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THE EFFECT OF NEUTRAL SALTS

ON THE ETHYL ACETATE EQUILIBRIUM.

A thesis submitted in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

to the Graduate School of the
University of Cincinnati

1929

by

Robert D. Billinger
Ch. E. Lehigh University 1921
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Grateful acknowledgement is made to Dr. R. C. Cantelo, under whose supervision this investigation was made. The interest and encouragement of Dr. Cantelo contributed in a large measure to the results of this work.

CONTENTS

PART I - LITERATURE REVIEW

INTRODUCTION

The classic researches of Berthelot and St. Gilles on the limits of esterification were among the first investigations of homogeneous equilibria. From these and subsequent studies there arose the Law of Mass Action, which has been more appropriately termed the Law of Molecular Concentration.

Next came a series of investigations of the effect of various catalysts on the rate of esterification. The increased velocity of esterification and hydrolysis in the presence of acids was attributed to the increase in hydrogen ion concentration. It was also found that the velocity was increased by the addition of neutral salts and this so-called "neutral salt effect" was explained by Arrhenius as due to one or more of three causes: (1) the increase in the ionization of the acid, (2) the increased ionization of the water, (3) the shift in equilibrium "inactive $\rightleftharpoons$ active " molecules to the right on the addition of neutral salts.

However, the results of many researches have shown that the original idea of Arrhenius and Ostwald, based on the electrolytic dissociation theory , that H^+ and $\overline{OH}$ ions are the sole catalysts in such reactions as cane sugar inversion and ester hydrolysis, is inadequate. The velocity is not always

proportional to the H^+ or $\overline{OH}$ ion concentration. The new method of approach which is mainly due to Bronsted, is to recognize that the net action that occurs to the substrate is either the acceptance or loss of a proton (H^+) or its transference from one position in the molecule to another. Hence, in the presence of molecules which are ready acceptors of protons and of others that are ready donors the prototropic change is facilitated, and the reaction catalyzed.

Although the literature contains much of importance on the subjects of esterification and hydrolysis, there is still no explanation of catalysis, which is universally accepted. Hence, this research was undertaken in the attempt to add another drop to the already large quantity of water - or ethyl acetate - which has gone under the bridge.

The objects of this investigation were fourfold : -

(1) To review in so far as possible the facts and theories of esterification catalysis,

(2) To determine whether certain neutral salts displace the limit of esterification, and therefore change the equilibrium as expressed by the ordinary mass action expression,

(3) To determine also the extent to which these neutral salts alter the rate of esterification,

(4) To attempt an interpretation of these results in the light of recent theories of catalysis.

EARLY RESEARCHES ON LIMITS OF ESTERIFICATION.

Ethyl acetate belongs to that series of organic salts, the esters, which early interested chemists. The first preparation of ethyl acetate is attributed to Lauroguais in 1759 [1]. The composition and structure of ethyl acetate was much in question during the early period of organic chemistry when the Etherin Theory, the Nucleus Theory and the Type Theory, etc. were all proposed to explain the structure of organic compounds.

The formation of ethyl acetate, i.e. the problem of esterification, was one of the first experimental investigations of homogeneous equilibrium in the liquid phase. Berthelot and Pean de St. Gilles [2] in their classical research on the reaction between acetic acid and ethyl alcohol proved it to be reversible and showed that their data could be represented by the equation -

$$K = \frac{\text{mols ester x mols water}}{\text{mols acid x mols alcohol}},$$

where K represents the equilibrium concentrations of the four constituents.

Berthelot and Pean de St. Gilles mixed alcohol and acetic acid in varying proportions in sealed glass tubes and heated the

tubes until no further change in composition occured, i.e. until equilibrium was established. They then analyzed the mixtures for acetic acid, and calculated the composition of the equilibrium mixture from this measurement. Suppose (a) represents the number of mols of alcohol taken, (b) the number of mols of acetic acid, and (x) the number of mols of ester and water formed. Their results show that at equilibrium the proportions of the constituents are represented by the equation -

$$K = \frac{x^2}{(a - x)(b - x)}$$

where K has the numerical value of 4.0. This value for K was obtained after heating mixtures for 500 hours at a temperature of 100° C. The value is approximately the same at all temperatures, but the time required to attain equilibrium varies greatly with temperature. Thus at 25° C. the reaction was found to be incomplete after continuing for 240 days.

From the above investigations we learn that the combination of alcohols and acids is always incomplete, in contrast to the combination of inorganic bases and acids where the process continues practically to completion. There is a fixed limit towards which the proportions of alcohol, acid, ester and water tend. On mixing one molecule of ethyl alcohol with one molecule of acetic acid, only the limiting proportion of 66.5% of alcohol and 66.5% of acid enter

into combination; and we finally obtain a system whose composition is -

Alcohol	+	Acid	$\rightleftharpoons$	Ester	+	Water
1/3 mol.		1/3 mol.		2/3 mol.		2/3 mol.

For equivalent amounts of ethyl alcohol and acetic acid, Berthelot found the following values of the limit:

In the cold	(10 years)	65.2%
At 100°	(200 hours)	65.6%
" 170°	(42 ")	66.5%
" 200°	(24 ")	67.3%

Berthelot's researches have an important bearing on the formulation of the Law of Mass Action and as Moureu[3] says, "The so-called "law of mass action" was first recognized by Berthelot in the course of his researches on esterification (1862), and expressed shortly afterwards in its final form by the Swedish chemists Guldberg and Waage" (1864) .

Menschutkin [4] corroborated much of Berthelot's work. His experiments consisted in heating glass tubes of about 1 c.c. capacity, containing mixtures of alcohol and different organic acids in molecular proportions, in a bath of glycerin maintained at a temperature of 153-154°. The amount of ester thus formed in a given time was estimated by withdrawing a tube from the bath, cooling it quickly and determining the residual acid by titration with baryta water. The results are given in the following form -

(1) The initial rate of esterification (that is the proportion of ether formed in the first hour, expressed in percentage of the total theoretical amount) and

(2) the limit of esterification, similarly expressed. The most important data are :

	Initial Rate	Limit
Methyl Acetate	57.25	71.45
Ethyl "	46.60	69.61
Propyl "	46.39	70.90
Isobutyl "	45.40	73.46
Octyl "	46.56	82.24
Cetyl "	-	87.17
Allyl "	36.80	61.88
Benzyl "	37.77	63.97
Styryl "	37.21	64.58

Menschutkin said that the limit of esterification of primary saturated alcohols (omitting methyl alcohol) increases with the molecular weight, being about two greater for each higher homologue.

Both Berthelot and Menschutkin stress the fact that an excess of one constituent in the esterification will increase the amount of the other combined. Thus when 2 molecular weights of ethyl alcohol are taken with 1 molecular weight of acetic acid the limit is 82%. When 10 molecules of alcohol are taken with 1 molecule of acid, the esterification is nearly complete, and conversely almost all of the alcohol is esterified by a large excess of acid. This means that the mass-action constant is maintained, and that therefore in the presence of excess alcohol a higher per-

centage of acid is transformed to ester.

The fact that the limit of esterification varies only slightly with change of temperature, e.g. 65.2% at 10° C. and 66.5% at 170° C., illustrates a general principle. When a reaction is accompanied by only a small thermal change there should be only a very slight displacement of the equilibrium when the temperature is varied [5]. This follows from a consideration of the van't Hoff "reaction isochore"; - $\frac{d(\ln K_c)}{dT} = \frac{Q_v}{RT^2}$

When Qv, the heat absorbed, when no external work is performed, is small the extent of change in K_c is likewise small.

The measure of the rate of esterification by electric conductivity measurements was made by M. Negreano[6]. He verified results of previous investigators, showing the limit of esterification to be approximately 2/3 when equivalent amounts of alcohol and acid were used.

In 1877 van't Hoff [7] treated the subject of esterification from a mathematical viewpoint and arrived at the conclusions: -

(1) Within certain limits the maximum of ether (ester) formed is independent of temperature.

(2) The different acids behave approximately in the same manner; for instance, if the same number of molecules of

two different acids are added to the same quantity of alcohol, the same amount of each is capable of forming ether. The different alcohols behave in the same way.

(3) Alcohol and acid behave nearly similarly, viz., a certain quantity of acid molecules being brought in contact with a double quantity of alcohol, the circumstances being the same in both cases, then taking acid instead of alcohol, or vice versa, similar quantities of ether will be formed.

(4) A quantity of ether added at the commencement influences the new formation of this substance in almost the same manner as a corresponding greater addition of water.

(5) The maximum quantity of ether formed is independent of neutral bodies (e.g. acetone) added to the mixture. It is also independent of the whole volume occupied by the mixture.

EFFECT OF CATALYSTS ON ESTERIFICATION.

Sabatier[8] says that catalysts for esterification in liquid systems are chiefly the mineral acids, hydrochloric and sulphuric, and several salts, ammonium salts, alkaline bisulphates, zinc chloride, and sodium acetate mixed with water.

Berthelot [9] had found that a little hydrochloric or sulphuric acid caused an abundant formation of ethyl acetate. Thus with hydrochloric acid he obtained the following results by adding to a mixture of equal molecules of ethyl alcohol and acetic acid (106 g.), small quantities of HCl -

HCl added	Amount of Ester Formed After 6 Hours
0.67 g. = 0.017 mole	9.6%
4.77 g. = 0.125 "	73.6%
11.84 g. = 0.33 "	75.8%

These experiments were performed at ordinary temperature. Without the HCl present, the limit of 66.6% is attained only after several years. Berthelot explained the elevation of the limit by the taking part of the hydrochloric acid in the equilibrium, in which it increases the total amount of acid relative to the alcohol. Similar results were obtained with sulphuric acid. Here the explanation is the formation of acid ethyl sulphate, which reacts with acetic acid to form ethyl acetate and regenerate sulphuric

acid, which then repeats the operation.

Another paper [10] of Berthelot's shows the influence of various metallic chlorides on the union of alcohol and acetic acid. In these experiments 62 1/2 parts of glacial acetic acid were mixed with 100 parts of absolute alcohol and the mixture placed in a flask with 5 grams of metallic chloride. The flasks were frequently shaken and from time to time the amount of acid in the solution was estimated on a sample of the liquid, by means of baryta water. Some of his results reported in terms of weight of acid converted into acetic ether are : -

Salt Used	After 2 Months
KCl	46.4
KBr	52.2
NaCl	47.3
$BaCl_2$	52.4
$BaCl_2 + 2\ H_2O$	53.7
$MgCl_2$	63.6
$CaCl_2$	64.7
$CaCl_2 + 6\ H_2O$	77.6
$SrCl_2$	70.6
$SrCl_2 + 6\ H_2O$	69.5
$CuCl_2$	77.0

His conclusions were that small quantities of such salts accelerated the etherification, the rate being more marked when the more easily decomposable chlorides were used; (decomposable, either by water with the formation of hydrochloric or oxychloric

acid, or by acetic acid, with the production of hydrochloric acid and acid acetate.)

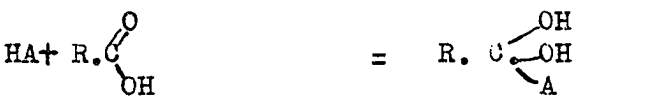
Reid[11] says "It is curious how many chemists have given entirely different explanations for the action of hydrochloric and sulphuric acids. All the facts go to show that all acids act alike and that whatever explanation is given in one case must fit all others".

The relative influence of hydrogen bromide and hydrogen chloride on the esterification of ethyl alcohol with benzoic acid has been studied by Phelps and Eddy [12]. They claim that the amount of ester produced is not proportional to the concentration of the hydrogen ions. Although in all cases the esterification proceeds more completely as the amount of the catalytic agent is increased up to a certain limit, any further increase causes a reduction in the quantity of ester produced. This is thought by them to be due to the fact that all the catalysts employed have a strong affinity for water, and consequently, when they are present in large quantities, absolute alcohol is not able to effect dehydration as thoroughly as is necessary for complete esterification.

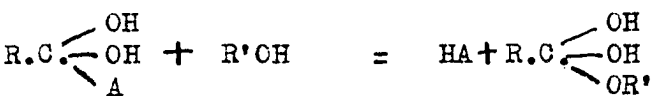
Phelps [13] and his co-workers also studied the effect of the hydrogen sulphates of K, NH_4, Na, pyridine and aniline on the esterification of benzoic and succinic acids. None of these

sulphates is so efficient as sulphuric acid. The catalytic action of metallic chlorides was also investigated, but little attempt was made to explain the results.

Bodroux[14] has explained the catalytic action of mineral acids by the temporary formation of an addition compound of the mineral acid with the organic acid considered as an anhydride of the ortho acid : -



then



and finally by the immediate loss of water : -

Many directions for esterification specify the saturation of the mixture of alcohol and acid with hydrogen chloride. However, Emil Fischer and Speier[15] investigated this subject and showed that the use of small quantities of the mineral acids is more convenient and quite satisfactory. Fischer showed that limited quantities of hydrochloric or sulphuric acid were sufficient not only for esterification of aliphatic acids, but also to a large

number of types of acids, either aliphatic or aromatic. The yields obtained are approximately 75% of theoretical, when employing 1 to 2% of mineral acid.

INFLUENCE OF STRUCTURE ON THE RATE OF ESTERIFICATION

Sudborough and Lloyd [16] have determined etherification constants of Substituted Acetic Acids. They used a large excess of alcohol and treated the reaction as monomolecular. N/20 HCl was used as catalyst. Their results confirm the work of Kistiakowsky [17] that the velocity constant of hydrolysis of an ester $RCOOC_2H_5$ by a solution of hydrogen chloride in a mixture of water and alcohol is identical with the esterification constant of the acid RCOOH when an aqueous alcoholic solution of hydrogen chloride of exactly the same concentration is employed.

