

1942

A study of cyanamide as a solvent and reaction medium

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A STUDY OF CYANAMIDE AS A SOLVENT AND
REACTION MEDIUM

by

Everett Cromwell Buckner

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

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I. INTRODUCTION

Cyanamide has been known, as a specific compound, since 1851. Many methods of preparation have been published and the physical properties of the compound have been determined. Its chemical reactions have been studied and many compounds have been prepared. Most of these reactions have been carried out in aqueous or liquid ammonia solutions. No investigations have been made of the properties of cyanamide as a solvent and reaction medium.

The theory of electrolytic dissociation stimulated inquiry into the electrical conductivity of solutions. Aqueous solutions were first studied, then solutions in which solvents were mixtures of water and other liquids, especially alcohols. Lastly, attention has been turned to the investigation of the conductivity of solutions that contain no water.

Liquid ammonia and liquid hydrogen cyanide have been used as solvents and as reaction media. Solutions in which these substances were solvents have been found to be conductors of electricity.

Cyanamide can be looked upon as a derivative of ammonia and of hydrogen cyanide. Since the parent substances are reasonably good solvents and their solutions are fair conductors, cyanamide might be expected to have the same properties.

This investigation was undertaken in order to determine the properties of cyanamide as a solvent, as a reaction medium, and as an ionizing medium.

II. REVIEW OF LITERATURE

Cyanamide and related compounds were the objects of intensive study over a hundred years ago. During the period, 1834 - 1855, Liebig (1, 2, 3, 4) published a series of papers on the preparation and properties of these compounds. In the first of these papers, he gives a reaction of cyanogen chloride with ammonia to give, what he called, a cyanamide compound. But it was Cloez and Cannizzaro (5) who, in 1851, proved that cyanamide and ammonium chloride were the products of the reaction.

Volhard (6) first suggested the use of thiourea as the best material for the preparation of pure cyanamide. Freshly precipitated mercuric oxide was suspended in water and added to a cold solution of thiourea. After the sulfur was removed, a few drops of acetic acid were added to the filtrate and the latter was evaporated on a water bath. The residue was extracted with ether and upon evaporating this solution, pure cyanamide was left.

Traube (7) modified the method used by Volhard. The desulfurization of pure thiourea by mercuric oxide was found to be incomplete, even upon standing several days. When a little ammonium thiocyanate was added to a solution of thiourea, the latter was readily converted into cyanamide.

Walther (8) dissolved thiourea in a 10 or 20 per cent solution of potassium hydroxide. Upon the addition of a 30 per cent lead acetate solution, lead sulfide was precipitated and could be filtered. The filtrate, containing the cyanamide, was acidified with acetic acid and extracted with ether. By distillation of the ether solution pure cyanamide was obtained.

Urea may be used as the starting material for the preparation of cyanamide. Moureau (9) treated urea with thionyl chloride and obtained excellent yields of cyanamide. Fenton (10) obtained the compound by gently heating urea with metallic sodium. Hydrogen was evolved and the solid residue contained cyanamide in the form of its sodium salt. The residue was dissolved in water, treated with ammonia and silver nitrate and the precipitated silver cyanamide filtered off. The silver salt was covered with ether and treated with hydrogen sulfide. The ether solution was filtered from silver sulfide and evaporated to obtain the pure cyanamide.

During the period 1895 - 1898, Caro and Frank (11) endeavored to synthesize cyanide compounds by the action of atmospheric nitrogen on barium carbide at a temperature of 700° C. They obtained only small yields of barium cyanide but much larger amounts of barium cyanamide. By using calcium carbide, they were able to get a yield of 90 per cent calcium cyanamide at 1000° C. At the present time, calcium cyanamide is produced by heating calcium carbide with nitrogen in the electric furnace. The commercial product contains 80 per cent

calcium cyanamide.

With calcium cyanamide as an inexpensive raw material, new methods of producing cyanamide were originated. Baum (12) extracted commercial cyanamide with water and precipitated the calcium as the sulfate by neutralizing the extract with sulfuric acid. The cyanamide solution was concentrated in a vacuum and the residue extracted with ether.

Caro and his associates, Schuck and Jacoby (13), extracted commercial cyanamide with water and precipitated the calcium with oxalic acid or aluminum sulfate. The filtrate was evaporated in a vacuum and the cyanamide was extracted and purified with ether.

Werner (14) found the evaporation of a water solution of cyanamide, even in a vacuum, to be a decidedly tedious operation. Since cyanamide is stable in the presence of acetic acid, Werner originated the method of treating calcium cyanamide with acetic acid until the mass is slightly acid throughout. The pasty mass is exposed to the air for 24 hours and then extracted with ether in a Soxhlet apparatus. The ether solution is evaporated and the residue dried over sodium hydroxide.

Osterberg and Kendall (15) tried the existing methods of obtaining cyanamide from thiourea and from calcium cyanamide and abandoned them because of the tedious procedures and poor yields. They suspended calcium cyanamide in water and passed in carbon dioxide until the solution was neutral or

only slightly alkaline to litmus. The calcium carbonate was filtered off and the solution evaporated under diminished pressure until the residue solidified on cooling. The cyanamide was extracted from the residue with ether. They were able to get yields of 93 per cent of the theoretical.

The foregoing methods for the preparation of cyanamide may be summarized by the following equations:



Cyanamide is a deliquescent, colorless solid. It crystallizes from ether solutions in the form of needles. The compound is very soluble in water, alcohol and ether. Some physical properties are shown in Table I.

TABLE I
SOME PHYSICAL PROPERTIES OF CYANAMIDE

Property	Value	Authority	Literature Cited
Melting Point ° C.	40°	Gloez	(5)
	41° - 42°	Caro	(13)
	42°	Drechsel; Lemoult	(16, 17)
	43°	Osterberg	(15)
	43° - 44°	Colson	(18)
	45°	Reis; Maze	(19, 20)
Boiling Point ° C.	140° at 19 mm.	Colson	(18)
	132°-138° at 12 mm.	Maze	(20)
Specific Gravity	1.07288 at 48° C.	Colson	(18)

Bader (21) found that cyanamide, in aqueous solution, is slightly dissociated and shows no distinct acid properties. The solution is a very poor conductor of electricity and Kameyama (22) found the primary dissociation constant, as an acid, to be 5.42×10^{-11} at 25° C. Lemoult (17) stated that in aqueous solution the acidity of cyanamide is comparable with that of hydrogen cyanide.

Working with Franklin, Kraus (23) determined the conductivity of many liquid ammonia solutions. Among these were solutions of cyanamide which conducted electricity with fair facility. Since there must have been an increase in hydrogen-ion concentration above that of the pure solvent, the investigators considered cyanamide a much stronger acid in ammonia than in water.

Many metallic salts of cyanamide have been prepared. It has been found that one or both of the hydrogen atoms in the compound may be replaced by metals. In this respect, cyanamide behaves as an acid. Table II shows the metallic salts recorded in the literature.

TABLE II

METALLIC SALTS OF CYANAMIDE

Compound	Reaction	Reaction Medium	Literature Cited
CaCN_2	$\text{CaC}_2 + \text{N}_2$		(11)
NaHCN_2	$\text{Na} + \text{H}_2\text{N}_2\text{CN}$	Ether	(16)
Ag_2CN_2	$\text{AgNO}_3 + \text{H}_2\text{N}_2\text{CN}$	Water	(16)
BaCN_2	$\text{BaO} + \text{H}_2\text{N}_2\text{CN}$	Methyl alcohol	(16)
PbCN_2	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{N}_2\text{CN}$	Water	(24)
NaKCN_2	$\text{KCN} + \text{N}_2 + \text{Na}$	Fusion	(25)
$\text{Ca}(\text{HCN}_2)_2$	$\text{CaCN}_2 + \text{H}_2\text{O}$		(26)
CuCN_2	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{N}_2\text{CN}$	Water	(27)
HgCN_2	$\text{HgO} + \text{H}_2\text{N}_2\text{CN}$	Water	(27)
$\text{KHCN}_2 \cdot \text{NH}_3$	$\text{KNH}_3 + \text{H}_2\text{N}_2\text{CN}$	Ammonia	(28)
$\text{Mg}(\text{HCN}_2) \cdot 6\text{NH}_3$	$\text{Mg} + \text{H}_2\text{N}_2\text{CN}$	Ammonia	(28)
$\text{Ca}(\text{HCN}_2) \cdot 2\text{NH}_3$	$\text{Ca}(\text{NH}_3)_2 + \text{H}_2\text{N}_2\text{CN}$	Ammonia	(28)

Not only may cyanamide react as a weak acid but also as a weak base. It forms salts with strong acids which are easily hydrolyzed. Drechsel (16) first prepared the hydrochloride, $H_2N.CN.2HCl$, and the hydrobromide, $H_2N.CN.2HBr$. He also mentioned a nitrate which was very unstable.

