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The Hydrolysis of Sodium Sulfide in  
Mixtures with Sodium Hydroxide

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THE HYDROLYSIS OF SODIUM SULFIDE IN  
MIXTURES WITH SODIUM HYDROXIDE

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## INTRODUCTION AND OBJECTIVES

In the sulfate or kraft process, wood is cooked in a solution, the active chemicals of which are sodium hydroxide and sodium sulfide. Considerable sodium carbonate is also present in the cooking liquor.

Cooking conditions vary a great deal within the sulfate industry. Most mills, however, operate with 17 to 22 per cent active alkali (as  $\text{Na}_2\text{O}$  and based upon the dry wood weight), cooking from two to six hours at a maximum temperature of 165 to 180° C., with a liquor-to-wood ratio between 3:1 and 5:1. Sulfidities  $\left( \frac{\text{Na}_2\text{S}}{\text{Na}_2\text{S} + \text{NaOH} + \text{Na}_2\text{CO}_3} \right)$  (all as  $\text{Na}_2\text{O}$ ) in modern kraft mills are approximately 25 per cent, although the optimum value is somewhat higher. A typical cooking liquor analysis, translated into molarities, gives a solution 1.3 molar in sodium hydroxide, 0.25 molar in sodium sulfide, and 0.13 molar in sodium carbonate, although there is a wide range of variation in the industry both above and below these values.

As is the case with many of our modern industrial developments, the technology of sulfate pulping has far outstripped its theoretical background. Although the process is more than sixty years old and the annual production of sulfate pulp in the United States is now well over four million tons, the chemical reactions by which this pulp is produced from wood are only vaguely defined.

The heterogeneity of the reactions is one of the greatest obstacles preventing their exact definition. Another, less evident factor is the lack of information as to the state of the simple inorganic compounds in the liquor under the conditions of reaction. Before attempting

to decide how these compounds react with the wood, it would seem necessary to know, for example, whether they are reacting as unhydrolyzed compounds, partially hydrolyzed compounds, or completely hydrolyzed compounds and, if partially hydrolyzed, to know (at least approximately) the position of the hydrolytic equilibria.

The purpose of this thesis was to investigate these hydrolytic equilibria for the more important compounds undergoing partial hydrolysis in a sulfate cooking liquor. Sodium sulfide, sodium carbonate, sodium acetate, and the sodium salts of a few of the higher organic acids might be of interest in this respect. This investigation was concentrated upon sodium sulfide, with some work being done on sodium carbonate. Data were obtained on sodium sulfide at temperatures as high as 165° C., whereas the work on sodium carbonate was limited to room temperature.

Finally, it was the object of this thesis to combine the information obtained on hydrolytic equilibrium conditions with a critical examination of existing sulfate pulping theory and, thus, to formulate as complete a picture as possible of the reactions taking place in a sulfate digester.

## HISTORICAL REVIEW

### SULFATE PULPING

The amount of wood pulp produced annually by the sulfate, or kraft, process has shown a rapid increase since Dahl (U. S. patent 296,936 (1884)) suggested the use of sodium sulfate as the make-up chemical for alkaline pulping. In the United States, 4,588,016 tons of sulfate pulp were produced during 1946 (1), and the process is now by far the most important of the pulping processes from a tonnage standpoint.

In the sulfate process, the wood is cooked in a liquor containing sodium hydroxide and sodium sulfide as the active chemicals in a ratio of roughly 2:1 as will be discussed later. The sodium sulfide is formed by the reduction of sodium sulfate with carbon in the chemical recovery operation. Hodges (2) gives the following typical analyses for undiluted cooking liquor (white liquor) in several kraft mills:

	Grams per liter		
	<u>A</u>	<u>B</u>	<u>C</u>
$\text{Na}_2\text{CO}_3$	19	17	19
$\text{Na}_2\text{S}$	26	22	41
$\text{NaOH}$	71	77	68
$\text{Na}_2\text{SO}_4$	1.7	2	1.7
$\text{Na}_2\text{S}_2\text{O}_3$	2.5	2.5	6.2
$\text{Na}_2\text{SO}_3$	6.0	0.24	1.1

There are mills using white liquors with concentrations considerably higher than these.

Some of the terms commonly used in connection with sulfate pulping are defined below.

Total chemical: all sodium salts expressed as  $\text{Na}_2\text{O}$ .

Green liquor: the term for the liquor (before it has been causticized) made by dissolving the recovered chemicals in water and weak liquor.

Total alkali:  $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ , all expressed as  $\text{Na}_2\text{O}$ .

Active alkali:  $\text{NaOH} + \text{Na}_2\text{S}$ , expressed as  $\text{Na}_2\text{O}$ .

Total titratable alkali:  $\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$ , all expressed as  $\text{Na}_2\text{O}$ .

Liquor ratio: the total weight of liquor and diluent put into the digester divided by the dry weight of the wood chips.

Sulfidity:  $\text{Na}_2\text{S}$ , expressed as  $\text{Na}_2\text{O}$ , divided by total titratable alkali, the result expressed as per cent.

Kress and McGregor (3) showed that a sulfidity of 33 per cent gave optimum results for screened yield and permanganate number, although Bray, Martin, and Schwartz (4) stated that the sulfidity could be increased almost indefinitely, as long as the total sodium hydroxide concentration (that added plus that formed by hydrolysis of sodium sulfide) was kept above a certain minimum. They assumed complete hydrolysis of the sodium sulfide. Hanson (5) supported Bray and his co-workers with his findings, which indicated that optimum sulfidity increased as the ratio of active chemical to wood was increased. Mitchell and Yorston (6) believed that all the sodium hydroxide in a kraft cook could be replaced by sodium sulfide if enough sodium sulfide was furnished to keep the liquor alkaline throughout the cook.

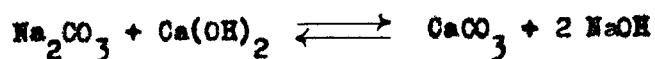
The 33 per cent figure given by Kress and McGregor is the optimum for the active chemical ratios used in commercial practice. In



the early days of sulfate pulping, it happened that the amount of make-up chemical required in the recovery process was such that the sulfidity was maintained near this value. With more efficient modern recovery practice, however, the sulfidity has dropped to about 25 per cent or less, and the pulping quality of the liquor has dropped with it. The drop is not a serious one, fortunately, although it is of sufficient importance to cause many modern mills to experiment with various methods for raising the sulfidity without increasing the inventory of sodium salts.

Niter cake ( $\text{NaHSO}_4$ ) has been added in the furnace. Sulfur or sulfur dioxide has been added to the black liquor before burning, and the use of sulfur through the blow pipes of the Tomlinson recovery furnace has been recommended. The use of gypsum in the furnace is another method that has received consideration. Savell (7) claims that a sodium carbonate-sulfur mixture, formed by melting sulfur with the carbonate, is a complete substitute for ordinary salt cake as a make-up chemical. Bray and Singer (8) suggested the use of by-product sodium sulfite as a make-up chemical and, also, the possibility of diluting kraft cooking liquor with spent, neutral sulfite, semichemical liquor. Their results have indicated that both sodium sulfite and sodium thio-sulfate are active pulping agents when used with sodium hydroxide to replace part or all of the usual sodium sulfide.

In addition to its more evident effects on the cooking process, the sulfidity influences the degree of completion of the causticizing reaction in the recovery process.



According to Hodges (2), increased sulfidity gives increased sodium hydroxide from the hydrolysis of sulfide and thus limits the completeness of the causticizing during the time that the slurry of sodium carbonate and calcium hydroxide is retained in the causticizing agitators. In the Dorr recausticizer this period is about an hour at a temperature of 85 to 90° C.

The chemical reactions that occur during sulfate pulping are still largely unknown. Hisey (9) stated that these reactions have a heterogeneous nature and that both carbohydrates and lignin decompose in the presence of alkali at elevated temperatures. Kleson was one of the school which believe that the so-called protective effect of sodium sulfide on the fiber is a result of the fact that the sodium sulfide becomes available as alkali only in the amount that caustic is consumed.

This theory, that the sodium sulfide acts largely as a reservoir of sodium hydroxide to permit a sufficient degree of pulping to be accomplished without the use of high initial alkalinity, was investigated in some work carried out under the direction of Koon (10) at The Institute of Paper Chemistry. Koon stated that the dissociation constants of hydrogen sulfide and carbonic acid were of the same order but that, when sodium sulfide was replaced with increasing amounts of sodium carbonate in a series of kraft cooks on loblolly pine, the pulping action decreased to the point of scarcely defibering the wood when only sodium hydroxide and sodium carbonate were present. Substantiation of the poor pulping action of sodium carbonate is found in the work of Aronovsky (11), who concluded that this compound is not a true pulping agent and

is inert as far as delignification is concerned. On the other hand, Jayne, Wagenbach, and Deloff (12), in sulfate cooks on European beech, credited a certain degree of reactivity to small amounts of sodium carbonate present in the liquor because of incomplete recausticizing.

Hodges (2) stated that, in the presence of proper initial concentrations, the attack of sulfate liquor on cellulose was inhibited to a large extent by the reduced concentration of sodium hydroxide, the buffer action of the sodium-lignin complex, and the reducing action of sodium sulfide. The extent of buffer action in a highly alkaline cooking liquor would seem to be very limited, however. Hanson (5) attributed the pulping action of sodium sulfide to a practically complete hydrolysis to hydrosulfide and the introduction of sulfur groups into the lignin by the action of this compound, thus increasing the acidity of the lignin and rendering it more soluble in alkali. Hanson also stated that wood could be pulped with sodium hydrosulfide alone but, in subsequent experiments, Buchanan and Koon (13), in an attempt to duplicate this work, found that carefully prepared and analysed sodium hydrosulfide had no pulping action. They concluded that the hydrosulfide used by Hanson was actually largely sodium sulfide. Hossfeld, Gortner, and Kaufert (14) gave further evidence in support of this conclusion. Alcohol-benzene extracted aspen sawdust was not pulped when cooked with aqueous solutions of pure sodium hydrosulfide; the presence of sodium sulfide, however, even in small amounts, resulted in good pulping action. These authors proposed that lignin may be present in wood as a labile complex of monomeric units, and that sodium hydrosulfide from the hydrolysis of sodium sulfide breaks down this primary lignin complex to give sulfur-

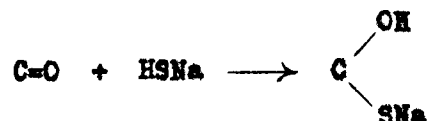
containing oils which are immediately soluble in the alkaline liquor. These oils are polymerized by the excess alkali at high temperatures to give lignin as it appears in the black liquor.

Bray, Martin, and Schwartz (4) assumed that the hydrolysis of sodium sulfide to hydrosulfide is complete in a sulfate cooking liquor. Their results, from experiments in which the sodium hydroxide concentration (including that from the assumed, complete hydrolysis of sodium sulfide) was held at 20 per cent and the sulfidity varied from 0 to 100 per cent, indicated that sodium sulfide had a specific pulping action in addition to its contribution of alkali through hydrolysis. Bixler (15) found, from a series of microdigestions of sprucewood sections followed by microscopic examination, that both sulfate and soda liquors had a selective action, reacting with the highly lignified intercellular material before having any noticeable action on the slightly-lignified secondary wall. This was not the case in a sulfite cook, where the liquor acted simultaneously on the ligneous intercellular material and the secondary fiber wall. Bixler stated further that the delayed action of the liquor on the small amount of lignin present with the carbohydrates in the secondary wall is probably the reason for the difficulty in removing the last two per cent of lignin in an alkaline cook.

According to Brauns (16), the lignin in sulfate black liquor is precipitated, together with some hemicelluloses, when the liquor is acidified with mineral acids. The lignin, after purification, is obtained as a light brown powder, consisting of a mixture of thioglignin and alkali lignin. Although the exact mechanism of the reaction between

sodium sulfide and lignin is not yet known, Brauna stated that there is little doubt that a mercapto group is formed in the lignin molecule as a result of the partial hydrolysis of sodium sulfide to hydrosulfide.

Ahlm (17) investigated the thiolignin obtained by cooking black spruce with sodium sulfide. This thiolignin contained 3.7 per cent sulfur, or one sulfur group per lignin building unit (molecular weight of 840). Methylation with methanol and hydrochloric acid gave one new methoxyl group, whereas methylation with diazomethane gave three new methoxys per building unit. The thiolignin also formed a mercury salt. From this evidence, it is postulated that sodium hydrosulfide formed by hydrolysis reacts with a carbonyl group in the lignin to form a labile mercapto group and a hydroxyl group, giving three groups per building unit capable of forming sodium salts (one mercapto and two hydroxyl groups). The presence of the sulfur in the structure increases the alkali solubility of the lignin. The formation of the mercapto group allegedly occurs according to the following reaction:



Hanson (5), pulping with what was actually a sodium sulfide-sodium hydrosulfide mixture, introduced a maximum of ten per cent of sulfur, or three groups per lignin building unit.

Hagglund (18), in a recent work on thiolignin in sulfate cooking, gives a very interesting theory of the role of sulfur. He states that, at the beginning of the cook, the wood takes up large

amounts of sulfur which can be largely split off with hydrochloric acid. As the cook progresses, carbohydrates also take up sulfur. Ten per cent of the lignin goes into solution below 100° C., but the rapid dissolution of the lignin decreases when the lignin content drops to 25 per cent of the original lignin. The lignin in the middle lamella is attacked last and thus has a chance to condense and become less soluble during the cook. Hagglund<sup>11</sup> proposes this as the reason for the slow solution of lignin toward the end of a sulfate cook. The hydrosulfide group is purported to act on the lignin by splitting a very labile oxygen bridge or by addition to a double bond, similar to the behavior of the sulfonic acid group in a sulfite cook.

Arrhenius (19), working with the data of Bruun, determined the relative rates of solution of cellulose and "incrustants" in sodium hydroxide under varying conditions of temperature. He found that the ratio of the rate of solution of "incrustants" to that of cellulose decreased with rising temperature. Values at 160° C. and 170° C. were 12.5 and 8.7, respectively. The "incrustants" were found to dissolve in sodium sulfide at about the same rate as in sodium hydroxide, but the rate of solution of cellulose was greatly diminished.

Hodges (2) has divided the sulfate cooking cycle into three parts: (1) the penetration and pressure-raising period, (2) the full-pressure period, and (3) the gassing-down period. Most of the chemical reactions are practically complete at the end of the first period; in fact, some mills cook without a full-pressure period. According to Hodges, during this first period air is removed from the digester, the

liquor penetrates the chips, and the volatile oils distill with the steam. The more soluble carbohydrates are attacked to a greater extent than the lignins under these conditions. Somewhere between a pressure of 40 and 60 pounds per square inch ( $131^{\circ}$  C. and  $145^{\circ}$  C.), mercaptans and sulfides begin to form. It is apparently in this region that the sulfur combines with the lignin and increases its solubility in alkali, thus bringing about a rapid increase in the rate of delignification and in the ratio of lignin to carbohydrates dissolved. As a pressure of sixty pounds per square inch is approached, the evolution of noncondensable gases begins to taper off, and the attack on the cellulose increases. This attack is said to be inhibited to a large extent by the reduced sodium hydroxide concentration, the buffer action of the sodium-lignin complex, and the reducing action of sodium sulfide. Noncondensable gases should be removed from the digester as formed since, through the exertion of false pressures, they will inhibit the steam distillation and cause some ordinarily volatile reaction products to remain in the digester. These products supposedly slow down the delignification, but not the degradation, of cellulose.

Scandinavian mills obtain a more uniform and stronger pulp by prolonging the period at low temperatures, using twenty minutes to an hour in the region of 25 to 700 pounds per square inch of gage pressure.

Borlew and Pascoe (20) disclosed some interesting data on sodium hydroxide and sodium sulfide consumption during a mill-scale kraft cook. Their data indicated that, although consumption of caustic followed a hyperbolic relationship with cooking time throughout the cook,

consumption of sodium sulfide was essentially confined to the first hour.

After sixty minutes of cooking, 63 per cent of the sodium hydroxide and 24 per cent of the sodium sulfide in the white liquor had been consumed. After four hours, the consumption was 91 per cent of the sodium hydroxide and 30 per cent of the sodium sulfide. These authors do not believe that sodium hydrosulfide exists in sulfate black liquors and state further that this compound cannot exist at a pH higher than 8.3.

Mitchell and Torston (21) have applied the laws of monomolecular reaction to the rate of delignification of wood with sodium hydroxide and with sodium sulfide. Their equations were in fairly good agreement with experimental results on sodium hydroxide, except for the latter part of the digestion. They attributed this disagreement to the location in the cell wall of the last portion of the lignin to be removed and the consequent hindrance to its diffusion. In experiments with sodium sulfide at 150° C., 160° C., and 170° C., the following equation was developed:

$$- \frac{d Ly}{dt} = k(Na_2S)(Ly - a)$$

where  $Ly$  = amt. of lignin remaining in the wood

$a$  = a constant to account for the small amount of lignin in the cell wall

$k$  = 1.25 at 150° C., 2.96 at 160° C., and 5.30 at 170° C.

An unexpected direct proportionality of the rate of delignification to the sodium sulfide concentration was indicated, although the hydrolysis of sodium sulfide supposedly changes with concentration. The equation



did not apply to the removal of the initial portion of the lignin, which was much more rapid.

Although there is a considerable range of applicability for these equations, numerous investigations have shown that the reaction of sodium hydroxide on wood is actually heterogeneous, and that any equations based on the laws of reaction of a definite order are purely empirical. Larocque and Masses (22) suggest that the reaction between sodium hydroxide and wood takes place in three stages: (1) the acid phenolic groups in the lignin bring about adsorption of the alkali at the interface, (2) either immediately after adsorption or after a certain amount of time, chemical combination takes place between the lignin and the adsorbed alkali, and (3) a chemical hydrolysis and the separation of one alkali-lignin complex from the lignin surface and its solution in the liquor occurs.

