

The mesomorphic thermal stabilities of the compounds of the present series (series A) are comparatively less than those of the corresponding compounds of the benzylidene series, *p-n*-alkoxybenzylidene-4-aminobiphenyls⁶ (series B). This is expected as series (A) contains a 1,4 substituted naphthalene nucleus at one end of the molecule which increases the molecular breadth resulting in the decrease of the thermal stabilities of the mesophases. It is of interest to note that only the last member of the series (A), *i.e.*, the octadecyl derivative exhibits smectic mesophase which is monotropic in nature. In the case of series (B) the smectic phase appears at the pentyl derivative and purely smectic in nature. The reason for this late from the dodecyl derivative onwards the series is commencement of smectic mesophase in series (A) can be attributed to the increased breadth of the molecules of series (A) due to the introduction of the naphthalene moiety which not only reduces the thermal stabilities of the mesophases but also delays the commencement of the smectic mesophase.

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ION-EXCHANGE KINETICS STUDY USING HYDROUS CERIC OXIDE AS AN ION-EXCHANGER

STUDY of the kinetics of ion-exchange is of importance in the use of ion-exchange resins for chemical separations. There is, however, a paucity of such data on inorganic ion-exchangers¹. The present paper describes an investigation of the kinetics of exchange reactions in hydrous CeO₂ using amines of Co³⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ as exchanging ions. The study includes (1) dependence of the exchange rate on the concentra-

tion of the exchanging ion and (2) effect of the size of the exchanger particle and exchanging ion on the rate of exchange.

Materials and Method

All the reagents used were of A.R. quality. Hydrous CeO₂ was prepared by adding excess of aqueous ammonia to a saturated solution of ceric ammonium sulphate². The resulting precipitate was washed free of sulphate and dried at 100–110° C. Ammine complexes of Co³⁺, Cu²⁺ and Ni²⁺ were prepared by the usual methods³ and those of Zn²⁺ and Cd²⁺ by dissolving appropriate quantities of the metal salts in water followed by the addition of excess of aqueous ammonia.

Procedure for the Rate-Study.—Samples of 20 ml of the metal amines were added to a series of stoppered conical flasks, each containing 100 mg of the exchanger. The resulting mixtures were shaken mechanically up to equilibrium. The solutions were immediately centrifuged and the supernatants (5 ml) were analysed for Co³⁺ and Cu²⁺ iodometrically^{4,5} and Ni²⁺, Cd²⁺ and Zn²⁺, complexometrically⁶ and the amount of metal ions sorbed, hence their F-values were found out from the relation⁷

$$F = \frac{\text{Amount of the metal ion sorbed at time } t}{\text{Total amount of the metal ion sorbed at equilibrium}}$$

The samples of CeO₂ with an average particle radius 9.0×10^{-3} cm and 0.85×10^{-3} cm were obtained with the help of standard sieves. The particle sizes were further checked by microscopic measurements.

Results and Discussion

The results presented in Tables I and II indicate that

- (i) The ion-exchange kinetics exhibit two distinctly separate stages, relatively quick process in the first stage followed by a slower one towards the end.
- (ii) Smaller the size of the exchanger particle as well as exchanging ion faster is the rate of exchange.
- (iii) Amongst the ammine complexes under study, the exchange rate follows the order :
Co > Cu > Zn > Ni > Cd.

It is well known⁸ that sorption of metal ions on hydrous oxides takes place by the mechanism of ion-exchange. It is also known⁹ that the overall exchange process is mainly governed by two types of diffusion processes. The first process, *i.e.*, film diffusion depends on (a) stirring characteristics, (b) the external concentration of the exchanging ions and (c) the size of the exchanger particle. The second process, *i.e.*, particle diffusion depends only on the size of the exchanger particle¹⁰. In very dilute solutions the rate of diffusion of electrolyte across the film barrier about the

TABLE I
Dependence of *F*-values on the concentration of different amines
Particle radius = 9.0×10^{-3} cm. Amount of the exchanger = 100 mg.
Total volume = 20 ml, pH = 10.5

