Enthalpy of *cis*-2-Pentene and a Mixture with *n*-Pentane

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A flow calorimeter was used to measure the enthalpy of *cis*-2-pentene and an equimolar mixture of *cis*-2-pentene and *n*-pentane. The measurements ranged from 300–450°F, with pressures up to 1400 psia. The critical temperature and pressure of *cis*-2-pentene were measured in a phase boundary apparatus and had values of 395.2°F and 535 psia.

This work is a presentation of measured enthalpy values for the olefin *cis*-2-pentene (bp 98.5°F) and for the close-boiling equimolar mixture of *cis*-2-pentene with *n*-pentane (bp 96.9°F). Little information is available for the enthalpy of olefins in the moderate boiling point ranges. Enthalpy values for the ideal gas state for *cis*-2-pentene have been presented by Kilpatrick et al. (*4*) and in the API Project 44 tables (*3*). Liquid phase heat capacities are shown below 300°K by Todd et al. (*10*) for pure *cis*-2-pentene and by Parks and Huffman (*8*) for a mixture of *cis*- and *trans*-2-pentene. No thermal information was found for a mixture of *cis*-2-pentene with *n*-pentane.

The *cis*-2-pentene used had a liquid density of 0.6538 g/cc at 75°F and a refractive index of $n^{20}D = 1.3833$. The API data book (*2*) shows values of 0.6516 g/cc for density and 1.3830 for the refractive index. An analysis performed with a Loenco Model 15A chromatograph showed the material to be 96.3 mol % *cis*-2-pentene (bp 98.5°F), 3.5 mol % *trans*-2-pentene (bp 97.4°F), and about 0.2 mol % trace of other materials. The *n*-pentane had a liquid density of 0.6223 g/cc at 60°F with refractive index of 1.3574. The corresponding data book values (*2*) are 0.6225 and 1.35748. The purity was evaluated in previous work (*6*) as better than 99.0 mol % containing a trace of isopentane.

The enthalpy of the *cis*-2-pentene and the mixture with *n*-pentane were measured using a flow calorimeter with design features previously described (*6*). In brief, the calorimeter functions by passing the hydrocarbon through the calorimeter at a constant flow rate, with the fluid entering at a measured inlet temperature ranging from 150–585°F and always leaving at 75°F and the liquid phase condition. The measurements were made isobarically with pressure differential never exceeding 0.2 psi as the hydrocarbon passed through the calorimeter.

The change in enthalpy was measured by the quantity of Freon-11 evolved as heat transferred in the calorimeter from the hydrocarbon fluid to surrounding Freon-11 maintained precisely at its boiling point and 75°F. Repeated and frequent measurements of *n*-pentane and water have shown that the calorimeter measures enthalpy differences with an average deviation below 1.5 Btu/lb when compared with the literature values (*3*, *7*). The calorimeter measures enthalpy relative to 75°F and the pressure of measurement with the fluid in the liquid state. Table I lists the results of these measurements.

The API data book (*2*) uses −200°F and the saturated liquid state for the pure components as the basis where enthalpy equals zero. To convert the measurements to this −200° F basis requires two corrections. By graphical integration of the heat capacity values of Todd et al. (*10*) with respect to temperature, the enthalpy difference for the estimated liquid *cis*-2-pentene was established between −200° and 75°F. The enthalpy of saturated liquid *cis*-2-pentene at 75°F was 128.7 Btu/lb higher than at −200° F. This differ-

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Table I. Measured Enthalpy Difference Relative to 75°F and Pressure of Measurement in Liquid Phase

Material	Press, psia	Temp, °F	Enthalpy, Btu/lb	Press, psia	Temp, °F	Enthalpy, Btu/lb	Press, psia	Temp, °F	Enthalpy, Btu/lb
cis-2-Pentene	20	159.8	195.4	450	384.5	261.5	540	397.3	220.8
		197.8	211.5		387.4	264.7		398.4	242.2
		248.7	233.3		391.0	267.5		400.8	246.4
		298.7	257.1		392.6	268.4		400.9	253.5
		350.3	283.7		394.9	271.4		410.0	251.9
		380.5	298.6		400.3	274.6		401.5	253.2
		399.1	306.9		419.4	288.4		401.7	255.9
		408.5	314.1	480	381.8	198.9		403.1	256.6
		428.6	324.4		384.0	245.0		404.2	258.9
		448.2	335.8		389.4	259.4		404.5	259.9
		499.2	359.8		394.0	264.5		409.2	265.8
		545.9	389.3		398.7	267.4		414.3	271.5
		585.0	414.3		403.9	273.0		418.8	276.9
	300	329.9	169.1		410.4	278.2		428.4	284.7
		329.9	163.7	500	359.2	177.4		438.3	291.5
		330.2	181.0		378.9	196.0	570	388.6	204.5
		330.5	192.2		382.0	200.3		394.0	209.6
		331.0	205.2		387.4	209.2		399.3	218.7
		331.2	223.1		388.3	239.9		402.7	228.0

