Ideal Gas Thermodynamic Properties of Ethylene and Propylene

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The ideal gas thermodynamic properties [$H^\circ - H_0^\circ$, $(G^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S°, C_p°, ΔHf°, ΔGf°, and log K_f] for ethylene and propylene in the temperature range 0 to 1500 K and at 1 atm have been calculated by the statistical thermodynamic method employing the most recent fundamental and molecular spectroscopic constants. The internal rotational contributions to thermodynamic properties for propylene were generated based on an internal rotation partition function formed by summation of internal rotation energy levels. The energy levels were derived from the potential function $V(\text{cm}^{-1}) = 349.2\ (1 - \cos 3\theta) - 6.5\ (1 - \cos 6\theta)$. The calculated heat capacities and entropies were compared with the available experimental values.

Key words: Critically evaluated data; enthalpy; enthalpy function; enthalpy of formation; entropy; equilibrium constant of formation; ethylene; Gibbs energy function; Gibbs energy of formation; heat capacity; ideal gas thermodynamic properties; internal rotation; internal rotation barrier height; propylene; torsional frequency.

Contents

1. Introduction

Ethylene (ethene, $CH_2 = CH_2$) and propylene (propene, $CH_3CH = CH_2$) are two key alkenes whose thermodynamic properties were investigated extensively for decades. In order to improve the reliability of the thermochemical calculations involving these two compounds, the thermodynamic properties for ethylene and propylene in the ideal gaseous state in the temperature range from 0 to 1500 K and at 1 atm were reevaluated using recent molecular and spectroscopic constants. In all computations, the most recent fundamental constants [1][1], the 1971 Atomic Weights: C = 12.011 and H = 1.0079 [2], and SI units [3], were employed except for the unit of energy where the calorie was used (1 cal = 4.184 J).

This work thoroughly reviews the past research studies on the molecular structure, vibrational frequency assignments, enthalpy of formation, and other related properties for each compound. Propylene exhibits internal rotation, i.e., the methyl group (CH_3) in the molecule can rotate around the C—C bond, and produces a special internal rotational contribution to the thermodynamic properties. Many investigators have studied the effect of the methyl rotor on the physical and thermodynamic properties of propylene. In this work, the reported observed torsional frequencies and potential barriers to internal rotation in propylene were critically reviewed and discussed.

The ideal gas thermodynamic properties were calculated by the statistical thermodynamic method based on a rigid-rotor harmonic-oscillator model. The internal rotation contributions to thermodynamic properties for propylene were evaluated by using a partition function formed by summation of internal rotational energy levels generated from a selected potential function. The calculated results were added to the other usual contributions (translation, rotation, vibration, and electronic) to yield the final property values.

[1]Figures in brackets indicate literature references in section 6.

2. Ethylene

The molecular structure of ethylene has been studied by electron diffraction [4, 5, 9], infrared [6, 7, 61], and Raman [8] spectra. Lerberghe, Wright, and Duncan [61] observed the high-resolution infrared spectrum of ethylene and determined the ground state rotational constants: $A_0 = 4.86596 \pm 0.00018\ cm^{-1}$, $B_0 = 1.001329 \pm 0.000061\ cm^{-1}$, and $C_0 = 0.828424 \pm 0.000062\ cm^{-1}$. These values were adopted to derive the product of the three principal moments of inertia: $I_A I_B I_C = 5.4345 \times 10^{-117}\ g^3\ cm^6$ for calculation of the rotational contribution to the thermodynamic properties of ethylene in the ideal gaseous state.

Many researchers have investigated the vibrational frequencies of ethylene by infrared spectra [10–13, 61] and Raman spectra [14–17, 45]. Recently Shimanouchi [18] has critically reviewed the reported spectral data and selected a complete set of vibrational wavenumbers for ethylene which was accepted for use. Five typical sets of vibrational assignments for ethylene are presented in table 1.

Using the above selected molecular and spectroscopic constants and other pertinent data, as given in table 2, we calculated the ideal gas thermodynamic functions for ethylene in the temperature range 0–1500 K and at 1 atm. The results are presented in table 3.

TABLE 1. Vibrational assignments for ethylene (cm^{-1})

Mode no.	Symmetry species	Reference				
		Gallaway and Barker, 1942 [a]	Crawford et al. 1953 [b]	Smith-Mills 1964 [c]	Herzberg 1966 [d]	Shimanouchi 1972 [e]
ν_1	a_{1g}	3019.3	3019.3	3026.4	3026.4	3026
ν_2	a_{1g}	1623.3	1623.3	1622.9	1622.6	1623
ν_3	a_{1g}	1342.4	1342.4	1342.2	1342.2	1342
ν_4	a_{1u}	825	1027	1023.0	1027	1023
ν_5	b_{1g}	3069	3075	3102.5	3102.5	3103
ν_6	b_{1g}	1055	1236	1222	1236	1236
ν_7	b_{1u}	949.2	949.2	949.3	949.2	949
ν_8	b_{2g}	943	943	943	950	943
ν_9	b_{2u}	3105.5	3105.5	3105.5	3105.3	3106
ν_{10}	b_{2u}	995.0	810.3	826.0	810.3	826
ν_{11}	b_{3u}	2989.4	2989.5	2988.7	2988.7	2989
ν_{12}	b_{3u}	1443.9	1443.5	1443.5	1443.5	1444

[a] Reference [6].
[b] Reference [11].
[c] Reference [13].
[d] Reference [19].
[e] Reference [18]; adopted in this work.