Cyanamide possesses considerable interest as the natural starting point in a large number of organic syntheses. Undoubtedly its use would be wide spread were it not for the fact that the compound is extremely hygroscopic and has a tendency to polymerize.

For these reasons the salt, cyanamide hydrochloride, should be of interest. It is much less hygroscopic and is more stable than cyanamide itself. In many syntheses it may be used in the place of cyanamide.

Three methods have been proposed for the preparation of $H_2N.CN.2HCl$. Drechsel (16) passed dry hydrogen chloride into an absolute ether solution of cyanamide. Hantsch and Vagt (29) recommended dissolving cyanamide in concentrated hydrochloric acid and evaporating the solution in a vacuum desiccator.

The latest method is that of Pinck and Hetherington (30). In this method, dry hydrogen chloride is passed into 95 per cent ethyl alcohol and then solid cyanamide is added. The hydrochloride precipitates when enough cyanamide has been added to react with 95 per cent of the hydrogen chloride.

After the removal of the solid product the mother liquor is used for the next batch.

The physiological properties of cyanamide are of interest. The compound is poisonous, as is to be expected. Stutzer and Söll (31) investigated the action of cyanamide and some of its derivatives and found the fatal dose of cyanamide for the guinea pig to be 0.4 g. per kilogram of body weight. When the compound comes into contact with the skin a mild exanthemata results.

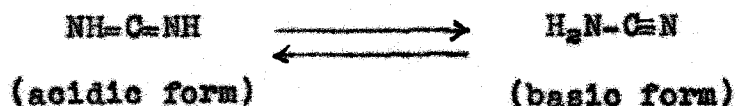
Since the publication of the earliest researches on cyanamide, two possible structural formulas have been suggested. The substance was named as an amide which gave it the structure $CN.NH_2$. But many of the reactions of the compound correspond to the diimide formula $HN=C-NH$.

Mulder (32) urged that the existence of a silver derivative required cyanamide to have the formula $HN=C-NH$, as only in imides can the hydrogen be displaced by metals. But Fileti and Schiff (33) believed that this argument was not conclusive, for metallic derivatives of several amines and amides were known. Moreover, they cited the reaction of amides with chloral as evidence that cyanamide has the formula $CN.NH_2$. No compound of chloral with an imide was known.

Refractometric methods have often been used to determine the structure of compounds in difficult cases. Cyanamide, which is easily polymerized, belongs in this category.

Colson (18) considered the formula of the dialkylcyanamides to be well-established as NC.NR_2 . He determined the refractive power of cyanamide and diethylcyanamide and concluded that the CN_2 group in cyanamide has the same refractometric value as that in its derivative. Therefore, the formula of cyanamide must be NC.NH_2 .

Werner (34) concluded that the properties of cyanamide in neutral solutions are those of a tautomeric substance. He assumed that an electrostatic equilibrium exists in such a solution, as shown by the following equation:



The addition of acid or base will disturb the equilibrium and polymerization will begin.

The polymerization reactions of cyanamide are of industrial importance. The dimer, dicyandiamide, is used to synthesize barbiturates, and in the production of guanidine and biguanide compounds. The trimer, melamine, is used in the manufacture of resins.

When heated alone, or in aqueous solution, cyanamide undergoes polymerization with the production of dicyandiamide. The speed with which the polymerization takes place and the temperature at which it begins are still debatable questions.

Morrell and Burgen (35) maintained neutral aqueous solutions of cyanamide at a temperature of 100°C . for two hours

without appreciable polymerization. Colson (18) kept molten cyanamide at 48° C. for three hours without change.

When warmed in aqueous solution, in the presence of ammonia, cyanamide is converted into dicyandiamide as represented by the equation:



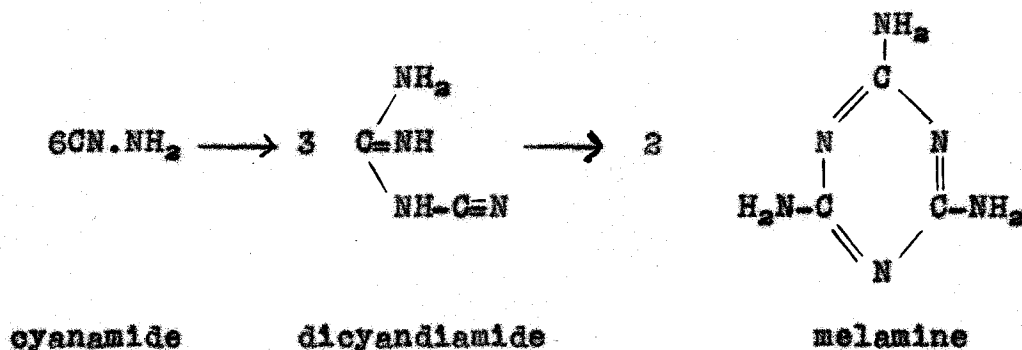
Grube and his associates, Kruger (36) and Motz (37) reported that the speed of polymerization is increased with increasing concentration of ammonia. They found that sodium hydroxide and calcium hydroxide had the same effect as ammonia but that there is an optimum concentration above or below which the polymerization is slower. Pinck and Hetherington (38) recommended using small amounts of ammonia and raising the temperature to about 100° C.

Acids also accelerate the polymerization of cyanamide. But the pH must be kept above 4 or the cyanamide hydrolyzes to urea. In more strongly acid solutions the hydrolysis is proportional to the concentration of acid, as was shown by Hetherington and Braham (39). If the solution is too strongly acid there is complete hydrolysis to urea and no dicyandiamide is formed. Moreover, if the solution is too strongly alkaline, above a pH of 9.6, as found by Buchanan and Barsky (40), urea is formed along with the polymer.

The trimer of cyanamide, melamine, is formed by heating cyanamide at temperatures above its melting point. Franklin

(41) prepared melamine by heating cyanamide in liquid ammonia and a modification of this process is the one that is most widely used on a commercial scale.

Cyanamide and dicyandiamide are used as raw materials and are heated at temperatures from 100° to 400° C. in the presence of anhydrous ammonia. A pressure of 10 to 100 atmospheres is employed. The reaction can be shown as follows:



Melamine is used in making thermo-setting resins which have superior heat resistance. Hodgins (42) and his associates have made a thorough study of the properties of melamine-formaldehyde resins and have found them to be equal and superior in some respects to the corresponding urea-alkyd resins.

III. EXPERIMENTAL

A. Preparation of Cyanamide Used

Part of the cyanamide used in this investigation was purchased from the Eastman Kodak Company*, Rochester, New York. This was made by suspending five kilograms of fresh technical calcium cyanamide in 15 liters of water at 30° - 35° C. After stirring for one hour, the sludge was filtered off and washed until the filtrate was about 15 liters. The filtrate was chilled and ice cold 30 per cent sulfuric acid was added until just acid to Congo Red. The precipitated calcium sulfate was filtered off and washed until the volume of filtrate and washings was about 16 liters. The filtrate was vacuum evaporated on a steam bath until the temperature of the residue reached 80° - 85° C.

The residue was extracted with ether and the ether solution well cooled and dried with calcium chloride. The ether was evaporated off and the small amount of liquid which adhered to the crystals was poured off. The melting point was 40° - 41° C.

