Table VI. Comparison of Distillation Data for Separation of Trioxane and Solvent[b]

particulars	dichlorobenzene	benzene
important solvent properties		
boiling point, °C	172-179	80.1
specific gravity, d_4^{20}	1.299	0.879
change in enthalpy ($H_T - H_{298}$), kcal/kg-mol	5963 at 114.5 °C (l)	9960 at 80 °C (g)
toxicity (allowable limit), ppm	*o*-, 50 *p*-, 75	10
wt % trioxane in distillate or bottom product	99.9	99.9
min reflux ratio	0.5	1.0
operating reflux ratio	1.0	1.5
no. of theoretical stages	11.8	24.9
condenser duty,[a] kcal/h	2200	4700
reboiler duty,[a] kcal/h	2500	4900

[a] Calculated for processing extract, containing 10 kg/h trioxane.
[b] Trioxane bp 114.5 °C.

aldehyde and water contents being higher, the operating costs for purification of trioxane to bring it to the monomer grade would be more.

Finally, trioxane has to be separated from the extracts by distillation. The data for the distillation from the extracts obtained at a solvent-to-feed ratio of 1.0 at 50 °C were calculated and are given in Table VI. The boiling points of benzene, *o*-dichlorobenzene, and trioxane are 80.1, 179, and 114.5 °C, respectively. Therefore, in the case of benzene extract, benzene would be the overhead product (at 80 °C) whereas, from the dichlorobenzene extract, trioxane would be distilled over at 114.5 °C. But in the former case the entire quantity of the benzene has to be separated by rectification. This would require a higher number of theoretical stages as well as operation at a higher reflux ratio. The consumption of energy will thus be higher. For the recovery of trioxane from dichlorobenzene extract, the requirements of theoretical stages, operating reflux, and heat load would be considerably lower. Moreover, benzene is more toxic than dichlorobenzene, and the allowable limits are 10 and 50 ppm, respectively (*16*). Hence, the expenses for safety precautions would be higher for benzene.

Glossary

C	solute
P	plait point
S	solvent
W	formaldehyde solution
X_{ss}	weight fraction of solvent in solvent layer
X_{ww}	weight fraction of formaldehyde solution in aqueous layer

Literature Cited

(1) Sharan, K. M.; Sagu, M. L.; Swarup, Janardan *Chem. Era* **1976**, *12*, 283.
(2) Charles, E. F. U.S. Patent 2 304 080; *Chem. Abstr.* **1943**, *37*, 2748^2.
(3) Joseph, F. W. U.S. Patent 2 347 447; *Chem. Abstr.* **1945**, *39*, 91^9.
(4) Natov, M.; Kabanvanov, V.; Godishink, M. M. *Chem. Tech. Inst.* **1961**, *7*, 203.
(5) Badische Aniline and Soda Fabrik A.-G. (by Rolf Platz), Belgium Patent 620 257; *Chem. Abstr.* **1963**, *59*, 7544A.
(6) Adamek, M.; Dykyj, J.; Glask, S.; Gregor, F.; Kordik, J.; Patek, V. Czechoslovakia Patent 129 711; *Chem. Abstr.* **1969**, *71*, 81440j.
(7) Dojcasky, J.; Neinrich, J.; Surovy, J. *Chem. Prum.* **1969**, *19*, 413.
(8) Yamase, Y.; Kutsuma, T. Japan Patent 7 033 184; *Chem. Abstr.* **1971**, *74*, 54361q.
(9) Dykyji, J.; Kovac, A.; Zlak, J.; Adamek, M.; Gregor, F. Czechoslovakia Patent 136 865; *Chem. Abstr.* **1971**, *75*, 36153q.
(10) Sperber, H.; Fuchs, H.; Libowitzky, H. German Patent 1 668 867; *Chem. Abstr.* **1972**, *77*, 114438u.
(11) Slivkin, L. G.; Orechkin, D. B.; Ovsyannikov, L. F. *Khim. Prom.* **1965**, *41*, 740.
(12) Meissner, J. *Brit. Chem. Eng.* **1969**, *14*, 757.
(13) Kuchhal, R. K.; Kumar, Basant; Mathur, H. S.; Gupta, P. L. *Z. Anal. Chem.* **1979**, *294*, 410.
(14) Sherwood, T. K. "Absorption and Extraction"; McGraw-Hill: New York, 1937; p 242.
(15) Othmer, D. F.; Tobias, P. S. *Ind. Eng. Chem.* **1942**, *34*, 693.
(16) "Occupational Exposure Limits for Airborne Toxic Substances"; Occupational Safety and Health Series no. 37, International Labour Office, Geneva, Switzerland, 1977.

