

Fig. 1.—X-Ray diffraction patterns obtained from hydrocarbon synthesis catalyst.

tion from an iron target X-ray tube monochromatized with a pentaerythritol crystal.

The d/n values and relative line intensities obtained for this compound are given in Table I. The d/n values were obtained with a 214.86-mm. powder camera using an iron target X-ray tube with manganese oxide filters. An internal standard of NaCl was used. The relative line intensities were obtained from Fig. 1(b).

TABLE I

X-RAY DIFFRACTION DATA FOR THE NEW IRON CARBIDE

d/n , kX. units	Relative intensity	d/n , kX. units	Relative intensity
1.112	10	1.346	15
1.128	10	1.716	15
1.144	25	1.801	30
1.149	25	2.012	100
1.167	30	2.115	45
1.201	35	2.250	35

The new carbide is ferromagnetic and, within the limits of our experimental error, its Curie temperature is the same as that of Fe_2C (Hägg) which is $250 \pm 3^\circ$.

After heating the sample of the new carbide for ten minutes at 600° , an X-ray diffraction pattern showed that the new carbide had been converted partially to cementite, Fe_3C ; after thirty minutes an X-ray diffraction pattern showed that all the carbide had been converted into Fe_3C .

The chemical analysis is complicated by the presence of condensed hydrocarbon products and free carbon. After magnetic separation in a solution of xylene to reduce the amounts of these materials, chemical analysis gave 77.4% iron and 17.4% carbon. This gives an iron to carbon atom ratio of 0.96 so that the new phase could be equivalent to "FeC."

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EFFECT OF $p\text{H}$ IN THE MUTAROTATION AND HYDROLYSIS OF GLYCOSYLAMINES

Sir:

A study of the behavior of the glycosylamines in the presence of acids and bases has revealed a striking dependence of the reactions of these compounds on the $p\text{H}$ of the solution. Attention was first called to this important property when it was discovered that if a glycosylamine is mixed quickly with one or more equivalents of strong acid, hydrolysis requires a period of many hours, but if the acid is added dropwise to an aqueous solution of the amine, hydrolysis is complete in a few minutes. It has been found that glycosylamines in general undergo a mutarotation reaction involving establishment of an equilibrium of the various modifications. The mutarotation is followed by a hydrolysis reaction that is remarkable in that it takes place rapidly only in a limited $p\text{H}$ range. Both reactions may be studied by means of the accompanying changes in optical rotation. An investigation is now in progress on the properties of a number of glycosylamines; results are reported here for L-arabinosylamine and the properties of this compound may be considered typical of the group.

Samples of L-arabinosylamine were dissolved in buffer solutions at various $p\text{H}$ values, and the ensuing reactions were followed by observing the change in optical rotation. Two reactions occurred, the relative rates of which depended upon the $p\text{H}$ of the solution. The first of these, which in the case of L-arabinosylamine was accompanied by a decrease in optical rotation, is ascribed to a mutarotation reaction; the second, accompanied by an increase in optical rotation, is ascribed to hydrolysis of the amine to the corresponding sugar. In solutions less alkaline than about $p\text{H}$ 8, the mutarotation was too fast to be measured, and in more alkaline solutions, the hydrolysis was negligibly slow.

By application of the customary equation for a pseudo-unimolecular reaction, satisfactory rate

constants were obtained for the mutarotation in the pH range 8.6 to 12, and for the hydrolysis in the pH range 0 to 9.5. For L-arabinosylamine, the mutarotation constant equals $(2.1 \times 10^8 [\text{H}^+]) / (1 + 1.6 \times 10^9 [\text{H}^+])$, and the rate constant for the hydrolysis reaction equals $1 / (7.9 + 6.1 \times 10^4 [\text{H}^+] + 4.2 \times 10^8 [\text{OH}^-])$. The curves of the figure correspond to these equations, and the points represent experimental values. The mutarotation of glycosylamines, in marked contrast to the mutarotation of sugars, is strongly catalyzed by oxonium ion, but not appreciably by hydroxyl ion. The hydrolysis, like certain enzymic reactions, takes place rapidly only in a limited pH range.