Of the cooking variables in sulfate pulping, active chemical ratio (percentage of active alkali based on dry wood weight) and active chemical concentration are the most important. Experiments at The Institute of Paper Chemistry under the direction of Koon (10) indicated that the effects of maximum temperature and time at maximum temperature are secondary, and are not effective means of controlling the reaction unless the active chemical ratio is kept sufficiently high.

It is common practice in the sulfate industry to add substantial amounts of black liquor to the charge of chips and white liquor in the digester. Wells and Arnold (23) found that black liquor had a beneficial effect as a preliminary impregnant and suggested that this was

caused by the action of the organic salts present as buffering agents, thus maintaining an even distribution of active chemical. Crandall and Enderlein (24), in a series of experiments with constant total-active chemical, found that the partial use of black liquor as a diluent gave increased cooking efficiency. The maximum efficiency (lowest permanganate number and percentage of screenings) was obtained when about 60 per cent of black liquor by volume was used. Under these conditions, 11.1 per cent of the total active chemical was furnished by the black liquor. These authors suggested the possibility that more alkali may actually be realized from highly ionized salts or from readily hydrolyzed organic combinations under conditions of heat and pressure than is shown to be present by analytical procedure.

#### DETERMINATION OF THE HYDROLYTIC EQUILIBRIUM OF SODIUM SALTS

A hydrolytic equilibrium for a pure solution of a salt can be determined if the initial concentration of the salt and the concentration of one of the ions participating in the hydrolysis are known. For example, the hydrolysis of sodium sulfide can be determined if the initial concentrations of sodium sulfide and the sulfide, hydrosulfide, or hydroxide ion are known. The usual analytical methods are of no value in determining the concentration of participating ions. Recourse must be had to methods which permit the measurement of these concentrations without disturbing the equilibrium.

Practically all the methods that have been used for determining hydrolysis come under one of the following classifications: (1) electrical conductivity measurements; (2) potentiometric measurements;

(3) indirectly, calculation from acidic or basic ionization constants and the ionization product for water; (4) measurement of the distribution of one product of the partially hydrolyzed salt between two solvents; (5) measurement of the catalytic effect of the  $H^+$  or  $OH^-$  ion as determined from the rate of a catalysable reaction such as the inversion of sugar, or the decomposition of diazoacetic ester, diacetone alcohol, or nitroso-amine compounds, and (6) specific methods for a certain salt or type of salt.

#### ELECTRICAL CONDUCTIVITY MEASUREMENTS

The conductometric approach appeared to be a very promising one for this study. With relatively simple apparatus, conductance readings have been made at temperatures far beyond those encountered in sulfate pulping. In addition, conductance readings lead to other valuable data, such as equivalent conductances of compounds and ions at infinite dilution, transference numbers, and solubilities of slightly soluble salts.

Bredig (25), in 1894, applied the conductometric method to a determination of the hydrolysis of aniline hydrochloride. The hydrolysis was calculated from the equation,

$$x = \frac{\Lambda - \Lambda_v}{\Lambda_{HCl} - \Lambda_v} ,$$

where  $x$  is the degree of hydrolysis,  $\Lambda$  the observed equivalent conductance,  $\Lambda_v$  the equivalent conductance of aniline hydrochloride with no hydrolysis, and  $\Lambda_{HCl}$  the equivalent conductance of hydrochloric acid.  $\Lambda_v$  was determined with  $N/32$  aniline in solution to suppress the hydrolysis. The

validity of this method is dependent upon the assumption that the conductivity of the base is negligible as compared with that of the salt. In the case of stronger bases than aniline, their conductivity is not negligible as compared with  $\Delta_{\nu}$  when their concentration is large. In such cases more dilute solutions of the base must be employed.

"The electrical conductivity of aqueous solutions," published in 1907, represents more than four years of intensive research by Noyes and his co-workers (26). The work was carried out under exacting conditions in a platinum-lined bomb with vapor baths for temperature control. Conductance data were obtained at temperatures as high as 306° C. for some aqueous solutions. Of special interest in connection with this thesis are the hydrolysis studies on sodium acetate and ammonium acetate. Sodium acetate exhibits only a small degree of hydrolysis and the results obtained at various concentrations do not give very good agreement when used to calculate  $K_w$ , the ionization product for water, at a given temperature. Much better agreement was obtained for the more highly hydrolyzed ammonium acetate solutions.

Knox (27) mentioned the work of Schaeffer in a dissertation at Leipzig. Schaeffer determined the hydrolytic equilibrium for sodium sulfide at 25° C. by conductance. He arrived at a value of 94.3 per cent hydrolyzed for 0.06 M sodium sulfide. The value used for the specific conductance of sodium hydroxide, however, differs from the value given in International Critical Tables by almost nine per cent.

The determination of conductance is an important, generally applicable, and rapid measurement once the equipment is installed. The

relationships between conductance and other properties of a solution, such as temperature, pressure, and concentration, are not exact ones and the literature abounds with equations that have been developed in an effort to correlate them. The basic relationships between composition and conductance in solutions are contained in the classic, partial dissociation theory of Arrhenius (28), for weak electrolytes and the Debye-Hückel theory (29), which is applicable to both weak and strong electrolytes.

These theories were derived for very dilute solutions and apply strictly only at infinite dilution. When they are employed for concentrated solutions, careful consideration must be given to the various effects arising from ionic and, in the case of weak electrolytes, molecular interaction. The interaction between solvent and solute must also be considered.

Hückel ascribed the failure of the simple Debye-Hückel equations at higher concentrations to a lowering of the dielectric constant in solution with the addition of electrolyte, whereas Onsager (30) believed that the failure is due mainly to a covolume effect, similar to that recognized in the (V-b) term of the van der Waal gas equation.

Scatchard (31), in 1936, made a notable contribution to the theoretical knowledge of concentrated solutions by a detailed extension of the Debye-Hückel theory. He derived an expression for the activity in a concentrated solution, consisting of four terms: the first is the limiting Debye-Hückel term and includes the effect of finite ion

size; the second, third, and fourth terms describe three effects superimposed upon an electrostatic attraction term. The second term is a function of ionic radii, molal volume of the electrolyte in solution, and molality; it corrects the charge-charge interaction for the reduction in dielectric constant of the solvent with the addition of electrolyte. The third term gives a correction for the "salting-out" effect due to a charge-solvent molecule interaction. The fourth term represents the nonelectrolyte molecule-molecule attraction.

Robinson and Harned (32), in a comprehensive review of research on activity coefficients, advanced the following views on concentrated electrolytes: (1)  $a^0$ , the mean distance of approach of the ions, cannot be determined exactly; (2) no exact, quantitative treatment of all the factors involved has been approached; (3) there must be a factor in the equation for the net short-range repulsive forces between the ions; and (4) the structure of liquid water molecules and their orientation around ions should be considered.

In recent years, Grinnell Jones and his associates (33, 34, 35), have made an exhaustive study of the apparatus and techniques of conductance measurements. This work has resulted in such contributions as more accurate values for the conductance of standard potassium chloride solutions (33), improved a. c. Wheatstone bridge design (34), and improved equipment for detection of the balance point by application of the cathode ray oscilloscope (35).

## ELECTROMETRIC MEASUREMENTS (pH)

The determination of hydroxyl ion concentration through the measurement of pH seemed to be a feasible method for determining the position of a hydrolytic equilibrium, in which sodium hydroxide appeared as one of the products. Certain limitations as to temperature and very high alkalinity were recognized at the outset.

Typical hydrogen ion concentrations in aqueous solution cover the range from one gram-ion per liter in a normal solution of a strong acid to  $10^{-14}$  in a N solution of alkali. Sørensen (36), in 1909, suggested the negative logarithm of the hydrogen ion activity as a convenient means of expressing such concentrations, and his scale has come into general use. The normal hydrogen electrode is the standard for all pH determinations, since all other electrode potentials are referred to it as zero. Because the use of this electrode is limited and often involves serious experimental difficulties, other electrodes, reversible with respect to hydrogen ions, have been developed. Naturally, the difference between the standard electrode potential in each case and that of the standard hydrogen electrode must be included in the expression for pH. The glass electrode is the one most widely used for pH measurement and was used in this thesis.

The glass electrode can be used in almost all solutions and special sodium-free glass electrodes, such as the Beckman Type E, can be used for pH's as high as 13. F. Haber discovered in 1909 that the potential difference between a glass surface and a solution varied regularly with the pH of the latter. This observation is the basis of

the glass electrode, which is made from a thin-walled bulb of low melting point glass of high electrical conductivity. The bulb contains a buffer solution together with a little quinhydrone and a platinum wire to serve as a connection. The bulb is immersed in the solution being measured and the potential difference between the platinum wire and the external solution is determined.

#### CALCULATION FROM $K_a$ OR $K_b$ AND $K_w$

The hydrolysis of a salt can be calculated from  $K_w$ , the ionization product for water, and  $K_a$  or  $K_b$ , the acidic or basic ionization constant. Hydrolysis is related to these quantities according to the equation,

$$K_h = K_w/K_a \quad \text{or} \quad K_h = K_w/K_b$$

Dissociation constants may be determined conductometrically, or from pH measurements on a solution containing a known amount of the acid and its salt with a strong base. The most accurate method involves electromotive force measurements, and has been described by Harned and Owen (37).

#### MEASUREMENT OF THE CATALYTIC EFFECT OF THE HYDROGEN OR HYDROXYL ION

By definition, a catalyst is not permanently affected by a reaction it catalyzes. Several methods for determining hydrolysis have been developed, based upon a measurement of the catalytic effect of the hydroxyl or hydrogen ion on the inversion or decomposition of a small amount of an organic material introduced into the solution. In these methods, a simple relationship exists between the magnitude of the catalytic effect and the concentration of hydrogen or hydroxyl ion.



Ley (38), in 1899, used the rate of inversion of cane sugar to determine the hydrolysis of aluminum chloride at room temperature and at 100° C. Bredig and Fraenkel (39) measured the rate of decomposition of diazoacetic ester by hydrogen ions, and Koelichen (40) determined the rate at which acetone was formed from diacetone alcohol by the catalytic effect of hydroxyl ions.

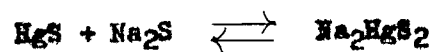
Francis and co-workers (41, 42, 43) have made a thorough study of the decomposition of certain nitrosoamines in the presence of hydroxyl ions and have proposed a method which gave good agreement with conductivity and electromotive force measurements on the hydrolysis of sodium carbonate. Their method involves the measurement of the rate at which nitrogen is generated from the nitrosoamine.

Beedle and Bolam (44) and McBain (45) applied the nitrosoamine method to the hydrolysis of soaps. King and Marion (46) adapted the method to the determination of ionization constants of very weak acids.

#### MEASUREMENT OF THE SOLUBILITY OF MERCURIC SULFIDE

Knox (27), in 1908, published some very interesting work on the hydrolysis of sodium sulfide at room temperature. He determined the hydrolysis by a method based upon the solubility of mercuric sulfide in sodium sulfide and its insolubility in sodium hydrosulfide, sodium hydroxide, and water. The mercuric sulfide apparently goes into solution by forming a soluble complex. Electromotive force measurements indicate that the complex formed is  $\text{Na}_2\text{HgS}_2$  and, thus, one mole of mercuric sulfide goes into solution for every mole of sodium sulfide present in the

unhydrolyzed form.



Solubility is determined after prolonged mixing of an excess of mercuric sulfide with the solution in question; the undissolved mercuric sulfide is allowed to settle and an aliquot of the clear supernatant liquid is pipetted off and analyzed for mercuric sulfide.

## EXPERIMENTAL PROCEDURES

### DETERMINATION OF HYDROLYTIC EQUILIBRIUM BY ELECTRICAL CONDUCTIVITY METHODS

#### APPARATUS AT 25° C.

A Pyrex conductivity cell with latimized platinum electrodes and a closed solution chamber, fitted with a ground-glass stopper, was used for the conductance measurements at 25° C. The cell had a volume of about fifty ml. and a cell constant of 0.2745.

Before use, the electrodes were cleaned and platinized. They were cleaned in 15 per cent hydrochloric acid by the application of a potential from three dry cells in series through a 10,000-ohm variable resistance. The current was adjusted for a gentle evolution of gas at the electrodes and was reversed every minute by means of a double-pole, double-throw switch in the line. The current was permitted to flow for a total of five minutes in each direction. All the old platinization was removed from the electrode surfaces by this treatment. After the cleaned electrodes had been washed thoroughly with distilled water, they were immersed in a platinizing solution containing three grams of platinum chloride and 20 milligrams of lead acetate per 100 ml. Potential was applied and the current reversed every minute as described above, until platinum precipitated out in the solution. The electrodes were washed thoroughly with distilled water and kept in distilled water when not in use.

For measurements at 25° C., the cell was immersed in a large Pyrex water bath, with vigorous agitation provided by a Cenco variable-

speed stirrer. The bath was heated by a 250-watt, Cenco knife-type immersion heater controlled by a Cenco DeKhotinsky thermo-regulator. A 76-mm. immersion thermometer, compared with a thermometer calibrated at the National Bureau of Standards, was used to indicate the temperature of the bath. The temperature was maintained at  $25 \pm 0.1^\circ \text{C}$ .

The a. c. Wheatstone bridge used in the conductance measurements was a Model RC-1 conductivity bridge, manufactured by Industrial Instruments, Inc. A conductivity cell filled with an electrolyte is not a pure resistance; therefore, external condensers were used with the bridge to correct the phase difference in the bridge arms caused by the capacitance effect at the cell electrodes and, thus, to obtain a sharper and more sensitive balance point. External variable capacitance ranging from 10 micromicrofarads to 11.11 microfarads was incorporated into the bridge circuit.

The balance points were still not of satisfactory sharpness after the capacitative effects were reduced. The difficulty was apparently traceable to polarization effects in the more concentrated solutions of electrolytes. When the frequency of the alternating voltage applied to the bridge (balancing voltage) was changed from 60 cycles to 1000 cycles, a distinct improvement was noted.

Taps and a double-pole switch were installed in the RC-1 instrument in that part of the transformer secondary supplying the balancing voltage to the bridge. The output terminal of a Hewlett-Packard audio oscillator, Model 200B, were connected to these taps through a coupling transformer as shown in Figure 1.

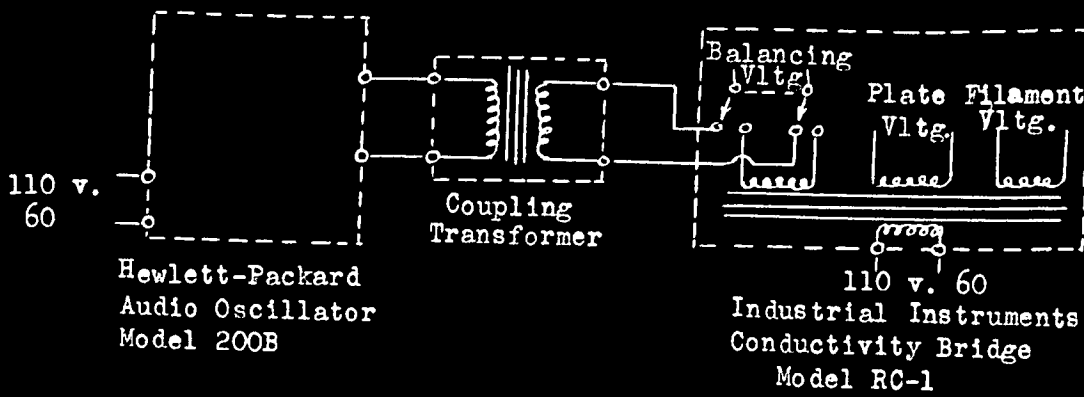


Figure 1

Circuit for Use of External Oscillator  
with Conductivity Bridge

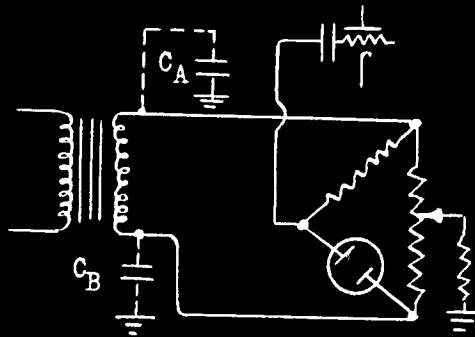


Figure 2a

Distributive Capacitance in Coupling of  
Oscillator to Conductivity Bridge

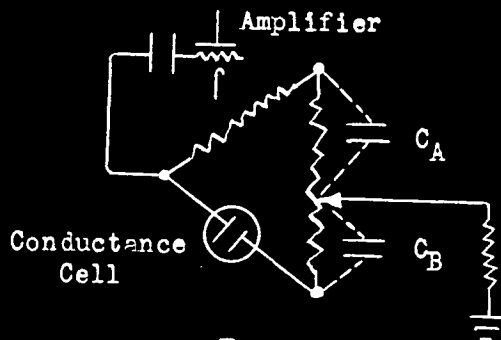


Figure 2b

Equivalent Circuit of Figure 2a

The voltage supplied at the taps by the audio oscillator was measured with a vacuum tube voltmeter in order to determine the proper setting of the oscillator output dial to give three to four volts of balancing voltage. This measurement was made with various resistors connected into the bridge at the conductivity cell terminals; the correct setting of the oscillator output dial was recorded in each case and a plot was made for using the external oscillator with the bridge.