Received for review October 30, 1979. Accepted July 30, 1980.

Heat Capacity and Enthalpy of Phosphoric Acid

Basil B. Luff

Division of Chemical Development, National Fertilizer Development Center, Tennessee Valley Authority,
Muscle Shoals, Alabama 35660

Measurements of the heat capacity of phosphoric acid were made over the ranges of concentration of 61.8–83.0% and temperature of 25–367 °C. A possible transition was found at ~77 °C. Values for enthalpy were derived.

Previous studies (*1*) of the enthalpies of phosphoric acids and the derived heat capacities were made by using a high-temperature drop calorimeter. This study, using a Perkin-Elmer differential scanning calorimeter Model DSC-2, more precisely defines the heat capacities and entropies of the acids over a somewhat broader concentration range (61.8–83.0% P_2O_5) and temperature range (25–370 °C).

Materials and Procedure

The most concentrated superphosphoric acid (83.0% P_2O_5) was prepared by dissolving reagent P_2O_5 in reagent H_3PO_4 at 145 °C and filtering the hot solution through a coarse glass frit. Portions of this acid were diluted with reagent H_3PO_4 to form acids of the desired concentrations. All the solutions were held overnight at 100 °C to ensure equilibrium distribution of the phosphate species. Final concentrations of the acids were determined by chemical analyses.

The acid samples (17.56–29.87 mg) and a synthetic sapphire reference standard (40.09 mg) were hermetically sealed in weighed gold pans. The sample enclosure of the scanning calorimeter was cooled by an aluminum cold finger partially immersed in ice water and was purged continuously with dry nitrogen. The scanning rate for all measurements was 10 deg/min, and the sensitivity of the recorder was 2 mcal s^{-1}.

A weighed empty pan was placed in the sample holder and scanned over the desired temperature range. The empty pan was replaced with the pan containing the sapphire, and it was scanned over the same temperature range. The pan containing the sapphire was then replaced with the pan containing the acid