* From private correspondence with Dr. C. R. Lee, Eastman Kodak Company

Some of the cyanamide used was made by the method of Werner (14). To a mixture of 120 g. of water and 125 g. of glacial acetic acid was gradually added 100 g. of crude calcium cyanamide. The mixture was stirred during the addition and the temperature was never allowed to rise above 55° C. Toward the end of the operation, the mixture became a thick pasty mass and was slightly acid throughout. The product was exposed to the air for 24 hours, then pulverized and extracted with anhydrous ether in a Soxhlet apparatus. The ether solution was evaporated and the crystals of cyanamide dried in a vacuum over sodium hydroxide. The melting point was 41° - 42° C.

B. Study of Solubilities

Since cyanamide is a solid at room temperature, a water-bath was used as a heating medium. The bath was kept at a temperature of 54° - 55° C. by means of a Genco-Dekhotinsky Thermoregulator.

The solid cyanamide was quickly placed in a 4 ml. test tube which was stoppered and placed in the water-bath. The compound melted and the liquid was used as a solvent. From 0.5 to 0.75 ml. of the liquid was used for each test. In doubtful cases check determinations were made.

If the substance to be tested was a liquid, it was added a drop at a time. If as much as 0.25 ml. dissolved, the

substance was listed as soluble, if one drop produced two layers, the substance was classified as insoluble. Other liquids were listed as slightly soluble. In the case of solid substances, from 0.05 to 0.07 g. of the solid was added in small portions. If this amount dissolved, the substance was considered as soluble. If less than half this quantity dissolved, the solid was considered slightly soluble. In some cases there was a violent reaction, in others a precipitate formed or there was a distinct color change.

The solubilities of 75 different substances were determined and the results are given in Table III. The compounds have been grouped as soluble, slightly soluble, insoluble and reactive.

TABLE III

<u>Soluble</u>	
Aluminum chloride	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$
Aluminum ammonium sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$
Ammonium acetate	$\text{CH}_3\text{COONH}_4$
Ammonium carbonate	$(\text{NH}_4)_2\text{CO}_3$
Ammonium chloride	NH_4Cl
Ammonium nitrate	NH_4NO_3
Cadmium nitrate	$\text{Cd}(\text{NO}_3)_2$
Cadmium nitrate	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Calcium chloride	CaCl_2
Chromic acid (anhydride)	CrO_3
Chromic chloride	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
Cobaltous nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Cupric sulfate	CuSO_4
Cupric sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Ferric chloride	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
Ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Lead nitrate	$\text{Pb}(\text{NO}_3)_2$
Lithium iodide	LiI
Mercuric chloride	HgCl_2
Nickel chloride	NiCl_2
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

TABLE III (Continued)

	<u>Soluble</u>
Potassium acid tartrate	$\text{KHC}_8\text{H}_4\text{O}_4$
Potassium bromide	KBr
Potassium iodide	KI
Potassium phosphate	K_3PO_4
Silver nitrate	AgNO_3
Sodium bromide	NaBr
Sodium nitrate	NaNO_3
Butyric acid	$\text{CH}_3(\text{CH}_2)_2\text{COOH}$
Cinnamic acid	$\text{C}_6\text{H}_5\text{CH}:\text{CH}\text{COOH}$
Glycolic acid	HOCH_2COOH
Tartaric acid	$\text{HOOC}(\text{CHOH})_2\text{COOH}$
Valeric acid	$\text{CH}_3(\text{CH}_2)_3\text{COOH}$
Isomyl alcohol	$(\text{CH}_2)_3\text{CH}\text{CH}_2\text{CH}_2\text{OH}$
Butyl alcohol	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$
Glycerol	$\text{C}_3\text{H}_7(\text{OH})_3$
Methyl alcohol	CH_3OH
Phenol	$\text{C}_6\text{H}_5\text{OH}$

TABLE III (Continued)

Soluble

Amyl acetate	$\text{CH}_3\text{COOC}_5\text{H}_{11}$
Ethyl acetate	$\text{CH}_3\text{COOC}_2\text{H}_5$
Ethyl benzoate	$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$
Ethyl malonate	$\text{CH}_2(\text{COOC}_2\text{H}_5)_2$
Methyl salicylate	$\text{HO.C}_6\text{H}_4.\text{COOCH}_3$
Acetone	$\text{CH}_3.\text{CO}.\text{CH}_3$
Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$
Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$

Slightly Soluble

Chloroform	CHCl_3
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O}$
Succinic acid	$\text{COOH}(\text{CH}_2)_2\text{COOH}$
Aluminum sulfate	$\text{Al}_2(\text{SO}_4)_3.18\text{H}_2\text{O}$
Ammonium acid phosphate	$(\text{NH}_4)_2\text{HPO}_4$
Barium chloride	$\text{BaCl}_2.2\text{H}_2\text{O}$
Boric acid	H_2BO_3
Bismuth sulfate	$\text{Bi}_2(\text{SO}_4)_3$
Cobaltous oxalate	CoC_2O_4
Ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3$
Cobaltous sulfate	CoSO_4

TABLE III (Continued)

Slightly Soluble

Lead chloride	$PbCl_2$
Magnesium oxide	MgO
Manganous sulfate	$MnSO_4$
Sodium chloride	$NaCl$

Insoluble

Benzene	C_6H_6
Butyl chloride	C_4H_9Cl
Carbon disulfide	CS_2
Carbon tetrachloride	CCl_4
Xylene	$C_6H_4(CH_3)_2$

Reactive

Antimony chloride	$SbCl_3$
Hydrogen chloride	HCl
Potassium cyanide	KCN
Potassium hydroxide	KOH
Potassium permanganate	$KMnO_4$
Sodium chromate	Na_2CrO_4
Sodium cyanide	$NaCN$
Sodium hydroxide	$NaOH$

C. Reactions

When some of the solid compounds were added to the molten cyanamide, gelatinous precipitates formed. These compounds are listed in Table IV.

TABLE IV

COMPOUNDS FORMING GELATINOUS PRECIPITATES

Aluminum ammonium sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ (slight)
Aluminum sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (slight)
Bismuth sulfate	$\text{Bi}_2(\text{SO}_4)_3$ (slight)
Chromic acid (anhydride)	CrO_3 (slight)
Cobaltous sulfate	CoSO_4 (slight)
Cupric sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (whole mass jelled)
Ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (slight)
Magnesium oxide	MgO (slight)
Manganous sulfate	MnSO_4 (slight)

Sodium chromate formed a deep red solution and potassium permanganate was reduced with the formation of manganese dioxide. Potassium hydroxide, sodium hydroxide and potassium cyanide were all soluble but upon standing a few seconds, a violent reaction took place. A yellowish-white solid was formed in each case.

When a solution of silver nitrate in cyanamide was added to cyanamide solutions of soluble chlorides, bromides, iodides, carbonates and phosphates, precipitates were produced immediately. The colors of these precipitates were the same as those of the silver salts precipitated from water solutions.

Ferric chloride and ferric sulfate dissolved in cyanamide to give brown solutions. Crystals of anhydrous nickel chloride turned blue when added to cyanamide. These blue crystals dissolved to form a blue solution. Cobalt salts formed pink solutions.

When anhydrous cupric sulfate was added to cyanamide, the particles of the salt became deep green in color, then dissolved to form a green solution. When this solution was warmed, for about ten minutes, a small amount of a black precipitate formed.

Antimony chloride was soluble in cyanamide but the solution became cloudy immediately. A white crystalline precipitate settled out upon standing. This precipitate

was insoluble in alcohol and ether.

Potassium phosphate was found to be soluble in cyanamide. A small amount of the salt dissolved readily. As more salt was added, the solution became viscous and white needles separated from the solution.

Dry hydrogen chloride formed a white crystalline compound when passed into liquid cyanamide.

D. Analyses of Compounds

Antimony Compound

The white crystalline compound formed when antimony chloride was added to liquid cyanamide settled rapidly and could be separated from the supernatant liquid. It was found to be insoluble in alcohol.

Since both antimony chloride and cyanamide are soluble in absolute alcohol, the excess solvent and reagent were removed by repeated extractions with this solvent. The compound was finally washed with absolute ether and dried in an oven at 65° C. It was found to be perfectly stable at this temperature.

The compound was analyzed for nitrogen by the micro Dumas method and for chlorine by the Volhard method (43).