It was found that the coupling transformer between the bridge and the external oscillator had to be of the isolation type--i. e., the primary coil had to be isolated from the secondary. If an isolation-type transformer is not used, distributed capacitance between the primary and the secondary provides an additional path to ground for 1000 cycles in the secondary (Figure 2 a), and appears in the equivalent circuit as two distributed capacitances shunting the slidewire (Figure 2 b). These capacitances do not change in value as the slidewire is moved and, thus, impart spurious effects as the cell resistance varies. With the isolation-type transformer the distributed capacitance is eliminated, and the only path to ground in the secondary circuit is through the slidewire and slider arm.

#### PREPARATION OF SOLUTIONS

In conductance work, elaborate precautions must be taken in the preparation and handling of the solutions to be measured. Exposure of the solutions to the atmosphere was kept at a minimum and, when necessary, was carried out under a protective stream of nitrogen. The nitrogen was passed from the gas cylinder through a train consisting of a calcium

chloride tube for removal of moisture and two ascarite tubes for removal of carbon dioxide.

#### Conductance Water

A Pyrex still with a 50 cm. Widmer column and ground-glass joints throughout was used. Distilled water from the laboratory supply was distilled twice more in the Pyrex still. Before the first distillation, a gram of potassium permanganate and a few ml. of five per cent sodium hydroxide were added to 800 ml. of water from the laboratory supply. Distillation of water containing alkaline permanganate frees it from organic impurities. The distillate was treated with a few ml. of 85 per cent phosphoric acid before the second distillation to remove the dissolved ammonia.

The distillate from the phosphoric acid solution had a specific conductance of  $1.62 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ , sufficiently low for use in most of the solutions to be measured. For use in the more dilute solutions, this water was subjected to a third distillation in the Pyrex still. The distillate then had a specific conductance of  $1.36 \times 10^{-6} \text{ ohm}^{-1} \text{ cm.}^{-1}$ . The water was stored in glass-stoppered Pyrex bottles. Periodic checks revealed little if any increase in its conductance.

Immediately before use, the conductance water was refluxed for half an hour in a Pyrex flask fitted with a Pyrex condenser topped by an ascarite tube. Practically all dissolved carbon dioxide was removed in this manner. As soon as the water stopped boiling, the condenser was removed and a siphon assembly quickly inserted into the flask. Air pressure for siphoning water from the flask was furnished through an ascarite tube.

### Carbonate-free Sodium Hydroxide

Reagent-quality sodium hydroxide pellets were used and, in all cases where it was necessary to expose either the caustic or the dilution water to the atmosphere, a stream of nitrogen was passed over the open vessel. One hundred and fifty grams of sodium hydroxide were dissolved in 150 ml. of refluxed conductance water. The solution was filtered through a fine, sintered-glass crucible. Sodium carbonate is insoluble in highly concentrated sodium hydroxide and is removed by the filtration. The filtrate was carefully transferred to a paraffin-coated bottle and diluted with three liters of refluxed conductance water, giving approximately a normal sodium hydroxide solution. An arrangement was made for siphoning directly into a microburette. All the rubber stoppers were sealed with paraffin. Potassium biphthalate reagent (99.95% pure) was used for standardization. The solution was tested for carbonate periodically by filling a test tube almost to the top with the sodium hydroxide, adding 1 ml. of 0.5 N barium chloride, and quickly stoppering the test tube. No turbidity should appear.

### Sodium Bicarbonate, Unhydrolyzed

C. p. sodium bicarbonate was dried for 1-1/2 hours at 110° C. and cooled in a desiccator before being weighed. The solution was made up with conductance water saturated with carbon dioxide in order to prevent any decomposition of the bicarbonate. Bodlaender and Breull (48) stated that only 0.04 per cent of sodium bicarbonate hydrolyzes in solutions saturated with carbon dioxide. When conductance-concentration curves were run on the bicarbonate, all dilutions were made with carbon



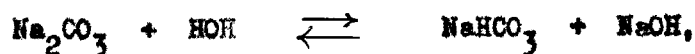
dioxide-saturated water, and all exposures of the solutions were made under a protective stream of carbon dioxide rather than nitrogen, which was used for all other solutions.

### Sodium Carbonate

Sodium carbonate reagent was heated for one-half hour at 270-300° C., cooled in a desiccator for one-half hour, and weighed out from a weighing bottle by difference. Precautions against atmospheric contamination must also be taken with sodium carbonate solutions. According to Mellor (49), solutions of sodium carbonate absorb carbon dioxide from the atmosphere because the partial pressure of carbon dioxide in the atmosphere is about four times that in N sodium carbonate. Dilute solutions at low temperatures are the worst offenders, since the partial pressure differential is greatest under these conditions.

### Sodium Carbonate, Unhydrolyzed

The hydrolysis of sodium carbonate was reduced considerably by the addition of an equimolar amount of carbonate-free sodium hydroxide to the carbonate solution. Originally, it was believed that the hydrolysis equilibrium,



was driven almost completely to the left by such an addition, but later experiments proved that such was not the case.

### Sodium Hydrosulfide, Unhydrolyzed

Normal carbonate-free sodium hydroxide was saturated with

hydrogen sulfide by bubbling the gas through the solution until a constant sulfide content was obtained. Dilutions were made with conductance water saturated with hydrogen sulfide.

Analysis for sulfide was made according to a procedure based upon that given by Scott (50). One hundred ml. of standard 0.1 N iodine solution were pipetted into a 250-ml. Erlenmeyer flask and acidified with 15 ml. of N hydrochloric acid. Five ml. of the hydrosulfide solution were pipetted in slowly with good mixing. The solution was back-titrated with standard 0.1 N sodium thiosulfate, one ml. of starch solution being added when the iodine color began to fade. Calculations were based upon the premise that, in the presence of an excess of hydrogen sulfide, none of the sodium exists in the form of sodium sulfide.

The total sodium content of the solution was checked by Institute Method 109. Ten ml. of the hydrosulfide solution were pipetted into a tared platinum evaporating dish and placed in an oven at 105° C. for a few hours. The residue was moistened with water and a drop of methyl orange was added. Concentrated sulfuric acid was then added dropwise to the development of a bright pink color, thus converting all sodium to sodium sulfate. The material was warmed gently at first to remove the excess sulfuric acid and was finally ignited quite strongly, cooled in a desiccator, and weighed.

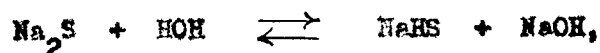
#### Sodium Sulfide

Hydrogen sulfide was bubbled gently through 90 ml. of standard N carbonate-free sodium hydroxide in a 100-ml. volumetric flask for about

one half hour, at which point the solution began to take on a yellowish tint. An expansion of a few ml. in the volume of the solution was evident at this time. In order to consider this expansion, the flask was filled to the mark with carbonate-free distilled water before the solution was analyzed for sulfide. From the normality of sulfide and the known normality of sodium (0.9 of the original normality), the amount of carbonate-free standard sodium hydroxide to be added for an exact equivalency between sodium and sulfide was calculated.

### Sodium Sulfide, Unhydrolyzed

As in the case of sodium carbonate, sodium sulfide in the unhydrolyzed state was obtained by adding sufficient standard sodium hydroxide to drive the hydrolytic equilibrium,



substantially completely to the left.

In conductance work on sodium sulfide and hydrosulfide solutions, the solutions were made up immediately before measurement in each case. These solutions proved to be extremely sensitive to atmospheric oxidation.

### Analytical Solutions

Standard solutions for analytical procedures, such as iodine, potassium dichromate, hydrochloric acid, and sodium thiosulfate, and indicator solutions, such as phenolphthalein, methyl orange, and methyl red, were prepared according to Kolthoff and Sandell (21).

# PROCEDURES FOR CONDUCTANCE CURVES AT 25° C.

In running conductance-concentration curves on the various solutions, a careful technique was required. The conductivity cell was rinsed thoroughly with the solution to be measured before filling. Dilution water was handled as described above under "Conductance water." All fillings and dilutions were made under a protective stream of nitrogen, or carbon dioxide in the case of unhydrolysed sodium bicarbonate.

The solutions in the conductivity cell were allowed to stand at least five minutes in the water bath to attain temperature equilibrium with the bath before the conductance was measured. Five minutes had been found to be sufficient for water within five degrees of bath temperature to reach equilibrium.

The bridge was balanced four times, twice from each side of the null point, and the average reading was taken as the cell resistance. The maximum spread in the readings seldom exceeded one per cent, even for the more concentrated solutions.

## METHODS OF CALCULATION

The various calculations made in the course of the work can best be described by illustrations.

### Determination of Cell Constant

Cell Constant = Cell Resistance x Specific Conductance

$$\underline{K} = \underline{R} \times \underline{k}$$

For 0.1 N potassium chloride the cell resistance was 21.32 ohms. Jones and Prendergast (33) give 0.0128862 as the specific conductance of 0.1 N KCl.

$$\begin{aligned}\underline{k} &= 21.32 \times 0.0128862 \\ &= 0.2745.\end{aligned}$$

#### Determination of Equivalent Conductance

A 0.2 N solution of sodium hydroxide gave a cell resistance of 7.06 ohms at 25° C.

$$\begin{aligned}\underline{k} &= \underline{k}/\underline{R} = 0.2745/7.06 \\ &= 3.89 \times 10^{-2}\end{aligned}$$

$$\text{Equivalent Conductance } (\underline{\Lambda}) = \frac{\underline{k} \times 10^3}{\text{Normality}}$$

$$\begin{aligned}\underline{\Lambda} &= \frac{(3.89 \times 10^{-2}) \times 10^3}{0.2} \\ &= 194.5 \text{ at } 0.2 \underline{N}\end{aligned}$$

#### Determination of the Equivalent Conductance at Infinite Dilution ( $\underline{\Lambda}_0$ )

Kohlrausch's method. Kohlrausch (52) obtained  $\underline{\Lambda}_0$  by extrapolating to zero concentration from a plot of  $\underline{\Lambda}$  vs.  $\sqrt{C}$ . For univalent electrolytes, the plots were closer to straight lines when ionic strengths were used instead of concentrations.

Ionic strength is a measure of intensity of the electrical field caused by the presence of ions in a solution. It supposedly represents the variation of activity coefficient with concentration.

$$\underline{I} = 1/2 \sum \underline{C}_i \underline{Z}_i^2.$$

where  $\underline{C}_i$  is the molarity of the ion "i" and  $\underline{Z}_i$  is its valence.

Shedlovsky's method. The Onsager equation (30) has been modified to make it applicable up to 0.1 N for strong uni-univalent electrolytes. Shedlovsky (53) made this modification of the Onsager Theory by the addition of a "BC" term, giving the equation

$$\Lambda_o = [\Lambda + 2\beta \sqrt{C}] / [1 - \alpha \sqrt{C}] - BC,$$

where B is a constant for each electrolyte and C is the equivalent concentration.  $\alpha$  and  $\beta$  are constants for a given solvent at a given temperature. For water at 25° C.,  $\alpha = 0.2274$  and  $\beta = 59.79$ .

To obtain  $\Lambda_o$ ,  $[2\beta \sqrt{C} + \Lambda] / [1 - \alpha \sqrt{C}] = \Lambda_o$  is plotted against C. The slope of the line obtained is B and the intercept at C = 0 is  $\Lambda_o$ . When the calculation is made for strong uni-bivalent electrolytes, ionic strength is used instead of concentration.

#### Calculation of Degree of Hydrolysis from Conductance Data

Bredig's method. Applying the general method of Bredig (25) to the hydrolysis of sodium carbonate,



$$\text{Percentage of hydrolysis} = \frac{[\Lambda_{\text{Na}_2\text{CO}_3} - \Lambda_{\text{Na}_2\text{CO}_3(\text{unhyd.})}] \times 100}{\frac{\Lambda_{\text{NaOH}}}{2} + \frac{\Lambda_{\text{NaHCO}_3(\text{unhyd.})}}{2} - \Lambda_{\text{Na}_2\text{CO}_3(\text{unhyd.})}} \quad (2)$$

The chemical methods for obtaining  $\text{Na}_2\text{CO}_3$  (unhydrolyzed) were given on page 32. The calculation again assumes Kohlrausch's laws for additivity of conductances. For the solution of carbonate and hydroxide,

$$k_t = k_{\text{Na}_2\text{CO}_3(\text{unhyd.})} + k_{\text{NaOH}}$$

$$k_t = (\frac{E\Lambda}{2})_{\text{Na}_2\text{CO}_3(\text{unhyd.})} + (\frac{E\Lambda}{2})_{\text{NaOH}}$$

$\Delta$  for NaOH is again taken from the  $\Delta$  vs. concentration curve at the total ionic strength of the solution. From  $k_2$  (as measured) and the known normalities of carbonate and hydroxide,  $\Delta$   $\text{Na}_2\text{CO}_3$  (unhydrolyzed) is calculated.

By analogy, for the case of sodium sulfide, Equation (2) becomes

$$\text{Percentage of hydrolysis} = \frac{[\Delta \text{Na}_2\text{S} - \Delta \text{Na}_2\text{S}(\text{unhyd.})] \times 100}{\Delta/2 \text{ NaOH} + \Delta/2 \text{ NaHS}(\text{unhyd.}) - \Delta \text{Na}_2\text{S}(\text{unhyd.})}$$



Schaeffer's method. The method of Schaeffer is most easily described through an example:

$$\text{specific conductance } 0.05917 \text{ N NaOH} = 11.61 \times 10^{-3} \Delta^{-1}$$

$$\text{specific conductance } 0.05917 \text{ N NaHS} = 5.50 \times 10^{-3} \Delta^{-1}$$

( $\text{H}_2\text{S}$  in excess to prevent hydrolysis)

$$\begin{aligned} \text{specific conductance of a mixture } 0.05917 \text{ N in each} \\ = 16.44 \times 10^{-3} \Delta^{-1} \end{aligned}$$

Schaeffer assumed that the conductance of unhydrolyzed sodium sulfide would be approximately the same as that of sodium hydrosulfide and set up the following equation.

$$16.44 = x(11.61 + 5.50) + (1-x)5.50$$

$$x = 94.3 \text{ per cent hydrolyzed}$$

#### DETERMINATION OF HYDROLYTIC EQUILIBRIUM BY ELECTROMETRIC MEASUREMENTS (pH)

APPARATUS AT 25° C.

Measurements of pH were made with a Beckman pH meter, Model G.

The Beckman Type F glass electrode, catalogue no. 1190-E, was used. This electrode is recommended for solutions of high alkalinity. The "sodium error," characteristic of glass electrodes in solutions of high sodium ion concentration, is reduced to a very small value when the Type F electrode is used. A correction chart for this error is furnished with the electrode. The meter was standardized at pH 11.62 with a disodium hydrogen phosphate-sodium hydroxide-sodium chloride buffer, the preparation of which is given by Bates (24). Before use, the Type F electrode was allowed to stand for several hours in a solution of pH 10. The solution to be measured and the electrodes were contained in a closed vessel under an atmosphere of nitrogen. The vessel was inserted in the same water bath used for the conductance measurements.

#### PREPARATION OF SOLUTIONS

Solutions for the measurements were prepared as described in the section concerning electrical conductivity methods.

#### CALCULATION OF DEGREE OF HYDROLYSIS FROM pH MEASUREMENT

$$\begin{aligned} \text{NaCO}_3^- + \text{HOH} &\rightleftharpoons \text{NaHCO}_3 + \text{OH}^- \\ K_{\text{hydrolysis}} &= \frac{[\text{NaHCO}_3][\text{OH}^-]}{[\text{NaCO}_3^-]} \\ &= \frac{[\text{OH}^-]^2}{[\underline{c} - \text{OH}^-]} = \frac{h^2 c}{1 - h} \end{aligned} \quad (1)$$

since  $[\text{OH}^-] = \underline{h}c$ , where  $\underline{h}$  is the degree of hydrolysis and  $\underline{c}$  is the concentration of sodium carbonate.



These equations are strictly true only if the activities rather than the concentrations are used for both  $[\text{OH}^-]$  and  $\underline{c}$ .

In order to calculate  $\underline{a}_{\text{OH}^-}$  (activity of the hydroxyl ion) from pH,  $\underline{K}_w$ , the ionization product of water at the concentration of the solution measured, must be known. At  $25^\circ \text{C}$ .  $\underline{K}_w = 1.008 \times 10^{-14}$  for pure water.

$$\underline{K}_w = \gamma_w^2 \underline{a}_{\text{H}^+} \underline{a}_{\text{OH}^-}$$

$$\underline{K}_w = \gamma_w^2 \times 1.008 \times 10^{-14}$$

where  $\underline{a}_{\text{H}^+}$  = concentration of hydrogen ion in pure water, and  
 $\underline{a}_{\text{OH}^-}$  = concentration of hydroxyl ion in pure water.

Values for  $\gamma_w^2$ , the ionic activity coefficient product, are not available for either sodium sulfide or sodium carbonate solutions. Harned (32), however, gives  $\gamma_w^2$  values for aqueous potassium chloride solutions at  $25^\circ \text{C}$ . Values from these data at the ionic strength of the solution measured were used. Activity data for sodium sulfide are given at this temperature in the same reference. Since data for sodium carbonate were not available, the data given for sodium sulfate were used for this calculation.