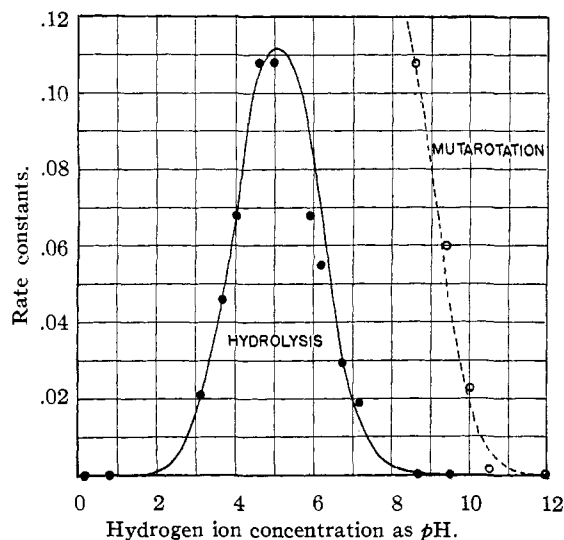


Fig. 1.

It has been found that the velocities of other reactions of the glycosylamines, now being studied, exhibit a similar dependence upon the pH of the reaction medium. In a forthcoming publication mechanisms will be presented to account for this striking property. The mechanisms seem pertinent to reactions of the N-glycosides and to reactions involving imine and aldehyde ammonia compounds in general.

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COHERENT ION-EXCHANGE GELS AND MEMBRANES

Sirs:

At the recent Gordon Research Conference on ion exchange a brief account was given by us of some electrochemical and exchange properties and uses of coherent cation- and anion-exchange membranes and gels which have been prepared in this laboratory. These materials may be classified as permselective electronegative and electro-

positive membranes. Other materials have been made and so defined by C. E. Marshall and collaborators [THIS JOURNAL, 63, 1911 (1941)] and by Karl Sollner and collaborators [J. Gen. Physiol., 24, 467 (1941)]. Recently J. R. Wyllie described cation membranes made by embedding granular Amberlite IR-100 (Rohm and Haas) in a plastic binder [see Chem. Eng. News, 27, 1797, June 20 (1949)]. In contrast with these membranes and with the collodion and clay membranes, the new materials have unusually high specific electric conductivities and exchange capacities.

A typical resinous sulfonic cation-exchange membrane, now available in the hydrogen or sodium form under the name Ionics¹ permionic membrane, cast in the form of disks, 9 cm. in diameter and 2-3 mm. thick, was tested as shown in Fig. 1, measuring at 25° its characteristic concentration potentials in the system

Calo-	Satd. KCl		Satd. KCl	Calo-
mel	soln.	0.1 M Mem-	0.01 M soln.	mel
elec-	diffusion	HCl	HCl	elec-
trode	protected	soln.	protected	trode

The order of magnitude of its specific conductivities was measured in the same apparatus by comparing the internal resistance in 6 N hydrochloric acid in the presence and absence of the membrane. Similar anion-exchange membranes have also been prepared and are under investigation.

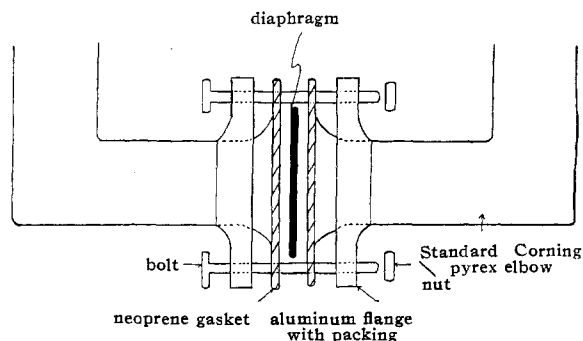


Fig. 1.—Exploded section of diaphragm cell. Ion-exchange diaphragm, 3 mm. thick, 75 mm. diameter.

This resinous sulfonic cation exchanger was found to have a characteristic concentration potential of 54-55 millivolts, a specific conductivity of the order of 0.02-0.03 ohms⁻¹ × cm.⁻¹, an exchange capacity of 0.4-0.6 milliequivalent per gram of wet hydrogen form material, and a moisture content of the order of 65% of the wet hydrogen form.

Numerous theoretical and practical applications of these materials in ion exchange as well as in the study and use of electrolytic systems are under active investigation.

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