Absolute Entropies of the Methyl Alkyl Ketones at 298.15° K.

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Low temperature heat capacities of the key members of the methyl alkyl ketones have been measured in an automatic low temperature adiabatic calorimeter. From these results, which include the data of 2-pentanone and 2-octanone presented in this paper, together with the data of 2-butanone given in an earlier publication from this laboratory, and the measurements of acetone from the literature, the third law entropies of the liquid at 298.15° K. have been computed for acetone through 2-octanone.

MUCH of the work in experimental thermodynamics is aimed at obtaining certain thermodynamic functions on one particular compound, and very little application of these results is made on closely related compounds. There are actually very few cases where the experimental work has been performed on a number of key compounds in order to estimate accurately the thermodynamics of the remainder of the particular series. The advantages of such a program are immediately obvious since experimental thermodynamics can be quite time consuming.

A thorough search of the literature revealed that low temperature heat capacity data on the ketones were nonexistent other than the work of Kelley (*3*) on acetone. Thus, ketones would be an ideal series of organic compounds for a key program investigation. To simplify the situation, the methyl alkyl ketone series was chosen because the only concern is with the methylene increment along one of the alkyl chains while the other chain remains constant—i.e., the methyl group.

The methyl alkyl ketone series will be considered here as a group of six members, acetone through 2-octanone. By knowing entropy values for the first, second, third, and sixth member, the entropies of the remaining members could be accurately estimated. Since Kelley (*3*) has reported the work on acetone and this laboratory has reported the work on 2-butanone (*8*), the entropies of the third and sixth members, 2-pentanone and 2-octanone, had to be determined. These results are reported below.

EXPERIMENTAL

Calorimeter. The calorimeter and its method of operation have been described in detail (*2, 5, 9*).

The reliability of this calorimeter has been demonstrated with the calorimetric standard, *n*-heptane, to be ±0.3% in the heat capacity measurements above 60° K. and better than ±0.3% in the entropy at 298.15° K. (*4*). The heat capacity measurements were taken using the platinum sample container No. 1 (laboratory designation), and the temperature measurements were taken by the platinum resistance thermometer No. 4 (laboratory designation) which has an ice point resistance of approximately 94 ohms. The ice point is taken as 273.15° K. and one defined calorie is equivalent to 4.1840 absolute joules.

Sample. Samples of both 2-pentanone and 2-octanone were obtained from the Matheson Co., dried with Drierite, and purified by a 100-plate distillation process. The compound, 2-octanone, was further purified by vapor phase chromatography. The melting point studies described later showed the 2-pentanone to be 99.81 mole % pure and the 2-octanone to be 99.68 mole % pure. The 2-pentanone sample was transferred to a high vacuum line, completely degassed, and loaded into the sample container by a one-plate distillation. Approximately 2 cm. of helium gas were admitted to the sample container before sealing off. The 2-pentanone sample weighed 50.7094 grams in vacuum, and the molecular weight was taken as 86.135. The 2-octanone sample was loaded into the sample container with a syringe in an atmosphere of helium and then sealed off. The sample of 2-octanone weighed 54.7209 grams in vacuum, and the molecular weight was taken as 128.216.

2-Pentanone. Six series of heat capacity measurements were made on 2-pentanone. The experimental results are given in Table I. The heat capacity curve is similar to those usually found for organic materials, being interrupted by the melting point at 196.35° K. The heat of melting was determined in Series I and VI by a continuous heat input and in Series III and V by incremental heat inputs. The results are given in Table II where the mean value for the heat of melting of 2-pentanone is 2539.0 ± 1.1 cal. per mole with the maximum deviation from the mean taken as the uncertainty. The purity of this sample of 2-pentanone is 99.81 mole % as determined from the equilibrium melting data taken in Series III and V as given in Table III. The melting point of this sample is 196.29 ± 0.05° K. whereas the 100% pure material would theoretically melt at 196.35° ± 0.05° K.

