

Ideal Gas Thermodynamic Properties of Ethylene and Propylene

Jing Chao and Bruno J. Zwolinski

Thermodynamics Research Center, Department of Chemistry, Texas A&M University, College Station, Texas 77843

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° , ΔH_f° , ΔG_f° , 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

	Page		Page
1. Introduction.....	251	Table 5. Reported Potential Barriers to Internal Rotation in Propylene.....	254
2. Ethylene.....	252	Table 6. Observed Torsional Frequency in Propylene.....	254
3. Propylene.....	253	Table 7. Molecular Constants for Propylene.....	255
4. Discussion.....	256	Table 8. Ideal Gas Thermodynamic Properties for Propylene.....	255
5. Acknowledgment.....	260	Table 9. Comparison of Calculated and Measured Heat Capacities of Ethylene.....	256
6. References.....	260	Table 10. Comparison of Calculated and the Third Law Entropy for Ethylene.....	257
		Table 11. Reported Gaseous Entropies of Propylene.....	258
		Table 12. Comparison of Calculated and Measured Heat Capacities of Propylene.....	259

List of Tables

Table 1. Vibrational Assignments for Ethylene...	252
Table 2. Molecular Constants for Ethylene.....	252
Table 3. Ideal Gas Thermodynamic Properties for Ethylene.....	253
Table 4. Vibrational Assignments for Propylene.....	254

1. Introduction

Ethylene (ethene, $\text{CH}_2 = \text{CH}_2$) and propylene (propene, $\text{CH}_3\text{CH}=\text{CH}_2$) 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.

¹Figures in brackets indicate literature references in section 6.



TABLE 3. Ideal gas thermodynamic properties for ethylene

<i>T</i>	$H^\circ - H_0^\circ$	$(G^\circ - H_0^\circ)$	$(H^\circ - H_0^\circ)$	S°	C_p°	ΔH_f°	ΔG_f°	log K_f
		T	T					
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 $\Delta H_f^\circ(298.15, C_2H_6, g) = -20.24$ kcal mol⁻¹ [32], the average value of $\Delta H_f^\circ(298.15, C_2H_4, g)$ was obtained as 12.36 kcal mol⁻¹.

In view of the above difference in the values of $\Delta H_f^\circ(298.15, C_2H_4, g)$, 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 H₂(g) from [34] and for C₂H₄(g) from this work, the values of ΔH_f° , ΔG_f° , 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 rota-

tional 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 cm². The product was 1.6873×10^{-115} g³ cm⁶ 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 $V_3 =$



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 $163.8 \pm 1 \text{ cm}^{-1}$ ($2 \rightarrow 3A?$) 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 $V_6 = -63 \text{ cal mol}^{-1}$ 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 $170.2 \pm 0.5 \text{ cm}^{-1}$. They combined the infrared and microwave spectral data and evaluated the two potential barriers as $V_3 = 1953 \text{ cal mol}^{-1}$ and $V_6 = -14 \text{ cal mol}^{-1}$.

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 $\Delta H_f^\circ(298.15 \text{ K, g}) = 4.88 \text{ kcal mol}^{-1}$ for propylene was taken from the API44 tables [32]. The values of $H^\circ - H_0^\circ$ and $(G^\circ - H_0^\circ)/T$ for the elements C (graphite) and $\text{H}_2(\text{g})$, used for calculation of ΔH_f° , ΔG_f° , 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, $I_A I_B I_C$, $\text{g}^3 \text{cm}^6$	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, ΔH_f° (298.15 K), kcal mol^{-1}	4.89

TABLE 8. Ideal gas thermodynamic properties for propylene

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}	$\text{cal K}^{-1} \text{mol}^{-1}$			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.

