Thermochimica Acta, 64 (1983) 285–303
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC PROPERTIES OF SIMPLE ALKENES

JING CHAO, KENNETH R. HALL

Thermodynamics Research Center, Texas A&M University, College Station, TX 77843 (U.S.A.)

JIAN-MIN YAO

Nanjing Institute of Chemical Technology, Nanjing, Jiangsu (The People's Republic of China)

(Received 5 November 1982)

ABSTRACT

Employing low temperature thermal measurements, heat capacities (C_s) in the crystal and liquid states, and phase transition data, T_m and ΔH_m, the condensed phase thermodynamic properties, $(G_s - H_0^\circ)/T$, $H_s - H_0^\circ$, S_s and C_s, in the temperature range 0–360 K were evaluated for the following eleven alkenes: ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, 1-pentene, *cis*-2-pentene, *trans*-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene. The sources of experimental data, methods of evaluation, and the calculated results are described in detail.

INTRODUCTION

Although the simple alkenes like ethylene (C_2H_4), propylene (C_3H_6) and butylenes (butenes, C_4H_8) are important feedstocks for the manufacture of organic polymers in chemical industries, low temperature thermal measurements using modern technology are unavailable for these substances. Consequently, for evaluation of the thermodynamic properties C_s, S_s, $H_s - H_0^\circ$, and $(G_s - H^\circ{}_0)/T$ for eleven alkenes in the carbon range C_2 to C_5, old thermal data from the literature were adopted. The eleven alkenes selected for evaluation of thermodynamic properties in the crystal and liquid states are: ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, 1-pentene, *cis*-2-pentene, *trans*-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene.

The low temperature thermal data needed are heat capacities (C_s) of the given substance in the crystal and liquid states, the melting temperature (T_m), and the enthalpy of fusion (ΔH_m). Employing these basic data and the standard thermodynamic relationships, the condensed phase thermodynamic properties for each of the alkenes were calculated.

CALCULATION METHODS

For old C_s data, temperature scale and molecular weight corrections were applied. Whenever possible the heat capacities reported were corrected to base upon the International Practical Temperature Scale of 1968 as described in ref. 1. The molecular weights of the alkenes were calculated using the International Atomic Weights of 1979 [2]. In all computations, recent physical constants, 1979 Atomic Weights ($C = 12.011$ and $H = 1.0079$) and SI units [3] were employed.

In low temperature heat capacity measurements, the sample is sealed in a calorimeter with a small amount of inert gas, e.g. He or H_2, to aid heat transfer. The measured heat capacity is denoted as C_s.

High temperature heat capacities at constant pressure, C_p, for propylene, 1-butene, *cis*-2-butene and 1-pentene in the liquid state were determined by Sage and co-workers [14,16,18]. The reported heat capacities (C_p) were derived from measured $q/\mathrm{d}T$ values for each substance. We derived the corresponding C_s values for these compounds from the reported $q/\mathrm{d}T$ data points, employing the equations

$$C_{\mathrm{s(liq)}} = \left(\frac{q_1}{\mathrm{d}T} - \frac{q_2}{\mathrm{d}T}\right)\frac{(1 - V_l/V_g)}{(n_1 - n_2)} + \frac{V_l}{V_g} C_{\mathrm{s(g)}} + T\frac{\mathrm{d}P}{\mathrm{d}T}\left[\frac{\mathrm{d}V_l}{\mathrm{d}T} - \left(\frac{V_l}{V_g}\right)\left(\frac{\mathrm{d}V_g}{\mathrm{d}T}\right)\right] \quad (1)$$

$$C_{\mathrm{s(g)}} = C_{p(\mathrm{g})} - T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)\frac{\mathrm{d}P}{\mathrm{d}T} \quad (2)$$

$$C_{\mathrm{p(g)}} = C^{\circ}_{p(\mathrm{g})} + \left(\frac{\mathrm{d}H_{\mathrm{R}}}{\mathrm{d}T}\right)_p \quad (3)$$

$$C_{\mathrm{s(g)}} = T\frac{\mathrm{d}S}{\mathrm{d}T} \quad (4)$$

where the quantities $q_1/\mathrm{d}T$ and q_2/dT represent the net electrical energy required per unit temperature change of a constant-volume calorimeter with sample weights n_1 and n_2 of the given compound, respectively.

The terms V_l and V_g are molar volumes of liquid and vapor of the compound at temperature T under equilibrium conditions. The necessary volumetric data, including the ratio of change of bubble-point and dew-point specific volumes with temperature and rate of change of vapor pressure with temperature, were taken from recent data available in the literature [4–8].

In eqn. (3), the quantity $C^{\circ}_{p(\mathrm{g})}$ is the heat capacity at constant pressure of the substance in the perfect gas state, which is obtained by statistical mechanical calculation; H_{R} is the residual enthalpy, i.e. the enthalpy difference between the real gas and the perfect gas at temperature T and constant pressure P. The value of H_{R} is evaluated from an equation of state.

The term $\mathrm{d}S/\mathrm{d}T$ in eqn. (4) is the rate of change of entropy with temperature. This equation was used for evaluating $C_{\mathrm{s(g)}}$ for propylene, where the entropy data of this compound as a function of T were available [6].

