[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHILLIPS PETROLEUM COMPANY]

Solubility of Boron Fluoride in Normal Pentane

BY GEORGE N. CADE, ROBERT E. DUNN AND HAROLD J. HEPP

The use of boron fluoride as a catalyst and as a catalyst promoter for isomerizing and for alkylating paraffins has been described by several investigators.[1,2] Data on the solubility of boron fluoride in paraffins are desirable for further study of these reactions. Since a literature search indicated that no such data were available, the solubility of boron fluoride in normal pentane was determined at 49, 66 and 93° and absolute pressures ranging from 3.8 to 14.8 atmospheres.

Experimental

Materials.—The pure grade *n*-pentane (minimum purity, 99%; chief contaminant, isopentane) supplied by the Phillips Petroleum Company was dried by distillation and used without further purification.

The boron fluoride supplied by The Harshaw Chemical Company was used without additional purification.

Apparatus.—The equilibrium vessel was a 7500-ml., copper-plated steel reactor equipped with a motor-driven stirrer, a calibrated Bourdon-tube pressure gage, a thermocouple well, sample outlets for the liquid and vapor phases, and a valved pipe for charging and evacuation. The vapor sample outlet was electrically heated to prevent condensation during sampling. The equilibrium temperatures were obtained by immersion of the equilibrium vessel in a water- or an oil-bath provided with an immersion heater and a stirrer. Temperature was measured with a chromel–alumel thermocouple and a potentiometer and was controlled within ±0.5° by a Cenco–de Khotinsky thermoregulator.

Vapor and liquid samples were collected in 5- and 25-ml, stainless steel containers equipped with brass Hoke needle valves.

Procedure.—About 3 liters of *n*-pentane was charged to the evacuated equilibrium vessel and heated to the desired temperature. Sufficient boron fluoride to obtain the desired pressure was then forced into the equilibrium vessel. The mixture was stirred intermittently during a period of eight to twelve hours. Constancy of pressure during the last four hours of this period was found to be a suitable indication of equilibrium, as evidenced by constant liquid-phase composition. Stirring was discontinued for about thirty minutes, and vapor and liquid samples were withdrawn into the tared containers and analyzed.

The boron fluoride content of the samples was determined by completely vaporizing, diluting the vapor with dry nitrogen, passing the diluted vapor through a tared Ascarite tube, and measuring the increase in weight of the tube. Any condensed pentane in the tube was removed by continuing the flow of nitrogen until constant weight was obtained.

A rough check on the boron fluoride content of the vapor was obtained by cooling a weighed sample in an octane–Dry Ice-bath, pumping out the boron fluoride with an aspirator, and measuring the decrease in weight after constant weight was attained. The results obtained agreed within 2% with those obtained by absorption in Ascarite.

The hydrocarbon remaining in the equilibrium vessel after the solubility determinations had been completed was freed of boron fluoride by treatment with sodium hydroxide and was found, by low-temperature fractionation, to comprise 99.7% normal pentane and 0.3% isopentane.

Experimental Data

Phase compositions for the *n*-pentane–boron fluoride system are given in Table I. The average error is believed to be about ±5%.

TABLE I

PHASE COMPOSITIONS FOR THE *n*-PENTANE–BORON FLUORIDE SYSTEM

Temp., °C.	Total press., atm.	Vapor, mole%		Liquid, mole%	
		C_5H_{12}	BF_3	C_5H_{12}	BF_3
49	4.0	38.1	61.9	99.45	0.55
	6.7	24.1	75.9	98.73	1.27
	9.2	19.5	80.5	98.12	1.88
	11.9	16.1	83.9	97.11	2.89
	14.7	15.5	84.5	96.36	3.64
66	3.8	62.1	37.9	99.76	0.24
	6.5	32.9	67.1	99.14	0.86
	9.2	23.8	76.2	98.47	1.53
	11.9	22.2	77.8	97.84	2.16
	14.8	17.3	82.7	96.88	3.12
93	6.5	77.3	22.7	99.73	0.27
	8.9	57.1	42.9	99.14	0.86
	9.1	50.4	49.6	98.94	1.06
	12.2	..	..	98.09	1.91
	12.4	44.4	55.6	98.00	2.00

Solubility isotherms are plotted in Fig. 1. Positive deviation from Henry's law is evident from the upward concavity. The solubilities in cc. of boron fluoride (STP) per g. of *n*-pentane were calculated, by means of the ideal gas law, from the liquid-phase compositions given in Table I. The pressures corresponding to zero solubility are the vapor pressures of pure *n*-pentane.

The relation of solubility to temperature at constant partial pressure of boron fluoride is shown in Fig. 2. To construct the curves in Fig. 2, the partial pressures of boron fluoride corresponding to the phase compositions in Table I were calculated by multiplying the total pressures by the corresponding mole fractions of boron fluoride in the vapor phase. The calculated partial pressures were then plotted against solubility. The boron fluoride partial pressure–solubility curves so obtained are not shown; they are similar to the isotherms in Fig. 1 except that they are shifted so that all three pass through the origin. From the boron fluoride partial pressure–solubility curves, the solubilities corresponding to constant partial pressures of boron fluoride were obtained and plotted against temperature to obtain the curves in Fig. 2. Since experimental data were obtained at only three temperatures, the curves in Fig. 2 are approximations. Minimum solubilities at about 70° are,

---

[1] J. D. Heldman, THIS JOURNAL, **66**, 1786–1788 (1944).

