U. S. Department of Commerce
National Bureau of Standards

Research Paper RP2026
Volume 43, September 1949

Part of the Journal of Research of the National Bureau of Standards

Heats, Equilibrium Constants, and Free Energies of Formation of the Dimethylcyclopentanes [1]

By Morton B. Epstein,[2] Gordon M. Barrow,[3] Kenneth S. Pitzer,[4] and Frederick D. Rossini [5]

For the five dimethylcyclopentanes, values are presented for the following thermodynamic properties to 1,500° K: heat content function, free energy function, entropy, heat content, heat capacity, heat of formation from the elements, free energy of formation from the elements, and logarithm of the equilibrium constant of formation from the elements. Equilibrium constants and concentrations are given in tabular and graphical form for some reactions of isomerization.

I. Introduction

As part of the work of the American Petroleum Institute Research Project 44 at the National Bureau of Standards and the University of California, values have been compiled for the thermodynamic properties in the gaseous state to 1,500 °K of the heat content function, free energy function, entropy, heat content, heat capacity, heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation for the five dimethylcyclopentanes. Calculations have also been made of the free energies and equilibrium constants of some reactions of isomerization.

II. Constants

The values of the constants used in the present calculations are the same as in the previous report [1].[6]

III. Heat Content Function, Free Energy Function, Entropy, Heat Content, and Heat Capacity

For the dimethylcyclopentanes, the available thermal, spectroscopic, and other molecular data are either insufficient or too uncertain to permit a satisfactory statistical treatment at the present time. However, the thermodynamic functions may be calculated by adding the necessary increment to the corresponding function of methylcyclopentane, for which the appropriate values have already been calculated [2].

For the calculation by the method of increments, the following equation was used:

$$G(\text{dimethlcyclopentane}) = G(\text{methylcyclopentane}) + G(\text{methyl}) + 2G(\text{restricted rotation of methyl group with appropriate barrier}) - 2G(\text{restricted rotation of methyl group with barrier as in methylcyclopentane}). \quad (1)$$

In eq 1, G represents the contribution to the heat content function, the free energy function, or the heat capacity, the entropy and heat content being simply derived from these functions. In calculating the contribution of the restricted rotation of the methyl group in methylcyclopentane, the barrier was taken to be 3,600 cal/mole [2].

The barriers restricting the internal rotation of the methyl groups in the dimethylcyclopentanes have been chosen to fit the known entropies of 1,1-dimethylcyclopentane, *cis*-1,2-dimethylcyclopentane, and *trans*-1,3-dimethylcyclopentane [3]. These barriers are 5,320, 4,680, and 4,360 cal/mole, respectively. For *trans*-1,2-dimethylcyclopentane and *cis*-1,3-dimethylcyclopentane, the barriers were taken to be equal to that in *trans*-1,3-dimethylcyclopentane. The barrier restricting ring puckering for all of the dimethylcyclopentane isomers is taken unchanged from that in methylcyclopentane [2].

[1] This investigation was performed as a part of the work of the American Petroleum Institute Research Project 44 at the National Bureau of Standards and the University of California.

[2] Research Associate on the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

[3] Junior Research Fellow on the American Petroleum Institute Research Project 44 at the University of California, Berkeley, California.

[4] Associate Director of the American Petroleum Institute Research Project 44 at the University of California, Berkeley, California, on leave.

[5] Director of the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

[6] Figures in brackets indicate the literature references at the end of this paper.