Table I. Observed Heat Capacities of Phosphoric Acids

	61.8% P_2O_5		67.0% P_2O_5		70.6% P_2O_5		72.6% P_2O_5		74.1% P_2O_5		78.0% P_2O_5		83.0% P_2O_5	
T, K	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]	C_s, cal K^{-1} g^{-1}	SD[a]
300	0.4507	0.0006	0.4218	0.0006	0.3883	0.0003	0.3783	0.0007	0.3675	0.0004	0.3607	0.0004	0.3250	0.0005
310	0.4584	0.0004	0.4276	0.0003	0.3916	0.0006	0.3811	0.0008	0.3740	0.0004	0.3642	0.0007	0.3286	0.0003
320	0.4617	0.0004	0.4308	0.0004	0.3948	0.0002	0.3855	0.0005	0.3791	0.0004	0.3694	0.0012	0.3324	0.0003
330	0.4668	0.0010	0.4352	0.0002	0.3980	0.0004	0.3890	0.0007	0.3831	0.0003	0.3746	0.0014	0.3354	0.0004
340	0.4710	0.0005	0.4394	0.0003	0.4018	0.0007	0.3933	0.0007	0.3889	0.0005	0.3783	0.0013	0.3382	0.0006
350	0.4751	0.0008	0.4434	0.0004	0.4074	0.0012	0.3976	0.0009	0.3954	0.0002	0.3828	0.0014	0.3417	0.0010
360	0.4799	0.0011	0.4485	0.0008	0.4116	0.0014	0.4050	0.0012	0.4014	0.0003	0.3867	0.0016	0.3446	0.0011
370	0.4844	0.0016	0.4532	0.0012	0.4178	0.0022	0.4124	0.0013	0.4102	0.0002	0.3906	0.0014	0.3476	0.0013
380	0.4892	0.0017	0.4586	0.0013	0.4252	0.0028	0.4233	0.0020	0.4192	0.0004	0.3943	0.0018	0.3506	0.0015
390	0.4950	0.0017	0.4645	0.0011	0.4363	0.0033	0.4388	0.0029	0.4290	0.0002	0.3973	0.0019	0.3534	0.0018
400	0.4990	0.0014	0.4694	0.0008	0.4444	0.0033	0.4520	0.0036	0.4331	0.0001	0.4005	0.0022	0.3559	0.0021
410	0.5027	0.0015	0.4728	0.0005	0.4448	0.0024	0.4540	0.0014	0.4326	0.0005	0.4036	0.0021	0.3588	0.0023
420	0.5068	0.0018	0.4769	0.0006	0.4432	0.0016	0.4485	0.0027	0.4350	0.0005	0.4068	0.0025	0.3611	0.0025
430			0.4808	0.0003	0.4442	0.0008	0.4480	0.0014	0.4386	0.0007	0.4093	0.0028	0.3637	0.0027
440			0.4850	0.0002	0.4470	0.0008	0.4509	0.0017	0.4419	0.0008	0.4117	0.0030	0.3660	0.0029
450			0.4890	0.0006	0.4501	0.0008	0.4535	0.0018	0.4454	0.0010	0.4141	0.0032	0.3681	0.0029
460					0.4538	0.0009	0.4561	0.0018	0.4484	0.0010	0.4172	0.0033	0.3709	0.0032
470					0.4573	0.0005	0.4599	0.0019	0.4511	0.0012	0.4195	0.0033	0.3727	0.0034
480					0.4608	0.0003	0.4634	0.0017	0.4536	0.0010	0.4212	0.0033	0.3750	0.0034
490							0.4657	0.0017	0.4552	0.0011	0.4226	0.0033	0.3766	0.0033
500							0.4681	0.0014	0.4571	0.0011	0.4245	0.0034	0.3786	0.0033
510							0.4703	0.0013	0.4586	0.0010	0.4260	0.0033	0.3803	0.0033
520							0.4735	0.0012	0.4603	0.0008	0.4274	0.0033	0.3823	0.0031
530							0.4754	0.0014	0.4610	0.0005	0.4286	0.0033	0.3838	0.0031
540									0.4628	0.0005	0.4296	0.0033	0.3850	0.0029
550											0.4305	0.0034	0.3866	0.0028
560											0.4315	0.0035	0.3882	0.0027
570											0.4332	0.0030	0.3903	0.0024
580											0.4338	0.0033	0.3919	0.0021
590											0.4356	0.0029	0.3936	0.0018
600											0.4376	0.0026	0.3956	0.0015
610											0.4396	0.0025	0.3980	0.0012
620											0.4415	0.0024	0.4004	0.0008
630											0.4436	0.0020	0.4025	0.0004
640											0.4468	0.0021	0.4056	0.0005

[a] SD = standard deviation.

and the scan repeated. The acid sample then was cooled as quickly as possible to the starting temperature and rescanned. The entire procedure was repeated several times for each acid sample, allowing at least 24 h between replicates. The pans containing the acid samples were weighed periodically to ascertain that no weight loss occurred during the measurements.