The entropy summary of 2-pentanone from 0° to 298.15° K. is given in Table IV. The entropy increment from 0° to 12° K. was calculated using the following Debye-Einstein equation which fits the experimental data from 12° to 26° K. to better than 2%.

$$C_v = 3D(95.25)/T + 4E(157.83)/T + 1E(100.50)/T$$

Table V gives the smoothed values of C_p, S_T, $H_T - H_0/T$, $-(F_T - H_0)/T$, and $H_T - H_0$ up to 330° K.

2-Octanone. Three series of heat capacity measurements were made on 2-octanone. The experimental results are given in Table I. The heat capacity curve is not unusual and requires no further discussion. The heat of melting was determined in all three series of heat capacity measure-

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Table I. Experimental Heat Capacity Data

T, ° K.	C_p, Cal./(Mole ° K.)
2-Pentanone	
Series I (crystal)	
11.66	0.810
13.18	1.108
14.76	1.498
16.67	2.003
18.54	2.500
20.42	3.005
22.41	3.571
24.45	4.136
26.76	4.827
29.56	5.704
32.59	6.697
50.12	11.27
54.90	12.24
60.19	13.40
65.50	14.32
71.03	15.12
82.81	16.97
94.83	18.62
124.64	22.21
130.51	22.97
136.23	23.67
141.82	24.25
147.28	25.01
152.62	25.78
157.84	26.56
162.93	27.50
168.41	28.59
174.24	29.74
179.91	30.67
185.43	32.19[a]
190.63	36.57[a]
M.p. 196.35° K. (liquid)	
202.13	41.38
208.78	41.47
215.41	41.41
222.01	41.43
228.59	41.61
241.59	41.90
248.09	41.97
254.56	42.21
260.99	42.45
267.38	42.69
273.74	42.97
280.06	43.27
Series II (crystal)	
18.90	2.592
20.14	2.911
20.90	3.212
22.82	3.803
24.73	4.214
26.57	4.768
28.91	5.394
31.91	6.344
34.07	7.035
34.82	7.346
36.30	7.730
48.33	10.90
55.46	12.31
59.86	13.24
64.84	14.22
69.82	15.02
75.06	15.76
81.09	16.72
87.31	17.68
Series III (crystal)	
90.73	17.98
96.54	18.68
102.14	19.38
107.55	20.09
112.80	20.67
117.92	21.25
122.90	21.83
127.77	22.41
132.53	23.04
137.20	23.66
141.76	24.34
146.24	24.91
150.63	25.50
154.94	26.18
159.17	26.87
163.31	27.57
167.37	28.34
171.35	29.14
176.71	30.11
183.37	31.55[a]
189.72	35.22[a]
M.p. 196.35° K. (liquid)	
203.08	41.29
210.58	41.40
218.04	41.37
225.49	41.46
240.20	41.85
247.54	41.92
254.84	42.13
262.10	42.47
269.31	42.73
276.48	42.97
283.61	43.34
290.68	43.63
297.71	43.99
304.68	44.34
311.61	44.75
Series IV (liquid)	
249.83	42.13
256.28	42.30
262.69	42.59
269.06	42.75
275.39	43.08
281.69	43.19
287.95	43.62
294.17	43.93
300.34	44.22
306.47	44.43
312.57	44.91
318.62	45.24
Series V (crystal)	
91.89	18.17
97.67	18.89
103.24	19.60
108.64	20.10
Series V (cont.) (crystal)	
113.68	20.87
118.54	21.37
123.79	22.01
129.16	22.68
134.41	23.33
139.53	24.06
144.53	24.58
149.44	25.29
154.24	25.99
158.94	26.73
163.54	27.57
168.04	28.38
172.44	29.31
176.76	30.06
180.99	30.79
185.14	32.00[a]
189.14	34.05[a]
M.p. 196.35° K. (liquid)	
202.02	41.45
208.63	41.52
260.33	42.38
266.68	42.70
272.99	42.93
279.27	43.13
285.51	43.40
291.72	43.77
297.88	44.06
304.01	44.32
310.11	44.81
316.15	45.11
322.14	45.39
328.10	45.75
334.02	46.00
Series VI (crystal)	
90.56	18.04
96.38	18.71
102.29	19.40
108.29	20.19
114.09	20.84
130.48	22.99
135.67	23.68
140.75	24.16
145.73	24.72
150.61	25.42
155.39	26.12
160.07	27.00
164.64	27.71
169.12	28.58
173.50	29.52
177.80	30.06
182.02	31.05
186.63	32.57[a]
191.30	38.02[a]
M.p. 196.35° K. (liquid)	
202.05	41.32
208.72	41.50
215.35	41.48