TABLE 2. Molecular constants for ethylene

Molecular weight	28.0536
Point group	D_{2h}
Symmetry number	4
Ground state configuration	^1A_g
Products of the three principal moments of inertia, $g^3\ cm^6$	5.4345×10^{-117}
Vibrational wavenumbers, cm^{-1}	3026, 1623, 1342, 1023, 3103, 1236, 949, 943, 3106, 826, 2989, 1444

Rossini and Knowlton [20] measured the enthalpy of combustion (ΔH_c°) of ethylene in oxygen at 298.15 K and 1 atm to form CO_2(g) and $H_2O(\ell)$ as -337.28 ± 0.07 kcal mol^{-1}, by flame calorimetry. Based on ΔHf°(298.15, CO_2, g) $= -94.051$ and ΔHf°(298.15, H_2O, ℓ) $= -68.315$ kcal mol^{-1} [21], the enthalpy of formation for ethylene was evaluated to be ΔHf°(298.15, C_2H_4,g) $= 12.55 \pm 0.10$ kcal mol^{-1}.

Numerous other ΔH_c° values for ethylene have been reported in the literature [22–29]. Some investigations

TABLE 3. Ideal gas thermodynamic properties for ethylene

T	$H^\circ - H_0^\circ$	$\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°	ΔH_f°	ΔG_f°	$\log K_f$
K	cal mol^{-1}	cal K^{-1} mol^{-1}				kcal mol^{-1}		
0	0	0	0	0	0	14.54	14.54	infinite
50	397	29.66	7.949	37.61	7.95	13.92	14.14	−61.784
100	795	35.17	7.949	43.12	7.95	13.78	14.40	−31.459
150	1194	38.40	7.960	46.36	8.05	13.55	14.75	−21.485
200	1605	40.69	8.024	48.72	8.45	13.23	15.19	−16.602
273.15	2264	43.23	8.290	51.52	9.69	12.69	15.99	−12.791
298.15	2513	43.96	8.430	52.39	10.24	12.50	16.31	−11.952
300	2532	44.01	8.441	52.45	10.28	12.49	16.33	−11.897
400	3679	46.54	9.198	55.74	12.67	11.75	17.73	−9.686
500	5060	48.69	10.121	58.81	14.92	11.10	19.30	−8.435
600	6652	50.62	11.088	61.71	16.87	10.53	20.99	−7.646
700	8426	52.40	12.038	64.44	18.56	10.06	22.78	−7.111
800	10357	54.07	12.947	67.01	20.03	9.66	24.62	−6.726
900	12426	55.64	13.806	69.45	21.31	9.33	26.51	−6.438
1000	14614	57.14	14.614	71.75	22.43	9.07	28.44	−6.217
1100	16908	58.57	15.370	73.94	23.42	8.87	30.37	−6.033
1200	19294	59.94	16.078	76.01	24.28	8.71	32.35	−5.892
1300	21760	61.25	16.739	77.99	25.04	8.58	34.32	−5.770
1400	24298	62.51	17.356	79.87	25.70	8.49	36.32	−5.671
1500	26898	63.73	17.932	81.66	26.28	8.42	38.31	−5.581

1 cal = 4.184 J.

[22–25] may now be considered as of historical importance only. The results of the remaining measurements have been critically reviewed and discussed by Rossini and Knowlton [20]. Due to lack of high purity sample material and high precision calorimetric apparatus, these early ΔH_c° values were not adopted.

Kistiakowsky et al. [30, 31] measured the enthalpy of hydrogenation of ethylene to form ethane at 355 K with Cu and Pt catalysts. Kistiakowsky and Nickle [33] determined the equilibrium constants of the reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ at 723.2 and 653.2 K. From the above results, using $\Delta Hf^\circ(298.15, C_2H_6, g) = -20.24$ kcal mol^{-1} [32], the average value of $\Delta Hf^\circ(298.15, C_2H_4, g)$ was obtained as 12.36 kcal mol^{-1}.

In view of the above difference in the values of $\Delta Hf^\circ(298.15, C_2H_4, g)$, the best adjusted value, 12.50 kcal mol^{-1}, listed in API44 Tables [32] was adopted for gaseous ethylene in this work. Incorporating this value with the enthalpies $(H^\circ - H_0^\circ)$ and Gibbs energy functions $-(G^\circ - H_0^\circ)/T$ for C (graphite) and $H_2(g)$ from [34] and for $C_2H_4(g)$ from this work, the values of ΔHf°, ΔGf°, and log K_f in the temperature range 0 to 1500 K were calculated and presented in table 3.