(*Continued on next page*)

Table I. (Continued)

Material	Press, psia	Temp, °F	Enthalpy Btu/lb	Press, psia	Temp, °F	Enthalpy, Btu/lb	Press, psia	Temp, °F	Enthalpy Btu/lb
cis-2-Pentene (*contd.*)	300	357.9	264.5		388.9	248.8		404.1	237.3
		377.7	278.6		391.3	254.4		405.1	244.1
		398.5	289.7		391.8	254.8		406.2	244.6
		418.8	301.8		393.0	256.9		407.2	248.9
		439.1	314.6		393.7	258.4		407.7	253.7
	350	335.7	159.8		394.7	259.7		408.8	257.9
		337.2	161.8		395.0	258.7		410.2	258.0
		346.7	176.6		396.8	260.8		414.6	264.7
		347.8	189.8		399.2	263.0		419.4	271.1
		347.8	202.8		400.9	266.3		424.5	276.1
		348.1	220.0		404.9	270.4	600	386.5	201.5
		350.9	247.5		407.0	272.5		391.1	204.2
		355.0	255.9		409.5	274.2		397.1	210.4
		359.9	258.6		414.8	279.5		403.4	221.3
		364.8	263.1	519	349.5	169.0		406.8	227.9
		369.6	266.5		368.8	185.3		408.4	232.2
	400	348.7	169.3		379.1	195.6		411.5	243.7
		353.2	173.3		383.1	198.8		414.3	252.2
		359.6	179.4		383.9	201.3		417.5	259.6
		360.4	184.5		388.4	206.0		427.1	272.9
		361.1	191.8		389.4	210.1		437.9	284.6
		361.1	213.8		390.6	207.3	650	405.0	218.0
		361.6	201.8		391.6	210.5		409.6	224.1
		361.8	211.8		393.2	224.7		413.7	230.7
		362.5	218.6		394.3	248.0		413.7	230.7
		362.5	226.2		394.8	253.7		415.7	231.9
		365.7	254.2		396.0	250.9		418.1	238.6
		366.5	252.7		396.2	253.3		423.6	250.4
		367.6	255.7		396.5	250.4		429.0	262.1
		370.3	257.0		399.5	260.2	700	401.8	212.2
		374.8	261.5		400.2	258.2		408.0	218.9
		377.7	263.9		402.2	263.7		416.9	228.6
		382.5	267.9		404.6	266.0		430.4	251.9
		396.0	278.8		406.2	268.0		448.7	278.3
	450	363.8	183.4		409.1	270.5	800	404.3	208.2
		370.4	187.3		418.6	280.4		416.3	222.6
		373.8	192.8		427.6	288.3		439.8	248.2
		374.7	199.5		447.1	301.2	1000	376.9	186.5
		375.0	207.6	540	379.5	194.3		408.2	210.0
		375.1	206.0		384.0	199.9		448.1	244.5
		375.5	215.3		389.7	205.4	1400	356.7	167.3
		375.7	223.8		390.3	204.3		377.0	181.4
		375.9	230.6		394.5	212.8		397.1	196.4
		376.9	249.2		395.5	214.9		417.4	211.6
		381.1	257.0		396.2	217.3		437.6	227.2
50.2 Mol % *n*-pentane in *cis*-2-pentene	20	378.8	300.0	450	381.7	260.5	600	350.6	175.2
		389.9	308.0		401.0	279.6		370.1	191.9
		409.5	318.8		410.3	287.8		391.1	210.6
		419.6	324.0		420.1	294.9		393.1	214.4
	300	349.3	262.1	500	355.0	180.3		400.0	221.0
		379.6	283.2		365.7	189.4		407.3	238.3
		409.1	300.7		375.8	200.0		410.9	247.8
		448.2	326.8		381.8	206.7		415.6	258.6
	350	341.2	170.6		387.5	226.3		419.8	267.2
		361.3	264.5		392.0	256.1		438.9	289.2
		380.2	278.4		396.4	264.2	700	410.1	228.5
		399.6	290.6		401.7	270.5		410.3	229.9
	400	331.3	161.7		420.8	287.9		416.7	236.7
		341.2	169.6	515	360.4	183.9		429.8	256.8
		351.8	178.8		374.8	199.1	800	393.5	207.9
		355.8	182.6		387.2	213.9		406.2	219.3
		361.3	199.4		392.2	245.2		415.5	228.3
		364.6	253.6		394.6	255.1		426.7	240.1
		369.8	261.6		396.3	258.4		435.5	251.0
		372.7	263.0		398.3	262.2	1000	410.9	220.0
		397.7	283.3		401.5	265.6		430.7	237.1
		419.7	298.7		406.5	271.5		450.2	253.8
		448.8	320.6		411.4	275.6	1400	349.2	168.1
	450	350.3	175.7		421.3	285.9		368.9	182.5
		360.0	183.4		431.1	294.1		390.1	197.8
		365.9	190.9		450.1	308.8		410.3	214.0
		371.1	196.4					430.8	231.4
		377.8	253.8					449.0	243.5

