

$\Delta H_{F-11}$  = latent heat of vaporization of Freon-11 at 75° F.  
 $P$  = pressure, p.s.i.a.  
 $T$  = temperature, ° F.  
 $T_1$  = inlet temperature of hydrocarbon to calorimeter, ° F.  
 $T_2$  = outlet temperature of hydrocarbon from calorimeter, ° F.  
 $V_{F-11}$  = volume rate of flow of Freon-11, cc. per second  
 $V_{HC}$  = volume rate of flow of hydrocarbon, cc. per second  
 $\rho_{F-11}$  = density of liquid Freon-11, grams per cc.  
 $\rho_{HC}$  = density of hydrocarbon at atmospheric pressure, grams per cc.

#### LITERATURE CITED

- (1) Allied Chemical Co., General Chemical Division, New York, "Genetron-11 Refrigerant, Thermodynamic Properties," 1957.
- (2) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds," Thermodynamic Research Center, Texas A & M University, College Station, Tex., April 30, 1969.
- (3) Benning, A. F., McHarness, R. C., "Thermodynamic Properties of Freon-11," E. I. du Pont de Nemours & Co., Wilmington, Del., 1938.
- (4) Connolly, J. F., Kandalic, G. A., J. CHEM. ENG. DATA 7, 137 (1962).

- (5) Eubank, P. T., Smith, J. M., *Ibid.*, 7, 75 (1962).
- (6) Graue, D. J., Berry, V., Sage, B. H., *Hydrocarbon Process. Petrol. Refiner* 45 (6), 191 (1966).
- (7) Kozicki, W., Sage, B. H., J. CHEM. ENG. DATA 5, 331 (1966).
- (8) McCracken, P. G., Smith, J. M., *A.I.Ch.E. J.* 2, 498 (1956).
- (9) McCracken, P. G., Storvick, T. S., Smith, J. M., J. CHEM. ENG. DATA 5, 130 (1960).
- (10) Meyer, C. A., McClintock, R. B., Silvestri, G. J., Spencer, R. C., "Thermodynamic and Transport Properties of Steam," Am. Soc. Mech. Engrs., New York, 1967.
- (11) Nelson, J. M., Holcomb, D. E., *Chem. Eng. Progr. Symp. Ser. No. 7*, 49, 93 (1953).
- (12) Organick, E. I., Studhalter, W. R., *Chem. Eng. Progr.* 44, 847 (1948).
- (13) Sahgal, P. M., Geist, J. M., Jambhekar, A., Wilson, G. M., *Advan. Cryog. Eng.* 10, 224 (1965).
- (14) Storvick, T. S., Smith, J. M., J. CHEM. ENG. DATA 5, 133 (1960).
- (15) Wiener, L. D., 50th National A.I.Ch.E. Meeting, Dallas, Tex., 1966.

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## Enthalpies of Mixtures of *n*-Octane and *n*-Pentane

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**Enthalpy measurements have been made with a flow calorimeter for *n*-octane and mixtures of *n*-octane with *n*-pentane. The results are presented in tabular and graphical form for pressures up to 140 p.s.i.a. and temperatures from 75° to 600° F.**

**E**XPERIMENTAL MEASUREMENTS of enthalpy difference have been made for *n*-octane and for mixtures containing 21.8, 39.2, 59.7, and 80.9 mole % pentane. The data extend from 150° to 600° F., with pressures from 15 to 1400 p.s.i.a. The apparatus is a flow calorimeter previously described (3) and shown to be capable of measuring enthalpy differences of 1.5 B.t.u. per pound. Both the *n*-octane and *n*-pentane were obtained from the Phillips Petroleum Co., as the pure grade, and used as received. The *n*-octane was specified as 99% pure. The *n*-pentane was examined and found to have a purity better than 99%, containing only a trace of isopentane (2-methylbutane).

A literature search found few thermal measurements for *n*-octane and none for the pentane-octane mixtures.

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McKay and Sage (4) measured latent heat of vaporization for *n*-octane from 100° to 340° F. Das and Kuloor (2) summarized the available thermal data for *n*-octane and tabulated enthalpy values for the saturated loci, the superheated vapor, and subcooled liquid, based upon computations using the Benedict-Webb-Rubin equation. The enthalpy values presented here are essentially an original measurement study.