T, ° K.	C_p, Cal./(Mole ° K.)
2-Octanone	
Series I (crystal)	
12.94	1.147
14.61	1.585
16.43	2.062
18.12	2.589
19.76	3.221
21.38	3.839
22.97	4.406
24.62	5.000
26.51	5.787
28.77	6.633
31.55	7.743
34.60	9.183
45.53	12.91
50.04	14.31
55.02	15.87
60.51	17.47
65.96	18.98
71.66	19.99
77.54	21.25
83.04	22.46
88.75	23.65
94.70	24.65
100.41	25.55
105.91	26.56
111.23	27.42
116.39	28.12
121.42	28.92
126.33	29.58
131.13	30.40
135.82	31.09
140.42	31.74
144.93	32.45
149.37	32.93
166.57	35.69
178.91	37.67
184.89	38.61
191.32	39.89
198.18	41.06
204.87	42.54[a]
211.40	43.94[a]
217.79	45.77[a]
223.98	47.63[a]
230.63	49.80[a]
237.67	52.50[a]
244.34	57.87[a]
M.p. 252.86° K. (liquid)	
274.76	63.81
280.26	64.20
Series I (liquid) (cont.)	
285.68	64.57
301.77	65.66
307.08	65.99
328.01	67.57
333.18	68.07
Series II (crystal)	
94.97	24.69
100.75	25.68
106.91	26.79
113.45	27.78
119.76	28.74
125.89	29.60
131.85	30.57
137.66	31.37
143.34	32.14
148.91	32.95
154.38	33.72
159.74	34.62
165.00	35.35
170.18	36.11
175.27	36.91
180.28	37.83
185.21	38.70
190.06	39.77
195.86	40.71
202.57	41.96
209.12	43.55[a]
215.49	45.02[a]
221.69	46.79[a]
227.72	48.79[a]
233.55	50.82[a]
239.18	53.48[a]
244.62	57.99[a]
M.p. 252.86° K. (liquid)	
257.77	63.10
263.25	63.26
268.71	63.62
274.15	63.69
279.57	64.06
284.96	64.44
Series II (liquid) (cont.)	
290.33	64.79
295.66	65.10
300.98	65.48
306.27	65.79
311.54	66.24
316.77	66.65
321.98	67.05
Series III (crystal)	
128.09	29.87
133.84	30.71
140.14	31.73
146.96	32.59
153.62	33.60
160.12	34.64
166.48	35.57
172.70	36.47
178.79	37.50
184.77	38.48
190.62	39.60
196.35	40.65
201.98	41.69
207.49	43.02[a]
212.89	44.25[a]
218.17	45.53[a]
223.33	47.19[a]
228.37	48.83[a]
233.26	50.75[a]
238.01	52.75[a]
243.07	56.12[a]
M.p. 252.86° K. (liquid)	
258.00	63.07
263.54	63.36
274.53	63.89
278.00	64.18
285.42	64.51
306.83	65.96
312.11	66.34
322.57	67.14
327.76	67.71

[a] Premelting.

Table II. Heat of Melting in Calories/Mole

2-Pentanone	
Series I	2538.9
Series III	2537.9
Series V	2539.7
Series VI	2539.5
Accepted value	2539.0 ± 1.1 cal./mole
2-Octanone	
Series I	5836.0
Series II	5835.7
Series III	5837.3
Accepted value	5836.3 ± 1.0 cal./mole

ments; Series I and III by a continuous heat input and Series II by incremental heat inputs. The results are given in Table II, where the mean value for the heat of melting of 2-octanone is 5836.3 ± 1.0 cal. per mole with the maximum deviation from the mean taken as the uncertainty. The purity of this material is 99.68 mole % as determined from the equilibrium melting data from Series II as given in Table III. The melting point of this sample is 252.79 ± 0.05° K., whereas the melting point of 100% pure material would be, theoretically, 252.86 ± 0.05° K.

