Summary

It has been proved that if the equilibrium pressure of each gas in a mixture equals its mole fraction-total pressure product for various values of the variables, then the laws of Boyle and of Avogadro apply to all the gases.

The system, $BaCl_2$-$BaCl_2.8NH_3$ has been used as the equivalent of a semi-permeable membrane for ammonia in the experimental determination of the equilibrium pressures of ammonia in mixtures of ammonia and nitrogen at 45° and over a pressure range from 10 to 60 atm.

The Dalton partial pressures were found to differ from the observed equilibrium pressures by 2 to 21%.

Several hypotheses were used for numerical calculation of the equilibrium pressures, and one of these was found to give values which do not differ greatly from the observed values over the whole pressure range to 60 atm. The deviations are possibly within the experimental error.

A similar calculation for the case of carbon dioxide and nitrogen, studied by Pollitzer and Strebel, was reasonably successful in spite of the fact that an equation of state was used at densities at which it is inexact.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VERMONT]

THE EQUILIBRIUM BETWEEN BENZENE, HYDROGEN AND CYCLOHEXANE

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Introduction

That cyclohexane may be synthesized from benzene and hydrogen in the presence of metallic catalysts, and that the reaction is a reversible one, have been known for some years through the work of Sabatier and Senderens,[1] and others. The first quantitative study to be published, from the standpoint of the reversibility of the reaction, is that of Taylor and Dougherty.[2] They measured the velocity of reaction between benzene and hydrogen at several temperatures, by measuring the changes of pressures undergone at constant volume. They also measured the extent of interaction, that is, the equilibria attained by means of the flow method. In their experiments the catalyst was nickel.

In the present work nickel was at first used as a catalyst. It led to erratic results through the usual but seemingly not invariable formation of side products. At the suggestion of Professor Taylor, platinum was substituted for nickel. With platinum, at the temperatures employed,

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[1] Sabatier and Senderens, *Compt. rend.*, **132**, 210 (1901).

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

the reaction proceeded regularly and smoothly. The results recorded are those gained with this metal.

Experimental Method

Hydrogen was bubbled slowly and at constant rate, as indicated by a flowmeter, through benzene held at a constant temperature. The resulting mixture passed immediately to a glass tube, containing platinized asbestos and supported in an electric furnace. To favor attainment of equilibrium at a definite temperature, this tube was twice bent back upon itself, permitting a length of 150 cm. to lie within the part of the furnace that maintained a uniform and constant temperature. Approximately 100 cm. of this length was filled with catalyst.

The reaction products passed from the furnace through a capillary tube into a receiver which was immersed in ether and carbon dioxide snow, leading to condensation of the residual benzene and of the cyclohexane formed. The residual hydrogen was collected and measured in a second receiver. The rate of passage of the substances through the reaction space was such that about 500 cc. of hydrogen collected in from one to two hours.

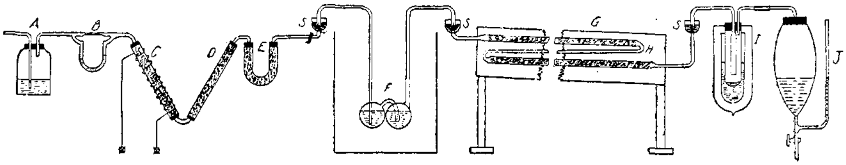

Fig. 1.

In Fig. 1, A, **B**, C, D and E represent, respectively, a wash bottle of alkaline permanganate solution, a flowmeter, hot copper gauze, calcium chloride and phosphorus pentoxide tubes, through which the hydrogen gas was passed before it bubbled into the benzene of constant temperature at F. The catalyst-filled reaction tube is shown at H, lying in the electrically-heated and controlled air-bath G. Connections to and from bubbler and furnace were by mercury cups S,S,S. The test-tube constituting the receiver for benzene and cyclohexane is shown at I, immersed in a Dewar flask containing carbon dioxide snow and ether. The residual hydrogen collected over water in the vessel J, the water dripping out at such a rate as to maintain the gas at atmospheric pressure.

The mixture of benzene and cyclohexane was weighed and then analyzed. The analysis was accomplished through determination of the refractive index of the mixture, determinations of the indices of synthetic mixtures of pure benzene and pure cyclohexane having been made and plotted. The points gained lie precisely on a smooth curve that is gently convex as observed from the percentage side (Fig. 2). The precision of the analysis is favored by the wide difference between the refractive indices of the pure components.

Materials

Benzene.—Eastman thiophene-free benzene was used. Its index of refraction, $n_D^{25} = 1.50144$, indicated a high degree of purity, and further purification was not undertaken.

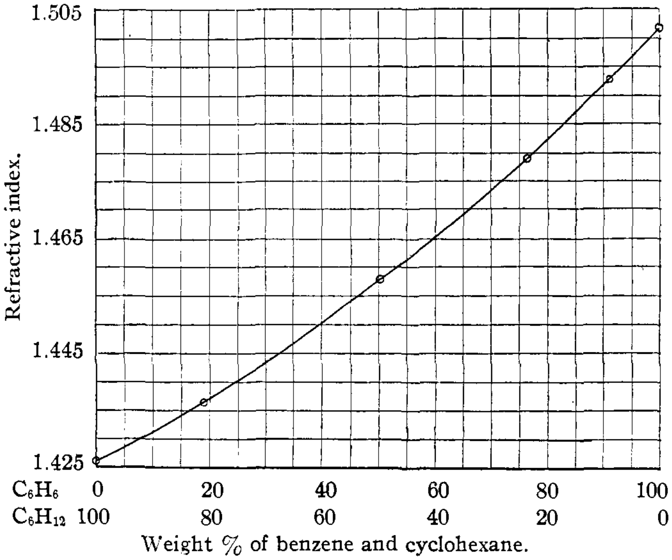

Fig. 2.