3. Propylene

Propylene is the simplest alkyl derivative of ethylene. The molecular structure of this compound has been elucidated by Lide and Christensen [35] and Lide and Mann [36] from the microwave spectra of seven isotopic species. In a more recent analysis of the microwave spectrum, Hirota [37] evaluated the three rotational constants as $A_0 = 1.54375$, $B_0 = 0.31039$, and $C_0 = 0.27133$ cm^{-1}. From these constants, we obtained $I_A = 1.8133 \times 10^{-39}$, $I_B = 9.0187 \times 10^{-39}$, and $I_C = 1.0317 \times 10^{-38}$ g cm^2. The product was 1.6873×10^{-115} g^3 cm^6 which was adopted in this work.

The vibrational spectra of propylene have been studied by many investigators. From observed infrared [39, 40, 63–70] and Raman [63, 66, 69, 71, 72] spectra, the fundamental vibrational modes for propylene were assigned. Table 4 lists five sets of fundamental vibrational assignments reported. In a recent study Silvi et al. [66] recorded the infrared and Raman spectra between 4000 and 200 cm^{-1} for four isotopic species of propylene in the gaseous and liquid states. Their vibrational assignments were accepted in this work.

In 1937 Pitzer [43] suggested a hindered internal rotation for the methyl group in propylene. Since that time, many chemists have concerned themselves with this problem. Due to lack of a reliable observed torsional frequency, Pitzer selected the internal rotation barrier height as an adjustable parameter to make the calculated heat capacities and entropies agree with the reported experimental data. Table 5 summarizes the internal rotation potential barriers in propylene as reported by different investigators. The discrepancies among these V_3 values are caused in part by the fact that different investigators used different molecular structural parameters and vibrational frequencies for the evaluation.

In 1957, Lide and Mann [36] analyzed satisfactorily the splittings of the microwave lines of propylene as a result of internal rotation by the methods of Hecht and Dennison [44]. They derived the barrier height $V_3 =$

TABLE 4. Vibrational assignments for propylene (cm^{-1})

Mode no.	Symmetry species	Reference				
		Herzberg (1945) [a]	Kilpatrick and Pitzer (1947) [b]	Lord and Venkateswarlu (1953) [c]	Sverdlov (1956) [d]	Silvi et al. (1973) [e]
ν_1	a'	3081	3050	3089.7	3090	3091.0
ν_2	"	3012	3050	(3013)	3013	3022
ν_3	"	2979	3050	2991.5	2992	2991.0
ν_4	"	2916	2950	2932.7	2954	2973
ν_5	"	2852	2950	2869.8	2933	2931.9
ν_6	"	1647	1649	1651.6	1652	1652.8
ν_7	"	1448	1444	1473.6	1474	1458.5
ν_8	"	1416	1415	1419.2	1419	1414
ν_9	"	1399	1370	1377.6	1378	1378.0
ν_{10}	"	1289	1297	1298	1298	1298.0
ν_{11}	"	1224	1042	1229	1172	1177.5
ν_{12}	"	1043	1172	1171.9	963	934.5
ν_{13}	"	919	920	920.4	920	919
ν_{14}	"	417	417	427.5	428	428
ν_{15}	a''	2960	2950	2954.0	2954	2952.8
ν_{16}	"	1472	1444	1442.6	1443	1442.5
ν_{17}	"	1166	1050	1044.7	912	1044.7
ν_{18}	"	996	990	990.6	1045	990.0
ν_{19}	"	936	911	912.4	578	912
ν_{20}	"	578	580	577.6	991	575.2
ν_{21} (tors.)	"			(174)		188

[a] Reference [67].
[b] Reference [38].
[c] Reference [39].
[d] Reference [63].
[e] Reference [66]; the reported values were adopted in this work.

TABLE 5. Reported potential barriers to internal rotation in propylene.

V_3	V_6	Investigator (year)	Reference
cal mol^{-1}			
800		Pitzer (1937)	[43]
600–800		Kistiakowsky et al. (1938)	[42]
2119		Crawford et al. (1939)	[41]
800		Kistiakowsky and Rice (1940)	[50], [43]
2100		Kistiakowsky and Rice (1940)	[50], [52]
2100		Kistiakowsky et al. (1940)	[52]
2000		Telfair (1942)	[53]
1950		Kilpatrick and Pitzer (1946)	[38]
1978		Lide and Mann (1957)	[36]
2033	−46	Fateley and Miller (1963)	[46]
1997	−37	Hirota (1966)	[37]
2038	−63	Moller et al. (1967)	[47]
1952	−14	Souter and Wood (1970)	[48]
2680 [a]		Durig and Hawley (1972)	[54]
1997	−37	Selected value in this work	

[a] Refer to propylene in the solid state.