=====

=====

=====

1

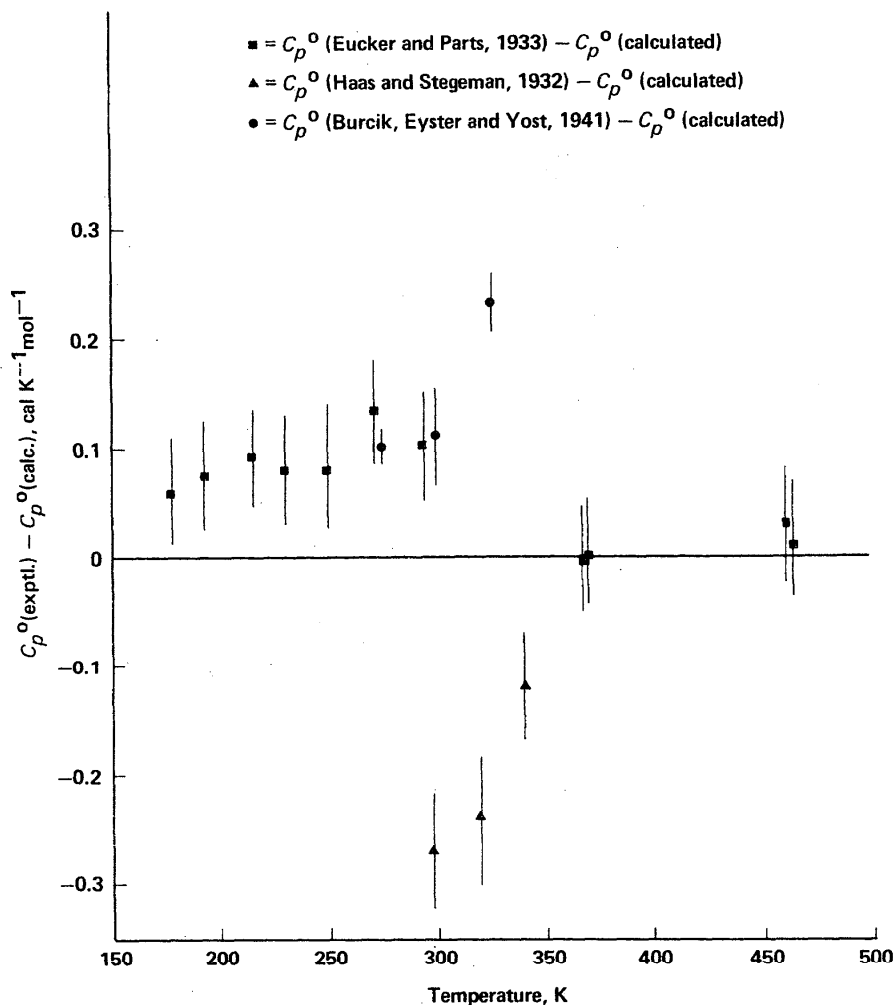


Figure 1. Comparison of Heat Capacity Data for Ethylene

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 $S^\circ(298.15$ 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 $S^\circ(15$ K) = 0.482 cal K⁻¹ mol⁻¹ from Debye extrapolation, the above meas-

urements, and correction for gas imperfection = 0.19 cal K⁻¹ mol⁻¹, they calculated the entropy for propylene $S^\circ(225.35$ K, g) = 59.93 ± 0.1 cal K⁻¹ mol⁻¹. In these calculations, the values $0^\circ\text{C} = 273.10$ 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.