847618—49——5

TABLE 1. *Values of the thermodynamic functions, for the ideal gas state, to 1,500 ° K, for the five dimethylcyclopentanes*

Compound (gas)	Temperature in ° K														
	0	298.16	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
	HEAT CONTENT FUNCTION, $(H°-H_0°)/T$, IN CAL/DEG MOLE														
1,1-Dimethylcyclopentane	0	18.66	18.77	23.51	28.59	33.63	38.32	42.64	46.69	50.38	53.77	56.92	59.78	62.42	64.87
cis-1,2-Dimethylcyclopentane	0	18.86	18.95	23.63	28.71	33.71	38.38	42.70	46.69	50.36	53.73	56.86	59.72	62.36	64.79
trans-1,2-Dimethylcyclopentane	0	18.94	19.05	23.71	28.78	33.77	38.42	42.68	46.69	50.34	53.69	56.82	59.68	62.30	64.73
cis-1,3-Dimethylcyclopentane	0	18.94	19.05	23.71	28.78	33.77	38.42	42.68	46.69	50.34	53.69	56.82	59.68	62.30	64.73
trans-1,3-Dimethylcyclopentane	0	18.94	19.05	23.71	28.78	33.77	38.42	42.68	46.69	50.34	53.69	56.82	59.68	62.30	64.73
	FREE ENERGY FUNCTION, $(F°-H_0°)/T$, IN CAL/DEG MOLE														
1,1-Dimethylcyclopentane	0	−67.21	−67.36	−73.36	−79.14	−84.72	−90.28	−95.75	−101.02	−106.13	−111.05	−115.87	−120.51	−125.04	−129.51
cis-1,2-Dimethylcyclopentane	0	−68.65	−68.81	−74.91	−80.71	−86.35	−91.91	−97.36	−102.65	−107.76	−112.70	−117.50	−122.12	−126.63	−131.10
trans-1,2-Dimethylcyclopentane	0	−68.73	−68.87	−75.01	−80.81	−86.45	−92.03	−97.54	−102.79	−107.90	−112.84	−117.64	−122.26	−126.77	−131.24
cis-1,3-Dimethylcyclopentane	0	−68.73	−68.87	−75.01	−80.81	−86.45	−92.03	−97.54	−102.79	−107.90	−112.84	−117.64	−122.26	−126.77	−131.24
trans-1,3-Dimethylcyclopentane	0	−68.73	−68.87	−75.01	−80.81	−86.45	−92.03	−97.54	−102.79	−107.90	−112.84	−117.64	−122.26	−126.77	−131.24
	ENTROPY, $S°$, IN CAL/DEG MOLE														
1,1-Dimethylcyclopentane	0	85.87	86.13	96.87	107.73	118.35	128.60	138.39	147.71	156.51	164.82	172.79	180.29	187.46	194.38
cis-1,2-Dimethylcyclopentane	0	87.51	87.76	98.54	109.42	120.06	130.29	140.06	149.34	158.12	166.43	174.36	181.84	188.99	195.89
trans-1,2-Dimethylcyclopentane	0	87.67	87.92	98.72	109.60	120.22	130.45	140.22	149.48	158.24	166.53	174.46	181.94	189.07	195.97
cis-1,3-Dimethylcyclopentane	0	87.67	87.92	98.72	109.60	120.22	130.45	140.22	149.48	158.24	166.53	174.46	181.94	189.07	195.97
trans-1,3-Dimethylcyclopentane	0	87.67	87.92	98.72	109.60	120.22	130.45	140.22	149.48	158.24	166.53	174.46	181.94	189.07	195.97
	HEAT CONTENT, $(H°-H_0°)$, IN CAL/MOLE														
1,1-Dimethylcyclopentane	0	5564	5631	9404	14300	20180	26820	34110	42020	50380	59150	68300	77710	87390	97300
cis-1,2-Dimethylcyclopentane	0	5623	5685	9452	14360	20230	26870	34160	42020	50360	59100	68230	77640	87300	97180
trans-1,2-Dimethylcyclopentane	0	5647	5715	9484	14400	20260	26890	34140	42020	50340	59060	68180	77580	87220	97100
cis-1,3-Dimethylcyclopentane	0	5647	5715	9484	14400	20260	26890	34140	42020	50340	59060	68180	77580	87220	97100
trans-1,3-Dimethylcyclopentane	0	5647	5715	9484	14400	20260	26890	34140	42020	50340	59060	68180	77580	87220	97100

