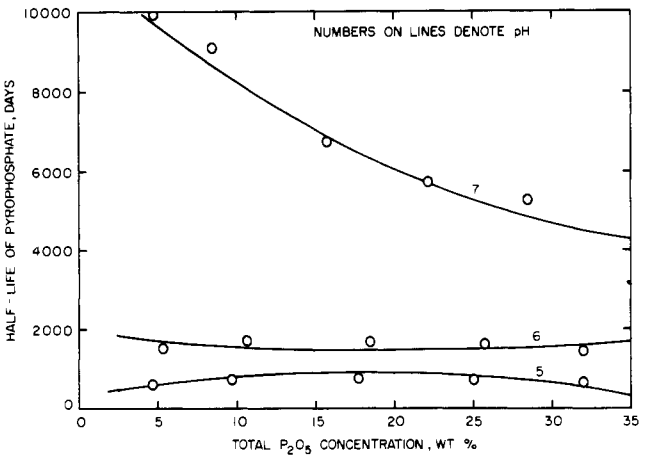

Figure 7. Effect of P_2O_5 concentration and pH on half-life of pyrophosphate at 25 °C (lines are predicted values from eq 4).

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.

Literature Cited

(1) Crowther, J. P.; Westman, A. E. R. *Can. J. Chem.* **1954**, *32*, 42-8.
(2) Van Wazer, J. R.; Griffith, E. J.; McCullough, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 287-91.
(3) Green, J. *Ind. Eng. Chem.* **1950**, *42*, 1542-6.
(4) Friess, S. L. *J. Am. Chem. Soc.* **1952**, *74*, 4027-9.
(5) Shen, C. Y.; Dyroff, D. R. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 97-100.
(6) Shen, C. Y.; Metcalf, J. S.; O'Grady, E. V. *Ind. Eng. Chem.* **1959**, *51*, 717-8.
(7) Quimby, O. T. *J. Phys. Chem.* **1954**, *58*, 603-18.
(8) Bell, R. N. *Ind. Eng. Chem.* **1947**, *39*, 136-40.
(9) Griffith, E. J. *Ind. Eng. Chem.* **1959**, *51*, 240.
(10) Thilo, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1061-71.
(11) Farr, T. D.; Williard, J. W.; Hatfield, J. D. *J. Chem. Eng. Data* **1972**, *17*, 313-7.
(12) Van Wazer, J. R. "Phosphorus and Its Compounds"; Interscience: New York, 1966; Vol. 1.
(13) Frazier, A. W.; Dillard, E. F. *J. Agric. Food Chem.* **1981**, *29*, 695-8.
(14) Perrin, C. H. *J. Assoc. Off. Anal. Chem.* **1958**, *41*, 758-63.
(15) Karl-Kroupa, E. *Anal. Chem.* **1956**, *28*, 1091-7.
(16) Williard, J. W.; Farr, T. D.; Hatfield, J. D. *J. Chem. Eng. Data* **1975**, *20*, 276-83.

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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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Table I. P-x Data for Ethylene Glycol (1)/Acetone (2)/Water (3) at 50 °C

