

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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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°.

TABLE (Concluded)
Reaction II. Na β -Bromopropionate + Na₂S₂O₃

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 \pm 690	20.00
$a = b = 0.05 M$ 0-12.5 12.5-25.0 0-25	None	.447	22,900 \pm 150 24,400 \pm 480 23,600 \pm 220	15.5
$a = b = 0.005 M$ 0-25	0.03 M LaCl ₃	.447	24,000 \pm 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 negative² 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's⁶ 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.

(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 $E_{\text{act.}}$, the velocity nevertheless increases due to an increase in $S_{\text{act.}}$ 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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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.