Enthalpies of Reaction of Phosphoric Acid Solutions and Urea at 25°C and Some Physical Properties of Solutions in System $CO(NH_2)_2$–H_3PO_4–H_2O

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Measurements at 25°C were made of the compositions of saturated solutions in the system $CO(NH_2)_2$–H_3PO_4–H_2O; the enthalpies of solution of urea orthophosphate in water, in 20.37% urea, and in 19.99% H_3PO_4; the enthalpies of solution of urea in 49.91%, 60.12%, and 75.03% H_3PO_4; the enthalpy of formation of urea orthophosphate; and the densities and heat capacities in the system $CO(NH_2)_2$–H_3PO_4–H_2O. The enthalpy of forming crystalline urea orthophosphate from urea and phosphoric acid solutions was calculated from the measurements and published data.

Crystallization of the urea adduct, $CO(NH_2)_2 \cdot H_3PO_4$, from wet-process phosphoric acid is a promising method for separating the acid from its impurities. Because thermal and physicochemical data are useful in the development of a process for this purpose, measurements at 25°C were made of the compositions of saturated solutions in the system $CO(NH_2)_2$–H_3PO_4–H_2O; the enthalpies of solution of urea orthophosphate in water, in 20.37% urea, and in 19.99% H_3PO_4; the enthalpies of solution of urea in 49.91%, 60.12%, and 75.03% H_3PO_4; the enthalpy of formation of urea orthophosphate; and the densities and heat capacities in the system $CO(NH_2)_2$–H_3PO_4–H_2O.

Materials

Urea. Reagent grade urea was dissolved in water at 70°C. The solution was filtered through fritted glass and cooled slowly to room temperature. The resultant crystals were separated by suction on fritted glass, dried at 57°C for 16 hr, cooled, and ground lightly to pass a 20-mesh screen. The product, when dried to constant weight at 57°C, contained 46.6% N (theoretical, 46.65% N).

Urea orthophosphate. Five kg of reagent urea was dissolved in 10 liters of 60% H_3PO_4 at 60°C. The solution was filtered and cooled slowly to room temperature. The coarse crystals were centrifuged, rinsed with cold water, and centrifuged again. The product was air dried on filter paper and then dried under vacuum desiccation over Dehydrite. It then was ground lightly to pass a 20-mesh screen and dried to constant weight under vacuum over Dehydrite. It contained 17.6% N and 44.91% P_2O_5 (theoretical, 17.72% N and 44.91% P_2O_5).

Phosphoric acid. The phosphoric acid solutions were prepared by diluting recrystallized reagent phosphoric acid with distilled water.

Compositions of Saturated Solutions in System $CO(NH_2)_2$–H_3PO_4–H_2O at 25°C

A determination of the integral enthalpy of solution at saturation requires a knowledge of the composition of the saturated solutions. Twelve saturated solutions were prepared by adding urea orthophosphate to various solutions of urea and phosphoric acid at 50°C until no more would dissolve readily. The solutions were cooled slowly to 25°C and held in stoppered flasks for three days, during which time large crystals formed in the bottom of the flasks. The crystals were identified petrographically as urea orthophosphate in each flask. The supernatant liquids were analyzed chemically for P_2O_5 and N, and the equivalent amounts of H_3PO_4 and $CO(NH_2)_2$, as calculated from the results, are shown in Table I and Figure 1.

Calorimeter and Procedure

The solution calorimeter used to determine integral enthalpies of solution was similar to that used by Southard (*5*). A 900-ml Dewar flask was supported in a constant-temperature water bath by cork rings clamped between stainless-steel plates. A flanged stainless-steel collar that fitted closely around the neck of the Dewar flask was silver soldered to the

Table I. Solutions Saturated with Urea Orthophosphate at 25°C

	Composition, %	
Soln no.	H_3PO_4	$CO(NH_2)_2$
5	28.02	38.65
6	29.37	31.71
3	30.24	28.76
1	32.19	19.73
2	36.33	14.69
4	45.54	9.56
7	46.67	9.90
8	53.49	8.02
9	62.11	6.90
10	69.04	7.18
11	72.20	8.77
12	71.38	15.97

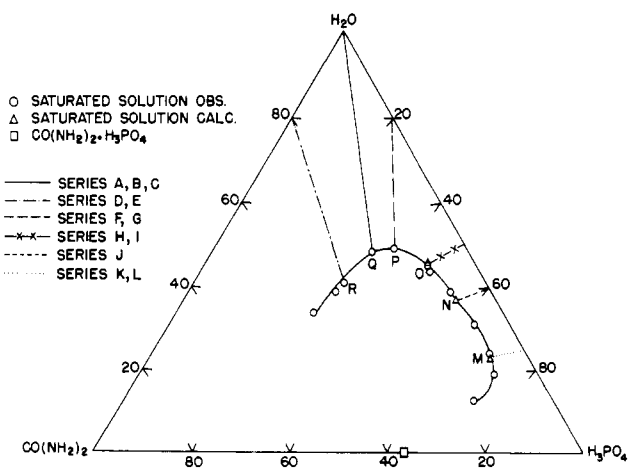

Figure 1. System $CO(NH_2)_2$–H_3PO_4–H_2O at 25°C

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top plate. The space between the collar and the neck of the flask was filled with Apiezon W wax. A stainless-steel plate, provided with three small stuffing boxes for the thermometer and heater supports and with a stainless-steel ball bearing guide, 4 in. long, for the stirrer, was clamped to the flanged collar with six spring clamps. A neoprene gasket sealed the cover plate to the collar.

A 4-lead helical constantan heater was mounted in a 5-mm glass tube that had been shaped into a helix. The head of a platinum resistance thermometer was sealed with Apiezon W

Table II. Observed Properties of Solution of Urea Orthophosphate in Water at 25°C

Solution concentration						
Wt %		Molality urea orthophosphate, m	Density, d, g/ml	Specific heat, s, cal/°C/g	Enthalpy of solution	
H_3PO_4	$CO(NH_2)_2$				Q, cal/run	ΔH, cal/mol
			Solution Series A			
0	0	0	0.9958	...	...	...
1.30	0.79	0.135	1.0065	0.9853	879.25	7675
2.65	1.63	0.283	1.0168	0.9682	951.43	7683
3.86	2.37	0.420	1.0256	0.9559	879.29	7696
4.97	3.05	0.552	1.0337	0.9435	824.26	7689
6.20	3.80	0.704	1.0424	0.9302	934.99	7675
7.31	4.48	0.846	1.0509	0.9192	861.55	7657
8.46	5.18	1.000	1.0599	0.9059	904.30	7631
9.52	5.83	1.148	1.0683	0.8962	861.76	7610
10.65	6.53	1.313	1.0777	0.8850	940.28	7587
11.70	7.17	1.471	1.0853	0.8740	883.20	7562
12.68	7.77	1.627	1.0931	0.8626	853.57	7539
13.65	8.36	1.785	1.1011	0.8438	854.39	7517
14.56	8.92	1.942	1.1087	0.8438	828.25	7495
15.43	9.46	2.096	1.1160	0.8351	802.95	7475
16.33	10.01	2.263	1.1232	0.8260	852.57	7454
17.25	10.57	2.439	1.1311	0.8170	882.48	7429
18.12	11.10	2.612	1.1386	0.8085	856.51	7409
18.94	11.61	2.782	1.1458	0.8005	823.43	7389
19.80	12.13	2.967	1.1533	0.7923	885.30	7369
20.52	12.57	3.129	1.1591	0.7854	760.98	7352
21.33	13.07	3.319	1.1662	0.7783	875.59	7333
22.10	13.54	3.503	1.1728	0.7700	840.45	7315
22.87	14.02	3.698	1.1798	0.7638	870.76	7297
23.64	14.49	3.899	1.1859	0.7565	882.61	7278
24.40	14.96	4.106	1.1927	0.7496	891.95	7260
25.13	15.40	4.313	1.1997	0.7434	875.09	7242
25.74	15.77	4.490	1.2054	0.7382	739.75	7228
26.42	16.19	4.699	1.2119	0.7313	858.62	7212
27.07	16.59	4.903	1.2177	0.7258	822.62	7196
27.71	16.98	5.113	1.2248	0.7200	833.97	7180
28.30	17.35	5.314	1.2312	0.7143	779.86	7163
28.87	17.69	5.512	...	0.7094	760.22	7149
			Solution Series B			
0	0	0	0.9971	0.9980	...	...
0.72	0.44	0.074	1.0027	0.9927	478.84	7614
2.01	1.23	0.212	1.0123	0.9780	900.98	7709
3.27	2.01	0.353	1.0216	0.9630	908.52	7725
4.65	2.85	0.513	...	0.9473	1013.03	7713
0.17	0.11	0.018	...	0.9983	105.74	6983[a]
0.35	0.22	0.036	...	0.9965	226.05	7345[a]
			Dilution Series C			
31.49	19.30	6.532	1.2622	...	...	7094
30.99	18.99	6.324	1.2570	0.6923	37.68	7105
30.47	18.67	6.115	1.2519	0.6965	37.94	7117
29.95	18.36	5.913	1.2468	0.7011	37.94	7128
29.46	18.05	5.728	1.2419	0.6973	35.40	7139
28.94	17.73	5.537	1.2366	0.7094	37.09	7151
28.45	17.43	5.364	1.2313	0.7148	34.04	7162
27.97	17.14	5.199	1.2269	0.7198	33.06	7173
27.48	16.84	5.035	1.2223	0.7243	33.17	7184
27.01	16.55	4.884	1.2182	0.7282	31.04	7194[b]
26.55	16.27	4.739	1.2139	0.7317	29.65	7205
26.06	15.97	4.589	1.2093	0.7275	31.17	7216
25.58	15.67	4.443	...	0.7410	30.81	7227

