[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF DAVIS AND ELKINS COLLEGE AND PRINCETON UNIVERSITY]

Equilibrium in the System Cyclohexane–Benzene–Hydrogen[1]

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In a previous paper,[2] attention was called to the anomalous temperature coefficient of the rate of hydrogenation of benzene between 200 and 300° in the presence of a copper catalyst. It was known from the work of Zelinskii[3] and of Dougherty and Taylor[4] that the reverse reaction in this range was considerable, but at that time no satisfactory quantitative measurements of equilibrium were available. Such measurements were consequently undertaken. Since then data at two temperatures have been presented by Burrows and Lucarini.[5] These will be considered in connection with our own results. In addition, Parks and Huffman[6] have calculated free energies from thermal data by means of the Nernst Heat Theorem.

Apparatus and Procedure

The experiments consisted of passing cyclohexane–benzene–hydrogen mixtures of known composition slowly over a copper catalyst and determining whether hydrogen was consumed or evolved. The composition was then shifted until no change in hydrogen volume resulted.

The apparatus was like that used in our previous investigation except that parallel saturators (one set each for benzene and cyclohexane) of a new type were used. One of these is illustrated in Fig. 1. Small round cotton wicks, E, hanging from rings of platinum wire, which were supported on the bulges, A, dipped into the liquid in the bulbs, B, of the presaturators. The condensers, C, were submerged in a thermostat at the temperatures at which it was desired to saturate the hydrogen. The presaturators were held at a temperature slightly higher than the condensers. This set-up avoided the bubbling of hydrogen through the liquids. These saturators were tested by absorbing the vapors in silica gel and weighing. They were proved to be perfectly satisfactory for the purpose employed.

The hydrogen was generated electrolytically, the rate of flow being determined by the current through the generators. Two sets of generators were used, the hydrogen from the one passing through the benzene saturator, and from the other through the cyclohexane saturator.

The temperature of the furnace containing the copper catalyst was

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[1] This investigation was carried out in the years 1924–1925 in the Cobb Chemical Laboratory, University of Virginia, while the senior author was du Pont Fellow in Chemistry. It was submitted by him in partial fulfilment of the requirements for the degree of Doctor of Philosophy in 1926.

[2] Pease and Purdum, THIS JOURNAL, **47**, 1435 (1925).

[3] Zelinskii, *Ber.*, **44**, 3121 (1911).

[4] Dougherty and Taylor, *J. Phys. Chem.*, **27**, 533 (1923).

[5] Burrows and Lucarini, THIS JOURNAL, **49**, 1157 (1927).

[6] Parks and Huffman, "Free Energies of Organic Compounds," Chemical Catalog Co., New York, 1932, p. 94.

controlled by regulating the heating current. This current was obtained from a storage battery. Constancy was obtained by "floating" another storage battery on the line. Temperatures were read on a calibrated mercury thermometer.

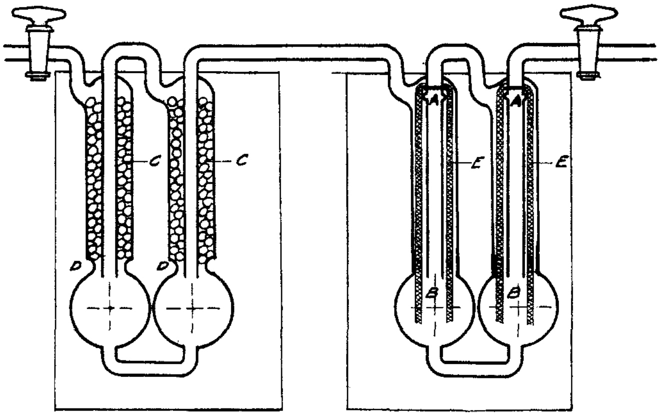

Fig. 1.—Apparatus for saturating hydrogen with benzene and cyclohexane vapors.