[2] Grosse and Ipatieff, *J. Org. Chem.*, **8**, 438–447 (1943).

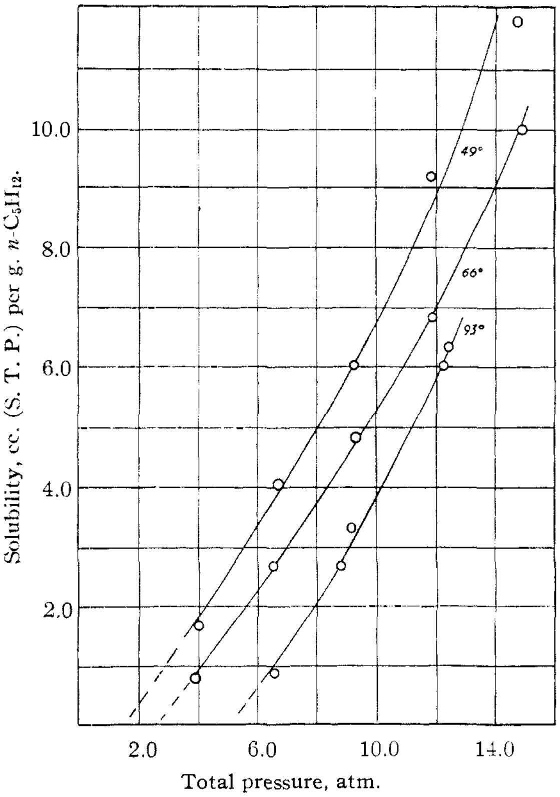

Fig. 1.—Solubility of boron fluoride in n-pentane at constant temperature.

however, clearly shown. Similar minima were reported by Wiebe, Gaddy and Heins[3] for the solubility in nitrogen in water.

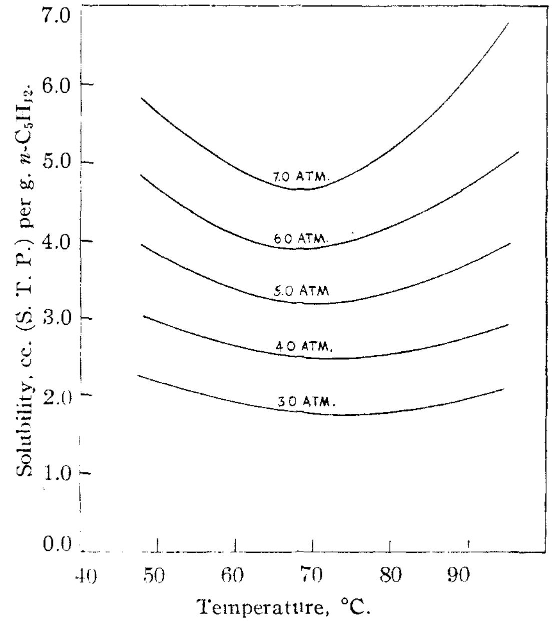

Fig. 2.—Solubility of boron fluoride in n-pentane at constant partial pressure of boron fluoride.

Summary

The solubility of boron fluoride in n-pentane was determined, with an average error of about ±5%, at 49, 66 and 93° and total absolute pressures ranging from 3.8 to 14.8 atmospheres and was found to be of the order of 1 to 12 cc. (STP) of boron fluoride per gram of normal pentane.

At constant partial pressure of boron fluoride, the solubility is a minimum at about 70°.

BARTLESVILLE, OKLAHOMA RECEIVED AUGUST 1, 1946

---

[3] Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947–953 (1933).

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP SUSTAINED BY THE CORNING GLASS WORKS AT MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

The Application of Bond Refractions to Organo-silicon Chemistry

BY E. L. WARRICK

A recent publication by R. O. Sauer[1] proposes a mixed system of group and bond refractions for application in the field of organo-silicon chemistry. It is the purpose of this work to present a simplified and more easily applied uniform system of bond refractions of wider utility.

These bond refractions are complementary to the work of Dr. Sauer, which represented a considerable step forward from the use of atomic refractions in organosilicon chemistry. A still greater simplification and wider utility is possible if we follow the work of Denbigh,[2] who established a rather complete uniform system of organic bond refractions. Denbigh's work was not used in the course of deriving the more cumbersome mixed system of group and bond refractions. Many of the required organic group refractions are not initially provided and have to be specially derived in Dr. Sauer's system.

The system of organo-silicon bond refractions herein developed when used with the organic bond system established by Denbigh[2] will expand the utility of refraction data to cover most of the probable organo-silicon compounds.

In organic chemistry the differences between the two systems of atomic or bond refraction constants are small. This may be the result of a nearly uniform character of bonding which is largely of a purely covalent type. In organo-silicon chemistry the differences between the two systems of

---

[1] Sauer, THIS JOURNAL, **68**, 954 (1946).

[2] Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).