[a] Initial solution was water. [b] Calculated from Series A.

wax to a flared 5-mm glass support tube. The heater and the thermometer were suspended from the calorimeter cover by anchoring three sections of ⅛-in. Inconel tubing in the stuffing boxes and sealing the glass tubes to the Inconel tubes with Apiezon W wax. The heater and thermometer leads passed through these tubes. An inert plastic draft tube was fastened inside the glass helix with platinum wire, and the thermometer was located just inside the draft tube. A glass stirrer was sealed to a ¼-in. stainless-steel tube just below the calorimeter cover with Apiezon W wax so that the impeller blades were only a few millimeters below the tip of the thermometer capsule.

The initial bulk charge of liquid for each experimental run was adjusted to 851 ml at 25°C and weighed. Each incremental addition to the bulk liquid was contained in a thin-walled glass bulb that was suspended from a glass rod inside the hollow stirrer shaft. The bulb was crushed against the bottom of the Dewar flask to start the solution period.

The calorimeter system was calibrated electrically immediately before and after each measurement. The platinum resistance thermometer was calibrated by the National Bureau of Standards. The Wenner potentiometer, Ayrton shunt, and standard resistors used in the energy measurements were calibrated against standard resistors and a potentiometer calibrated by the Redstone Arsenal, Huntsville, Ala., and traceable to the National Bureau of Standards. The defined calorie was taken as 4.1840 absolute joules.

Conventional "normal" and "reverse" readings of the resistance of the platinum resistance thermometer on a Leeds and Northrup G-2 Mueller bridge were made during rating periods to establish heat-leak corrections. Only normal readings were taken during the solution period, and to these were applied both the usual bridge corrections and an adjustment to compensate for the absence of reverse measurements. The observed temperature rise was the difference between the temperatures at the end and at the beginning of the solution period as calculated from linear equations for the rating periods. The correction to the observed temperature for heat leak was calculated by integration by the trapezoidal rule of the heat leak as a function of time from measurements taken at half-minute intervals. The calculation was simplified by the linear relationship of heat leak to temperature over the temperature range of the measurements.

The average temperature during the solution period for each measurement was 25.00° ± 0.04°C, and no temperature corrections were necessary. As the water bath around the calorimeter was held at 28.00° ± 0.02°C, heat leaks were always in the same direction. Raoult's law was applied to correct for the heat of vaporization of water into the vapor space above the calorimeter liquid for each measurement. A correction for the energy of bulb breaking (1.1 ± 0.1 cal) was based on the results of 10 measurements in which bulbs filled with water were broken in the Dewar flask containing water.

Table III. Integral Enthalpies of Solution of Urea Orthophosphate in Water at 25°C

Concentration			
Wt %		Urea orthophosphate molality, m	ΔH, cal/mol urea orthophosphate
H_3PO_4	$CO(NH_2)_2$		
0.20	0.12	0.02	7050
0.49	0.30	0.05	7510
0.96	0.59	0.1	7660
1.90	1.16	0.2	7730
4.54	2.78	0.5	7690
8.46	5.19	1.0	7620
11.88	7.28	1.5	7550
14.89	9.13	2.0	7490
17.56	10.76	2.5	7430
19.94	12.22	3.0	7370
24.02	14.72	4.0	7270
27.37	16.77	5.0	7190
30.18	18.49	6.0	7120
32.19	19.73	6.83[a]	7080

[a] Saturated solution.

Measurements

For enthalpy of solution measurements, the solute was added to the solvent in successive increments; for enthalpy of dilution measurements, the solvent was added to a nearly saturated solution in successive increments.

The observed integral enthalpy of solution of the solute at each final molality was determined by solving the equation

$$\Delta H = \Sigma Q/M \quad (1)$$

where ΔH refers to the observed integral enthalpy of solution in cal/mol; Q, the enthalpy change in calories for each measurement of the series to that molality; M, the moles of solute at that molality; and Σ indicates the summation process. Manipulative details in adjusting the final solution from one experimental run to a weighed fixed volume for the following experimental run entailed a loss of 1–2% of the solution; therefore, linear corrections were made in the accumulated weights of solute and solvent and in the accumulated enthalpy changes for each measurement.

The enthalpy of dilution is equal to the difference between the integral enthalpy of solution in the initial (ΔH_I) and final (ΔH_F) solutions, thus

$$\Delta H_I = \Delta H_F - Q/M \quad (2)$$

For one solution of the enthalpy of dilution series, ΔH_F was calculated from an equation for the integral enthalpy of solution as a function of molality for the corresponding enthalpy of solution series. Solving Equation 2 for each dilution gave the observed integral enthalpy of solution for each measurement of the dilution series. These values of the observed integral enthalpies of solution were combined with those from the corresponding enthalpy of solution series, and equations expressing integral enthalpy of solution as a function of molality were fitted to the observed values by the method of least squares. The equations were extrapolated to the molality of the saturated solutions to determine the integral enthalpies of solution at saturation. The concentration of each saturated solution was calculated by solving simultaneously the first-degree equation of percent solute as a function of percent solvent from pure solvent to pure solute and a similar first-degree equation between two adjacent points on the saturation isotherm that intersects the first equation.

The total weight of solution in the calorimeter, the temperature rise, and the electrical energy input during the second electrical calibration for each measurement made possible a calculation of the heat capacity, s, of each solution at the average temperature of the calibration (25.3° ± 0.3°C). The average water equivalent of the calorimeter was 67.4 ± 0.2 grams, based on 19 determinations.

The initial bulk charge of the liquid for each enthalpy of solution measurement was weighed at room temperature (25.0° ± 0.5°C) in a modified volumetric flask that held 851.3 ± 0.2 ml. From these weights the densities, d, of the solutions were determined.

Enthalpies of Solution

Urea orthophosphate in water. The enthalpies of solution over the concentration range 0–6.53m urea orthophosphate were measured in three series. In Series A, crystalline urea orthophosphate was added to distilled water in successive in-

crements to a final concentration of 5.51*m* urea orthophosphate. Series B was similar to Series A to a final concentration of 0.51*m* urea orthophosphate to more clearly define the peak in the integral enthalpy of solution at about 0.4*m*. Two additional enthalpy of solution measurements were made in which the urea orthophosphate was added to water to more clearly define the slope of the integral enthalpies of solution in the dilute range.