	298.16°	300°	400°	500°	600°	700°	800°	900°	1000°	1100°	1200°	1300°	1400°	1500°
	HEAT CAPACITY, C_p°, IN CAL/DEG MOLE													
1,1-Dimethylcyclopentane	0	31.86	32.16	43.55	54.01	62.78	70.08	76.18	81.38	85.83	89.62	92.89	95.75	98.19	100.31
cis-1,2-Dimethylcyclopentane	0	32.06	32.34	43.67	54.03	62.72	69.92	75.98	81.14	85.57	89.38	92.65	95.51	97.97	100.11
trans-1,2-Dimethylcyclopentane	0	32.14	32.44	43.71	54.03	62.66	69.88	75.84	80.98	85.43	89.24	92.51	95.39	97.85	100.01
cis-1,3-Dimethylcyclopentane	0	32.14	32.44	43.71	54.03	62.66	69.88	75.84	80.98	85.43	89.24	92.51	95.39	97.85	100.01
trans-1,3-Dimethylcyclopentane	0	32.14	32.44	43.71	54.03	62.66	69.88	75.84	80.98	85.43	89.24	92.51	95.39	97.85	100.01
	HEAT OF FORMATION, ΔHf°, IN KCAL/MOLE													
1,1-Dimethylcyclopentane	−22.69	−33.05	−33.10	−35.92	−38.14	−39.79	−41.04	−41.91	−42.39	−42.59	−42.55	−42.29	−41.94	−41.49	−40.94
cis-1,2-Dimethylcyclopentane	−20.66	−30.96	−31.01	−33.84	−36.05	−37.72	−38.96	−39.83	−40.36	−40.58	−40.57	−40.33	−39.99	−39.54	−39.03
trans-1,2-Dimethylcyclopentane	−22.39	−32.67	−32.72	−35.54	−37.75	−39.41	−40.67	−41.58	−42.09	−42.33	−42.35	−42.11	−41.78	−41.36	−40.85
cis-1,3-Dimethylcyclopentane	−21.65	−31.93	−31.98	−34.80	−37.01	−38.67	−39.93	−40.84	−41.35	−41.59	−41.61	−41.37	−41.04	−40.62	−40.11
trans-1,3-Dimethylcyclopentane	−22.19	−32.47	−32.52	−35.34	−37.55	−39.21	−40.47	−41.38	−41.89	−42.13	−42.15	−41.91	−41.58	−41.16	−40.65
	FREE ENERGY OF FORMATION, ΔFf°, IN KCAL/MOLE													
1,1-Dimethylcyclopentane	−22.69	+9.33	9.58	24.26	39.58	55.34	71.29	87.33	103.51	119.75	136.02	152.24	168.48	184.62	200.64
cis-1,2-Dimethylcyclopentane	−20.66	+10.93	11.18	25.67	40.83	56.39	72.17	88.07	104.08	120.15	136.23	152.31	168.42	184.43	200.29
trans-1,2-Dimethylcyclopentane	−22.39	+9.17	9.42	23.90	39.04	54.60	70.36	86.19	102.22	118.27	134.34	150.41	166.50	182.50	198.35
cis-1,3-Dimethylcyclopentane	−21.65	+9.91	10.16	24.64	39.78	55.34	71.10	86.93	102.96	119.01	135.08	151.15	167.24	183.24	199.09
trans-1,3-Dimethylcyclopentane	−22.19	+9.37	9.62	24.10	39.24	54.80	70.56	86.39	102.42	118.47	134.54	150.61	166.70	182.70	198.55
	LOGARITHM OF EQUILIBRIUM CONSTANT OF FORMATION, $\log_{10}Kf$													
1,1-Dimethylcyclopentane	Infinite	−6.8372	−6.9791	−13.2550	−17.3002	−20.1566	−22.2561	−23.8567	−25.1361	−26.1704	−27.0236	−27.7258	−28.3238	−28.8208	−29.2335
cis-1,2-Dimethylcyclopentane	Infinite	−8.0107	−8.1413	−14.0255	−17.8445	−20.5399	−22.5337	−24.0595	−25.2729	−26.2579	−27.0664	−27.7393	−28.3132	−28.7903	−29.1818
trans-1,2-Dimethylcyclopentane	Infinite	−6.7224	−6.8651	−13.0564	−17.0648	−19.8865	−21.9662	−23.5465	−24.8213	−25.8483	−26.6914	−27.3930	−27.9912	−28.4890	−28.8986
cis-1,3-Dimethylcyclopentane	Infinite	−7.2648	−7.4042	−13.4607	−17.3882	−20.1561	−22.1972	−23.7487	−25.0009	−26.0101	−26.8384	−27.5277	−28.1156	−28.6046	−29.0064
trans-1,3-Dimethylcyclopentane	Infinite	−6.8690	−7.0108	−13.1657	−17.1522	−19.9594	−22.0286	−23.6011	−24.8698	−25.8921	−26.7311	−27.4294	−28.0248	−28.5203	−28.9278