Sudborough and Gittins [18] have obtained esterification constants of the normal fatty acids, by the method above described. Their values of E represent velocity constants for esterification of the respective acids with methyl alcohol at 15° C. They were obtained from the equation for a molecular reaction, k equals 1/t log. $\frac{a}{a-x}$, where (t) represents time expressed in hours. The acid content of the reaction mixture was obtained from titration of small portions with standard baryta solution at various intervals.

The following values were obtained:

Acid		E(at 15°C. with Methyl Alcohol)
Formic	HCOOH	1124
Acetic	CH_3COOH	104
Propionic	CH_3CH_2COOH	91.9
n-Butyric	$CH_3(CH_2)_2COOH$	50.0
n-Valeric	$CH_3(CH_2)_3COOH$	53.5
n-Hexoic	$CH_3(CH_2)_4COOH$	51.5
n-Heptoic	$CH_3(CH_2)_5COOH$	52.5
n-Octoic	$CH_3(CH_2)_6COOH$	54.6
n-Nonoic	$CH_3(CH_2)_7COOH$	53.6
Decoic	$CH_3(CH_2)_8COOH$	51.8
Lauric	$CH_3(CH_2)_{10}COOH$	52.9
Myristic	$CH_3(CH_2)_{12}COOH$	52.5
Palmitic	$CH_3(CH_2)_{14}COOH$	49.7
Stearic	$CH_3(CH_2)_{16}COOH$	53.7

The results as the authors say "clearly show the inhibiting effect produced by introducing small radicles, such as methyl and ethyl, into the formic acid molecule. Equally clear is the fact that butyric acid onward the rates are very nearly the same for the different acids, so that an increase in the length of the normal chain produces little or no effect on the rate of esterification".

Michael and Wolgast[19] studied the relation between the structure of the aliphatic alcohols and their rate of esterification. They criticize Menschutkin's results, because the percentages of

alcohol esterified in the first hour, which he termed the "initial velocities" are not proportional to the rates of esterification, since in many cases an appreciable quantity of water is formed in that time. Their method consisted in determining at definite intervals the decrease of the acid titration of an alcoholic solution containing a known amount of acid. The results are summarized as follows, the values given being for $k \times 10^5$, in which k is the constant of the reaction calculated from the equation of the second order, k equals $1/t \cdot x/A(a - x)$, A being the number of gram molecules of acid to which 1 liter of alcohol is added, (a) the number of c.c. of N/10 ammonia required to neutralize 2 g. or 2 c.c. at the beginning, a - x the amount required to neutralize the same quantity at time (t). The values of k are either means of the series obtained from any one experiment, or, in cases where a regular increase or decrease in the value found for successive times was observed, the values were extrapolated graphically, for t equals 0.

Esterification with Acetic Acid at 50°, -

Methyl alcohol	808 equals ($k \times 10^5$)
Ethyl alcohol	159
n-butyl alcohol	234
Cetyl alcohol	436

They also ran extensive experiments on esterification of trichloracetic acid. They concluded that the velocity of esterification increases as the carbon chain becomes longer. Menschutkin

had said that the velocity of esterification was constant from ethyl alcohol onwards. The increase is not an additive one, but a constitutive influence depending on the position of the methyl group.

The Esterification Law, discovered by Victor Meyer [20] in 1894 and experimentally established by him and others, is usually stated - "If in a substituted benzoic acid both of the hydrogen atoms next to the carboxyl group are replaced by radicles, the resulting acid cannot be esterified by means of alcohol and acid".

However, Rosanoff and Prager [21] claim that diortho-substituted aromatic acids, which are generally assumed to be unesterifiable, can be esterified quantitatively at higher temperatures; and state that the law should be "Aromatic acids with one or both positions next to the carboxyl occupied by substituting groups, combine with alcohols more slowly, though to no less extent than acids otherwise constituted".

IONIZATION THEORIES OF ESTERIFICATION CATALYSIS.

Many investigators have attempted to correlate the catalytic effect and the tendency of the molecules to form compounds with the catalyst. Kastle[22] explained the catalytic effect of the hydrogen ion by assuming the formation of an intermediate product between hydrogen ion and catalyzed molecule and

later a splitting of the product formed.

Euler [23] assumes that "all substances, without exception, are split up into ions, although the part ionized is frequently a very small fraction of the whole ..... all reactions are ion reactions .....only collisions between ions are chemically fruitful". He defines a catalytic agent as a substance which modifies the velocity of chemical reactions by changing the concentration of the ions of the reacting substances.

In the hydrolysis of ethyl acetate, Euler assumes that the ethyl alcohol, acetic acid, ethyl acetate, and water are all more or less dissociated, and that for equilibrium: -

$$C_{H^\bullet}\, C_{OH'} = K_1 C_{H_2O} \quad ; \qquad C_{C\ H\ O'}\, C_{H^\bullet} = K_2\, C_{C_2H_5OH} \quad ;$$

and $$C_{CH_3CO^\bullet}\, C_{OH'} = K_3 C_{CH_3COOH} \quad ; \quad \text{and}$$

$$C_{C_2H_5O'}\, C_{CH_3CO^\bullet} = K_4 C_{CH_3COOC_2H_5} \ , \ \text{then}$$

$$K_4 C_{CH_3COOC_2H_5}\ K_1 C_{H_2O} = K_2 C_{C_2H_5OH}\ C_{CH_3COOH} \quad \text{or}$$

$$C_{C_2H_5O'}\ C_{CH_3CO^\bullet} C_{H^\bullet}\ C_{OH'} = K C_{C_2H_5O'}\ C_{H^\bullet}\ C_{CH_3CO}\ C_{OH'}$$

Wegscheider [24] says that the last equation is a "self-evident identity", unless we make the assumption that there are different kinds of $H^\bullet$, OH' and other ions.

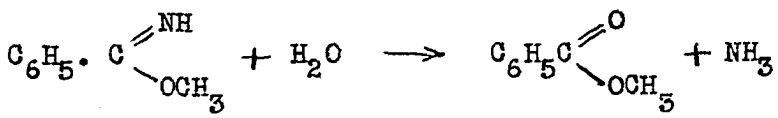
Euler made determinations of the constants of hydrolysis

for the methyl, ethyl, and propyl esters of formic, acetic propionic, chloracetic and hydrochloric acids. It was found that the methyl esters were least, the ethyl esters most hydrolyzed, and that the hydrolysis was greater the greater the dissociation constant of the acid. When K is the equilibrium constant of the reaction and k and k' the velocity constants of the two opposite component reactions, then K equals k/k'. The catalytic agent, Euler claims, has no effect on the ratio k/k', but alters the absolute value both of k and k' in the proportion 1: 1 + kH where H is the concentration of the hydrogen ions yielded by the catalytic agent. Since the ratio k/k' is unaltered by the catalytic agent, the free energy of the reaction (= RT log k/k') is also unaltered.

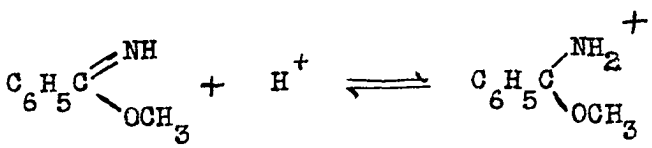
Acree and Johnson [25] state that the velocity of catalyzed esterification and ester hydrolysis are usually nearly proportional to the concentration of catalyst, where the latter is a powerful acid, and to the concentration of the carbonyl compound (ester or carboxylic acid), and that the activity of the catalyst is roughly proportional to its so-called degree of dissociation as given by conductivity measurements.

Stieglitz [26] studied the catalysis of esters and of imidoesters by acids. He says that in considering how an acid can affect the decomposition of an ester by water, "we are led to re-

call the most fundamental property of acids, that of combining with bases and oxides to form ionizable salts". Reasoning thus he assumes that perhaps an ester like methyl acetate may have basic functions and that salt formation with the acid may be the explanation of catalysis in the hydrolysis of the ester. However, the basic properties of most simple esters may be so weak that a quantitative estimation of the conditions of equilibrium of its salts cannot be made. Hence Stieglitz studied the decomposition of imido esters, RC(:NH)OR', acid esters which show definite basic functions and claimed the results were analogous to the case of ordinary esters. The decomposition of methyl-imido benzoate by water according to the scheme: -

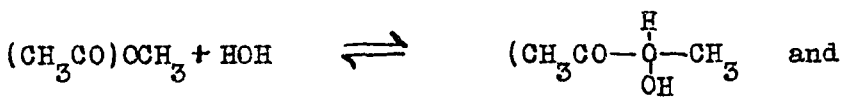


proceeds very slowly without catalysts, but is greatly accelerated in the presence of acid. Stieglitz assumes the catalytic effect to be due to the formation of a positive ion: -



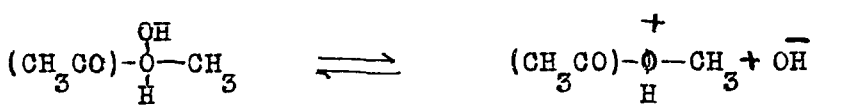
which then reacts spontaneously with the solvent: -

Hence Stieglitz says that the catalytic effect of the hydrogen ion is interpreted in accordance with the ionization theory and a similar explanation holds for ordinary ester hydrolysis. He claims that methyl acetate forms an oxonium base with water in the same way that ammonia combines with water to form ammonium hydroxide,



$$C_{ester} \times C_{H} \times C_{OH} = k' \times C_{base} \qquad (1)$$

The oxonium base ionizes: -



for which we have

$$C_{ester\ pos.\ ion} \times C_{OH} = k_{base} \times C_{base} \qquad (2)$$

Combining (1) and (2) we have : -

$$C_{ester\ pos.\ ion} = \frac{k_{base}}{k'} \times C_{ester} \times C_{H} \qquad (3)$$

Then, if as was shown for the imidoesters, it is only the positive ions which will react with water to give acetic acid and methyl alcohol, we would have for the velocity of this reaction of saponification,

$$\frac{dx}{dt} = K_S \times C_{\text{ester pos.ion}} \times C_H \times C_{OH} \quad (4)$$

Since for water, $C_H \times C_{OH} = K_w \times C_{H_2O}$ (5)

Substituting the values of (3) and (5) in (4), we have,

$$\frac{dx}{dt} = K_S \times \frac{k_{\text{base}}}{k'} \times C_{\text{ester}} \times C_H \times k_w \times C_{H_2O} =$$

$$K_S \times C_{\text{ester}} \times C_{H_2O} \times C_H$$

as representing the velocity of the decomposition of methyl acetate by water in the absence of any acid.

When hydrochloric acid is added to the mixture of methyl acetate and water, we obtain the hydrochloride of the oxonium base, but the salt is almost completely hydrolyzed,

$$(CH_3CO)-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{O}}-CH_3 + HOH \rightleftharpoons (CH_3CO)-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{O}}-CH_3 + HCl$$

By reasoning as above-Stieglitz says that the velocity of the decomposition of methyl acetate in the presence of hydrochloric acid is represented,

$$\frac{dx}{dt} = K_S \times C_{ester} \times C'_H \times C_{H_2O}$$

Similarly, considering the reverse process of esterification in the presence of hydrochloric acid, the velocity is represented by,

$$\frac{dx}{dt} = K_e \times C_{acetic\ acid} \times C'_H \times C_{CH_3OH}$$

The addition of hydrochloric acid would therefore, through salt and ion formation, accelerate the reactions in the reversed directions in the same proportions, and therefore not measurably affect the final condition of equilibrium.

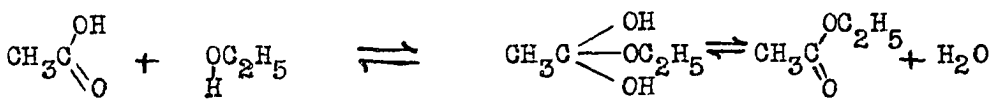
Acree [27] in commenting on Stieglitz's article "Studies in Catalysis" claims that every one of his fundamental assumptions and "especially Stieglitz's keynote, acceleration through salt and ion formation, had already been made by Kastle [28], Euler[29], Acree[30], Bredig[31], and Lapworth[32]."

Lowry [33] in discussing the mechanism of hydrolysis and esterification applies the electronic theory of valency in formulating the addition compounds. In explaining esterification he says "the condensation of the alcohol and acid therefore appears to involve (1) the repression of the ionization of the organic acid, with a development of its ketonic functions, the addition of a proton to the alcohol, thereby giving to the alcohol the

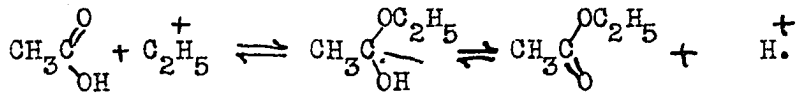
proton- donating functions, of an acid, (3) the coordination of proton of this complex with the carbonyl oxygen of the acid as a preliminary to (4) the addition of the proton-donating complex of the alcohol to the carbonyl group of the acid, according to the normal rules for the addition of a hydride such as HCN to an aldehyde or keton, (5) the elimination of the proton of the catalyst, and of a molecule of water, from the intermediate condensation product.

Lowry says that some of these intermediate compounds have been isolated. Thus an addition compound of sodium methoxide with ethyl benzoate has been isolated by von Pechmann[34], and an unstable addition compound of ethyl acetate with hydrogen bromide, m.p. = 36°, has been isolated by Maass and McIntosh[35].

