selected to facilitate comparison of the total fertilizer nutrient contents, $N + P_2O_5$, of the saturated solutions in the several systems.

The 0°C isotherm of the multiphosphate system over the pH range studied comprises three branches representing solutions saturated, respectively, with $(NH_4)_2HPO_4$, $(NH_4)_4P_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$; $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$; and $NH_4H_2PO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$. Only one invariant solution was determined. It was saturated with $(NH_4)_2HPO_4$, $(NH_4)_3HPO_7 \cdot H_2O$, $(NH_4)_4P_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$, and contained 12.61% N and 41.04% P_2O_5 distributed as ortho- 21, pyro- 35, tripoly- 14, and tetrapolyphosphate 29%. It had a pH of 6.39, a value near that (6.50) of the invariant solution of the ternary system NH_3–$H_4P_2O_7$–H_2O saturated with tri- and tetraammonium pyrophosphate and near that (6.44) of the invariant solution of the quaternary system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O saturated with tri- and tetraammonium pyrophosphates and diammonium orthophosphate. A second invariant point, representing a solution saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_5P_3O_{10} \cdot H_2O$, and $(NH_4)_6P_4O_{13} \cdot 2H_2O$, was estimated from plots of pH vs. N or P_2O_5 to contain 12.6% N and 44.2% P_2O_5 and to have a pH of 5.9.

As shown in Figure 1, the total fertilizer nutrient contents of the solutions saturated with ammonium ortho-, pyro-, tripoly-, and tetrapolyphosphates are significantly higher than those of solutions with the same ratio $N:P_2O_5$ that are saturated with only a single phosphate species. As shown in Figure 2, at each ratio $N:P_2O_5$, a solution of the six-component system saturated with ammonium ortho-, pyro-, tripoly-, and tetrapolyphosphates has a nutrient content ($N + P_2O_5$) 5–10% higher than that of a solution of the five-component system saturated with only ammonium ortho-, pyro-, and tripolyphosphates, and 10–25% higher than that of a solution of the four-component system saturated with only ammonium ortho- and pyrophosphates.

The isotherms in Figure 2 will be useful in the preparation of ammonium polyphosphate solutions in the most desirable pH range with maximum fertilizer nutrient contents that will not salt out at 0°C.

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Measured Enthalpies for Mixtures of Benzene with *n*-Pentane

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A flow calorimeter was used to measure four compositions of benzene with *n*-pentane between 260° and 700°F, with pressures ranging up to 1400 psia.

This experimental study reports the calorimetric measurements of four mixtures of benzene with *n*-pentane, a paraffin of lower boiling point and molecular weight than benzene. This present work complements an earlier study of benzene and *n*-octane mixtures (*7*). The measurements were made with a flow calorimeter that operates isobarically and measures the enthalpy difference relative to 75°F and the pressure of measurements. The details of the calorimeter and its operation have been discussed (*8*).

Prior to this present study the accuracy of the calorimeter was determined by making measurements with pure pentane and liquid water, and comparing with published literature values (*2*, *3*, *6*, *9*). These reported results showed an average deviation of 1.2 Btu/lb for pentane and 0.98 Btu/lb with water, and it was concluded that the enthalpy measurements have an uncertainty of about 1.5 Btu/lb. For the period of measurements on the pentane–benzene mixtures, 144 additional measurements were made with pure pentane showing an average deviation from the literature values of 0.93 Btu/lb. An additional 66 measurements were performed with water, with average deviation of 0.69 Btu/lb. During the time period of approximately four years' operation of the calorimeter, the measurement accuracy has not declined, and an expectation of an accuracy of 1.5 Btu/lb is considered justified.

Enthalpy values have already been presented for the pure components, benzene and pentane, as discussed (*7*, *8*). At the outset of this present study, it was believed that no previous enthalpy measurements had been made on the benzene–

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pentane system. After a portion of the measurements had been made, Wiener (*10*) disclosed that Kemp (*5*) had measured enthalpies of pentane–benzene mixtures using a heat exchanger. Kemp's results were presented in a thesis which appears not to have been published.