x_1	x_2	x_3	P/kPa
0.2939	0.0194	0.6867	19.003
0.2849	0.0497	0.6655	31.688
0.2701	0.0989	0.6310	45.021
0.2553	0.1483	0.5964	53.113
0.2403	0.1983	0.5614	58.269
0.2253	0.2483	0.5264	61.694
0.2103	0.2984	0.4913	64.088
0.1953	0.3484	0.4563	65.872
0.1802	0.3986	0.4211	67.296
0.1652	0.4487	0.3861	68.458
0.1502	0.4988	0.3510	69.511
0.6844	0.0205	0.2951	12.355
0.6638	0.0500	0.2862	23.113
0.6292	0.0995	0.2713	36.441
0.5951	0.1483	0.2566	45.597
0.5603	0.1980	0.2416	52.070
0.5254	0.2481	0.2266	56.628
0.4905	0.2979	0.2115	59.892
0.4559	0.3476	0.1966	62.291
0.4206	0.3980	0.1814	64.147
0.3858	0.4478	0.1664	65.616
0.3507	0.4981	0.1512	66.861
0.0212	0.6847	0.2941	74.214
0.0499	0.6646	0.2855	73.393
0.0998	0.6296	0.2705	72.065
0.1243	0.6125	0.2632	71.490
0.1473	0.5964	0.2563	70.922
0.2036	0.5570	0.2394	69.622
0.2597	0.5178	0.2226	68.343
0.3155	0.4787	0.2058	67.067
0.3706	0.4402	0.1892	65.692
0.4255	0.4018	0.1727	64.146
0.4798	0.3638	0.1564	62.391
0.5004	0.3495	0.1502	61.618
0.0200	0.2939	0.6862	65.781
0.0506	0.2846	0.6648	65.213
0.1001	0.2698	0.6301	64.152
0.1502	0.2548	0.5950	62.939
0.2006	0.2397	0.5597	61.503
0.2503	0.2248	0.5249	59.903
0.3003	0.2098	0.4899	58.039
0.3504	0.1948	0.4548	55.948
0.4002	0.1799	0.4199	53.592
0.4503	0.1649	0.3848	50.936
0.5003	0.1500	0.3498	47.981
0.2941	0.6849	0.0209	69.371
0.2854	0.6645	0.0501	69.412
0.2703	0.6292	0.1005	69.425
0.2551	0.5938	0.1512	69.322
0.2402	0.5591	0.2007	69.167
0.2101	0.4892	0.3007	68.599
0.1951	0.4540	0.3509	68.281
0.1801	0.4191	0.4009	67.727
0.1642	0.3821	0.4538	67.075
0.1500	0.3491	0.5009	66.370
0.6863	0.2929	0.0208	56.048
0.6659	0.2841	0.0501	55.990
0.6307	0.2690	0.1003	55.850
0.5957	0.2541	0.1502	55.640
0.5610	0.2392	0.1998	55.324
0.5252	0.2240	0.2508	54.916
0.4902	0.2090	0.3008	54.436
0.4554	0.1942	0.3505	53.843
0.4203	0.1792	0.4005	53.143
0.3853	0.1643	0.4503	52.185
0.3502	0.1493	0.5005	51.187
0.6876	0.2928	0.0196	56.055
0.6664	0.2837	0.0499	55.995
0.6313	0.2688	0.1000	55.850
0.5959	0.2537	0.1504	55.622
0.5608	0.2387	0.2006	55.315
0.5258	0.2237	0.2505	54.917

reported earlier (*1–3*) are given in Table IV along with required ancillary data. The second virial coefficients B_{ij} come from the correlation of Hayden and O'Connell (*8*).

Table II. P-x Data for Acetonitrile (2)/Water (3) at 50 °C

x_2	x_3	P/kPa	x_2	x_3	P/kPa
0.0208	0.9792	19.413	0.5002	0.4998	37.491
0.0499	0.9501	26.267	0.5490	0.4510	37.622
0.1010	0.8990	32.405	0.5985	0.4015	37.778
0.1500	0.8500	34.787	0.6485	0.3515	37.943
0.1997	0.8003	35.844	0.6987	0.3013	38.062
0.2506	0.7494	36.395	0.7491	0.2509	38.128
0.2999	0.7001	36.715	0.7995	0.2005	38.094
0.3500	0.6500	36.964	0.8485	0.1515	37.867
0.4000	0.6000	37.154	0.8990	0.1010	37.315
0.4501	0.5499	37.326	0.9471	0.0529	36.222
0.4988	0.5012	37.482	0.9783	0.0217	35.074