Table II. Saturated Enthalpy Values for *cis*-2-Pentene

Units: Btu/lb
Base level: Pure saturated liquid at −200°F

Temp, °F	Press, psia	Liquid phase enthalpy	Vapor phase enthalpy
331	300	286.3	376.3
348	350	298.6	379.2
362	400	309.8	380.9
375.6	450	321.8	381.1
383	480	329.4	380.3
387.5	500	335.1	378.6
391.6	519	341.8	375.5
395.2[a]	535	360.2	360.2

[a] Critical temperature.

ence has been previously established for *n*-pentane at 129.4 Btu/lb (*6*).

For the equimolar mixture the saturated liquid enthalpy at 75°F was computed at 129.1 Btu/lb, established as a weight average of the two pure component values. This procedure presumes the heat of mixing for *cis*-2-pentene and *n*-pentane to be negligibly small. As a second correction the enthalpy difference between the saturated liquid state and the liquid at the pressure of measurement, both at 75°F, was added to the measured enthalpies. This enthalpy was small, never exceeding 3.6 Btu/lb, and was computed by using the thermodynamic equation of state discussed previously (*6*). This correction of enthalpy in the liquid phase is small because the temperature of 75°F is much lower than the critical temperature. The computation of this small difference is accomplished with an accuracy exceeding that of the measurements.

The measurements converted to the −200°F basis were plotted on large sheets of graph paper, and smoothed values of enthalpy were established by cross-plotting. Table II shows the resulting smoothed enthalpy values for *cis*-2-pentene along the saturation locus, and Table III the enthalpies for the single phase gas and liquid conditions. Table IV shows the results for the mixture of *cis*-2-pentene and *n*-pentane. These smoothed values show a standard error of estimation of 1.0 Btu/lb compared to the measured results.

Although the measurements for pure *cis*-2-pentene are capable of establishing vapor pressures, it was not possible to establish the critical temperature from the enthalpy values alone with sufficient certainty. A search of the literature showed a confusing set of critical values. The data book (*2*) listed a critical temperature of 406°F and a critical pressure of 518.8 psia. These values were presented in brackets to indicate that the numbers were uncertain. Kobe and Lynn (*5*) tabulated values of 396.3°F and 494 psia. A critical temperature of 390.9°F results from using the equation presented by Ambrose et al. (*1*). None of these values seemed to fit well with the measured enthalpy; therefore, the critical constants were measured independently in a phase boundary apparatus described previously (*9*).

Briefly, a small sample of *cis*-2-pentene was entrapped over mercury in a heavy walled capillary tube closed at one end. By systematically manipulating both temperature and pressure, the point of criticality was observed. The results showed a critical temperature of 395.2°F with a critical pressure of 535 psia. These newly measured critical constants were consistent with the previously measured enthalpy values. The API data book (*2*) shows that the critical temperature of *trans*-2-pentene is 3°F lower than for *cis*-2-pentene. Similarly, the critical pressure of the trans isomer is 3 psi lower than the cis form. Although 3.5% *trans*-2-pentene exists in the material, the small difference between the cis and trans critical constants should result in negligible error, below the measurement accuracy level.

In the cross-plotting work the enthalpy of the equimolar mixture may be accurately computed as a weight average of the enthalpy values of *cis*-2-pentene and *n*-pentane except near the critical point where the relationship becomes nonlinear.

