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Heats, Equilibrium Constants, and Free Energies of Formation of Cyclopentene and Cyclohexene[1]

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

For cyclopentene and cyclohexene, 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 are given in graphical form for some reactions of isomerization, dehydrogenation, and disproportionation.

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 cyclopentene and cyclohexene. Calculations have also been made of the free energies and equilibrium constants of a number of reactions involving isomerization, dehydrogenation, and disproportionation of these compounds.

The values of the constants used in the present calculations are as follows [1,2] [5]: The calorie is the conventional thermochemical calorie defined as 4.1840 absolute joules; the absolute temperature of the ice point is 273.16 ±0.010° K; the gas constant is 1.98719 ±0.00013 cal/deg mole.

For cyclopentene and cyclohexene, the values of the heat-content function, free-energy function, and heat capacity were taken from reference [3]. As usual, the value of the entropy is given by the value of the heat-content function less the value of the free-energy function, and the heat content is obtained by multiplying the value of the heat-content function by the temperature.

The resulting values of the thermodynamic functions are given in table 1, which includes values of the following properties from 0° to 1,500° K: heat-content function, free-energy function, entropy, heat content, and heat capacity.

Values of the standard heat of formation at 25° C of gaseous cyclopentene and cyclohexene, from carbon (solid, graphite) and hydrogen (gaseous), were calculated from the values for the standard heat of formation for the liquid state calculated by Prosen, Yenchius, and Rossini [4] from experimental values for the heats of combustion, together with values for the standard heat of vaporization calculated by Wagman and Rossini [6] from vapor pressure data of Forziati and Rossini [7]. The values for the standard heat of formation from the elements, at 25° C, $\Delta Hf°$, from reference [4] are as follows: Cyclopentene (liquid), 1.16 ±0.16 kcal/mole; cyclohexene (liquid), −9.70 ± 0.19 kcal/mole. The values for the standard heat of vaporization at 25° C, $\Delta Hv°$, from reference [6], are as follows: cyclopentene, 6.71 ±0.07 kcal/mole; cyclohexene, 8.00 ±0.08 kcal/mole.

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

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

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

TABLE 1.—*Values of the thermodynamic functions, for the ideal gas state, to 1,500° K, for cyclopentene and cyclohexene*

Compound (gas)	Formula	Temperature in °K															
		0	200	298.16	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	1,500
		Heat-content function, $(H°-H_0°)/T$, in cal/deg mole															
Cyclopentene	C_5H_8	0	9.97	11.61	11.65	14.12	16.98	19.90	22.71	25.36	27.82	30.09	32.19	34.13	35.92	37.57	39.10
Cyclohexene	C_6H_{10}	0	10.75	13.98	14.05	18.04	22.20	26.20	29.93	33.35	36.47	39.33	41.94	44.34	46.53	48.55	50.42
		Free-energy function, $(F°-E_0°)/T$, in cal/deg mole															
Cyclopentene	C_5H_8	0	−53.37	−57.62	−57.69	−61.37	−64.82	−68.18	−71.46	−74.67	−77.80	−80.85	−83.81	−86.70	−89.50	−92.23	−94.87
Cyclohexene	C_6H_{10}	0	−55.43	−60.29	−60.38	−64.96	−69.43	−73.84	−78.16	−82.38	−86.49	−90.48	−94.36	−98.12	−101.75	−105.27	−108.68
		Entropy, S°, in cal/deg mole															
Cyclopentene	C_5H_8	0	63.43	69.23	69.34	75.49	81.80	88.08	94.17	100.03	105.62	110.94	116.00	120.83	125.42	129.80	133.97
Cyclohexene	C_6H_{10}	0	66.18	74.27	74.43	83.00	91.63	100.04	108.09	115.73	122.96	129.81	136.30	142.46	148.28	153.82	159.10
		Heat content, $(H°-H_0°)$, in cal/mole															
Cyclopentene	C_5H_8	0	1,994	3,462	3,495	5,648	8,490	11,940	15,900	20,290	25,040	30,090	35,410	40,960	46,700	52,600	58,650
Cyclohexene	C_6H_{10}	0	2,150	4,168	4,215	7,216	11,100	15,720	20,950	26,680	32,820	39,330	46,130	53,210	60,490	67,970	75,630
		Heat capacity, $C_p°$, in cal/deg mole															
Cyclopentene	C_5H_8	0	12.33	17.95	18.08	25.08	31.62	37.19	41.86	45.78	49.11	51.94	54.37	56.45	58.24	59.79	61.13
Cyclohexene	C_6H_{10}	0	16.32	25.10	25.28	34.64	42.78	49.45	54.92	59.49	63.34	66.62	69.43	71.85	73.92	75.72	77.27
		Heat of formation, $\Delta Hf°$, in kcal/mole															
Cyclopentene	C_5H_8	7.05	3.14	1.16	1.12	−0.74	−2.28	−3.51	−4.49	−5.22	−5.75	−6.09	−6.29	−6.35	−6.35	−6.27	−6.15
Cyclophexene	C_6H_{10}	−2.24	−7.44	−9.70	−9.74	−11.69	−13.21	−14.35	−15.18	−15.74	−16.07	−16.19	−16.14	−15.95	−15.70	−15.36	−14.96
		Free energy of formation, $\Delta Ff°$ in kcal/mole															
Cyclopentene	C_5H_8	7.05	-------	19.77	19.89	26.43	33.41	40.66	48.11	55.66	63.31	71.01	78.73	86.46	94.20	101.9	109.6
Cyclohexene	C_6H_{10}	−2.24	-------	17.12	17.28	26.60	36.36	46.38	56.58	66.86	77.22	87.60	97.96	108.3	118.7	129.0	139.3
		Logarithm of equilibrium constant of formation, $\log_{10} Kf$															
Cyclopentene	C_5H_8	∞	-------	−14.491	−14.487	−14,439	−14.602	−14.811	−15.019	−15.206	−15.374	−15.519	−15.642	−15.746	−15.837	−15.909	−15.975
Cyclohexene	C_6H_{10}	∞	-------	−12.548	−12.592	−14.533	−15.892	−16.895	−17.664	−18.266	−18.750	−19.143	−19.462	−19.727	−19.951	−20.136	−20.294