Table III. P-x Data for Ethylene Glycol (1)/Acetonitrile (2)/Water (3) at 50 °C

x_1	x_2	x_3	P/kPa
0.6854	0.2936	0.0210	24.659
0.6650	0.2848	0.0503	24.933
0.6305	0.2700	0.0996	25.394
0.5948	0.2547	0.1505	25.813
0.5597	0.2397	0.2007	26.198
0.5243	0.2245	0.2512	26.548
0.4895	0.2096	0.3009	26.853
0.4544	0.1945	0.3511	27.099
0.4194	0.1796	0.4010	27.298
0.3842	0.1645	0.4513	27.426
0.3483	0.1491	0.5025	27.501
0.2955	0.6844	0.0201	30.130
0.2863	0.6630	0.0507	30.700
0.2711	0.6277	0.1012	31.540
0.2558	0.5923	0.1520	32.246
0.2410	0.5580	0.2011	32.844
0.2257	0.5227	0.2515	33.358
0.2106	0.4876	0.3018	33.797
0.1955	0.4527	0.3518	34.162
0.1804	0.4177	0.4019	34.476
0.1653	0.3827	0.4520	34.704
0.1502	0.3477	0.5022	34.837
0.0203	0.2918	0.6879	36.409
0.0500	0.2830	0.6670	35.932
0.1002	0.2680	0.6318	35.040
0.1501	0.2531	0.5967	34.095
0.2004	0.2382	0.5615	33.028
0.2504	0.2233	0.5263	31.853
0.3002	0.2084	0.4913	30.576
0.3503	0.1935	0.4561	29.157
0.4004	0.1786	0.4209	27.622
0.4503	0.1638	0.3859	25.959
0.5003	0.1489	0.3508	24.173
0.6856	0.0198	0.2945	7.240
0.6647	0.0497	0.2856	12.099
0.6300	0.0993	0.2706	18.076
0.5954	0.1488	0.2558	22.213
0.5603	0.1991	0.2407	25.079
0.5254	0.2488	0.2257	27.043
0.4909	0.2983	0.2109	28.402
0.4559	0.3483	0.1959	29.367
0.4210	0.3982	0.1809	30.057
0.3859	0.4483	0.1658	30.581
0.3510	0.4982	0.1508	30.984
0.0203	0.6814	0.2983	37.457
0.0500	0.6634	0.2866	36.649
0.1012	0.6276	0.2712	35.461
0.1509	0.5929	0.2562	34.477
0.2008	0.5580	0.2412	33.599
0.2508	0.5231	0.2261	32.778
0.3009	0.4881	0.2110	31.997
0.3510	0.4531	0.1959	31.208
0.4011	0.4181	0.1807	30.395
0.4511	0.3833	0.1657	29.514
0.5010	0.3484	0.1506	28.530

Data for the ternary systems are adequately correlated by the three-parameter Wohl equation:

$$g_{123} = g_{12} + g_{13} + g_{23} + (C_0 + C_1x_1 + C_2x_2)x_1x_2x_3 \quad (2)$$

Correlations for the g_{ij} are given by eq 1; parameters C_0, C_1,

Table IV. Summary of Results for Binary Systems at 50 °C

	ethylene glycol (1)/ acetone (2)[a]	acetone (2)/ water (3)[b]	ethylene glycol (1)/ acetonitrile (2)[a]	acetonitrile (2)/ water (3)	ethylene glycol (1)/ water (3)[c]
P_i^{sat}, kPa	0.114	81.83	0.104	33.94	0.116
P_j^{sat}, kPa	81.83	12.32	33.90	12.34	12.345
V_i^L, cm³/mol	57	77	57	55	57
V_j^L, cm³/mol	77	18	55	18	18
B_{ii}	−1970	−1446	−1970	−4153	−1970
B_{jj}	−1446	−1137	−4153	−1137	−1137
B_{ij}	−1477	−870	−2354	−1764	−1246
A_{ij}	2.07715	2.2767	2.37232	2.53621	−0.14939
A_{ji}	1.59982	1.7251	1.64781	2.04616	−0.14939
λ_{ij}	1.02225	1.3226	1.63867	1.00655	0.0
λ_{ji}	0.06055	0.6172	0.40608	1.66742	0.0
η_{ij}	0.61533	0.5489	1.30570	−0.75813	0.0
η_{ji}	−0.39262	0.5489	0.20963	2.76872	0.0
rms δP, kPa	0.046	0.033	0.011	0.029	0.025
max $\|\delta P\|$, kPa	0.175	0.058	0.036	0.074	0.048