Both the pentane and the benzene were obtained from the Phillips Petroleum Co. The *n*-pentane used was very pure. Examination by chromatography indicated only a trace of isopentane, indicating a purity of 99.9%. Its density at 75°F was 0.6219 g/cc, with refractive index of $\eta^{20}D = 1.35757$. The benzene density was 0.8730 g/cc, with refractive index of $\eta^{20}D = 1.50030$, with a purity exceeding 99.0%. The Phillips Petroleum Co. states that the average composition is 99.84% benzene for the material they supply. After performing this enthalpy study, an analysis was made with a Loenco chromatograph showing 99.87 mol % benzene, 0.07% methylcyclopentane, 0.02% cyclopentane, 0.02% methylcyclohexane, 0.01% toluene, and 0.01% heptane. Mixtures were prepared by weighing the pure materials for samples of 5000 grams. With a weighing precision of 2.5 grams, the composition was established to 0.1%. Table I shows the compositions of the mixtures studied, with density at 75°F, and heat of mixing in the liquid phase at 75°F as obtained from the data of Hoskyns et al. (*4*). In addition, Table I shows the enthalpy needed to convert the measurements relative to 75°F in the saturated liquid condition to the enthalpy basis of −200°F recommended by the API data book (*1*). This conversion number for pure benzene was established (*7*) as 88.1 Btu/lb,

Table I. Properties of Liquid Phase at 75°F and 1 Atm for Benzene Systems with *n*-Pentane

Material	Wt % benzene	Liquid density, g./cm.³	Heat of mixing, Btu/lb	Enthalpy to add, Btu/lb
100% Benzene	100.0	0.8730	0	88.1
81.4 Mol % benzene	82.6	0.8186	3.41	98.6
60.0 Mol % benzene	61.9	0.7584	5.02	108.9
40.6 Mol % benzene	42.6	0.7096	4.71	116.5
19.9 Mol % benzene	21.2	0.6631	2.95	123.6
100% *n*-Pentane	0.0	0.6219	0	129.4

Table II. Smoothed Values of Enthalpy for 82.6 Wt % Benzene with 17.4 Wt % *n*-Pentane

Units. Btu/lb
Datum. Pure saturated liquid components at −200°F

Temp, °F	Psia												
	0	200	300	400	500	560	600	640	662	700	800	1000	1400
75		99.1	99.3	99.6	99.8	99.9	100.0	100.1	100.2	100.2	100.4	100.9	101.8
300		209.2											
320		220.6											
340		232.0											232.9
353.8		240.0[a]											
360	377.3	264.9	243.8										244.1
375.7		370.8[a]											
380	386.1	372.6	255.9										255.9
400	394.9	380.9	268.8										267.5
404.0			271.2[a]										
420	403.9	390.0	377.0	289.9									279.3
425.3			385.8[a]										
438.9				294.6[a]									
440	413.1	399.2	392.5	301.1	295.3					293.6	293.0	292.3	291.4
459.3				394.7[a]									
460	422.3	409.4	402.5	395.0	309.0					307.2	306.7	305.6	304.0
468.2					314.9[a]								
480	431.5	419.5	413.0	405.9	389.0	323.0				321.5	320.5	319.1	316.9
485.4					399.8[a]								
485.8						327.2[a]							
490	436.2	424.7	418.3	411.5	402.4	345.8	330.8			329.4	328.1	326.1	323.2
496.4							336.3[a]						
498.5						398.2[a]							
500	441.0	429.9	423.8	417.0	408.4	401.0	355.3	339.8		338.0	336.3	333.2	330.0
506.0							397.3[a]	346.0					
508.1								348.7[a]					
510	445.8	435.0	429.1	422.7	414.5	408.0	401.4	372.6	351.1	346.8	344.7	340.9	336.9
513.0								391.0[a]	359.2				
514.1									366.4[b]				
515	448.1	437.6	432.0	425.4	417.5	411.4	406.0	396.1	380.3	352.4	349.0	344.8	340.2
517							407.9	399.9	392.0	355.0			
520	450.7	440.1	434.6	428.2	420.6	415.0	410.3	404.0	398.5	360.4	353.5	348.8	344.0
525							414.3	409.0	405.0	383.6	358.8	352.8	347.3
530	455.5	445.5	440.0	433.9	426.8	421.9	418.1	413.3	409.8	397.2	364.7	357.0	351.0
540	460.5	450.6	445.3	439.8	432.9	428.5	425.2	421.6	418.7	410.8	381.2	365.4	358.2
550	465.5	455.9	451.0	445.5	439.0	435.1	432.3	429.0	426.4	419.8	397.2	375.3	365.8
560	470.1	461.5		451.4	445.0		438.8		433.4	428.3	411.8	385.7	372.7
580	479.8	471.9		463.1	457.4		450.9		447.3	444.2	435.1	410.9	388.2
600	489.9	482.4		474.4	469.3		463.3		460.0	457.5	449.6	432.4	404.4
620	500.0	493.2		485.5	481.2		475.4		472.4	470.4	463.6	448.6	421.2
640	510.4	504.0		497.0			487.6			482.7	477.0	463.6	438.2
660	520.7	508.3		508.5			499.9				490.1	477.5	454.8
680	531.0	525.9		520.1			512.0				502.9	491.4	471.4
700	541.5	536.8		531.5			523.8				515.7	504.9	487.5

[a] On two-phase boundary. [b] At critical point.