The term G(methyl) represents the contribution of a methyl group with a barrier to internal rotation of 3,600 cal/mole and is calculated from the following relation:

G(methyl) = G(methylcyclopentane) − G(cyclopentane) − G(restricted rotation of ring puckering in methylcyclopentane),

where the term G(cyclopentane) includes all contributions to that function for cyclopentane exclusive of symmetry. From the method of calculation of the function for methylcyclopentane [2], the term G(methyl) is the same as the contribution of a methyl group to the functions for methylcyclohexane with a barrier of 3,600 cal/mole. This contribution is equal to the difference between the functions for methylcyclohexane and cyclohexane, exclusive of contributions due to symmetry and to equatorial-polar tautomerism [4].

For 1,1-dimethylcyclopentane, *trans*-1,2-dimethylcyclopentane, and *trans*-1,3-dimethylcyclopentane, an additional symmetry term, R ln 2, was subtracted from the entropy and the negative of the free energy function. For *trans*-1,2-dimethylcyclopentane and *trans*-1,3-dimethylcyclopentane, a mixing term R ln 2 was added to allow for the mixing of equal amounts of the dextro and levo optical isomers. The values tabulated for these two compounds, therefore, are for the mixture of the optical isomers. It will be noted that the mixing term, where applicable, exactly cancels the symmetry term. The resulting values for the heat content function, the free energy function, the entropy, the heat content, and the heat capacity are included in table 1. Where the second decimal place is given, the uncertainty is several tenths of a unit.

IV. Heat, Free Energy, and Equilibrium Constants of Formation

Values for the standard heat of formation at 25° C of the five dimethylcyclopentanes in the gaseous state, from carbon (solid, graphite) and hydrogen (gaseous), are taken from reference [5].

The method of calculating values of the standard heat of formation, the standard free energy of formation, and the logarithm of the equilibrium constant of formation for the different temperatures in the range 0° to 1,500° K is the same as that described in section IV–1 of reference [6].

The resulting values for the formation of the given hydrocarbon in the gaseous state, from the elements carbon (solid, graphite) and hydrogen (gaseous), each in its thermodynamic standard reference state, are included in table 1, which gives values of the following properties to 1,500° K: heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation.

V. Free Energies and Equilibria of Some Reactions of Isomerization

In figure 1 are plotted, as a function of temperature, for the five dimethylcyclopentanes and ethylcyclopentane, the amounts, in mole fraction, of each of the isomers present at equilibrium with the other isomers in the gaseous state. The corresponding numerical values are given in table 2.

