Chemical Thermodynamic Properties of the Pentadienes

Third Law Studies

JOHN F. MESSERLY, SAMUEL S. TODD, and GEORGE B. GUTHRIE
Bartlesville Petroleum Research Center, Bureau of Mines, U. S.
Department of the Interior, Bartlesville, Okla. 74003

The chemical thermodynamic properties of the seven pentadienes are determined from adiabatic calorimetric studies over the range 12° to 320° K. Properties measured include the heat capacities in the solid and liquid state, heats of fusion, melting points, and purities of the samples. The heats of vaporization at 298.15° K are calculated from vapor pressure data, and the entropies of all seven pentadienes in the ideal gas state at 298.15° K are determined. Free energies of formation and the logarithm of the equilibrium constants of formation at 298.15° K are calculated.

LOW-TEMPERATURE calorimetric studies of the seven isomeric pentadienes were included in the continuing program of the Bureau of Mines for obtaining thermodynamic properties of materials important in petroleum technology. In many thermodynamic applications, particularly in isomerization studies, high relative accuracy of the experimental thermodynamic functions of the isomers is necessary for mole-fraction calculations. All of the values reported here are related to the same methods of measurement and correlation, and the same calibrated standards. Thus, systematic errors tend to cancel and uncertainties will be smaller than those that are found when comparing work of different laboratories. Previously, low-temperature thermal data had been reported by Bekkedahl and Wood (*1*) for 2-methyl-1,3-butadiene, and by Parks, Todd, and Shomate for 1,4-pentadiene (*10*).

To obtain values of the thermodynamic properties in the ideal gas state at 298.15° K, the experimental low-temperature properties were combined with enthalpies of formation (*3, 4*) and vapor pressure data (*9*). The available literature values of the thermodynamic functions of the pentadienes are those reported by Kilpatrick *et al.* (*8*), from a correlation based on data obtained from lower molecular weight alkanes, alkenes, and alkadienes.

EXPERIMENTAL

Materials. The compound samples were purified and made available in glass, internal breakoff-tip ampoules through American Petroleum Institute Projects 44 and 58B at Carnegie-Mellon University. Before the ampoules were opened they were immersed in liquid nitrogen to test the samples for cloudiness, as an indication of polymer, and for the formation of ice crystals. The sample of 1,4-pentadiene which showed no ice or cloudiness and the sample of 2-methyl-1,3-butadiene which showed only a trace of ice crystals were used as received. The other pentadiene samples showed a marked cloudiness upon melting which disappeared, as they warmed, well below the melting point of ice; therefore they were given a bulb-to-bulb distillation to remove polymer and, except for 3-methyl-1,2-butadiene, were dried by passing their vapors through magnesium perchlorate. 3-Methyl-1,2-butadiene was dried by passing its vapor through molecular sieve. The magnesium perchlorate turned yellow to brown upon passage of the vapors of 1,2-pentadiene, 1,*cis*-3-pentadiene, 1,*trans*-3-pentadiene, and 2,3-pentadiene.

Each sample was placed in the calorimeter without exposure to air or a temperature above 25°. In the case of 2-methyl-1,3-butadiene 34 mm. of Hg of helium gas was added to promote thermal equilibration during the calorimetric measurements.

Apparatus and Physical Constants. The measurements were made with an adiabatic apparatus described as Rig 1 by Huffman and coworkers (*6, 7, 12, 13*). The samples were contained in a copper calorimeter (laboratory designation 3-C) which was designed to hold a platinum thermometer (laboratory designation 6) in its re-entrant well. Identical operating techniques, including manual control of the adiabatic shield temperatures, were used on all seven isomers. The molecular weight of pentadiene, based on 1961 International Atomic Weights (*2*), was 68.1195. Conversion of observed quantities to standard data forms was made with the aid of recent values of the fundamental physical constants (*11*). Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale of 1948 (*16*) from 90° to 400° K, and the provisional scale of the National Bureau of Standards (*5*) from 11 to 90° K. Celsius temperatures were converted to Kelvin temperatures by adding 273.15° (*15*). Energy was measured in joules and converted to calories by the relation 1 cal = 4.184J. Measurements of mass, electrical potential, and resistance were made in terms of secondary standard devices that had been calibrated at the National Bureau of Standards.