The entropy summary of 2-octanone from 0° to 298.15° K. is given in Table IV. The entropy increment from 0° to

Table III. Melting Point and Purity Data

2-Pentanone[a, b]				2-Octanone[c, d]	
1/Fraction Melted	T, °K.	1/Fraction Melted	T, °K.	1/Fraction Melted	T, °K.
Series III		Series V		Series II	
5.23	196.054	5.87	196.017	5.43	252.389
3.76	196.135	4.07	196.127	3.85	252.571
2.93	196.178	3.12	196.177	2.98	252.648
2.40	196.208	2.52	196.209	2.42	252.684
2.03	196.233	2.12	196.231	2.04	252.709
1.00	196.29	1.87	196.250	1.77	252.729
0.00	196.35	1.00	196.29	1.56	252.745
		0.00	196.35	1.39	252.758
				1.26	252.768
				1.15	252.778
				1.05	252.789
				1.00	252.79
				0.00	252.86

[a] M.p. this sample 196.29 ± 0.05° K. [b] M.p. 100% pure sample 196.35 ± 0.05° K. [c] M.p. this sample 252.79 ± 0.05° K. [d] M.p. 100% pure sample 252.86 ± 0.05° K.

Table IV. Entropy Summary

2-Pentanone	
$S_{12^\circ \text{K.}}$ (Debye-Einstein)	0.293 cal./(mole ° K.)
$S_{196.35-12^\circ \text{K.}}$ ($\int C_p \, d \ln T$) crystal	34.28
S_{melting} (2539/196.35)	12.93
$S_{298.15-193.35^\circ \text{K.}}$ ($\int C_p \, d \ln T$) liquid	17.61
$S_{298.15^\circ \text{K.}}$	65.11 ± 0.15
2-Octanone	
$S_{13^\circ \text{K.}}$ (Debye-Einstein)	0.399
$S_{252.86-13^\circ \text{K.}}$ ($\int C_p \, d \ln T$) crystal	55.34
S_{melting} (5836.3/252.86)	23.08
$S_{298.15-252.86}$ ($\int C_p \, d \ln T$) liquid	10.53
	89.35 ± 0.15

13° K. was determined by empirically fitting a Debye-Einstein equation of the following form

$$C_v = 6D(118.9)/T + 6E(182.0)/T$$

to the experimental data between 13° and 31° K. Table V gives the smoothed values of C_p, S, $H_T - H_0/T$, $-(F_T - H_0)/T$, and $H_T - H_0$ up to 330° K.

Table V. Molal Thermodynamic Functions[a]

T, °K.	C_p, Cal./°K.	S, Cal./°K.	$H_T - H_0/T$, Cal./°K.	$-(F_T - H_0)/T$, Cal./°K.	$H_T - H_0$, Cal.
		2-Pentanone			
12.00	0.874	0.293	0.261	0.032	3.1
15.00	1.544	0.557	0.448	0.109	6.7
20.00	2.891	1.181	0.886	0.295	17.7
25.00	4.339	1.980	1.431	0.550	35.8
30.00	5.810	2.900	2.037	0.863	61.1
35.00	7.357	3.911	2.686	1.226	94.0
40.00	8.768	4.987	3.359	1.628	134.4
45.00	10.06	6.096	4.033	2.063	181.5
50.00	11.23	7.217	4.695	2.522	234.7
55.00	12.31	8.339	5.339	3.000	293.6
60.00	13.29	9.452	5.961	3.491	357.7
70.00	15.03	11.63	7.136	4.500	499.5
80.00	16.54	13.74	8.218	5.524	657.4
90.00	17.96	15.77	9.222	6.551	830.0
100.00	19.16	17.73	10.16	7.571	1016
110.00	20.35	19.61	11.03	8.581	1213
120.00	21.54	21.42	11.85	9.576	1422
130.00	23.81	23.23	12.67	10.56	1648
140.00	24.08	25.00	13.47	11.52	1886
150.00	25.37	26.70	14.22	12.48	2133
160.00	26.96	28.38	14.96	13.42	2394
170.00	28.83	30.07	15.72	14.35	2673
180.00	30.66	31.77	16.50	15.27	2970
190.00	32.51	33.48	17.29	16.18	3286
196.35	33.70	34.57	17.81	16.76	3496
		Liquid			
196.35	41.39	47.50	30.74	16.76	6035
200.00	41.40	48.26	30.93	17.33	6186
210.00	41.43	50.28	31.43	18.85	6600
220.00	41.48	52.21	31.89	20.32	7015
230.00	41.60	54.06	32.30	21.75	7430
240.00	41.79	55.83	32.70	23.13	7847
250.00	42.07	57.54	33.06	24.48	8266
260.00	42.40	59.20	33.42	25.78	8689
270.00	42.80	60.80	33.76	27.05	9115
273.15	42.93	61.30	33.86	27.44	9250
280.00	43.20	62.37	34.09	28.28	9545
290.00	43.66	63.89	34.41	29.48	9979
298.15	44.06	65.11	34.67	30.44	10336
300.00	44.16	65.38	34.73	30.65	10418
310.00	44.72	66.84	35.04	31.80	10862
320.00	45.30	68.27	35.35	32.92	11312
330.00	45.85	69.67	35.66	34.01	11768