The heat capacities of the acids were determined at even temperature intervals by comparison of the ordinate displacement of the recording of the sample with that of the sapphire, the heat capacity of which is well-known (*2*), according to eq 1, where $C_s(\mathrm{S})$ = observed heat capacity of acid (cal $\deg^{-1}$ g^{-1}),

$$C_s(\mathrm{S}) = (\mathrm{WR}/\mathrm{WS})[(\mathrm{DS} - \mathrm{DE})/(\mathrm{DR} - \mathrm{DE})]C_p(\mathrm{R}) \qquad (1)$$

$C_p(\mathrm{R})$ = heat capacity of sapphire (cal $\deg^{-1}$ g^{-1}), WS = weight of acid sample (mg), WR = weight of sapphire (mg), DS = ordinate displacement of pan plus acid (% of full scale), DR = ordinate displacement of pan plus sapphire (% of full scale), and DE = ordinate displacement of empty pan (% of full scale). Corrections based on the differences in weight between the empty pan and the sample pans and the heat capacity of gold were applied.

Heat Capacity and Enthalpy

The average observed heat capacities under the equilibrium vapor pressures, C_s, at even increments of absolute temperature along with their standard deviations are listed in Table I. An anomaly in the heat-capacity curves, possibly indicating a pronounced redistribution of phosphate species, was observed in the acids of lower concentration (61.8–74.1% P_2O_5) starting at ~350 K. The anomaly was rather small with the two acids of lowest concentration (61.8–67.0% P_2O_5), and no significant differences could be detected between the first scan and the scan immediately after cooling, indicating that equilibrium at the starting temperature was attained quickly upon cooling. The average observed heat capacities for these acids were obtained from all of the scans. The anomaly was more pronounced with three of the acids (70.6, 72.6, and 74.1% P_2O_5), and significant differences could be detected in the anomaly between the first scan and the scan immediately after cooling, indicating that, although the acids were converting back to the low-temperature form, equilibrium had not been attained. The heat capacities for these acids at temperatures below and above the anomaly showed no significant differences between the first and second scan; so for these acids, all of the observed heat capacities at temperatures below and above the anomaly were used to determine the average values. Only those from the first scans were used for the average values in the anomaly. The anomaly was not observed in the heat-capacity curves of the two acids of highest concentration (78.0 and 83.0% P_2O_5), and no significant differences could be detected between the first and second scans; so for these acids, all of the observed heat capacities were used to determine the average values. Poly-

Table II. Enthalpies of Transition of Phosphoric Acids at 350 K

concn, % P_2O_5	ΔH_{TR}, cal g^{-1}
61.8	0.004
67.0	0.111
70.6	0.974
72.6	1.740
74.1	0.692

Table III. Heat Capacity and Enthalpy Change above 298.15 K of Phosphoric Acids

temp, K	61.8% P_2O_5 C_s, cal deg^{-1} g^{-1}	61.8% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	67.0% P_2O_5 C_s, cal deg^{-1} g^{-1}	67.0% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	70.6% P_2O_5 C_s, cal deg^{-1} g^{-1}	70.6% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	72.6% P_2O_5 C_s, cal deg^{-1} g^{-1}	72.6% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	74.1% P_2O_5 C_s, cal deg^{-1} g^{-1}	74.1% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	78.0% P_2O_5 C_s, cal deg^{-1} g^{-1}	78.0% P_2O_5 $(H_T - H_{298})$, cal g^{-1}	83.0% P_2O_5 C_s, cal deg^{-1} g^{-1}	83.0% P_2O_5 $(H_T - H_{298})$, cal g^{-1}
298.15	0.452	0.000	0.422	0.000	0.388	0.000	0.377	0.000	0.368	0.000	0.360	0.000	0.325	0.000
310	0.457	5.386	0.427	5.026	0.392	4.616	0.381	4.491	0.374	4.391	0.365	4.295	0.329	3.874
330	0.466	14.623	0.435	13.643	0.398	12.514	0.389	12.197	0.384	11.965	0.374	11.684	0.335	10.513
350	0.476	24.044	0.444	22.430	0.405	20.547	0.397	20.063	0.394	19.741	0.382	19.246	0.341	17.279
ΔH_{TR}, cal g^{-1}		0.004		0.111		0.974		1.740		0.692	no transition		no transition	
350	0.477	24.048	0.450	22.541	0.418	21.521	0.426	21.803	0.405	20.433	0.382	19.246	0.341	17.279
370	0.486	33.680	0.457	31.611	0.424	29.939	0.431	30.371	0.415	28.627	0.390	26.972	0.348	24.169
390	0.494	43.481	0.465	40.838	0.431	38.488	0.437	39.051	0.424	37.011	0.397	34.850	0.353	31.178
410	0.503	53.453	0.473	50.221	0.437	47.169	0.442	47.844	0.432	45.566	0.404	42.867	0.359	38.300
430			0.481	59.760	0.444	55.981	0.448	56.749	0.439	54.275	0.410	51.006	0.364	45.527
450			0.489	69.455	0.450	64.925	0.454	65.768	0.445	63.118	0.415	59.254	0.368	52.851
470					0.457	74.000	0.459	74.899	0.451	72.079	0.419	67.593	0.373	60.264
490							0.465	84.144	0.455	81.137	0.423	76.010	0.377	67.758
510							0.471	93.501	0.459	90.276	0.426	84.493	0.380	75.326
530							0.476	102.971	0.461	99.477	0.428	93.032	0.384	82.963
550											0.431	101.621	0.387	90.666
570											0.433	110.258	0.390	98.436
590											0.436	118.948	0.394	106.275
610											0.439	127.699	0.398	114.190
630											0.444	136.529	0.403	122.193