The initial solution of Series C contained 22.74% P_2O_5 and 9.03% N or 6.53*m* urea orthophosphate. Successive increments of distilled water were added to this solution to a final concentration of 4.44*m* urea orthophosphate.

The observed properties of solutions of urea orthophosphate in water are shown in Table II. Equations derived from the observed values are

$$\Delta H = 7809 - 15.2m^{-1},\ m = 0.02 \text{ to } 0.21 \quad (3)$$

and

$$\Delta H = 7770 - 158m + 8.3m^2,\ m = 0.21 \text{ to } 6.53 \quad (4)$$

where ΔH = integral enthalpy of solution (cal mol^{-1}), and m = molality of urea orthophosphate. The observed values fit Equation 3 with a standard deviation of 38 cal mol^{-1} and

Table IV. Observed Properties of Solution of Urea Orthophosphate in 20.37% Urea at 25°C

Solution concentration, Wt %		Molality urea orthophosphate, m	Density, d, g/ml	Specific heat, s, cal/°C/g	Enthalpy of solution	
H_3PO_4	$CO(NH_2)_2$				Q, cal/run	ΔH, cal/mol
			Solution Series D			
0	20.37	0	1.0517	...	...	...
1.15	20.70	0.119	1.0598	0.8726	608.40	5692
2.30	21.02	0.243	1.0676	0.8628	689.82	5995
3.54	21.38	0.383	1.0761	0.8533	779.60	6136
4.81	21.74	0.533	1.0850	0.8430	829.01	6212
5.94	22.06	0.670	1.0926	0.8344	755.02	6259
7.11	22.39	0.819	1.1013	0.8256	807.93	6293
8.19	22.70	0.963	1.1093	0.8194	767.18	6312
9.31	23.02	1.117	1.1164	0.8104	810.72	6326
10.27	23.29	1.257	1.1241	0.8028	722.62	6336
11.28	23.58	1.407	1.1315	0.7955	769.41	6345
12.20	23.84	1.551	1.1389	0.7884	726.70	6351
13.14	24.11	1.702	1.1461	0.7809	752.12	6355
14.00	24.35	1.845	1.1524	0.7742	702.72	6358
14.93	24.62	2.007	1.1595	0.7669	790.04	6361
15.78	24.86	2.160	1.1654	0.7604	731.15	6362
16.70	25.12	2.332	1.1736	0.7533	809.49	6363
17.61	25.38	2.509	1.1807	0.7468	826.07	6364
			Dilution Series E			
29.52	28.56	5.750	1.2800	...	...	6390
28.97	28.41	5.549	1.2750	0.6658	−2.04	6390
28.45	28.26	5.366	1.2701	0.6751	−0.95	6389
27.98	28.13	5.204	1.2660	0.6709	−1.53	6389
27.48	27.99	5.037	1.2615	0.6744	−1.79	6388
27.00	27.86	4.880	1.2578	0.6786	−1.87	6388
26.49	27.72	4.719	1.2541	0.6818	−2.03	6387
26.01	27.59	4.572	1.2503	0.6858	−1.96	6386
25.59	27.47	4.446	1.2468	0.6884	−1.55	6386
25.17	27.35	4.323	1.2432	0.6917	−1.51	6385
24.75	27.24	4.203	1.2395	0.6950	−1.74	6385
24.31	27.11	4.079	1.2358	0.6981	−2.67	6384
23.86	26.99	3.957	1.2321	0.7011	−2.53	6383
23.43	26.87	3.843	1.2280	0.7042	−2.77	6382
23.02	26.76	3.735	1.2255	0.7075	−2.74	6381
22.59	26.64	3.626	1.2213	0.7106	−2.48	6380
22.20	26.53	3.529	1.2184	0.7136	−2.53	6378
21.78	26.41	3.427	1.2149	0.7163	−2.88	6377
21.36	26.30	3.325	1.2117	0.7194	−2.75	6376
20.96	26.19	3.231	1.2080	0.7248	−2.65	6375
20.59	26.08	3.145	1.2055	0.7241	−2.27	6374
20.22	25.98	3.062	1.2024	0.7266	−2.81	6373
19.85	25.88	2.980	1.1992	0.7302	−3.03	6371
19.51	25.78	2.904	1.1964	0.7321	−2.97	6370
19.19	25.69	2.836	1.1933	0.7348	−2.59	6368
18.84	25.60	2.762	1.1911	0.7380	−2.68	6367
18.48	25.50	2.686	1.1883	0.7406	−3.21	6365
18.13	25.40	2.615	1.1856	0.7431	−3.19	6364
17.81	25.31	2.550	...	0.7455	−2.63	6362[a]

[a] Calculated from Series D.

Table V. Integral Enthalpies of Solution of Urea Orthophosphate in 20.37% Urea at 25°C

Concentration			
Wt %		Urea ortho-phosphate molality, m	ΔH, cal/mol urea ortho-phosphate
H_3PO_4	$CO(NH_2)_2$		
0.96	20.64	0.1	5630
1.90	20.91	0.2	5910
4.54	21.66	0.5	6200
8.46	22.78	1.0	6334
11.88	23.75	1.5	6345
14.89	24.60	2.0	6355
17.56	25.36	2.5	6364
19.94	26.04	3.0	6372
22.08	26.65	3.5	6378
24.02	27.20	4.0	6383
25.77	27.70	4.5	6387
27.37	28.15	5.0	6389
28.83	28.57	5.5	6389
30.18	28.95	6.0	6389
30.24	28.97	6.02[a]	6388

[a] Saturated solution.

Equation 4 with a standard deviation of 10 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from the equations are shown in Table III.

Urea orthophosphate in 20.37% urea. The initial solution of Series D was prepared by dissolving recrystallized urea in distilled water. Chemical analysis showed it to contain 9.50% N or 20.37% urea. Crystalline urea orthophosphate was added to this solution in successive increments to a final concentration of 2.51m urea orthophosphate. The initial solution of Series E was prepared by adding urea orthophosphate to 20.37% urea solution. Chemical analysis showed it to contain 13.32% N and 21.38% P_2O_5 or 5.75m urea orthophosphate. Successive increments of 20.37% urea were added to this solution to a final concentration of 2.55m urea orthophosphate.

The observed properties of solutions of urea orthophosphate in 20.37% urea are shown in Table IV. Equations derived from the observed values are

$$\Delta H = 5179 + 5533m - 11578m^2 + 11206m^3 - 4006m^4,\ m < 1 \quad (5)$$

$$\Delta H = 6306 + 30.4m - 2.77m^2,\ m > 1 \quad (6)$$

Table VI. Observed Properties of Solutions of Urea Orthophosphate in 19.99% H_3PO_4 at 25°C

Solution concentration					Enthalpy of solution	
Wt %		Molality urea orthophosphate, m	Density, d, g/ml	Specific heat, s, cal/°C/g	Q, cal/run	ΔH, cal/mol
H_3PO_4	$CO(NH_2)_2$					
			Solution Series F			
19.99	0	0	1.1122	...	...	...
20.80	0.73	0.125	1.1193	0.8402	905.75	7682
21.65	1.50	0.260	1.1277	0.8303	964.97	7658
22.53	2.30	0.407	1.1363	0.8210	1032.66	7639
23.33	3.02	0.546	1.1431	0.8115	955.05	7615
24.05	3.67	0.676	1.1514	0.8032	875.79	7594
24.82	4.37	0.821	1.1588	0.7949	958.11	7573
25.50	4.99	0.955	1.1655	0.7872	871.21	7554
26.21	5.63	1.100	1.1724	0.7800	920.28	7532
26.95	6.29	1.256	1.1803	0.7715	967.40	7505
27.62	6.90	1.405	1.1869	0.7646	918.58	7487
28.26	7.48	1.550	1.1935	0.7577	873.13	7469
28.92	8.07	1.707	1.2003	0.7508	932.57	7450
29.54	8.64	1.861	1.2064	0.7433	892.81	7431
30.09	9.14	2.003	1.2122	0.7374	813.69	7414
30.60	9.60	2.138	1.2180	0.7324	756.48	7398
31.14	10.08	2.285	1.2235	0.7267	809.32	7381
31.69	10.59	2.443	1.2295	0.7212	861.90	7363
32.22	11.06	2.598	1.2355	0.7158	826.51	7346
32.76	11.55	2.762	1.2417	0.7101	861.98	7327
33.23	11.98	2.912	...	0.7064	767.42	7310
			Dilution Series G			
35.95	14.34	3.835	1.2758	...	...	7235
35.57	14.09	3.730	1.2738	0.6828	22.42	7244
35.30	13.85	3.629	1.2704	...	19.89	7252
35.03	13.60	3.528	1.2671	0.6863	19.91	7260
34.75	13.35	3.429	1.2643	0.6906	19.47	7268
34.49	13.12	3.335	1.2613	0.6931	18.37	7275
34.20	12.86	3.235	1.2581	0.6973	20.17	7284
33.93	12.60	3.140	1.2549	0.6989	19.01	7292
33.66	12.36	3.050	1.2523	0.7013	17.83	7300
33.41	12.14	2.971	1.2499	0.6963	15.44	7307
33.16	11.91	2.889	...	0.7068	16.20	7315[a]

[a] Calculated from Series F.