T, °K.	C_p, Cal./°K.	S, Cal./°K.	$H_T - H_0/T$, Cal./°K.	$-(F_T - H_0)/T$, Cal./°K.	$H_T - H_0$, Cal.
		2-Octanone			
13.00	1.161	0.399	0.298	0.101	3.9
15.00	1.694	0.601	0.448	0.153	6.7
20.00	3.333	1.304	0.956	0.348	19.1
25.00	5.186	2.245	1.615	0.630	40.4
30.00	7.122	3.358	2.368	0.989	71.0
35.00	9.310	4.617	3.201	1.416	112.0
40.00	10.98	5.969	4.068	1.900	162.7
45.00	12.70	7.361	4.931	2.429	221.9
50.00	14.31	8.783	5.789	2.993	289.5
55.00	15.83	10.22	6.634	3.585	364.9
60.00	17.27	11.66	7.461	4.198	447.7
70.00	19.66	14.51	9.041	5.468	632.9
80.00	21.86	17.28	10.51	6.772	840.7
90.00	23.77	19.97	11.88	8.090	1069
100.00	25.56	22.57	13.16	9.408	1316
110.00	27.21	25.08	14.36	10.72	1580
120.00	28.73	27.51	15.50	12.02	1859
130.00	30.23	29.87	16.57	13.30	2154
140.00	31.68	32.17	17.60	14.57	2464
150.00	33.06	34.40	18.58	15.81	2788
160.00	34.63	36.58	19.54	17.04	3126
170.00	36.09	38.73	20.47	18.26	3480
180.00	37.72	40.84	21.38	19.45	3849
190.00	39.57	42.92	22.29	20.63	4235
200.00	41.40	45.00	23.20	21.80	4640
210.00	43.19	47.06	24.11	22.95	5063
220.00	44.93	49.11	25.02	24.10	5504
230.00	46.61	51.15	25.92	25.23	5961
240.00	48.24	53.17	26.82	26.35	6436
250.00	49.82	55.17	27.70	27.46	6926
252.86	50.27	55.74	27.96	27.78	7069
		Liquid			
252.86	62.95	78.82	51.04	27.78	12905
260.00	63.18	80.57	51.37	29.21	13355
270.00	63.59	82.96	51.81	31.15	13989
273.15	63.75	83.70	51.95	31.75	14190
280.00	64.16	85.29	52.24	33.05	14628
290.00	64.76	87.55	52.66	34.89	15272
298.15	65.31	89.35	53.00	36.35	15802
300.00	65.44	89.76	53.08	36.68	15923
310.00	66.17	91.91	53.49	38.43	16581
320.00	66.92	94.03	53.90	40.13	17247
330.00	67.74	96.10	54.30	41.79	17920

[a] To retain internal consistency, some of the values in the table are given to more decimal places than are justified by their absolute accuracy.