Cyclohexane.—The cyclohexane used in establishing the refractive index-composition curve was prepared from benzene and hydrogen, using nickel as catalyst. After thorough treatment with fuming sulfuric acid, washing and drying, it distilled between 80.2 and 80.4° (uncorr.); $n_D^{20} = 1.42640$. Auwers, Hinterseber and Treppmann[3] give for cyclohexane the value $n_D^{11.2} = 1.43199$. The molecular refractivities calculated from these values by the formula of Lorentz and Lorenz are 27.77 and 27.68, respectively, showing close agreement.

Hydrogen.—Hydrogen from a commercial cylinder, found essentially free of oxygen, was washed with alkaline permanganate, passed through copper gauze heated to redness, and dried by phosphorus pentoxide, before being bubbled through the benzene.

The Experimental Data and Calculations

The data used in plotting the composition-refractive index curve are exhibited in Table I.

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[3] Auwers, Hinterseber and Treppmann, *Ann.*, **410**, 257 (1915).

TABLE I

COMPOSITION AND REFRACTIVE INDICES OF BENZENE-CYCLOHEXANE MIXTURES

Benzene, %	Cyclohexane, %	n_D^{25}
0	100	1.42624
18.96	81.04	1.43710
50.24	49.76	1.45806
75.92	24.08	1.47880
91.46	8.54	1.49334
100.00	0	1.50144

The data of the equilibria measurements are given in Table II.

TABLE II

EQUILIBRIUM DATA

Expt. No.	Benzene bath temp., °C.	Reaction temp., °C.	Residual H_2, cc. (corr.)	Condensed mixture, g.	n_D^{25}	Compn. of condensed mixture C_6H_6, %	Compn. of condensed mixture C_6H_{12}, %	$K = \frac{p_{C_6H_{12}}}{p_{C_6H_6}\, p^3_{H_2}}$ Pressure, atm.
1	43.4	266–267	577	0.8628	1.44816	34.3	65.7	5.10
2	43.5	266–267	577	.6525	1.44424	27.9	72.1	5.49
3	43.2	266–267	582	.5364	1.44213	25.6	74.4	5.40
4	48.2	266–267	570	1.8620	1.46274	54.65	55.35	5.51
							Av.	5.38
						Av., omitting 1st		5.47
6	46.2	280	564	0.5304	1.46492	56.35	43.65	1.52
7	41.0	280	555	.7389	1.46780	61.3	38.7	1.60
8	47.8	280	558	.7877	1.46858	61.95	38.05	1.63
							Av.	1.58
						Av., omitting 1st		1.62

After the furnace was brought to the selected temperature and the reaction started, approximately two hours was necessary fully to attain equilibrium conditions in the reaction tube. Expts. 1 and 6 of Table II were made during the second hour of this period. On this account, the results from them are not included in the final averages.

Accepting the constants 5.47 and 1.62 at the temperatures 266.5 and 280°, respectively, the heat of reaction, assumed constant over this narrow temperature range, and as calculated by the equation $2.303 \log (p_2/p_1) = (\Delta H/R)[(1/T_1) - (1/T_2)]$, is C_6H_6 (vapor) + $3H_2$ = C_6H_{12} (vapor); $\Delta H = -53{,}260$ cal.

The upper temperature is believed to have been slightly higher than 280°, more probably 280.5°. Using this value, ΔH becomes 51,400 cal.

Using the value of Richards and Davis[4] for the heat of combustion of benzene, and that given by Swietoslawski[5] for cyclohexane, we obtain from thermochemical data, at 20°, C_6H_6 (liquid) + $3H_2$ = C_6H_{12} (liquid); $\Delta H = -51{,}600$ cal. As the effect of the changed conditions cannot be

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[4] Richards and Davis, THIS JOURNAL, **42**, 1614 (1920).

[5] Swietoslawski, *ibid.*, **42**, 1094 (1920).

great, the results from equilibrium and from thermochemical data seem in good agreement.

The constants also agree well with those calculated from Nernst's approximation formula,[6] especially if the thermochemical data just quoted are employed. Thus Nernst's formula, $\log K_p = -(51{,}600/4.57T) + 3\ (1.75 \log T) + 3\ (1.6)$, yields for the temperature 266.5°, $\log K_p = -1.82$, our experimental value being $\log K_p = -1.73$. (The constant here is the reciprocal of that of Table II.)

An equilibrium constant based on the stoichiometric equation, involving the cube of the hydrogen pressure, is inconsistent with the data of Dougherty and Taylor, with nickel as catalyst, which yield a constant on inserting the first power of this pressure. They point out that this seems in agreement with experiments which show the concentration of hydrogen on the surface of a nickel catalyst to be practically independent of the hydrogen pressure, over a rather wide range of pressures. It appears possible, however, that their result may be due to the disturbing effect of side-product formation when nickel is used. Our experience that side products with nickel as catalyst are usual, but not invariable, suggests that further study of the reaction in the presence of this metal would prove of interest.

Summary

The equilibrium pressures in the reaction between benzene and hydrogen leading to cyclohexane have been measured at two temperatures.

The heat of reaction calculated from the constants found is in accord with that from thermochemical data.

The constants are of the magnitude predicted by the Nernst approximation formula.

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[6] Ref. 2, p. 536. See also Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1925**, vol. 2, p. 1164.