Table III. Values of Enthalpy for Mixture of 61.9 Wt % Benzene with 38.1 Wt % *n*-Pentane

Units. Btu/lb
Datum. Pure saturated liquid components at −200°F

Temp, °F	Psia														
	0	200	300	400	500	560	580	600	620	640	660	700	800	1000	1400
75		109.4	109.6	109.9	110.1	110.2	110.3	110.3	110.4	110.4	110.5	110.6	110.7	111.2	112.2
260		202.8													
280		214.8													
300		226.8													
320	371.6	239.1													
328.2		244.5[a]													
340	380.3	303.9	252.0												
354.3		372.9[a]													
360	389.7	375.8	265.1												265.7
376.8			276.2[a]												
380	399.2	385.5	290.0	278.3											277.5
400	408.9	395.9	382.0	291.9											289.8
404.1			389.8[a]												
412.7				300.2[a]											
420	418.8	406.4	398.4	336.0	305.4								303.8	303.0	302.1
432.7				395.3[a]											
440	428.3	416.9	409.7	400.0	320.2							319.0	318.1	317.0	315.0
441.0					321.0[a]										
450	433.3	422.1	415.1	406.0	369.1	328.6						327.2	326.0	324.8	321.9
457.5					396.7[a]										
457.9						336.1[a]									
460	438.2	427.7	420.9	412.1	399.8	348.0	338.2					336.1	334.5	332.3	328.7
464.0							342.8[a]								
468.9						391.5[a]									
470	443.2	433.1	426.5	418.3	408.0	393.7	376.0	352.5	349.4	347.7		345.9	342.8	340.2	335.6
471.8							386.5[a]	357.0							
474.0					411.1	399.4	394.4	365.3[b]	357.9	352.8		350.0	346.1	343.2	338.4
477					413.3	403.1	399.3	389.7	371.5	358.2	354.8	353.1	348.8	345.7	340.4
480	448.3	438.5	432.1	424.6	415.7	406.6	403.2	397.1	387.1	367.6	359.8	356.4	351.3	348.0	342.7
485					419.3			404.4	398.0	389.0	376.6	362.2	355.9	352.0	346.2
490	453.3	444.0	438.0	430.8	422.9	417.1	413.8	410.1	404.6	398.4	391.8	369.5	361.1	355.9	350.0
495					426.2			415.1	410.1	405.2	400.0	387.1	366.9	359.9	353.5
500	458.5	449.2	443.8	436.9	429.6	424.8	422.7	419.8	415.1	411.1	406.1	396.7	373.0	364.0	357.2
510	463.9	454.7	449.5	443.0	436.0			427.7	424.5	420.3	417.0	409.1	387.2	372.0	365.0
520	469.0	460.1	455.2	449.2	442.2			434.6	432.1	428.2	426.2	419.3	402.2	380.3	372.7
540	479.3	471.2	467.1	461.8	455.0			448.2	446.2	444.4	442.5	438.8	425.8	403.0	388.0
560	490.0	482.8	478.8	474.0	467.1			461.4				454.7	445.2	428.3	403.8
580	500.8	494.8	490.8	486.3	479.4			474.5				468.8	461.9	447.6	420.0
600	511.8	506.0		498.5	491.8			487.8				482.4	476.4	464.0	436.2
620	533.8	517.6		510.5	504.2			500.8				496.0	490.8	479.1	454.5
640	533.9	528.9		522.9				513.8				509.3	504.1	493.4	471.5
660	545.0	540.3		534.8				526.8				522.8	517.8	507.8	488.2
680	556.1	552.0		547.0				539.8					531.2	522.1	504.2
700	568.0	563.9		559.0				552.5					544.9	536.2	520.0

[a] On two-phase boundary. [b] At critical point.