As an illustration of the calculation, 0.4 M sodium carbonate had a pH of 11.42 at  $25^\circ \text{C}$ .

$$-\log \underline{a}_{\text{H}^+} = 11.42$$

$$\underline{a}_{\text{H}^+} = 3.80 \times 10^{-12}$$

$$\underline{a}_{\text{OH}^-} = \frac{\underline{K}_w}{\underline{a}_{\text{H}^+}} = \frac{\gamma_w^2 \times 1.008 \times 10^{-14}}{3.80 \times 10^{-12}}$$

From the data for potassium chloride, at an ionic strength of 1.2 ( $\mu = 3c$ ),  $\gamma_{\text{Cl}^-}^2 = 0.620$ .

$$a_{\text{OH}^-} = \frac{0.620 \times 1.00\% \times 10^{-14}}{3.80 \times 10^{-12}} = 1.646 \times 10^{-3}.$$

For 0.4 M sodium sulfate and sodium carbonate,

$$\gamma_{\text{NaCO}_3} = \frac{\gamma_{\text{Na}_2\text{CO}_3}}{\gamma_{\text{Na}}} \approx \frac{\gamma_{\text{Na}_2\text{SO}_4}}{(\gamma_{\text{NaOH}})^{1/2}} = \frac{0.295}{(0.681)^{1/2}} = 0.358$$

$\gamma_{\text{Na}_2\text{SO}_4}$  for a 0.4 M solution is 0.295. For a solution of ionic strength of 1.2,  $\gamma_{\text{NaOH}}$  is 0.681.

$$\gamma(c) = 0.358 \times 0.4 = 0.1432$$

Now, if activities are included in equation (1),

$$\frac{(a_{\text{OH}^-})^2}{\gamma[c] - a_{\text{OH}^-}} = \frac{h^2 \gamma(c)}{1 - h} \quad \text{or} \quad \frac{h^2}{1 - h} = \frac{(a_{\text{OH}^-})^2}{(\gamma[c] - a_{\text{OH}^-}) \gamma[c]}$$

$$\frac{h^2}{1 - h} = \frac{(1.646 \times 10^{-3})^2}{(0.1432 - 0.0016) \cdot 0.1432} = 1.337 \times 10^{-4}.$$

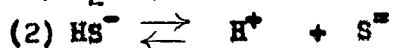
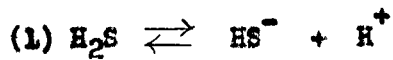
$$h = 1.15 \times 10^{-2},$$

Hydrolysis = 1.15 per cent.

#### CALCULATION OF THE DEGREE OF HYDROLYSIS FROM THE SECOND IONIZATION CONSTANT OF THE ACID OF THE SALT

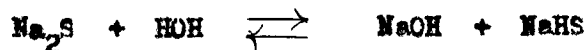
The indirect determination of the hydrolytic equilibrium is demonstrated below. The  $K_h = K_w/K_a$  relationship is used to calculate the degree of hydrolysis of 0.394 M sodium sulfide at 25° C.

For the reactions,



$$K_1 = \frac{(\text{HS}^-)(\text{H}^+)}{(\text{H}_2\text{S})} \quad \text{and} \quad K_2 = \frac{(\text{H}^+)(\text{S}^{=})}{(\text{HS}^-)} .$$

For the hydrolysis reaction,



$$K_h = \frac{(\text{NaOH})(\text{NaHS})}{(\text{Na}_2\text{S})} = \frac{(\text{OH}^-)(\text{HS}^-)}{(\text{S}^{=})}$$

$$= \frac{(\text{H}^+)(\text{OH}^-)(\text{HS}^-)}{(\text{H}^+)(\text{S}^{=})} = K_w/K_2$$

$$K_h = K_w/K_2 = \frac{\gamma_1^2 (c)h^2}{\gamma_2 (1-h)}$$

$\gamma_1$  = activity coefficient for the univalent ion, and

$\gamma_2$  = activity coefficient for the bivalent ion.

According to the Debye-Huckel equation for calculating activities in dilute solutions,

$$-\log \gamma_1 = \frac{A z_1^2 \sqrt{\mu}}{1 + B a}$$

where  $\gamma_1$  = activity coeff. for ion "1",

$A$  = a constant,

$z_1$  = valence of ion "1", and

$\mu$  = ionic strength in solution.

From this equation it is evident that the activity coefficient of the bivalent ion is equal to the fourth power of that for the univalent ion. Data from Robinson and Harned (32) for  $\gamma_{\text{NaS}^-}$  were used for the calculation

$$\gamma_1 = (\gamma_{\text{NaS}^-})^{0.2} \qquad \gamma_2 = (\gamma_{\text{NaS}^-})^{0.8}$$

$K_2$  values for hydrogen sulfide are quite scarce in the literature. Kolthoff and Sandell (51) list  $1.2 \times 10^{-15}$  at  $25^\circ \text{C}$ .

Thus for 0.394 M sodium sulfide,

$$\gamma_{\text{NaS}^-} = 0.647 \qquad \gamma_1 = (0.647)^{0.2} = 0.917$$

$$\gamma_2 = (0.647)^{0.8} = 0.706$$

$$\frac{K_1}{K_2} = \frac{K_w}{K_2} = \frac{\gamma_1^2 (c) h^2}{\gamma_2 (1 - h)}$$

$$\frac{h^2}{1 - h} = \frac{K_w \gamma_2}{K_2 \gamma_1^2 (c)} = \frac{1.008 \times 10^{-14} \times 0.706}{1.2 \times 10^{-15} \times (0.917)^2 \times 0.394}$$

$$= 0.18$$

$$h = 0.35$$

$$\text{Hydrolysis} = 35 \text{ per cent}$$

#### DETERMINATION OF HYDROLYTIC EQUILIBRIUM BY THE MERCURIC SULFIDE SOLUBILITY METHOD OF KNOX

APPARATUS AT  $25^\circ \text{C}$ .

For the work at  $25^\circ \text{C}$ ., a Dorrco Flocculator, manufactured by the Dorr Co., Inc., was adapted to fit a large Pyrex bath. Four 60-ml. ground-glass stoppered Pyrex bottles containing the solutions under investigation and an excess of mercuric sulfide, were fastened to the paddles with heavy rubber bands and rotated in the bath at about five r.p.m. Twenty-four hours of mixing were found to be sufficient for

reaching equilibrium. The bottles were then removed from the agitator and allowed to stand in the water bath for at least an hour for settling of the excess mercuric sulfide. A ten-ml. portion of the clear supernatant liquid was then removed for analysis.

#### APPARATUS FOR HIGH-TEMPERATURE HYDROLYSIS DETERMINATIONS

For the determination of the position of the sodium sulfide hydrolysis at sulfate cooking temperatures, equipment was designed and constructed to permit an investigation of the mercuric sulfide method at elevated temperatures. The apparatus in its final form is shown in Figure 3.

High temperature solubility determinations were carried out in sealed tubes (A in Figure 3) bent at the center to an angle of about 130 degrees. The tubes, about half filled with the solution under investigation and an excess of mercuric sulfide, were rotated end-over-end at about ten r.p.m. for 24 hours in an oven at 165° C., after which the excess mercuric sulfide was allowed to settle at one end of the tube. After settling was complete, the slight bend in the center permitted the decantation of some of the clear supernatant liquid. The tube was then allowed to cool and the separated supernatant liquid was removed at room temperature. An aliquot of this liquid was analyzed for mercuric sulfide as in the case of the low temperature application of the method. Figure 4 shows cross sectional views of a tube in the "settling" and "decanting" positions, and indicates the method for isolation of a sample of the supernatant liquid in the right-hand end of the tube by decantation.

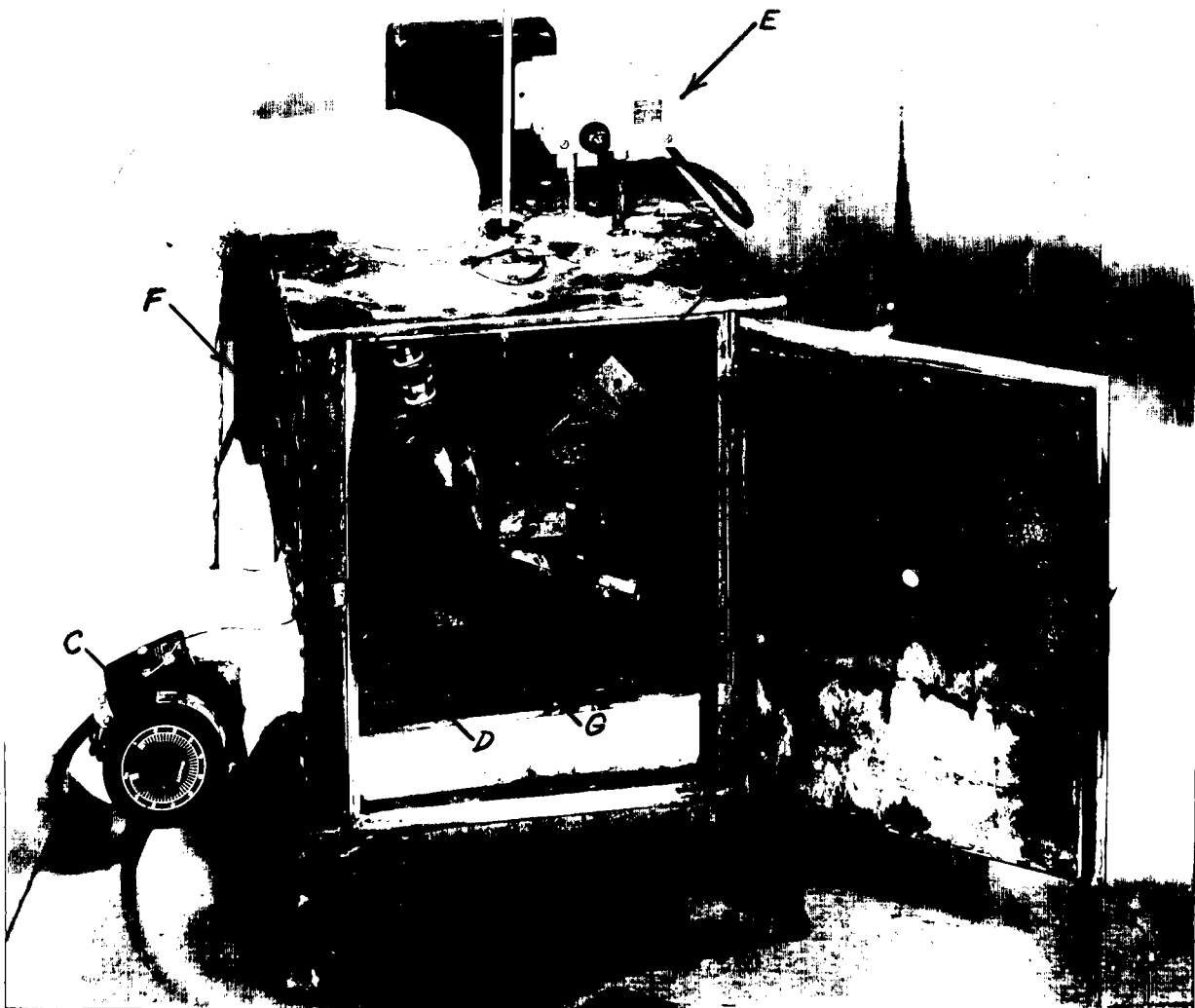
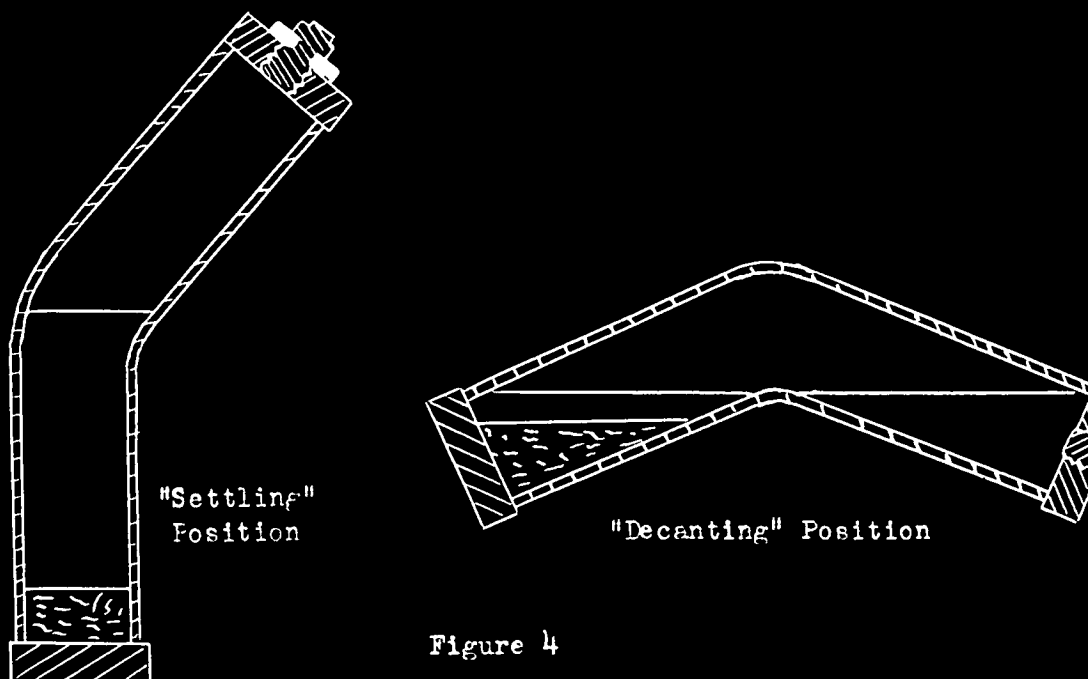


Figure 3

Apparatus for High Temperature Hydrolysis Determinations

- |                              |                    |
|------------------------------|--------------------|
| A Stainless steel tube       | F AC-DC relay      |
| B Blower motor               | G Removable cradle |
| C Blower motor speed control | H Trough           |
| D Strip heater               | I Steel clip       |
| E Thermo-regulator           | J Counterbalance   |



Cross Section--Stainless Steel Tubes for  
High Temperature Hydrolysis Determination

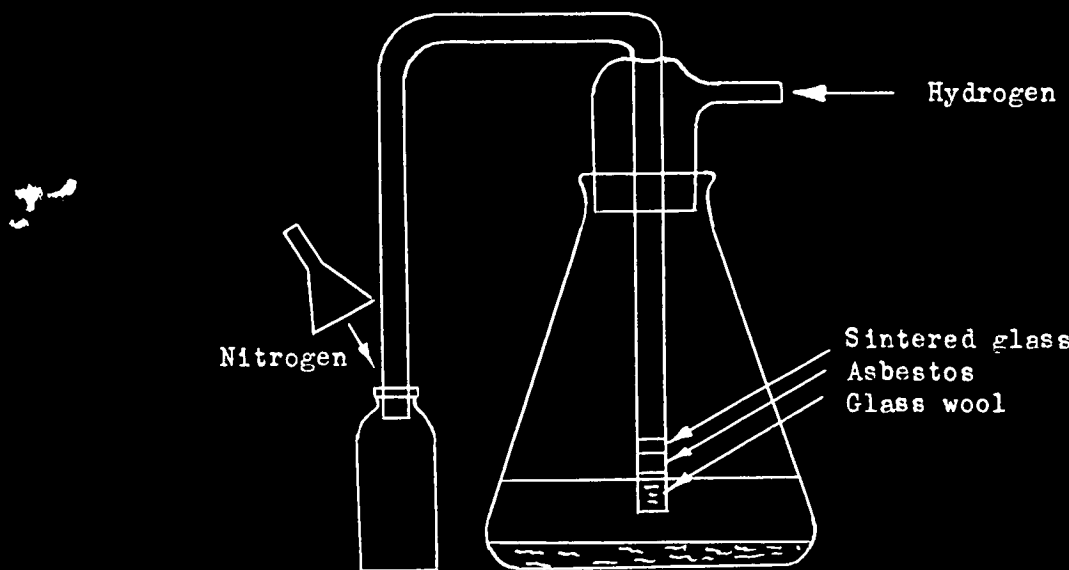


Figure 5

Apparatus for Filtration at 100° C.

A Thelco 700-watt oven, manufactured by the Freese Electric Furnace Co., Irvington, N. J., was modified for the purposes of this investigation. A blower system was installed, consisting of a 2-1/2-inch blower (B and C), and 2-1/2-inch copper tubing lagged with asbestos. The system was arranged to take air from the top of the oven and blow it back in along the bottom. An auxiliary 150-watt strip heater (D) was installed on the oven floor. Temperature control within  $0.5^{\circ}$  C. at  $165^{\circ}$  C. was maintained by means of a Genco-DeVotinsky thermo-regulator (E) and an AC-DC relay (F) in series with the main heating element of the oven. The thermometer used was compared with a thermometer calibrated at the Bureau of Standards.

A removable cradle (G) was constructed for rotation of the tubes. This device consisted of five troughs (H), made of 1/2-inch conduit, brazed to a 5/16-inch steel shaft. The tubes were held in the troughs by thin steel clips (I). The shaft rotated in sleeve-type brass bearings and was coupled through a reduction gear (56:1) to a small motor mounted to the back of the oven. Dow-Corning stop-cock grease (a silicone preparation) was found to be a fairly good bearing lubricant at  $165^{\circ}$  C. A 500-ohm, 0.31-ampere potentiometer in series with the motor gave control of the speed of the rotation. An adjustable counterbalance (J) was brazed onto the shaft in order to provide a more balanced load for the motor.

The shaft was marked where it extended out of the oven at the rear, so that rotation could be stopped with the tubes in "settling" position and in "decanting" position after settling was complete, without opening the oven.



The tubes were first made from heavy-wall Pyrex tubing (19 x 25 mm.). Several explosions resulted when these tubes were heated to 165° C. Evidently slight strains were set up in the glass during the bending operation. After an explosion that damaged the oven severely, the idea of using glass tubes was abandoned.