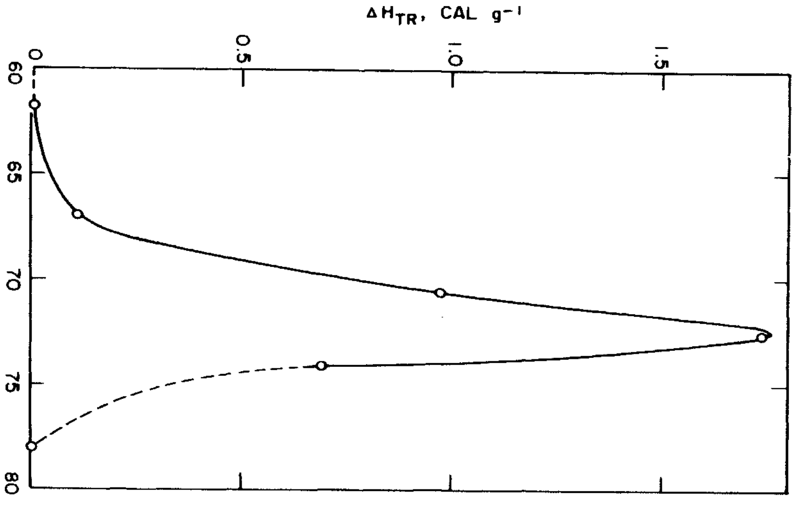

Figure 1. Enthalpy of transition of phosphoric acids.

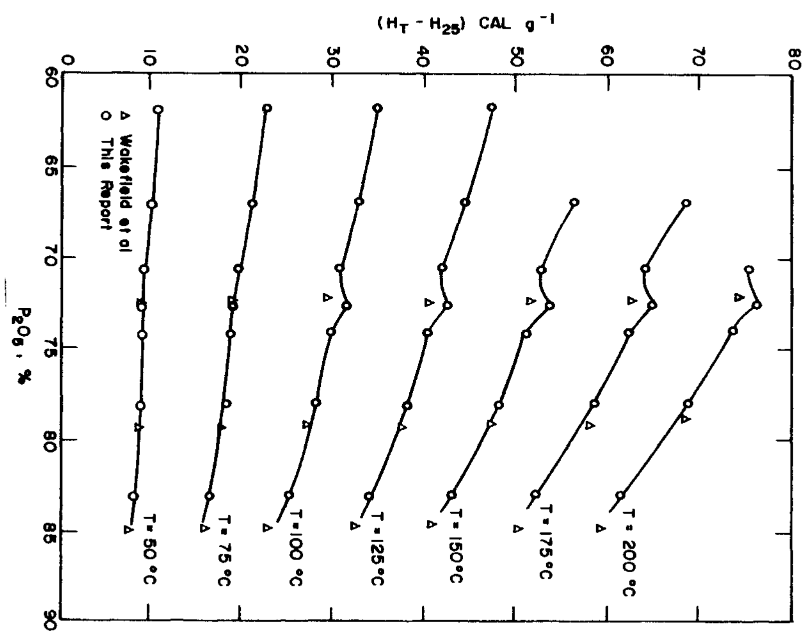

Figure 2. Enthalpy change above 25 °C for phosphoric acids.