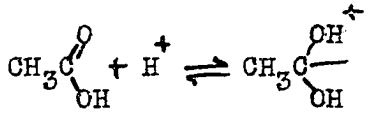
Another view [36] of esterification is to represent the mechanism as a process of association -



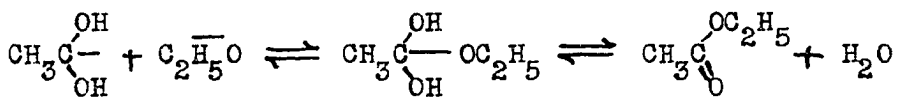
Lapworth [37] has proposed a compromise between the ionic theory and the association hypothesis, that "the production of complex ions is at the bottom of a large number of organic reactions". Lapworth offers two possible reactions :

(1) 

or the alternative -

(2)  a slow reaction followed

by the more rapid changes -

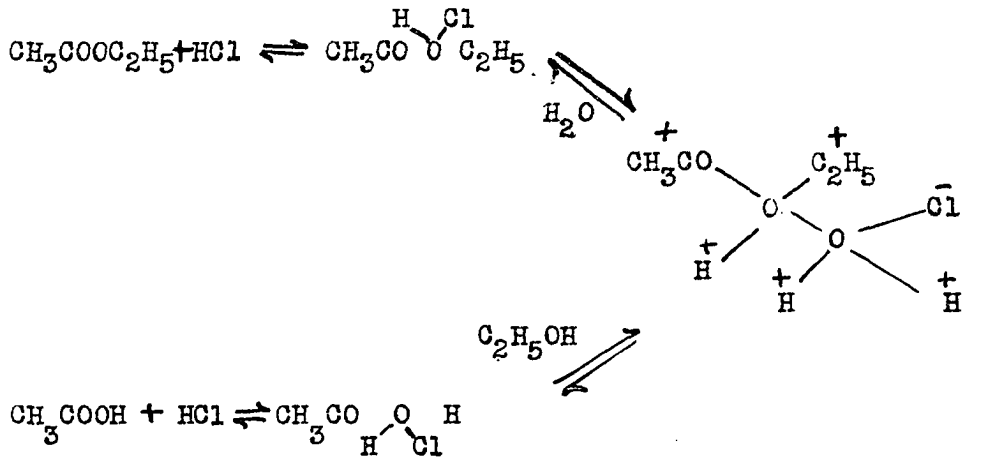


which harmonizes with the fact that the velocity of hydrolysis of ethyl acetate is directly proportional to the concentration of hydrogen ions.

Kendall [38] states that "the hypothesis of the catalytic activity of the undissociated molecule which purports to explain why the speed of reactions such as ester catalysis is not exactly proportional to hydrogen ion concentration may be discarded in favor of a view which recognizes several types of hydrogen ion (e.g., H^+, $(H(H_2O)^+)$, $(H(R.COOR)^+)$ each possessing a different catalytic activity.

The action of acids as catalytic agents may be explained on the basis of "onium" compound formation [39]. This involves the formation of an intermediate complex in which an oxygen atom seems to be quadrivalent. The theory assumes the

catalytic effect to be due to unionized acid molecules. The hydrolysis and esterification of ethyl acetate is thus formulated : -



According to Falk and Nelson [40] this scheme accounts for the following facts : -

1. "The hydrogen chloride bears the same relation to the acid and the ester. It therefore catalyzes the reaction in both directions.

2. The onium compound formation depends on the strength of the acid catalyst. This is measured by the degree to which it breaks up in solution to form ions, a physical property similar to the chemical property of onium addition, which controls the rate of reaction with water or alcohol.

3. Increasing the concentration of water favors the production of acid; increasing the concentration of alcohol favors the production of ester."

INFLUENCE OF SOLVATION IN CATALYSIS BY HYDRIONS.

Arrhenius and the early supporters of the ionization theory emphasized the parallelism between the electrical conductivity of an acid solution and its catalytic activity in ester hydrolysis. But more accurate measurements showed that direct proportionality could not be claimed. It was found that the rate of hydrolysis increased more rapidly than the hydrogen-ion concentration, and it also increased with the ester concentration. So other theories have been offered to account for these divergences.

Bronsted [41] has recently reviewed the theories of Acid and Basic Catalysis and showed the failure of some of the older theories to adequately explain the phenomena.

Arrhenius' views on the subject of acid catalysis do not distinguish between hydrogen ions in the free and in the hydrated state. According to Lapworth [42] the catalytic effect in acid catalysis is due solely to the non-hydrated or non-solvated hydrogen ion. The solvated hydrion is supposed to be inactive. He says that the addition of water to a mixture of alcohol and acid causes a reduction in the number of hydrogen ions which accounts for the retarding effect of water in esterification.

Lapworth [43] later offers an explanation of the properties of acids, not necessarily involving the conception of hydrogen ions. From this standpoint the properties of acids when dissolved in solvents containing bases may merely depend on (1) the extent to which they combine, (2) the manner in which they are partitioned between the bases, and (3) the degree to which the resulting salts are dissociated.

The most important experimental basis of Lapworth's theory consists of showing the effect of small quantities of water in retarding the hydrazobenzene-benzidene rearrangement, and the bromination of ketones in non-aqueous solutions. He explains the effect by assuming that most of the hydrions in aqueous solution are hydrated and form a complex H_3O^+. There is then supposed to be an equilibrium between this oxonium ion H_3O^+ and H_2O and H^+ as expressed by the equation -

$$H_3O^+ \rightleftharpoons H_2O + H^+$$

The diminution of H^+ ions (on addition of H_2O) is now explained, with consequent formation of oxonium ions which are assumed to be catalytically inactive.

To support his views on free hydrions, Lapworth [44] has investigated the variations in electromotive force in cells of this type -

H	HCl alcohol	HCl alcohol + H_2O	H,

The quantity of water was small compared to the amount of alcohol, but great as compared to the acid.

The electromotive force of such a cell is given by the equation -

E equals $\frac{RT}{F}$ log. $\frac{P}{P'}$, where P and P' are the "availabilities" of the acid in the two liquids. The "availbility" of the acid is perhaps synonymous with the present "activity".

The fall in availability due to the addition of water is represented : -

$$\frac{P'}{P} = \frac{r}{r + w}$$

where P' is the availability of the acid in moist solution, P that of the acid in anhydrous alcohols, w is the concentration of water in gram molecules per liter, and r a constant.

Goldschmidt[45] explains the catalytic effect of acids as due to the formation of hydrogen ion alcoholate $C_2H_5OH_2^+$. From this view, the anti-catalytic effect of water depends upon the partial decomposition of the alcoholate according to the scheme : -

$$C_2H_5OH_2^+ + H_2O \rightleftharpoons C_2H_5OH + H_3O^+$$

In Goldschmidt's work the alcohol was present in large excess and hence can be considered present in constant concentration. Hence the reaction velocity was interpreted by means of the unimolecular equation $K = \frac{1}{t} \log \frac{a}{a - x}$. Using this method Goldschmidt showed that as an approximation it could be stated that the reaction constant varied proportionately to the hydrogen ion concentration, and that the activity of different acid catalysts was in direct relation to the strength of the acid as determined by the hydrogen ion concentration from conductivity data. Thus, in order of diminishing catalytic power, came hydrochloric, picric, trichloroacetic, trinitrobenzoic, trichlorobutyric, and dichloroacetic acids. As stated above the active agent in esterification is the alcoholate $C_2H_5OH_2^+$, while the ion hydrate H_3O^+ is considered non-active.

The falling constant, K, obtained from the ordinary unimolecular equation and caused by the retarding influence of the water formed in the reaction was corrected by using an equation $k.c.t. = n + r + a \cdot \log \frac{a}{a - x} - x$, in which

c equals the H ion concentration in absolute alcohol,
t " time in hours,
n " initial concentration of added water,
r " equilibrium constant of hydrolysis of the alcoholate ion,
a " original concentration of acid undergoing esterification,

x equals concentration of acid esterified and therefore of water formed in the reaction.

Bronsted[46] shows that on the basis of Goldschmidt's views there can be obtained a relation : -

$$\frac{C_{C_2H_5OH_2}}{C_H} = \frac{r}{r + w}$$

where r represents the dissociation constant of the oxonium ion in alcoholic solutions. This leads to an expression

$$\frac{k}{k_0} = \frac{r}{r + C_{H_2O}}$$

If the hydrion alcoholate functions as the catalyst: k_0 and k being the velocity constants in alcoholic solutions with and without water respectively. The expressions of Lapworth and Goldschmidt show that the assumptions of the free hydrion or the active alcoholate ion as the active catalyst, lead to the same formula for the anti catalytic effect of water. Hence, the experimental facts cannot offer a choice between the two theories. However, Taylor and Rideal[47] state that "Lapworth's theory is applicable without modification to all the various acid catlaytic processes here considered, whilst Goldschmidt's view requires adjustment to meet particular cases".

Bronsted considers that catalysis due to free hydrion is improbable. An argument advanced for this belief is based on

some work of Fajans[48] who found the enormous heat effect of 232,000 calories per gram ion when the free hydrion united with water. Using this quantity as a measure of the affinity of the hydrion for water, Bronsted calculates the concentration of free hydrion in an acid solution to be as low as 10^{-150}. Hence, he says "the catalytic effect must consequently be assigned to the hydrion hydrate or the oxonium ions, while in alcoholic solutions the hydrion alcoholate should be considered as the active catalyst".

Rice[49] has adopted Lapworth's views of free hydrion catalysis in his views on "chemical activity". He assumes that the reactivity of the molecules is independent of the medium in which the reaction proceeds. He distinguishes between a catalytically neutral point and a stoichiometric neutrality; and claims that it is not until the hydrogen ion concentration has a value about $P_h 5$ that the concentrations of the unhydrated ions become equal. When this point is reached there is a minimum of catalytic activity.

CATALYSTS AND EQUILIBRIUM

Mellor[50] gives as general characteristics of catalytic reactions the following "articles of faith" -

(1) "The catalyst has the same chemical composition at the beginning as at the end of the reaction.

(2) A small quantity of the catalytic agent is sufficient to effect the transformation of an indefinitely large quantity of the reacting substance.

(3) A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.

(4) A catalytic agent cannot affect the final state of equilibrium.

(5) The velocity of two inverse reactions is affected by the catalyst to the same extent.

(6) The state of equilibrium is independent of the nature and quantity of the catalytic agent.

(7) The phenomenon of catalysis is universal."

Article (4) is generally assumed to be correct because otherwise it might conceivably be possible to allow substances to react alternately with and without the catalyzer, and so utilize the process to perform work. This would be in reality a perpetual motion principle, which is denied.

If we consider a general reaction involving a moles of A and b moles of B to form c moles of C and d moles of D, under the influence of x moles of catalyst X,

$$aA + bB + xX = cC + dD + xX$$

we may express the equilibrium conditions in terms of concentrations:

$$K_c = \frac{C_C{}^c \times C_D{}^d \times C_X{}^x}{C_A{}^a \times C_B{}^b \times C_X{}^x} = \frac{C_C{}^c \times C_D{}^d}{C_A{}^a \times C_B{}^b}$$

provided that we are dealing with very dilute solutions in which the laws of dilute solutions hold. It is evident that the equilibrium conditions remain unchanged in the catalyzed process, because the catalyst is present in equal concentrations on both sides of the equation and these values cancel.

Since actual systems deviate from the ideal conditions, it is now customary to employ the concept of activity. The activity of a species may be defined by the equation,

$$F_A = RT \ln a_A + C_A$$

where F_A is the molal free energy of the substance A under given conditions, a_A is its activity, and C_A is a constant which may be arbitrarily defined. The increase in free energy when a substance changes from one set of conditions A to another A' is given

by the expression,

$$F_{A'} - F_A = \Delta F_A = RT\ln \frac{a_{A'}}{a_A}$$

where a_A and $a_{A'}$ represent the activities in the initial and final stages respectively and F_A represents the increase in free energy accompanying the change. The condition for equilibrium is that $F = 0$.

When the reaction $aA + bB = cC + dD$ is at equilibrium,

$$aF_A + bF_B = cF_C + dF_D$$

Now by substituting for each free energy term its corresponding activity equivalent, $aRT\ln a_A + aC_A + bRT\ln a_B + bC_B =$ $cRT\ln a_C + cC_C + dRT\ln a_D + dC_D$ or $aC_A + bC_B - cC_D - dC_D =$ $RT\ln \frac{a^c_C \times a^d_D}{a^a_A \times a^b_B}$ or since the quantities on the left hand side are constants, $K_a = \frac{a^c_C \times a^d_D}{a^a_A \times a^b_B}$, which represents the equilibrium constant K_a at any given temperature in terms of the activities of the reacting substances. It is evident that this equilibrium constant will be unchanged in the presence of any

substance occurring (as a catalyst) on both sides of the equation. However, in homogeneous systems it is possible that the equilibrium concentrations may be modified by the presence of a catalyst. For example the mineral acid catalyst may affect the activity of water (and possibly the other constituents), so that the molecular concentration of water may be quite different from that in the absence of a catalyst. "It is to this varying effect, state Rideal and Taylor[51] of a catalytic agent on the activities of the individual reacting species that most of the abnormalties in the determination of equilibria in the presence of catalysts are to be attributed. The effect is particularly apt to occur in equilibria which involve electrolytes either as reactants or as catalysts".

There are a number of examples to be found in the literature which show an apparent displacement of equilibrium constants by means of added electrolytes. Thus Jones and Lapworth[52] found that the hydrolysis constant of ethyl acetate could be changed by adding varying amounts of hydrochloric acid as catalyst. The value of four for the esterification constant of Berthelot and St. Gilles could be increased to nine, with increasing concentrations of hydrochloric acid. The phenomenon is to be ascribed to the influence of the acid on the activity of water.

Poma and Albonico[53] examined the action of neutral

salts on the velocity of formation and saponification of esters. They found the order of influence of the cations to be K, Na, Li, Ca, Mg, i.e. decreasing with the electroaffinity of the cations. The order of the anions was apparently smaller but not to be neglected. In their study of the effect of anions, $LiNO_3$ and LiBr were used as neutral salts and HBr and HNO_3 as catalysts.