Analysis for antimony was made by dissolving the compound in hydrochloric acid solution (1:4) and then saturating with hydrogen sulfide. The antimony sulfide was

precipitated, filtered through a Gooch filter and washed. The sulfide was dissolved in concentrated hydrochloric acid, powdered tartaric acid added and the solution warmed on a water bath. The excess acid was neutralized with sodium hydroxide and sodium bicarbonate. Excess bicarbonate was added and the antimony solution was titrated with standard iodine solution, using starch as an indicator.

The analyses were made from samples prepared under the same conditions but at different times. They were not necessarily uniform.

From the results of the analyses, the compound was determined to be $Sb(HN.CN)_2.HCl$. The results of the analyses are shown in Table V.

TABLE V
ANALYSIS OF ANTIMONY COMPOUND

Calculated for $Sb(HN.CN)_3.HCl$		Per Cent Found	Average
Antimony	43.29	44.46 43.39 44.09	43.98
Nitrogen	29.87	28.84 29.89	29.37
Chlorine	12.61	14.75 15.06 16.26	15.36

Copper Compound

The fact that anhydrous cupric sulfate, when added to pure liquid cyanamide, gives a dark green compound indicates the formation of a solvated compound. This green compound was separated from excess solvent by treatment with anhydrous ether. It was very hygroscopic and became a brown sticky mass when exposed to the air. When placed in an oven, the compound charred. It was possible to wash the substance with anhydrous ether and to dry it in a vacuum desiccator.

Several samples of the green compound were prepared by adding anhydrous cupric sulfate to cyanamide. The excess cyanamide was quickly removed with anhydrous ether. After washing thoroughly with ether, the compound was dried in a

vacuum desiccator.

The compound, after drying, was quickly transferred to a small weighing bottle with a ground glass stopper. Samples were weighed out and ignited in crucibles to cupric oxide. The cupric oxide, after weighing, was dissolved in dilute nitric acid, the solution neutralized with ammonia and then glacial acetic acid was added. Potassium iodide was then added and the liberated iodine titrated with standard thio-sulfate solution.

The analyses were made with samples prepared under the same conditions but at different times. The results are found in Table VI.

TABLE VI
ANALYSIS OF COPPER COMPOUND

Sample	Per Cent Cu Based on Weight of CuO	Per Cent Cu Based on Liberated I ₂
1	22.86	
2	26.15	26.43
3	23.46	23.55
4	24.73	25.00
5	24.28	24.60

Several samples of the solvated compound were prepared and dried as described above. These samples were then added to more liquid cyanamide. The color of all but one of these samples did not change and analyses for copper gave an average of 25.76 per cent copper.

One of the samples became very dark green and, when washed with ether, became a liquid which crystallized only after standing several hours. An analysis of this compound gave 16.41 per cent copper.

The per cent copper in various solvated compounds is given in Table VII.

TABLE VII
PER CENT COPPER IN VARIOUS SOLVATED COMPOUNDS

Compound	Per Cent Cu
$\text{CuSO}_4 \cdot \text{H}_2\text{NCN}$	31.53
$\text{CuSO}_4 \cdot 2\text{H}_2\text{NCN}$	26.09
$\text{CuSO}_4 \cdot 3\text{H}_2\text{NCN}$	23.26
$\text{CuSO}_4 \cdot 4\text{H}_2\text{NCN}$	19.40
$\text{CuSO}_4 \cdot 5\text{H}_2\text{NCN}$	17.20

There was a decided difference in the color of the solvated compound analyzing 23.55 per cent copper and that giving 26.43 per cent copper. The former was much darker

green than the latter. These results would indicate the formation of $\text{CuSO}_4 \cdot 2\text{H}_2\text{NCN}$ or $\text{Cu}_2\text{SO}_4 \cdot 3\text{H}_2\text{NCN}$. The rapidity with which the salt was added to the solvent, the length of time before removal of excess solvent and the temperature would account for the different degrees of solvation.

The one sample which gave 16.41 per cent copper would indicate $\text{CuSO}_4 \cdot 5\text{H}_2\text{NCN}$. But the conditions which gave this solvate were not duplicated in any other preparation.

Hydrochloride

When dry hydrogen chloride was passed into liquid cyanamide at $54^\circ - 55^\circ \text{C}$., a white crystalline compound was formed. This compound could be washed with ether and dried in an oven at 65°C . It was stable at room temperature.

The hydrogen chloride was obtained by dropping concentrated sulfuric acid into concentrated hydrochloric acid. The liberated gas was dried by passing it through concentrated sulfuric acid, and then introduced into a flask containing the liquid cyanamide. The flask was fitted with a Bunsen valve to prevent moisture from entering the reaction chamber.

When the hydrogen chloride came into contact with the cyanamide, a white crystalline compound began to form. But the reaction soon became vigorous and enough heat was generated to break the flask.

It was decided to generate the hydrogen chloride by

passing dry nitrogen gas through concentrated hydrochloric acid solution. The mixture of gases was dried by passing through concentrated sulfuric acid and then passed into the flask containing the cyanamide. The flask was fitted with a Bunsen valve and the delivery tube did not extend into the liquid cyanamide.

The reaction proceeded quietly and the hydrogen chloride was passed over the cyanamide for a period of 48 hours. At the end of that time, all the cyanamide had been converted into the crystalline compound.

The white powder was washed with ether and dried in an oven at 65° C. It was then analyzed for chlorine by the Volhard method (43). The results of the analyses indicated a compound with the formula $H_2N.CN.HCl$. In Table VIII may be found the results of the analyses.

TABLE VIII
ANALYSIS OF CYANAMIDE HYDROCHLORIDE

Calculated for $H_2N.CN.HCl$	Per Cent Cl Found	Average
Chlorine	45.20	43.54
		43.49
		43.57
		43.45
		43.51

Since cyanamide has a tendency to polymerize in the presence of acids, some dicyandiamide was undoubtedly formed. The polymer is only very slightly soluble in ether and repeated washings failed to remove all of it. This would account for the low results.

Reaction of Potassium Phosphate with Cyanamide

When potassium phosphate was added to cyanamide, the solution became viscous. Upon the continued addition of the salt, a white crystalline compound separated from the solution. The excess solvent was removed with absolute alcohol. The compound was washed thoroughly with absolute alcohol and then with ether and dried in the oven at 65° C.

This compound was examined under the microscope and was found to be composed of colorless needles. There were occasional spots of a white powder on the needles.

A small amount of the substance was dissolved in water and qualitative tests were made for phosphate with silver nitrate, magnesia mixture and molybdate reagent. Only faint tests for phosphate could be obtained. When a small amount of the compound was heated on a platinum foil a slight residue remained.

Mr. R. N. Meals, Chemistry Department, Iowa State College, determined the per cent nitrogen in the compound by the micro Dumas method. His analyses gave an average of 66.11 per cent nitrogen. A melting point of 200° C. was

obtained by the micro method.

These data would indicate dicyandiamide, contaminated with a slight amount of potassium phosphate. The polymer has 66.61 per cent nitrogen and a melting point of 207° C.

E. Study of the Electrical Conductivity of Cyanamide and Solutions

Apparatus

The apparatus used in this part of the investigation was of the standard type consisting of a conductivity cell, resistance box, hummer, ear-phones, and Wheatstone bridge. The current was generated with an oscillating circuit composed of radio tubes with proper capacities and inductances.

The cell was of standard type but was built to have a volume of about 5 ml. It consisted of two circular platinum plates set vertically in a cylindrical cell. Connection was made through platinum wires sealed through the glass and leading into wells containing mercury by which the circuit was completed with copper leads from the apparatus.

The electrodes were platinized by using a three per cent solution of chloroplatinic acid and reversing the poles every half minute. In ten minutes a very satisfactory deposit was secured. This was freed from occluded gases by electrolyzing a dilute solution of sulfuric acid in the cell for half an hour.

The cell was calibrated at 55° C. and was found to contain 4.30 ml. The cell constant was determined by using a 0.02 molar solution of potassium chloride. Assuming that the specific conductivity of a potassium chloride solution is a linear function of the temperature, a 0.02 molar solution was calculated to have a specific conductance of 0.004416 reciprocal ohms at 55° C. This calculation was based on the values at 30° to 35° C. The cell constant was found to be 0.8444.

Method

The conductivity measurements were made with liquid cyanamide solutions of various salts. These were placed in the cell and maintained at the temperature at which the solubilities were determined, 54° to 55° C., by means of a thermoregulator.