RESULTS

Heat Capacities. Heat capacity determinations reveal no instances of polymorphism in the pentadienes. Not only was a single crystalline form readily obtained upon freezing each sample, but little if any supercooling of the liquids was observed. Experimental values of the heat capacities of the crystalline and liquid phases are recorded (Table I) in the order of ascending mean temperature which, however, is not necessarily the chronological order of the observations. The energy increments were kept small enough so that nominal heat capacities in the incremental temperature ranges were, within experimental error, linear functions of temperature. Corrections to heat capacity determinations for the effect of heterophase premelting have not been applied to the values in Table I; however, such corrections were applied to the smoothed heat capacity values in Table II. The experimental temperature incre-

Table I. Molal Heat Capacity (Cal °K^{-1})

T, °K^a	C_s^b	T, °K^a	C_s^b	T, °K^a	C_s^b
1,2-Pentadiene					
Crystals					
12.97	0.7304	32.09	5.250	89.73	14.771
13.29	0.7867	35.16	5.986	90.90	14.902
14.53	1.004	38.68	6.782	95.07	15.358
14.66	1.027	42.71	7.640	100.51	15.946^c
16.10	1.309	47.10	8.509	106.16	16.531^c
17.12	1.543	51.93	9.409	108.99	16.823^c
17.94	1.729	53.95	9.763	110.61	16.982^c
20.03	2.209	57.17	10.301	112.09	17.147^c
20.10	2.236	58.99	10.598	113.86	17.319^c
22.26	2.765	64.00	11.391	114.81	17.419^c
22.32	2.790	69.05	12.112	117.81	17.763^c
24.57	3.370	74.67	12.869	118.58	17.832^c
24.89	3.439	80.40	13.634	119.99	17.985^c
26.86	3.945	85.01	14.216	125.45	18.643^c
27.79	4.170	85.78	14.318	130.27	19.836^c
29.30	4.557				
Liquid					
142.31	31.32	181.87	31.58	247.74	33.55
144.95	31.30	190.28	31.73	259.16	34.06
149.28	31.29	192.31	31.77	270.75	34.61
151.16	31.30	203.01	32.03	282.17	35.18
158.91	31.33	213.96	32.33	293.73	35.81
169.21	31.41	225.13	32.69	297.20	36.00
179.80	31.54	236.51	33.10	307.50	36.59
1,*cis*-3-Pentadiene					
Crystals					
11.19	0.799	27.82	4.530	82.19	14.003
12.26	0.971	28.59	4.708	87.58	14.675^d
13.00	1.109	30.75	5.213	87.95	14.717^d
13.66	1.249	33.96	5.957	91.85	15.148^d
14.05	1.322	37.35	6.694	94.33	15.403^d
15.25	1.577	40.87	7.436	96.68	15.662^d
15.29	1.584	44.83	8.226	99.49	15.973^d
16.73	1.905	49.44	9.100	102.57	16.287^d
17.07	1.983	53.84	9.873	105.27	16.563^d
18.59	2.332	55.11	10.081	107.69	16.817^d
19.05	2.437	58.48	10.651	111.35	17.182^d
20.70	2.829	60.09	10.899	113.64	17.406^d
21.24	2.953	65.36	11.727	117.20	17.777^d
22.89	3.352	70.97	12.508	119.38	18.006^d
23.62	3.527	76.52	13.245	122.85	18.417^d
25.25	3.928				
Liquid					
138.21	31.152	193.97	30.773	256.29	32.698
142.63	31.028	203.96	30.930	266.35	33.194
143.92	31.014	204.01	30.932	276.26	33.722
148.24	30.921	214.67	31.166	286.37	34.306
153.48	30.828	225.27	31.463	296.67	34.939
163.39	30.710	235.74	31.825	307.14	35.620
173.65	30.663	246.08	32.235	316.12	36.240
183.85	30.683				
1,*trans*-3-Pentadiene					
Crystals					
11.56	0.760	55.04	10.110	104.30	17.522