The low temperature C_s values are fitted into algebraic heat capacity equations for derivation of condensed phase thermodynamic properties. The heat capacity equation adopted was

$$C_s = a + bT + cT^2 + dT^3 + eT^4$$

for fitting the experimental C_s data points by the least-squares method.

To achieve a better fit of C_s data in the heat capacity equations, the adopted C_s data points in each condensed phase, crystal or liquid, for the given substance were divided into several groups. Each group of data points covered a narrow temperature range. Within each temperature range, the heat capacity points were fitted by a simple polynomial as shown above, where a, b, c, d, and e are numerical coefficients. Each C_s datum was weighted for evaluation.

The least-squares method simultaneously determined the coefficients of the required heat capacity equations for the same condensed phase. The calculation method met the constraint that the two derived heat capacity curves of the adjacent temperature regions joined smoothly at the intersection.

Division of each condensed phase temperature range into regions and the degree of polynomial to be used for fitting the heat capacity data within each region were determined by trial and error. The set of heat capacity equations which fitted the experimental data points with least deviations from the least-squares criterion was selected for each alkene.

The selected heat capacity equations together with the best values of phase transition data, T_m and ΔH_m, were employed for calculating the required thermodynamic properties. The formulas used for evaluating these thermodynamic functions have been described in textbooks on chemical thermodynamics and will not be repeated here.

SOURCES OF DATA

Ethylene (ethene)

Egan and Kemp [9] measured the heat capacities of ethylene in the crystal (16.00–103.83 K) and liquid (106.67–168.68 K) states. They also determined the melting point and enthalpy of fusion. Their results were adopted for evaluation of the thermodynamic properties of ethylene in the temperature range 10–170 K.

The low temperature thermal measurements on ethylene in condensed phases were reported by Eucken and Hauck [10]. Pall and Maass [11] made specific heat measurements for ethylene near the critical point. However, the C_s data of Eucken and Hauck were 3 to 17% higher than those of Egan and Kemp. Therefore, the data of Eucken and Hauck were not adopted for evaluation. The heat capacities reported by Pall and Maass were not used because of uncertainties involved when extrapolating these data to the normal boiling point of ethylene.

Propylene (propene)

Employing an aneroid calorimeter, Huffman et al. [12] determined the heat capacities of propylene in the crystal (68.9–81.6 K) and liquid (93.1–210.3 K) states. The values of T_m and ΔH_m were reported to be 88.2 K and 16.67 cal g^{-1}, respectively, where 1 cal = 4.184 J.

Powell and Giauque [13] measured the condensed phase heat capacities (14.18–86.19 K, Cryst.; 93.93–223.44 K, liq.), melting point (87.85 K) boiling point (225.35 K), and enthalpies of fusion (717.6 cal $mole^{-1}$) and vaporization (4402 cal $mole^{-1}$) for propylene. Their results were adopted.

The isobaric heat capacity along the bubble point has been determined at temperatures in the range 80–160°F (299.42–344.26 K) for propylene by Auerback et al. [14]. The reported q/dT data points were converted to C_s values, as mentioned previously, for evaluation. The adopted C_s data were combined with equal weight for each point and fitted into heat capacity equations.

1-Butene

For evaluation of the thermodynamic properties of 1-butene, the low temperature thermal measurements reported by Aston et al. [15] (12.86–258.50 K) and Schinger and Sage [16] were employed. The given q/dT data points in the temperature range 101.93–187.65°F (132.00–359.62 K) were calculated as C_s heat capacities, using the method described previously. The two sets of heat capacity data were applied along with temperature scale, molecular weight, and energy unit corrections as usual, and combined with the proper weight for each datum for fitting into C_s equations.

Todd and Parks [19] determined the specific heats, 81.3–253.4 K, and the fusion data for liquid 1-butene with an aneroid calorimeter. These results, combined with estimated missing data, were employed for calculating the entropy, enthalpy, and Gibbs energy of formation at 298.1 K for 1-butene (g). Because they were unable for unknown reasons to crystallize the 1-butene sample, which was kept at 78 K for several days, their heat capacities were not adopted for evaluation.

cis-*2-Butene*

The heat capacities of this compound have been measured between 93.6 and 266.6 K by Todd and Parks [19]. Later, Scott et al. [17] determined the specific heat of crystalline and liquid *cis*-2-butene from 15 to 300 K. The values of the triple point (T_{tp}) and ΔH_m at T_m were reported as 134.26 K and 7309 J mole^{-1}, respectively. For internal consistency, the results of Scott et al. [17] were used.

Schlinger and Sage [18] investigated the isobaric heat capacities (C_p) at the bubble point in the temperature range 133.15–366.48 K for this compound. The data above 300 K were adopted for recalculation to C_s and added to the low temperature data of Scott et al. [17] for fitting into heat capacity equations.

trans-*2-Butene*

Todd and Parks [19] measured the heat capacities of *trans*-2-butene in the crystal (93.6–149.5 K) and liquid (176.0–259.6 K) states. The entropy and Gibbs energy of formation at 298.1 K have been derived from these results in conjunction with other data for *trans*-2-butene (g).