nomial equations of the heat capacity as a function of temperature were fitted to the observed values below and above the anomaly. The enthalpies of transition, ΔH_{TR}, in cal g^{-1} were determined from eq 2. The first term on the right side of eq

$$\Delta H_{TR} = \int_{350}^{T} (C_s)_a \, dT - \int_{350}^{T} (C_s)_t \, dT \qquad (2)$$

Table IV. Heat Capacity of Phosphoric Acid, cal g^{-1} $°C^{-1}$

T, °C	P_2O_5, wt %	62	64	66	68	70	72	74	76	78	80	82
25		0.450	0.441	0.429	0.414	0.395	0.380	0.368	0.365	0.360	0.351	0.337
40		0.457	0.448	0.436	0.420	0.400	0.386	0.376	0.372	0.366	0.358	0.343
50		0.462	0.452	0.440	0.424	0.403	0.390	0.381	0.376	0.371	0.362	0.346
60		0.467	0.457	0.444	0.428	0.407	0.393	0.386	0.381	0.375	0.366	0.350
70		0.471	0.461	0.448	0.432	0.410	0.397	0.391	0.386	0.379	0.369	0.353
80		0.478	0.469	0.458	0.444	0.426	0.424	0.407	0.392	0.384	0.373	0.356
90		0.482	0.473	0.462	0.448	0.429	0.427	0.412	0.397	0.388	0.376	0.359
100		0.486	0.477	0.466	0.451	0.432	0.430	0.416	0.402	0.391	0.379	0.361
110		0.491	0.481	0.470	0.455	0.436	0.433	0.421	0.406	0.395	0.382	0.364
120		0.495	0.486	0.474	0.459	0.439	0.436	0.425	0.411	0.399	0.385	0.366
130		0.499	0.490	0.478	0.462	0.442	0.439	0.429	0.415	0.402	0.387	0.369
140		0.504	0.494	0.482	0.466	0.446	0.442	0.433	0.419	0.405	0.390	0.371
150		0.508	0.498	0.486	0.469	0.449	0.445	0.437	0.422	0.408	0.392	0.373
160			0.503	0.490	0.473	0.452	0.448	0.441	0.426	0.411	0.394	0.375
170				0.494	0.477	0.456	0.451	0.444	0.429	0.413	0.396	0.377
180					0.480	0.459	0.454	0.447	0.432	0.416	0.398	0.379
190					0.484	0.462	0.457	0.450	0.434	0.418	0.400	0.381
200						0.465	0.460	0.453	0.437	0.420	0.401	0.383
210						0.469	0.463	0.456	0.439	0.421	0.403	0.384
220							0.466	0.459	0.441	0.423	0.405	0.386
230							0.469	0.461	0.442	0.425	0.406	0.388
240								0.464	0.443	0.426	0.408	0.390
250								0.466	0.445	0.427	0.409	0.391
260								0.468	0.445	0.429	0.411	0.393
270									0.446	0.430	0.412	0.395
280									0.446	0.431	0.414	0.396
290									0.446	0.432	0.415	0.398
300									0.446	0.434	0.417	0.400
310									0.446	0.435	0.419	0.401
320										0.436	0.420	0.403
330										0.438	0.422	0.405
340										0.440	0.424	0.407
350										0.442	0.426	0.409
360										0.445	0.428	0.411
370										0.448	0.430	0.413