TABLE 6. Observed torsional wavenumber in propylene

Experimental method	Torsional wavenumber, cm^{-1}	Reference
Infrared, overtone band	174	[39]
Far infrared spectrum	$188 \pm 1 (0 \rightarrow 1)$	[46]
	$170.4 \pm 1 (1 \rightarrow 2)$	
	$163.8 \pm 1 (2 \rightarrow 3A?)$	
	$188.0 (0 \rightarrow 1)$	[47]
	$171.5 (1 \rightarrow 2)$	
	$188.0 \pm 0.5 (0 \rightarrow 1)$	[48]
	$170.2 \pm 0.5 (1 \rightarrow 2)$	
	$188 (0 \rightarrow 1)$	[66]
Theoretical calculation	$189 (0 \rightarrow 1)$	This work
	$170 (1 \rightarrow 2)$	
	$161 (2 \rightarrow 3A)$	

1978 ± 17 cal mol^{-1} for propylene, which is in agreement with the values determined previously from calorimetric measurements as listed in table 5. By use of the moment of inertia of the methyl group about its symmetry axis $I_\alpha = 5.186 \times 10^{-40}$ g cm^2 [35], instead of 5.153×10^{-40} g cm^2 [36], the value of V_3 was reevaluated by Hirota [37] as 1957 ± 17 cal mol^{-1}

Fateley and Miller [46] observed a series of transitions between CH_3 torsional levels: 188 ± 1 ($0 \rightarrow 1$), 170.4 ± 1 ($1 \rightarrow 2$), and 163.8 ± 1 cm^{-1} ($2 \rightarrow 3A?$) in the far-infrared spectrum for propylene. From these data, the potential function for internal rotation of the methyl group in propylene was determined as V (in cal mol^{-1}) $= \frac{1}{2} V_3 (1 - \cos 3\theta) + \frac{1}{2} V_6 (1 - \cos 6\theta)$, where $V_3 = 2033$ and $V_6 = -46$. Moller et al. [47] derived the potential function parameters as $V_3 = 2038$ and $V_6 = -63$ cal mol^{-1} from two strong torsional bands, observed at 188 and 171.5 cm^{-1}, in the far infrared spectrum for propylene. Table 6 summarizes the observed torsional wavenumbers.

The microwave rotational spectra in the first and second excited states of the methyl torsion were observed by Hirota [37]. Based on his analysis, Hirota determined the internal rotation potential function as $V = \frac{1}{2}(1997)(1 - \cos 3\theta) - \frac{1}{2}(37)(1 - \cos 6\theta)$. Souter and Wood [48] reported two torsional bands at 188.0 ± 0.5 and 170.2 ± 0.5 cm^{-1}. They combined the infrared and microwave spectral data and evaluated the two potential barriers as $V_3 = 1953$ cal mol^{-1} and $V_6 = -14$ cal mol^{-1}.

The differences in the results listed in table 5 between the values of torsional barriers determined by microwave splitting and those obtained from far infrared transitions can be attributed to the different models used in the analysis.

The selected molecular, spectroscopic, and thermal constants, employed for the evaluation of the ideal gas thermodynamic properties for propylene, are given in table 7. The calculated thermodynamic properties are presented in table 8.

For calculation of thermodynamic properties due to internal rotation, we adopted the potential function and related molecular constants determined by Hirota [37] for the generation of 104 internal rotation energy levels up to 20178 cm^{-1}. The procedure developed by Laane [49] was adopted for generation of these energy levels.

The enthalpy of formation $\Delta Hf°(298.15\ \text{K, g}) = 4.88$ kcal mol^{-1} for propylene was taken from the API44 tables [32]. The values of $H°-H_0^\circ$ and $(G°-H_0^\circ)/T$ for the elements C (graphite) and H_2(g), used for calculation of $\Delta Hf°$, $\Delta Gf°$, and log K_f at various temperatures, were obtained from the recent values reported in the TRC Data Project tables [34].

TABLE 7. Molecular constants for propylene

Molecular weight	42.0804
Point group	C_s C_{3v} (for methyl top)
Symmetry number	3
Ground state configuration	$^1A'$
Product of the three principal moments of inertia, $I_A I_B I_C$, g^3 cm^6	1.6873×10^{-115}
Reduced moment, I_r, g cm^2	3.945×10^{-40}
Potential barrier height, cal mol^{-1}	$V_3 = 1997$
Vibrational wavenumber, cm^{-1}	3091.0, 3022, 2991, 2973, 2932, 1653, 1459, 1414, 1378, 1298, 1178, 935, 919, 428, 2953, 1443, 1045, 990, 912, 575
Enthalpy of formation, $\Delta Hf°$ (298.15 K), kcal mol^{-1}	4.89