Guttman and Pitzer [20] investigated the potential barrier to the rotation of a methyl group attached to an olefinic structure. They determined the heat capacities of this compound in the crystal (14.56–160.40 K) and liquid (170.66–271.03 K) states. The values of T_m and ΔH_m were obtained as 167.62 K and 9757 J mole^{-1}, respectively. This set provided more data and covered a wider temperature range than that reported by Todd and Parks. In this work, the results of Guttman and Pitzer were employed for evaluating the thermodynamic properties for *trans*-2-butene.

Pentenes

Low temperature calorimetric studies have been made on six pentenes, over the temperature range 12–300 K by Todd et al. [21]. Their results were employed for calculating the condensed phase thermodynamic properties for 1-pentene, *cis*-2-pentene, *trans*-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene. Table 1 gives the temperature range and number of C_s data points in the crystal and liquid states, and the phase transition data, T_m and ΔH_m, for each pentene, which were adopted for evaluation.

Schlinger and Sage [16] determined the isobaric heat capacities of 1-pentene at the bubble point in the temperature range 91.40–204.97°F (306.15–369.24 K), using three different weights of sample material in the calorimeter. The reported $q/\mathrm{d}T$ values were converted to C_s heat capacities using the method described previously. The results were added to the low-temperature heat capacities of 1-pentene reported by Todd et. al. [21] for evaluation.

Parks and Huffman [22] have made low temperature calorimetric studies on 2-methyl-2-butene over the temperature range 92.7–293.9 K and have also made measurements on liquid 2-pentene which was a mixture of *cis* and *trans*-2-pentenes. Because of uncertainty in the sample purity these results were not adopted for evaluation in this work.

TABLE 1

Low temperature thermal measurements of alkenes

Compound	Heat capacity of crystal		Phase transition data		Heat capacity of liquid	
	Temperature range (K)	No. of points	Temperature (K)	ΔH_m J mole^{-1}	Temperature range (K)	No. of points
Ethylene	16.00–103.83	29	103.97	3351	106.67–168.68	12
Propylene	14.18– 86.19	20	87.85	3003	93.93–340.00	48
1-Butene	12.86– 85.51	23	87.82	3848	89.80–360.93	40
cis-2-Butene [a]	5.00–134.26	27	134.26	7309	134.26–366.48	50
trans-2-Butene	14.56–160.40	43	167.62	9757	170.66–271.03	14
1-Pentene	12.72–105.00	25	107.90	5807	125.73–353.15	28
cis-2-Pentene	13.15–120.00	45	121.78	7112	128.69–295.26	37
trans-2-Pentene	12.77–130.00	34	132.93	8352	134.98–301.67	21
2-Methyl-1-butene	12.69–135.00	44	135.60	7911	133.58–292.85	23
3-Methyl-1-butene	13.27–100.00	31	104.71	5359	103.08–298.34	23
2-Methyl-2-butene	12.52–135.00	31	139.40	7579	140.89–300.97	23

[a] The reported data points in the temperature range 5–300 K were smoothed values.

TABLE 2

Coefficients for the heat capacity equation, $C_s = a + bT + cT^2 + dT^3 + eT^4$ C_s in J K^{-1} mole^{-1} and T in K.

Temperature range (K)	a	b	$c \times 10^3$	$d \times 10^6$	$e \times 10^5$
Ethylene					
0.00– 34.00				1168.570	−2.028520
34.00– 80.00	−22.07780	1.617421	−14.39756	64.89300	
80.00– 99.00	−745.8604	28.65341	−351.0242	1461.990	
99.00–103.97	−67695.45	2049.051	−206.7444	69605.86	
103.97–170.00	−64.11394	0.2390014	−2.645468	7.960437	
Propylene					
0.00– 15.00				2999.372	−9.416469
15.00– 40.00	1.813643	−0.4313202	54.51417	−667.7873	
40.00– 75.00	−9.627300	1.273572	−9.278438	40.23715	
75.00– 87.85	840.7915	−29.26645	351.5660	−1357.490	
87.85–300.00	125.9890	−0.5783180	2.583000	−3.062330	
300.00–340.00	−7688.020	78.44460	−263.7690	296.1540	
1-Butene					
0.00– 19.00				1496.24	−2.36332
19.00– 51.00	−6.352400	0.3494196	24.54071	−286.1860	
51.00– 70.00	67.81260	−2.679927	57.79652	−332.6740	
70.00– 87.82	−797.2361	33.61802	−449.6670	2031.052	
87.82–200.00	98.95370	0.3821720	−4.255350	13.23970	
200.00–360.00	−289.1130	4.624890	−17.57760	22.29110	
cis-*2-Butene*					
0.00– 18.00				1120.710	−1.330120
18.00– 45.00	−3.666270	0.1181890	25.12430	−250.6420	
45.00–110.00	−23.57310	1.574620	−10.11440	31.67130	
110.00–134.26	−99.6630	3.469430	−25.70030	73.93250	
134.26–240.00	150.0370	−0.5669730	1.898660	−1.265220	
240.00–360.00	61.72400	0.6902880	−3.510110	6.483310	