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 [5].

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.

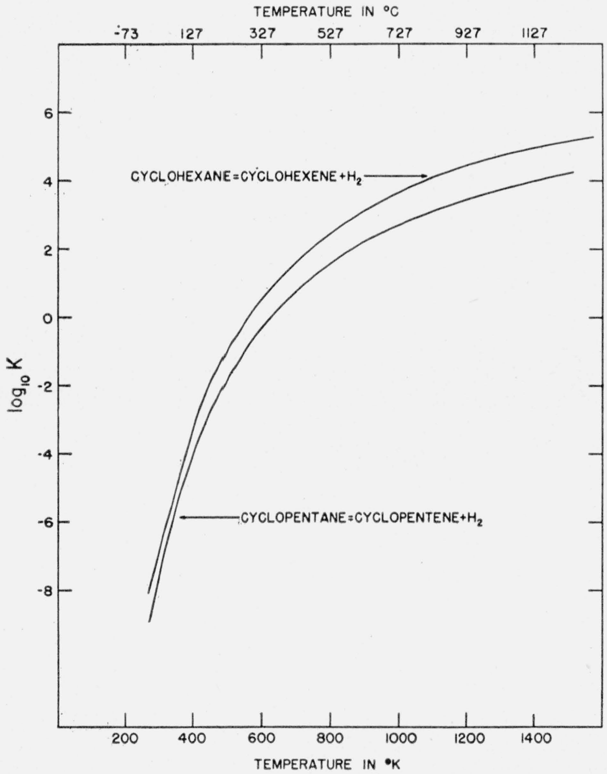

FIGURE 1. *Dehydrogenation of cycloparaffins to cycloolefins.*

The curves give the logarithm of the equilibrium constant as a function of temperature for the following reactions in the gaseous state:

C_5H_{10} (gas, cyclopentane) = C_5H_8 (gas, cyclopentene) + H_2 (gas).

C_6H_{12} (gas, cyclohexane) = C_6H_{10} (gas, cyclohexene) + H_2 (gas).

In figure 1 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the reactions of dehydrogenation of cyclopentane to cyclopentene and of cyclohexane to cyclohexene.