The observed values fit Equation 5 with a standard deviation of 10 cal mol^{-1} and Equation 6 with a standard deviation of 3 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from the equations are shown in Table V.

Urea orthophosphate in 19.99% H_3PO_4. In Series F, urea orthophosphate was added to 19.99% H_3PO_4 in successive increments to a final concentration of 2.91*m* urea orthophosphate. The initial solution of Series G was prepared by adding urea orthophosphate to 19.99% H_3PO_4. Chemical analysis showed it to contain 6.69% N and 26.04% P_2O_5 or 3.84*m* urea orthophosphate. Successive increments of 19.99% H_3PO_4 were added to this solution to a final concentration of 2.89*m* urea orthophosphate.

The observed properties of solutions of urea orthophosphate in 19.99% H_3PO_4 are shown in Table VI. The equation derived from the observed values is

$$\Delta H = 7704 - 171.0m + 12.72m^2 \quad (7)$$

The observed values fit Equation 7 with a standard deviation of 2 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from Equation 7 are shown in Table VII.

Urea in 49.91% H_3PO_4. In Series H and I, crystalline urea was added to 49.91% H_3PO_4 in successive increments to final concentrations of 1.73 and 1.65*m* urea, respectively.

The observed properties of solutions of urea in 49.91% H_3PO_4 are shown in Table VIII. The equation derived from the observed values is

$$\Delta H = 613 + 270.3m_1 - 30.2m_1^2 \quad (8)$$

Table VII. Integral Enthalpies of Solution of Urea Orthophosphate in 19.99% H_3PO_4 at 25°C

Concentration			
Wt %		Urea orthophosphate molality, *m*	ΔH, cal/mol urea orthophosphate
H_3PO_4	$CO(NH_2)_2$		
20.64	0.59	0.1	7687
21.28	1.16	0.2	7670
23.07	2.78	0.5	7622
25.72	5.19	1.0	7546
28.04	7.28	1.5	7476
30.08	9.13	2.0	7413
31.89	10.76	2.5	7356
33.50	12.22	3.0	7306
34.95	13.53	3.5	7261
36.23	14.69	3.99[a]	7224

[a] Saturated solution.

Table IX. Integral Enthalpies of Solution of Urea in 49.91% H_3PO_4 at 25°C

Concentration			
Wt %		Urea molality, *m*	ΔH, cal/mol urea
H_3PO_4	$CO(NH_2)_2$		
49.61	0.60	0.1	639
49.32	1.19	0.2	665
48.45	2.92	0.5	740
47.08	5.67	1.0	853
45.79	8.26	1.5	950
45.19	9.45	1.74[a]	991

[a] Saturated solution.

Table VIII. Observed Properties of Solutions of Urea in 49.91% H_3PO_4 at 25°C

Solution concentration						
Wt %		Urea molality, *m*	Density, *d*, g/ml	Specific heat, *s*, cal/°C/g	Enthalpy of solution	
H_3PO_4	$CO(NH_2)_2$				*Q*, cal/run	ΔH, cal/mol
			Solution Series H			
49.91	0	0	1.3296	...	...	...
49.38	1.06	0.179	1.3296	0.6416	134.22	664
48.72	2.39	0.407	1.3303	0.6396	198.12	726
48.24	3.35	0.576	1.3308	0.6408	156.25	759
47.77	4.29	0.747	1.3310	0.6410	169.30	792
47.34	5.14	0.902	1.3293	0.6406	166.86	826
46.89	6.04	1.071	1.3310	0.6403	188.28	860
46.41	7.01	1.256	1.3308	0.6397	218.40	897
45.95	7.94	1.436	1.3320	0.6390	223.00	932
45.49	8.86	1.619	1.3322	0.6385	235.50	966
45.21	9.42	1.732	...	0.6385	150.08	987
			Solution Series I			
49.91	0	0	1.3295	...	...	...
49.65	0.53	0.088	1.3288	0.6418	62.60	626
49.13	1.57	0.266	1.3297	0.6413	142.47	684
48.64	2.53	0.433	1.3300	0.6409	147.04	725
48.17	3.49	0.601	1.3303	0.6408	161.87	766
47.72	4.39	0.765	1.3300	0.6401	168.46	804
47.23	5.36	0.944	1.3310	0.6400	196.06	844
46.72	6.39	1.136	1.3314	0.6394	223.73	885
46.28	7.27	1.306	1.3310	0.6399	205.21	918
45.81	8.22	1.490	1.3316	0.6391	236.27	955
45.42	9.00	1.646	...	0.6400	206.63	986

Table X. Observed Properties of Solutions of Urea in 60.12% H_3PO_4 at 25°C

Solution concentration					Enthalpy of solution	
Wt %		Urea	Density, d,	Specific heat, s,		
H_3PO_4	$CO(NH_2)_2$	molality, m	g/ml	cal/°C/g	Q, cal/run	ΔH, cal/mol
			Solution Series J			
60.12	0	0	1.4216	...	...	...
59.55	0.95	0.160	1.4212	0.5765	−89.22	−461.6
59.04	1.80	0.305	1.4193	0.5762	−63.54	−415.5
58.48	2.73	0.468	1.4181	0.5767	−52.13	−365.6
57.89	3.71	0.642	1.4182	0.5767	−34.56	−312.2
57.31	4.67	0.816	1.4186	0.5774	−13.41	−259.7
56.76	5.59	0.986	1.4179	0.5775	6.32	−209.3
56.17	6.57	1.170	...	0.5783	26.21	−156.6
55.64	7.44	1.339	...	0.5776	41.73	−108.9

Table XI. Integral Enthalpies of Solution of Urea in 60.12% H_3PO_4 at 25°C

Concentration			
Wt %		Urea	ΔH, cal/mol
H_3PO_4	$CO(NH_2)_2$	molality, m	urea
59.41	1.19	0.2	−448.9
58.71	2.35	0.4	−386.1
58.03	3.48	0.6	−324.6
57.36	4.58	0.8	−264.5
56.71	5.67	1.0	−205.6
56.08	6.72	1.2	−148.1
55.45	7.77	1.40[a]	−91.1

[a] Saturated solution.

where m_1 = molality urea. The observed values fit Equation 8 with a standard deviation of 6 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from Equation 8 are shown in Table IX.

Urea in 60.12% H_3PO_4. In Series J, crystalline urea was added to 60.12% H_3PO_4 in successive increments to a final concentration of 1.34m urea.

The observed properties of solutions of urea in 60.12% H_3PO_4 are shown in Table X. The equation derived from the observed values is

$$\Delta H = -513.0 + 323.9m_1 - 16.44m_1^2 \quad (9)$$

The observed values fit Equation 9 with a standard deviation of 0.3 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from Equation 9 are shown in Table XI.

Urea in 75.03% H_3PO_4. In Series K crystalline urea was added to 75.03% H_3PO_4 in successive increments to a final concentration of 0.61m urea. The initial solution of Series L was prepared by adding urea to 75.03% H_3PO_4. Chemical analysis showed it to contain 50.41% N and 3.36% P_2O_5 or 1.29m urea. Successive increments of 75.03% H_3PO_4 were added to this solution to a final concentration of 0.65m urea.