TABLE 2 (continued)

Temperature range (K)	a	b	$c \times 10^3$	$d \times 10^6$	$e \times 10^5$
trans-*2*-*Butene*					
0.00– 17.00				789.9308	0.1841391
17.00– 35.00	−1.854299	−0.1496550	36.32306	−420.1531	
35.00–135.00	−17.31682	1.279568	−7.479444	25.27425	
135.00–167.62	−0.8008469	1.650224	−15.68925	59.03750	
167.62–280.00	32.11994	1.139366	−5.713168	10.07708	
1-*Pentene*					
0.00– 18.00				2362.282	−5.149123
18.00– 34.00	−5.604552	0.3202371	32.99511	−425.0149	
34.00– 70.00	−25.85754	2.096481	−18.93017	80.94659	
70.00–107.90	−27.25545	2.015224	−15.75263	56.21204	
107.90–230.00	141.9603	−0.1925667	0.5891156	0.7986254	
230.00–360.00	151.6486	−0.4504791	2.282400	−2.484290	
cis-*2*-*Pentene*					
0.00– 19.00				1913.335	−3.966871
19.00– 37.00	−3.319858	0.05531081	36.08704	−408.8881	
37.00–100.00	−23.12568	1.7375692	−11.44383	37.91583	
100.00–121.78	−71.07068	−1.1182577	17.41381	−59.27431	
121.78–205.00	190.9506	−0.8385866	3.591069	−4.269856	
205.00–300.00	202.0362	−0.9061456	3.458821	−3.303925	

trans-2-*Pentene*					
0.00– 16.00				1439.915	−1.606129
16.00– 35.00	−2.237281	−0.07584295	39.81017	−462.7295	
35.00– 80.00	−18.92055	1.467023	−7.496515	18.52374	
80.00–132.93	−17.97756	1.455379	−7.647473	20.38826	
132.93–310.00	137.3285	−0.2072887	1.081041	−0.5507399	
2-Methyl-1-butene					
0.00– 14.00				2011.349	−2.571097
14.00– 28.00	0.03851828	−0.4582275	69.91046	−1018.373	
28.00– 90.00	−18.15028	1.677801	−13.06257	49.00636	
90.00–135.60	−15.31888	1.393264	−7.788181	21.64618	
135.60–180.00	166.0353	−0.4878377	2.018998	−1.569632	
180.00–300.00	159.8715	−0.4078404	1.700859	−1.214373	
3-Methyl-1-butene					
0.00– 15.00				2406.938	−5.344432
15.00– 25.00	−1.593489	−0.1024494	46.93151	−596.0066	
25.00– 85.00	−19.682373	1.755460	−14.87466	61.26757	
85.00–104.71	−200.8002	7.565509	−76.37683	275.5846	
104.71–180.00	145.0400	−0.472938	2.805464	−3.894342	
180.00–300.00	114.2646	0.01789267	0.2013391	0.7008493	
2-Methyl-2-butene					
0.00– 17.00				1995.437	−3.917521
17.00– 35.000	−3.403906	0.07646469	37.66044	−457.6083	
35.00– 90.00	−18.71139	1.543419	−8.677783	25.85440	
90.00–139.40	−35.88031	2.015316	−12.80555	37.01079	
139.40–200.00	191.0816	−0.9299609	4.576543	−6.696576	
200.00–310.00	165.2303	−0.4500645	1.716411	−1.161884	

TABLE 3

Condensed phase thermodynamic properties for alkenes

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
Ethylene (crystal)				
10	0.087	2.5	0.339	0.966
20	0.617	33.8	2.305	6.10
30	1.808	138.0	5.409	15.12
40	3.637	334.0	11.987	23.74
50	5.912	608.2	18.076	30.91
60	8.456	949	24.27	37.15
70	11.156	1349	30.43	42.85
80	13.947	1806	36.52	48.40
90	16.791	2321	42.58	55.44
100	19.869	2944	49.12	71.13
103.97	20.869	3253	52.26	88.04
Ethylene (liquid)				
103.97	20.869	6604	84.38	69.31
110	24.46	7020	88.28	68.99
120	30.03	7708	94.26	68.46
130	35.18	8390	99.72	67.96
140	39.98	9067	104.74	67.57
150	44.45	97.42	109.39	67.31
160	48.65	10414	113.7	67.2
170	52.60	11087	117.8	67.4
Propylene (crystal)				
10	0.203	5.6	0.764	2.06
20	1.250	60.8	4.288	9.65
30	3.182	207.8	10.110	19.91
40	5.783	455.2	17.162	29.05
50	8.783	780.5	24.39	35.88
60	11.978	1170.7	31.49	42.08
70	15.262	1620.6	38.41	47.86
80	18.581	2129.1	45.19	54.46
87.85	21.201	2588	50.66	62.62
Propylene (liquid)				
87.85	21.201	5591	84.84	93.04
90	22.75	5791	87.09	92.63
100	29.68	6708	96.76	90.92
110	36.17	7610	105.36	89.55
120	42.27	8500	113.10	88.49
130	47.99	9381	120.15	87.73
140	53.38	10256	126.63	87.25
150	58.46	11127	132.64	87.02
160	63.28	11997	138.26	87.04
170	67.85	12868	143.54	87.28
180	72.19	13743	148.54	87.72
190	76.34	14623	153.30	88.35
200	80.30	15511	157.85	89.15