Table IV. Values of Enthalpy for Mixture of 42.6 Wt % Benzene with 57.4 Wt % *n*-Pentane

Units. Btu/lb
Datum. Pure saturated liquid components at −200°F

Temp, °F	Psia												
	0	200	300	400	500	560	575	600	660	700	800	1000	1400
75		117.0	117.2	117.5	117.7	117.9	117.9	118.1	118.2	118.2	118.5	119.1	120.0
260		216.2											
280		228.9											
300	371.9	241.6											
311.9		249.9[a]											
320	381.3	296.2	255.2										
333.5		371.2[a]											
340	391.1	374.8	269.1										
357.0			281.1[a]										
360	401.0	385.5	292.0	283.1									282.9
380	411.1	396.6	387.8[a]	297.8									296.1
391.6				306.5[a]									
400	421.1	408.0	399.8	348.0	312.9				311.7			309.3	309.3
410	426.7	413.8	405.8	394.8[a]	321.1				319.0			316.5	316.0
419.5					329.0[a]								
420	432.0	419.4	411.7	401.0	330.9				326.9			324.0	323.0
430	437.1	425.1	417.7	407.9	382.4	338.6			335.6			331.7	329.9
433.7					395.9[a]								
437.1						346.7[a]							

(*Continued on next page*)

Table IV. (Continued)

Units. Btu/lb
Datum. Pure saturated liquid components at −200°F

Temp., °F	Psia												
	0	200	300	400	500	560	575	600	660	700	800	1000	1400
440	442.4	430.9	423.8	414.7	401.0	363.5	351.0		345.4			339.3	336.9
442					402.8	375.6	354.7		347.6				
444					404.4	384.1[a]	362.8		349.8	346.1		342.9	
444.5							365.7[b]						
446					406.1	389.5	379.5		352.1	348.1		344.4	
448					407.9	392.8	387.7	360.1	354.5	350.2		346.1	
450	447.8	436.6	429.8	421.4	409.5	395.7	392.0	365.1	357.0	352.3		347.9	344.0
455					413.7	402.1	399.8	384.9	364.1	357.8		351.9	347.5
460	453.0	442.3	435.8	428.1	417.7	407.9	405.9	396.0	372.2	364.2	358.5	356.0	351.1
470	458.3	448.1	441.8	434.9	425.4	418.0		410.5	396.1	379.1	367.9	364.3	358.6
480	463.8	453.9	447.9	441.7	433.0	426.7		420.8	411.0	398.6	378.8	373.0	366.1
490	469.0	459.5	454.0	448.3	440.2	434.8		429.9	421.2	413.6	393.0	382.1	373.9
500	474.5	465.1	460.1	455.0	447.4	442.1		438.0	430.0	423.2	408.4	391.1	381.8
520	485.5	477.6	472.8	467.7	460.3			452.9		442.2	431.7	413.0	397.6
540	497.2	489.7	485.1	480.4	473.6			467.6		459.2	450.9	434.6	413.3
560	508.4	501.7	497.4	493.0	487.1			481.4		474.7	468.0	454.2	429.4
580	519.9	513.9	509.9	505.9	500.4			494.8		489.7	483.9	472.1	446.6
600	531.3	525.8	522.8	518.9	513.6			508.4			498.7	488.2	464.4
620	543.3	538.1		531.7	527.0			522.1			513.5	503.3	482.2
640	555.4	550.2		544.8				535.7			528.2	518.2	499.2
660	567.4	562.5		557.5				549.5			542.4	533.2	515.3
680	579.5	575.2		570.5				563.3			556.5	547.5	531.3
700	592.1	588.1		583.4				577.1			570.4	562.1	547.4

[a] On two-phase boundary. [b] At critical point.

Table V. Values of Enthalpy for Mixture of 21.2 Wt % Benzene with 78.8 Wt % *n*-Pentane