TABLE 8. Ideal gas thermodynamic properties for propylene

T	$H°-H_0^\circ$	$-\frac{(G°-H_0^\circ)}{T}$	$\frac{(H°-H_0^\circ)}{T}$	$S°$	$C_p°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
K	cal mol^{-1}	cal K^{-1} mol^{-1}				kcal mol^{-1}		
0	0	0	0		0	8.47	8.47	infinite
50	400	37.05	7.996	45.04	8.21	7.35	8.24	−36.006
100	838	42.69	8.376	51.07	9.34	6.98	9.26	−20.240
150	1336	46.19	8.903	55.09	10.60	6.53	10.49	−15.289
200	1900	48.83	9.499	58.33	12.01	6.00	11.89	−12.997
273.15	2865	51.93	10.488	62.42	14.45	5.16	14.17	−11.337
298.15	3238	52.87	10.859	63.72	15.37	4.88	15.02	−11.010
300	3266	52.93	10.887	63.82	15.44	4.86	15.09	−10.989
400	5000	56.28	12.500	68.78	19.23	3.77	18.67	−10.198
500	7102	59.25	14.204	73.46	22.75	2.82	22.50	−9.834
600	9534	61.99	15.890	77.88	25.81	2.02	26.51	−9.656
700	12251	64.56	17.501	82.07	28.46	1.36	30.65	−9.569
800	15215	67.00	19.018	86.02	30.77	0.82	34.87	−9.526
900	18394	69.32	20.438	89.76	32.77	0.41	39.16	−9.508
1000	21761	71.55	21.761	93.31	34.52	0.11	43.49	−9.505
1100	25291	73.68	22.992	96.67	36.05	−0.10	47.80	−9.498
1200	28964	75.73	24.137	99.87	37.38	−0.25	52.20	−9.506
1300	32762	77.70	25.201	102.9	38.54	−0.34	56.56	−9.509
1400	36667	79.61	26.190	105.8	39.55	−0.38	60.97	−9.518
1500	40668	81.45	27.112	108.6	40.43	−0.39	65.34	−9.520

1 cal = 4.184 J.

4. Discussion

The vapor heat capacity of ethylene in the temperature range 178.6–464.0 K was measured calorimetrically by Eucken and Parts [55]. Haas and Stegeman [56] determined C_p° of ethylene at 298.16, 319.6, and 339.96 K, using a flow calorimeter. By the adiabatic expansion method of Lummer and Pringsheim, employing pure nitrogen as the standard comparison gas, Burcik, Eyster, and Yost [57] obtained the C_p° values at 270.7, 300.0, and 320.7 K for ethylene. A comparison of the differences in the observed and calculated heat capacities for ethylene are presented in table 9 and figure 1. The results indicate that our calculated values are in reasonable agreement with the experimental measurements; the differences are expected to be within their experimental uncertainties.

TABLE 9. Comparison of calculated and measured heat capacities of ethylene [a]

T K	C_p°		C_p° (calc.) − C_p° (exptl.)	Percent deviation
	Experimental	Calculated		
Burcik, Eyster, and Yost (1941) [b]				
270.7	9.74	9.64	−0.10	−1.0
300.0	10.39	10.28	−0.11	−1.1
320.7	10.99	10.76	−0.23	−2.1
Eucken and Parts (1933) [c]				
178.15	8.283	8.224	−0.059	−0.7
178.65	8.305	8.229	−0.076	−0.9
179.05	8.290	8.232	−0.058	−0.7
192.35	8.438	8.362	−0.076	−0.9
192.75	8.452	8.366	−0.086	−1.0
193.15	8.460	8.370	−0.090	−1.1
210.40	8.673	8.583	−0.090	−1.0
210.80	8.672	8.588	−0.084	−1.0
211.15	8.696	8.593	−0.103	−1.2
230.90	8.975	8.893	−0.082	−0.9
231.40	9.008	8.901	−0.107	−1.2
231.85	9.021	8.909	−0.112	−1.2
250.60	9.327	9.243	−0.084	−0.9
251.00	9.336	9.250	−0.086	−0.9
251.25	9.332	9.255	−0.077	−0.8
271.80	9.803	9.666	−0.137	−1.4
272.10	9.808	9.672	−0.136	−1.4
272.45	9.815	9.679	−0.136	−1.4
293.45	10.238	10.136	−0.102	−1.0
293.55	10.266	10.138	−0.128	−1.2
367.70	11.887	11.890	+0.003	0.0
368.10	11.900	11.900	0.000	0.0
368.70	11.905	11.915	0.010	0.1
463.60	14.160	14.129	−0.031	−0.2
464.00	14.151	14.138	−0.013	−0.1
Haas and Stegeman (1932) [d]				
298.16	9.97	10.24	+0.27	+2.7
319.16	10.40	10.64	0.24	2.3
339.96	10.98	11.10	0.12	1.1

[a] Unit = cal K^{-1} mol^{-1}; 1 cal = 4.184 J.
[b] Reference [57].
[c] Reference [55].
[d] Reference [56].