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
210	84.10	16407	162.22	90.09
220	87.74	17313	166.44	91.17
230	91.26	18231	170.52	92.36
240	94.64	19161	174.48	93.6
250	97.91	20104	178.33	95.0
260	101.08	21061	182.08	96.4
270	104.14	22032	185.7	97.9
273.15	105.09	22341	186.9	98.3
280	107.12	23018	189.3	99.3
290	110.02	24019	192.8	101
290.15	112.3	24846	195.7	102
300	112.8	25034	196.3	102
310	115.6	26066	199.7	104
320	118.3	27129	203.0	109
330	120.9	28254	207.0	117
340	123.5	29491	210.0	131
1-Butene (crystal)				
10	0.113	3.3	0.440	1.26
20	0.808	44.7	3.044	8.16
30	2.370	177.5	8.285	18.49
40	4.669	413.7	15.012	28.57
50	7.465	742.4	22.31	36.70
60	10.546	1141.7	29.57	43.23
70	13.776	1605.5	36.71	49.31
80	17.077	2122	43.60	54.24
87.82	19.677	2574	48.99	62.74
1-Butene (liquid)				
87.82	19.677	6423	92.81	108.66
90	21.48	6659	95.47	108.53
100	29.46	7741	106.87	107.86
110	36.97	8816	117.12	107.12
120	44.04	9884	126.41	106.42
130	50.71	10945	134.90	105.81
140	57.01	12001	142.73	105.38
150	62.97	13053	149.99	105.22
160	68.62	14106	156.78	105.39
170	74.00	15163	163.19	105.99
180	79.12	16228	169.28	107.09
190	84.02	17306	175.11	108.76
200	88.72	18405	180.74	111.09
210	93.23	19528	186.22	113.38
220	97.58	20670	191.53	114.96
230	101.78	21825	196.67	115.97
240	105.83	22988	201.62	116.5
250	109.76	24155	206.38	116.8
260	113.57	25324	210.97	116.9
270	117.26	26493	215.4	117.0

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mo
273.15	118.39	26861	216.7	117.0
280	120.84	27663	219.6	117.1
290	124.31	28836	223.7	117
298.15	127.1	29796	227.0	118
300	127.7	30014	227.7	118
310	131.0	31202	231.6	119
320	134.2	32406	235.5	121
330	137.3	33632	239	124
340	140.4	34888	243	128
350	143.4	36185	247	132
360	146.3	37534	251	138
cis-*2-Butene (crystal)*				
10	0.087	2.5	0.340	0.99
20	0.641	36.3	2.453	6.74
30	1.925	147.5	6.842	15.72
40	3.861	352.4	12.672	25.22
50	6.273	648.8	19.25	33.83
60	9.004	1025.4	26.09	41.33
70	11.938	1472.5	32.97	47.95
80	14.993	1982.2	39.77	53.88
90	18.118	2548.4	46.43	59.30
100	21.276	3167.2	52.95	64.42
110	24.446	3836.3	59.32	69.41
120	27.614	4555.1	65.57	74.34
130	30.771	5323.7	71.72	79.46
134.26	32.111	5667	74.32	81.80
cis-*2-Butene (liquid)*				
134.26	32.111	12976	128.76	114.08
140	36.172	13629	133.52	113.40
150	42.925	14758	141.31	112.44
160	49.303	15878	148.54	111.74
170	55.342	16993	155.30	111.31
180	61.073	18105	161.66	111.12
190	66.527	19217	167.67	111.18
200	71.728	20330	173.38	111.47
210	76.699	21447	178.83	111.99
220	81.461	22570	184.05	112.73
230	86.031	23702	189.08	113.68
240	90.43	24844	193.95	114.8
250	94.66	25999	198.66	116.2
260	98.75	27170	203.25	117.9
270	102.70	28358	207.7	119.8
273.15	103.92	28736	209.1	120.5
280	106.53	29567	212.1	122.1
290	110.25	30802	216.5	125
298.15	113.2	31829	220	127
300	113.9	32065	221	128