11.70	0.797	55.42	10.183	106.85	17.893
12.76	0.986	55.46	10.178	110.38	18.379
12.97	1.019	59.57	10.872	110.86	18.591
14.11	1.266	61.24	11.155	112.65	18.876
14.47	1.333	64.53	11.710	117.08	19.742
15.77	1.632	67.25	12.125	121.31	20.636
16.03	1.679	70.00	12.544	123.28	21.521
17.50	2.025	73.33	13.025	128.16	22.758
17.53	2.034	75.53	13.359	129.01	23.101
17.73	2.076	79.60	13.951	133.71	24.277
19.41	2.483	81.09	14.189	134.53	24.454^e
19.60	2.529	85.15	14.756	140.58	25.563^e
21.50	2.995	86.30	14.948	146.42	26.367^e
1,*trans*-3-Pentadiene					
Crystals					
21.69	3.042	86.72	15.025	152.53	26.731^e
23.82	3.579	91.53	15.708	157.90	26.845^e
23.98	3.616	92.05	15.736	158.01	26.808^e
26.37	4.209	92.44	15.820	159.15	26.855^e
26.49	4.235	92.98	15.868	164.05	26.995^e
28.87	4.802	94.28	16.015	165.13	27.072^e
29.60	4.978	97.84	16.588	170.43	27.256^e
32.96	5.763	98.29	16.638	171.43	27.354^e
36.74	6.606	98.52	16.632	173.01	27.513^e
41.02	7.501	100.74	16.944	177.99	28.450^e
45.53	8.387	100.86	16.978	182.21	34.133^e
50.22	9.270				
Liquid					
189.20	31.143	222.22	31.758	267.83	33.824
194.20	31.106	227.40	31.938	277.92	34.394
196.32	31.141	237.72	32.331	288.19	35.036
201.84	31.217	247.90	32.793	298.29	35.692
204.06	31.274	257.94	33.290	308.23	36.372
211.71	31.448			316.41	36.959
1,4-Pentadiene					
Crystals					
11.37	0.756	26.52	4.682	91.32	15.997
12.55	0.979	28.34	5.196	93.64	16.279^f
13.31	1.133	29.39	5.493	97.71	16.793^f
13.84	1.251	32.50	6.356	98.90	16.933^f
14.63	1.420	35.81	7.217	99.93	17.117^f
15.37	1.605	39.63	8.135	100.17	17.099^f
16.25	1.815	43.95	9.079	103.78	17.645^f
17.14	2.046	48.22	9.944	105.86	17.985^f
18.10	2.290	53.04	10.773	106.16	18.019^f
19.06	2.552	53.70	10.884	106.37	18.106^f
20.00	2.814	58.49	11.665	109.55	18.566^f
21.14	3.134	63.75	12.452	111.85	18.972^f
21.83	3.330	69.57	13.220	115.04	19.616^f
23.37	3.770	75.48	13.963	117.27	20.078^f
23.94	3.943	81.44	14.734	119.99	20.525^f
25.73	4.453	87.48	15.515		
Liquid					
127.99	30.564	174.37	30.387	241.96	32.178
132.47	30.486	184.57	30.515	252.13	32.627
133.21	30.482	194.66	30.699	262.17	33.102
138.15	30.398	204.66	30.922	272.07	33.604
139.76	30.385	214.55	31.199	281.82	34.136
145.27	30.325	224.33	31.518	291.44	34.691
154.11	30.287	234.00	31.873	300.93	35.258
164.08	30.309				
2,3-Pentadiene					
Crystals					
11.74	0.578	27.08	4.029	87.72	15.576
12.30	0.667	27.91	4.245	93.48	16.265
13.32	0.829	29.61	4.664	93.54	16.268
13.68	0.899	30.81	4.971	99.49	16.950
14.91	1.134	34.30	5.837	100.54	17.060
15.18	1.193	38.37	6.805	106.52	17.703^g
16.58	1.474	42.67	7.802	108.83	17.949^g
16.81	1.534	47.04	8.752	112.52	18.333^g
18.34	1.873	52.06	9.793	114.71	18.560^g
18.53	1.918	56.24	10.602	118.87	18.986^g
20.25	2.321	57.44	10.834	120.94	19.177^g
20.57	2.401	60.77	11.454	123.93	19.427^g
22.34	2.833	65.66	12.319	125.56	19.606^g
22.90	2.980	71.08	13.162	129.41	19.992^g
24.62	3.408	76.64	14.007	134.73	20.547^g
25.32	3.593	82.18	14.817	139.88	21.412^g
Liquid					
150.70	32.489	189.38	32.713	253.95	34.416