Table V. Enthalpy of Phosphoric Acid, $H_T - H_{25}$, cal g^{-1}

T, °C	P_2O_5, wt %	62	64	66	68	70	72	74	76	78	80	82
40		6.8	6.7	6.5	6.3	6.0	5.7	5.6	5.5	5.4	5.3	5.1
50		11.4	11.2	10.9	10.5	10.0	9.6	9.4	9.3	9.1	8.9	8.5
60		16.1	15.7	15.3	14.7	14.0	13.5	13.2	13.1	12.9	12.6	12.0
70		20.7	20.3	19.7	19.0	18.1	17.5	17.1	16.9	16.6	16.2	15.5
80		25.5	25.0	24.3	23.6	23.0	23.2	21.8	20.9	20.5	19.9	19.1
90		30.3	29.7	28.9	28.1	27.2	27.5	25.9	24.9	24.3	23.7	22.6
100		35.1	34.4	33.6	32.6	31.5	31.8	30.1	28.9	28.2	27.5	26.2
110		40.0	39.2	38.3	37.1	35.9	36.1	34.2	32.9	32.1	31.3	29.9
120		44.9	44.1	43.0	41.7	40.3	40.4	38.5	37.0	36.1	35.1	33.5
130		49.9	48.9	47.7	46.3	44.7	44.8	42.7	41.1	40.1	39.0	37.2
140		54.9	53.9	52.5	50.9	49.1	49.2	47.0	45.3	44.1	42.8	40.9
150		60.0	58.8	57.4	55.6	53.6	53.6	51.4	49.5	48.2	46.8	44.6
160			63.8	62.2	60.3	58.1	58.1	55.8	53.7	52.3	50.7	48.4
170				67.2	65.1	62.6	62.6	60.2	58.0	56.4	54.6	52.1
180					69.9	67.2	67.1	64.7	62.3	60.6	58.6	55.9
190					74.7	71.8	71.7	69.2	66.6	64.7	62.6	59.7
200						76.4	76.3	73.7	71.0	68.9	66.6	63.5
210						81.1	80.9	78.2	75.4	73.1	70.6	67.4
220							85.5	82.8	79.8	77.3	74.7	71.2
230							90.2	87.4	84.2	81.6	78.7	75.1
240								92.0	88.6	85.8	82.8	79.0
250								96.7	93.0	90.1	86.9	82.9
260								101.3	97.5	94.4	91.0	86.8
270									101.9	98.7	95.1	90.7
280									106.4	103.0	99.2	94.7
290									110.9	107.3	103.4	98.6
300									115.3	111.6	107.5	102.6
310									119.8	116.0	111.7	106.6
320										120.3	115.9	110.7
330										124.7	120.1	114.7
340										129.1	124.3	118.8
350										133.5	128.6	122.9
360										137.9	132.9	127.0
370										142.4	137.1	131.1

2 was determined by tabular integration of the average observed heat capacities as a function of temperature in the anomaly, and the last term was determined by integrating the heat capacity equation above the anomaly over the temperature range of the tabular integration. The values for the enthalpy of transition calculated in this manner are listed in Table II and shown in Figure 1.

Values for heat capacity and enthalpy change above 298.15 K at even intervals of temperature for the phosphoric acids were calculated from the heat-capacity equations, their integrals with the proper integration constants, and the heats of transition listed in Table II. These values are listed in Table III. Enthalpy changes above 298.15 K also were calculated at the same temperatures as those reported by Wakefield et al. (*1*), and the values compared in Figure 2. The results are in good agreement except at 72.6% P_2O_5, a concentration in which the enthalpy of transition is quite pronounced, and above 350 K (77 °C), the temperature of the transition. This discrepancy probably can be explained by the fact that only the energy released as the acid cools from the higher temperature to 298.15 K in a short period of time would be measured by the drop calorimeter. The slow release of energy as the acid converts from the high-temperature form to the low-temperature form, which takes several hours, would not be detected.

Values of heat capacity of the phosphoric acid calculated from the heat-capacity equations were plotted against concentration at each 10-degree interval of temperature, and smooth curves were drawn through the points. Values of heat capacity at each 10-degree interval of temperature for phosphoric acids at even intervals of concentration then were read from the curves. Values of the enthalpy of transition at even intervals of concentration were read from Figure 1. Equations were fitted to these values, and the heat capacities and enthalpy changes above 298.15 K were determined as described above and are listed in Tables IV and V, respectively. The temperatures were converted to Celsius to make the report compatible with the previous one (*1*).