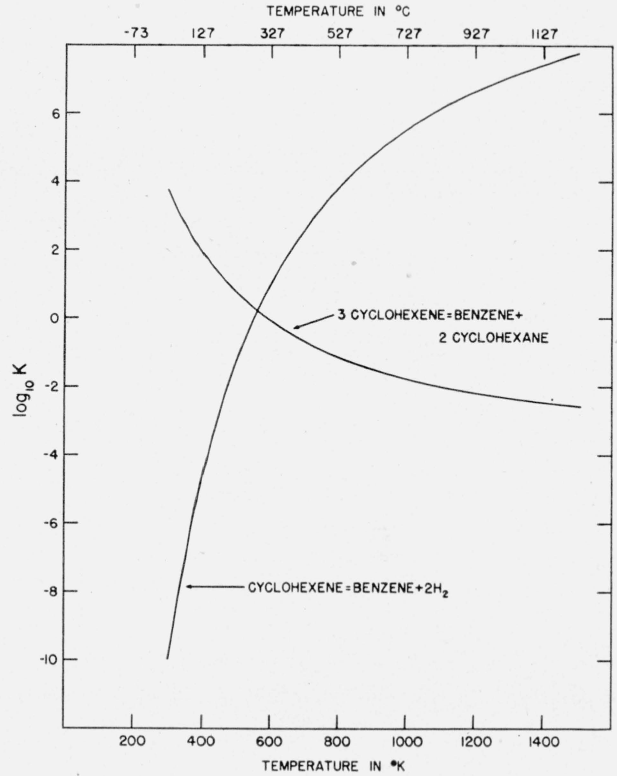

FIGURE 2. *Dehydrogenation of cyclohexene to benzene and disproportionation of cyclohexene to benzene and cyclohexane.*

The curves give the logarithm of the equilibrium constant as a function of temperature for the following reactions in the gaseous state:

C_6H_{10} (gas, cyclohexene) = C_6H_6 (gas, benzene) + $2H_2$ (gas).

$3C_6H_{10}$ (gas, cyclohexene) = C_6H_6 (gas, benzene) + $2C_6H_{12}$ (gas, cyclohexane).

In figure 2 are plotted, as a function of temperature, values of the logarithm of the equilibrium constant for the dehydrogenation of cyclohexene to benzene and for the disproportionation of cyclohexene to cyclohexane and benzene.

In figure 3 are plotted, as a function of temperature, values of the logarithm of the equilibrium

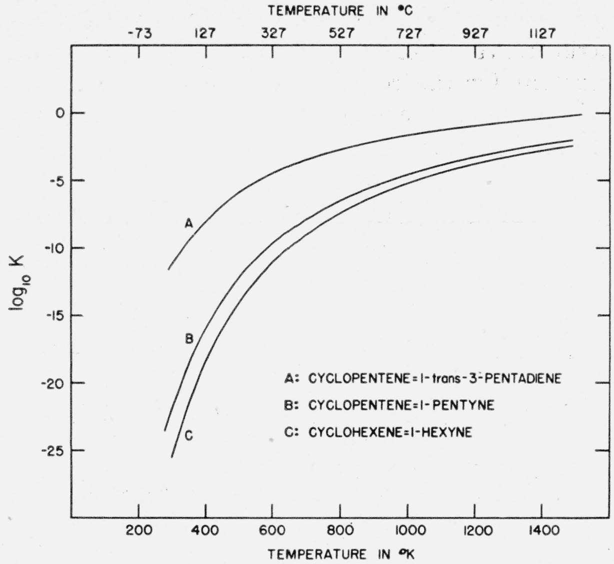

FIGURE 3. *Isomerization of cycloolefins to diolefins and to acetylenes.*

The curves give the logarithm of the equilibrium constant as a function of temperature for the following reactions in the gaseous state:

(A) C_5H_8 (gas, cyclopentene) = C_5H_8 (gas, 1-*trans*-3-pentadiene).

(B) C_5H_8 (gas, cyclopentene) = C_5H_8 (gas, 1-pentyne).

(C) C_6H_{10} (gas, cyclohexene) = C_6H_{10} (gas, 1-hexyne).

constant for the isomerization of cyclopentene to 1-pentyne, of cyclopentene to 1-*trans*-3-pentadiene, and of cyclohexene to 1-hexyne.

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[1] Selected values of chemical thermodynamic properties (December 31, 1947). National Bureau of Standards.

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