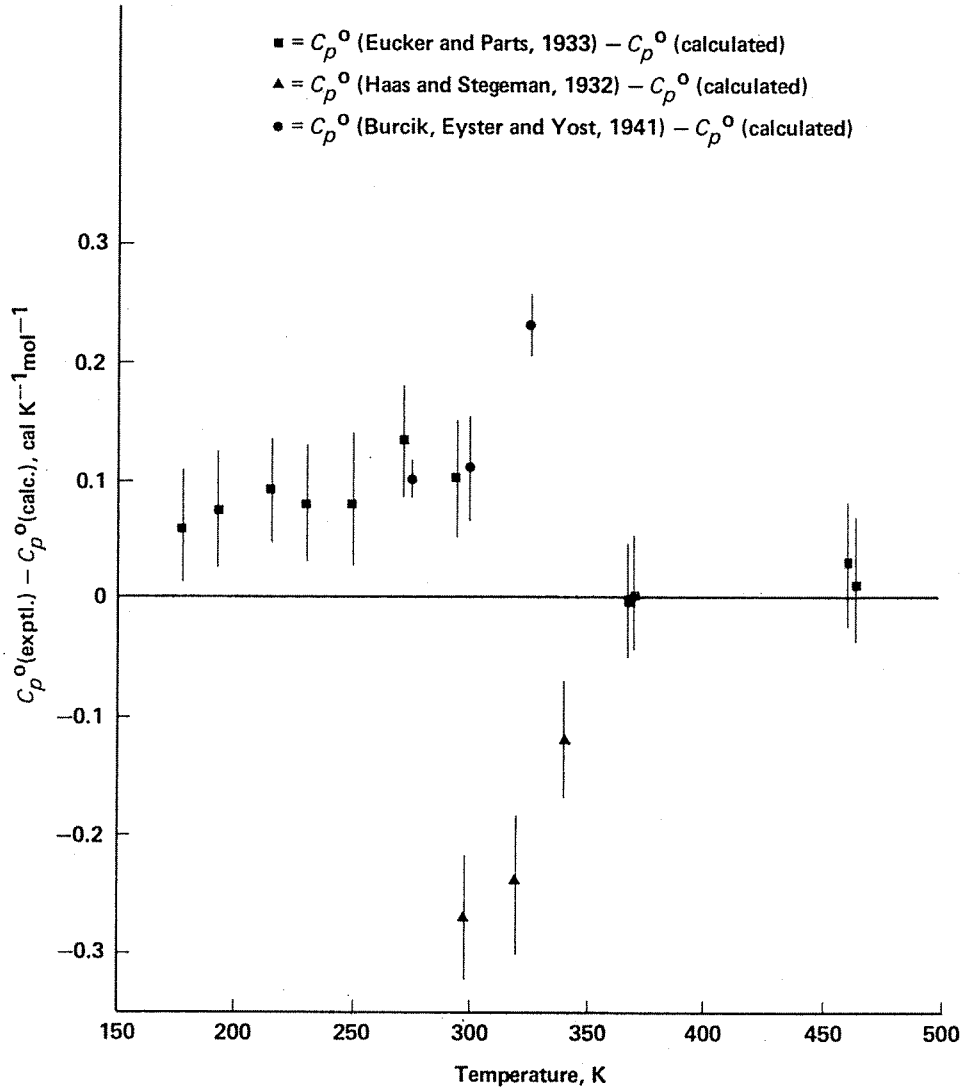

Figure 1. Comparison of Heat Capacity Data for Ethylene

Egan and Kemp [58] have measured calorimetrically the low temperature heat capacities of ethylene from 15 K to the boiling point (169.40 ± 0.05 K). The melting point was found to be 103.95 ± 0.05 K, the enthalpy of fusion 800.8 ± 0.8 cal mol^{-1}, and the enthalpy of vaporization 3237 ± 3 cal mol^{-1}. Based on these data, the entropy of ideal gas at the boiling point and 1 atm was evaluated to be 47.36 ± 0.1 cal K^{-1} mol^{-1} (see table 10 for details) which compares favorably with our entropy value of 47.35 cal K^{-1} mol^{-1}.

Huffman et al. [59] have measured the low temperature heat capacities for propylene in the crystal (68.9–81.6 K) and liquid (93.1–210.3 K) states. From the experimental measurements and the estimated missing data, they obtained the entropy of propylene as $S°$ (298.15 K, g) = 63.1 cal K^{-1} mol^{-1}.