Time	Fractional attainment of equilibrium (F)									
	Co (NH ₃) ₆ ³⁺		Cu (NH ₃) ₄ ²⁺		Zn (NH ₃) ₄ ²⁺		Ni (NH ₃) ₆ ²⁺		Cd (NH ₃) ₄ ²⁺	
	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M
30 secs	0.09	0.20	0.015	0.11	..	0.10	..	0.05	..	0.02
1 min	0.13	0.36	0.03	0.14	0.02	0.13	0.01	0.12	0.025	0.10
2 min	0.20	0.42	0.09	0.40	0.08	0.39	0.05	0.30	0.075	0.25
5 min	0.34	0.60	0.25	0.55	0.28	0.54	0.26	0.52	0.21	0.50
10 min	0.60	0.70	0.36	0.66	0.45	0.65	0.42	0.64	0.40	0.62
20 min	0.70	0.80	0.62	0.80	0.70	0.78	0.65	0.76	0.625	0.75
30 min	0.82	0.86	0.74	0.85	0.81	0.84	0.78	0.82	0.765	0.81
45 min	0.89	0.89	0.82	0.88	0.89	0.89	0.88	0.87	0.86	0.86
60 min	0.93	0.93	0.89	0.92	0.925	0.925	0.91	0.91	0.90	0.90
75 min	0.95	0.95	0.93	0.94	0.95	0.95	0.94	0.94	0.93	0.93
90 min	0.97	0.97	0.96	0.96	0.97	0.97	0.96	0.96	0.96	0.96
100 min	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
110 min	1.00	1.00	1.00	1.00	0.99	0.99	0.99	0.99	0.99	0.99
120 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE II
Dependence of *F*-values on the concentration of different amines
Particle radius = 0.85×10^{-3} cm. Amount of the exchanger = 100 mg. Total volume = 20 ml, pH = 10.5

Time	Fractional attainment of equilibrium (F)									
	Co (NH ₃) ₆ ³⁺		Cu (NH ₃) ₄ ²⁺		Zn (NH ₃) ₄ ²⁺		Ni (NH ₃) ₆ ²⁺		Cd (NH ₃) ₄ ²⁺	
	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M	0.05 M	0.10 M
30 secs	0.31	0.32	0.18	0.24	0.10	0.18	0.015	0.14	0.01	0.05
1 min	0.41	0.40	0.20	0.38	0.12	0.36	0.025	0.28	0.04	0.10
2 min	0.45	0.46	0.28	0.49	0.15	0.47	0.08	0.39	0.10	0.35
5 min	0.66	0.65	0.42	0.57	0.27	0.55	0.24	0.53	0.26	0.50
10 min	0.80	0.82	0.58	0.74	0.47	0.72	0.48	0.70	0.52	0.68
20 min	0.92	0.94	0.79	0.90	0.72	0.88	0.71	0.85	0.76	0.83
30 min	0.99	0.99	0.90	0.93	0.86	0.94	0.84	0.92	0.87	0.90
45 min	1.00	1.00	0.96	0.99	0.96	0.98	0.96	0.965	0.95	0.95
60 min	1.00	1.00	0.99	1.00	1.00	1.00	0.99	1.00	0.98	0.98
75 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.99	0.99
90 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
100 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
110 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
120 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

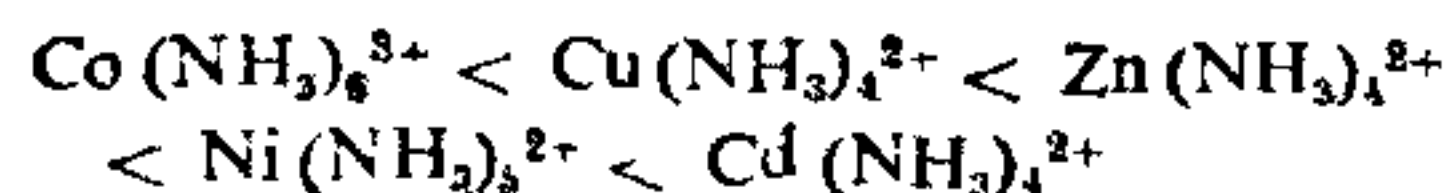
exchanger is rate-controlling. As the concentration is increased, the kinetics is determined by both the diffusion across the film and the diffusion in the solid. At still higher concentrations, particle diffusion becomes the sole rate determining step⁹ and the rate of diffusion becomes concentration independent¹¹, i.e., *F* becomes independent of concentration. Our results (Tables I and II) show both film and particle diffusion are responsible for the overall exchange process. Since, *F*-values initially increase with the increase of exchanging ion concentration

from 0.05 M to 0.10 M, followed by a more or less identical *F*-values.

From Tables I and II it is seen that the exchange rate in smaller (0.85×10^{-3} cm) particle is very much faster than the same in the bigger (9.0×10^{-3} cm) size particles due to the increase in specific surface area.

The faster rate of exchange of Co(III)-amine as compared to the other metal amines under study may be explained on the basis of their known covalent radii¹²⁻¹⁴; Octahedral Co(III), 1.22 Å

and Ni (II), 1.39 Å; Tetrahedral Zn (II), 1.31 Å and Cd (II), 1.48 Å; square planar Cu (II), 1.28 Å. Therefore their sizes follow the order:



From our results (Tables I and II) it seems smaller the size of the exchanging ion, faster will be the rate of exchange through the pores of the exchanger solid, resulting in a faster rate of exchange.