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
310	117.4	33362	225	132
320	120.8	34698	229	136
330	124.2	36077	233	140
340	127.4	37505	238	145
350	130.6	38988	242	151
360	133.8	40533	246	158
trans-*2-Butene (crystal)*				
10	0.067	2.0	0.268	0.808
20	0.541	32.5	2.165	6.321
30	1.727	138.3	6.337	15.003
40	3.549	331.7	11.843	23.516
50	5.810	605.6	17.923	31.122
60	8.352	951.7	24.214	37.990
70	11.070	1363.5	30.549	44.27
80	13.899	1835.7	36.846	50.12
90	16.796	2364.9	43.073	55.69
100	19.731	2949	49.222	61.12
110	22.689	3587	55.302	66.57
120	25.659	4281	61.334	72.20
130	28.634	5033	67.346	78.15
140	31.614	5846	73.371	84.72
150	34.601	6733	79.486	92.98
160	37.602	7713	85.807	103.41
167.62	39.91	8536	90.83	113.04
trans-*2-Butene (liquid)*				
167.62	39.91	10868	104.75	110.04
170	40.83	11130	106.30	110.21
180	44.64	12236	112.62	110.87
190	48.38	13348	118.63	111.47
200	52.03	14465	124.36	112.08
210	55.61	15589	129.85	112.76
220	59.10	16721	135.11	113.56
230	62.52	17861	140.18	114.56
240	65.86	19013	145.08	115.79
250	69.12	20178	149.84	117.3
260	72.32	21361	154.47	119.3
270	75.44	22565	159.0	121.6
273.15	76.42	22949	160.4	122.4
280	78.51	23795	163.5	124.4
1-Pentene (crystal)				
10	0.171	4.9	0.659	1.85
20	1.163	61.5	4.238	10.60
30	3.211	225.4	10.725	22.22
40	6.060	502.6	18.625	32.89
50	9.403	877.2	26.95	41.76
60	13.020	1333.2	35.24	49.27
70	16.776	1859.6	43.34	55.90

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
80	20.591	2449.3	51.21	61.93
90	24.418	3096.6	58.83	67.50
100	28.230	3798.8	66.22	72.95
107.90	31.221	4393	71.93	77.40
1-Pentene (liquid)				
107.90	31.221	10200	125.75	129.04
110	33.05	10471	128.24	128.97
120	41.46	11759	139.45	128.72
130	49.40	13046	149.75	128.64
140	56.91	14333	159.28	128.74
150	64.03	15621	168.17	129.03
160	70.81	16914	176.52	129.50
170	77.26	18212	184.39	130.17
180	83.42	19518	191.85	131.04
190	89.31	20833	198.96	132.12
200	94.97	22161	205.77	133.40
210	100.40	23502	212.32	134.90
220	105.63	24859	218.63	136.61
230	110.68	26235	224.74	138.55
240	115.56	27361	230.68	140.7
250	120.28	29049	236.47	142.9
260	124.85	30489	242.12	145.2
270	129.30	31952	247.6	147.5
273.15	130.68	32418	249.4	148.3
280	133.62	33439	253.0	149.9
290	137.83	34950	258.4	152
298.15	141.2	36200	262.6	154
300	141.9	36486	263.6	155
310	145.9	38047	268.7	157
320	149.9	39633	273.7	160
330	153.7	41243	279	162
340	157.4	42878	284	165
350	161.1	44537	288	167
360	164.7	46219	293	169
cis-*2-Pentene (crystal)*				
10	0.140	4.0	0.539	1.52
20	0.958	51.1	3.515	8.95
30	2.692	193.9	9.154	19.78
40	5.184	446.3	16.34	30.49
50	8.194	799.2	24.18	39.88
60	11.525	1240	32.19	48.12
70	15.048	1759	40.17	55.43
80	18.680	2346	48.01	62.05
90	22.367	2998	55.68	68.20
100	26.07	3710	63.17	74.11
110	29.78	4480	70.51	79.88
120	33.48	5306	77.69	85.21

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
121.78	34.13	5458	78.95	86.09
cis-*2-Pentene (liquid)*				
121.78	34.13	12570	137.35	134.37
130	40.94	13669	146.09	133.24
140	48.80	14996	155.92	132.22
150	56.25	16315	165.02	131.55
160	63.32	17629	173.50	131.22
170	70.04	18940	181.45	131.20
180	76.44	20253	188.95	131.45
190	82.55	21570	196.07	131.97
200	88.39	22894	202.86	132.72
210	94.00	24225	209.36	133.68
220	99.39	25568	215.61	134.91
230	104.57	26924	221.63	136.40
240	109.57	28297	227.47	138.12
250	114.40	29687	233.2	140.05
260	119.08	31099	238.7	142.2
270	123.61	32532	244.1	144.5
273.15	125.01	32988	245.8	145.3
280	128.00	33989	249.4	147.0
290	132.28	35471	254.6	149.6
298.15	135.68	36699	258.8	151.8
300	136.44	36981	259.7	152.3
trans-*2-Pentene (crystal)*				
10	0.112	3.3	0.440	1.28
20	0.830	46.7	3.164	8.47
30	2.444	182.3	8.521	18.82
40	4.797	422.1	15.35	28.95
50	7.647	757.8	22.80	38.00
60	10.810	1179	30.46	46.11
70	14.166	1677	38.13	53.39
80	17.635	2245	45.69	59.95
90	21.166	2874	53.10	65.93
100	24.72	3562	60.34	71.47
110	28.28	4303	67.40	76.72
120	31.83	5095	74.29	81.78
130	35.36	5938	81.03	86.77
132.93	36.39	6194	82.98	88.24
trans-*2-Pentene (liquid)*				
132.93	36.39	14546	145.81	127.58
140	42.08	15449	152.43	127.99
150	49.73	16732	161.28	128.70
160	56.97	18024	169.62	129.58
170	63.83	19325	177.50	130.63
180	70.36	20637	185.00	131.83
190	76.58	21962	192.17	133.19
200	82.53	23301	199.04	134.71