Units. Btu/lb
Datum. Pure saturated liquid components at −200°F

Temp, °F	Psia											
	0	200	300	400	500	528	560	600	700	800	1000	1400
75		124.1	124.4	124.6	124.8	124.9	125.0	125.1	125.4	125.6	126.0	127.1
260		231.8										
280		244.7										
298.1		256.0[a]										257.9
300	382.8	267.9	257.5									
310.5		368.0[a]										
320	392.8	375.6	272.5									272.2
340	403.1	387.9	287.9									285.9
342.5			290.0[a]									
354.7			382.8[a]									
360	414.0	399.6	387.5	303.1								299.9
375.5				315.7[a]					313.2	312.5	311.6	311.0
380	424.5	410.8	402.5	365.9	319.1				317.0	316.0	315.0	314.2
383.6				388.2[a]								
400	435.3	422.1	415.1	404.5	337.5[a]			336.0	334.0	332.6	331.0	329.1
405				408.2	359.2	342.9		341.0	338.1	336.8	335.0	332.9
407.9					387.0[a]	346.5						
410				412.0	392.5	349.1	347.8	346.2	342.8	341.0	339.0	336.7
413.2					397.4	367.2[b]	352.8	350.0				
415				415.8	399.8	388.0	355.8	352.1	347.0	345.1	342.9	340.2
420	446.8	434.0	427.4	419.2	405.1	397.5	374.0	358.6	351.5	349.8	347.0	341.1
425.5				422.9	410.1	406.1	391.0	366.0	356.2			
430	452.2	440.0	433.8	426.3	414.9	410.0	401.7	380.0	361.2	359.0	355.1	351.9
440	457.9	445.8	440.0	433.2	423.0	419.9	413.8	403.2	374.7	369.0	364.0	359.7
460	469.1	458.1	452.6	446.8	438.1	436.0	431.8	427.4	406.1	391.8	381.8	375.1
480	480.8	471.0	465.6	460.0	452.8		447.6	444.0	431.0	417.2	399.5	391.1
500	492.8	483.9	479.0	473.1	467.0		462.4	460.0	450.1	439.1	418.5	407.3
520	504.9	496.1		486.4	480.7			474.7	466.6	456.9	439.9	423.4
540	516.9	508.9		499.4				488.9		473.6	459.0	439.7
560	529.2	521.7		512.9				502.8		489.9	477.2	457.0
580	541.1	534.6		526.7				516.9		505.7	494.7	474.8
600	553.7	547.2		540.4				530.9		520.8	510.9	492.6
620	566.2	560.4		553.9				544.9		535.7	526.9	509.8
640	579.0	573.6		567.9				559.2		550.8	542.9	526.9
660	591.9	587.0		581.8				573.3		565.8	558.1	542.6
680	604.9	600.2		595.5				587.9		580.4	573.0	558.6
700				609.4				602.9		595.0	587.7	574.7

[a] On two-phase boundary. [b] At critical point.

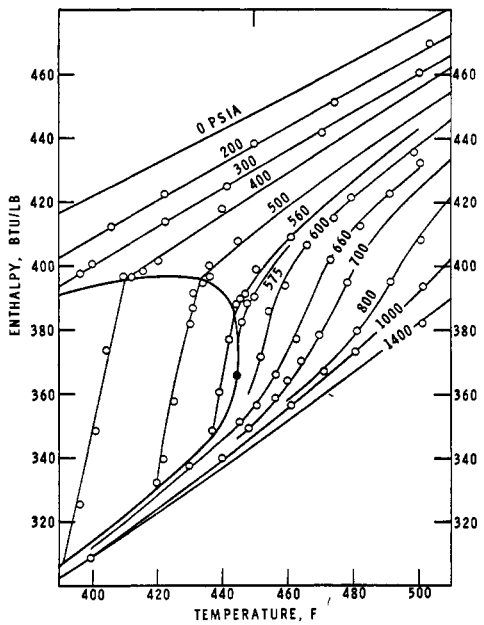

Figure 1. Enthalpy of 42.6 wt % benzene with *n*-pentane

and for *n*-pentane, 129.4 Btu/lb (*8*). For the mixtures, the conversion number is the weight average of the pure component values plus the heat of mixing. An additional correction was made to the calorimeter measurements to account for the change in enthalpy with increasing pressure at 75°F in the liquid phase. This correction was made using the thermodynamic equation of state (*8*). This correction, needed to adjust the data to the saturated liquid condition at 75°F, never exceeded 3.5 Btu/lb and was evaluated with greater precision than the accuracy of measurement.

A total of 1005 measurements was made on the four mixtures of benzene with pentane. These measurements, relative to the 75°F liquid state and the pressure of measurement, have been tabulated and are deposited with the ACS Microfilm Depository Service. Also deposited are the results obtained with pure *n*-pentane and water, measured for the purpose of accuracy evaluation. Cross-plotting the mixture measurements on large-sized graph paper gave smoothed enthalpy values. These are presented in Tables II, III, IV, and V relative to the API data book (*1*) basis of −200°F. The temperature range extends from as low as 260°F up to 700°F, and from pressures of 0–1400 psia. These smoothed values deviated from the measured enthalpies by a standard error of estimation of 1.96 Btu/lb. Figure 1 illustrates the behavior of the enthalpy isobars in the critical region for the system with 57.4 wt % benzene. The dark point along the saturated locus represents the critical point.

The compositions measured by Kemp (*5*) were almost identical to those chosen for this study, but his values were obtained at different pressure levels. The values obtained by Kemp were cross-plotted to determine the enthalpy values corresponding to the pressure levels in this measurement study. In this manner, the interpolated enthalpy values were found to deviate from the results of this study by an average of 2.5 Btu/lb, with a maximum discrepancy of 8.1 Btu/lb, found in the region of the dew point vapor approaching the critical point. Because the cross-plotting of the Kemp data introduces uncertainty, it is difficult to assess precisely the deviation between these two sets of data, but there appear to be no gross discrepancies.

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