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ADSORPTION OF HYDROGEN ON PRECIPITATED FISCHER-TROPSCH IRON CATALYSTS

ADSORPTION of hydrogen has been studied on two catalysts containing originally (A) Fe_2O_3 , CuO and K_2O in the ratio of approximately 90 : 8 : 0.4 and (B) Fe_2O_3 and K_2O in the proportion of 98 : 0.4 respectively. These catalysts are being tried in the Fischer-Tropsch synthesis of hydrocarbons at the Institute,

The catalysts were prepared by precipitation with Na_2CO_3 from a solution of the nitrates of the metals. The dry precipitate was reduced at 300° C for 6 hr.

The adsorption of hydrogen was measured in a volumetric gas adsorption unit in the temperature range 99°–275° C. The time for equilibration at each pressure was one hour. The degassing of the catalysts was carried out at 400° C, for 5 hr.

The adsorption isotherms in the case of both catalysts exhibit, as shown in Figs. 1 and 2, an

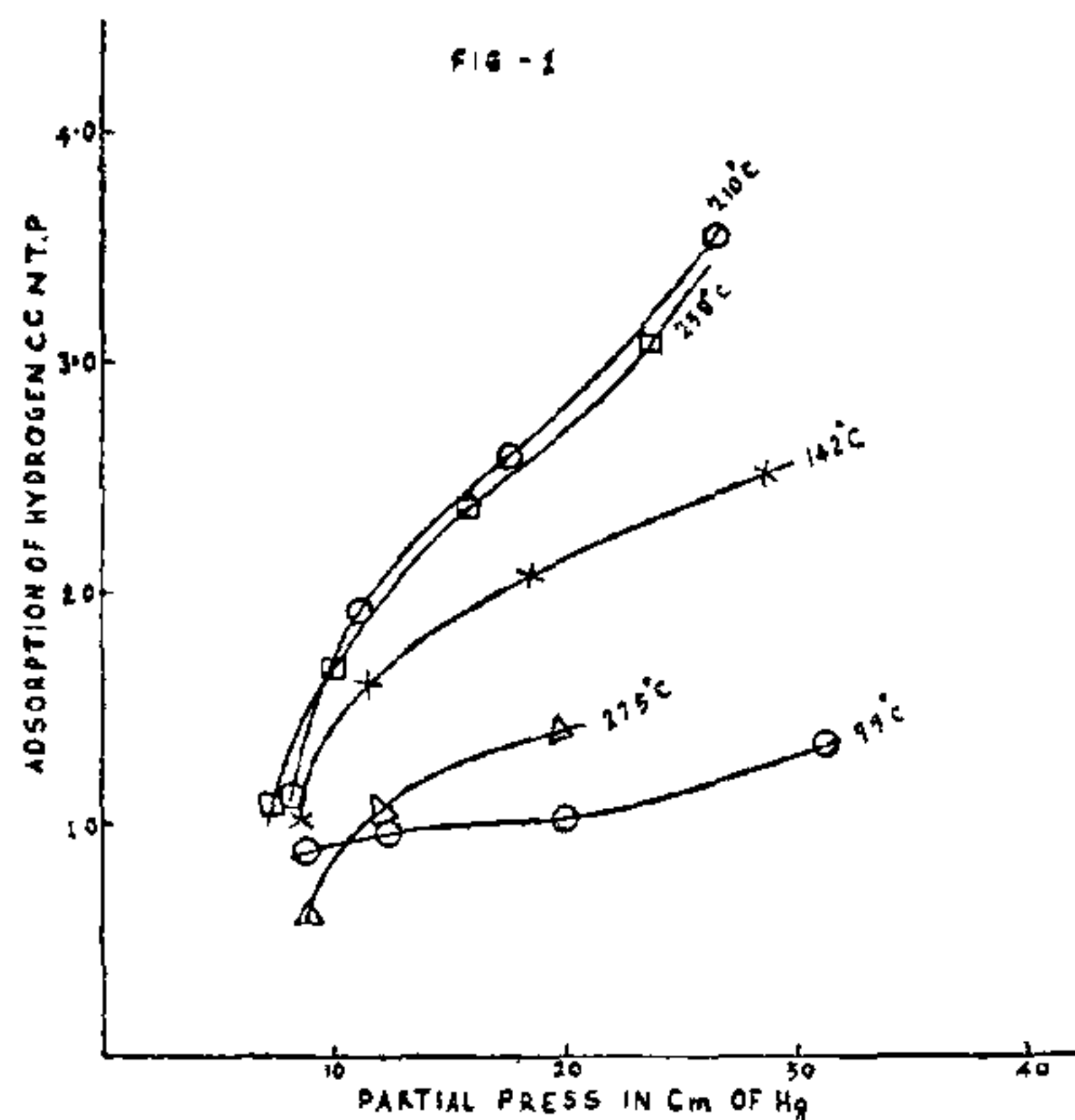


FIG. 1. Adsorption isotherms of hydrogen on catalyst (A) (7.5 g. dry).

