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).

INSECTICIDE DIVISION
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WASHINGTON, D. C.

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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% Al_2O_3 and 1.59% K_2O, pure iron catalyst 973, and singly promoted catalyst 921 containing 1.31% Al_2O_3 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.

BUREAU OF CHEMISTRY AND SOILS
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P. H. EMMETT
STEPHEN BRUNAUER

RECEIVED FEBRUARY 14, 1933 PUBLISHED APRIL 6, 1933

ENERGY OF ACTIVATION

Sir:

During the past two years, we[1] have extended our investigation of the kinetics of the ionic reactions (I) sodium bromoacetate + sodium thiosulfate, and (II) sodium β-bromopropionate + sodium thiosulfate, to determine the energy of activation, $E_{\text{act.}}$, and the constant B in the equation $\log k = B - E_{\text{act.}}/2.3\ RT$ 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	$\sqrt{\mu}$	$E_{\text{act.}}$ Cal.	B (time unit minutes)
0–12.5	None	0.1414	16,062 ± 83	11.40
12.5–25	None	.1414	15,962 ± 68	11.28
25–37.5	None	.1414	15,849 ± 64	11.20
0–25	0.18 M NaCl	.447	15,960 ± 53	11.58
–25	.06 M $BaCl_2$	.447	16,299 ± 41	11.94
–25	.03 M $LaCl_3$	.447	17,695 ± 55	13.40

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

TABLE (*Concluded*)

Reaction II. Na β-Bromopropionate + $Na_2S_2O_3$

t, °C.	Added salt	$\sqrt{\mu}$	$E_{act.}$ Cal.	B (time unit minutes)
$a = b = 0.005\ M$				
0–25	None	0.1414	28,900 ± 690	20.00
$a = b = 0.05\ M$				
0–12.5	None	.447	22,900 ± 150	
12.5–25.0	None	.447	24,400 ± 480	
0–25	None	.447	23,600 ± 220	15.5
$a = b = 0.005\ M$				
0–25	0.03 M $LaCl_3$	.447	24,000 ± 500	16.4
$a = b = 0.015\ M$				
0–25	0.0567 M $LaCl_3$	.633	22,000	14.5

$E_{act.}$ decreases with T for reaction I but increases for reaction II by an amount outside the probable error. That $E_{act.}$ may vary with T is not surprising since the partial molal heat capacities of ions are large negative[2] values, which are dependent upon the total charge, concentration, and specific properties; hence the heat capacity of the reactive complex need not be equal to the sum of the heat capacities of the reacting ions.

A study of the most reliable data on the reactions: (III) diacetone alcohol decomposition; (IV) sodium phenolate + various alkyl iodides in alcohol; (V) acetone dicarboxylic acid decomposition, furnishes evidence that our findings are not restricted to ionic reactions.[3,4,5] For reaction III, $E_{act.}$ (20–30°) = 17,040; $E_{act.}$ (25–35°) = 18,098, an increase which is eight times the experimental error. For reaction IV, using the ethyl iodide $E_{act.}$ (30.1–42.5°) = 21,067; (42.5–58.5°) = 21,604; (58.5–80.1) = 21,263. The increase in $E_{act.}$ at low temperatures followed by a decrease at higher temperatures is repeated uniformly by the eight primary alkyl iodides. The same behavior is indicated by reaction V.

The temperature dependence of $E_{act.}$ requires consideration of the following activation quantities: heat capacity $C_{act.}$; free energy $F_{act.}$; and entropy $S_{act.}$. Brönsted's equation for the influence of the medium follows readily in terms of $F_{act.}$; but the derivation in the light of R. C. Tolman's[6] statistical expression for $E_{act.}$ shows that *in general* f_X is a kinetic and not a pure thermodynamic activity coefficient. The collision number Z and the Arrhenius B are related by the equation $B = \log Z + S_{act.}/2.3\ R$. The simple collision theory consequently is valid only if $S_{act.} = 0$, which in turn requires the improbable assumption that $C_{act.}$ remains equal to zero down to absolute zero.

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[2] La Mer and Cowperthwaite, THIS JOURNAL, **55**, 1004 (1933); Randall and Rossini, *ibid.*, **51**, 323 (1929).

[3] G. M. Murphy, *ibid.*, **53**, 977 (1931).

[4] D. Segaller, *J. Chem. Soc.*, **105**, 106 (1914).

[5] E. O. Wiig, *J. Phys. Chem.*, **34**, 596 (1930).

[6] Tolman, "Statistical Mechanics," 1927, p. 261.