TABLE 2. *Values of the equilibrium concentrations for the isomerization of the* C_7 *alkylcyclopentanes in the ideal gaseous state to 1,500° K*

Temperature	Composition, in mole fraction, of equilibrium mixture of isomers					
	Ethylcyclopentane	1,1-Dimethylcyclopentane	*cis*-1,2-Dimethylcyclopentane	*trans*-1,2-Dimethylcyclopentane	*cis*-1,3-Dimethylcyclopentane	*trans*-1,3-Dimethylcyclopentane
°K						
298.16	0.031	0.264	0.018	0.343	0.099	0.245
300	.032	.264	.018	.342	.099	.245
400	.075	.201	.034	.318	.125	.247
500	.122	.168	.048	.289	.137	.236
600	.164	.143	.059	.267	.142	.225
700	.196	.127	.068	.249	.145	.215
800	.221	.116	.075	.235	.147	.206
900	.243	.108	.080	.223	.147	.199
1000	.262	.102	.084	.213	.147	.192
1100	.278	.098	.087	.204	.147	.186
1200	.292	.094	.089	.197	.146	.182
1300	.303	.090	.091	.193	.145	.178
1400	.310	.088	.094	.188	.145	.175
1500	.313	.087	.097	.185	.144	.174

In figure 2 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the isomerization to methylcyclohexane of ethylcyclopentane and each of the five dimethylcyclopentanes.

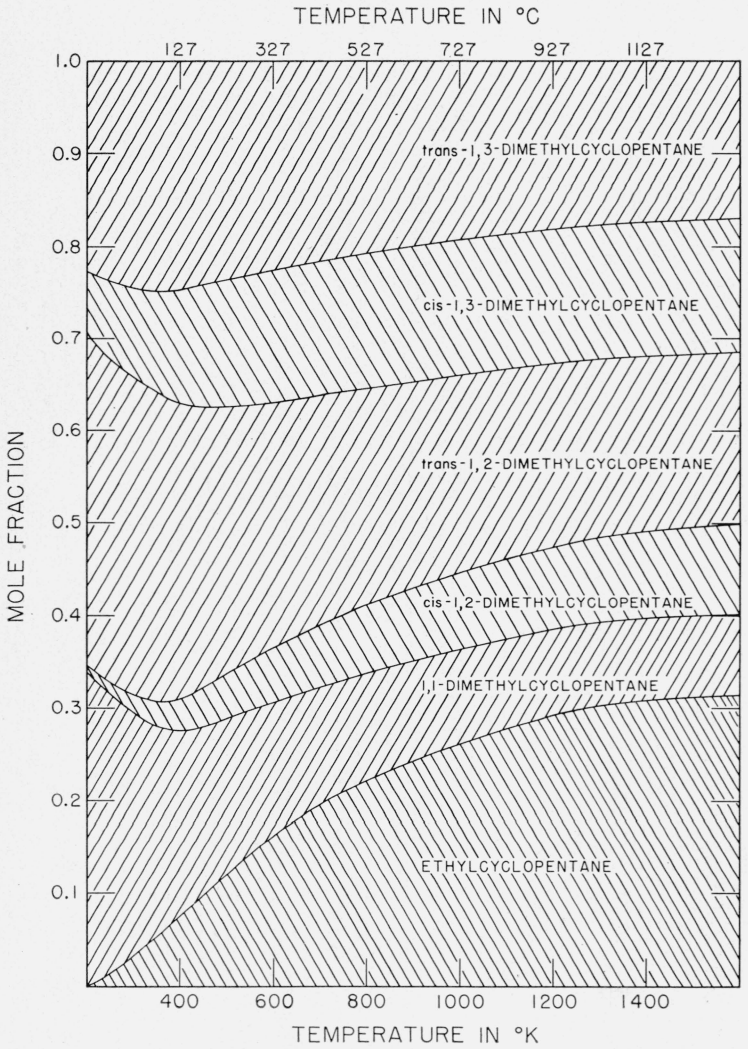

FIGURE 1. *Equilibrium concentrations of the six* C_7H_{14} *alkyl cyclopentanes.*

The vertical width of a band measures the mole fraction as a function of temperature of a given isomer when at equilibrium with all of the isomeric alkylcyclopentanes in the gas phase.