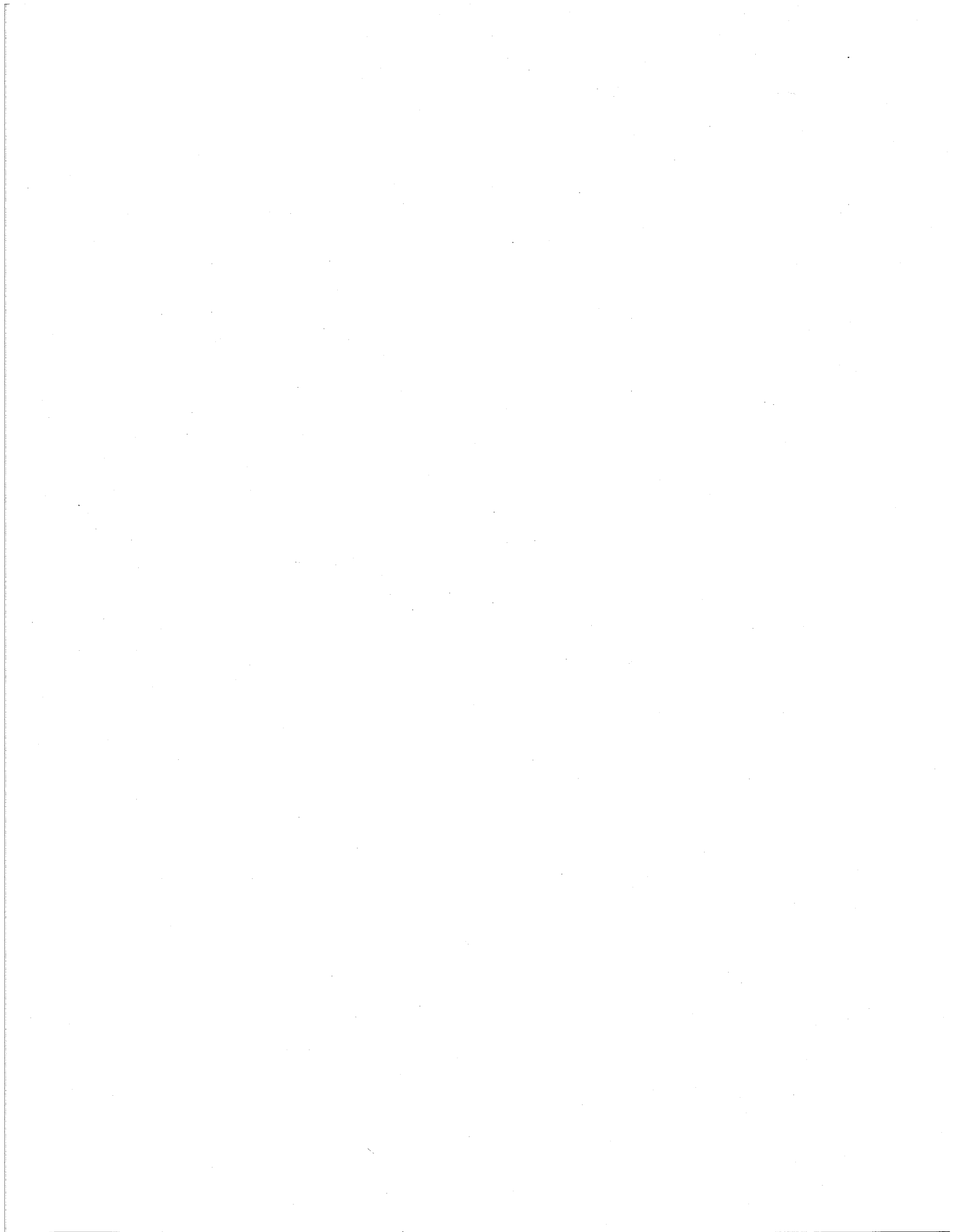
^b Reference [58].



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

T K	C _p ^o		C _p ^o (calc.) - C _p ^o (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].