The flow calorimeter measures the difference between the enthalpy of the fluid at some temperature higher than 100° F. at the pressure of measurement, and the fluid at 75° F. in the liquid state at the same pressure. The enthalpy differences evaluated directly from the calorimeter measurements without correction have been tabulated and deposited with ASIS.

The use of the uncorrected data requires adjustment to a common base level. The enthalpy value of the liquid phase at 75° F. is different at each composition and

pressure level. As the pressure rises, the liquid enthalpy increases in accordance with the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (1)$$

The use of Equation 1 to correct the liquid-phase enthalpy requires experimental evaluation of the density and the rate of change of density with temperature at constant pressure at 75° F. Because the correction is small, amounting to between 3 and 4 B.t.u. per pound at 1400 p.s.i.a. compared to atmospheric pressure, it is only necessary to establish the liquid density at one pressure, selected as 1 atm. for convenience. The pro-

cedure for correction has been described in more detail (3). The measured densities were 0.7000, 0.6896, 0.6768, 0.6659, and 0.6422, respectively, for *n*-octane and the 21.8, 39.2, 59.7, and 80.4 mole % pentane mixtures. This correction for the isothermal effect of pressure placed all the enthalpy values upon a basis of 75° F. and the pressure of the saturated liquid being studied.

For the *n*-octane and for each mixture, a large scale plot was made showing enthalpies corrected for pressure level dependent upon temperature for isobars of 15.2, 200, 400, 500, 600, 800, 1000, and 1400 p.s.i.a. From the smoothed isobars, enthalpy values at zero pressure were established by extrapolating isothermally. Zero pressure enthalpies were determined in this manner for the gas

Table I. Smoothed Values of Enthalpy for *n*-Octane Units

Temp., ° F.	Units. B.t.u. per lb.								
	Datum. Pure saturated liquid octane at -200° F.								
	P.S.I.A.								
	0	200	360	400	500	600	800	1000	1400
75	271.6	115.8		116.4	116.6	116.9	117.4	117.9	119.0
200		187.1		187.3	187.4	187.6	187.8	188.0	188.3
300		250.3		250.3	250.3	250.3	250.3	250.3	250.3
360		290.3		290.3	290.3	290.3	290.3	290.3	290.3
380	418.3	303.9		303.8	303.8	303.8	303.7	303.7	303.7
400	430.3	317.6		317.5	317.5	317.5	317.4	317.4	317.3
420	441.9	332.6		332.3	332.2	332.1	332.0	331.8	331.5
440	453.6	347.9		347.3	347.2	347.0	346.7	346.1	345.5
460	465.5	364.0		363.3	362.9	362.7	362.1	361.6	360.6
480	477.4	379.2		378.5	378.1	377.8	377.1	376.4	375.1
500	490.9	469.2		394.3	393.9	393.4	392.5	391.6	389.8
510	497.4	476.3		402.3	401.8	401.3	400.3	399.3	397.3
520	502.8	482.5		410.4	409.5	409.1	408.4	407.2	405.0
530	510.1	489.3		418.8	417.5	417.2	416.8	415.0	412.6
540	516.4	495.6		427.4	426.5	425.8	424.3	423.0	419.9
550	522.7	502.5		437.3	435.6	434.3	432.8	430.8	427.3
560	529.2	509.5	456.3	448.5	444.9	442.9	441.2	438.8	435.3
570	535.6	516.5	486.6	463.3	454.5	452.2	449.5	446.9	443.3
580	542.3	523.6	498.3	485.6	465.3	461.5	458.1	455.3	451.6
590	548.8	530.8	508.8	498.7	476.7	470.9	466.9	463.8	460.0
600	555.3	540.8	518.8	510.3	488.8	480.3	475.4	472.3	468.3

Table II. Smoothed Values of Enthalpy for Mixture of 21.8 Mole % Pentane with 78.2 Mole % Octane