Table I. Molal Heat Capacity (Cal ° K^{-1}) (*Continued*)

T, ° K^a	C_s^b	T, ° K^a	C_s^b	T, ° K^a	C_s^b
Liquid					
155.41	32.468	199.20	32.879	264.47	34.838
155.94	32.475	208.95	33.065	274.85	35.287
162.85	32.481	218.61	33.297	285.11	35.760
170.22	32.513	228.18	33.549	295.23	36.264
170.45	32.513	233.56	33.708	305.22	36.785
179.47	32.599	243.65	34.037	315.09	37.334
3-METHYL-1,2-BUTADIENE					
Crystals					
11.32	0.460	27.58	3.981	86.64	14.371
12.77	0.653	28.67	4.246	89.34	14.772
13.36	0.752	30.72	4.734	92.29	15.079
14.22	0.897	34.07	5.524	93.48	15.219
14.82	1.004	37.60	6.301	95.45	15.495
15.79	1.194	41.43	7.104	98.69	15.833
16.48	1.332	45.80	7.958	99.92	15.970
17.63	1.576	50.79	8.887	106.54	16.736
18.23	1.705	54.88	9.610	113.35	17.516
19.53	2.004	56.26	9.842	120.24	18.274^h
20.20	2.164	59.90	10.460	127.23	19.019^h
21.57	2.492	65.35	11.341	133.95	19.712^h
22.46	2.715	71.30	12.218	140.45	20.399^h
23.87	3.064	77.29	13.077	142.94	20.644^h
24.87	3.308	83.29	13.966	147.34	21.202^h
26.17	3.627	86.01	14.297		
Liquid					
161.86	31.212	196.37	31.943	266.89	34.745
167.19	31.302	206.57	32.256	276.88	35.238
169.44	31.341	216.65	32.596	286.73	35.780
169.60	31.334	226.61	32.957	296.45	36.327
175.66	31.444	236.45	33.346	306.04	36.890
179.55	31.539	246.50	33.776	314.56	37.411
189.92	31.781	256.76	34.249		
2-METHYL-1,3-BUTADIENE					
Crystals					
11.51	0.912	24.31	3.882	60.56	10.598
12.46	1.088	24.94	4.029	61.63	10.742
13.77	1.358	26.99	4.524	66.68	11.405
14.62	1.553	27.53	4.645	71.82	12.028
15.17	1.686	30.01	5.227	77.08	12.645
16.19	1.896	30.47	5.324	82.51	13.279^i
16.72	2.028	33.32	5.970	88.11	13.903^i
18.03	2.328	36.79	6.683	92.13	14.341^i
18.44	2.434	40.40	7.398	93.43	14.428^i
19.96	2.797	44.28	8.090	97.83	14.884^i
20.39	2.905	49.14	8.905	103.41	15.482^i
21.99	3.302	54.92	9.794	109.29	16.151^i
22.59	3.448	56.61	10.044	115.35	17.633^i
Liquid					
130.32	29.293	176.84	29.644	249.51	32.774
134.95	29.260	187.40	29.904	259.69	33.406
137.13	29.248	197.83	30.243	260.91	33.464
140.93	29.243	208.10	30.638	271.26	34.158
146.05	29.247	218.23	31.080	282.10	34.912
155.73	29.301	228.57	31.594	293.09	35.733
166.14	29.435	239.13	32.151	303.86	36.540

[a] Mean, temperature of each heat capacity measurement. [b] Heat capacity of 1 mole of compound in condensed phase under saturation pressure. Values of C_s for crystals not corrected for effect of premelting. [c, d, e, f, g, h, i] Temperature increment ΔT, of these measurements are, in order of increasing temperature, in ° K: [c] 5.245, 6.049, 4.945, 3.614, 5.818, 4.793, 4.787, 5.626, 4.653, 5.562, 5.374, 4.256; [d] 4.342, 6.042, 4.183, 4.935, 5.478, 5.381, 6.300, 6.195, 6.068, 5.958, 5.837, 5.749, 5.645, 5.548; [e] 6.169, 5.927, 5.755, 6.470, 5.371, 5.674, 5.607, 6.421, 6.342, 6.343, 6.260, 5.427, 4.518, 3.934; [f] 6.459, 6.219, 7.168, 6.122, 6.142, 5.915, 6.751, 5.835, 6.758, 5.632, 5.559, 5.354, 5.285, 5.000; [g] 6.111, 5.988, 5.887, 5.773, 6.814, 6.694, 5.555, 6.578, 5.394, 5.249, 5.066; [h] 7.131, 6.852, 6.604, 6.416, 4.057, 4.753; [i] 5.759, 5.447, 5.969, 5.204, 5.706, 5.470, 6.284, 5.850.

ments in the premelting regions are contained in a footnote to Table I to make available documented data for studies of premelting behavior.

Heat capacity curves for crystalline pentadienes are normally sigmoidal, and for liquid pentadienes are concave upward. Except for one isomer, 3-methyl-1,2-butadiene, the heat capacity curves of the liquids show minima over a range 50° above the melting points. Cubic equations in T were fitted to the molal heat capacities of the liquids. The constants for these equations are given (Table III) with values of the average and maximum deviations of the observed points from smooth curves.

Above 30° K the estimated precision uncertainty of the heat capacity measurements is less than 0.1%, and the estimated accuracy uncertainty is 0.2%. Below 30° K the estimated precision uncertainty and estimated accuracy uncertainty increase and reach a value of 1% at the lowest experimental temperature. Just below the melting points

Table II. Molal Thermodynamic Properties of Pentadienes in Solid and Liquid States[a,b]