The importance of considering the entropy of activation is well illustrated by the $BaCl_2$ and $LaCl_3$ additions in Reaction I. In spite of an increase of 1800 calories in $E_{act.}$, the velocity nevertheless increases due to an increase in $S_{act.}$ as shown by the marked increase in B.

Reaction III and the rearrangement of acetylchloroaminobenzene are being studied over wider ranges of temperature for a more convincing test of the conclusions drawn.

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VICTOR K. LA MER

RECEIVED FEBRUARY 17, 1933 PUBLISHED APRIL 6, 1933

MODIFICATION OF THE WILLARD-WINTER METHOD FOR FLUORINE DETERMINATION

Sir:

The use of standard thorium nitrate solutions for the titration of fluorine, as developed by Willard and Winter [*Ind. Eng. Chem., Anal. Ed.*, **5**, 7–10 (1933)], affords an accurate method for the determination of soluble fluorides. However, the end-point of the titration, when the amount of the zirconium–alizarin indicator specified by the writers is being used, is so faint as to be difficult to detect. Larger amounts of indicator cannot be employed, especially when one is titrating small quantities of fluorine, since zirconium combines with fluorine.

This difficulty can be avoided by the use of a 0.05% aqueous solution of sodium alizarin sulfonate alone as the indicator. The procedure is essentially the same as that employed by Willard and Winter. Three drops of the indicator solution are added to 40 cc. of solution containing 20 cc. of alcohol. Dilute hydrochloric acid (1:50) is added dropwise until the solution is colored yellow. A further drop of acid is then added. The end-point of the titration is recognized by the appearance of a faint, permanent pink color due to the formation of the thorium lake. The use of an arbitrary reference solution of the lake with a slight pink color makes for more accurate results, because the titrated solution shades from yellow to pink as the end-point is approached. The procedure succeeds best with fractional quantities of a milligram of fluorine, since the troublesome adsorption of the dye and lake on the precipitated thorium fluoride is rendered less noticeable.

The results tabulated below were obtained when solutions of sodium fluoride were titrated with a thorium nitrate solution of such strength that 1.0 cc. was equivalent to 0.2 mg. of the fluorine. The microburet readings were rounded off to the nearest 0.005 cc., and 0.030 cc. was subtracted from each of the readings to account for the thorium required to form the lake. The analyst did not know the fluorine content of the solutions marked with an asterisk.

$Th(NO_3)_4$, cc.	F Calcd., mg.	F Found, mg.	$Th(NO_3)_4$, cc.	F Calcd., mg.	F Found, mg.
0.260	0.050	0.052	0.990	0.200	0.198
.245		.049	1.020		.204
.520	.100	.104	1.000	.201*	.200
.505		.101	1.155	.230*	.231
.760	.150	.152	1.490	.300	.298
.865	.175*	.173	2.000	.400	.400

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W. D. ARMSTRONG

RECEIVED MARCH 8, 1933 PUBLISHED APRIL 6, 1933

A NEW BAND IN THE WATER VAPOR DISCHARGE

Sir:

In a spectrographic study of the electrodeless discharge in water vapor the writers have observed a band of moderate intensity with a head of wave length 3564 Å. This band is degraded toward the red and appears to have the structure of a hydride. It does not belong to any known system of hydroxyl bands and may prove to be due to OH^+. Other fainter bands were also observed which have not been measured accurately or identified. The analysis of these bands is being carried out under the direction of Professor F. W. Loomis of the Department of Physics.

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RECEIVED MARCH 20, 1933 PUBLISHED APRIL 6, 1933

NEW BOOKS

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, de Biologie et de Technologie. (Annual Tables of Constants (A T C) and Numerical Data, Chemical, Physical, Biological and Technological.) Published under the Patronage of the International Research Council and of the International Union of Chemistry. American Agents, McGraw-Hill Book Co., Inc., 330 West 42d St., New York, 1931–1932. Vol. VIII, 2 parts (1927–1928), 2706 pp. Vol. IX (1929), 1607 pp.; Index to Vol. IX, 124 pp. 22 × 28 cm. Price, cloth, Vol. VIII, $20.00; Vol. IX, $16.00.

With the appearance of Volume IX for 1929 and of Volume VIII in two parts covering 1927–1928, Dr. Marie and the International Committee have finally completed the Herculean task of bringing the Annual Tables up to date, after the serious interruption and delay incident to the World War. Volume IX was issued at the end of 1931, and its Index a few months later. This resumption of prompt publication is of great importance to the scientific world, and Dr. Marie and the Committee are to be congratulated