- [34] Zwolinski, B. J., et al., "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center Data Project, Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843 (loose-leaf data sheets, extant, 1973).
- [35] Lide, D. R., Jr., and Christensen, D., *J. Chem. Phys.* **35**, 1374 (1961).
- [36] Lide, D. R., Jr., and Mann, D. E., *J. Chem. Phys.* **27**, 868 (1957).
- [37] Hirota, E., *J. Chem. Phys.* **45**, 1984 (1966).
- [38] Kilpatrick, J. E., and Pitzer, K. S., *J. Res. Nat. Bur. Stand.* **38**, 191 (1947).
- [39] Lord, R. C., and Venkateswarlu, P., *J. Opt. Soc. Amer.* **43**, 1097 (1953).
- [40] Wilson, E. B., Jr., and Wells, A., *J. Chem. Phys.* **9**, 319 (1941).
- [41] Crawford, B. L., Jr., Kistiakowsky, G. B., Rice, W. W., Wells, A. J., and Wilson, E. B., Jr., *J. Amer. Chem. Soc.* **61**, 2980 (1939).
- [42] Kistiakowsky, G. B., Lacher, J. R., and Ransom, W. W., *J. Chem. Phys.* **6**, 900 (1938).
- [43] Pitzer, K. S., *J. Chem. Phys.* **5**, 473 (1937).
- [44] Hecht, K. T., and Dennison, D. M., *J. Chem. Phys.* **26**, 31 (1957).
- [45] Blumenfeld, S. M., Reddy, S. P., and Welsh, H. L., *Can. J. Phys.* **48**, 513 (1970).
- [46] Fateley, W. G., and Miller, F. A., *Spectrochim. Acta* **19**, 611 (1963).
- [47] Moller, K. D., De Meo, A. R., Smith, D. R., and London, L. H., *J. Chem. Phys.* **47**, 2609 (1967).
- [48] Souter, C. E., and Wood, J. L., *J. Chem. Phys.* **52**, 674 (1970).
- [49] Lewis, J. D., Malloy, T. B., Jr., Chao, T. H., and Laane, J., *J. Mol. Struct.* **12**, 427 (1972).
- [50] Kistiakowsky, G. B., and Rice, W. W., *J. Chem. Phys.* **8**, 610 (1940).
- [51] Crawford, B. L., *J. Chem. Phys.* **8**, 273 (1940).
- [52] Kistiakowsky, G. B., Lacher, J. R., and Ransom, W. W., *J. Chem. Phys.* **8**, 970 (1940).
- [53] Telfair, D., *J. Chem. Phys.* **10**, 167 (1942).
- [54] Durig, J. R., and Hawley, C. W., *J. Chem. Phys.* **57**, 1426 (1972).
- [55] Eucken, A., and Parts, A., *Z. Phys. Chem.* **B20**, 184 (1933).
- [56] Haas, M. E., and Stegeman, G., *J. Phys. Chem.* **36**, 2127 (1932).
- [57] Burcik, B. J., Eyster, E. H., and Yost, D. M., *J. Chem. Phys.* **9**, 118 (1941).
- [58] Egan, C. J., and Kemp, J. D., *J. Amer. Chem. Soc.* **59**, 1264 (1937).
- [59] Huffman, H. M., Parks, G. S., and Barmore, M., *J. Amer. Chem. Soc.* **53**, 3876 (1931).
- [60] Powell, T. M., and Giauque, W. F., *J. Amer. Chem. Soc.* **61**, 2366 (1939).
- [61] Lerberghe, D. V., Wright, I. J., and Duncan, J. L., *J. Mol. Spectrosc.* **42**, 251 (1972).
- [62] Bier, K., Ernst, G., Kunze, J., and Maurel, G., *Verfahrenstechnik Mainz* **6**, 261 (1972).
- [63] Sverdlov, L. M., *Dokl. Akad. Nauk SSSR* **106**, 80 (1956).
- [64] Zerbi, G., Peraldo, M., and Mantice, E., *Int. Symp. Mol. Struct. Spectrosc.*, Tokyo (1962).
- [65] Gross, B., and Forel, M. T., *J. Chim. Phys. Physiochim. Biol.* **63**, 1163 (1966).
- [66] Silvi, B., Labarbe, P., and Perchard, J. P., *Spectrochim. Acta, Part A* **29**, 263 (1973).
- [67] Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945.
- [68] Farina, M., and Peraldo, M., *Gazz. Chim. Ital.* **90**, 973 (1960).
- [69] Avery, W. H., and Ellis, C. F., *J. Chem. Phys.* **10**, 10 (1942).
- [70] Rasmussen, R. S., and Brattain, R. R., *J. Chem. Phys.* **15**, 120 (1947).
- [71] Anantkrishnan, R., *Proc. Indian Acad. Sci. Sect. A* **3**, 527 (1936).
- [72] Bourguel, M., and Piaux, L., *Bull. Soc. Chim. Fr.* **2**, 1958 (1935).