When the temperature of the water-bath became constant, about 4.00 ml. of cyanamide were placed in the cell. The specific conductivity of the pure substance was determined and then a weighed amount of salt was introduced. The volume was then brought up to 4.30 ml. by the addition of cyanamide. After the solution became homogeneous, the specific conductivity was determined. Then one-sixth of the original volume of the solution was removed with a clean dry capillary pipette and an equal amount of pure cyanamide

was added. The specific conductivity of this more dilute solution was then measured. The solutions were progressively diluted until at least seven different concentrations were obtained for each solute.

Results

Reagent grade salts were used in making the solutions. They were ammonium chloride, ammonium nitrate, potassium iodide, potassium phosphate, and sodium nitrate.

The results of the conductivity measurements are shown in Tables IX through XIV. The normality, the volume of solution containing one gram-equivalent of salt, the specific conductance, and equivalent conductance are given for each solution. The conductivity is expressed in reciprocal ohms. In each case the specific conductivity of the pure solvent has been deducted from that of the solution.

The data for the most dilute solution studied, potassium iodide, show a gradual increase in equivalent conductance with dilution. The other solutions, with the exception of potassium phosphate, show an increase for several dilutions and then the conductivity drops. As the dilution continues, the equivalent conductivity again increases.

In addition to the tables, the data obtained from these studies are presented graphically by Figures 1 through 6. These graphs have been prepared by plotting the volume in liters containing one gram-equivalent of salt against the

equivalent conductance.

Smooth curves have been drawn through the points. These curves, with the exception of those for potassium iodide and potassium phosphate, show peaks.

It is known that acids and bases cause the polymerization of cyanamide. There are indications that salts cause the same effect. The form of the curve for potassium phosphate, Figure 3, indicates polymerization. That for the more dilute solutions of sodium nitrate, Figure 1, can be interpreted as showing polymerization which reaches a maximum after eight dilutions. The depressions in the other curves may be due to the polymerization effect. The more concentrated the salt solution, the greater would be this effect.

The liquid cyanamide used in making the dilutions was held in a state of fusion for periods as long as six hours. There was no appreciable polymerization, which would be shown by partial insolubility in ether. However, even a small amount of polymerization in the cyanamide and in the solutions would introduce errors in the conductivity determinations.

TABLE IX
 CONDUCTANCE OF SOLUTIONS OF SODIUM NITRATE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.0326	30.67	0.002851	87.44
0.0272	36.76	0.002390	87.86
0.0227	44.05	0.002010	88.55
0.0189	52.91	0.001689	89.37
0.0158	63.29	0.001422	90.00
0.0132	75.76	0.001200	90.91
0.0110	90.91	0.000977	88.82
0.0092	108.70	0.000801	87.06
0.0077	129.87	0.000678	88.05
0.0064	156.25	0.000571	89.22
Specific Conductivity of Cyanamide = 0.000629			

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TABLE X
 CONDUCTANCE OF SOLUTIONS OF SODIUM NITRATE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.3283	3.05	0.019885	60.35
0.2736	3.66	0.017440	63.83
0.2280	4.39	0.014930	65.54
0.1900	5.26	0.012700	66.80
0.1583	6.32	0.011181	70.66
0.1320	7.58	0.009264	70.22
0.1100	9.09	0.008086	73.51
0.0917	10.91	0.006614	72.16
0.0764	13.09	0.005609	73.42
0.0637	15.70	0.004753	74.62
Specific Conductivity of Cyanamide = 0.000710			

TABLE XI
 CONDUCTANCE OF SOLUTIONS OF POTASSIUM PHOSPHATE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.0133	75.19	0.000873	65.64
0.0111	90.09	0.000700	63.06
0.0093	107.53	0.000534	57.42
0.0077	129.83	0.000431	55.97
0.0064	156.25	0.000355	55.47
0.0053	188.68	0.000269	50.75
0.0044	227.27	0.000216	49.09
0.0037	270.27	0.000177	47.84
0.0031	322.59	0.000154	49.68

Specific Conductivity of Cyanamide = 0.000799

TABLE XII
 CONDUCTANCE OF SOLUTIONS OF POTASSIUM IODIDE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.0097	103.10	0.001089	112.28
0.0081	123.45	0.000912	112.60
0.0068	147.06	0.000776	114.12
0.0057	175.44	0.000680	119.30
0.0048	208.34	0.000595	123.96
0.0040	250.00	0.000507	126.75
0.0033	303.03	0.000453	137.28
0.0028	357.14	0.000394	140.72
0.0023	434.78	0.000330	143.48
Specific Conductivity of Cyanamide = 0.000704			

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TABLE XIII

CONDUCTANCE OF SOLUTIONS OF AMMONIUM NITRATE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.0215	46.51	0.002198	102.23
0.0179	55.87	0.001846	103.14
0.0149	67.11	0.001553	104.22
0.0124	80.65	0.001320	106.46
0.0103	97.09	0.001083	105.15
0.0086	116.28	0.000917	106.63
0.0072	138.89	0.000770	106.94

Specific Conductivity of Cyanamide = 0.000752

TABLE XIV

CONDUCTANCE OF SOLUTIONS OF AMMONIUM CHLORIDE

Normality	Dilution in Liters	Specific Conductance	Equivalent Conductance
0.1567	6.38	0.014647	93.45
0.1306	7.66	0.012285	94.14
0.1088	9.19	0.010259	94.28
0.0907	11.03	0.008782	96.86
0.0755	13.24	0.007283	96.43
0.0629	15.88	0.006273	99.62
0.0524	19.09	0.005037	96.16
0.0437	22.88	0.004232	96.83
0.0364	27.47	0.003538	97.19
0.0303	33.01	0.002965	97.87