The observed properties of solutions of urea in 75.03% H_3PO_4 are shown in Table XII. The equation derived from the observed values is

$$\Delta H = -2805 + 494m_1 - 49m_1^2 \quad (10)$$

The observed values fit the equation with a standard deviation of 5 cal mol^{-1}. Integral enthalpies of solution at even values of molality and at saturation as calculated from Equation 10 are shown in Table XIII.

Enthalpy of Formation of Urea Orthophosphate

The standard enthalpy of formation of urea orthophosphate was determined from the enthalpy of Reaction 11 (ΔH_{11}) at 25°C

$$CO(NH_2)_2(c) + H_3PO_4 \cdot 1.00H_2O(l) = CO(NH_2)_2 \cdot H_3PO_4(c) + 1.00H_2O(l) \quad (11)$$

in combination with published values for the enthalpy of formation of $CO(NH_2)_2$ and $H_3PO_4 \cdot 1.00H_2O$, the enthalpy of dilution of phosphoric acid solutions, and the integral enthalpy of solution of urea orthophosphate in H_2O at 25°C.

The phosphoric acid solution contained 61.15% P_2O_5. The calorimetric solvent was distilled water.

The enthalpy of reaction for Equation 11 was determined by the scheme:

Ampul $H_3PO_4 \cdot 1.00H_2O$ + solvent = solution A $\quad \Delta H_x$

Ampul $CO(NH_2)_2$ + solution A = solution B $\quad \Delta H_y$

Ampul $CO(NH_2)_2 \cdot H_3PO_4$ + solvent = solution B $\quad \Delta H_z$

$$\Delta H_{11} = \Delta H_x + \Delta H_y - \Delta H_z$$

The enthalpies of solution of ampuls of urea in the solvent to which the stoichiometric amounts of $H_3PO_4 \cdot 1.00H_2O$ had been added, ΔH_y; the enthalpies of solution of the stoichiometric amounts of $H_3PO_4 \cdot 1.00H_2O$, ΔH_x, calculated from the data of Egan and Luff (*2*); and the enthalpies of solution of the stoichiometric amount of $CO(NH_2)_2 \cdot H_3PO_4$, ΔH_z, calculated from Equation 4; and the enthalpy of Reaction 11 are listed in Table XIV.

The standard enthalpies of formation from the elements at 25°C (*4*) are $H_3PO_4 \cdot 1.00H_2O$, −304.69 ± 0.1; and $CO(NH_2)_2$, −79.56 ± 0.1 kcal mol^{-1}. Substitution of these values, along with the enthalpy of reaction of Equation 11 (−7799 cal), in the equation

$$\Delta H_f^\circ CO(NH_2)_2 \cdot H_3PO_4(c) = \Delta H_f^\circ H_3PO_4 \cdot 1.00H_2O(l) + \Delta H_f^\circ CO(NH_2)_2(c) + \Delta H_R \quad (12)$$

gives −392.05 ± 0.14 kcal mol^{-1} for the standard enthalpy of formation of $CO(NH_2)_2 \cdot H_3PO_4$ at 25°C.

Integral Enthalpy of Solution at Saturation of Urea Orthophosphate in Concentrated H_3PO_4 Solutions

Attempts to determine the enthalpy of solution of urea orthophosphate in 40% H_3PO_4 were unsuccessful because of the small temperature change and the low dissolution rate in the solution calorimeter. The integral enthalpy of solution at saturation of urea orthophosphate in more concentrated solutions of H_3PO_4 can be determined by the scheme

Table XII. Observed Properties of Solutions of Urea in 75.03% H_3PO_4 at 25°C

Solution concentration					Enthalpy of solution	
Wt %		Urea	Density, d,	Specific heat, s,		
H_3PO_4	$CO(NH_2)_2$	molality, m	g/ml	cal/°C/g	Q, cal/run	ΔH, cal/mol
			Solution Series K			
75.03	0	0	1.5701	...	...	...
74.35	0.91	0.153	1.5673	0.4966	−560.46	−2746
73.65	1.84	0.312	...	0.4959	−535.46	−2646
73.03	2.67	0.457	...	0.4960	−455.47	−2576
72.38	3.54	0.610	...	0.4961	−460.35	−2513
			Dilution Series L			
69.60	7.20	1.292	1.5518	...	...	−2242
69.75	7.03	1.259	1.5525	0.4998	−22.18	−2256
69.88	6.87	1.227	1.5530	0.4998	−20.55	−2269
69.99	6.72	1.200	1.5529	0.4998	−17.61	−2281
70.09	6.58	1.172	1.5537	0.4994	−17.14	−2292
70.21	6.42	1.143	1.5546	0.4995	−17.75	−2305
70.32	6.28	1.116	1.5555	0.4990	−15.58	−2316
70.42	6.14	1.090	1.5550	0.4991	−14.27	−2326
70.53	6.00	1.063	1.5553	0.4990	−15.39	−2338
70.63	5.86	1.037	1.5554	0.4987	−13.76	−2348
70.73	5.73	1.012	1.5556	0.4987	−12.89	−2358
70.83	5.60	0.987	1.5558	0.4986	−12.49	−2368
70.93	5.47	0.963	1.5567	0.4985	−12.34	−2378
71.02	5.34	0.939	1.5568	0.4984	−11.57	−2388
71.11	5.22	0.917	1.5569	0.4982	−10.56	−2397
71.20	5.10	0.895	1.5575	0.4982	−9.90	−2405
71.29	4.99	0.875	1.5582	0.4981	−8.91	−2413
71.37	4.88	0.854	1.5580	0.4980	−9.28	−2422
71.45	4.77	0.834	1.5584	0.4979	−8.29	−2429
71.53	4.67	0.816	1.5586	0.4981	−7.18	−2436
71.60	4.57	0.797	1.5584	0.4977	−7.00	−2443
71.68	4.46	0.778	1.5590	0.4979	−8.22	−2451
71.75	4.37	0.760	1.5587	0.4981	−7.12	−2458
71.82	4.28	0.744	1.5590	0.4979	−5.95	−2465
71.89	4.19	0.727	1.5593	0.4976	−6.02	−2471
71.96	4.10	0.712	1.5595	0.4978	−5.81	−2477
72.02	4.01	0.695	1.5588	...	−5.69	−2484
72.08	3.93	0.680	1.5598	0.4976	−5.08	−2489
72.15	3.84	0.665	1.5592	0.4964	−4.67	−2495
72.22	3.75	0.648	...	0.4976	−5.53	−2501[a]

[a] Calculated from Series K.

Table XIII. Integral Enthalpies of Solution of Urea in 75.03% H_3PO_4 at 25°C

Concentration			
Wt %		Urea	ΔH, cal/mol
H_3PO_4	$CO(NH_2)_2$	molality, m	urea
74.14	1.19	0.2	−2708
73.27	2.35	0.4	−2615
72.42	3.48	0.6	−2526
71.59	4.58	0.8	−2441
70.78	5.67	1.0	−2360
69.99	6.72	1.2	−2283
69.48	7.40	1.33[a]	−2234

[a] Saturated solution.

$$H_3PO_4 \cdot aH_2O + bCO(NH_2)_2 = H_3PO_4 \cdot aH_2O \cdot bCO(NH_2)_2 \quad (13)$$

$$H_3PO_4 + aH_2O = H_3PO_4 \cdot aH_2O \quad (14)$$

$$H_3PO_4 + a/(1-b)H_2O = H_3PO_4 \cdot a/(1-b)H_2O \quad (15)$$

$$H_3PO_4 + CO(NH_2)_2 = CO(NH_2)_2 \cdot H_3PO_4 \quad (16)$$

$$1/b\{(13) + (14) - (1-b)(15) - b(16)\} = (17)$$
$$\{(1-b)/b\}\{H_3PO_4 \cdot a/(1-b)H_2O\} + CO(NH_2)_2 \cdot H_3PO_4 =$$
$$1/b\{H_3PO_4 \cdot aH_2O \cdot bCO(NH_2)_2\} \quad (17)$$

The value for a can be calculated from the concentration of the phosphoric acid solution to which the urea is to be added, and b can be calculated from the composition of the phosphoric acid solution saturated with urea. The enthalpy of Reaction 13, ΔH_{13}, can be determined from the integral enthalpy of solution of urea in the phosphoric acid to saturation. The value for $a/(1-b)$ can be calculated from a and b. The formula $H_3PO_4 \cdot a/(1-b)H_2O$ gives the concentration of phosphoric acid to which urea phosphate must be added to obtain the saturated solution of the third term of Equation 13. A linear equation for percent phosphoric acid as a function of percent urea from the composition of urea phosphate through the composition of the saturated solution of Equation 13 extrapolated to 0% urea also gives the concentration of phosphoric acid corresponding to $H_3PO_4 \cdot a/(1-b)H_2O$.