Edgar and Schuyler[54] studied the esterification equilibria in the gaseous phase and found high values ranging from 347 to 559 for the equilibrium constants in the vapor phase at 75° C. They mention recent work by Miss Tobin (Dissertation, Bryn Mawr College, 1920) which indicates that the constant for the liquid phase is more nearly 3.7 than the value 4.0 given by earlier investigators. This value corresponds more closely to results of our determination.

Schlesinger[55] investigated the influence of LiCl, NaCl, KCl and $CaCl_2$ on the equilibrium between EtOAc and its saponification products at 100° C, using 0.2 Normal HCl as a catalyst. His equilibrium constants expressed as

$$K = 10^4 \times \frac{\text{millimols HAc} \times \text{millimols EtOH}}{\text{millimols EtOAc} \times \text{millimols } H_2O},$$

show values decreasing with increasing salt concentration. When NaCl, LiCl and $CaCl_2$ respectively, were used, the equilibrium constant could be calculated with sufficient accuracy from the linear equation $K = 3045 - 21.217\ c$ (c being the salt

concentration in milli-equivalents per mol. of water).

Schlesinger emphasizes the fact that these equilibrium displacements are not contradictions of the second law of thermodynamics. He is inclined to trace the equilibrium displacement to a loss of water content through formation of hydrates, but is apparently unable to explain why $CaCl_2$, which takes up both alcohol and water, should act similar to NaCl which binds only water. He suggests a possible relation to the theory of action of neutral salts as outlined by Debye and McAulay[56]. It is difficult, however, to see how the removal of water due to the formation of salt hydrates, will explain the changes in the numerical value of the equilibrium constant.

NEUTRAL SALT EFFECT

Arrhenius[57] studied the influence of neutral salts on the rate of hydrolysis of ethyl acetate. This influence as a rule is small. He used an equation $-\frac{dC}{dt} = k.C.C_1$ for the rate of saponification; where t is the time, C the concentration of the base, and C_1 that of the salt. The units are seconds and gram equivalents per cubic centimeter. Some of the results are as follows: -

Temperature	Salt Concentration	Average k	Deviation in %
24.4 C.	0.025 normal KOH	6.30	
	1 " KNO_3	5.15	- 18.3
	1 " KCl	5.74	- 8.9
	1 " KBr	5.21	- 17.3
	1 " KI	4.60	- 27.0
	1 " K_4Cy_6Fe	5.68	- 8.2
	1 " $K_6Cy_{12}Fe$	5.90	- 8.0
	1 " K_2SO_4	6.72	6.6

Here we see that halogens depress the value of k, while sulphates raise the value. The influence of KI is greater than that of KBr, which is greater than that of KCl, the three being very nearly in the ratio 3: 2: 1. Ammonium salts showed abnormal effects; the values of k being large, and varying distinctly with the amount of salt in solution.

Arrhenius[58] offered several explanations for this effect. He attributed the increase in velocity to one or more of three causes: -

(1) The increase in the ionization of the acid.

(2) The increased ionization of the water.

(3) The shift in the equilibrium "inactive active" molecules, to the right on the addition of neutral salts.

Euler's theory[59] which is merely an enlargement of that of Arrhenius, accounts for the "salt effect" on the basis of an increasing dissociation of water.

Numerous other postulates have been advanced to explain the neutral salt effect. Lamble and Lewis[60] offer the suggestion that catalysis is a "radiation phenomenon." According to this, reactions are catalyzed by the absorption of radiation which the hydrogen ion emits due to its vibration to and fro between two neighboring molecules. They attempted to test Arrhenius' idea of the existence of "active" and "inactive" molecules, by assuming that if such forms exist, then a catalyst merely acts in shifting the equilibrium between the two forms. Determinations of the velocity of hydrolysis of methyl acetate were made at different temperatures with different amounts of catalyst. Their results

show that there is no tendency for the temperature coefficient of a strongly catalyzed reaction to be less than that of a weakly catalyzed reaction. Hence, they assume the non existence of so-called "active" and "inactive" molecules.

Acree[61] suggests that "reactive" and "less reactive" double salts are formed between the added salt and the reacting substance. These compounds speed up or retard the reaction. Changes in solvation, viscosity, vapor pressure or osmotic pressure are also considered to play a part; and the general effect is ascribed to a change in the thermodynamic potential caused by a change in the field surrounding the reacting substances.

Wilson[62] concluded that removal of solvent by hydration of the salt accounts for the rise in the hydrogen ion concentration. His conclusions came as a result of some researches on acidity of chrome tanning solutions. Manning [63], on the contrary, states that hydration of the solute is not likely the cause of the changing hydrogen ion concentration, because studies of reaction velocities of hydrolysis of ethyl formate in H_2O alone and in aqueous solutions of sucrose, glucose and various salts show that the non-electrolytes exert little or no influence on the rate of hydrolysis. In other words hydration of the solute does not affect k.

Taylor[64] emphasizes the fact that the activity of the undissociated molecule as well as the hydrogen ion must be considered in acid catalysis. Akerlof[65] however, concludes that the hypothesis of the catalytic activity of the non-ionized molecule is incorrect. His conclusions result from a study of neutral salt action on velocity of hydrolysis at constant acid concentration. The hydrogen ion activity of the catalyst in various reaction mixtures has been determined by means of E.M.F. measurements. A relationship between reaction velocity and hydrion activity is given $K = C.\ a.\ f.\ (n)\sqrt[3]{a}$ in which K is the reaction velocity , n the acid titre and a the hydrion activity. The formula is claimed to hold for all concentrations of catalyst, and is not influenced by the nature or concentration of the added salt.

Akerlof proposes a hypothesis that the water sheath of the hydrogen ion is changed by the addition of neutral salts, which accounts for the concentration of hydrogen ion remaining constant while its activity changes. The various neutral salt actions are controlled by the various forces with which the different ions attract the water molecules.

Dhar[65] says the effect of neutral salts is highly specific, some accelerating and others retarding the speed of reaction. He claims that neither the order of the reactions nor

the temperature coefficient is affected by the presence of neutral salts. His article contains a chart summarizing many of the experiments on the influence of salts on reaction rate.

L. E. Bowe[66] studied cane sugar inversion and ester hydrolysis by hydrochloric acid in the presence of concentrated alkali halides and also determined electrometrically the hydrogen ion activity (termed apparent hydrogen ion concentration). Since sugar inversion is catalyzed by acid, the rate of inversion is used as a measure of the hydrogen ion concentration. Experiments were conducted on the increase in the rate of inversion upon addition of the neutral salts NaCl, Na Br and NaI. He found a parallelism between speed and hydrogen ion activity. However, in the hydrolysis of ethyl acetate the addition of neutral salt has a much smaller effect. The work was done under the direction of Bancroft [67] who says that neutral salt action is due to a shift in the water equilibrium. Liquid water is assumed to be mainly $(H_2O)_2$ "dihydrol"; but the addition of salts may cause the formation of more molecules of "monohydrol" (H_2O) . This amounts to a change in solvent, in which concentrations, reaction velocities, ionization, etc. will be different from those in the original solvent. This is really a view proposed by Stieglitz[68] based on Arrhenius' interpretations previously mentioned.

RECENT VIEWS ON THE INFLUENCE OF STRONG ELECTROLYTES ON REACTION VELOCITY.

The relationship between ionization and reaction velocity of hydrolysis, established by Ostwald and Arrhenius, which holds for weak acids and salts with a common ion, does not hold for strong acids and neutral salts with a common ion. The reaction velocity in the presence of strong acids increases at a greater rate than the concentration of the acid, and in presence of a salt of common ion there is an increased velocity, whereas the common ion effect would demand a decreased velocity due to a decrease in hydrogen ions. Taylor[69] gives the following data on the rate of hydrolysis of ethyl acetate at 25° C. -

C	0.25	0.10	0.05	0.025	0.01 n.
k(c.HCl) x 10^5	71.6	28.3	13.8	7.0	2.9
k(c.HCl 1.0n KCl) x 10^5	85.7	34.45	16.9	8.7	3.6

Various empirical formulae have been proposed to account for such results.

Arrhenius suggested that the velocity could be expressed by an equation,

$$k = a(H.) + b(H.)^2$$

Another formula which considers the catalytic effect as due not

only to hydrogen ion, but also to the undissociated molecule was used by Snethlage,

$$k = n_H \cdot K_H + n_m K_m,$$

where n refers to the concentration and K to the catalytic activity of hydrogen ion. However in strong acids the ionic and molecular concentrations are unknown, and so the above equations can only be applied to weak acids.

The more recent view of reaction velocity attempts to express results in terms of the activities of the catalyst. Work in this field has been done by Harned[70], Akerlof[71], Lewis[72], Bray[73] and Livingston[74], and Bronsted[75].

Thus in a reaction velocity equation where the concentration of the reacting species is C_S and those of the catalyst species are C_A and C_B the reaction velocity equation is expressed,

$$\frac{dx}{dt} = k \cdot C_S \cdot C_A \cdot C_B \cdot f_A \cdot f_B$$

where f_A and f_B are the activity coefficients of the catalyst species.

Harned and Selz[76] successfully applied such an equation to the velocity of change of acetyl chloraminobenzene to chloracetanilide in presence of HCl. Likewise Bray and Livingston showed its application to the decomposition of hydrogen peroxide in the

presence of HBr. In these cases A is the H ion and B the halogen (-) ion.

Bronsted assumes that such reactions involve two steps, the slow formation of an unstable intermediate complex, followed by a rapid decomposition to the final reaction products; thus -

$$\underset{\text{Slow}}{A + B \rightleftharpoons AB} \qquad \underset{\text{Fast}}{AB \longrightarrow C}$$

He then formulates the velocity equation on the assumption that the velocity is determined by the ratio of the activities of the reactants to that of the products,

$$\frac{dx}{dt} = k\, C_A \cdot C_B \cdot \frac{f_A\, f_B}{f_{AB}}$$

Bronsted assumes the following : -

"The probability of a molecular system passing from its normal state, into a state characterized by great improbability, is proportional to the ratio between the activity coefficients in the normal and the improbable state."

ACTIVITY AND NEUTRAL SALT ACTION.

Important applications of the new velocity theory have been made by Bronsted to some results of Holmberg on hydrolysis of halogenated organic compounds in alkaline solutions in presence

and absence of neutral salts.

Holmberg first studied the reaction between alkalies and dibromsuccinic acid, a reaction which, stoichiometrically and kinetically, proceeds according to the scheme,

$$\begin{matrix} CHBrCOO^{--} \\ | \\ CHBrCOO \end{matrix} + OH^{-} = \begin{matrix} CH.COO^{--} \\ | \\ CBrCOO \end{matrix} + Br^{-} + H_2O$$

The velocity constants of the process, with varying concentrations of the reactants and also in the presence of salts, show a marked dependence on the total ionic concentration. Holmberg called the phenomenon cation catalysis, since the velocity with unchanged cation apparently depends on the total ion concentration, and not upon the nature of the anions. He also showed that variation of the cation, especially a change to calcium and barium salts, produced a large increase in the velocity.

Bronsted showed that these results could be interpreted by his activity theory of salts. He formulates the reaction by the equation

$$S^{--} + OH^{-} = (S.OH)^{---} ,$$

where S refers to the dibromsuccinic, OH^{-} to the hydroxyl ion, and $(S.OH)^{---}$ to a trivalent complex formed by the association of two anions. In terms of Bronsted's activity theory of reaction velocity,

the velocity is expressed,

$$v = k \times (C_{S^{--}}) \times (C_{OH^-}) \times \frac{(f_2 f_1)}{(f_3)}$$

where f_1 , f_2 , and f_3 , refer to the activity coefficients of the several ions, subscripts indicating valencies of the ions.

PART II - EXPERIMENTAL

PRELIMINARY EXPERIMENTS.

Before a satisfactory procedure was adopted, several preliminary experiments were run. It was first thought possible to esterify a fairly large mixture of alcohol and acid in a 500 c.c. round bottomed flask heated on a water bath; the flask being connected with a reflux condenser. The idea was to periodically withdraw certain fractions of the mixture and analyze for the free acetic acid. However, the losses of constituents through volatilization were so great, no matter how well refluxed, that this course was abandoned.

It was also deemed advisable to see whether stirring had any considerable influence on the rate of esterification. A wide mouthed flask of 500 c.c. capacity was connected with an electric stirrer, which passed through a mercury seal. The experiment was conducted at room temperature, and portions of the esterification mixture sampled periodically. The results indicated that the rate of esterification is not appreciably influenced by stirring. A similar result was obtained by Huber and Reid (77) in a study of the influence of rate of stirring on reaction velocity. They found that the saponification of ethyl benzoate was independent of the speed of stirring.

DETERMINATION OF EQUILIBRIUM CONSTANTS.

The method finally adopted was essentially the same as that employed by Berthelot and St. Gilles, and other early investigators, and more recently by Schlesinger [78]. It has been briefly described in a recent paper by Cantelo and Billinger [79]. The detailed procedure was as follows: -

Weighed quantities of acetic acid, ethyl alcohol and water (or salt solution) were mixed together in a weighed flask. From this mixture small glass tubes were filled and sealed by means of a blast lamp. The tubes were made from soft glass tubing of 9 mm. bore, and 1 mm. wall. Each tube was approximately 6 cm. in length. The tubes were weighed before and after filling to obtain the weight of sample taken.

The method of filling the tubes was to fit up the weighed flask as a wash bottle with a capillary jet; then by means of a current of air, dried by passing through calcium chloride, it was possible to force the liquid into the small tubes. Each tube had a number scratched on it for identification.

The acetic acid, ethyl alcohol and neutral salts used were all c.p. chemicals which were tested for impurities. The acid contained 99.39% of acetic acid by weight and the alcohol 95.75% by weight. The salts were all thoroughly dried before using.