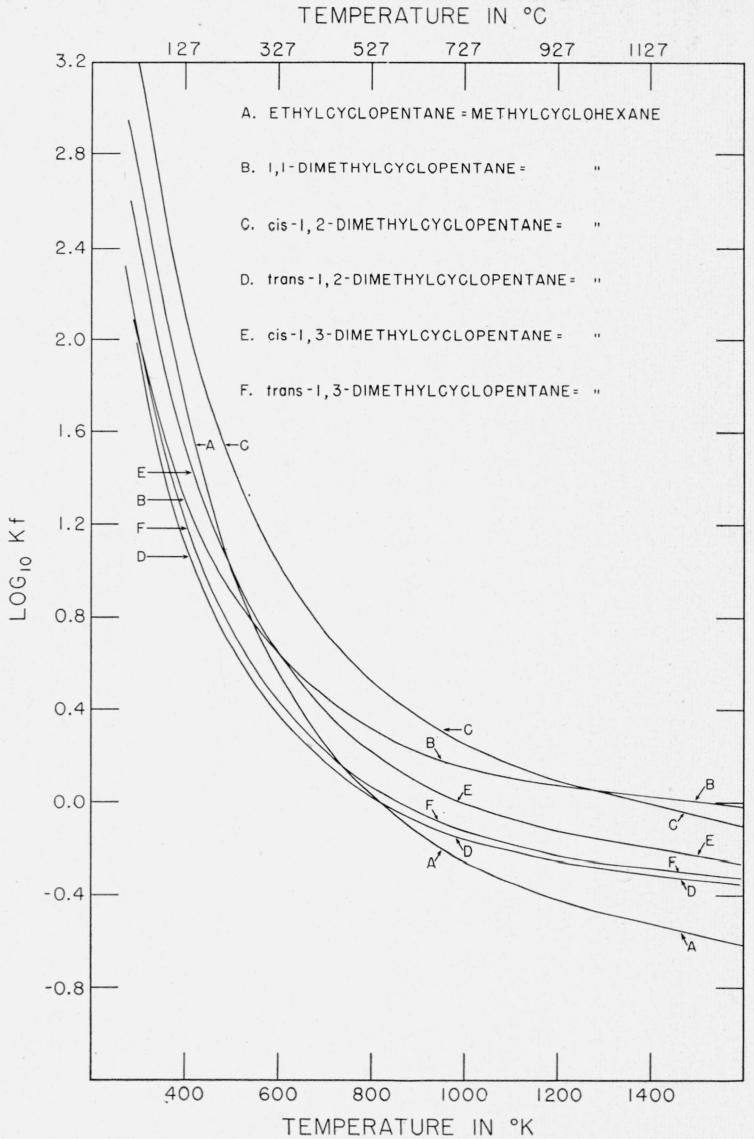

FIGURE 2. *Isomerization of ethylcyclopentane and each of the five dimethylcyclopentanes to methylcyclohexane.*

The curves give the logarithm of the equilibrium constant as a function of temperature for the following reactions in the gaseous state: C_7H_{14} (gas, ethylcyclopentane or a dimethylcyclopentane) = C_7H_{14} (gas, methylcyclohexane).

VI. References

[1] M. B. Epstein, K. S. Pitzer, and F. D. Rossini, J. Research NBS **42,** 379 (1949) RP1976.

[2] J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer, and F. D. Rossini, J. Research NBS **39,** 523 (1947) RP1845.

[3] H. M. Huffman and others, U. S. Bureau of Mines, Bartlesville, Oklahoma. Unpublished.

[4] C. W. Beckett, K. S. Pitzer, and R. Spitzer, J. Am. Chem. Soc. **69,** 2488 (1947).

[5] W. H. Johnson, E. J. Prosen, and F. D. Rossini, J. Research NBS **42,** 251 (1949) RP1966.

[6] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, J. Research NBS **34,** 143 (1945) RP1634.

WASHINGTON, May 13, 1949.