Table III. Smoothed Values of Enthalpy for *cis*-2-Phentene

Units: Btu/lb
Base level: Pure saturated liquid at −200°F

Temp, °F	Psia							
	0	200	300	400	450	480	500	519
330	402.7	389.0	285.7					
340	407.8	394.4	382.5	292.7				
350	412.8	399.9	389.0	300.1				
360	417.8	405.2	395.5	308.1				
370	423.0	410.7	402.0	387.4	315.3			
380	428.1	416.0	408.3	395.7	386.6	326.1		
390	433.4	421.5	414.4	403.9	396.1	390.1	382.8	358.8
395	436.1	424.3	417.4	407.9	400.1	395.0	389.2	383.1
400	438.9	427.1	420.4	411.7	404.1	399.3	395.1	391.0
410	443.9	433.0	426.4	418.5	411.9	407.8	405.0	401.1
420	449.0	438.8	432.5	425.0	419.0	415.6	413.5	410.3
440	459.9	450.0	444.6	437.9	433.4	430.8	428.8	426.6
	Psia							
	540	570	600	650	700	800	1000	1400
350			299.0			297.8	296.9	296.0
370			314.8			312.9	311.1	309.1
380		324.7	323.5		321.7	320.2	318.3	316.1
390	336.3	335.2	333.0		330.5	328.8	326.1	323.3
395	344.1	341.2	338.2		335.2	333.0	330.1	327.1
400	379.6	350.1	344.0	342.0	340.1	337.5	334.2	330.7
410	396.8	387.5	370.0	354.6	351.0	346.9	342.5	338.2
420	407.0	401.9	393.4	372.7	363.0	357.0	350.7	346.0
430	416.0	412.0	406.0	394.2	381.1	367.9	359.1	353.7
440	424.2	421.0	416.8	408.1	398.7	379.4	368.1	361.4
450					410.0	391.9	377.8	369.7

Table IV. Smoothed Values of Enthalpy for Mixture of 49.1 Wt % *cis*-2-Pentene and 50.9 Wt % *n*-Pentane

Units: Btu/lb. Base level: Pure saturated liquid components at −200°F

Temp, °F	Psia										
	0	300	400	450	500	515	600	700	800	1000	1400
350	416.6	392.1	306.9				305.0		303.1	301.9	300.7
360	421.9	398.6	315.1				313.2		311.5	310.0	308.0
360.4			315.6[a]								
365			387.2[a]								
370	427.1	405.1	391.5	324.1			321.7		319.9	318.1	315.3
375.8				329.9[a]							
377.8				385.1[a]							
380	432.4	411.6	399.6	388.5	334.4		330.7		328.2	326.0	322.5
386.6					343.2[a]						
389					378.2[a]						
390	438.0	418.1	407.2	400.1	382.1	350.6	340.4		336.5	334.0	330.2
391.6						361.3[b]					
391.9						374.3[c]					
395	440.7	421.2	411.1	405.0	392.2	386.0	345.8	342.2	340.7	338.0	333.9
400	443.3	424.6	415.0	409.2	399.0	394.5	352.0	347.7	345.0	341.8	337.6
410	449.1	431.1	422.0	417.4	409.1	405.9	375.8	359.3	354.1	350.2	345.7
420	454.8	437.9	429.1	424.3	417.9	415.0	398.0	371.9	364.2	359.3	353.9
430	460.7	444.4	436.0		425.5	423.5	410.7	388.0	375.3	367.9	361.8
440	466.6	451.1	443.0		433.2	431.2	420.8	403.0	387.1	376.5	370.1

[a] Enthalpy value on two-phase boundary. [b] Enthalpy at critical point. [c] Enthalpy at cricondentherm.

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RECEIVED for review January 18, 1971. Accepted June 16, 1971. The authors appreciate the funds made available by the American Petroleum Institute for the performance of these measurements.

Thermodynamic Properties of Gases in Propellants

Solubilities of Gaseous NH_3, CO, CO_2, and SF_6

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Ordinary gases are generally used for blanketing and pressurizing liquid propellants. Absorption and desorption of these gases cause undesirable mechanical and hydrodynamic effects in space vehicles. A series of investigations was therefore carried out to measure the solubilities of He, N_2, O_2, Ar, and N_2O_3 in liquid N_2O_4; and He, N_2, and Ar in liquid hydrazine, methylhydrazines, and their mixtures (*1–3*). The present investigation is on the solubilities of NH_3(g) in liquid hydrazine (N_2H_4), in methylhydrazine (MH; $N_2H_3CH_3$), and in unsymmetrical dimethylhydrazine [UDMH; 1,1-$N_2H_2(CH_3)_2$]; CO(g) in UDMH; SF_6(g) in MH and in N_2O_4; and CO_2(g) in N_2O_4.

There are no available data on these gas–liquid systems except on the NH_3–N_2H_4 system at very high concentrations of ammonia (*6*). A small amount of ammonia in N_2H_4 improves the performance of N_2H_4 in special engines, and CO and CO_2 are potential pressurization gases for UDMH and N_2O_4. Compounds of sulfur and fluorine, in particular SF_6, have electrophyllic properties in engines using MH and N_2O_4. An accurate investigation of these gas–liquid systems is therefore warranted.

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EXPERIMENTAL

The apparatus and the method for measuring the solubilities of gases are described elsewhere in detail (*1, 4*). Briefly, the apparatus for solubility measurements consists of three calibrated volumes for measuring the amounts of gases, a container