Stainless steel tubes were developed for the determination. The tubes were made from 3/4-inch stainless steel tubing. They were bent at red heat. The end pieces were made from stainless steel of 3/8-inch thickness. One end piece was drilled and tapped for a 3/8-inch plug. These tubes were tested hydrostatically for leaks at 300 pounds per square inch before use. The ends were first welded to the tubes with a stainless steel rod and an electric arc. It was discovered, however, that welding brought about rapid oxidation of the stainless steel with the development of pinholes. Efforts to weld over these pinholes resulted in the development of others in greater number. Silver-soldering of the end pieces with an oxyacetylene torch and a liberal application of flux proved to be the answer to the problem, giving a pressure-tight union.

Ease of removal was a very important consideration in the design of the plugs and the selection of gasket material for them. After some of the supernatant liquid in one end of the tube was separated by decantation, it was very important that none of the material from the other end of the tube should be mixed with it. Thus, delicate handling of the tubes was required.

Various materials--copper, lead, asbestos, Neoprene, silicone rubber, and ten-mm. sparkplug gaskets--were tried as gaskets by measuring the amount of water in the tube before and after twenty-four hours at 165° C. Dow-Corning silicone rubber of 5/64-inch thickness was found to combine the advantages of complete retention of the test solution, inertness, and ease of plug removal. The resiliency of the material made possible a perfect seal without excessive tightening of the plugs.

#### SPECIAL APPARATUS AT 100° C.

A special piece of apparatus, shown in Figure 5, was constructed to permit a check on the completeness of settling of the excess mercuric sulfide at elevated temperatures. The apparatus was arranged so that the supernatant liquid from a hydrolysis determination could be forced through an asbestos mat and a sintered-glass disk in a filter stick by hydrogen pressure, while the entire system was held in a boiling water bath. In this manner, complete removal of excess mercuric sulfide was insured. The filtered, supernatant liquid was collected under a protective stream of nitrogen to minimize atmospheric oxidation.

#### PREPARATION OF SOLUTIONS

Solutions for the measurements were prepared as described in the section on electrical conductivity measurements. Sodium sulfide solutions were used for several days before being discarded. While not in use, they were kept under hydrogen and near the cooling coils of a refrigerator, as is recommended by Horlew and Pascoe (20). The mercuric sulfide used was the red c. p. powder of Berck and Co., Inc. Knox (27) found that the black, less stable form of mercuric sulfide did not form

a true complex with sodium sulfide.

#### ANALYSIS OF THE SUPERNATANT LIQUID FOR DISSOLVED MERCURIC SULFIDE

Ten ml. of the clear supernatant liquid were carefully pipetted into a 50-ml. Erlenmeyer flask containing ten ml. of 6 N hydrochloric acid. The transfer was made under a protective stream of nitrogen in order to minimize atmospheric oxidation. Hydrogen sulfide was then bubbled through the solution for ten minutes to complete the precipitation. The solution was filtered through a weighed Pyrex "fine" sintered-glass crucible to which an asbestos mat had been added. The precipitate was washed with 30 ml. of 95 per cent ethyl alcohol, followed by an equal amount of carbon disulfide. The crucibles were dried for at least two hours at 110° C., cooled in a desiccator for thirty minutes, and weighed.

#### CALCULATION OF THE DEGREE OF HYDROLYSIS FROM MERCURIC SULFIDE SOLUBILITY

The method of calculation is illustrated by the following example: 10 ml. of the supernatant liquid from a solution 0.25 M in sodium sulfide and 0.25 M in sodium hydroxide, after 24 hours' mixing with an excess of mercuric sulfide, contained 0.1173 g. of dissolved mercuric sulfide.

$$\begin{aligned}
 \text{molarity HgS} &= \frac{\text{wt. HgS}}{\text{HgS}} \times \frac{1000}{10} \\
 &= \frac{0.1173}{232.67} \times 100 \\
 \text{M HgS} &= 0.0504
 \end{aligned}$$

In the presence of a large excess of  $\text{HgS}$ ,



$$\text{molarity HgS} = \text{molarity Na}_2\text{S as Na}_2\text{S}$$

$$\therefore M \text{ Na}_2\text{S} = 0.0504$$

$$\text{Hydrolysis of Na}_2\text{S} = 100 - \frac{0.0504 \times 100}{0.25}$$

$$= 79.8 \text{ per cent.}$$

#### CALCULATION OF THE STANDARD ERROR FOR MERCURIC SULFIDE HYDROLYSIS DETERMINATIONS

The standard error for the hydrolysis determinations at  $25^\circ \text{C.}$ , at  $110^\circ \text{C.}$ , and at  $165^\circ \text{C.}$  was calculated from the standard error equation,

$$\underline{s}^2 = \frac{1}{\underline{n}-1} \frac{(\underline{n}\underline{x}^2 - (\sum \underline{x})^2)}{\underline{n}}.$$

where  $\underline{s}$  is the standard error,  $\underline{n}$  is the number of measurements on a solution of a given composition, and  $\underline{x}$  is the value of an individual measurement. A weighted average standard error was calculated for all measurements at a given temperature by summing the  $\frac{(\underline{n}\underline{x}^2 - (\sum \underline{x})^2)}{\underline{n}}$  terms and multiplying by the sum of the  $\frac{1}{\underline{n}-1}$  terms.

#### ANALYSIS OF BLACK LIQUOR SAMPLES

Black liquor samples from a mill cook were analysed for sodium sulfide and sodium hydroxide by a procedure suggested by Moltzau (55). According to TAPPI Standard T 625 M, the liquor is treated with barium chloride and the supernatant liquid is titrated to pH 8.3, at which point all of the hydroxide and half of the sulfide have been neutralized.

Moltzau pointed out that, in the presence of formaldehyde, sodium sulfide is completely neutralized at pH 8.3. Therefore, a black liquor can be analyzed for sodium hydroxide and sodium sulfide by titration to pH 8.3 with and without formaldehyde.

# EXPERIMENTAL DATA AND DISCUSSION

The hydrolysis of sodium carbonate and sodium sulfide has been studied by conductance measurements and hydrogen ion concentration determinations at 25° C. The hydrolysis of sodium sulfide at 25° C. and at elevated temperatures has been studied by the application of the mercuric sulfide solubility method of Knox.

## DETERMINATION OF HYDROLYSIS BY ELECTROCHEMATIC MEASUREMENTS (pH) AND BY CALCULATION FROM THE SECOND IONIZATION CONSTANT OF THE ACID OF THE SALT

Determination of the pH's of sodium carbonate, sodium bicarbonate, and sodium sulfide solutions of various concentrations are given in Table I. The measurements were made as described on page 38.

TABLE I

pH VALUES (25° C.)

Sodium Bicarbonate		Sodium Carbonate		Sodium Sulfide	
Molarity	pH	Molarity	pH	Molarity	pH
0.005	10.33	0.005	10.87	0.01202	11.61
0.010	10.47	0.010	10.96	0.0578	12.59
0.020	10.49	0.025	11.09	0.0688	12.53
0.050	10.43	0.050	11.20	0.1104	12.81
0.100	10.36	0.075	11.26	0.1674	12.98
0.200	10.24	0.100	11.30	0.394	13.01
0.875	9.97	0.125	11.34		
		0.150	11.37		

The determination of hydrolysis through pH measurements has a limited application. The upper limit of measurement is a pH of 13, even when the special Beckman Type K, blue-point electrode for high alkalinities is used. As is apparent from Table I, the pH of concentrated sodium sulfide solutions is in this region before the addition of any sodium hydroxide. Therefore, the method is not applicable to any solution with an alkalinity approaching that of a sulfate white liquor. A second limitation is that of temperature. The upper limit for the blue-point electrode is 40° C. To be accurate in the calculation of hydrolysis from pH, activity data for the hydroxyl ion and for the ionic activity coefficient product for water must be employed (see page 40).

The calculation of hydrolysis from the ionization product for water and the second ionization constant of either carbonic acid or hydrogen sulfide is only an approximate method. Once again, data on the ionic activity coefficient product for water and the activities of several of the ions participating in the hydrolytic equilibrium are required. In addition, the second ionization constants of carbonic acid and hydrogen sulfide are not known to an accuracy of greater than ten per cent. The method is not applicable to mixtures of sodium carbonate or sodium sulfide and sodium hydroxide, since the  $K_h = K_2/K_1$  relationship is not valid under these conditions. No calculations at elevated temperatures are possible because of the lack of the required activity and ionization data.

Hydrolysis data on sodium carbonate, sodium bicarbonate, and sodium sulfide at 25° C., as obtained by these methods, appear in Tables III, IV, and V.

# THE CONDUCTANCE METHOD OF HYDROLYSIS DETERMINATION

The application of Bredig's version of the conductance method for hydrolysis determination required equivalent conductance versus concentration curves for the compounds involved in the hydrolysis. The data obtained for this purpose permitted calculation of conductances at infinite dilution of the various compounds for extension of and comparison with data in the literature.

## EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

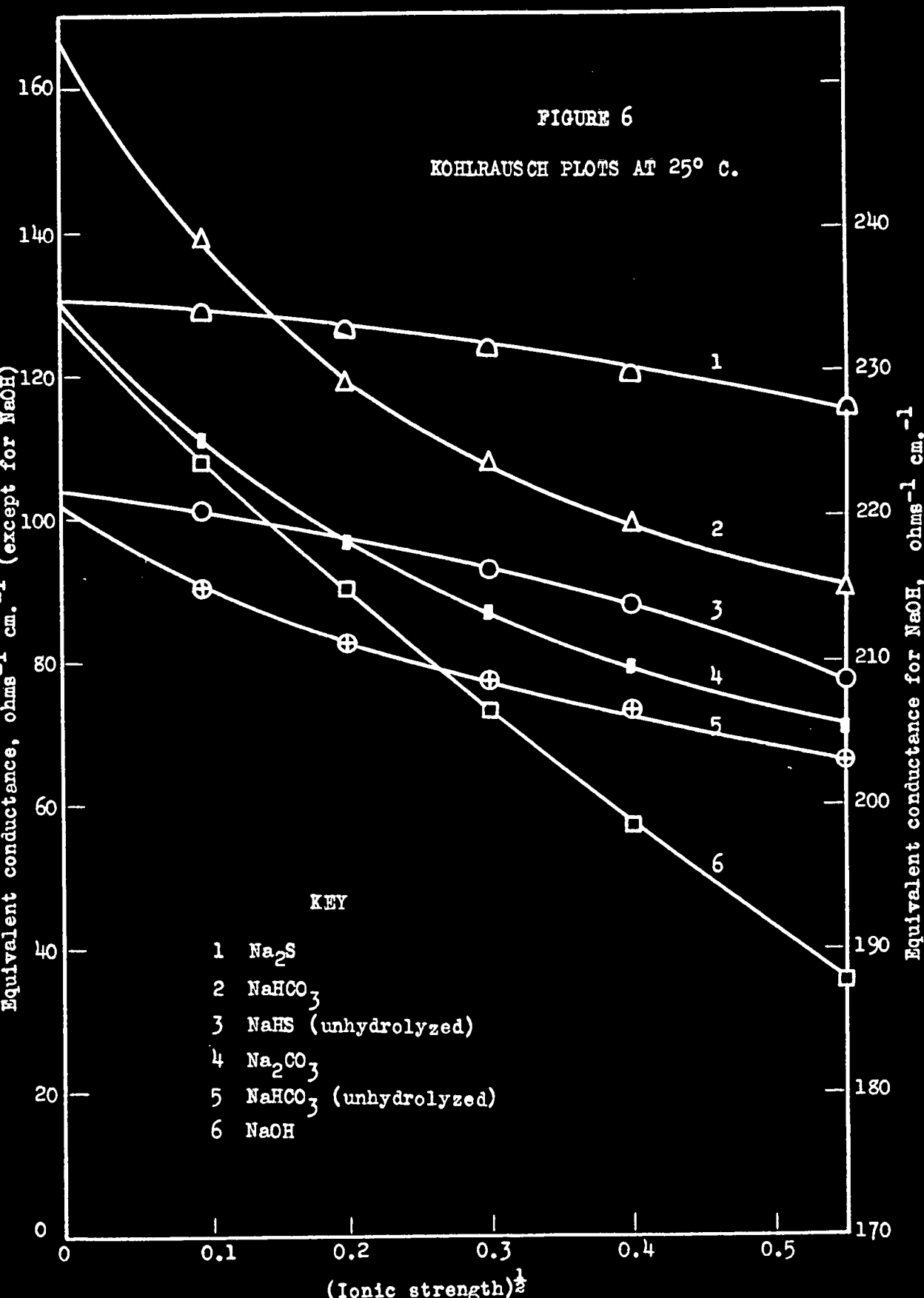
Equivalent conductances at infinite dilution ( $\Lambda_0$ ) at 25° C. are shown in Table II, as determined by Kohlrausch's method (page 36) and by Shedlovsky's method (page 37). The plots are given in Figures 6 and 7. The  $\Lambda_0$  values for the anions were obtained in each case by subtracting the equivalent conductance of the sodium ion at infinite dilution at 25° C. from the  $\Lambda_0$  value of the compound. Johnston (56) gives a value of 50.9 for sodium at 25° C.

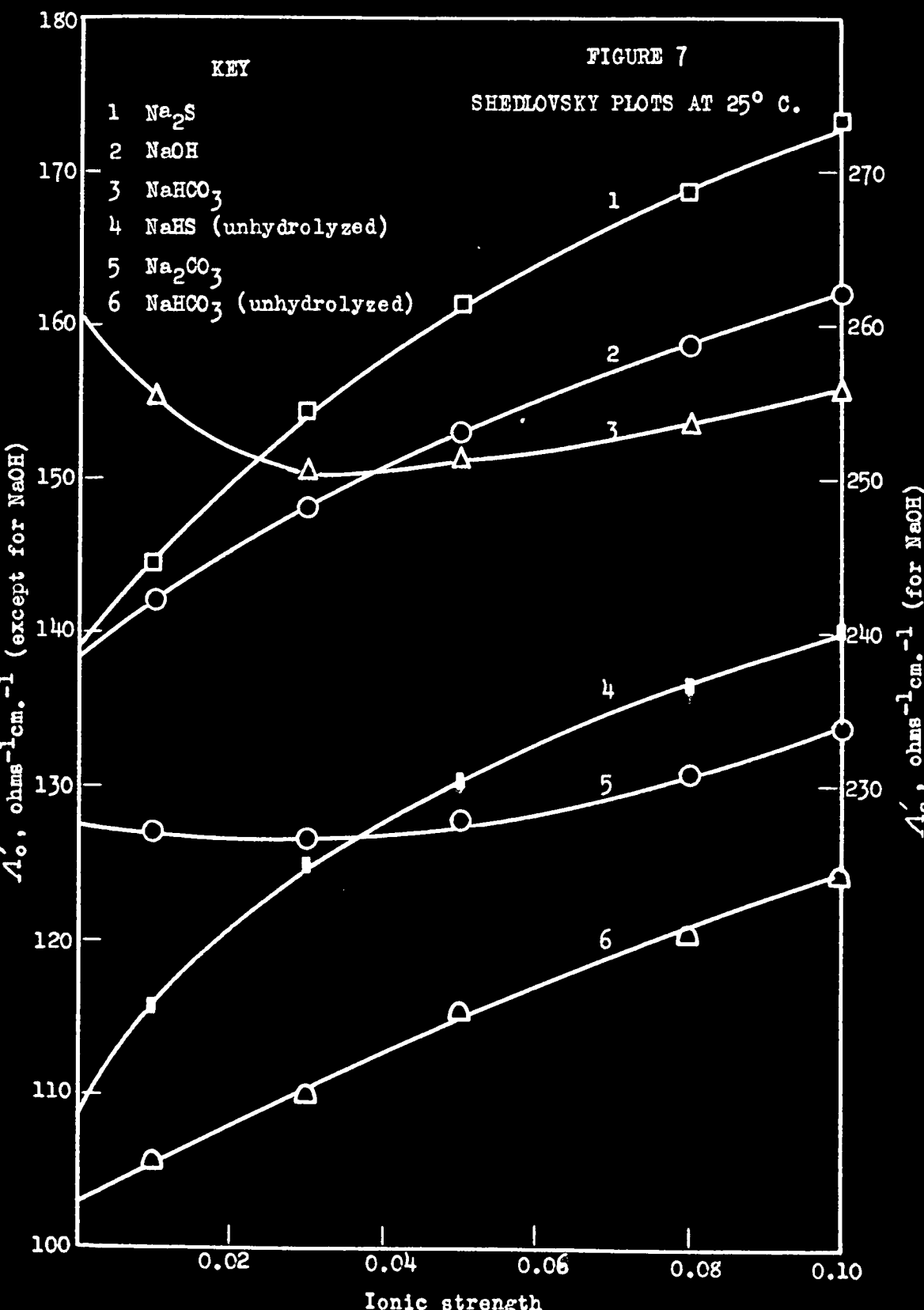
TABLE II

EQUIVALENT CONDUCTANCES ( $\text{ohm}^{-1} \text{ cm.}^{-1}/\text{equivalent}$ )  
AT INFINITE DILUTION (25° C.)

Compounds	Kohlrausch Method		Shedlovsky Method	
	$\Lambda_0$ Compound	$\Lambda_0$ Anion	$\Lambda_0$ Compound	$\Lambda_0$ Anion
NaOH	234.6	183.7	239.2	188.3
NaHCO <sub>3</sub> (unhydrolyzed)	102.3	51.4	102.8	51.9
NaHCO <sub>3</sub>	165.3	114.4	160.4	109.5
1/2 Na <sub>2</sub> CO <sub>3</sub>	130.9	80.0	127.7	76.8
NaHS (unhydrolyzed)	104.3	53.4	106.9	56.0
1/2 Na <sub>2</sub> S	131.1	80.2	138.8	87.9







It should be emphasized that the values for sodium carbonate and sodium sulfide are only apparent values. Actually, these values are the sum of the conductances of that portion of the salt that has remained unhydrolyzed plus those of the products of hydrolysis. The difference between an actual and an apparent value is illustrated in the case of sodium bicarbonate in Table II.