The sealed tubes were placed in a bath of carbon tetrachloride which was kept refluxing by a simple heater. The heater consisted of a 100-watt incandescent lamp in a can insulated with sheet asbestos. By this arrangement it was possible to keep the tubes containing the esterification mixture at a temperature of 78°. Two photographs are included which show a battery of heaters and flasks.

Esterification in the absence of a mineral acid catalyst is slow, even at this temperature, and it was necessary to continue the heating for from thirty to forty days. Then from time to time a tube was taken from the bath, cooled in ice, the capillary end broken and the contents placed in ice cold, freshly boiled water. The mixture was transferred to a volumetric flask and an aliquot portion taken for titration against standard barium hydroxide solution. By means of the titration value the concentration of acetic acid was known in the resulting mixture, and from the known initial concentrations it was possible to calculate the concentration of all four constituents in the equilibrium mixture. Concentrations were figured in terms of millimols of the constituents and the equilibrium constant K_E was then expressed as

$$K_E = \frac{\text{Millimols of } CH_3COOC_2H_5 \times \text{Millimols of } H_2O}{\text{Millimols of } CH_3COOH \times \text{Millimols of } C_2H_5OH}$$

When several successive samples gave approximately equal values of

K_E the equilibrium was assumed to have been reached.

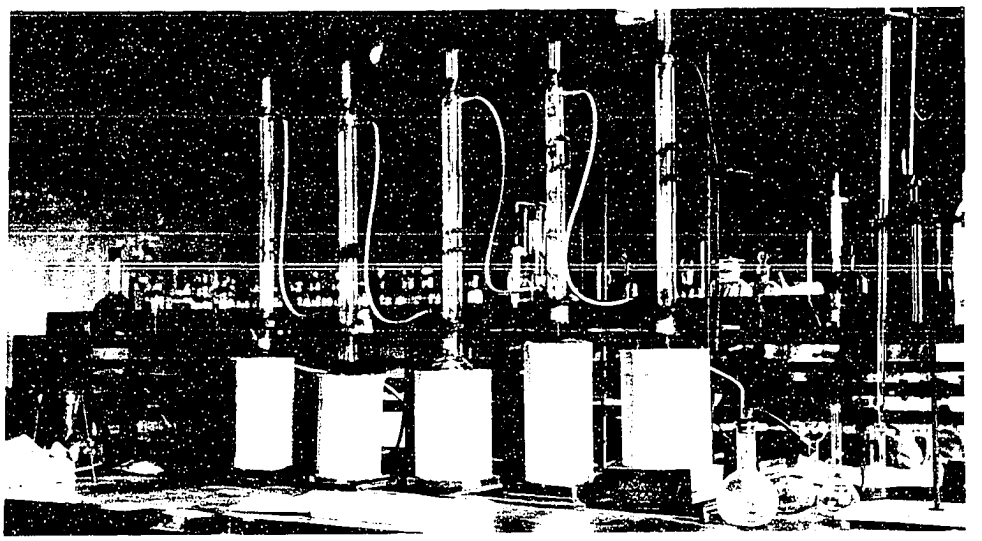
The salts used were high grade products; the sodium chloride, bromide and acetate were Kahlbaum products, while the sodium thiocyanate, iodide and nitrite were obtained from Coleman and Bell. In the case of the esterification in presence of sodium iodide, there was always a light brown coloration indicating the presence of free iodine. When sodium thiocyanate was used there was a pinkish tinge in the reaction mixture, probably due to a trace of iron. It is interesting to note that these two cases show the greatest departure from a linear relationship in their effect on the equilibrium constants. This is evident by comparing the curves for sodium iodide and thiocyanate with the curves for the other salts.

Eight tables of results are included in the data. Table Number One contains the equilibrium data for esterification with no added salt. The mixture started with consisted of 50 c.c. of alcohol, 50 c.c. of acetic acid and 25 c.c. of water. These quantities were pipetted and then weighed in the mixing flask and the molal concentration figured from the analysis. Tables Number Two to Seven inclusive, contain the data for esterification in the presence of added salts in various concentrations. It will be observed that the molal concentrations of alcohol, acid and water are not always the same, but the relative proportions are approximate-

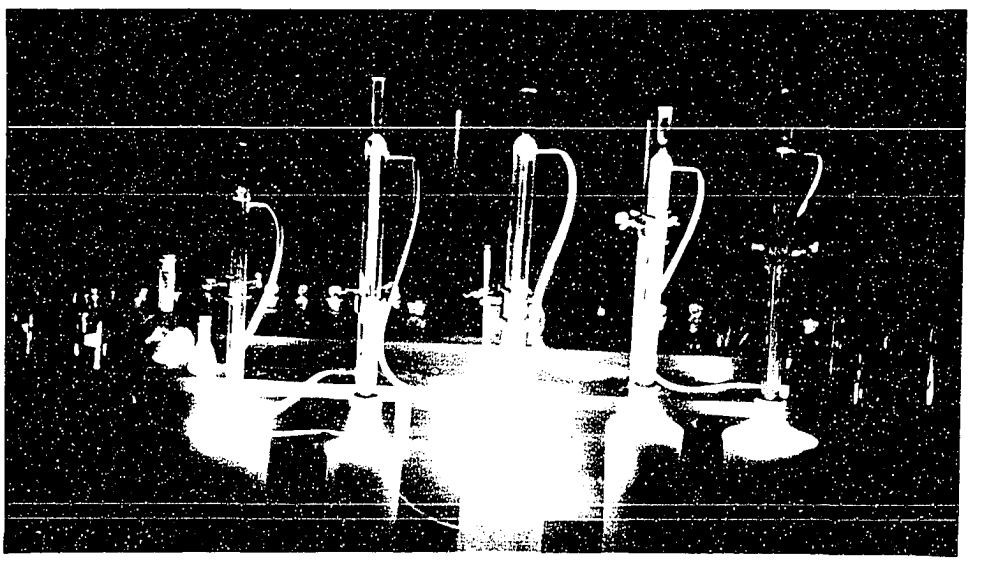
ly the same, because the volumes pipetted were always in the ratio 2, 2 and 1 for alcohol, acid and water respectively.

Table Number Eight gives results when esterification was performed in a mixture of alcohol, acetic acid and a solution of 0.020 Normal HCl. The relative volumes used in this case were the same as in the previous experiments, namely 2 volumes of alcohol to 2 of acetic acid to 1 volume of the aqueous solution of 0.1 Normal HCl.

The comparative effects of the several salts is shown graphically on the curve sheet No. 1 included. Here the values of K_E are plotted as ordinates against the corresponding values of salt concentration as abscissae.



Constant Temperature Baths - Consisting of 500 c.c. Soxlet Flasks attached to condensers. Each flask was heated by a 100 watt incandescent bulb in a tin can insulated with asbestos.



Apparatus photographed at night.

TABLE I.

ESTERIFICATION WITH NO ADDED SALT.

Run	K_E	Av. K_E	Concn. HAc Initial	HAc Final	Concn. ETOH Initial	ETOH Final	Concn. H_2O Initial	H_2O Final	Concn. ETAc Final
A	3.686	3.705	866.9	459.8	848.4	441.3	1430.4	1837.5	407.1
B	3.723		866.9	458.6	848.4	439.7	1430.4	1838.7	408.3
C	3.755	3.708	867.8	458.4	847.6	438.2	1433.0	1842.4	409.4
D	3.661		867.8	461.5	847.6	441.3	1433.0	1839.3	406.3

Note - The initial concentration refers to the concentration, expressed in millimols, in the original mixture before reaction occurs. The final concentration refers to the concentration after equilibrium is established.

TABLE II

ESTERIFICATION IN PRESENCE OF NaCl.

Neutral Salt Concn.	Run	K_E	Av. K_E	Concn. HAc Initial	HAc Final	Concn. ETOH Initial	ETOH Final	Concn. H_2O Initial	H_2O Final	Concn. ETAc Final
0.096 N.	A	3.872	3.902	170.9	91.5	163.4	84.0	296.2	375.5	79.3
	B	3.931		170.9	91.0	163.4	83.5	296.2	376.0	79.8
0.200 N.	A	4.089	4.082	865.3	444.7	848.4	427.8	1429.2	1849.8	420.6
	B	4.074		865.3	445.2	848.4	428.3	1429.2	1849.3	420.1
0.285 N.	A	4.221	4.235	866.7	443.5	857.7	434.5	1499.0	1922.2	423.2
	B	4.249		866.7	442.6	857.7	433.6	1499.0	1923.1	424.1
0.400 N.	A	4.413	4.438	866.8	435.4	848.8	417.5	1428.7	1860.0	431.3
	B	4.463		866.8	433.9	848.8	416.0	1428.7	1861.5	432.8

TABLE III.

ESTERIFICATION IN PRESENCE OF NaI.

Neutral Salt Concn.	Run	K_E	Av. K_E	Concn. HAc Initial	Concn. HAc Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETAc Final
0.095 N.	A	3.839	3.848	170.9	91.2	163.6	83.9	290.2	369.8	79.6
	B	3.857		170.9	91.1	163.6	83.8	290.2	369.9	79.7
0.189 N.	A	4.053	4.056	170.9	90.3	163.6	83.0	296.5	377.0	80.5
	B	4.059		170.9	90.2	163.6	82.9	296.5	377.1	80.6
0.289 N.	A	4.128	4.143	170.8	89.3	163.2	81.7	289.3	370.7	81.4
	B	4.159		170.8	89.2	163.2	81.6	289.3	370.8	81.5
0.380 N.	A	4.192	4.186	170.5	89.0	162.8	81.3	292.0	373.4	81.4
	B	4.179		170.5	89.1	162.8	81.4	292.0	373.3	81.3

TABLE IV.

ESTERIFICATION IN PRESENCE OF NaCNS.

Neutral Salt Concn.	Run	K_E	Av. K_E	Conc. HAc Initial	Conc. HAc Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETAc Final
0.095 N.	A	3.893	3.916	170.9	91.4	163.1	83.6	295.7	375.1	79.4
	B	3.939		170.9	91.1	163.1	83.3	295.7	375.4	79.7
0.188 N.	A	3.927	3.973	171.8	91.5	163.3	83.0	291.7	371.9	80.2
	B	4.018		171.8	90.9	163.3	82.4	291.7	372.5	80.8
0.281 N.	A	4.114	4.080	171.3	90.2	163.2	82.1	295.2	376.2	81.0
	B	4.046		171.3	90.6	163.2	82.5	295.2	375.8	80.6
0.368 N.	A	4.319	4.313	170.6	88.3	163.8	81.5	295.8	378.0	82.2
	B	4.307		170.6	88.4	163.8	81.6	295.8	378.0	82.2

TABLE V.

ESTERIFICATION IN PRESENCE OF NaAc.

Neutral Salt Concn.	Run	K_E	Av. K_E	Concn. HAc Initial	Concn. HAc Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETOAc Final
0.097 N.	A	3.488	3.477	170.9	93.8	163.6	86.5	290.5	367.5	77.0
	B	3.466		170.9	94.0	163.6	86.7	290.5	367.4	76.9
0.190 N.	A	3.556	3.552	170.8	93.4	163.1	85.7	290.7	368.1	77.4
	B	3.547		170.8	93.5	163.1	85.8	290.7	368.0	77.3
0.283 N.	A	3.604	3.604	170.8	93.3	163.5	86.0	295.3	372.8	77.5
	B	3.604		170.8	93.3	163.5	86.0	295.3	372.8	77.5
0.376 N.	A	3.621	3.652	170.3	93.1	162.4	85.2	295.5	372.7	77.2
	B	3.683		170.3	93.5	162.4	85.6	295.5	372.3	76.8

TABLE VI.

ESTERIFICATION IN PRESENCE OF NaBr.

Neutral Salt Concn.	Run	K_E	Av. K_E	Concn. HAc Initial	Concn. HAc Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETOAc Final
0.096 N.	A	4.059	4.068	170.7	89.5	163.5	82.3	287.3	368.5	81.2
	B	4.077		170.7	89.4	163.5	82.2	287.3	368.6	81.3
0.191 N.	A	4.094	4.103	170.7	89.6	163.1	81.9	290.1	371.3	81.2
	B	4.111		170.7	89.3	163.1	81.7	290.1	371.4	81.4
0.289 N.	A	4.254	4.256	170.9	88.7	163.3	80.9	289.7	372.1	82.4
	B	4.257		170.9	88.6	163.3	81.0	289.7	371.9	82.3
0.382 N.	A	4.461	4.480	171.1	87.4	163.9	80.2	290.5	374.2	83.7
	B	4.499		171.1	87.2	163.9	80.0	290.5	374.4	83.9

TABLE VII.

ESTERIFICATION IN PRESENCE OF $NaNO_2$.