Powell and Giauque [60] determined the heat capacities (14.18–86.17 K, c; 93.91–223.40 K, ℓ), melting point (87.85 K), boiling point (225.35 K), and enthalpies of fusion (717.6 cal mol^{-1}) and vaporization (4402 cal mol^{-1}) for propylene. Based on $S°$(15 K) = 0.482 cal K^{-1} mol^{-1} from Debye extrapolation, the above measurements, and correction for gas imperfection = 0.19 cal K^{-1} mol^{-1}, they calculated the entropy for propylene $S°$ (225.35 K, g) = 59.93 ± 0.1 cal K^{-1} mol^{-1}. In these calculations, the values 0 °C = 273.10 K and molecular weight = 42.078 were employed. Using the

TABLE 10. Comparison of calculated and the third law entropy for ethylene [a]

	Experimental [b]	
0–15 k	Debye extrapolation	0.25
15–103.95 K	graphical	12.226
800.8/103.95	fusion	7.704
103.95–169.40 K	graphical	7.924
3237/169.40 K	vaporization	19.11
	Entropy of real gas at T_b	47.21
	Correction for gas imperfection	0.15
	Entropy of ideal gas at T_b and 1 atm.	47.36
	Calculated	47.35

[a] Unit = cal K^{-1}mol^{-1}; 1 cal = 4.184 J.
[b] Reference [58].

correction for gas imperfection as 0.033 cal K^{-1} mol^{-1} [32], we obtained $S°(225.4\ K, g) = 59.77$ cal K^{-1} mol^{-1}, while our calculated entropy value is 59.80 cal K^{-1} mol^{-1}. The agreement is excellent. Therefore, the conclusion reached by Powell and Giauque, that the entropy discrepancy between the third law calorimetric entropy and the statistically calculated entropy was due to random end for end orientation of $CH_2 = CH - CH_3$ molecule in the crystal lattice, seems no longer valid.

The reported entropies of propylene, calculated by the statistical thermodynamic method from the molecular and spectroscopic constants, are compared with those obtained from calorimetric measurements in table 11.

The propylene vapor heat capacities have been determined by different experimental methods [50, 52, 53, 62]. The heat capacities reported by Kistiakowsky and Rice (272.29–367.11 K) [50] and Kistiakowsky et al. (148.1–291.1 K) [52] were evaluated by the Lummer-Pringsheim adiabatic expansion method. In this method, the values of $C_p°$ were derived from the measured low pressure thermal conductivities of propylene. Telfair [53] used sound velocity measurements as a means of determining the gaseous heat capacities of propylene. Bier et al. [62] measured the specific heat (298.15–473.15 K, 1–120 bar) for propylene calorimetrically. By extrapolation of measured heat capacities to zero pressure, they obtained the $C_p°$ values for propylene in the ideal gaseous state in the temperature range 298.15–473.15 K. Table 12 gives the comparison of our calculated results with the extrapolations of experimental measurements. The deviations in $C_p°$ are shown graphically in figure 2.

It should be mentioned that, using the selected potential function and derived reduced moment for internal rotation, we calculated the first three torsional transitions as 189 ($0 \rightarrow 1$), 170 ($1 \rightarrow 2$), and 161 ($2 \rightarrow 3A$) cm^{-1}, which are in good agreement with those observed by Fateley and Miller [46] as shown in table 6. This indicates that the generated internal rotation energy levels are reliable.

It is interesting to note that the use of the new 1973 physical constants [1] for the calculation produces insignificant changes in the derived thermodynamic properties for ethylene and propylene. For example in the temperature range from 50 to 1500 K, the increase in heat capacity and entropy are: 0.000–0.001 and 0.001–0.003 cal K^{-1} mol^{-1}, respectively, for ethylene; and 0.000–0.001 and 0.000–0.002 cal K^{-1} mol^{-1}, respectively, for propylene. There is essentially no enthalpy change for both ethylene and propylene. The maximum increase in enthalpy, at higher temperatures, is 1 cal mol^{-1}.

TABLE 11. Reported gaseous entropies of propylene

Investigator (year)	Method	$S°$, cal K^{-1} mol^{-1}	
		Reported	This work
Huffman et al. (1931) [a]	calorimetric	63.1 (298.15 K)	63.72 (298.15 K)
Pitzer (1937) [b]	calculated	65.1 ± 0.7 (298.15 K)	63.72 (298.15 K)
Powell and Giauque (1939) [c]	calorimetric	59.93 ± 0.1 (225.35 K)	
		59.77 ± 0.1 (225.35 K)	59.80 (225.35 K)
Crawford et al. (1939) [d]	calculated	59.87 (225.35 K)	59.80 (225.35 K)
Kilpartrick and Pitzer (1949) [e]	calculated	63.80 (298.15 K)	63.72 (298.15 K)

[a] Reference [59].
[b] Reference [43].
[c] Reference [60]; we recalculated the reported entropy 59.93 cal K^{-1} mol^{-1} as 59.77 cal K^{-1} mol^{-1}, see text.
[d] References [41] and [50].
[e] Reference [38].