Equivalent conductances at infinite dilution are difficult to find in the literature for several of the compounds listed in Table II. Randall and "callione (58) gave a  $\Lambda_0$  value of 243.9 for sodium hydroxide at 25° C., whereas Darken and Meier (59) reported 248. These values are comparable with that of 239.2 calculated from the data of this thesis by the Shedlovsky method. The Shedlovsky extension of the Onsager theory is well recognized as the most accurate method for the calculation of  $\Lambda_0$  values, although the Kohlrausch method is simpler and more rapid. Taylor (60) gave a value of 60 at 18° C. for the equivalent conductance at infinite dilution of the carbonate ion and noted it as "uncertain." Taylor also presented a value of 45.4 for the sodium ion at 18° C. When one considers that the equivalent conductance at infinite dilution of the sodium ion at 25° C. is 50.9 (56), the value of 76.8 obtained for the carbonate ion at that temperature in this work seems reasonable.

The equivalent conductance at infinite dilution for sodium sulfide was found to be 138.8. This is not consistent with a value of 171 for the equivalent conductance of 0.100 N sodium sulfide at 25° C. published by Jellinek and Czerwinski (61), but appears reasonable in the light of a  $\Lambda$  of 155 obtained for a 0.100 N solution at 35° C. by Goldschmidt

and Larsen (62). Jellinek and Czerwinaki gave 106.7 for 0.010 N sodium hydrosulfide at 25° C., Kendall (63) listed 94.4 for 0.0005 N sodium bicarbonate, and the International Critical Tables (64) noted 110.7 for 0.005 N sodium carbonate. These values seem compatible with the  $\Lambda_0$  values of 106.9, 102.8, and 127.7, respectively, found in this work.

Conductance values for sodium bicarbonate and sodium hydrosulfide in the unhydrolyzed state are not difficult to obtain. Carbon dioxide and hydrogen sulfide are used and these dissolved gases contribute little to the total conductivity. For sodium sulfide and sodium carbonate, however, extremely large concentrations of alkali must be added to suppress the hydrolysis, making the accurate calculation of the conductance of the unhydrolyzed salt an impossibility.

Difficulties of the same nature arise when the attempt is made to calculate the degree of hydrolysis of these salts from conductance data. The established theories relating conductance to other properties of the solution are valid only at infinite dilution. The extension of these theories to concentrations usually encountered in practice is a long and arduous procedure and does not give very good results.

#### HYDROLYSIS OF SODIUM CARBONATE

The percentage of hydrolysis of sodium carbonate in solutions at 25° C., as determined by three methods, is summarized in Table III. Hydrolysis was calculated from conductance data by two methods--those of Bredig (page 37) and Schaeffer (page 38). The calculation from pH values was made as shown on page 39, and the calculation from  $K_1$  and  $K_2$  data is illustrated on page 42. A value of  $5.70 \times 10^{-11}$  was used for the second

ionization constant of carbonic acid; this is the value of Kauko and Mantere (57).

#### HYDROLYSIS OF SODIUM BICARBONATE

The percentage of hydrolysis of sodium bicarbonate in solutions at 25° C. is summarized in Table IV. Calculations were made in the same manner as for sodium carbonate, although the Schaeffer method of calculating conductance data is not applicable to this type of salt.

#### HYDROLYSIS OF SODIUM SULFIDE

Table V presents hydrolysis values on sodium sulfide at 25° C. Calculations were made as for sodium carbonate. The Bredig method for handling conductance data gave negative hydrolysis values, evidently because of the failure of Kohlrausch's laws of additivity of conductances (see page 37) at the concentrations investigated. The conductance of unhydrolyzed sodium sulfide was obtained by subtracting the conductance of a pure solution of sodium hydroxide of the concentration added from the total conductance of a solution containing a given concentration of sodium sulfide and a large added excess of sodium hydroxide. This conductance value for unhydrolyzed sodium sulfide was larger than that for a sodium sulfide solution of the same concentration.

TABLE III  
HYDROLYSIS OF SODIUM CARBONATE (25° C.)

Molarity	Hydrolysis			
	From Conductance (Schaeffer), %	(Bredig), %	From pH, %	From $K_1/K_2$ , %
0.005	----	21.5	11.4	16.2
0.010	58.2	20.8	6.7	12.0
0.025	49.8	16.3	3.6	7.5
0.050	44.3	11.2	2.4	5.2
0.075	----	8.3	2.0	4.2
0.100	37.5	6.2	1.7	3.6
0.150	----	1.5	---	---
0.200	----	---	1.3	2.5
0.300	24.9	---	---	---
0.400	----	---	1.1	1.7
0.500	19.0	---	---	---

TABLE IV  
HYDROLYSIS OF SODIUM BICARBONATE (25° C.)

Molarity	Hydrolysis		
	From Conductance (Bredig), %	From pH, %	From $K_1/K_2$ , %
0.005	30.1	3.8	0.8
0.010	25.1	2.5	0.6
0.020	---	1.3	---
0.050	14.9	0.4	0.3
0.100	10.9	0.2	0.3
0.200	---	0.1	---
0.500	4.3	---	0.1
0.875	---	0.01	---
1.000	0.6	---	0.1

TABLE V

HYDROLYSIS OF SODIUM SULFIDE (25° C.)

Molarity	From Conductance (Schaeffer), %	Molarity	From pH, %	Molarity	From $\frac{K_w}{K_a}$ , %
0.0063	73.8	0.0050	62	0.0062	92
0.0126	81.8	0.0100	63	0.0123	87
0.0253	80.3	0.0250	63	0.0246	80
0.0505	79.3	0.0500	72	0.0493	69
0.1010	79.2	0.1000	76	0.0985	58
0.202	76.3	0.200	79	0.197	45
0.404	77.7	0.400	38	0.394	35

HYDROLYSIS OF SODIUM SULFIDE IN SODIUM SULFIDE-SODIUM HYDROXIDE MIXTURES

The data given in Table VI were obtained from plots of the percentage of hydrolysis vs. the sodium sulfide concentration for a given ratio of sodium hydroxide to sodium sulfide. The calculations for the plots were made from conductance data by the Schaeffer method. Once again the Bredig method gave negative hydrolysis values.

TABLE VI

HYDROLYSIS OF SODIUM SULFIDE IN MIXTURES WITH SODIUM HYDROXIDE (25° C.)

Molarity Na <sub>2</sub> S	0	Molarity NaOH	0.1	0.2	0.4
	%		%	%	%
0.050	80	69	---	---	---
0.100	78	72	68	---	---
0.200	77	76	72	69	---

A COMPARISON OF HYDROLYSIS RESULTS FROM THE CONDUCTANCE,  
ELECTROPHOTETIC, AND INDIRECT METHODS

A study of the hydrolysis values given in Tables III, IV, and V reveals the wide differences in results obtained from the methods discussed above. For sodium carbonate, conductance data gave the highest values for hydrolysis, whereas pH measurements gave the lowest. Calculation of the conductance data by the Schaeffer method gave higher degrees of hydrolysis than calculation by the Bredig method. Francis, Geake, and Roche (43) found by the nitrosoamine method (see page 24) that 0.05 M sodium carbonate was 5.2 per cent hydrolyzed at 15° C. and that an 0.10 M solution was 3.1 per cent hydrolyzed. These values agree quite well with those of 5.2 per cent and 3.6 per cent hydrolyzed, respectively, which are calculated for these solutions at 25° C. by the indirect method. For sodium bicarbonate, the conductance method gave a much higher hydrolysis than the other methods. In this case, a slightly greater hydrolysis was indicated by pH measurements than was determined by the indirect method. The Schaeffer method of calculating conductance data is not applicable to a salt of this type. In the case of sodium sulfide solutions, the Bredig method of calculation gave negative hydrolysis values. The values obtained by the Schaeffer method and from pH measurements are somewhat erratic. Too much significance cannot be attached to the results calculated by the indirect method, for the reasons mentioned above.

Table VI indicates some effect on the part of the sodium hydroxide in suppressing the hydrolysis, although one might expect a more pronounced effect. The increase in hydrolysis with increasing sodium sulfide concentration for 0.1 M and 0.2 M sodium hydroxide is also contrary to expectation.



To summarize, one might say that the conductance, pH, and indirect methods gave an indication of the positions of the sodium sulfide and sodium carbonate hydrolytic equilibria at 25° C. They showed that sodium sulfide is a more highly hydrolyzed salt than sodium carbonate. The results obtained were often erratic and contrary to theory, and lead one to conclude that none of the methods gave more than a semiquantitative estimation of the degree of hydrolysis.

#### MERCURIC SULFIDE SOLUBILITY METHOD OF HYDROLYSIS DETERMINATION

The poor results obtained by the methods thus far described led to an extensive search for other methods of measuring these hydrolyses, particularly that of sodium sulfide.

Much more reasonable and consistent data on the hydrolysis of sodium sulfide were obtained by the application of the mercuric sulfide solubility method of Knox. This method was free from severe limitations as to the alkalinity of the solution being measured, and was adapted to hydrolysis determinations at temperatures typical of those encountered in sulfate pulping.

The validity of the method was checked from every conceivable standpoint. The method as developed by Knox at 25° C. was based upon the mole for mole solubility of red mercuric sulfide in sodium sulfide and its insolubility in water, sodium hydrosulfide, and sodium hydroxide. These insolubilities were verified at 25° C. and were investigated at 165° C. The solubility in hydrogen sulfide was also measured, because an excess of this compound was present in the sodium hydrosulfide solutions. Table VII indicates that red mercuric sulfide is negligibly soluble in water and in sodium hydrosulfide at 165° C., as well as at room temperature, but that some solubility in sodium hydroxide exists at

the elevated temperature. Determinations of solubility were made at a number of sodium hydroxide concentrations in order that a correction could be applied in the hydrolysis calculations at 165° C. In the application of this correction, sodium hydroxide formed by hydrolysis, as well as that added, was considered. In no case did the correction change the calculated percentage of hydrolysis to an extent greater than two per cent. Determinations at 110° C. indicated negligible solubility in sodium hydroxide at this temperature.

#### SOLUBILITY DATA ON MERCURIC SULFIDE

The solubility of red mercuric sulfide (cinnabar) in components of sulfate white liquor other than sodium sulfide is shown in Table VII.

TABLE VII

#### SOLUBILITY OF MERCURIC SULFIDE

Solution	M HgS (25° C.)	Solution	M HgS (165° C.)	Solution (M NaOH)	M HgS (165° C.)
0.1 M NaOH	0	---	---	0.1000	.0003
2.5 M NaOH	0	---	---	0.464	.0024
9.7 M NaOH	0	---	---	0.927	.0022
0.25 M NaHS,		0.20 M NaHS,			
0.025 M H <sub>2</sub> S	0.0001	0.019 M H <sub>2</sub> S	0.0004	1.92	.0118
0.058 M H <sub>2</sub> S	0	0.044 M H <sub>2</sub> S	0	4.80	.0122
H <sub>2</sub> O	0	H <sub>2</sub> O	0.0006	9.60	.0902

#### QUANTITATIVE NATURE OF THE MERCURIC SULFIDE-SODIUM SULFIDE COMPLEX FORMATION

The next point of the Knox method to be investigated was the mole for mole solubility of mercuric sulfide in sodium sulfide. The basis for the calculation of the hydrolysis (page 50) is the proposition that, in the presence of an excess of red mercuric sulfide, there is a quantitative one-to-one relationship between moles of dissolved mercuric sulfide

and moles of sodium sulfide present in the unhydrolyzed form. Table VIII shows the hydrolysis values obtained for solutions in which the ratio of sodium hydroxide to sodium sulfide concentration was very high. Runs 4 through 7 gave very low degrees of hydrolysis. In Run 7, for example, 1.3 per cent hydrolysis was obtained, indicating that the amount of mercuric sulfide dissolved was 38.7 per cent of the total concentration of sodium sulfide (hydrolyzed and unhydrolyzed). With the large excesses of sodium hydroxide present in these solutions, a very low degree of hydrolysis would be expected, although values of a few per cent certainly seem possible. In any event, one may consider the data of Table VIII as very strong evidence that the mole for mole solubility relationship is quantitative or very nearly so at 25° C. Unfortunately, the appreciable solubility of mercuric sulfide in concentrated sodium hydroxide makes it impossible to obtain evidence of this sort at 105° C.

TABLE VIII  
HYDROLYSIS OF SODIUM SULFIDE IN CONCENTRATED  
SODIUM HYDROXIDE (25° C.)

Run	Na <sub>2</sub> S, M	NaOH, M	HgS in Solution, M	Hydrolysis, %
1	.0488	2.362	.0353	27.7
2	.0488	2.362	.0336	31.1
3	.1147	2.220	.0832	27.4
4	.0483	9.31	.0468	3.0
5	.0483	9.31	.0466	3.4
6	.1259	8.66	.1217	3.3
7	.1259	8.66	.1242	1.3

# REVERSIBILITY OF THE COMPLEX-FORMATION REACTION

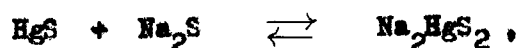
The reversibility of the reaction of  $\text{HgS}$  with  $\text{Na}_2\text{S}$  to form a soluble complex (page 24) was tested in the following manner: A solution of 0.3  $\text{M}$  in  $\text{Na}_2\text{S}$  and 1  $\text{M}$  in  $\text{NaOH}$  was rotated with an excess of mercuric sulfide at  $25^\circ \text{C}$ . for twenty-four hours. A sample of the supernatant liquid was analyzed at this time. Sufficient water was then added to make the solution 0.15  $\text{M}$  in  $\text{Na}_2\text{S}$  and 0.5  $\text{M}$  in  $\text{NaOH}$ . After twenty-four additional hours of mixing, the supernatant liquid was again analyzed. The results are shown in Table IX.

TABLE IX

## REVERSIBILITY OF MERCURIC SULFIDE-SODIUM SULFIDE COMPLEX FORMATION

	$\text{HgS}$ in Soln., $\text{M}$	Hydrolysis ( $25^\circ \text{C}$ .), $\%$
0.3 $\text{M}$ $\text{Na}_2\text{S}$ , 1 $\text{M}$ $\text{NaOH}$	0.1443	51.9
After dilution and 24 hrs. mixing, 0.15 $\text{M}$ $\text{Na}_2\text{S}$ , 0.5 $\text{M}$ $\text{NaOH}$	0.0590	66.7

The reversibility of the complex-formation reaction,

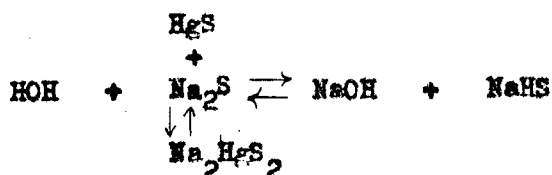


is a requisite of the high-temperature adaptation of the Knox hydrolysis determination. The reaction tubes are filled at room temperature with the solution in question and an excess of mercuric sulfide, and are then heated to the desired temperature. In order for the method to yield correct results at the elevated temperature, the soluble complex must be able to break down with the resultant precipitation of mercuric sulfide from solution, if the hydrolysis of the sodium sulfide increases. After

twenty-four hours of mixing with an excess of mercuric sulfide at 25° C., the hydrolysis of the sodium sulfide in a solution 0.3 M in sulfide and 1.0 M in sodium hydroxide was determined as 51.9 per cent or 0.1443 M mercuric sulfide in solution. After the addition of sufficient distilled water to make the solution 0.15 M in sodium sulfide and 0.5 M in sodium hydroxide and after twenty-four additional hours of mixing, the hydrolysis was determined as 66.7 per cent or 0.0590 M mercuric sulfide in solution. It is evident that considerable mercuric sulfide was thrown out of solution by the increase in hydrolysis upon dilution. In addition, both the hydrolysis values appear very reasonable when compared with the data at other concentrations in Table XII. The complex-formation reaction appears to be reversible.

#### EFFECT OF COMPLEX FORMATION ON THE SODIUM SULFIDE HYDROLYSIS EQUILIBRIUM

In the development of any method for the determination of the position of an equilibrium, the possibility of disturbing the equilibrium must be carefully considered. In the Knox method, the sodium sulfide in solution participates in two equilibrium reactions.



In the presence of a large excess of HgS, such as that used in this method, one would expect all sodium sulfide to be present as the sodium mercury sulfide complex. Information as to the properties of this soluble complex is very scarce in the literature, although Kolthoff, Griffith, and Koltzau (65) have published some work on the precipitation

of mercuric sulfide from the complex by means of zinc sulfide. There is considerable room for argument as to the interchangeability of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{HgS}_2$  in the sodium sulfide hydrolysis equilibrium.

In an effort to detect any shift in the hydrolytic equilibrium, pH measurements were made on 0.1 M sodium sulfide solution before and after twenty-four hours of mixing with an excess of mercuric sulfide. The readings appear in Table X.

TABLE X  
pH OF 0.1 M SODIUM SULFIDE (25° C.)