Corrections for converting C_s to C_p, the heat capacity at constant pressure, based on vapor pressures and enthalpies of vaporization taken from the literature (*3*) and the assumption that the liquids occupied 75% of the encapsulated volumes were less than 0.001 cal deg^{-1} g^{-1} over most of the temperature ranges but did increase to 0.002 cal deg^{-1} g^{-1} when the liquids were near their boiling points. These corrections, approximately the same magnitude as the differences between the observed and calculated heat capacities, were considered to be within the precision of the measurements.

Literature Cited

(1) Wakefield, Z. T.; Luff, B. B.; Reed, R. B. *J. Chem. Eng. Data* **1972**, *17*, 420-3.

(2) Ginnings, D. C.; Furukawa, G. T. *J. Am. Chem. Soc.* **1953**, *75*, 522-7.

(3) Brown, E. H.; Whitt, C. D. *Ind. Eng. Chem.* **1952**, *44*, 615-8.

Received for review June 2, 1980. Accepted October 27, 1980.

Solubility of Acetone and Isopropyl Ether in Compressed Nitrogen, Methane, and Carbon Dioxide

Paul J. Hicks, Jr., and John M. Prausnitz*

Chemical Engineering Department, University of California, Berkeley, California 94720

Vapor-phase solubilities are reported for acetone and isopropyl ether in compressed nitrogen, methane, and carbon dioxide, in the range -50 to 50 °C and 17-63 bar. The experimental solubilities are reduced to obtain second virial cross-coefficients. Experimental cross-coefficients are compared to those calculated by using the square-well potential or the Hayden-O'Connell correlation.

There is little fundamental information concerning the interaction between a small nonpolar molecule (*2*) and a large polar molecule (*1*). To obtain such information, it is useful to measure the second virial cross-coefficient B_{12} which is directly related to the intermolecular potential Γ_{12}. This work reports experimental measurements which yield B_{12} for a number of binary polar-nonpolar mixtures. The experimental data obtained are the solubilities of acetone and isopropyl ether in compressed nitrogen, methane, and carbon dioxide.

These measurements are also of interest in chemical engineering because they provide the fundamental information needed to calculate solvent losses in an absorption process operating at advanced pressure.

This work is similar to that of Lazalde et al. (*1*), who studied the solubility of methanol in compressed gases.

Experimental Section

The experimental apparatus is similar to that used by Lazalde (*1*). There are some minor modifications made primarily to facilitate changing pressures in the apparatus. A schematic of the flow apparatus is shown in Figure 1.

A light (gaseous) component is equilibrated with a heavy (liquid) component at a given temperature and pressure. The gas phase is sampled and analyzed.

The light component is fed from a gas cylinder through a pressure regulator and a precooling/preheating coil to the two equilibrium cells arranged in series. The gas enters the bottom of each equilibrium cell, containing the liquid being studied, through a stainless-steel sparger whose average pore size is 5 μm. The slowly flowing gas is saturated with the liquid as it bubbles through the liquid. Two cells in series are used to ensure that the exiting gas is in equilibrium with the liquid. The top of each cell is packed with glass wool to remove any possible entrainment of the liquid in the gas. The gas exits the second cell through a section of tubing heated to prevent condensation of the heavy component. In this section the gas is expanded to atmospheric pressure. The volumetric flow rate is always less than 0.3 cm^3/s where the measured solubility is independent of the flow rate.

The constant-temperature bath containing the equilibrium cells is controlled by a Hallikainen (Shell Development) thermotrol to ±0.05 °C or better except at -50 °C where it is controlled to ±0.15 °C or better. At low temperatures, the bath fluid is 95% ethanol; at high temperatures, it is water. Temperatures above -10 °C are measured with a set of liquid-in-glass calorimetric thermometers with an accuracy of ±0.1 °C. Temperatures between -10 and -25 °C are measured with a

0021-9568/81/1726-0074$01.00/0