T, ° K	$-(G_s - H_0^\circ)/T$, Cal ° K^{-1}	$-(H_s - H_0^\circ)/T$, Cal ° K^{-1}	$H_s - H_0^\circ$, Cal	S_s, Cal ° K^{-1}	C_s, Cal ° K^{-1}
1,2-PENTADIENE					
Crystals					
10	0.028	0.084	0.842	0.112	0.336
15	0.095	0.283	4.247	0.378	1.091
20	0.220	0.620	12.405	0.840	2.207
25	0.404	1.062	26.562	1.466	3.461
30	0.642	1.568	47.04	2.210	4.728
35	0.924	2.108	73.77	3.032	5.948
40	1.241	2.659	106.36	3.900	7.074
45	1.586	3.207	144.32	4.793	8.095
50	1.952	3.744	187.22	5.696	9.056
60	2.727	4.775	286.52	7.502	10.761
70	3.536	5.740	401.8	9.276	12.240
80	4.361	6.637	530.9	10.998	13.581
90	5.193	7.478	673.0	12.671	14.801
100	6.021	8.265	826.4	14.286	15.877
110	6.845	9.003	990.3	15.848	16.888
120	7.658	9.702	1164.2	17.360	17.889
130	8.461	10.370	1348.1	18.831	18.888
135.89	8.930	10.753	1461.3	19.683	19.482
Liquid					
135.89	8.930	24.047	3268.0	32.977	31.372
140	9.648	24.261	3396	33.909	31.33
150	11.338	24.731	3709	36.069	31.29
160	12.948	25.142	4022	38.090	31.33
170	14.484	25.508	4336	39.992	31.41
180	15.951	25.840	4651	41.791	31.54
190	17.356	26.145	4967	43.501	31.72
200	18.705	26.429	5285	45.134	31.95
210	20.000	26.699	5606	46.699	32.21
220	21.249	26.956	5930	48.205	32.51
230	22.452	27.205	6257	49.657	32.85
240	23.616	27.448	6587	51.064	33.23
250	24.740	27.688	6921	52.428	33.64
260	25.831	27.925	7260	53.756	34.09
270	26.890	28.162	7603	55.052	34.56
273.15	27.217	28.238	7713	55.455	34.72
280	27.918	28.400	7952	56.318	35.07
290	28.918	28.640	8305	57.558	35.60
298.15	29.717	28.836	8597	58.553	36.05
300	29.894	28.881	8664	58.775	36.15
310	30.845	29.125	9028	59.970	36.73
320	31.773	29.372	9398	61.145	37.31

[a] Values tabulated are Gibbs energy function, enthalpy function, enthalpy, entropy, and heat capacity of condensed phases at saturation pressure. [b] This part of table given for illustrative purposes only. Complete table available from ASIS.

Table III. Equation for Heat Capacity of Liquid

$C_s = A + BT + CT^2 + DT^3$, cal °K^{-1} mole^{-1}

Compound	A	B	C × 10^4	D × 10^7	Range, °K	Av. Dev., Cal °K^{-1}	Max. Dev., Cal °K^{-1}
1,2-Pentadiene	38.193	−0.10007	4.1059	−3.3210	142–316	0.003	0.009
1,*cis*-3-Pentadiene	44.719	−0.17584	6.3844	−5.2865	153–316	0.007	0.035
1,*trans*-3-Pentadiene	51.047	−0.25113	9.4359	−9.1898	189–316	0.015	0.057
1,4-Pentadiene	39.075	−0.12124	4.7654	−3.8494	128–301	0.006	0.014
2,3-Pentadiene	38.435	−0.080580	2.9801	−1.6936	151–315	0.004	0.009
3-Methyl-1,2-butadiene	34.932	−0.066215	3.0056	−2.0677	162–306	0.004	0.013
2-Methyl-1,3-butadiene	38.236	−0.13639	5.8779	−5.1748	130–304	0.006	0.014

accuracies decrease because of slow equilibration and uncertainties in the corrections for heterophase premelting. Fortunately, the uncertainties only slightly decrease the accuracy with which the enthalpy and entropy of the liquids are determined because these errors tend to cancel in enthalpy and entropy of fusion measurements.

Molal Heats of Fusion, Triple-Point Temperatures, and Sample Purities. Replicate determinations of the molal heat of fusion, ΔHm, were made from heat capacity data and from enthalpy measurements over ranges of temperatures that included triple-point temperatures. Because measurements are made on slightly impure compounds, the observed heat capacities and enthalpies of fusion have been corrected for the effects of these impurities. These premelting corrections are made empirically based on an "effective" impurity, footnote[c] Table V, a little smaller than the actual impurity as determined in the melting point studies. The exact causes of these differences in impurity behavior are unknown but they probably result from deviations from ideal behavior, presence of solid solutions, or nonattainment of thermodynamic equilibrium. The average of at least three heats of fusion is given in Table IV, and the uncertainty of ΔHm for each compound is the maximum deviation of any individual measurement from the arithmetic mean.