Specific Conductivity of Cyanamide = 0.000706

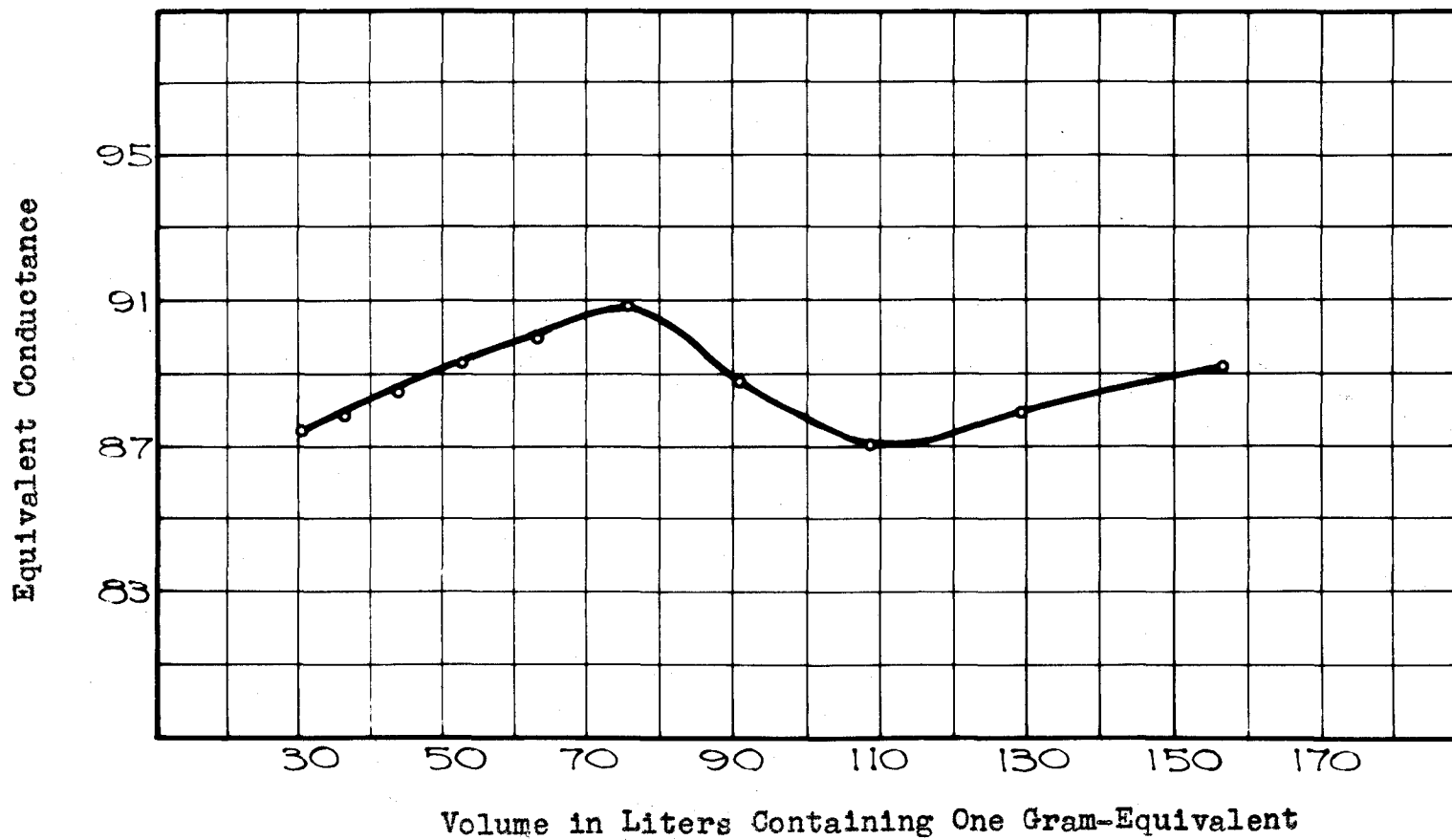


Figure 1. Conductance of Solutions of Sodium Nitrate. Curve 1.

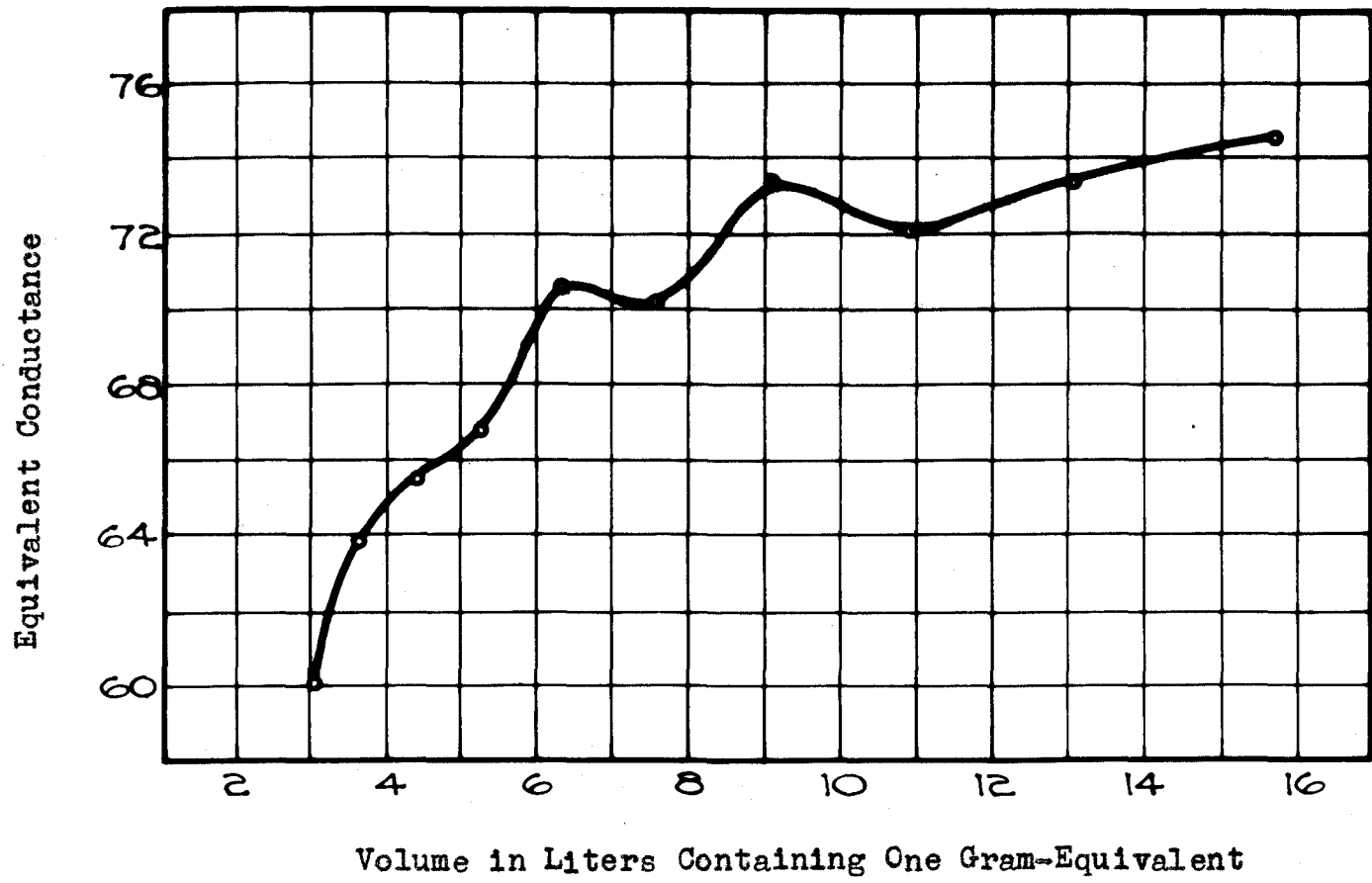


Figure 2. Conductance of Solutions of Sodium Nitrate. Curve 2.