TABLE 12. Comparison of calculated and measured heat capacities of propylene [a]

T K	C_p°		C_p° (calc.) − C_p° (exptl.)	Percent deviation
	Experimental	Calculated		
Kistiakowsky and Rice (1940) [b]				
272.3	14.36	14.42	0.06	0.4
299.3	15.47	15.42	−0.05	−0.3
333.9	16.74	16.72	−0.02	−0.1
367.1	17.93	17.99	+0.06	+0.3
Kistiakowsky, Lacher, and Ransom (1940) [c]				
148.1	10.63	10.55	−0.08	−0.8
148.3	10.64	10.55	−0.09	−0.8
157.3	10.86	10.79	−0.07	−0.6
157.6	10.86	10.80	−0.06	−0.6
158.0	10.87	10.81	−0.06	−0.6
212.3	12.46	12.39	−0.07	−0.6
213.9	12.50	12.44	−0.06	−0.5
219.9	12.68	12.63	−0.05	−0.4
220.2	12.70	12.64	−0.06	−0.5
223.4	12.82	12.74	−0.08	−0.6
223.9	12.83	12.76	−0.07	−0.5
256.4	13.90	13.85	−0.05	−0.4
258.3	13.97	13.92	−0.05	−0.4
258.4	13.98	13.92	−0.06	−0.4
259.0	14.04	13.95	−0.09	−0.6
291.1	15.16	15.11	−0.05	−0.3
Telfair (1942) [d]				
270	14.29	14.34	+0.05	+0.3
300	15.47	15.44	−0.03	−0.2
350	17.35	17.34	−0.01	−0.1
400	19.16	19.23	+0.07	+0.4
430	20.23	20.33	0.10	0.5
460	21.28	21.39	0.11	0.5
500	22.65	22.75	0.10	0.4
510	22.99	23.07	0.08	0.3
Bier, Ernst, Kunze, and Maurer (1972) [e]				
298.15	15.49	15.37	−0.12	−0.8
323.15	16.22	16.32	+0.10	+0.6
348.15	17.16	17.27	0.11	0.6
365.15	17.80	17.92	0.12	0.7
373.15	18.11	18.22	0.11	0.6
398.15	19.09	19.16	0.07	0.4
423.15	19.99	20.08	0.09	0.5
448.15	20.90	20.97	0.07	0.3
473.15	21.79	21.84	0.05	0.2

[a] Unit = cal K^{-1} mol^{-1}; 1 cal = 4.184 J.
[b] Reference [50].
[c] Reference [52].
[d] Reference [53].
[e] Reference [62].

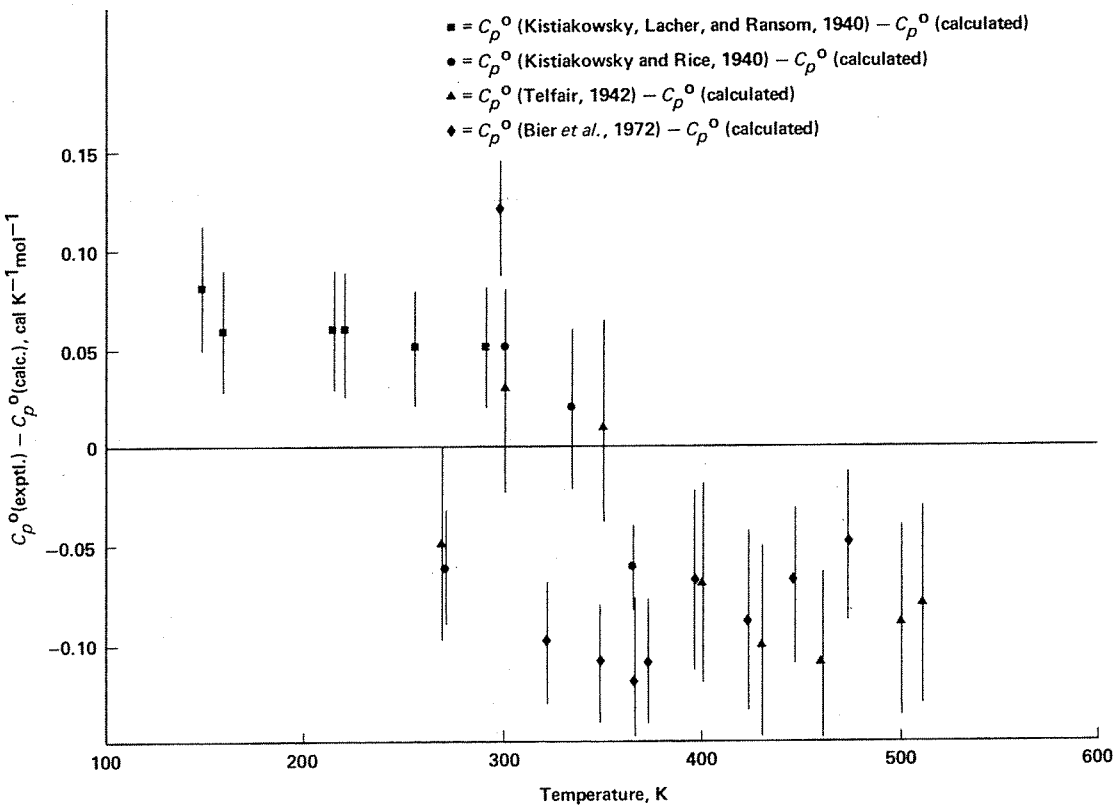

Figure 2. Comparison of Heat Capacity Data for Propylene

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