Temp., ° F.	Units. B.t.u. per lb.								
	Datum. Pure saturated liquid components at -200° F.								
	P.S.I.A.								
	0	200	400	432	500	600	800	1000	1400
75	274.6	118.1	118.7		119.0	119.2	119.4	120.2	121.2
200		189.0	189.3		189.4	189.6	189.8	190.0	190.5
300		253.4	253.4		253.4	253.4	253.4	253.4	253.4
360		293.7	293.7		293.7	293.7	293.6	293.6	293.5
380		308.8	308.7		308.7	308.7	308.6	308.6	308.5
400		322.5	322.4		322.3	322.2	322.0	321.8	321.6
420		340.7	337.6		337.5	337.4	336.9	336.6	336.0
440		389.6	353.4		353.0	352.7	352.4	351.7	350.8
460			368.9		368.6	368.3	367.6	366.7	365.3
480	480.5		385.6		384.9	384.5	383.4	382.2	380.5
500	493.8		402.2		401.5	400.8	399.2	397.6	395.3
520	506.6	487.0	421.2		418.7	417.2	414.3	412.1	410.5
530	512.6	493.8	438.6	431.7	427.8	425.6	422.4	420.0	417.7
540	519.1	500.7	464.6	447.7	437.2	434.2	430.7	428.1	425.0
550	525.6	507.6	479.8	472.4	448.9	443.7	439.5	435.9	432.6
560	532.1	514.3	489.6	484.6	463.8	453.8	447.4	444.4	440.4
580	545.4	529.4	507.1	503.0	493.6	475.6	466.1	461.2	455.6
600	558.6	545.0	523.9		512.8	498.4	483.4	478.2	470.9

phase at temperatures over 360°F. at about 40° F. intervals. The API data book (1) shows zero pressure enthalpies relative to -200° F. and the saturated liquid pressure. For *n*-octane, the addition of 115.3 B.t.u. per pound to the zero pressure enthalpies determined with 75° F. base level gave agreement to the API values within ±0.9 B.t.u. per pound. From the API data book

values, zero pressure mixture enthalpies were computed as a weight average of the zero pressure enthalpies of *n*-octane and *n*-pentane. Comparison with the results obtained by extrapolating the measured results to zero pressure showed that the addition of 117.6, 119.5, 122.4, and 126.3 B.t.u. per pound adjusted the enthalpy values for the 21.8, 39.2, 59.7, and 80.9 mole % pentane mix-

Table III. Smoothed Values of Enthalpy for Mixture of 39.2 Mole % Pentane with 60.8 Mole % Octane

Units. B.t.u. per lb.  
Datum. Pure saturated liquid components at -200° F.

Temp., ° F.	P.S.I.A.								
	0	200	400	500	540	600	800	1000	1400
75	276.8	120.0	120.5	120.7		121.0	121.5	122.1	123.2
200		189.1	189.5	189.6		189.7	190.2	190.5	191.2
300		254.5	254.6	254.7		254.8	255.3	255.6	255.8
360		296.5	296.5	296.5		296.5	296.5	296.5	296.5
380	421.1	312.5	312.1	311.7		311.6	311.4	310.8	310.5
400	435.5	337.5	328.3	327.6		327.4	326.5	325.5	324.4
420	447.3	382.3	343.5	342.7		342.4	341.3	340.3	338.4
440	458.9	432.7	358.5	358.2		357.4	356.2	355.0	352.7
460	471.5	446.9	374.3	373.2		372.3	370.6	369.5	367.9
470	478.0	454.3	383.7	381.2		380.2	379.1	377.5	375.5
480	484.1	461.8	397.5	389.8		388.8	387.3	385.5	383.5
490	490.4	469.0	414.3	398.5		397.0	395.0	393.0	391.1
500	496.5	476.4	435.0	408.4		405.4	402.9	400.9	389.1
510	503.0	483.9	453.8	417.7		414.1	410.8	408.5	406.9
520	509.3	491.0	467.2	433.0	426.2	424.0	418.4	416.4	414.5
540	522.1	505.5	484.5	464.1	453.6	445.5	435.5	432.8	430.7
560	534.7	519.8	500.5	484.5		469.5	454.3	449.4	446.5
580	548.0	534.5	515.5	504.0		492.5	474.2	465.7	463.1
600	561.1	549.2	532.5	523.4		512.0	492.8	483.0	480.4

