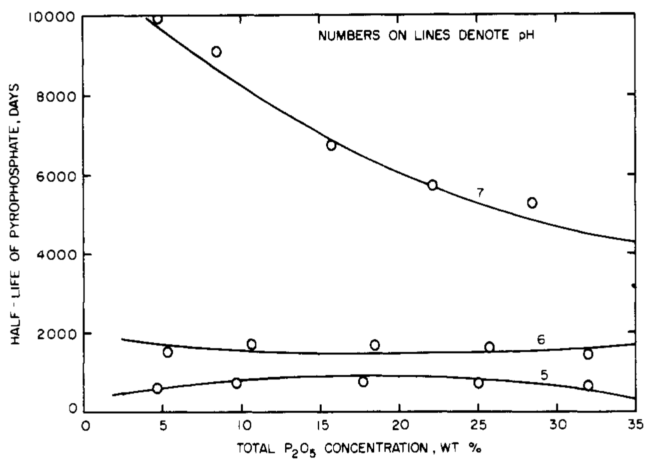

Figure 7. Effect of P_2O_5 concentration and pH on half-life of pyrophosphate at 25 °C (lines are predicted values from eq 4).

centration. Therefore, the tripolyphosphate hydrolyzes most rapidly at high P_2O_5 concentrations and low pH values. The same effect of P_2O_5 concentration and pH upon the half-life of tripolyphosphate is shown in Figure 5.

In the case of pyrophosphate, pk_2 values decrease when the P_2O_5 concentration increases at pH 7, but the effect is negligible when the pH is 6 or less (Figure 6). The data in Figure 7 show the half-life of pyrophosphate as a function of P_2O_5 concentration and pH. A study of the effect of P_2O_5 concentration on the rate of hydrolytic degradation of pyrophosphate is under way and results will be available soon.

Registry No. $P_3O_{10}{}^{5-}$, 14127-68-5.

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Supplementary Material Available: Complete Table I (calculated vs. observed concentrations of P_3O_{10}, observed P_2O_7, and observed PO_4 at 25 °C) (8 pages). Ordering information is given on any current masthead page.

Excess Thermodynamic Functions for Ternary Systems. 11. Total-Pressure Data and G^E for Ethylene Glycol/Acetone/Water and for Ethylene Glycol/Acetonitrile/Water at 50 °C

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Isothermal *P*-*x* data for the ternary systems ethylene glycol/acetone/water and ethylene glycol/acetonitrile/water at 50 °C are reported. Data reduction by Barker's method provides correlations for G^E.

Vapor/liquid equilibrium measurements are reported for ethylene glycol/acetone/water and for ethylene glycol/acetonitrile/water at 50 °C. Experimental values of total vapor pressure are measured for ternary mixtures formed by addition of a pure species to mixtures of the other two. The data for ethylene glycol/acetone/water come from seven such runs and for ethylene glycol/acetonitrile/water from five. Data are also reported for the binary system acetonitrile/water. Correlations for the ethylene glycol/water, acetone/water, ethylene glycol/acetone, and ethylene glycol/acetonitrile binaries have already been published (*1*-*3*).

The apparatus was that of Gibbs and Van Ness (*4*) as modified by DiElsi et al. (*5*). For the ethylene glycol/acetone/water system, the ethylene glycol was chromatoquality reagent with specified purity of >99.5 mol % from Matheson Coleman and Bell, and the acetone was OmniSolv reagent with an indicated purity of 99.5 mol % from MCB Manufacturing Chemists, Inc. For the ethylene glycol/acetonitrile/water system, the ethylene glycol was 99+ mol % reagent from MCB Manufacturing Chemists, Inc., and the acetonitrile was chromatoquality reagent with stated purity of >99.9 mol % from Matheson Coleman and Bell. The water was doubly deionized. All reagents were thoroughly degassed.

Results and Correlations

Table I presents data for ternary mixtures of ethylene glycol/acetone/water. Table II shows *P*-*x* data for the acetonitrile/water binary system, and Table III gives data for the ethylene glycol/acetonitrile/water ternary. Data reduction is by Barker's method, as described earlier (*6*, *7*).

For the binary systems, the Margules equation with up to six parameters provides suitable expression of G^E:

$$g_{ij} \equiv G^E{}_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_ix_j + (\eta_{ji}x_i + \eta_{ij}x_j)(x_ix_j)^2]x_ix_j \quad (1)$$

The binary system for which data are reported here requires all six parameters. Values for this system as well as for those

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