	Initial pH	Final pH
Run 1	12.90	12.83
Run 2	12.91	12.86

A shift in the hydrolysis means a change in the sodium hydroxide concentration and, therefore, a change in the pH of the solution. Unfortunately, we are dealing with very high pH's and an extensive shift in the hydrolytic equilibrium would be required to shift the pH to an extent greater than the experimental error involved in a pH measurement. For 0.1 M sodium sulfide at pH 12.90, a shift of 16 per cent in the hydrolysis equilibrium would only change the pH to 12.80. Table X indicates that changes in pH of 0.07 and 0.05 were obtained experimentally. The magnitude of these changes is very close to the reproducibility of a pH measurement and, thus, too much significance cannot be attached to them. They may be interpreted as evidence that, if a shift in hydrolytic equilibrium exists, it does not exceed the order of ten per cent or so.

A consideration of Tables VIII and XII, which present results as low as 1.3 per cent and as high as 92.7 per cent for the hydrolysis of sodium sulfide as determined by the Knox method, lends further support to the premise that the disruption of the hydrolytic equilibrium by complex formation is small. There is every reason to believe that, for sodium sulfide solutions more dilute than 0.15 M, the method will yield hydrolysis values higher than 92.7 per cent.

#### DEGREE OF COMPLETION OF SETTLING OF EXCESS MERCURIC SULFIDE

It was desired to check the efficiency of the separation of excess mercuric sulfide from the supernatant liquid in the stainless steel tubes at elevated temperatures. Special apparatus was constructed in which the supernatant liquid was actually filtered through asbestos and sintered-glass mats at 100° C. (see Figure 5). The hydrolysis values obtained appear in Table XI.

TABLE XI

HYDROLYSIS OF SODIUM SULFIDE (100° C.)  
(SUPERNATANT LIQUID FILTERED)

Solution	Hydrolysis, %
0.2 <u>M</u> Na <sub>2</sub> S, 0.5 <u>M</u> NaOH	
Run 1	64.9
Run 2	65.1

The average value of 65.0 per cent hydrolyzed at 100° C. obtained under these conditions compares well with that of 67.1 per cent hydrolyzed obtained for the same composition of solution at 110° C. (Table XII) by the regular high-temperature method. It is apparent that

satisfactory removal of excess mercuric sulfide is obtained by the settling and decanting procedure used.

# HYDROLYSIS OF SODIUM SULFIDE IN SULFIDE-HYDROXIDE MIXTURES

Table XII presents data on the hydrolysis of sodium sulfide at various sulfide and hydroxide concentrations and for several temperatures as obtained by the mercuric sulfide method. The concentrations and temperatures were selected to cover the ranges normally encountered in sulfate pulping.

TABLE XII

## HYDROLYSIS OF SODIUM SULFIDE

25° C. M Na <sub>2</sub> S	Molarity NaOH				
	0 %	0.25 %	0.50 %	0.75 %	1.5 %
0.15	92.7	79.7	66.7	56.8	37.8
0.25	91.9	80.3	----	58.7	41.0
0.35	83.8	71.9	----	55.1	33.1
110° C. M Na <sub>2</sub> S	Molarity NaOH				
	0 %	0.25 %	0.50 %	1.0 %	1.5 %
0.20	89.3	79.3	67.1	51.9	43.1
165° C. M Na <sub>2</sub> S	Molarity NaOH				
	0 %	0.25 %	0.50 %	1.0 %	1.5 %
0.20	92.0	84.5	72.0	53.5	46.9

An examination of these data reveals that the sodium sulfide concentration and the temperature of the solution exert only minor influences on the degree of hydrolysis. The determining factor seems to be the amount of sodium hydroxide present, although the effect of this compound in suppressing the hydrolysis is also surprisingly small. From Table XII, it appears that 1.5 M sodium hydroxide reduces the



hydrolysis by little more than one half for the concentrations of sodium sulfide investigated. Table VIII indicates that eight or nine molar sodium hydroxide is required to reduce the hydrolysis to less than four per cent for dilute sodium sulfide solutions.

Mitchell and Yorston (21), in experiments on the delignification of wood with sodium sulfide, found a direct proportionality between the rate of delignification and the sodium sulfide concentration. They considered this to be surprising, because of an expected change in the hydrolysis of sodium sulfide with concentration. The data in Table XII indicate that, at 25° C. at least, there is little change in the hydrolysis with change in sodium sulfide concentration, over a concentration range of 0.15 M to 0.35 M.

The small effect of temperature on the sodium sulfide hydrolysis, evidenced in Table XII, was contrary to expectation. It is well established that  $K_w$ , the ionization product for water, shows a rapid increase with temperature. Since  $K_h = K_w/K_a$  (see page 35), one might expect the hydrolysis to increase rapidly with  $K_w$ . Two possible reasons for the small change suggest themselves: (1) the increase of  $K_w$  with the temperature increase in a concentrated salt solution may be less than in the case of pure water and (2) the second ionization constant of hydrogen sulfide ( $K_a$ ) may increase with the temperature to such an extent as to balance the increase in  $K_w$ .

Unfortunately, data are not available in the literature on the variation of the second ionization constants of hydrogen sulfide and carbonic acid with temperature. Jenkins (66) presents an equation for

the ionization constant of acetic acid, which is satisfactory over a fifty degree temperature range. The equation is also applicable to formic, propionic, and butyric acids. Values of  $1.751 \times 10^{-5}$  at  $25^{\circ}$  C. and  $1.539 \times 10^{-5}$  at  $60^{\circ}$  C. were calculated for acetic acid.

Evidence for the idea that the second ionization of hydrogen sulfide increases with temperature is found when the heats of neutralization of certain weak acids are considered. The combination of hydrated hydrogen and hydroxyl ions to form water is accompanied by the evolution of 13.8 kilogram-calories per mole. In the neutralization of one mole of acetic acid by sodium hydroxide, 13.40 kilogram-calories are liberated. The difference between 13.8 and 13.40 is the heat consumed in the ionization of acetic acid in water. The neutralization of hydrogen cyanide ( $K_a = 7 \times 10^{-10}$ ) by sodium hydroxide liberates only 2.90 kilogram-calories of energy per mole. The lower the ionization constant the greater is the heat consumed in ionization of the acid, and one might expect that an acid with a high heat of ionization would exhibit an increase in ionization with increasing temperature. Thus it seems quite possible that the second ionization of hydrogen sulfide ( $K_2 = 1.2 \times 10^{-15}$ ) might be very sensitive to increased temperature.

It would seem that Koon (page 9) was making a rather extensive approximation when he assumed that sodium carbonate and sodium sulfide were practically equivalent as a source of sodium hydroxide by hydrolysis in a kraft cooking liquor. He based the assumption upon the premise that the dissociation constants of hydrogen sulfide and carbonic acid were about the same. It is true that the first ionization constants are quite

similar ( $3.313 \times 10^{-7}$  for hydrogen sulfide (67) and  $3.47 \times 10^{-7}$  for carbonic acid (57)). The second ionization constants, however, are the ones that determine the degree of hydrolysis of the salts in question, and these differ appreciably ( $1.2 \times 10^{-15}$  for hydrogen sulfide (51) and  $5.70 \times 10^{-11}$  for carbonic acid (57)). The data in Tables III and V indicate that sodium sulfide is a more highly hydrolyzed salt than sodium carbonate.

#### A COMPARISON OF HYDROLYSIS RESULTS ON SODIUM SULFIDE BY THE CONDUCTANCE AND MERCURIC SULFIDE METHODS

A comparison of the hydrolysis values in Table VI, obtained by the Schaeffer method of calculation from conductance data, with those of Table XII, obtained by the mercuric sulfide solubility method of Knox, reveals fair agreement. The Schaeffer method gave a value of 77 per cent hydrolyzed for 0.2 M sodium sulfide at 25° C., as compared with 92.7 per cent for 0.15 M and 91.9 per cent for 0.25 M sodium sulfide by the Knox method. For a solution 0.2 M in sodium sulfide and 0.2 M in sodium hydroxide, the conductance method gave 72 per cent hydrolyzed, whereas the mercuric sulfide determination yielded 79.7 per cent for a 0.15 M sodium sulfide-0.25 M sodium hydroxide mixture and 80.3 per cent for a 0.25 M-0.25 M mixture.

Schaeffer found that 0.05917 M sodium sulfide was 94.3 per cent hydrolyzed at 25° C. (see page 38). The close agreement of this result with the high values of Table XII for sodium sulfide solutions with no sodium hydroxide added appears to be a matter of coincidence. The use of conductance data obtained in this thesis gave a value of 71.7 per cent

hydrolyzed for 0.0505 M sodium sulfide. Schaeffer's value for the specific conductance of 0.05917 M sodium hydroxide seems questionable when compared with the data of Goldschmidt and Larsen (62), which appear in International Critical Tables.

Schaeffer's value for 0.05917 M NaOH at 25° C.	$11.61 \times 10^{-3} \Lambda^{-1}$
Goldschmidt and Larsen value	$12.61 \times 10^{-3} \Lambda^{-1}$
Value determined in this thesis	$12.53 \times 10^{-3} \Lambda^{-1}$

It is evident that the mercuric sulfide solubility method is much more precise than the conductance method for determining sodium sulfide hydrolysis. Small errors in the specific conductivity values involved in the Schaeffer determination produce large differences in the calculated percentage of hydrolysis. The response of the hydrolysis to changes in the sodium hydroxide and sodium sulfide concentrations is both more pronounced and more predictable by the mercuric sulfide method.

In brief, then, the mercuric sulfide solubility method was by far the best of the methods investigated for the determination of the sodium sulfide hydrolysis. It was applicable to all concentrations of sulfide and hydroxide and at all temperatures encountered in sulfite pulping. The calculation of hydrolysis from the solubility data was simple and direct, and required no data on activities. The results obtained were consistent and satisfactorily reproducible for the present purpose, standard errors being determined as 3.39 per cent for the work at 25° C., 3.70 per cent at 110° C., and 1.58 per cent at 165° C. The theoretical basis for the method, although not proved rigorously, was established sufficiently well to give the method a quantitative status. The general agreement at 25° C. of results obtained from the conductance,

pH, and indirect methods with those obtained by the mercuric sulfide method was an additional argument for the validity of this method.

#### APPLICATION OF HYDROLYSIS DATA TO MILL COOKING DATA

It was felt that components of a sulfate black liquor other than sodium hydroxide would have little bearing on the sodium sulfide hydrolysis. To confirm this idea, the high-temperature adaptation of the Knox method was applied directly to some mill black liquors which had been analyzed for sodium hydroxide and total sulfide. The liquor samples were obtained from the Mosinee Paper Mills, Mosinee, Wisconsin. The values obtained were of the same order of magnitude as the hydrolytic data on pure solutions of sodium hydroxide and sulfide, although the results obtained were somewhat erratic and are not presented. The reason for the erratic results was the coprecipitation of alkali lignin when the black liquors were acidified to precipitate dissolved mercuric sulfide. Thorough washing of the precipitate with alcohol removed most of this lignin, but it was evident that the direct application of the mercuric sulfide method to black liquors yielded data of little value.

Since satisfactory data on the hydrolysis of the sodium sulfide in cooking liquors could not be obtained directly, the hydrolysis values for the various liquor samples were estimated by application of the data in Table XII on the hydrolysis of sodium sulfide in mixtures with sodium hydroxide to the total sulfide and sodium hydroxide contents of the liquor samples as determined by analysis. From these estimated hydrolysis values, the total concentrations of sodium hydroxide, sodium sulfide, and sodium bisulfide existing in the solutions were calculated.

This procedure was applied to some analytical data on a Nekoosa-Edwards cook, as well as to those of the Rosine cook. The results obtained are tabulated in Tables XIII and XIV and are plotted in Figures 8 and 9. The term "M NaOH (free)" used in these tables and figures does not include sodium hydroxide formed by hydrolysis of the sodium sulfide.

The original analytical data on the Rosine cook are indicated by the points in Figure 9; those for the Nekoosa-Edwards cook were taken from Horlew and Pascoe (20).

TABLE XIII

MILL-SCALE COOKING DATA (NEKOOSA-EDWARDS)

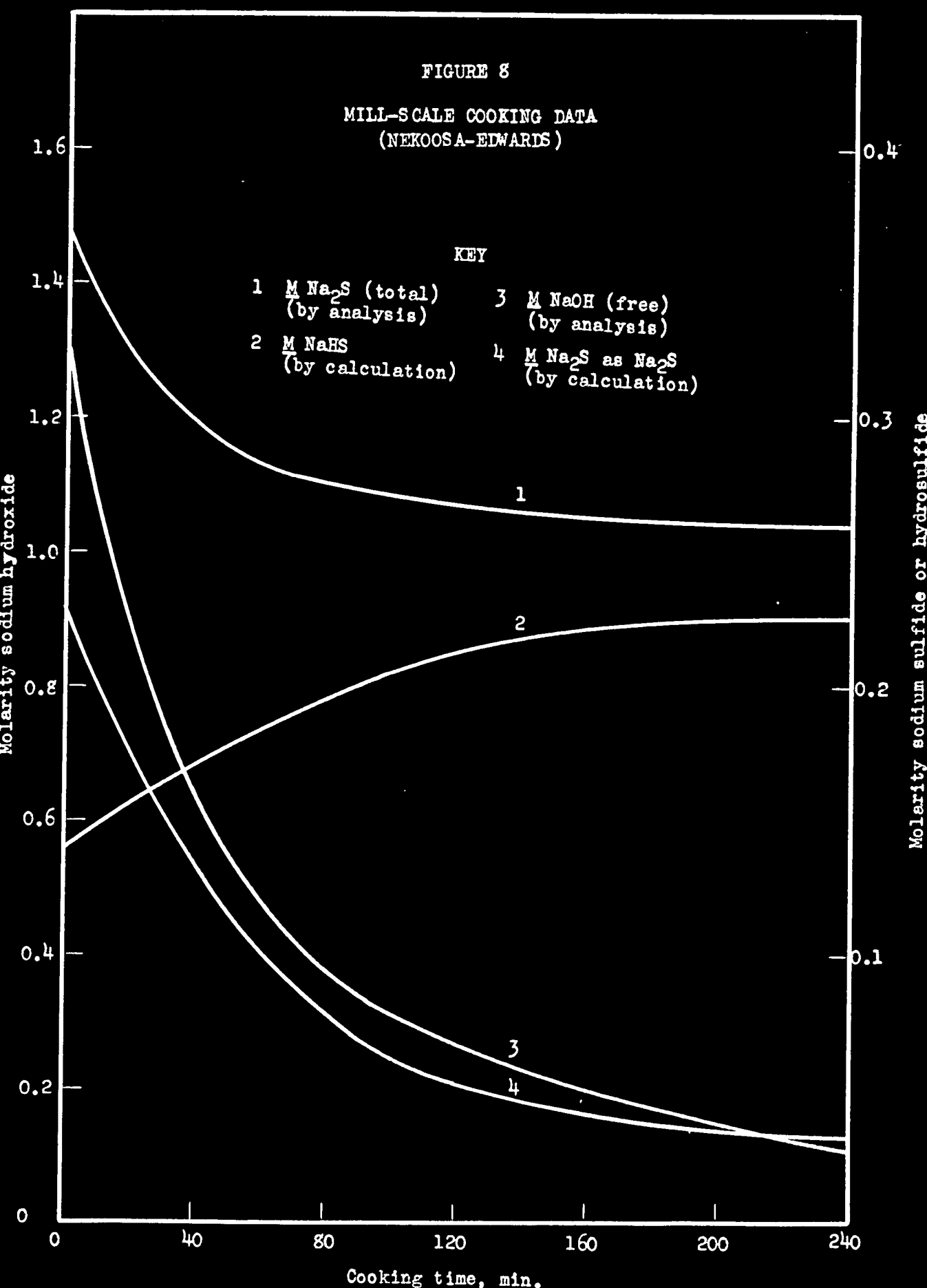
Time, min.	<u>M</u> NaOH, free	<u>M</u> Na <sub>2</sub> S, total	Estimated Hydrolysis, %	<u>M</u> NaOH	<u>M</u> Na <sub>2</sub> S	<u>M</u> NaHS
0	1.30	0.37	38	1.44	0.23	0.14
60	0.48	0.28	64	0.66	0.10	0.18
120	0.27	0.27	78	0.48	0.06	0.21
180	0.17	0.26	85	0.39	0.04	0.22
240	0.11	0.26	88	0.34	0.03	0.23