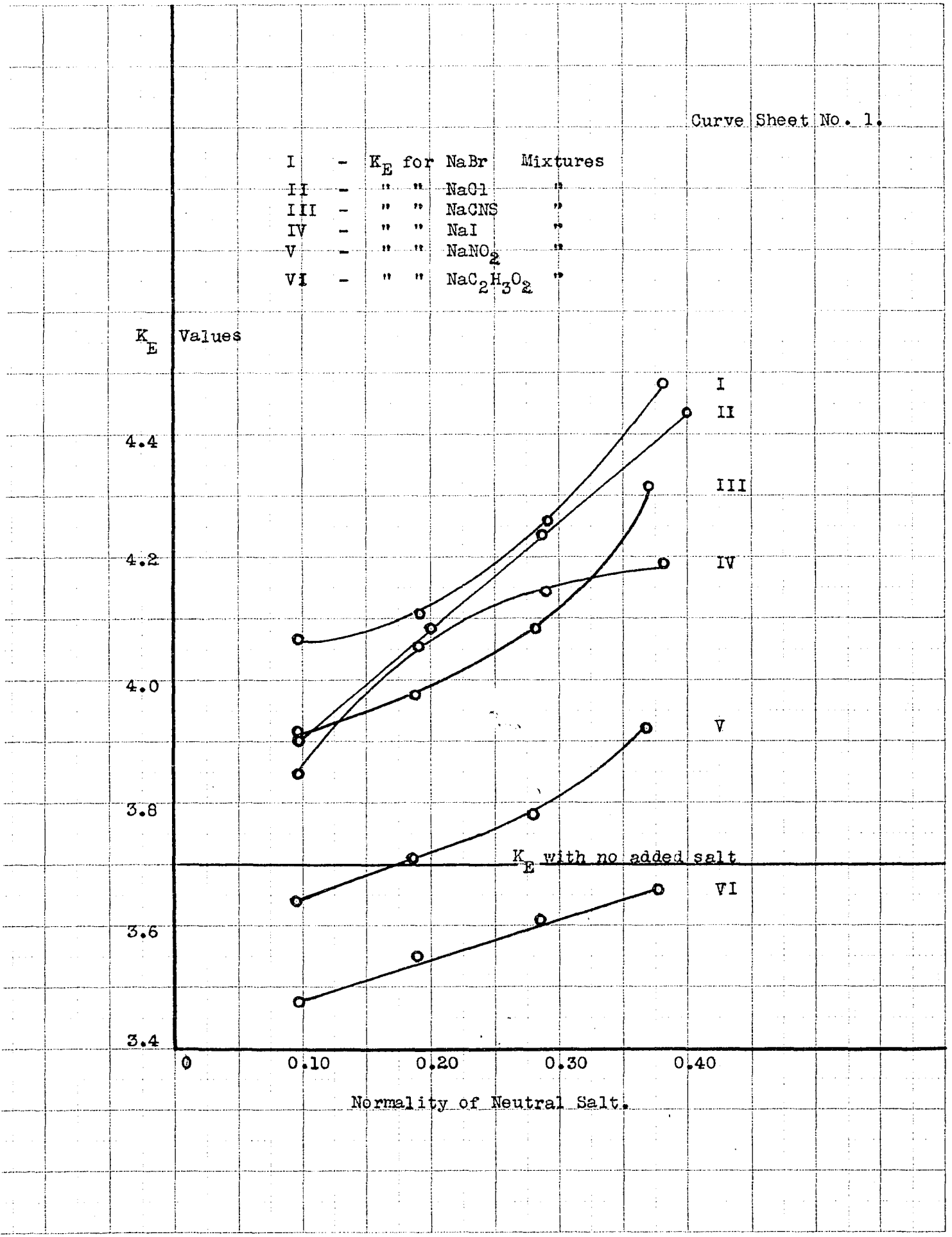
Neutral Salt Concn.	Run	K_E	Av. K_E	Concn. HAc Initial	Concn. HAc Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETOAc Final
0.093 N.	A	3.648	3.640	341.7	186.4	328.2	172.9	599.9	755.2	155.3
	B	3.632		341.7	186.6	328.2	173.1	599.9	755.0	155.1
0.184 N.	A	3.752	3.710	338.6	183.3	326.7	171.4	603.9	759.2	155.3
	B	3.668		338.6	184.5	326.7	172.6	603.9	758.0	154.1
0.279 N.	A	3.829	3.779	340.2	182.5	328.0	170.3	597.6	755.3	157.7
	B	3.729		340.2	183.9	328.0	171.7	597.6	753.9	156.3
0.367 N.	A	3.976	3.924	337.9	179.7	327.1	168.9	604.7	762.9	158.2
	B	3.871		337.9	181.1	327.1	170.3	604.7	761.5	156.8

TABLE VIII.

ESTERIFICATION IN PRESENCE OF HCl.

HCl Concn.	Run	K_E	Av. K_E	Concn. HAc. Initial	Concn. HAc. Final	Concn. ETOH Initial	Concn. ETOH Final	Concn. H_2O Initial	Concn. H_2O Final	Concn. ETOAc Final
0.020 N.	A	3.695	3.677	339.9	184.7	327.0	171.8	599.5	754.7	155.2
	B	3.660		339.9	185.1	327.0	172.2	599.5	754.3	154.8

Curve Sheet No. 1.



DETERMINATION OF REACTION VELOCITY CONSTANTS.

The general procedure in measuring the reaction velocity constants was similar to that described under the determination of equilibrium constants. However, in the latter case it was necessary to take samples frequently in the early stages of the esterification and record the time interval between start and time of removing samples. Since the reaction rate is very slow at room temperature, the actual starting time was not taken until the mixtures were sealed in tubes and the tubes immersed in boiling carbon tetrachloride. The time of stopping was taken when the tubes were withdrawn from the heating flask, and immersed in ice water, prior to titration. Thus the time recorded in the tables represents the time during which the samples were at the temperature of boiling carbon tetrachloride (78° C.)

The method of calculating the velocity constants is that given by Partington[80] . The reaction is reversible and therefore the velocities of both direct and reverse reactions must be considered.

In the equation : -

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Let a, b, c, d, denote the initial concentration in mols per liter of acid, alcohol, ester, and water; and let the amount of change after a

time t be called x.

The velocities of the direct and reverse reactions are

$$\frac{dx_1}{dt} = k_1(a - x)(b - x), \quad \frac{dx_2}{dt} = k_2(c + x)(d + x);$$

hence the velocity of esterification is

$$\frac{dx}{dt} = \frac{dx_1}{dt} - \frac{dx_2}{dt} = k_1(a - x)(b - x) - k_2(c + x)(d + x)$$

To integrate this equation we put

$$\frac{dx}{k_1(a - x)(b - x) - k_2(c + x)(d + x)} = dt.$$

The denominator on the left can be written

$$(k_1ab - k_2cd) - \{k_1(a + b) + k_2(c + d)\}x + (k_1 - k_2)x^2;$$

or dividing by k_2 and putting $k_1 / k_2 = K$,

$$(Kab - d) - \{K(a + b) + (c + d)\}x + (K - 1)x^2;$$

which is of the form $Lx^2 + mx + n$.

To factorize this expression we proceed as follows: -

Let a, β be the roots of the quadratic equation

$$Lx^2 + mx + n = 0.$$

Then, $$a = \frac{-m + \sqrt{m^2 - 4ln}}{2L},$$

$$\beta = \frac{-m - \sqrt{m^2 - 4ln}}{2L},$$

On comparing these results with the expression to be factorized, it is seen that

$$L = K - 1,$$
$$m = -(K(a + b) + (c + d)) = -Q \text{ say},$$
$$n = Kab - cd;$$

thence $a = \frac{1}{2(K-1)} \left(Q + \sqrt{Q^2 - 4(K-1)(Kab - cd)} \right)$,

$$\beta = \frac{1}{2(K-1)} \left(Q \sqrt{Q^2 - 4(K-1)(Kab - cd)} \right),$$

Put $\sqrt{Q^2 - 4(K-1)(Kab - cd)} = P$

Therefore $a = \frac{Q + P}{2(K-1)}$, $\beta = \frac{Q - P}{2(K-1)}$.

Thus $(Kab - cd) - (K(a + b) + (c + d)x + (K-1)x^2 = (x-a)(x-\beta)$.

Now, to split into partial fractions, assume

$$\frac{1}{(x-a)(x-\beta)} = \frac{A}{x-a} + \frac{B}{x-\beta},$$

and, by the usual methods, it is found that

$A = (K-1)/P$, $B = -(K-1)/P$.

The expression is now integrable: -

$$\frac{dx}{(x-a)(x-\beta)} = \frac{(K-1)\,dx}{P(x-a)} - \frac{(K-1)\,dx}{P(x-\beta)} = k_2\,dt$$

Integrating we obtain: -

$$\frac{K-1}{P}(\log(x-a) - \log(x-\beta)) - k_2 t = C$$

To find C put $x = 0$, $t = 0$. Then $C = \frac{K-1}{P} \cdot \log \frac{a}{\beta}$

Hence, $\frac{K-1}{P} \left(\log \frac{x-a}{x-\beta} \right) - k_2 t = \frac{K-1}{P} \cdot \log \frac{a}{\beta}$

or $k_2 = \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{\beta(x-a)}{a(x-\beta)}$

Substituting the values, $a = \frac{Q+P}{2(K-1)}$ and $\beta = \frac{Q-P}{2(K-1)}$

$$k_2 = \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{(Q-P)}{(Q+P)} \cdot \frac{\left(x - \frac{Q+P}{2(K-1)}\right)}{\left(x - \frac{Q-P}{2(K-1)}\right)}$$

$$= \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{(Q-P)\,(2(K-1)x - Q - P)}{(Q+P)\,(2(K-1)x - Q - P)}$$

$$\text{or} \quad k_2 = \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{(Q-P)\,(Q+P-2(K-1)x)}{(Q+P)\,(Q-P-2(K-1)x}$$

From the relationship $\frac{k_1}{k_2} = K_E$, it is now possible to determine the values for k_1 , because the values of K_E were previously obtained, and the values of k_2 are obtained from the above equation.

The values necessary in the equation for k_2 are: -

a equals mols of acetic acid initially
b " " " alcohol initially
c " " " ester "
d " " " water "
x " amount of change after time (t).

For any one mixture the values for Q and P will be the same throughout the course of the reaction, since they depend only on the values of K_E and the initial concentrations: -

$$Q = K(a+b) - (c+d)$$

$$P = \sqrt{Q^2 - 4(K-1)(Kab - cd)}$$

The only variables then in the equation for k_2 are (t) and (x) for a particular mixture. The time was recorded in minutes. It should be noted that the logarithm is to the base (e), and should be multiplied by 2.303 to change to the base 10.

The curves showing the relationship between average values of k_1 and salt concentration are shown on Curve Sheet No. 2. For the average value k_1 , the average of the last three values was taken, because the variation seemed much less than in the initial stages of the reaction.

TABLE IX.

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION WITH NO ADDED SALT.

Time Minutes	k_2	(k_1 = (k_2 x 3.705)
32	.000114	.000421
122	.000114	.000422
171	.000108	.000399
242	.000101	.000392
301	.000102	.000379
359	.000104	.000386
	Average	.000386

TABLE X.

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF NaCl.

Neutral Salt Concn.	Time in Minutes	k_2	$(k_1 = (k_2 \times 3.902)$
0.101 N.	25	.000162	.000633
	80	.000176	.000685
	151	.000163	.000637
	200	.000157	.000613
	260	.000155	.000606
	365	.000161	.000629
		Average	.000616
			$(k_1 = (k_2 \times 4.082)$
0.200 N.	73	.000261	.001070
	138	.000228	.000931
	198	.000222	.000906
	230	.000221	.000903
	288	.000215	.000878
	408	.000186	.000759
		Average	.000846
			$(k_1 = (k_2 \times 4.235)$
0.300 N.	68	.000277	.001173
	100	.000277	.001173
	133	.000259	.001095
	199	.000248	.001051
	227	.000237	.001003
	262	.000228	.000963
		Average	.001006
			$(k_1 = (k_2 \times 4.438)$
0.400N.	69	.000296	.001293
	100	.000273	.001212
	133	.000262	.001165
	161	.000254	.001129
	191	.000246	.001092
	229	.000239	.001060
		Average	.001090

TABLE XI.

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF NaCNS.

Neutral Salt Concn.	Time in Minutes	k_2	$(k_1 = (k_2 \times 3.916)$
0.100 N.	133	.000130	.000509
	165	.000123	.000482
	210	.000118	.000460
	240	.000111	.000436
	272	.000109	.000428
	304	.000105	.000412
		Average	.000425
			$(k_1 = (k_2 \times 3.973)$
0.201 N.	68	.000147	.000583
	106	.000133	.000529
	117	.000133	.000527
	182	.000117	.000463
	221	.000113	.000441
	245	.000109	.000426
		Average	.000443
			$(k_1 = (k_2 \times 4.08)$
0.298 N.	98	.000181	.000742
	137	.000119	.000485
	174	.000116	.000474
	263	.000113	.000452
	297	.000105	.000429
	329	.000108	.000440
		Average	.000441
			$(k_1 = (k_2 \times 4.313)$
0.403 N.	89	.000131	.000567
	124	.000122	.000527
	165	.000116	.000501
	201	.000121	.000520
	238	.000121	.000521
	278	.000120	.000519
		Average	.000520

TABLE XII

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF NaI.

Neutral Salt Concn.	Time in Minutes	k_2	$(k_1 = k_2 \times 3.848)$
0.100 N.	22	.000156	.000602
	42	.000176	.000679
	111	.000143	.000551
	141	.000140	.000539
	171	.000135	.000518
	202	.000133	.000513
		Average	.000523
			$(k_1 = k_2 \times 4.056)$
0.201 N.	62	.005170	.002100
	129	.000287	.001170
	418	.000161	.000653
	435	.000137	.000557
	496	.000145	.000587
	525	.000143	.000581
		Average	.000575
			$(k_1 = k_2 \times 4.143)$
0.301 N.	30	.000480	.001989
	61	.000299	.001241
	90	.000247	.001022
	200	.000147	.000609
	221	.000175	.000727
	319	.000160	.000663
		Average	.000683
			$(k_1 = k_2 \times 4.186)$
0.400 N.	60	.000239	.001005
	88	.000218	.000913
	114	.000266	.000675
	184	.000244	.000605
	320	.000229	.000504
	347	.000244	.000602
		Average	.000583

TABLE XIII

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF NaBr.