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
210	88.24	24656	205.65	136.37
220	93.72	26029	212.03	138.18
230	99.00	27420	218.22	140.14
240	104.09	28832	224.23	142.23
250	109.02	30266	230.1	144.47
260	113.78	31722	235.8	146.8
270	118.40	33203	241.4	149.3
273.15	119.83	33674	243.1	150.1
280	122.89	34709	246.9	152.0
290	127.26	36242	252.2	154.7
298.15	130.74	37512	256.6	157.0
300	131.52	37803	257.5	157.6
310	135.67	39394	262.7	160.5
2-Methyl-1-butene (crystal)				
10	0.155	4.5	0.606	1.75
20	1.125	61.6	4.204	10.69
30	3.176	224.7	10.666	21.75
40	5.986	490.8	18.25	31.20
50	9.224	843.9	26.10	39.21
60	12.686	1271	33.87	46.08
70	16.256	1763	41.44	52.10
80	19.863	2311	48.75	57.56
90	23.469	2913	55.84	62.77
100	27.05	3566	62.71	67.77
110	30.60	4268	69.39	72.51
120	34.10	5016	75.90	77.13
130	37.56	5810	82.26	81.74
135.60	39.48	6275	85.76	84.37
2-Methyl-1-butene (liquid)				
135.60	39.48	14186	144.10	133.09
140	42.84	14771	148.34	133.00
150	50.18	16101	157.52	132.99
160	57.16	17432	166.11	133.24
170	63.81	18766	174.20	133.74
180	70.16	20107	181.86	134.49
190	76.23	21457	189.16	135.45
200	82.05	22817	196.14	136.62
210	87.64	24190	202.83	137.99
220	93.03	25577	209.29	139.54
230	98.22	26981	215.53	141.27
240	103.23	28403	221.58	143.17
250	108.09	29845	227.5	145.24
260	112.79	31309	233.2	147.5
270	117.35	32795	238.8	149.8
273.15	118.76	33268	240.6	150.6
280	121.79	34306	244.3	152.4
290	126.11	35843	249.7	155.0

TABLE 3 (continued)

	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
298.15	129.54	37115	254.0	157.3
300	130.32	37407	255.0	157.8
3-Methyl-1-butene (crystal)				
10	0.174	4.9	0.669	1.87
20	1.175	61.5	4.248	10.36
30	3.192	219.9	10.521	21.25
40	5.943	480.8	17.96	30.66
50	9.117	828.0	25.68	38.56
60	12.517	1248	33.32	45.33
70	16.023	1732	40.77	51.33
80	19.570	2274	47.99	56.93
90	23.119	2870	55.01	62.34
100	26.65	3519	61.85	67.57
104.71	28.31	3844	65.02	70.36
3-Methyl-1-butene (liquid)				
104.71	28.31	9203	116.20	121.81
110	32.68	9848	122.20	121.78
120	40.59	11066	132.80	121.96
130	48.06	12288	142.58	122.41
140	55.14	13515	151.68	123.13
150	61.86	14751	160.20	124.08
160	68.26	15997	168.25	125.24
170	74.37	17256	175.88	126.59
180	80.22	18530	183.16	128.10
190	85.82	19819	190.13	129.74
200	91.20	21125	196.83	131.50
210	96.39	22449	203.29	133.39
220	101.39	23793	209.54	135.41
230	106.22	25158	215.61	137.56
240	110.90	26545	221.51	139.84
250	115.44	27955	227.3	142.27
260	119.85	29391	232.9	144.8
270	124.14	30853	238.4	147.6
273.15	125.47	31319	240.1	148.5
280	128.32	32343	243.8	150.4
290	132.40	33862	249.2	153.5
298.15	135.65	35123	253.5	156.1
300	136.38	35413	254.4	156.7
2-Methyl-2-butene (crystal)				
10	0.147	4.2	0.567	1.60
20	1.017	54.6	3.745	9.53
30	2.853	203.8	9.647	20.43
40	5.450	461.1	16.98	30.80
50	8.538	815.9	24.86	40.00
60	11.926	1258	32.89	48.24
70	15.494	1778	40.89	55.67
80	19.163	2369	48.78	62.46

TABLE 3 (continued)