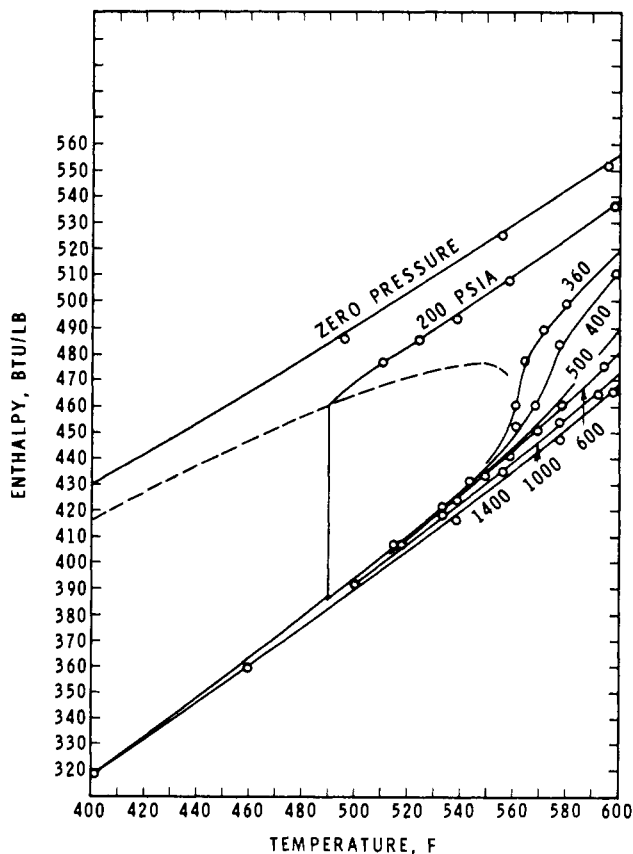


Figure 1. Enthalpy values for *n*-octane

Base level. -200° F. and saturated liquid

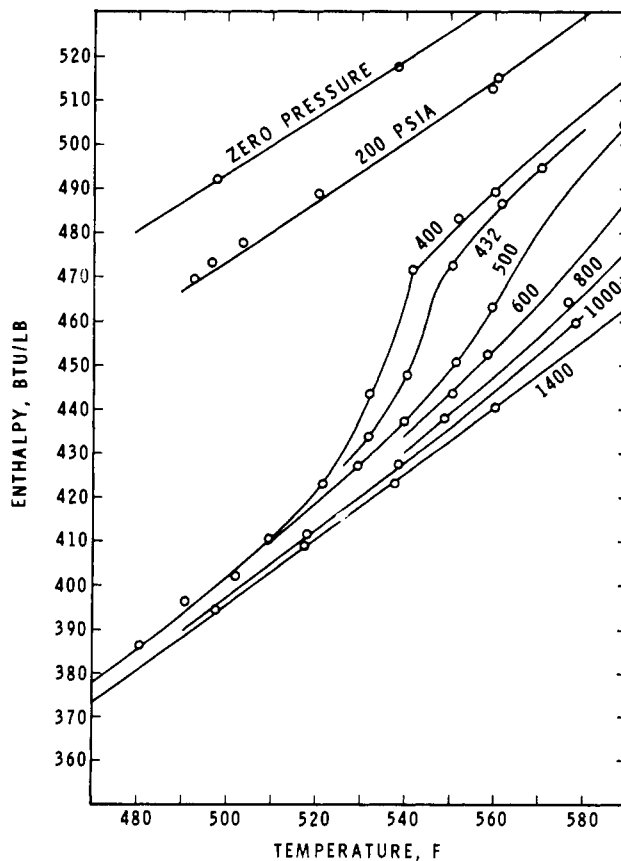


Figure 2. Enthalpy values for mixtures of 21.8 mole % *n*-pentane with 78.2% *n*-octane

Base level. Pure saturated liquid components at -200° F.

tures to the  $-200^{\circ}\text{F}$ . base level. This procedure assumes the liquid heat of mixing at  $75^{\circ}\text{F}$ . for pentane and octane to be negligible, and establishes the enthalpy values relative to the pure component enthalpies at their saturated liquid states and  $-200^{\circ}\text{F}$ .