The enthalpies of Reactions 14 and 15, ΔH_{14} and ΔH_{15}, respectively, can be calculated from the data of Luff et al. (*3*) and Egan and Luff (*2*). The enthalpy of Reaction 16, ΔH_{16},

Table XIV. Observed Enthalpies of Reaction for Equation 11

	Run no.				
	1	2	3	4	5
Solvent wt, grams	848.0695	848.0445	848.2818	848.3949	848.1967
Urea wt, grams	12.09067	12.43737	12.91616	13.26962	13.92902
Stoich. $H_3PO_4 \cdot 1.00H_2O$, grams	23.03708	24.03708	24.96821	25.64553	26.91992
Molality H_3PO_4, final soln	0.2364	0.2431	0.2524	0.2592	0.2721
φ_L H_3PO_4,[a] final soln cal mol^{-1}	180	182	186	188	193
ΔH_1, cal mol^{-1}	−3571	−3569	−3565	−3563	−3558
Stoich. $CO(NH_2)_2 \cdot H_3PO_4$, grams	31.81950	32.73192	33.99987	34.92219	36.65756
Molality $CO(NH_2)_2 \cdot H_3PO_4$, final soln	0.2364	0.2431	0.2524	0.2592	0.2721
ΔH_3, cal mol^{-1}	7733	7732	7730	7729	7727
ΔH_2, cal mol^{-1}	3505	3501	3497	3495	3486
ΔH_R, Equation 11	−7799	−7800	−7798	−7797	−7799
	Average ΔH_R = −7799 cal				

[a] φ_L ($H_3PO_4 \cdot 1.00H_2O$) = 3751 cal mol^{-1}.

Table XV. Calculation of Integral Enthalpies of Solution to Saturation of Urea Phosphate in Phosphoric Acid Solutions at 25°C

	% H_3PO_4 ~ $H_3PO_4 \cdot aH_2O$		
	49.91	60.12	75.03
ΔH_{T_1}, cal/mol[a]	991	−91.1	−2234
a	5.46	3.61	1.81
b	0.34	0.23	0.17
ΔH_{13}, cal	337	−21	−380
ΔH_{14}, cal	−4399	−3918	−2961
$a/(1-b)$	8.29	4.68	2.19
	% H_3PO_4 ~ $H_3PO_4 \cdot a/(1-b)H_2O$		
	39.63	53.77	71.29
ΔH_{15}, cal	−4780	−4230	−3235
ΔH_{16}, cal	−9948	−9948	−9948
ΔH_{17}, cal[b]	7280	6983	6089

[a] Integral enthalpy of solution of urea at saturation in $H_3PO_4 \cdot aH_2O$. [b] Integral enthalpy of solution of urea phosphate at saturation in $H_3PO_4 \cdot a/(1-b)H_2O$.

Table XVI. Enthalpy of Producing Crystalline Urea Orthophosphate from Equimolar Amounts of Urea and Phosphoric Acid at 25°C

% H_3PO_4	x, Eq. 21	ΔH_{19}, cal	d, Eq. 21	ΔH_{20}, cal	ΔH_{21}, cal	ΔH_c, cal/g
			Satd soln Q, Figure 1			
100	0	−9948	0	0	−9948	−62.94
95	0.2863	−8898	0.0352	250	−8648	−56.72
90	0.6044	−8228	0.0744	527	−7701	−52.64
85	0.9599	−7855	0.1182	837	−7018	−50.36
80	1.3599	−7393	0.1674	1185	−6208	−47.17
75	1.8132	−6985	0.2232	1580	−5405	−44.02
70	2.3312	−6624	0.2870	2032	−4592	−40.75
65	2.9290	−6306	0.3605	2553	−3753	−37.14
60	3.6264	−6024	0.4464	3161	−2863	−32.73
55	4.4505	−5775	0.5479	3879	−1896	−26.53
50	5.4396	−5553	0.6696	4741	−813	−15.55
45	6.6483	−5356	0.8185	5795	439	15.29

(−9948 cal) can be calculated by adding the enthalpy of dilution from H_3PO_4 to $H_3PO_4 \cdot 1.00H_2O$ (*2, 3*) (−2149 cal) to the enthalpy of Reaction 11 (−7799 cal). Combining ΔH_{13} through ΔH_{16} in the manner indicated will give the enthalpy of Reaction 17, ΔH_{17}, the integral enthalpy of solution of 1 mole of urea orthophosphate in sufficient phosphoric acid of the concentration expressed in the first term of Equation 17 to form a saturated solution.

Values for the integral enthalpies of solution to saturation (ΔH_{T_1}) of urea in 49.91, 60.12, and 75.05% H_3PO_4 along with the calculations of the integral enthalpies of solution to saturation (ΔH_{T_2}) of urea phosphate in 39.63, 53.77, and 71.29% H_3PO_4 by use of Equations 13–17 are summarized in Table XV.

Enthalpy of Crystallization of Urea Orthophosphate from Urea and Phosphoric Acid Solutions at 25°C

Subtracting the enthalpy of Reaction 18 (ΔH_{18})

$$H_3PO_4 \cdot 1.00H_2O + (x-1)H_2O = H_3PO_4 \cdot xH_2O \quad (18)$$

from ΔH_{11} (−7799 cal) gives the enthalpy of Reaction 19 (ΔH_{19}).

$$CO(NH_2)_2(c) + H_3PO_4 \cdot xH_2O(l) = CO(NH_2)_2 \cdot H_3PO_4(c) + xH_2O(l) \quad (19)$$

The value of ΔH_{18} was calculated from published data (*2, 3*).

Part of the urea orthophosphate remains in the saturated solution so

$$xH_2O(l) + d\{CO(NH_2)_2 \cdot H_3PO_4\}(c) = dH_3PO_4 \cdot dCO(NH_2)_2 \cdot xH_2O \quad (20)$$

where d is the number of moles of urea orthophosphate needed to saturate the water from the phosphoric acid solution (see Table III). The value of ΔH_{20} was calculated from the integral enthalpy of solution at saturation of urea orthophosphate in water (7080 cal/mol).

Adding ΔH_{20} to ΔH_{19} gives ΔH_{21}, the enthalpy of Reaction 21

$$CO(NH_2)_2(c) + H_3PO_4 \cdot xH_2O(l) = (1-d)\{CO(NH_2)_2 \cdot H_3PO_4\}(c) + dH_3PO_4 \cdot dCO(NH_2)_2 \cdot xH_2O \quad (21)$$

and $\Delta H_{21}/158.05114(1-d)$ gives the enthalpy of producing crystalline urea orthophosphate (ΔH_c) in calories per gram

from equimolar amounts of urea and phosphoric acid. Values of x, ΔH_{19}, d, ΔH_{20}, ΔH_{21}, and ΔH_c for different concentrations of phosphoric acid are listed in Table XVI.