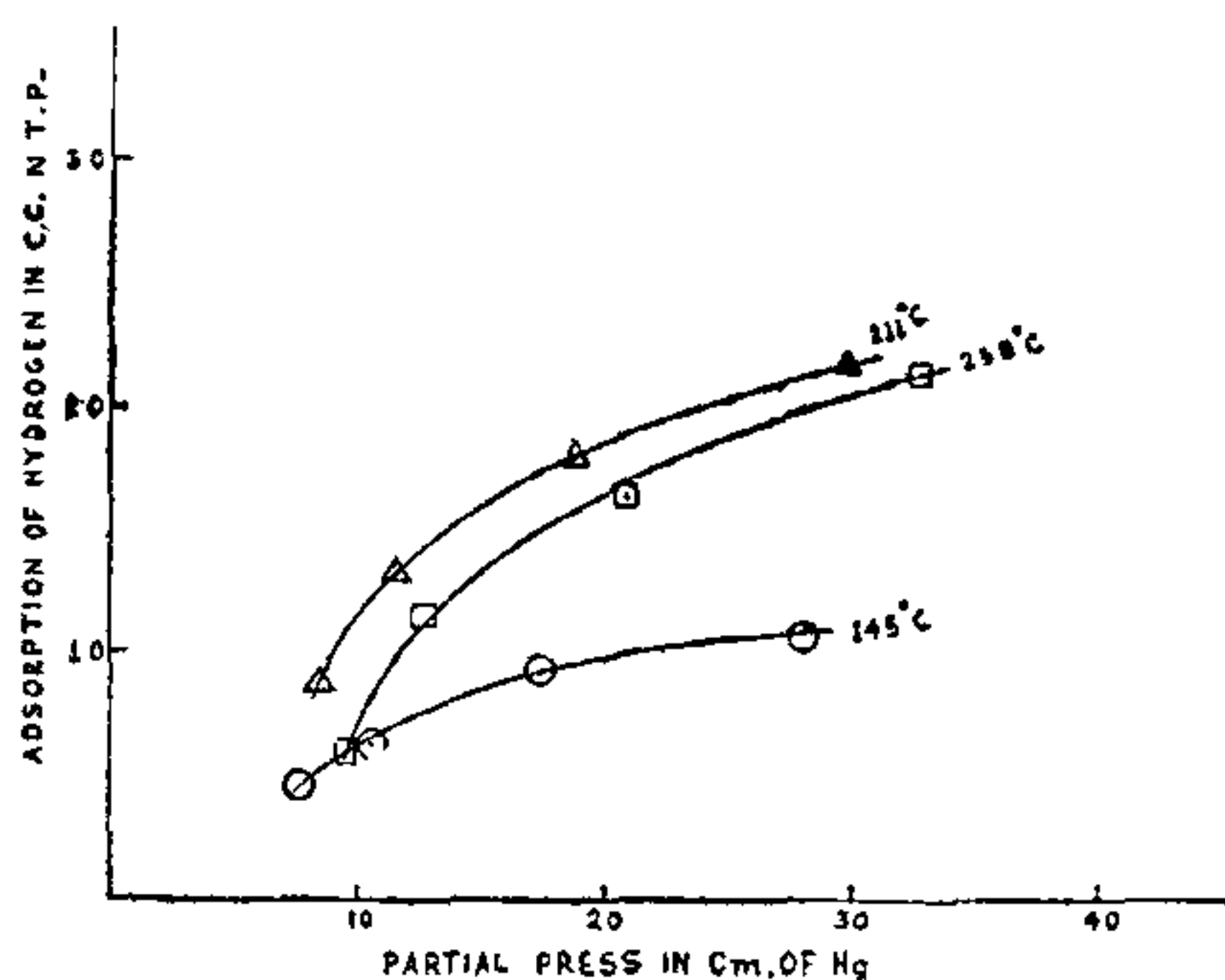


FIG. 2. Adsorption isotherms of hydrogen on catalyst (B) (6.65 g. dry).

increase of adsorption with increase in temperature upto about 210° C, and then a decrease. The surface area of the catalysts, as measured by the adsorption of argon at liquid nitrogen temperature, using the approach of de Boer and coworkers¹, was