Neutral Salt Concn.	Time in Minutes	k_2	$(k_1 = k_2 \times 4.068)$
0.099 N.	53	.000184	.000748
	74	.000174	.000707
	104	.000167	.000679
	129	.000166	.000677
	154	.000157	.000637
	175	.000162	.000659
		Average	.000658
			$(k_1 = k_2 \times 4.103)$
0.208 N.	108	.000225	.000925
	133	.000223	.000915
	166	.000215	.000883
	197	.000205	.000842
	225	.000208	.000854
	259	.000199	.000820
		Average	.000839
			$(k_1 = k_2 \times 4.256)$
0.299 N.	19	.000216	.000919
	38	.000284	.001207
	61	.000274	.001168
	83	.000265	.001128
	108	.000233	.000989
	126	.000266	.001134
		Average	.001083
			$(k_1 = k_2 \times 4.480)$
0.400 N.	141	.000289	.001296
	175	.000288	.001288
	207	.000274	.001229
	242	.000289	.001297
	271	.000281	.001289
	297	.000284	.001270
		Average	.001275

TABLE XIV

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF $NaC_2H_3O_2$.

Neutral Salt Concn.	Time in Minutes	k_2	$(k_1 = k_2 \times 3.477)$
0.099 N.	91	.0000203	.0000704
	315	.0000214	.0000742
	1126	.0000199	.0000692
	1368	.0000191	.0000663
	1597	.0000189	.0000659
	2752	.0000175	.0000607
		Average	.0000643
			$(k_1 = k_2 \times 3.552)$
0.200 N.	1362	.0000201	.0000865
	1582	.0000196	.0000713
	2649	.0000192	.0000682
	2826	.0000194	.0000687
	3054	.0000181	.0000643
		Average	.0000671
			$(k_1 = k_2 \times 3.604)$
0.298 N.	942	.0000189	.0000686
	1158	.0000187	.0000672
	1391	.0000182	.0000656
	2395	.0000189	.0000681
	2575	.0000166	.0000597
	2864	.0000164	.0000591
		Average	.0000623
			$(k_1 = k_2 \times 3.652)$
0.400 N.	1056	.0000173	.0000632
	1235	.0000184	.0000672
	1524	.0000183	.0000669
	2379	.0000179	.0000636
	2679	.0000164	.0000597
	2877	.0000174	.0000636
		Average	.0000623

TABLE XV.

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF $NaNO_2$.

Neutral Salt Concn.	Time in Minutes	k_2		$(k_1 = k_2 \times 3.64)$
0.101 N.	1354	.0000214		.0000779
	1893	.0000211		.0000768
	4365	.0000185		.0000673
	5654	.0000178		.0000648
	6585	.0000188		.0000683
			Average	.0000668
				$(k_1 = k_2 \times 3.71)$
0.200 N.	1215	.0000187		.0000692
	2223	.0000178		.0000609
	5223	.0000159		.0000588
	6612	.0000147		.0000545
	8082	.0000149		.0000554
	9462	.0000132		.0000489
			Average	.0000529
				$(k_1 = k_2 \times 3.78)$
0.300 N.	1393	.0000214		.0000807
	1639	.0000210		.0000792
	1785	.0000207		.0000783
	2906	.0000198		.0000747
	3179	.0000193		.0000730
			Average	.0000753
				$(k_1 = k_2 \times 3.92)$
0.394 N.	1020	.0000191		.0000748
	4020	.0000154		.0000603
	5400	.0000151		.0000591
	6870	.0000146		.0000571
	8250	.0000139		.0000548
	17280	.0000121		.0000475
			Average	.0000531

TABLE XVI.

REACTION VELOCITY CONSTANTS FOR ESTERIFICATION IN PRESENCE OF HCl.

Neutral Salt Concn.	Time in Minutes	k_2	($k_1 = k_2 \times 3.678$)
0.020 N.	41	.000925	.003400
	57	.000915	.003365
	71	.000830	.003051
	86	.000841	.003090
	101	.000818	.003005
	118	.000806	.002963
	132	.000794	.002919
	150	.000782	.002875
		Average	.002919

PART III

DISCUSSION OF RESULTS.

The value of the equilibrium constant for the esterification of ethyl acetate was found to be 3.705. This corresponds with a value 3.7 found by Euler[81], and a like value by Tobin (see page 34), but differs slightly from the value 4.0 given by Berthelot and St. Gilles.

An examination of Curve Sheet No. 1 shows the relation between apparent displacement of the equilibrium constants and the concentrations of the respective neutral salts. These equilibrium constants have been calculated by the classical method, in which the Law of Mass Action applied to equilibrium is expressed by the equation,

$$K_E = \frac{C_{EtAc} \times C_{H_2O}}{C_{HAc} \times C_{ETOH}}$$

The order of the anions in displacing the equilibrium is $Br > Cl > CNS > I > NO_2 > C_2H_3O_2$. It was thought that perhaps the order would be similar to the order of the Hofmeister series, which affect the swelling of gelatine in the order $SO_4 > Cl > NO_3 > Br > I > CNS$. While there is some similarity in these two series, they are not parallel. The effect of all of the salts is greater with increasing concentration. $NaNO_2$ at low concentration, and $NaC_2H_3O_2$ at

all the concentrations investigated gave values of K_E less than the normal 3.7 obtained in absence of salts.

PERCENTAGE OF ESTER FORMED WITH VARIOUS SALT CONCENTRATIONS

Salt Concn.	NaBr	NaCl	NaCNS	NaI	$NaNO_2$	$NaC_2H_3O_2$
0.1 N.	49.74	48.51	48.80	48.75	47.45	47.12
0.2	49.83	49.62	49.23	49.33	47.62	47.44
0.3	50.45	49.45	49.51	49.84	47.87	47.48
0.4	51.12	50.83	50.20	50.01	48.13	47.30

Ester formed with no Added Salt equals 48%
Ester formed in presence of 0.02 N-HCl equals 47.5%

The actual increase in percentage ester formed with salts never amounted to more than about 3% greater than in the absence of them. This increased value is considerable, however, when we consider the relatively large amount of water present in the reaction mixture. The ratio of the several constituents initially present in the reaction mixture was : - 1 mol acid: 0.97 mol alcohol: 1.7 mols water.

Viewed from the deviation in the equilibrium constants from the normal value 3.7, the results show a much wider variation.

PERCENTAGE DEVIATION OF THE EQUILIBRIUM CONSTANTS FROM THE NORMAL 3.7 .

Salt Concn.	NaBr	NaCl	NaCNS	NaI	$NaNO_2$	$NaC_2H_3O_2$
0.1 N.	9.92	5.40	5.84	4.02	- 1.63	- 6.03
0.2	10.90	10.28	7.37	9.14	0.27	- 4.00
0.3	15.01	14.48	10.30	12.00	2.18	- 2.59
0.4	21.10	19.90	16.57	13.18	6.05	- 1.30

An examination of the cause of the displacement of an equilibrium in terms of the classical mass action expression, shows that in general displacement is possible when any one of the conditions such as temperature, pressure or concentration changes.

In the case of the present investigation the latter condition - was the only variable which we believe may have been altered, because the temperature was kept approximately constant by the device mentioned in the experimental method, and the pressure was fairly uniform because the tubes were filled with liquid, in so far as practicable, before being sealed. (However, in the case of the mixtures containing sodium nitrite there was considerable pressure developed and a number of filled tubes broke in heating.)

When we say that the concentration may have been altered we do not mean that there was any variation in the proportion of the actual amounts of alcohol, acid and water initially present in the several mixtures, but that the effective water concentration may have been changed. This may be accounted for in either of two

ways -

(1) It is well known that liquid water exists in several forms H_2O, $(H_2O)_2$, $(H_2O)_n$, etc., hydrol, dihydrol, polyhydrol. There is at all times of course an equilibrium existing between these several polymerized forms of water. But it is possible that the addition of salts causes a shift in this water equilibrium. Bancroft[67] considers the greater peptizing action of potassium iodide over potassium chloride on gelation in water to the water equilibrium being shifted in the direction of more hydrol, which is the real peptizing agent. This goes back to one of the explanations offered by Arrhenius that there is a change from inactive to active molecules.

(2) Another, and in some respects more easily grasped explanation is that the equilibrium displacement is due to a loss of water content through formation of hydrates. Schlesinger has suggested this idea, but in his investigations he worked with $CaCl_2$ as well as NaCl, and found that the former salt which takes up both alcohol and water acts similar to NaCl which takes up only water.

If the formation of hydrates in solution is the cause of the displacement, then the results indicate the order of hydration of the respective anions, since the same cation sodium was used throughout.

The displacement of an equilibrium may be interpreted in terms of the activity theory as due to the influence of the added

salt in changing the activity of water and probably also the activities of the other constituents. Thus McBain and Kam [82] determined the vapor pressure of acetic acid over solutions containing added salt and concluded from their results that "the undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts." Such changes in chemical potential would result in a change in the value of K_a, the activity equilibrium constant.

This latter idea was also proposed by Acree [83] who states that "the thermodynamic potential, or driving force behind each reaction depends not only on the reacting substances, but also on the surrounding field; the addition of salt affects the field and therefore the thermodynamic potential."

The reaction velocities calculated according to the classical method for a bi-molecular reaction, are shown graphically on Curve Sheet No. 2. The effect of the anions in increasing the reaction velocity seems to be almost the same order as that indicated in the displacement of the equilibrium, except that here the iodide seems to have a greater effect than the thiocyanate ion. The iodide values must be accepted with some doubt because the reaction tubes containing these mixtures always showed the presence of free iodine, which no doubt affected the results.

Curve Sheet No. 2.

Reaction Rate Curves

I - K_1 for NaBr Mixtures

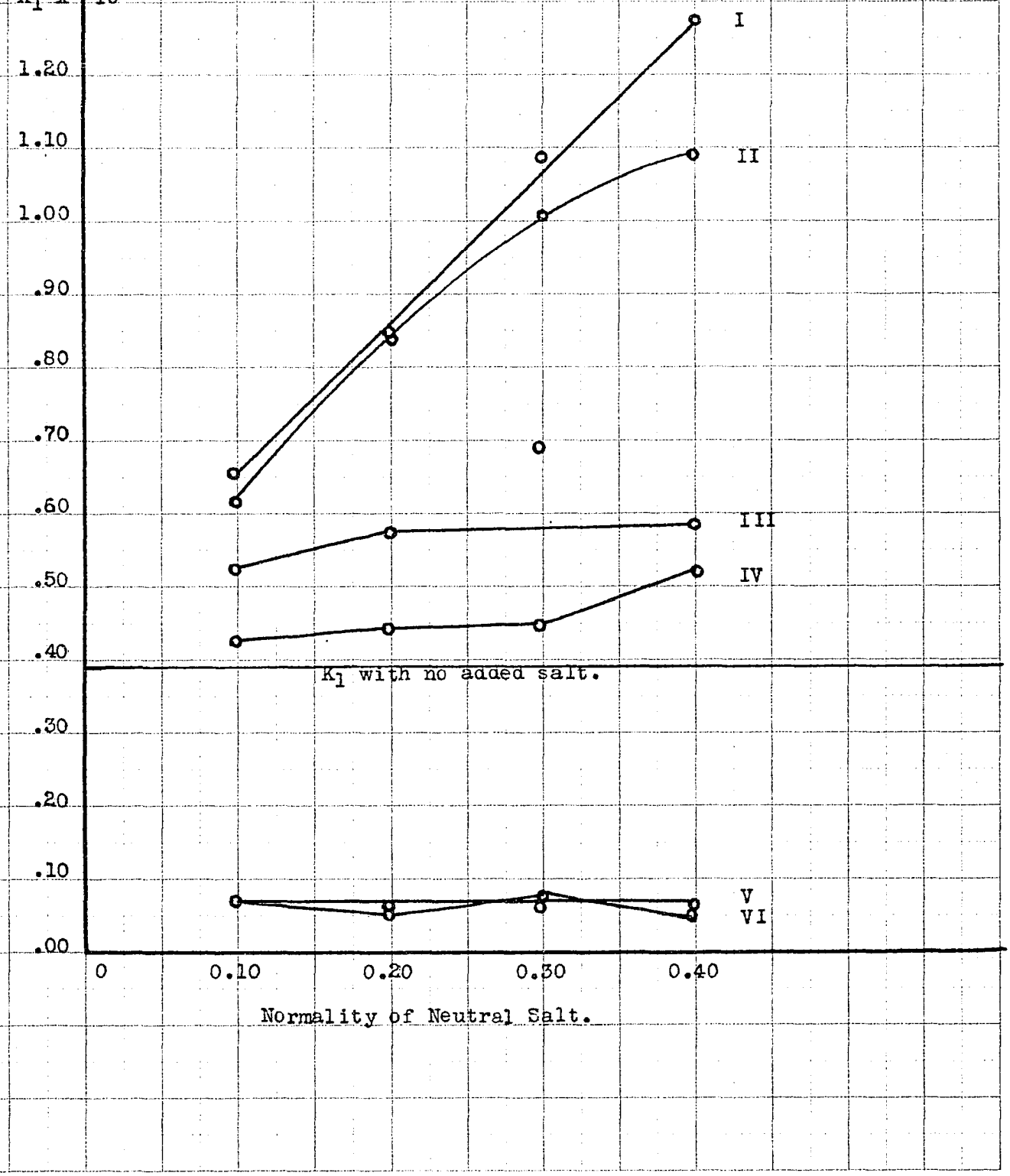
II - " " NaCl "

III - " " NaI "

IV - " " NaCNS "

V - " " $NaC_2H_3O_2$ "

VI - " " $NaNO_2$ "



The following summary shows the percent deviation of the velocity constants, from the normal value .000386.

Salt Concn.	NaBr	NaCl	NaI	NaCNS	$NaNO_2$	$NaC_2H_3O_2$
0.1 N.	70.5	59.5	35.5	10.1	- 82.6	- 83.2
0.2	117.5	119.0	48.9	14.79	- 86.1	- 82.6
0.3	180.7	160.5	76.9	14.28	- 80.5	- 83.7
0.4	230.2	182.0	51.0	34.70	- 86.4	- 83.7

Percent deviation with 0.2 N. HCl equals 655.