[a] Reference 3. [b] Reference 2. [c] Reference 1.

Table V. Summary of Results for Ternary Systems at 50 °C

	ethylene glycol (1)/ acetone (2)/ water (3)	ethylene glycol (1)/ acetonitrile (2)/ water (3)
P_1^{sat}, kPa	0.114	0.103
P_2^{sat}, kPa	81.83	33.92
P_3^{sat}, kPa	12.34	12.34
C_0	3.32716	3.34310
C_1	0.16465	0.30862
C_2	−0.98061	−0.99391
rms δP, kPa	0.095	0.046
max $\|\delta P\|$, kPa	0.359	0.113

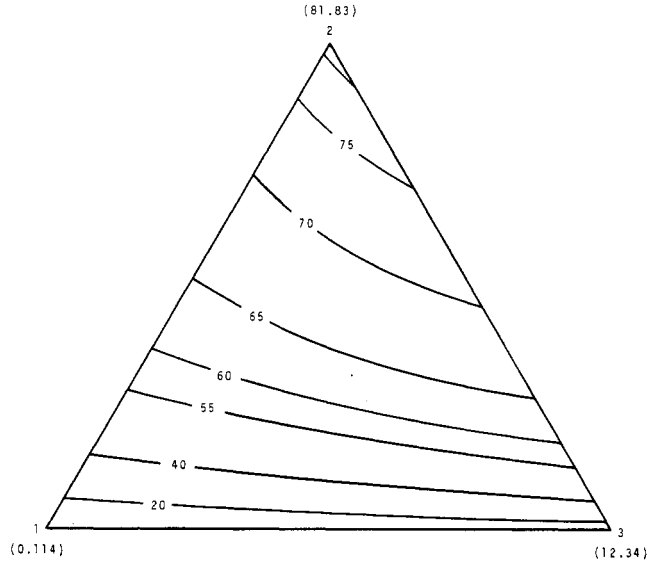

Figure 1. Lines of constant P (kPa) for the ethylene glycol (1)/acetone (2)/water (3) system at 50 °C.

and C_2 are found by regression of just the ternary data. The results of correlation for the ternary systems are given in Table V.

Discussion

The only literature data comparable with those reported here are for acetonitrile/water (9), also measured in our laboratory. The agreement is excellent, with the maxium $|\delta P| = 0.16$ kPa.

Results for the ternary systems are shown graphically by the contour diagrams of Figures 1–4. Lines of constant pressure are shown by Figures 1 and 2 and lines of constant G^E by Figures 3 and 4. Although the two ternary systems show differences in detail, their general behavior is similar. The only azeotrope is for acetonitrile/water at $x_{acetonitrile} = 0.7575$ and $P^{az} = 38.13$ kPa.