The results of a study of the equilibrium melting temperature T_{obsd}, as a function of the fraction of the total sample melted, F, are listed (Table V) with the amount of impurity found for each of the seven pentadienes. The triple-point temperatures and the cryoscopic constants, defined by the relations (*17*), $A = \Delta Hm/RT^2_{TP}$ and $B = (1/T_{TP}) - (\Delta Cm/2\Delta Hm)$, calculated from the observed values of T_{TP}, ΔHm and ΔCm (the heat capacity of the liquid minus that of the solid, at the melting point), are in Table IV.

Thermodynamic Properties in Solid and Liquid States. The experimentally determined values of heat capacity were used to provide "smoothed" values at selected temperatures by numerical methods. From these data and values of the heat of fusion the thermodynamic properties for the condensed phases were calculated for even temperatures from 10° to above 300° K by appropriate numerical integration. The values of the thermodynamic functions at 10° K were calculated from Debye functions fitted to the heat capacities from 12° to 20° K. The Debye parameters, θ, the characteristic temperature, and the degrees of freedom, are given for each compound in Table VI.

Entropy in Ideal Gas State. The entropies of all seven pentadienes in the ideal gas state at 298.15° K have been calculated from the entropy in the liquid by use of the vapor pressures as reported by Osborn and Douslin (*9*). The entropies of vaporization at 298.15° K were calculated from the Clapeyron equation, using gas volumes computed from the virial equation $PV = RT(1 + B/V)$; and values of B taken from the empirical equation of Scott *et al.* (*14*). Values of dp/dt were obtained from Cox equations, fitted to experimental values of the vapor pressure as reported by Osborn and Douslin (*9*). The entropies of compression at 298.15° K were calculated using the pressures interpolated from the same Cox equations. The corrections to the entropy of gas imperfection were made empirically from a linear correlation of calculated corrections from the published literature *vs.* vapor pressure at 298.15° K. A summary of these calculations and a comparison with the literature values at 298.15° K are given in Table VII.

Free Energies and Logarithm of Equilibrium Constants of Formation. The free energies of formation of all seven pentadienes at 298.15° K in the ideal gas state were calculated from the above entropies at 298.15° K in the ideal gas state and the heats of formation, as given by Fraser and Prosen (*3*), for six of the pentadienes and the heat of formation of 3-methyl-1,2-pentadiene as measured in this laboratory but reported separately (*4*). The calculations were made using the values of heats and entropies of formation of water and carbon dioxide and the entropy of graphite, from the National Bureau of Standards (*18*). The logarithms of the equilibrium constants of formation were calculated from the free energies of formation and are listed with a comparison with literature values in Table VIII.

DISCUSSION

Calorimetric Data. Previously low-temperature studies had been made for only two of the pentadienes. A comparison of the data here presented with those of Bekkedahl and Wood (*1*) for 2-methyl-1,3-butadiene shows that their values of heat capacity are higher than those of this laboratory

Table IV. Triple-Point Temperatures, Heats of Fusion, and Cryoscopic Constants

Compound	T_{TP}	ΔHm, Cal Mole^{-1}	A, °K^{-1}	B, °K^{-1}
1,2-Pentadiene	135.89 ± 0.05	1806.7 ± 0.3	0.04923	0.00407
1,*cis*-3-Pentadiene	132.35 ± 0.05	1347.7 ± 0.5	0.03870	0.00300
1,*trans*-3-Pentadiene	185.71 ± 0.05	1707.4 ± 0.8	0.02491	0.00447
1,4-Pentadiene	124.91 ± 0.05	1461.5 ± 0.4	0.04714	0.00492
2,3-Pentadiene	147.52 ± 0.05	1584.1 ± 1.8	0.03663	0.00327
3-Methyl-1,2-butadiene	159.53 ± 0.05	1901.6 ± 0.8	0.03760	0.00395
2-Methyl-1,3-butadiene	127.27 ± 0.05	1177.0 ± 0.6	0.03656	0.00476