Smoothed enthalpy values dependent on temperature and pressure with the  $-200^{\circ}\text{F}$ . API base level are pre-

sented in Tables I to V. Data for *n*-pentane have been presented on the same basis (*β*). The enthalpies are tabulated at 0, 200, 400, 500, 600, 800, 1000, and 1400 p.s.i.a. Around the critical region the enthalpy values are presented at  $10^{\circ}\text{F}$ . intervals, and less frequently where the rate of change of enthalpy with temperature is less. For the low temperature range at zero pressure,

Table IV. Smoothed Values of Enthalpy for Mixture of 59.7 Mole % Pentane with 40.3 Mole % Octane

Units. B.t.u. per lb.  
Datum. Pure saturated liquid components at  $-200^{\circ}\text{F}$ .

Temp., $^{\circ}\text{F}$ .	P.S.I.A.								
	0	200	400	470	500	600	800	1000	1400
75	280.4	122.9	123.4		123.7	124.0	124.4	124.9	126.0
200		192.3	192.7		193.0	193.2	193.6	194.1	195.0
300		257.7	258.3		258.4	258.5	258.6	259.0	259.6
360		300.6	300.6		300.6	300.6	300.6	300.6	300.6
380	428.4	358.9	315.0		314.9	314.8	314.7	314.6	314.5
400	439.8		333.7		333.0	332.6	331.0	330.2	329.0
420	451.4	428.5	346.7		346.3	346.0	345.7	345.4	343.6
440	463.4	441.9	374.0		363.4	362.4	361.7	360.9	358.6
450	469.4	448.5	393.4		372.6	371.2	370.1	368.5	366.4
460	475.4	455.4	414.5	383.6	382.4	380.6	378.3	376.4	374.3
470	481.2	462.3	438.6	400.3	394.5	390.0	386.5	384.3	382.0
480	487.6	469.3	448.2	422.5	410.9	400.4	394.5	392.3	389.6
490	493.8	476.6	456.5	441.8	431.2	410.4	402.6	400.4	397.4
500	500.3	483.5	464.6	452.2	447.5	421.7	411.3	408.5	405.5
510	506.3	490.9	473.0	462.0	458.3	437.4	420.6	417.0	413.5
520	512.6	498.4	481.3	471.8	467.4	451.2	429.9	425.2	421.5
540	525.4	512.1	497.4	489.2	485.7	471.4	450.4	442.4	437.6
560	538.5	526.3	512.8	505.8	503.0	490.6	469.9	460.3	454.9
600	565.3	555.6	541.8	536.2	533.7	525.5	507.8	496.6	486.3

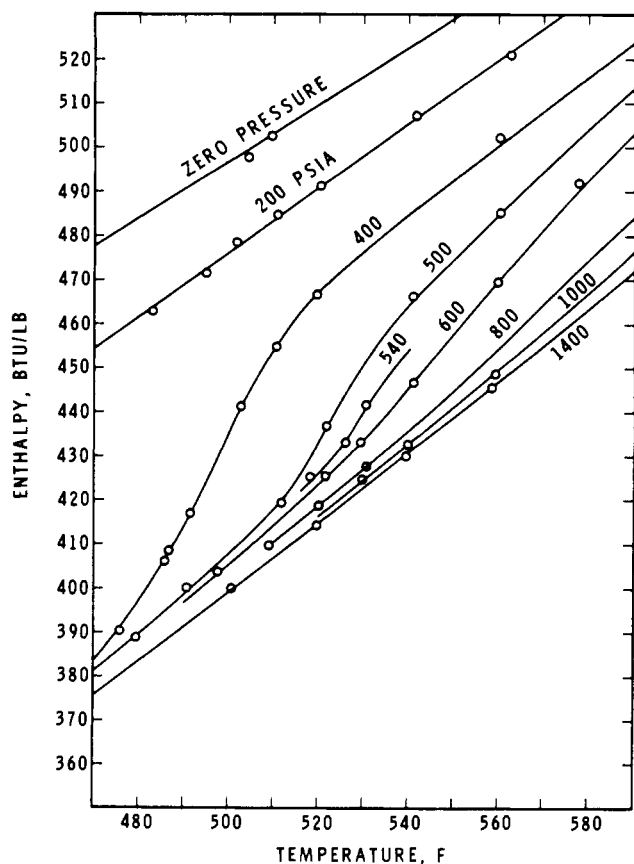


Figure 3. Enthalpy values for mixtures of 39.2 mole % *n*-pentane with 60.8 % *n*-octane

Base level. Pure saturated liquid components at  $-200^{\circ}\text{F}$ .