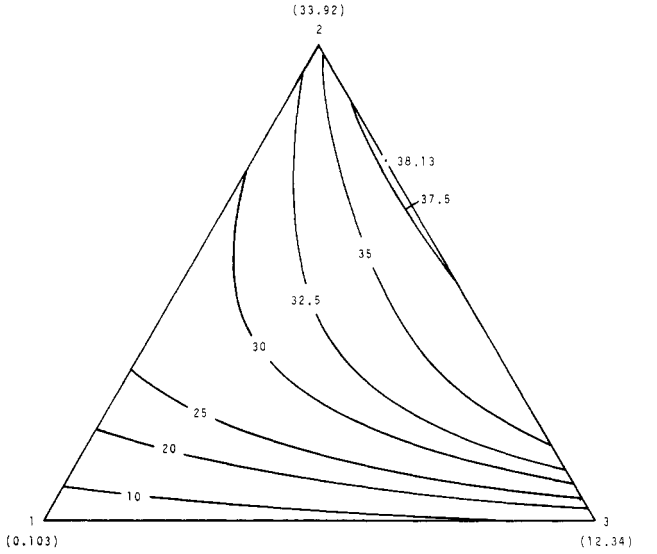

Figure 2. Lines of constant P (kPa) for the ethylene glycol (1)/ acetonitrile (2)/ water (3) system at 50 °C.

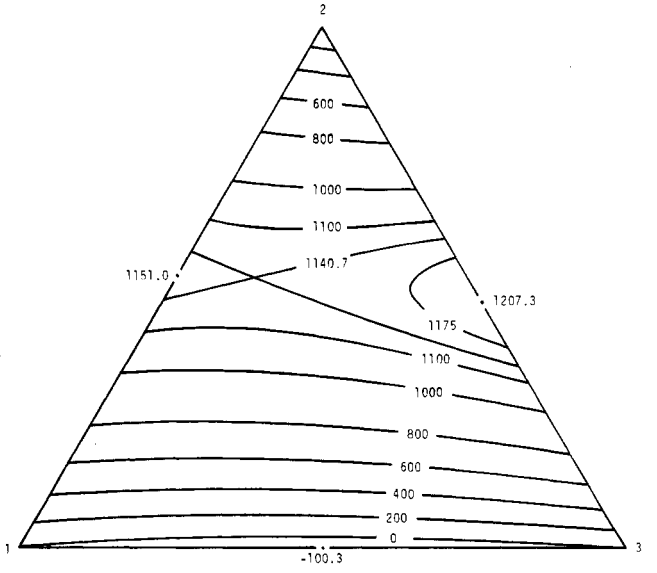

Figure 3. Lines of constant G^E (J/mol) for the ethylene glycol (1)/ acetone (2)/water (3) system at 50 °C. Note that there is a saddle point for $G^E = 1140.7$ J/mol.

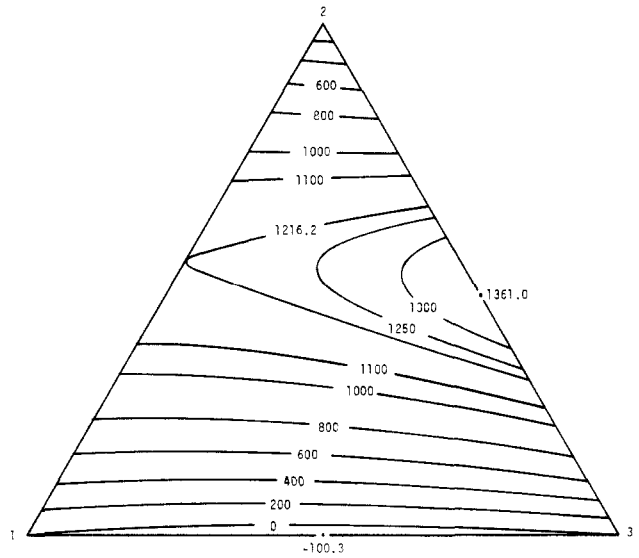

Figure 4. Lines of constant G^E (J/mol) for the ethylene glycol (1)/acetonitrile (2)/water (3) system at 50 °C.