Table VI. Entropies of the Liquid Methyl Alkyl Ketones at 298.15° K., Cal./(Mole ° K.)

	$S_{298.15^\circ \mathrm{K.}}$	$S_{\mathrm{increment}}$
Acetone	47.9[a] (49.28)[b]	7.80
2-Butanone	57.08[c]	8.03
2-Pentanone	65.11[d]	8.08
2-Hexanone	(73.19)	8.08
2-Heptanone	(81.27)	8.08
2-Octanone	89.35[d]	

[a] Reference (*3*). [b] *R* ln 2 is added because of symmetry. [c] Reference (*8*). [d] These data.

DISCUSSION

The low temperature heat capacity measurements on liquid acetone were taken by Kelley (*3*) from which he derived an entropy of 47.9 ± 0.3 cal./(mole °K.) at 298.15° K. A recent publication from this laboratory (*8*) on liquid methyl ethyl ketone (2-butanone) gave the third law entropy as 57.08 ± 0.15 cal./(mole ° K.). From these two values, it is possible to establish the entropy increment owing to the addition of a methylene group. In comparisons of this kind, however, one must also take into consideration the symmetry of each molecule. Since the symmetry number for acetone is two, *R* ln 2 must be added giving an entropy value of 49.28 cal./(mole ° K.). As the ketone, 2-butanone, has a symmetry number of one, no additional entropy is added. In this case, then, the entropy increment owing to the addition of a methylene group going from acetone to 2-butanone is found to be 7.8 cal./(mole ° K.).

The next member in the series is methyl propyl ketone (2-pentanone), whose entropy, 65.11 cal./(mole °K.), was established in the experimental section. The difference between 2-pentanone and 2-butanone is 8.03 cal./(mole ° K.) compared to the difference of 7.80 cal./(mole ° K.) between 2-butanone and acetone. The third law entropy of the sixth member of the series, 2-octanone, given earlier as 89.35 cal./(mole ° K.), shows the average entropy increment per methylene group to be 8.08 cal./(mole °K.) from 2-pentanone through 2-octanone. The results of these measured and interpolated values of the entropy at 298.15° K. of the methyl alkyl ketone series are shown in Table VI.

Parks, Kelley, and Huffman (*6*) have found that the average entropy increment per methylene group is 8.0 cal./(mole °K.) from formic acid to palmitic acid. The average increment for normal aldehydes is found to be 8.1 cal./(mole ° K.) from the work of Parks and coworkers (*7*) on *n*-butyraldehyde and *n*-heptaldehyde. The agreement between the entropy increment per methylene group of the normal ketones, acids, and aldehydes is considered to be satisfactory. It has been established, however, that the entropy increment is 7.72 cal./(mole ° K.) for the *n*-alkanes (*1*) and is 7.8 cal./(mole °K.) for the normal alcohols (*6*). This significant difference in entropy increment most certainly lies in the fact that the ketone-acid-aldehyde class contains the carbonyl group which is not present in the alkane-alcohol class.

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Molecular Diffusion Coefficients in Binary Gaseous Systems at One Atmosphere Pressure

N-Hexane–Methane and 3-Methylpentane–Methane Systems

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THERE are relatively few data on binary diffusion coefficients in hydrocarbon gaseous systems. Such data are necessary in calculations involving steady and nonsteady state mass transport. Few, if any studies on diffusion coefficients in isomeric systems have been reported. In the saturated hydrocarbon systems, it appears desirable to determine if there are measurable differences in the diffusion coefficients of isomeric compounds in the same gas. Data of these types are of considerable value in testing certain diffusional models such as those derived by use of intermolecular potential functions in conjunction with the kinetic theory.

EXPERIMENTAL

The experimental apparatus was an adaptation of the diffusion glass tube apparatus first described by Stefan (*8*), and which has been used extensively for measurement of gas diffusion coefficients. It consisted of the diffusion cell shown in Figure 1, which contained a capillary tube of 0.15 cm. I.D. The cell was thermostated in a well agitated water bath whose temperature was controlled to ±0.01° C. by a mercury temperature controller. The temperature of the bath was measured using a calibrated mercury in glass thermometer which was accurate within 0.1° C.