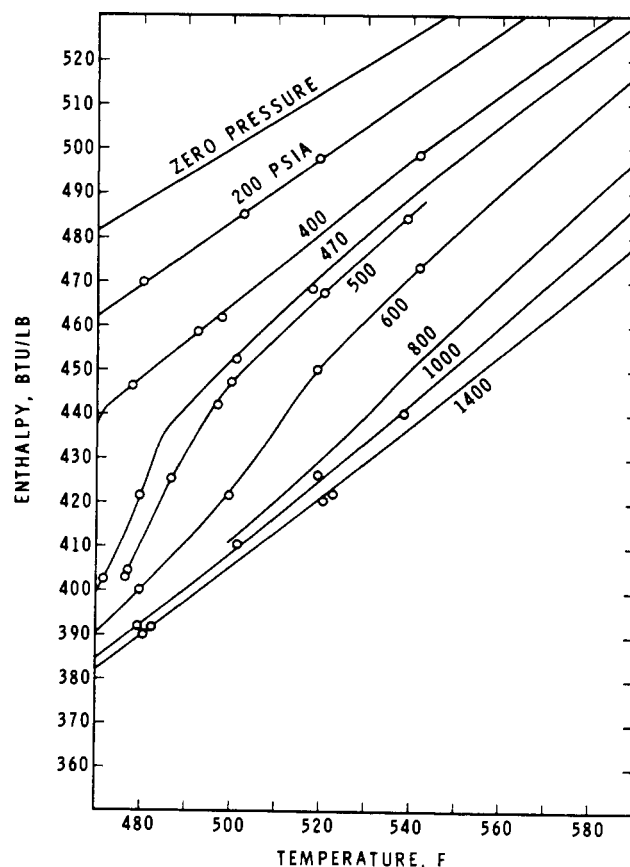


Figure 4. Enthalpy values for mixtures of 59.7 mole % *n*-pentane with 40.3 % *n*-octane

Base level. Pure saturated liquid components at  $-200^{\circ}\text{F}$ .

values of enthalpy are not presented, because they could not be successfully evaluated from the measured data. Some smoothed results are presented along the critical isotherm where data were taken.

Figures 1 to 5 show isobars of enthalpy relative to the  $-200^{\circ}\text{F}$ . base level for octane and the mixtures. Figures 1 through 4 show the temperature range from

$470^{\circ}$  to  $590^{\circ}\text{F}$ . Figure 5 shows the range  $410^{\circ}$  to  $530^{\circ}\text{F}$ . to illustrate the critical region for the 80.9% pentane. Since the apparatus does not directly distinguish phase differences, the figures do not attempt to show phase boundaries. An attempt to evaluate such boundaries would require an estimation technique not dependent on the measurements. Figure 6 shows the enthalpy beha-

Table V. Smoothed Values of Enthalpy for Mixture of 80.9 Mole % Pentane with 19.1 Mole % Octane

Temp., $^{\circ}\text{F}$ .	Units. B.t.u. per lb. Datum. Pure saturated liquid components at $-200^{\circ}\text{F}$ .							
	P.S.I.A.							
	0	200	400	500	600	800	1000	1400
75	285.1	126.7	127.2	127.4	127.6	128.1	128.4	129.2
200		196.9	197.0	197.1	197.4	197.6	197.9	198.5
300		263.0	263.2	263.3	263.4	263.6	263.8	264.0
360		396.3	309.5	309.4	309.3	309.0	308.3	306.4
380	433.4	417.3	326.3	325.9	325.5	324.6	323.5	321.4
400	444.8	428.0	362.4	342.8	342.2	340.5	339.3	336.2
420	456.4	440.3	411.1	361.6	359.7	356.8	354.7	352.4
430	462.4	446.4	425.9	383.3	369.5	365.2	362.6	360.3
440	468.5	452.5	433.7	409.8	381.1	373.6	370.4	368.2
450	474.5	459.0	441.0	423.3	396.4	382.0	378.2	376.0
460	480.6	465.3	448.6	433.5	411.6	391.5	386.5	384.2
470	486.8	472.0	456.0	442.7	426.3	401.4	395.2	392.1
480	493.0	478.3	463.4	451.4	438.9	411.9	404.5	400.5
490	499.1	484.9	470.4	459.3	448.5	422.2	413.6	408.9
500	505.3	491.2	477.5	467.2	457.2	432.5	423.0	417.5
520	517.9	505.2	492.3	482.4	473.4	451.5	441.4	435.0
540	530.4	519.0	506.8	498.0	489.9	470.0	459.9	452.0
560	543.7	532.5	521.5	513.4	505.4	487.5	477.3	468.6
580	556.9	546.1	536.0	529.0	521.3	505.2	495.0	485.0
600	570.4	560.3	550.4	544.4	537.3	522.5	512.3	501.3