Results

Results are presented in Table I and Fig. 2. The value of K_P is for atmospheres

$$K_P = P_{C_6H_{12}}/P_{C_6H_6}P^3_{H_2}$$

Parks and Huffman[6] give the following equation for $\Delta F°$ based on thermal data and the Nernst Heat Theorem

$$\Delta F° = -43{,}800 + 18.2\ T \ln T - 0.008\ T^2 - 30.0\ T$$

TABLE I

EQUILIBRIUM DATA

Temp., °C.	Press., mm.	Temp. satns., °C.	Equil. mixture, % by vol.[a] C_6H_{12}	C_6H_6	H_2	K_P, atm.	$\Delta F°$ Cal. Expt.	Equ.[c] P.-H.	Δ
251	742.5	35.0	17.29	2.75	79.96	13.19	−2690	−1980	− 640
251	740.7	23.2	10.51	1.44	88.05	11.59	−2550		
257	746.5	35.0	15.56	4.39	80.06	7.29	−2090	−1420	− 680
257	744.5	23.2	11.33	2.52	86.45	7.40	−2110		
261	750.3	23.2	9.34	2.47	88.22	5.72	−1850	−1050	− 800
266–7	(Burrows and Lucarini)[b]					5.47	−1820	− 540	(−1280)
268	746.8	35.0	11.77	8.11	80.12	2.97	−1170	− 390	− 790
268	753.6	23.2	7.85	3.86	88.29	3.03	−1190		
269	748.8	23.2	8.02	3.76	88.22	3.25	−1270	− 300	− 970
274	744.4	35.0	9.51	10.40	80.10	1.89	− 700	+ 190	− 900
274	753.4	23.2	6.60	5.10	88.15	1.94	− 720		
280	(Burrows and Lucarini)[b]					1.62	− 530	+ 750	(−1280)

[a] The vapors were assumed to be perfect gases. [b] The data of Burrows and Lucarini have been added for comparison. [c] $\Delta F°$ from equation of Parks and Huffman.

Values of ΔF° calculated from this equation are given in the next to last column of Table I for comparison with the values calculated from the experimental data. There is a consistent difference between the two (entered in the last column) which is somewhat larger for the two results of Burrows and Lucarini. This could be taken account of by altering the last term of the Parks–Huffman equation, from $-30.0\ T$ to $-31.5\ T$ for our data, or to $-32.4\ T$ for Burrows and Lucarini's data, or to $-31.7\ T$ for all the equilibrium data. The best value for this term is perhaps closer to $-31.0\ T$ than to $-30.0\ T$. All things considered, the agreement is very good.

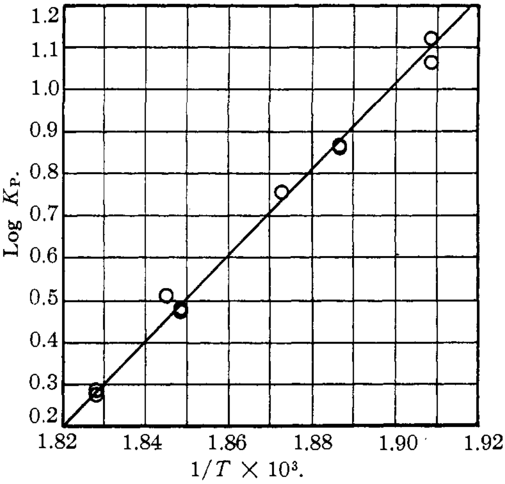

Fig. 2.—Effect of temperature on the equilibrium.

Summary

Equilibrium has been determined in the reaction $C_6H_6(g) + 3H_2 \rightleftharpoons C_6H_{12}(g)$ between 250 and 275°. The results suggest that the last term of Parks and Huffman's equation for the free energy of this reaction be slightly altered, giving $\Delta F^\circ = -43{,}800 + 18.2\ T \ln T - 0.008\ T^2 - 31.0\ T$.

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