Glossary

A_{ij}, A_{ji}	parameters in eq 1
B_{ij}	second virial coefficient
C_0, C_1, C_2	parameters in eq 2
G^E	excess Gibbs function, liquid phase
g	G^E/RT
P	total pressure
P_i^{sat}	vapor pressure of pure i
R	universal gas constant
T	absolute temperature
V_i^L	molar volume of pure liquid i
x	mole fraction, liquid phase

Greek Letters

λ_{ij}, λ_{ji}	parameters in eq 1
η_{ij}, η_{ji}	parameters in eq 1

Registry No. Ethylene glycol, 107-21-1; acetone, 67-64-1; acetonitrile, 75-05-8.

Literature Cited

(1) Gonzales, C.; Van Ness, H. C. *J. Chem. Eng. Data* **1983**, *28*, 410.
(2) Loehe, J. R.; Van Ness, H. C.; Abbott, M. M. *J. Chem. Eng. Data* **1981**, *26*, 178.
(3) Villamañán, M. A.; Allawi, A. J.; Van Ness, H. C. *Int. Data Ser., Sel. Data Mixtures, Ser. A* **1984**, 31-6.
(4) Gibbs, R. E.; Van Ness, H. C. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410.
(5) DiElsi, D. P.; Patel, R. B.; Abbott, M. M.; Van Ness, H. C. *J. Chem. Eng. Data* **1978**, *23*, 242.
(6) Abbott, M. M.; Van Ness, H. C. *AIChE J.* **1975**, *21*, 62.
(7) Abbott, M. M.; Floess, J. K.; Walsh, G. E.; Van Ness, H. C. *AIChE J.* **1975**, *21*, 72.
(8) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(9) Wilson, S. R.; Patel, R. B.; Abbott, M. M.; Van Ness, H. C. *J. Chem. Eng. Data* **1979**, *24*, 130.

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Dew Point Measurements for Nitrogen–Propane and Nitrogen–Butane Mixtures

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Dew point measurements were made for binary mixtures containing nitrogen and propane, *n*-butane, or isobutane. The temperature range was 188.2–350.4 K and the pressure range was 0.083–6.897 MPa. Nitrogen mole fractions ranged from 0.090 to 0.910.

Introduction

Accurate phase equilibria data for mixtures of nitrogen and hydrocarbons are needed to improve predictive procedures for estimation of properties of mixtures in natural gas processes. As part of an ongoing effort, dew point data were determined for binary mixtures of nitrogen with propane, *n*-butane, and isobutane. Measurements were made in ranges where data are not currently available.

Previous investigators have presented vapor–liquid equilibria data for the nitrogen–propane system (*1–4*), the nitrogen–*n*-butane system (*5–8*), and the nitrogen–isobutane system (*9*). These studies provided a data base to identify regions where additional data are necessary.

Experimental Section

Equipment. A schematic diagram for the dew point apparatus is shown in Figure 1. All of the piping, valves, and fittings are constructed from 316 stainless steel, and each piece was washed with acetone and flushed with nitrogen before assembly.

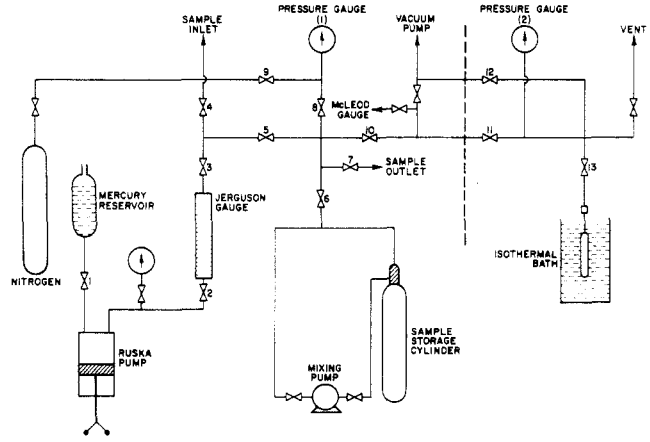

Figure 1. Schematic diagram of dew point equipment.

To preserve the uniformity of the gas composition charged into the cell, the system, with the exception of the cell, its

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