Table V. Melting Point Summaries

F	$1/F$	T_{osbd}, °K	T_{calcd}[a], °K
1,2-Pentadiene (Impurity[b] = 0.08 ± 0.04 Mole %)			
0.1095	9.132	135.7143	135.7364
0.2640	3.788	135.8264	135.8283
0.5064	1.975	135.8595	135.8595
0.7146	1.399	135.8694	135.8694
0.9054	1.104	135.8707	135.8745
1.0000	1.000		135.8763
Pure	0		135.8935[c]
1,*cis*-3-Pentadiene (Impurity[b] = 0.09 ± 0.04 Mole %)			
0.1232	8.117	132.2145	132.17
0.2560	3.906	132.2774	132.266
0.2653	3.769	132.2796	132.269
0.5170	1.934	132.3125	132.3104
0.5278	1.895	132.3125	132.3113
0.7070	1.414	132.3229	132.3221
0.7431	1.346	132.3236	132.3236
0.9210	1.086	132.3300	132.3295
0.9583	1.044	132.3304	132.3304
1.0000	1.000		132.3314
Pure	0		132.3539[c]
1,*trans*-3-Pentadiene (Impurity[b] = 0.10 ± 0.02 Mole %)			
0.1093	9.149	185.3992	185.3434
0.2588	3.864	185.5740	185.5624
0.5130	1.949	185.6397	185.6359
0.7166	1.395	185.6584	185.6584
0.9036	1.107	185.6701	185.6701
1.0000	1.000		185.6744
Pure	0		185.7151[c]
1,4-Pentadiene (Impurity[b] = 0.02 ± 0.001 Mole %)			
0.0993	10.070	124.8670	124.8670
0.2516	3.975	124.8921	124.8921
0.5134	1.948	124.8994	124.8993
0.7098	1.409	124.9014	124.9014
0.9062	1.104	124.9024	124.9026
1.0000	1.000		124.9030
Pure	0		124.9070[c]
2,3-Pentadiene (Impurity[b] = 0.12 ± 0.02 Mole %)			
0.1310	7.634	147.2565	147.2673
0.2813	3.555	147.4014	147.4014
0.4715	2.121	147.4501	147.4486
0.7005	1.428	147.4729	147.4714
0.8915	1.112	147.4818	147.4818
1.0000	1.000		147.4855
Pure	0		147.5184[c]
3-Methyl-1,2-butadiene (Impurity[b] = 0.02 ± 0.005 Mole %)			
0.1202	8.319	159.4731	159.4805
0.2665	3.752	159.5061	159.5061
0.5113	1.956	159.5161	159.5162
0.7071	1.414	159.5192	159.5192
0.9029	1.108	159.5204	159.5209
1.0000	1.000		159.5215
Pure	0		159.5271[c]
2-Methyl-1,3-butadiene (Impurity[b] = 0.17 ± 0.08 Mole %)			
0.04726	21.16	126.5155	126.2891
0.1651	6.057	127.0357	126.9900
0.4216	2.372	127.1651	127.1608
0.6154	1.625	127.1955	127.1955
0.8096	1.235	127.2136	127.2136
1.0000	1.000		127.2245
Pure	0		127.2709[c]

[a] Temperatures read from straight line through plot of T_{obsd} *vs.* $1/F$. [b] Impurity calculated from simplified relationship $N_2 = F \times A \times (T_{TP} - T_{obsd})$ where N_2 is the mole fraction of impurity. "Effective" impurity activities for pentadienes used in corrections to heat capacities and heats of fusion for effects of premelting are: 0.067, 0.050, 0.078, 0.020, 0.075, 0.020, and 0.160, respectively. [c] Triple-point temperature taken as extrapolated temperature for $1/F = 0$.

Table VI. Debye Parameters

Compound	θ, Deg	Degrees of Freedom
1,2-Pentadiene	136.2	5.5
1,*cis*-3-Pentadiene	98.6	3.5
1,*trans*-3-Pentadiene	101.0	3.5
1,4-Pentadiene	105.1	4.0
2,3-Pentadiene	128.6	5.0
3-Methyl-1,2-butadiene	138.6	5.5
2-Methyl-1,3-butadiene	95.2	3.5

throughout the entire range. The difference is 2% from 20° to 100° K, 0.3% at 130° K rising to 1% at 300° K. Despite this difference in heat capacity, their values of entropy at 298.15° K is only 0.25 cal °K^{-1} mole^{-1} higher than this work owing to their lower entropy at 20° and lower entropy of fusion. The triple point reported for 2-methyl-1,3-butadiene (126.4° K) by Bekkedahl and Wood differs markedly from that reported in this work and that reported by Streiff *et al.* (*17*). By use of the heat capacity data reported by Bekkedahl and Wood it is possible to make a rough calculation of the melting point of their sample. From this, the triple point is found to be 127.36° K and the impurity 1.7 mole %. The heat capacities reported for 1,4-pentadiene by Parks, Todd, and Shomate (*10*) differ from this work by more than the expected experimental error. Their values are from 0.5 to 1% higher from 80° to 100° K, 0.3% lower from 130° to 180° K, nearly the same from 180° to 220° K, and gradually increase to 1% higher at 300° K. The entropy reported by Parks *et al.* is 1.33 eu less than that found in this work. Most of the difference in entropy is due to Parks' extrapolation from 80° to 0° K which differed by 1.46 eu from the measured values reported in this paper.

