

equivalent to at least 1% rotenone or deguelin (both give the test). No further plant material was available. The remainder of the acetone extract, representing 6.3 g. of original material, was evaporated to dryness in a vacuum and the rotenone determined by crystallization from carbon tetrachloride.⁴ The amount of material so obtained corresponded to about 1% of rotenone in the original root. This material recrystallized from absolute alcohol gave large, hexagonal plates melting at 163°, with indices of refraction identical with those of pure rotenone.

There are numerous species of *Spatholobus*, most of them native to India, the Malay Peninsula or the Philippine Islands. Since rotenone has now been found in *S. roxburghii* it would be well for investigators in these countries to study the rotenone content of plants of this genus.

(4) Jones, *Ind. Eng. Chem., Anal. Ed.*, **5**, 23 (1933).

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COMMUNICATIONS TO THE EDITOR

THE ADSORPTION OF NITROGEN BY IRON SYNTHETIC AMMONIA CATALYSTS

Sir:

The experimental work of recent years upon the mechanism of ammonia synthesis over iron catalysts has culminated in the idea that the synthesis occurs through nitrogen molecules reacting with the surface atoms of the iron catalyst to form a layer of nitrogen held to the surface by activated adsorption [see Taylor, *THIS JOURNAL* **53**, 578 (1931)] or a surface iron nitride [see Frankenburger, Ullmann's "Enzyklopadie der technischen Chemie," 1928; Emmett, *J. Chem. Ed.*, **7**, 2571 (1930)] which in turn can be reduced by hydrogen to form ammonia. Various indirect lines of evidence have been advanced in support of this hypothesis. However, as yet no data have been published to show whether the adsorption of nitrogen by the surface of an iron catalyst at synthesis temperatures proceeds at a sufficient rate to permit it to be an essential step in the synthesis of ammonia. The present letter presents briefly the results that have been obtained recently relative to the rate and extent of nitrogen adsorption by various types of iron ammonia catalysts.

At 400° and one atmosphere pressure 10-cc. samples of doubly promoted iron catalyst 931 containing 1.3% Al₂O₃ and 1.59% K₂O, pure iron catalyst 973, and singly promoted catalyst 921 containing 1.31% Al₂O₃ adsorbed

2.4, 0.26 and 6.3 cc. of nitrogen, respectively, in the first minute out of total adsorptions of 4.2, 0.93 and 8.2 cc. attained at the end of one to two hours. These initial rates of adsorption are in approximately the same ratio as the rates of ammonia synthesis measured immediately after each adsorption run. Furthermore, the adsorption of nitrogen is sufficiently fast on each catalyst to permit it to constitute the first step in the synthesis of ammonia, in accordance with the hypothesis already advanced.

Measurements of the temperature coefficient of the rates of adsorption of nitrogen on catalyst 931 between 275 and 450° indicate an energy of activation of about 15,000 and 17,000 calories for the adsorption of 1.7 and 3.6 cc. of nitrogen, respectively. Isotherms at 400 and 450° correspond to a heat of adsorption between 34,000 and 40,000 calories. It appears therefore that the energy of activation of the desorption of nitrogen from the surface of the iron catalysts is between 49,000 and 57,000 calories. This seems to be in substantial agreement with the experiments of Winter [*Z. physik. Chem.*, **B13**, 401 (1931)] in which he found that the temperature coefficient of ammonia decomposition over iron catalysts was about 54,000 calories and was apparently determined by the rate at which nitrogen was desorbed from the iron.

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P. H. EMMETT
STEPHEN BRUNAUER

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ENERGY OF ACTIVATION

Sir:

During the past two years, we¹ have extended our investigation of the kinetics of the ionic reactions (I) sodium bromoacetate + sodium thio-sulfate, and (II) sodium β -bromopropionate + sodium thiosulfate, to determine the energy of activation, $E_{act.}$, and the constant B in the equation $\log k = B - E_{act.}/2.3 RT$ as functions of temperature and concentration. The table illustrates some of the salient features.

TABLE
Reaction I. Na Bromoacetate (0.005 M) + $Na_2S_2O_3$ (0.005 M)

t , °C.	Added salt	$\sqrt{\mu}$	$E_{act.}$, Cal.	B (time unit minutes)
0-12.5	None	0.1414	16,062 \pm 83	11.40
12.5-25	None	.1414	15,962 \pm 68	11.28
25-37.5	None	.1414	15,849 \pm 64	11.20
0-25	0.18 M NaCl	.447	15,960 \pm 53	11.58
-25	.06 M BaCl ₂	.447	16,299 \pm 41	11.94
-25	.03 M LaCl ₃	.447	17,695 \pm 55	13.40

(1) La Mer and Kammer, *THIS JOURNAL*, **53**, 2832 (1931), for data at 25°.