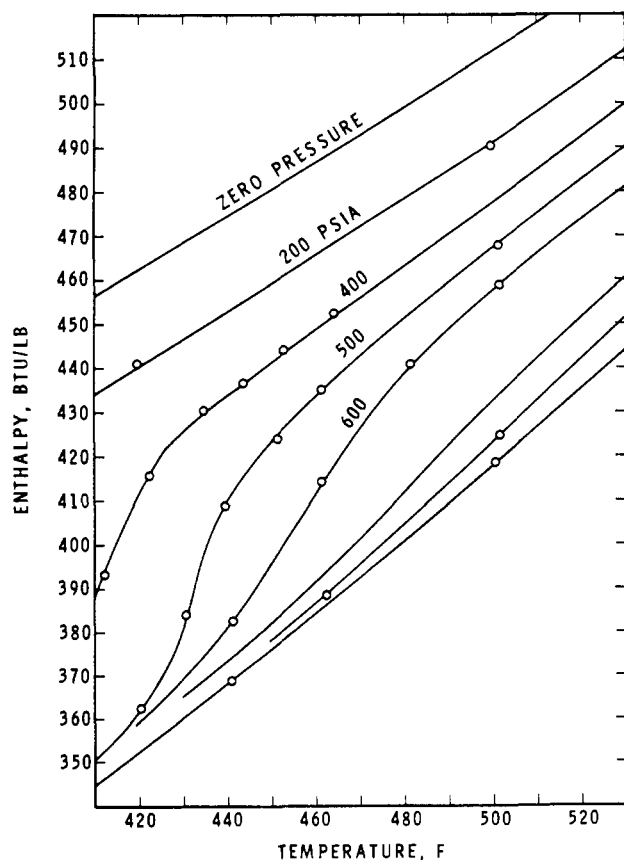


Figure 5. Enthalpy values for mixtures of 80.9 mole % *n*-pentane with 19.1 % *n*-octane

Base level. Pure saturated liquid components at  $-200^{\circ}\text{F}$ .

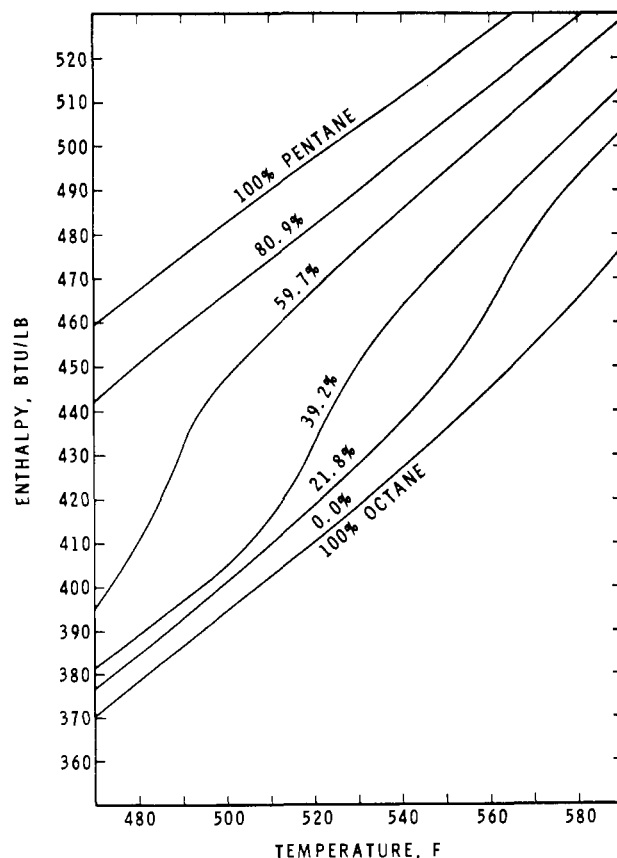


Figure 6. Enthalpy values of mixtures of pentane and octane dependent on composition at 500 p.s.i.a.

viator of the 500-p.s.i.a. isobar for octane, the mixtures, and pentane (3), showing the progressive decrease in enthalpy as the octane content increases.