Enthalpies of producing crystalline urea orthophosphate from solutions of phosphoric acid and excess urea were determined by adding the enthalpies of Reactions 22 (ΔH_{22})

$$xH_2O + d\{CO(NH_2)_2(c) = d\{CO(NH_2)_2 \cdot xH_2O \quad (22)$$

and 23 (ΔH_{23})

$$d\{CO(NH_2)_2 \cdot xH_2O + e\{CO(NH_2)_2 \cdot H_3PO_4\}(c) = (d + e)CO(NH_2)_2 \cdot eH_3PO_4 \cdot xH_2O \quad (23)$$

Table XVII. Enthalpy of Producing Crystalline Urea Orthophosphate from Phosphoric Acid and Excess Urea at 25°C

% H_3PO_4	x, Eq. 24	ΔH_{19}, cal	d, Eq. 24	ΔH_{22}, cal	e, Eq. 24	ΔH_{23}, cal	ΔH_{24}, cal	ΔH_c, cal/g
				Satd soln R, Figure 1				
100	0	−9948	0	0	0	0	−9948	−62.94
95	0.2863	−8898	0.0220	74	0.0390	249	−8574	−56.45
90	0.6044	−8228	0.0464	157	0.0824	526	−7545	−52.02
85	0.9599	−7855	0.0737	249	0.1309	836	−6770	−49.28
80	1.3599	−7393	0.1044	353	0.1854	1185	−5856	−45.48
75	1.8132	−6985	0.1391	471	0.2472	1579	−4935	−41.48
70	2.3312	−6624	0.1789	605	0.3179	2031	−3988	−36.99
65	2.9290	−6306	0.2248	760	0.3994	2551	−2995	−31.55
60	3.6264	−6024	0.2783	941	0.4945	3159	−1924	−24.08
55	4.4505	−5775	0.3415	1155	0.6069	3877	−743	−11.96
50	5.4396	−5553	0.4174	1412	0.7417	4738	597	14.62
45	6.6483	−5356	0.5102	1725	0.9066	5791	2161	146.31

Table XVIII. Enthalpy of Producing Crystalline Urea Orthophosphate from Urea and Excess Phosphoric Acid at 25°C

% H_3PO_4	x, Eq. 27	ΔH_{19}, cal	d, Eq. 27	ΔH_{25}, cal	e, Eq. 27	ΔH_{26}, cal	ΔH_{27}, cal	ΔH_c, cal/g
				Satd soln P, Figure 1				
100	0	−9948	0	0	0	0	−9948	−62.94
95	0.2863	−8898	0.0133	−57	0.0260	188	−8767	−56.95
90	0.6044	−8228	0.0286	−102	0.0558	403	−7927	−53.12
85	0.9599	−7855	0.0461	−148	0.0901	651	−7352	−51.12
80	1.3599	−7393	0.0666	−183	0.1302	941	−6635	−48.27
75	1.8132	−6985	0.0908	−213	0.1776	1283	−5915	−45.50
70	2.3312	−6624	0.1199	−237	0.2344	1693	−5168	−42.71
65	2.9290	−6306	0.1554	−258	0.3038	2195	−4369	−39.71
60	3.6264	−6024	0.1998	−276	0.3906	2822	−3478	−36.11
55	4.4505	−5775	0.2569	−290	0.5022	3628	−2438	−30.98
50	5.4396	−5553	0.3331	−302	0.6510	4702	−1153	−20.90
45	6.6483	−5356	0.4396	−313	0.8592	6207	538	24.19
				Satd soln O, Figure 1				
100	0	−9948	0	0	0	0	−9948	−62.94
95	0.2863	−8898	0.0358	−134	0.0185	135	−8897	−57.35
90	0.6044	−8228	0.0787	−241	0.0407	296	−8173	−53.91
85	0.9599	−7855	0.1310	−353	0.0678	494	−7715	−52.36
80	1.3599	−7393	0.1963	−439	0.1016	740	−7092	−49.95
75	1.8132	−6985	0.2801	−511	0.1449	1055	−6441	−47.66
70	2.3312	−6624	0.3915	−574	0.2026	1475	−5723	−45.41
65	2.9290	−6306	0.5467	−627	0.2829	2059	−4874	−43.00
60	3.6264	−6024	0.7782	−673	0.4026	2931	−3766	−39.89
55	4.4505	−5775	1.1603	−715	0.6003	4370	−2119	−33.55
50	5.4396	−5553	1.9108	−753	0.9887	7197	892	497.47
				Satd soln N, Figure 1				
100	0	−9948	0	0	0	0	−9948	−62.94
95	0.2863	−8898	0.0652	−207	0.0193	135	−8971	−57.87
90	0.6044	−8228	0.1484	−373	0.0439	306	−8294	−54.89
85	0.9599	−7855	0.2583	−552	0.0764	533	−7874	−53.94
80	1.3599	−7393	0.4100	−687	0.1212	846	−7233	−52.08
75	1.8132	−6985	0.6332	−802	0.1872	1307	−6480	−50.44
70	2.3312	−6624	0.9939	−900	0.2938	2052	−5473	−49.03
65	2.9290	−6306	1.6758	−985	0.4955	3460	−3832	−48.05
				Satd soln M, Figure 1				
100	0	−9948	0	0	0	0	−9948	−62.94
95	0.2863	−8898	0.1503	−328	0.0316	193	−9034	−59.03
90	0.6044	−8228	0.3810	−577	0.0802	488	−8317	−57.21
85	0.9599	−7855	0.7800	−891	0.1642	1000	−7746	−58.64
80	1.3599	−7393	1.6370	−1113	0.3446	2098	−6408	−61.86

to ΔH_{19} to give the enthalpy of Reaction 24 (ΔH_{24})

$$(1 + d)CO(NH_2)_2 + H_3PO_4 \cdot xH_2O = (1 - e)\{CO(NH_2)_2 \cdot H_3PO_4\}(c) + (d + e)CO(NH_2)_2 \cdot eH_3PO_4 \cdot xH_2O \quad (24)$$

The value d was calculated to make the third term of Equation 22 equivalent to 20.37% urea, and e was calculated to make the third term of Equation 23 equivalent to the saturated solution given in Table V. The value of ΔH_{22} was calculated from published values for the enthalpy of solution of urea (*1*), and ΔH_{23} was calculated from the integral enthalpy of solution at saturation of urea orthophosphate in 20.37% urea solution (6388 cal/mol). The expression $\Delta H_{24}/\{158.05114\ (1 - e)\}$ gives the enthalpy of crystallization of urea orthophosphate in calories per gram under the conditions of Equation 24. Values of x, ΔH_{19}, d, ΔH_{22}, e, ΔH_{23}, ΔH_{24}, and ΔH_c for different concentrations of phosphoric acid are listed in Table XVII.

Table XIX. Material Balance and Enthalpy Change in Addition of Urea to 1000 Grams of Phosphoric Acid Solution