Entropies and Free Energies of Formation. The only published data for the free energies and entropies of the pentadienes in the ideal gas state are those of Kilpatrick *et al.* (*8*). These data, dating from 1949, are essentially those published in the API Research Project 44 tables. A comparison of the entropies in the ideal gas at 298.15° K reported here with those calculated by Kilpatrick *et al.* shows that difference was less than the estimated uncertainty except in cases of 2,3-pentadiene and 1,*trans*-3-pentadiene, where the differences were about 1 cal ° K^{-1} mole^{-1}.

The Gibbs energies of formation of the seven pentadienes in the ideal gas state (Table VIII) show that, as expected, the 2-methyl-1,3-pentadiene and 1,*trans*-3-pentadiene were the most stable and 1,*cis*-3-pentadiene only a little less stable. All three of these have conjugated double bonds and the slightly greater Gibbs energy of formation of the *cis* form may be attributed to steric effects. The nonconjugated pentadienes were several orders of magnitude less stable than the three dominant forms, with the allene-like structures being the least stable. The differences in Gibbs energies of formation at 298.15° K between this work and that of Kilpatrick *et al.* are well within claimed accuracies for 1,*trans*-3-pentadiene, 1,4-pentadiene, 3-methyl-1,2-butadiene, and 2-methyl-1,3-butadiene but exceed 1 kcal for 1,2-pentadiene, 1,*cis*-3-pentadiene, and 2,3-pentadiene. The effect of these differences in Gibbs energy of formation is shown in Table IX as the equilibrium concentrations of each pentadiene at 298.152° K as calculated from the two sets of energies. The major change is the large difference in the relative stabilities of *cis*- and *trans*-1,3-pentadiene. The deviations between the new and old values at 298.15° K indicated that a complete revision of the thermodynamic properties of the pentadienes is needed, supported by gas phase equilibria studies at higher temperatures.

Table VII. Molal Entropies in Ideal Gas State (Cal °K^{-1}) at 298.15° K

Compound	$S°$ (liq)	ΔS_{vap}	ΔS_{comp}	Gas Imperfection	$S°$ (gas)	$S°$ (gas) Literature
1,2-Pentadiene	58.55	22.791	−1.444	0.12	80.02	79.7^{a}
1,*cis*-3-Pentadiene	55.747	22.659	−1.382	0.13	77.15	77.5^{a}
1,*trans*-3-Pentadiene	54.28	22.248	−1.224	0.13	75.43	76.4^{a}
1,4-Pentadiene	59.48	20.209	−0.068	0.20	79.82	79.7^{a}
2,3-Pentadiene	56.72	23.547	−1.718	0.11	78.66	77.6^{a}
3-Methyl-1,2-butadiene	55.40	22.377	−1.150	0.14	76.77	76.4^{a}
2-Methyl-1,3-butadiene	54.56	21.152	−0.643	0.16	75.23	75.4^{a}

[a] (*8*).

Table VIII. Molal Free Energies and Logarithms of the Equilibrium Constants of Formation at 298.15° K

Compound	$S°$ (gas), Eu	$\Delta S_f°$, Eu	$T\Delta S_f°$, Kcal	$\Delta H_f°$, Kcal	$\Delta G_f°$, Kcal	Log $K_f°$	$\Delta G_f°$ Literature, Kcal
1,2-Pentadiene	80.02	−51.672	−15.406	33.625^{a}	49.031	−35.94	50.29^{b}
1,*cis*-3-Pentadiene	77.15	−54.542	−16.262	19.785^{a}	36.047	−26.42	34.88^{b}
1,*trans*-3-Pentadiene	75.43	−56.262	−16.775	18.125^{a}	34.900	−25.58	35.07^{b}
1,4-Pentadiene	79.82	−51.872	−15.466	25.425^{a}	40.891	−29.97	40.69^{b}
2,3-Pentadiene	78.66	−53.032	−15.811	31.805^{a}	47.616	−34.90	49.22^{b}
3-Methyl-1,2-butadiene	76.77	−54.942	−16.381	30.852^{c}	47.228	−34.62	47.47^{b}
2-Methyl-1,3-butadiene	75.23	−56.462	−16.834	18.105^{a}	34.939	−25.61	34.87^{b}

[a] Values quoted from (*3*), but corrected to latest (20)NBS values of heats of formation of water and carbon dioxide. [b] (*8*). [c] (*4*).

Table IX. Equilibrium Concentrations at 298.15° K

Compound	This Work, Mole Fraction	Kilpatrick *et al.*, Mole Fraction
1,2-Pentadiene	2.1×10^{-11}	0.000
1,*cis*-3-Pentadiene	0.0696	0.367
1,*trans*-3-Pentadiene	0.481	0.263
1,4-Pentadiene	2.0×10^{-5}	0.000
2,3-Pentadiene	2.3×10^{-10}	0.000
3-Methyl-1,2-butadiene	4.4×10^{-10}	0.000
2-Methyl-1,3-butadiene	0.449	0.370

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