#### ACKNOWLEDGMENT

Gratitude is expressed to the American Petroleum Institute, which provided funds for the enthalpy measurement of these mixtures.

#### NOMENCLATURE

$H$  = enthalpy, B.t.u. per lb.  
 $P$  = pressure, p.s.i.a.  
 $V$  = specific volume, cu. ft. per lb.  
 $T$  = temperature, Rankine

#### LITERATURE CITED

- (1) American Petroleum Institute, Division of Refining, "Technical Data Book—Petroleum Refining," Section 7A1.3, New York, 1966.
- (2) Das, T. R., Kuloor, N. R., *Indian J. Technol.* 5 (2), 51 (1967).
- (3) Lenoir, J. M., Robinson, D. R., Hipkin, H. G., *J. CHEM. ENG. DATA* 15, 23 (1970).
- (4) McKay, R. A., Sage, B. H., *Ibid.*, 5, 21 (1960).

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## Solubility of Some Ammonium, Copper, Iron, Potassium, and Zinc Salts in Formamide

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**Solubilities of 21 compounds in formamide were determined. Most compounds were considerably less soluble in formamide than in water. Zinc oxide proved to be more soluble in formamide than in water.**

FORMAMIDE, like water, is a polar solvent with a high dielectric constant. The solubility of inorganic salts tends to be high in formamide because of solvation. Gopal and Husain (4) reported that the solubilities of the alkali and alkaline earth halides in formamide are less than the corresponding values in water, whereas the reverse is true for lead salts. Colton and Brooker (2) determined the solubility of a variety of alkali metal salts, but reported their data as grams of salt per liter of solution, which is not a very useful unit without density data. Consequently, some of their measurements were repeated and the data are reported here in more suitable units.

Most of the present data are for solutions of copper, iron, and zinc salts in formamide. Such solutions may be useful as liquid fertilizers, rich in both nitrogen and trace elements essential for proper plant growth (1, 7). No solubility data for copper, iron, or zinc salts in formamide have been reported in the literature.

#### EXPERIMENTAL

Matheson, Coleman and Bell formamide, 99%, was used in all solubility studies. This formamide melts at  $2.5^\circ \pm 0.1^\circ \text{C}$ ., which is in good agreement with the literature value of  $2.55^\circ \text{C}$ . (8). All salts were reagent grade chemicals and

were used without purification. Hygroscopic salts were stored in a dry box.

Formamide and an excess of the salt were weighed into a 100-ml. volumetric flask, in amounts such that the flask was about half full. The formamide was exposed to the air only briefly during addition, and all hygroscopic salts were added in the dry box. The flasks were closed with glass stoppers and attached to a shaker arm so that all of the flask except the top of the neck was immersed in a stirred constant-temperature water bath maintained at  $25^\circ \pm 1^\circ \text{C}$ . All samples were shaken for at least 48 hours, after which the mixtures were filtered rapidly in air at  $25^\circ \text{C}$ . A weighed aliquot of the filtrate was taken for analysis. Two or three separate solubility determinations were made for each compound.

Both water and air temperatures were determined with an Anschutz precision thermometer with a range of  $-5^\circ$  to  $+55^\circ \text{C}$ ., and  $0.2^\circ \text{C}$ . divisions. This thermometer had been checked previously at the ice point and against a calibrated copper-constantan thermocouple. The copper-constantan thermocouple, in conjunction with a Leeds and Northrup K-2 potentiometer, was used to measure the melting point of formamide.

Bath temperature was controlled with a Fisher immersion-type thermoregulator, which controlled an immersion heater in the bath. The heater worked against a cooling coil cooled with tap water. Air temperature was thermostatically controlled at  $25^\circ \text{C}$ .

Before analysis, formamide was removed by evaporating an aqueous solution of the sample to dryness. Copper was

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