			Satd soln, wt %		Reactants in soln, %		
% H_3PO_4	Wt urea, g	Wt urea orthophosphate, g	H_3PO_4	Urea	H_3PO_4	Urea	$-\Delta H_c$, kcal
95	506	1290	69.5	7.4	15.8	3.2	76.13
	547	1411	55.4	7.8	7.9	1.9	81.64
	562	1452	45.2	9.4	5.2	1.9	83.27
	575	1473	36.2	14.7	3.9	2.6	83.87
	582	1478	32.2	19.7	3.5	3.5	83.84
	595	1472	30.2	29.0	3.9	6.0	83.12
90	399	967	69.5	7.4	33.4	8.0	55.31
	480	1209	55.4	7.8	16.7	4.4	66.33
	511	1291	45.2	9.4	11.1	4.1	69.59
	536	1333	36.2	14.7	8.2	5.6	70.78
	552	1344	32.2	19.7	7.4	7.4	70.73
	577	1332	30.2	29.0	8.2	12.3	69.29
85	293	644	69.5	7.4	53.0	16.4	37.75
	414	1006	55.4	7.8	26.6	7.6	54.28
	461	1130	45.2	9.4	17.6	6.8	59.16
	498	1192	36.2	14.7	13.0	9.0	60.96
	521	1209	32.2	19.7	11.8	11.8	60.88
	559	1191	30.2	29.0	13.1	19.1	58.72
80	186	321	69.5	7.4	75.1	34.5	19.84
	348	804	55.4	7.8	37.7	12.1	41.88
	410	969	45.2	9.4	24.9	10.2	48.40
	460	1052	36.2	14.7	18.5	13.0	50.79
	490	1074	32.2	19.7	16.7	16.7	50.68
	541	1051	30.2	29.0	18.5	26.2	47.80
75	281	602	55.4	7.8	50.2	18.7	30.37
	359	808	45.2	9.4	33.2	14.5	38.51
	421	912	36.2	14.7	24.6	17.8	41.50
	460	940	32.2	19.7	22.3	22.3	41.36
	524	911	30.2	29.0	24.7	33.9	37.77
70	215	400	55.4	7.8	64.6	29.4	19.60
	308	647	45.2	9.4	42.7	20.3	29.38
	383	772	36.2	14.7	31.6	23.4	32.96
	429	805	32.2	19.7	28.7	28.7	32.80
	506	770	30.2	29.0	31.8	42.1	28.49
65	149	198	55.4	7.8	81.1	49.5	9.50
	258	486	45.2	9.4	53.6	28.3	20.90
	345	632	36.2	14.7	39.7	30.4	25.08
	398	670	32.2	19.7	36.1	36.1	24.89
	488	630	30.2	29.0	39.9	51.0	19.86
60	207	325	45.2	9.4	66.4	40.3	12.97
	306	491	36.2	14.7	49.2	39.1	17.75
	368	536	32.2	19.7	44.6	44.6	17.53
	470	489	30.2	29.0	49.4	60.5	11.78
55	156	164	45.2	9.4	81.5	60.0	5.51
	268	351	36.2	14.7	60.4	50.2	10.88
	337	401	32.2	19.7	54.8	54.8	10.64
	452	349	30.2	29.0	60.7	70.7	4.17
50	105	3	45.2	9.4	99.6	98.9	−1.56
	230	211	36.2	14.7	73.8	65.1	4.41
	306	266	32.2	19.7	67.0	67.0	4.14
	434	208	30.2	29.0	74.2	81.8	−3.05
45	192	71	36.2	14.7	90.2	85.9	−1.72
	276	132	32.2	19.7	81.8	81.8	−2.02
	416	68	30.2	29.0	90.7	93.8	−9.92

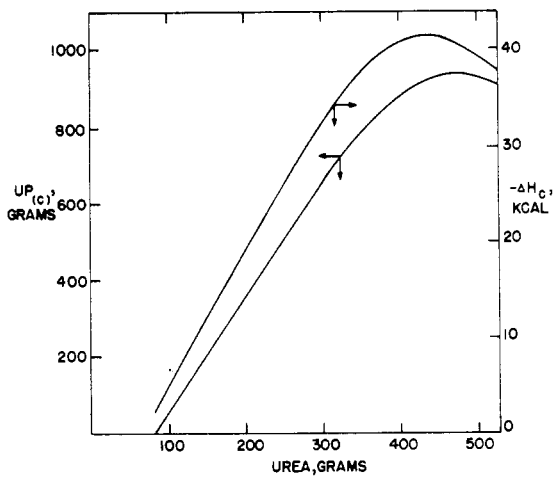

Figure 2. Enthalpy change and urea orthophosphate crystallized when urea is added to 1000 grams of 75% H_3PO_4

Table XX. Heat Capacity, cal $°C^{-1}$ g^{-1}, of Solutions Containing Phosphoric Acid and Urea at 25°C

	% Urea					
% H_3PO_4	0	5	10	15	20	25
0	1.000	0.971	0.943	0.915	0.887	
5	0.961	0.933	0.906	0.880	0.853	
10	0.923	0.896	0.870	0.845	0.820	
15	0.885	0.860	0.835	0.811	0.787	
20	0.848	0.824	0.801	0.778	0.755	0.733
25	0.812	0.789	0.767	0.745	0.724	0.703
30	0.776	0.755	0.734	0.713	0.693	0.673
35	0.742	0.721	0.702			
40	0.707	0.688	0.670			
45	0.674	0.656				
50	0.641	0.625				
55	0.609	0.594				
60	0.578	0.564				
65	0.547	0.534				
70	0.517	0.505				

Table XXI. Density, g ml^{-1}, of Solutions Containing Phosphoric Acid and Urea at 25°C

	% Urea					
% H_3PO_4	0	5	10	15	20	25
0	1.001	1.015	1.028	1.041	1.054	
5	1.025	1.040	1.055	1.069	1.083	
10	1.052	1.067	1.083	1.098	1.113	
15	1.080	1.097	1.113	1.129	1.145	
20	1.110	1.128	1.145	1.162	1.179	1.196
25	1.142	1.161	1.179	1.198	1.215	1.233
30	1.176	1.196	1.215	1.234	1.253	1.272
35	1.212	1.233	1.253			
40	1.250	1.271	1.293			
45	1.289	1.312				
50	1.331	1.355				
55	1.374	1.399				
60	1.420	1.445				
65	1.467	1.494				
70	1.516	1.544				

Enthalpies of producing crystalline urea orthophosphate from urea and excess phosphoric acid were determined by adding the enthalpies of Reactions 25 (ΔH_{25})

$$d(H_3PO_4 \cdot xH_2O) + xH_2O = dH_3PO_4 \cdot (x + dx)H_2O \quad (25)$$

and 26 (ΔH_{26})

$$dH_3PO_4 \cdot (x + dx)H_2O + e\{CO(NH_2)_2 \cdot H_3PO_4\}(c) = (d + e)H_3PO_4 \cdot eCO(NH_2)_2 \cdot (x + dx)H_2O \quad (26)$$

to ΔH_{19} to give the enthalpy of Reaction 27 (ΔH_{27})

$$CO(NH_2)_2 + (1 + d)\{H_3PO_4 \cdot xH_2O\} = (1 - e)\{CO(NH_2)_2 \cdot H_3PO_4\}(c) + (d + e)H_3PO_4 \cdot eCO(NH_2)_2 \cdot (x + dx)H_2O \quad (27)$$

The value d was calculated to give the phosphoric acid concentration of the third term of Equation 25 in which the integral enthalpies of solution of urea orthophosphate had been determined (19.99%, 39.63%, 53.77%, and 71.29% H_3PO_4, respectively), and e was calculated to make the third term of Equation 26 equivalent to the corresponding saturated solutions given in Tables VII, IX, XI, and XIII. The value ΔH_{25} was calculated from published values for the enthalpy of dilution of phosphoric acid solutions (*2*, *3*), and ΔH_{26} was calculated from the integral enthalpy of solution at saturation of urea orthophosphate in 19.99%, 39.63%, 53.77%, and 71.29% H_3PO_4. Values of x, ΔH_{19}, d, ΔH_{25}, e, ΔH_{26}, ΔH_{29}, and ΔH_c under conditions of excess H_3PO_4 described for different concentrations of phosphoric acid are listed in Table XVIII.

Calculations of material balance and enthalpy change based on the addition of urea to 1000 grams of various concentrations of phosphoric acid solutions to produce crystalline urea orthophosphate are listed in Table XIX. Values for the integral enthalpy of solution at saturation of urea in 75% H_3PO_4 from Table XIII were combined with the corresponding values from Table XIX for the same acid and are illustrated in Figure 2.

Densities and Heat Capacities in System $CO(NH_2)_2$–H_3PO_4–H_2O at 25°C

Second-degree equations in weight percent urea and weight percent phosphoric acid were fitted to the observed values of heat capacity, s, and density, d, for the solutions listed in Tables II, IV, VI, VIII, X, and XII.

$$s = 1.000 - 0.00787P - 0.00580U + 0.0000138P^2 + 0.0000082U^2 + 0.0000491PU \quad (28)$$

$$d = 1.001 + 0.00470P + 0.00279U + 0.0000381P^2 - 0.0000056U^2 + 0.0000400PU \quad (29)$$

where s = heat capacity, cal $°C^{-1}$ g^{-1} of solution; d = density, g ml^{-1}; P = weight percent H_3PO_4; and U = weight percent urea. The standard deviation of Equation 28 is 0.002 cal $°C^{-1}$ g^{-1} of solution, and that of Equation 29 is 0.001 g ml^{-1}. Heat capacities at even values of P and U are shown in Table XX. Densities at even values of P and U are shown in Table XXI.

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