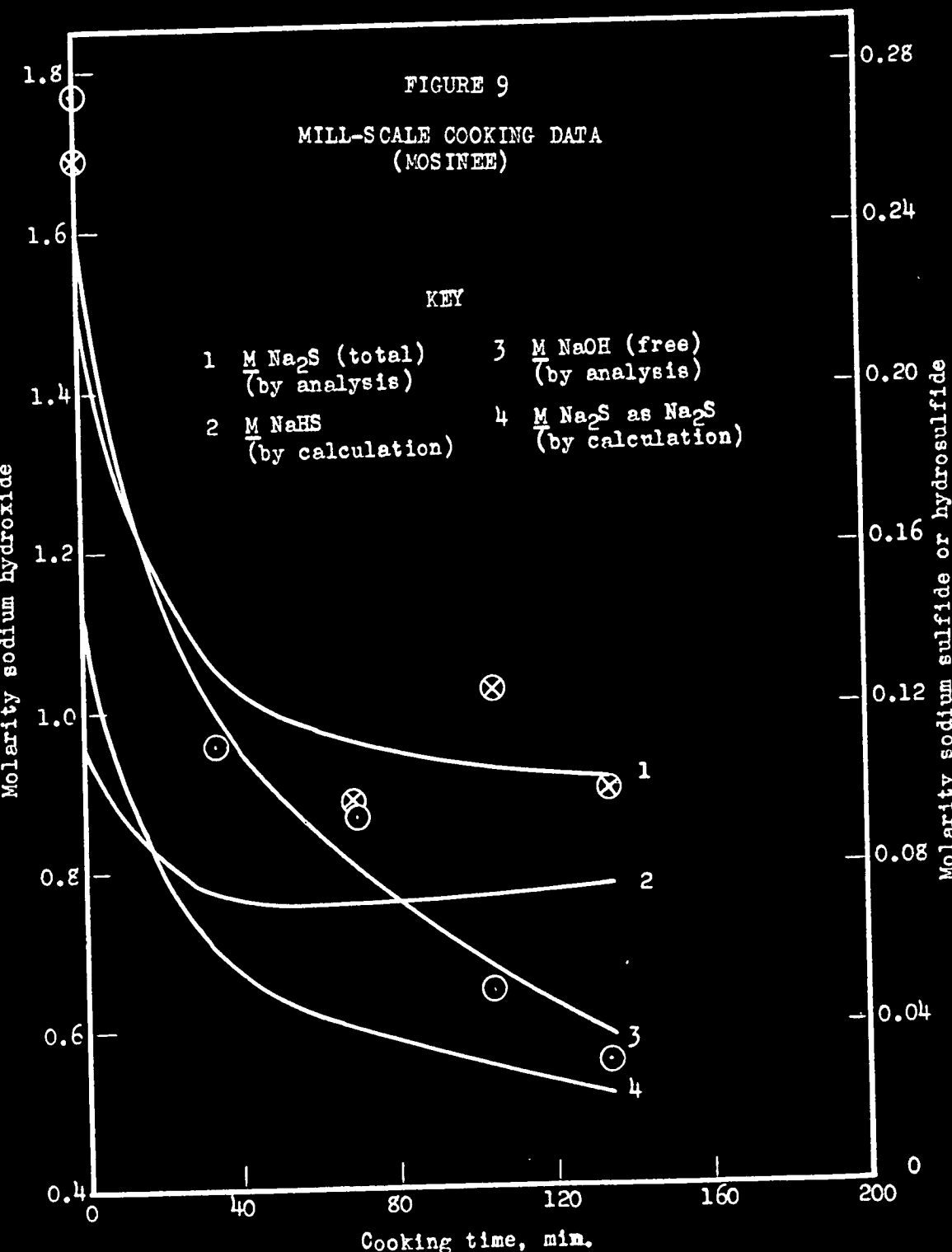
TABLE XIV

MILL-SCALE COOKING DATA (ROSINE)

Time, min.	<u>M</u> NaOH, free	<u>M</u> Na <sub>2</sub> S, total	Estimated Hydrolysis, %	<u>M</u> NaOH	<u>M</u> Na <sub>2</sub> S	<u>M</u> NaHS
0	1.77	0.26	42	1.88	0.15	0.110
35	0.98	0.13	57	1.05	0.06	0.074
70	0.80	0.11	65	0.87	0.04	0.072
105	0.67	0.10	73	0.74	0.03	0.073
135	0.58	0.10	76	0.66	0.02	0.076

FIGURE 8  
MILL-SCALE COOKING DATA  
(NEKOOSA-EDWARDS)







## THE SODIUM SULFIDE HYDROLYSIS IN SULFATE COOKING

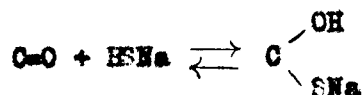
Many assumptions as to the hydrolysis of sodium sulfide in a sulfate cooking liquor appear in the literature. Bray, Martin, and Schwartz (4) and Hanson (5), on one hand, assumed complete or practically complete hydrolysis of the sodium sulfide to sodium hydroxide and sodium hydrosulfide. On the other hand, Borlew and Pascoe (20) assumed zero hydrolysis, stating that sodium hydrosulfide does not exist in a sulfate cooking liquor and, furthermore, that it cannot exist at a pH higher than 8.3. The data of Table XII indicate an appreciable hydrolysis, and substantiate Braun's (6) idea of a partial hydrolysis of sodium sulfide to hydrosulfide, from which compound a mercapto group is formed in sulfate lignin.

It should be mentioned again that these data were obtained from mixtures of pure solutions of sodium sulfide and sodium hydroxide and not from actual cooking liquors. It is felt, however, that the other components in a cooking liquor, or even in a black liquor, would have little effect upon the sodium sulfide hydrolysis.

Table XIII and Figure 8 present analytical data from a mill-scale cook, to which has been added an estimation of the sodium sulfide hydrolysis, based upon the data of Table XII. Some interesting observations in connection with various ideas that have been advanced on sulfate pulping can be made by considering the hydrolysis at several points during a typical cook. The ideas mentioned were expressed, with appropriate references, in the "Historical Review" section of the thesis.

Let us consider the cook described in Table XIII as a typical sulfate cook, in which the temperature is raised to 165° C. in one and one-half hours and held there for two and one-half hours before the digester is relieved and blown.

When the cook is first started, the sodium sulfide is only 38 per cent hydrolyzed; the total concentrations in solution are 1.44 M sodium hydroxide, 0.23 M sodium sulfide, and 0.14 M sodium bisulfide. During the first hour, air is removed from the digester, the liquor penetrates the chips, and the volatile oils distill off with the steam. The more soluble carbohydrates are attacked to a greater extent than the lignin during the very early part of the cook. The entrance of sulfur into the lignin, with the resulting increase of lignin solubility in alkali, may take a little time to reach appreciable proportions. The sulfur apparently enters the lignin from the sodium hydrosulfide and forms a mercapto group.



It is the presence of this mercapto group that is responsible for the increase in alkali solubility.

At the end of the first hour, the temperature is in the neighborhood of 140° C. and the sodium sulfide is 64 per cent hydrolyzed. The concentration of the sodium hydrosulfide in solution has actually increased to 0.18 M, whereas the sodium hydroxide is 0.66 M and the sodium sulfide is 0.10 M. It is in this region that the rate of delignification and the ratio of lignin to carbohydrates dissolved are approaching their maxima.

At the end of the second hour, maximum temperature has been reached and the sodium sulfide is 78 per cent hydrolyzed. The concentrations in solution are now 0.48 M for sodium hydroxide, 0.06 M for sodium sulfide, and 0.21 M for sodium bisulfide. The evolution of noncondensable gases has practically ceased and the more readily accessible lignin has been removed.

During the last two hours of the cook, there is a slow lignin removal and some degradation of the cellulose. The cooking liquor is rich in sodium hydrosulfide, but the alkali concentration has become rather low. Much of the lignin now being removed is coming from the middle lamella. This lignin may have been rendered less soluble by condensation reactions earlier in the cook.

Theoretical support for the recognized benefits of pre-impregnation with black liquor, as well as for sulfate injection pulping, is found in the hydrolysis and cooking data. From Table XIII it is evident that the black liquor has a high concentration of sodium hydrosulfide. Sulfur may enter the lignin in appreciable amounts during the pre-impregnation period. The thiolignin formed will then dissolve rapidly as soon as the white liquor, rich in sodium hydroxide, comes in contact with the wood.

In injection cooking, a more dilute liquor at the beginning of the cook should eliminate (or materially reduce) the period during which carbohydrates are dissolved at a more rapid rate than the lignin. It is felt that maximum benefits would be obtained by starting the cook with a high-sulfidity white liquor in the digester, and injecting a

liquor of lower sulfidity and higher sodium hydroxide content as the cook progressed. In this way, a high concentration of sodium hydro-sulfide would be present to enter the lignin during the early stages, and a sufficient amount of sodium hydroxide would be present toward the end of the cook to dissolve the more resistant lignin.

## CONCLUSIONS

- (1) A method has been developed for determining the hydrolysis of sodium sulfide in mixtures with sodium hydroxide, over the ranges of concentration and temperature encountered in sulfate pulping. The method, the principles of which were given by Knox, is based upon the quantitative solubility of mercuric sulfide in sodium sulfide and its insolubility in sodium hydrosulfide, sodium hydroxide, and water.
- (2) This method indicated that the sodium sulfide was about forty per cent hydrolyzed at the beginning of a typical sulfate cook and about ninety per cent hydrolyzed at the end.
- (3) The concentration of sodium hydroxide in the cooking liquor appeared to be the dominant factor in determining the degree of hydrolysis of the sodium sulfide; temperature and sodium sulfide concentration exerted only a minor influence.
- (4) Determination of hydrolysis by conductance measurements, pH measurements and, indirectly, by calculation from acidic ionization constants gave only approximate results. These methods had serious limitations as to concentration and/or temperature, although the order of magnitude of the hydrolysis results obtained at 25° C. was such as to lend additional support to the validity of the mercuric sulfide method.

LITERATURE CITED

1. United States Pulp Producers' Association. Wood Pulp Statistics. New York, The Association, 1947. 269 p.
2. Hodges, Paul. The sulfate process. In Sutermeister, The chemistry of pulp and paper making. 3rd ed. p. 94-167. New York, Wiley, 1941.
3. Kress, Otto and McGregor, George H., Paper Trade J. 96, no. 24:40-42 (T.S.302-304)(June 15, 1933).
4. Bray, Mark W., Martin, J. Stanley, and Schwartz, Sidney L., Paper Trade J. 109, no. 17:40-45(T.S.224-229)(Oct. 26, 1939); Tech Assoc. Papers 22:382-387, 83-85(1939).
5. Hanson, Fred S., Paper Trade J. 112, no. 2:32-38(T.S.16-22)(Jan. 9, 1941); Tech. Assoc. Papers 23:163-169(1940).
6. Mitchell, C. R., and Vorston, F. H., Forest Products Labs. Canada, Pulp Paper Lab., Quarterly Rev. no. 18:6-16(April-June, 1934).
7. Savell, Walter L., Paper Trade J. 111, no. 8:31-34(T.S.91-94)(Aug. 22, 1940); Tech Assoc. Papers 23:154-157, 64(1940).
8. Bray, Mark W., and Singer, Bernard, Paper Trade J. 125, no. 8:49-53 (T.S.81-85)(Aug. 21, 1947).
9. Hisey, W. O. Delignification of wood. Alkaline Delignification. In Wise, Wood chemistry. p. 716-730. New York, Reinhold, 1944.
10. Koon, Charles M. Preparation of cellulose from its natural sources. A. Wood pulp. In Ott, Cellulose and cellulose derivatives. p. 475-534. New York, Interscience Publishers, 1943.
11. Aronovsky, S. I., Paper Ind. 16:413-419(Sept., 1934).
12. Jayne, G., Wagenbach, H., and Deloff, W., Papier-Fabr. 37, no. 43/44: 353-357(1939).
13. Buchanan, M. A., and Koon, C. E., Paper Trade J. 115, no. 14:116 (T.S.190)(Oct. 1, 1942).
14. Hossfeld, Ralph L., Gortner, Ross Aiken, and Kaufert, Frank H., Ind. Eng. Chem. 35:717-720(1943).
15. Bixler, A. L. M., Paper Trade J. 107, no. 15:29-40(T.S.171-182)(Oct. 13, 1938); Tech. Assoc. Papers 21:181-192, 39-41(1938).
16. Brauns, F. E. Lignin and other noncarbohydrates. In Ott, Cellulose and cellulose derivatives. p. 449-472. New York, Interscience Publishers, 1943.

17. Ahlm, C. Edward, Paper Trade J. 113, no. 13:115-118(T.S.175-178)  
(Sept. 25, 1941); Tech. Assoc. Papers 25:687-690(1942).
18. Hagglund, Erik, Holz Roh u. Werkstoff 4:233-240(1941).
19. Arrhenius, Svante, Paper Trade J. 82, no. 15:65-66(T.S.202-203)  
(April 15, 1926); Tech. Assoc. Papers 9:85-86(1926).
20. Norlew, P. B., and Pascoe, T. A., Paper Trade J. 122, no. 10:31-34  
(T.S.99-102)(March 7, 1946); Tech. Assoc. Papers 29:166-168, 75-76  
(1946). Paper Trade J. 123, no. 15:178-180(T.S.194-196)(Oct. 10, 1946).
21. Mitchell, C. R., and Yorston, F. H., Forest Products Labs. Canada,  
Pulp Paper Lab., Quarterly Rev. no. 19:11-22(July-Sept., 1934).
22. Larocque, G. L., and Mass, O., Can. J. Research 19, B:1-16(Jan. 1941).
23. Wells, C. D., and Arnold, Kenneth A., Paper Trade J. 113, no. 9:39-42  
(T.S.103-106)(Aug. 28, 1941); Tech. Assoc. Papers 24:156-159(1941).
24. Crandall, Henry C., and Enderlein, G. F., Paper Trade J. 123, no.  
2:40-43(T.S.16-19)(July 11, 1946); Tech. Assoc. Papers 29:310-313,  
75(1946).
25. Bredig, G., Z. physik. chem. 13:191-326, especially p. 214(1894).
26. Noyes, Arthur A. The electrical conductivity of aqueous solutions.  
Washington, Carnegie Institution of Washington, 1907. 352 p.
27. Knox, Joseph, Trans. Faraday Soc. 4:29-50(1908).
28. Arrhenius, Svante, J. Chem. Soc. 105:1414-1426(1914).
29. Debye, P., and Hückel, H., Physik Z. 24:305-325(1923); C.A. 18:190  
(1924).
30. Onsager, Lars, Chem. Rev. 13:73-89, especially 84(1933).
31. Scatchard, George, Chem. Rev. 19:309-327(1936).
32. Robinson, Robert A., and Harned, Herbert S., Chem. Rev. 28:  
419-476(1941).
33. Jones, Grinnell, and Prendergast, Maurice Joseph, J. Am. Chem. Soc.  
59:731-736(1937).
34. Jones, Grinnell, and Josephs, Roswell Colt, J. Am. Chem. Soc.  
50:1049-1092(1928).
35. Jones, Grinnell, Mysels, Karol J., and Judin, Walter, J. Am. Chem.  
Soc. 62:2919-2922(1940).

36. Sørensen, S. P. L., Biochem. Z. 21:131-304(1909); quoted by Glasstone, Samuel. Textbook of physical chemistry. 2nd ed. New York, Van Nostrand, 1946. p. 982.
37. Harned, Herbert S., and Owen, Benton B., J. Am. Chem. Soc. 52:5079-5091(1930).
38. Ley, H., Z. physik. Chem. 30:193-257, especially p. 222(1899); quoted by (47), p. 248.
39. Bredig, G., and Fraenkel, W., Z. Elektrochem. 11:525-528(1905); quoted by (47), p. 249.
40. Koelichen, Karl, Z. physik. Chem. 33:129-177(1900).
41. Clibbens, Douglas Arthur, and Francis, Francis, J. Chem. Soc. 101: 2358-2371(1912).
42. Francis, Francis, and Geake, Frank Henry, J. Chem. Soc. 103:1722-1735(1913).
43. Francis, Francis, Geake, Frank Henry, and Roche, James William, J. Chem. Soc. 107:1651-1673(1915).
44. Beedle, F. C., and Bolam, T. R., J. Soc. Chem. Ind. 40:27-29T(1921).
45. McBain, James William, and Martin, Herbert Ernest, J. Chem. Soc. 105:957-977(1914).
46. King, Cecil V., and Marion, Alexander P., J. Am. Chem. Soc. 66:977-980(1944).
47. Lewis, William C. McC. A system of physical chemistry. Vol. 1. New York, Longmans, Green, 1929. 494 p.
48. Bodlaender, G., and Breull, P., Zeit. angew Chem. 14:381, 405-413 (1901); quoted by (49), p. 766.
49. Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. 2. p. 766. New York, Longmans, Green, 1927.
50. Scott, Wilfred W. Standard methods of chemical analysis. 5th ed. Vol. 2. p. 2181-2187. New York, Van Nostrand, 1939.
51. Kolthoff, I. M., and Sandell, E. B. Textbook of quantitative inorganic analysis. New York, MacMillan, 1937. 749 p.
52. Kohlrausch, F. W., and Holborn, L. Leitvermögen der electrolyte. B. G. Teubner, Leipzig, 1898; quoted by (26), p. 263.
53. Shedlovsky, Theodore, J. Am. Chem. Soc. 54:1405-1411(1932).



54. Bates, Roger G., Hamer, Walter J., Manov, George G., and Acree, W. F., J. Research Natl. Bur. Stds. 29:183-190(1942)(RP 1495).
55. Moltzau, D. Romund, Paper Trade J. 115, no. 5:38-42(T.S. 56-60) (July 30, 1942); Tech. Assoc. Papers 25:391-395(1942).
56. Johnston, John, J. Am. Chem. Soc. 31:1010-1020(1909).
57. Kauko, Y., and Mantere, V., Z. physik. Chem. 176:187-201(1936).
58. Randall, Merle, and Scalione, Charles C., J. Am. Chem. Soc. 49: 1486-1492(1927).
59. Darken, Lawrence S., and Meier, Harry F., J. Am. Chem. Soc. 64:621-623(1942).
60. Taylor, Hugh S. A treatise on physical chemistry. 2nd ed. Vol. 1. p. 673. New York, Van Nostrand, 1931.
61. Jellinek, Karl, and Czerwinski, Johannes, Z. physik. Chem. 102: 438-479(1922).
62. Goldschmidt, Heinrich, and Larsen, Halfdan, Z. physik. Chem. 71:437-512(1910).
63. Kendall, James, J. Am. Chem. Soc. 38:1480-1497(1916).
64. The National Research Council of the United States of America. International critical tables of numerical data, physics, chemistry, and technology. Vol. 6, p. 248. New York, McGraw-Hill Book Co., 1930.
65. Kolthoff, I. M., Griffith, Frank S., and Moltzau, D. Romund, J. Am. Chem. Soc. 60:1576-1582(1938).
66. Jenkins, H. O., Trans. Faraday Soc. 41:138-140(1945).
67. Eprecht, A. G., Helv. Chim. Acta 21:205-211(1938).