The cause for the increased velocities, i.e. the catalytic effect, has been explained by various theories. The generally accepted view, based on the original idea of Arrhenius and Ostwald, is that H^+ and $\bar{O}H$ ions are the sole catalysts in such reactions as cane sugar inversion and ester hydrolysis. However, the velocity of the reaction is not always proportional to the H^+ and $\bar{O}H$ ion concentration. Lapworth believes that catalysis is due to the non-hydrated hydrion. Goldschmidt ascribes the catalytic effect to the hydrogen ion alcholate. Some reactions seem to be catalyzed by both anion and cation of the catalyst, that is the velocity of the reaction is proportional to the square of the acid concentration. This gives rise to the "dual theory" of catalysis. A number of these theories have been reviewed in Part I.

Most of the investigations of others involving the study of the effect of neutral salts on esterification rate have been done in the presence of HCl and the increased velocity has been attributed to the increase in hydrogen ion concentration. Thus Wilson[62] says

that removal of solvent by hydration is the cause of the increased hydrogen ion concentration, while Akerlof[65] believes the water sheath of the hydrogen ion is changed by the addition of neutral salts. Dhar[65A] says the effect of neutral salts is highly specific, some retarding and others accelerating the speed of reaction.

Our results seem to confirm the last statement. The present investigations were made in the absence of mineral acid, so that if the addition of neutral salts varied the hydrogen ion concentration, it was the hydrogen ion concentration resulting from the reaction mixture acetic acid, ethyl alcohol and water.

Bronsted[41] points out that the dissociation of a weak acid is more dependent on the total salt concentration, the lower the dielectric constant of the solvent. Hence, whatever dissociation there is of acetic acid in water solution, would be enhanced in an esterification mixture of alcohol, acid, water and the added salt.

INTERPRETATION OF RESULTS IN TERMS OF THE ACTIVITY RATE THEORY.

The so-called activity rate theory has been developed by Harned[70], W. C. McC. Lewis[72], Scatchard[84] and Fales[85]. In this concept the velocity is assumed proportional to the activity of the reagents, and for the bimolecular process $A + B \longrightarrow C + D$, we represent:

$$\text{velocity} = V = k' a_A a_B = k \cdot c_A \cdot c_B \cdot f_A \cdot f_B \qquad (1)$$

where the symbols a, c and f stand respectively for activity, concentration and activity coefficient.

This differs from the classical theory which expresses the

$$\text{velocity} = V = k_1 \cdot C_A \cdot C_B , \qquad (2)$$

if the concentration of the reciprocal system is considered to have no effect upon the velocity with which A and B react. The latter expression holds only for dilute solutions in an unchanging medium.

Since activities for the reaction constituents were not available, in order to interpret our results in terms of the activity rate theory the following mathematical and graphical method was employed.

In the two equations given for velocity of esterification, the velocity (V) is the same. Therefore we can equate (1) and (2)

$$k_1 C_{EtOH} \cdot C_{HAc} = k' f_{EtOH} \cdot C_{EtOH} \cdot f_{HAc} \cdot C_{HAc}$$

or

$$k_1 = k' f_{EtOH} \cdot f_{HAc} \qquad (3)$$

Taking the logarithm of both sides of this equation,

$$\log k_1 = \log k' + \log f_{EtOH} + \log f_{HAc} \qquad (4)$$

Now according to Debye and McAuley[56] the variation of the activity coefficient of a non-electrolyte in an aqueous salt solution may be represented by an equation,

$$\log \frac{fo}{u} = k$$ where fo is the activity coefficient of the non-electrolyte and k is a constant which depends upon the properties of the salt and the non-electrolyte present[86], and u is the ionic strength of the salt. The value of $u = c. \frac{Z_1 + Z_2}{2}$, where c is equivalent concentration and Z_1 and Z_2 are the valences of the two ions of the uni-univalent salts employed. Hence (u) is equal to (c) for our case. Then substituting in (4) the value (uk) for log f we have

$$\log k_1 = \log k' + uk_{EtOH} + uk_{HAc}$$

and since (u) is the same we can represent the last two terms by mu where m is a constant equal to $(k_{EtOH} + k_{HAc})$. Hence

$$\log k_1 = mu + \log k' ,$$

which is the equation for a straight line, similar to the familiar

$$y = ax + b.$$

Using this equation the values of u (salt concentration) were plotted as abscissae against values of $\log (k_1 \times 10^5)$ as

ordinates. These curves are shown on Curve Sheet No. 3.

The intercepts on the y axis should then give the values of log k' which is the velocity constant of the activity theory. Extrapolating the curves to zero concentration and obtaining values of k' we get,

k'	from	NaBr	Curve	equals	.000537
k'	"	NaCl	"	"	.000457
k'	"	NaI	"	"	.000467
k'	"	NaCNS	"	"	.000437

While these values are not identical as should be the case at zero salt concentration, the three later values are quite close. They are somewhat higher than the value .000386 obtained from the ordinary velocity method using concentrations.

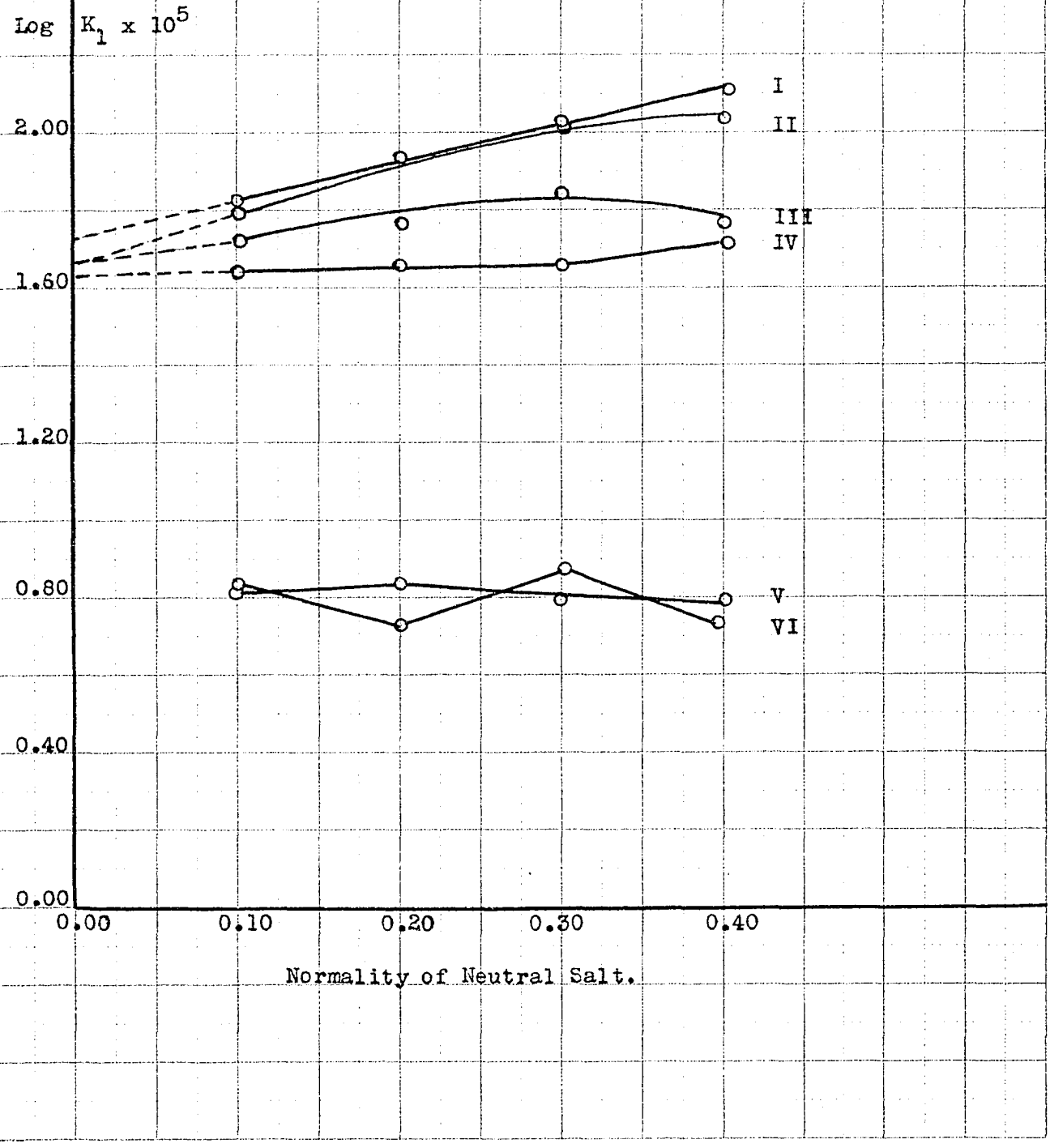
Pertaining to this interpretation of the results it may be mentioned that Harned and Seltz tried to employ an equation

$$K_T = \frac{k}{a_H \times a_{Cl}}$$

(where k is the velocity constant from the ordinary monomolecular equation, and K_T is a constant at any given temperature) to the study of the formation of parachloro-acetanilide from acetyl-chloro-amino benzene. They found that the equation held very well for HCl but failed to hold in the presence of the neutral salts.

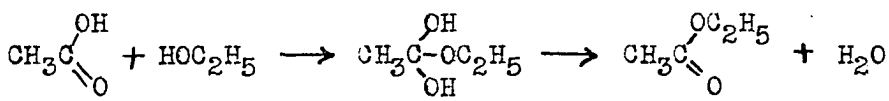
Curve Sheet No. 3.

I - Curve for NaBr Mixtures
II - " " NaCl "
III - " " NaI "
IV - " " NaCNS "
V - " " $NaC_2H_3O_2$ "
VI - " " $NaNO_2$ "



APPLICATION OF BRONSTED'S THEORY.

If we assume the type of mechanism, proposed by Bronsted, we will formulate an esterification as first involving the slow formation of an unstable intermediate complex, followed by a rapid decomposition to the final reaction products.



The reaction velocity is then formulated:

$$V = k.f_{EtOH}.C_{EtOH}.f_{HAc}.C_{Hac}.\frac{1}{f_x} \qquad (1)$$

in which k equals reaction velocity constant.
c " concentrations of substances indicated.
f " activity coefficient of " "
f_x " " " " the intermediate compound.

Since our data furnishes only concentration values, it was necessary in applying the above concept to use a method similar to the one employed for the activity rate theory. Comparing equation (1) with the equation

$$V = k_1 C_{EtOH} C_{HAc} \qquad (2)$$

we see that the velocities are equal and hence we can equate,

$$k_1 C_{EtOH} \cdot C_{HAc} = k\, f_{EtOH} \cdot C_{EtOH} \cdot f_{HAc} \cdot C_{Hac} \cdot \frac{1}{f_x}$$

or

$$k_1 = k \cdot \frac{f_{EtOH} \cdot f_{HAc}}{f_x} \qquad (3)$$

Now using the previously described idea of Debye and McAuley that the activity coefficient of a non-electrolyte is expressed by the relation,

$$\log \frac{f}{u} = \text{constant}$$

we will assume $\log f_{EtOH} = k'u = k'C$

$\log f_{HAc} = k''u = k''C$

$\log f_x = k'''u = k'''C$

If we take the logarithm of equation (3) and then substitute the values just given,

$$\log k_1 = \log k . \log f_{EtOH} \cdot \log f_{HAc} - \log f_x$$

and after substitution,

$$\log k_1 = \log k + (k' + k'' - k''')C$$

Now let $(k' + k'' - k''') = k_i$. Then the equation becomes,

$$\log k_1 = k_i C + \log k$$

which is the same as the equation obtained for the activity rate theory.

Bronsted says that the two theories lead to practically identical results when the critical complex is uncharged, i.e. when the two reacting ions carry charges of the same magnitude but of opposite sign.

SUMMARY

1. The ethyl acetate equilibrium depends upon the equality of the sum of the chemical potentials of the ethyl alcohol and acetic acid to the sum of the chemical potentials of the ethyl acetate and water. Any change in the thermodynamic environment may change the value of one or more of these potentials, thereby giving a new value for the equilibrium constant.

2. The value of the equilibrium constant for the esterification of ethyl acetate at 78° was found to be 3.705.

3. The displacement of the equilibrium constant, in the presence of six neutral salts, was measured and found to increase with increasing salt concentration. With sodium chloride the equilibrium constant increases linearly, but in the other cases the effect is more complicated. Sodium acetate depresses the value of the equilibrium constant.

4. The order of the effects of the anions upon the equilibrium constant is not that of the Hofmeister series, but each of the anions seems to exercise a specific effect.

5. The reaction velocities were calculated according to the classical method for bimolecular reactions, in which the velocity of both forward and back reaction is considered. Knowing

the values for the equilibrium constants (K_E) in the several mixtures and from the relation $K_E = \frac{k_1}{k_2}$ we obtain the value of $k_1 = K_E \cdot k_2$, after k is found from the integrated form of the equation,

$$\frac{dx}{dt} = k_1 (a - x) (b - x) - k_2 (c + x) (d + x)$$

which assumes a form,

$$k_2 = \frac{1}{t} \cdot \frac{K-1}{P} \log \frac{(Q-P)(Q+P-2(K-1)x)}{(Q+P)(Q-P-2(K-1)x)}$$

where $Q = K(a + b)(c + d)$

$$P = \sqrt{Q^2 - 4(K-1)(Kab - cd)}$$

6. The order of the anions in increasing the velocity of esterification was almost the same as the order of the effect in displacing the equilibrium. The increased velocity in the presence of neutral salts seems to be due to the increase in hydrogen ion concentration.

7. Interpretations of the results were made in terms of the activity rate theory, and the velocity reaction theory of Bronsted.

8. In addition to the experimental work done, which involved approximately six hundred esterifications in sealed tubes, a fairly exhaustive search of the literature of previous work was made. Abstracts of this phase of the work are given in Part I.

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