T(K)	$-(G_s - H_0^\circ)/T$ (J K^{-1} mole^{-1})	$H_s - H_0^\circ$ (J mole^{-1})	S_s (J K^{-1} mole^{-1})	C_s (J K^{-1} mole^{-1})
90	22.884	3026	56.50	68.75
100	26.63	3743	64.05	74.61
110	30.36	4517	71.42	80.12
120	34.09	5345	78.63	85.51
130	37.79	6227	85.69	91.01
139.40	41.24	7108	92.23	96.47
2-Methyl-2-butene (liquid)				
139.40	41.24	14705	146.73	132.24
140	41.69	14785	147.29	132.21
150	49.04	16105	156.41	131.96
160	56.02	17425	164.92	132.02
170	62.66	18746	172.93	132.35
180	69.00	20073	180.51	132.91
190	75.06	21405	187.72	133.67
200	80.87	22747	194.60	134.58
210	86.44	24098	201.19	135.65
220	91.80	25460	207.53	136.92
230	96.97	26837	213.65	138.38
240	101.95	28228	219.57	140.02
250	106.77	29637	225.3	141.84
260	111.44	31066	230.9	143.8
270	115.97	32514	236.4	146.0
273.15	117.37	32975	238.1	146.7
280	120.36	33986	241.7	148.3
290	124.64	35480	247.0	150.7
298.15	128.04	36717	251.2	152.8
300	128.80	37001	252.1	153.3
310	132.86	38547	257.2	156.0

RESULTS AND DISCUSSION

Table 1 indicates the temperature range and number of data points for the heat capacities of each alkene in the crystal and liquid states together with the phase transition data, T_m and ΔH_m, which were employed for evaluation of the condensed phase thermodynamic properties of the eleven alkenes selected.

The coefficients for heat capacity equations obtained by fitting the adopted C_s data points for each alkene appear in Table 2. The heat capacity equation $C_s = dT^3 + eT^4$ was used for extrapolating the C_s heat capacities in the lowest temperature region to 0 K for each alkene (cryst.). The number of significant figures reserved for each coefficient listed in Table 2 is sufficient for preserving accuracy in computer calculations.

The condensed phase thermodynamic properties evaluated for eleven simple alkenes in the carbon range from C_2 to C_5 appear in Table 3. These results are obtained by employing recent physical constants, temperature scale, and molecular weights. Our C_s and $H_s - H_0^\circ$ values are also consistent with those apppearing in the recent work of the Engineering Science Data Unit [23].

ACKNOWLEDGEMENT

This work was supported by the Thermodynamics Research Center (T.R.C.), Texas A&M University, College Station, Texas, and Nanjing Institute of Chemical Technology, Nanjing, Jiangsu, The People's Republic of China. The authors would like to thank the research staff C. Chen, R.C. Wilhoit and A. Kreglewski of T.R.C. for help in the computer calculations. The service provided for preparation of the manuscript for publication by the T.R.C. staff is acknowledged.

REFERENCES

1 T.B. Douglas, J. Res. Natl. Bur. Stand., 73 (1969) 451.
2 N.E. Holden, Pure Appl. Chem., 47 (1976) 77.
3 C.H. Page and P. Vigoureux, Natl. Bur. Stand. Special Publication No. 330, 1970. M.A. Paul, J. Chem. Doc., 11 (1971) 3.
4 Selected Values of Properties of Hydrocarbons and Related Compounds, Thermodynamics Research Center Hydrocarbon Project, Thermodynamics Research Center, Texas A&M University, College Station, TX. (Looseleaf data sheets, extent, 1982).
5 D.W. Morecroft, J. Inst. Pet. London, 44 (1958) 43.
6 S. Angus, B. Armstrong and K.M. de Reuck, International Thermodynamic Tables of the Fluid State, Vol. 7, Pergamon Press, New York, 1980.
7 J.H. Weber, AIChE J., 1 (1955) 210.
8 H.O. Day, D.E. Nicholson and W.A. Felsing, J. Am. Chem. Soc., 70 (1948) 1784.
9 C.J. Egan and J.D. Kemp, J. Am. Chem. Soc., 59 (1937) 1264.
10 A. Eucken and F. Hauck, Z. Phys. Chem. (Leipzig), 134 (1928) 161.
11 D.B. Pall and O. Maass, Can. J. Res. Sect. B, 16 (1938) 449.
12 H.M. Huffman, G.S. Park and M. Barmore, J. Am. Chem. Soc., 53 (1931) 3876.
13 T.M. Powell and W.F. Giauque, J. Am. Chem. Soc., 61 (1939) 2366.
14 C.E. Auerbach, B.H. Sage and W.N. Lacey, Ind. Eng. Chem., 42 (1950) 110.
15 J.G. Aston, H.L. Fink, A.B. Bestul, E.L. Pace and G.J. Szasz, J. Am. Chem. Soc., 68 (1946) 52.
16 W.G. Schlinger and B.H. Sage, Ind. Eng. Chem., 41 (1947) 1779.
17 R.B. Scott, W.J. Fergusen and F.G. Brickwedde, J. Res. Natl. Bur. Stand., 33 (1944) 1.
18 W.G. Schlinger and B.H. Sage, Ind. Eng. Chem., 44 (1952) 2454.
19 S.S. Todd and G.S. Parks, J. Am. Chem. Soc., 58 (1936) 134.
20 L. Guttman and K.S. Pitzer, J. Am. Chem. Soc., 67 (1945) 324.
21 S.S. Todd, G.D. Oliver and H.M. Huffman, J. Am. Chem. Soc., 69 (1947) 1519.
22 G.S. Parks and H.M. Huffman, J. Am. Chem. Soc., 52 (1930) 4381.
23 Eng. Sci. Data, Item No. 78015, Eng. Sci. Data Unit Ltd., London, 1978.