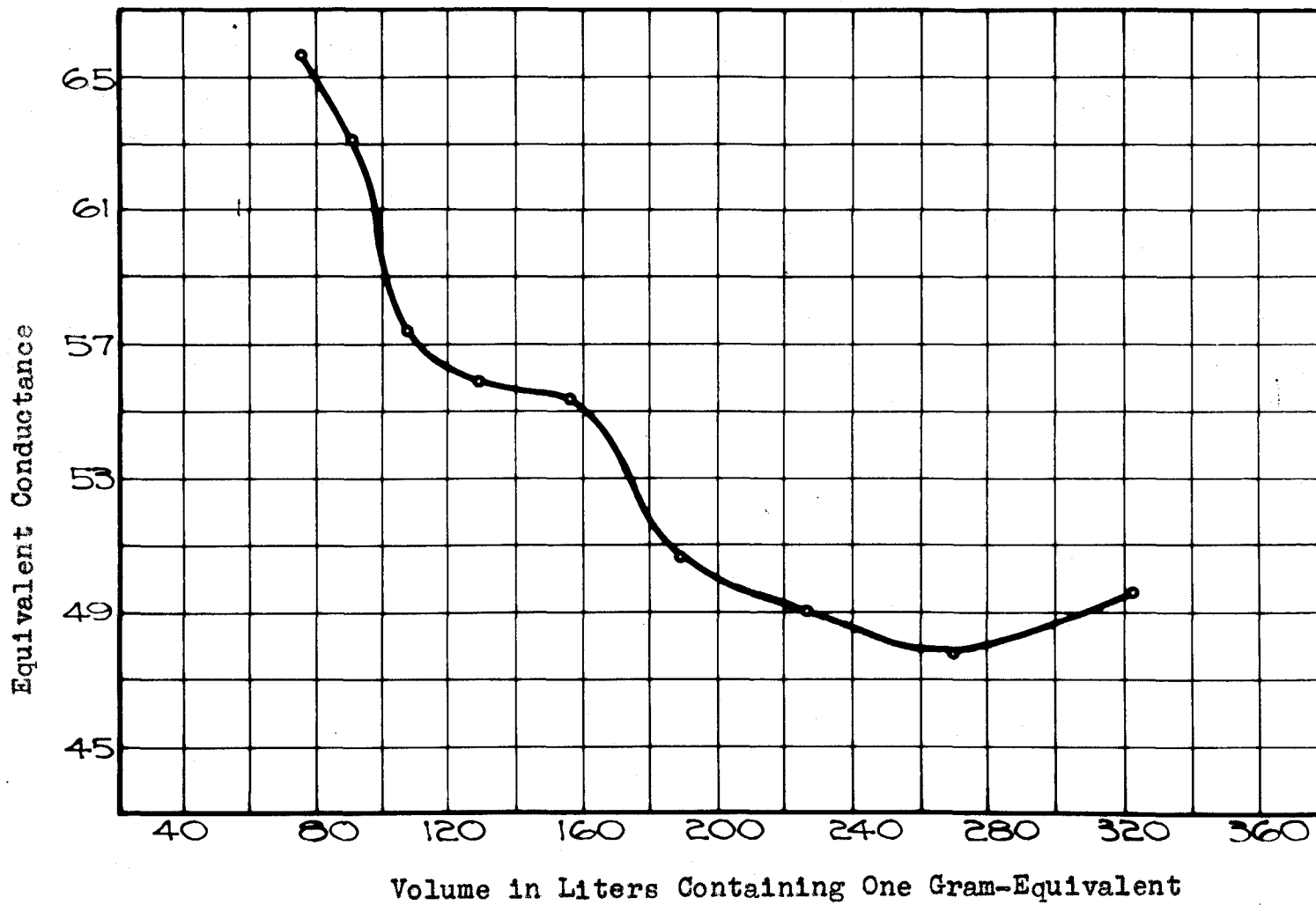


Figure 3. Conductance of Solutions of Potassium Phosphate

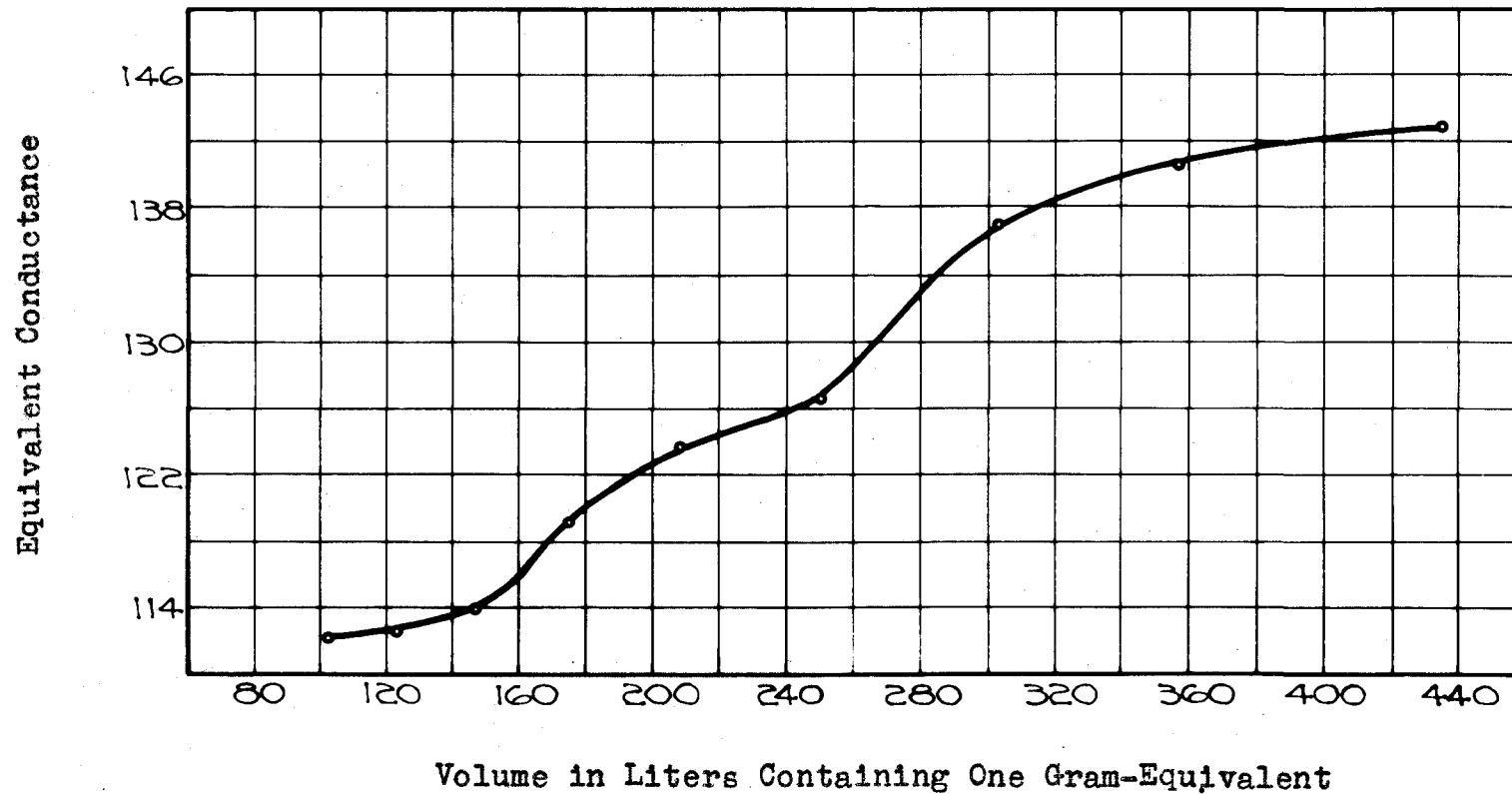


Figure 4. Conductance of Solutions of Potassium Iodide

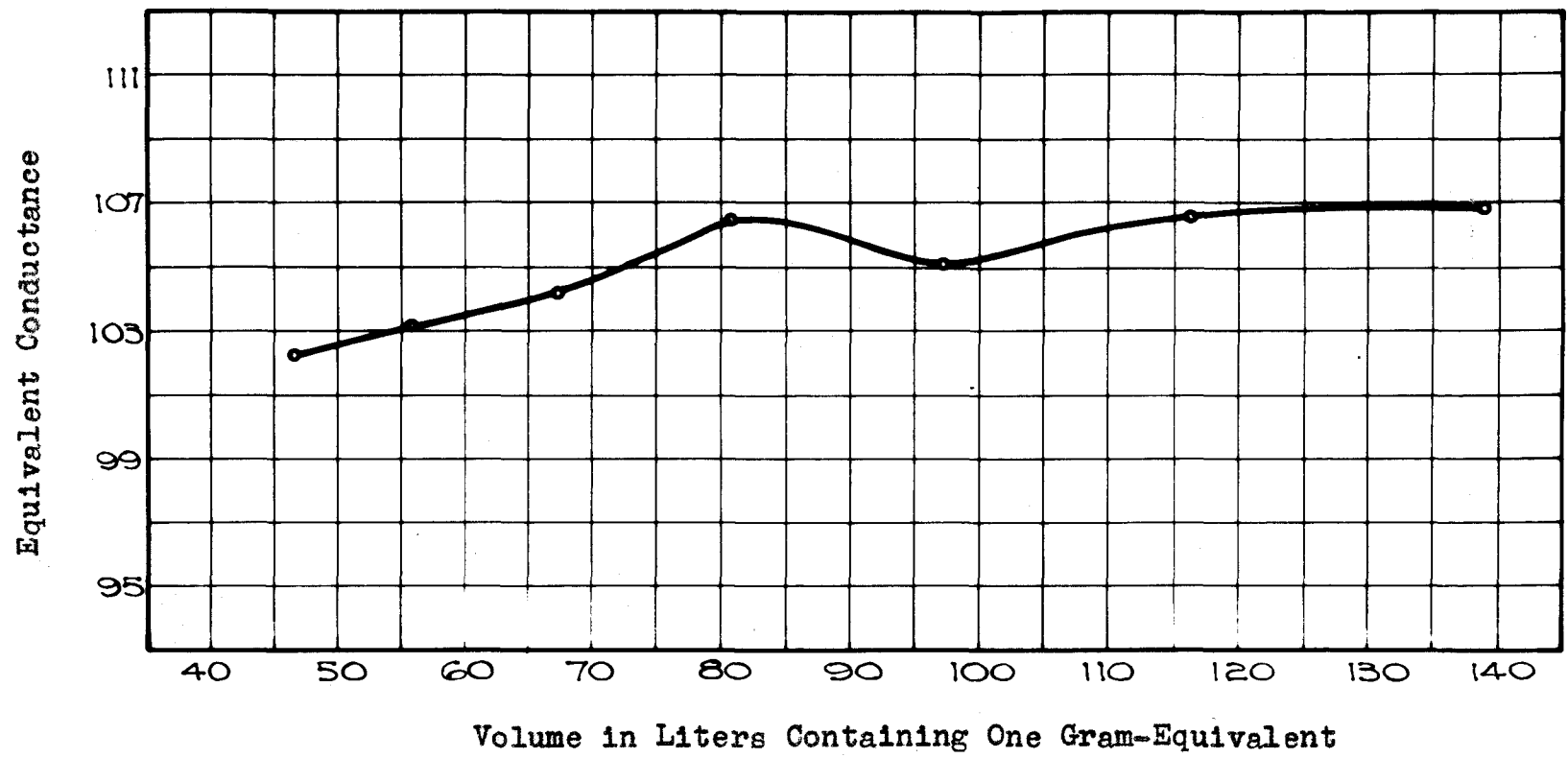


Figure 5. Conductance of Solutions of Ammonium Nitrate

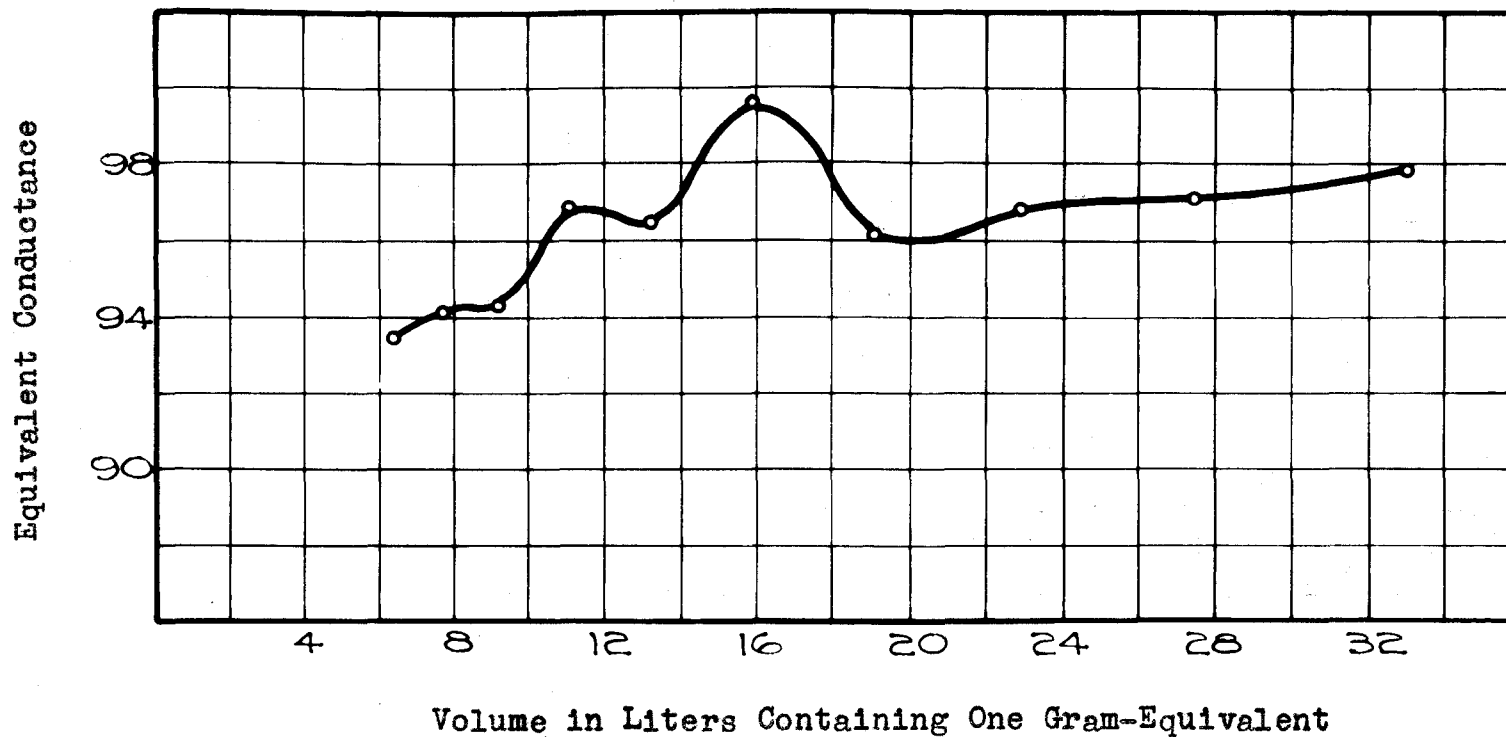


Figure 6. Conductance of Solutions of Ammonium Chloride

IV. DISCUSSION OF RESULTS

The study of solubilities of compounds in cyanamide shows that a great many inorganic compounds are soluble. In general, those substances which have a high solubility in water are soluble in cyanamide. Those found to be slightly soluble have, for the most part, low solubilities in water.

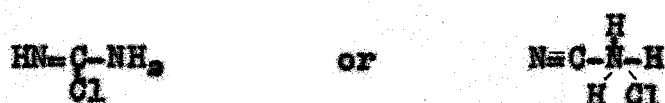
Since inorganic compounds were of primary interest in this investigation, the solubilities of comparatively few organic compounds were determined. The organic acids, alcohols, and esters tested were found to be soluble.

The temperature of the water-bath was kept at 54° to 55° C. during the solubility determinations. This temperature, some ten degrees above the melting point of cyanamide, was chosen so that the test tube containing the solution could be removed from the bath and shaken without solidification of the solvent.

Liquid cyanamide acts as an acid, for it forms a metallic compound with antimony chloride. The analysis of this compound corresponds very well with the formula $Sb(HN.CN)_2.HCl$, except in the case of chlorine. The per cent chlorine ran high in every sample analyzed and the precision was not good. Since the analyses were made on samples prepared

under the same conditions but at different times there was the possibility that some $\text{Sb}(\text{HN.CN})_3 \cdot 2\text{HCl}$ or $\text{Sb}(\text{HN.CN})_3 \cdot 3\text{HCl}$ was formed in some samples and not in others.

Fused cyanamide also acts as a base. It reacts with dry hydrogen chloride to form the hydrochloride, $\text{H}_2\text{N.CN.HCl}$. This compound might be assumed to have one of the following structural formulas:



The solvated compound formed with anhydrous cupric sulfate was difficult to work with. No method of getting consistent results was found. However, the results indicated the formation of $\text{CuSO}_4 \cdot 2\text{H}_2\text{NCN}$ or $\text{CuSO}_4 \cdot 3\text{H}_2\text{NCN}$.

In the conductivity measurements, certain errors creep in due to extra operations and calculations required. A small indeterminate error involved in determining the specific conductivity is multiplied several thousand times in calculating the equivalent conductivity. Undoubtedly certain other errors cancel or are diminished.

Every solution studied showed an increase in specific conductivity over that of the pure solvent. The plotted points in the graphical presentation of data do not fall on a curve of the type obtained with aqueous solutions of salts. It is possible that heat or the presence of salts causes the cyanamide to polymerize. Data have been presented which

it is believed show that salts cause polymerization in solutions in which cyanamide is the solvent.

Some results on the comparative equivalent conductivities of solutions of potassium iodide in water and in cyanamide show that water is the better ionizing medium. For solutions of equal normality, the equivalent conductance of aqueous solutions of potassium iodide is about twice that of cyanamide solutions of the same salt.

Cyanamide is a difficult substance with which to experiment. It is very hygroscopic and has a tendency to polymerize. In the preparation of the compounds, it was found that the salt could not be added rapidly. Violent reactions took place with rapid addition of the reagent.

V. CONCLUSIONS

1. Many inorganic compounds are soluble in liquid cyanamide.
2. Certain organic acids, alcohols, and esters are soluble in cyanamide.
3. Cyanamide reacts with antimony chloride to form $\text{Sb}(\text{HN}.\text{CN})_3.\text{HCl}$.
4. A solvated compound is obtained when anhydrous cupric sulfate is added to cyanamide. This compound is $\text{CuSO}_4.3\text{H}_2\text{NCN}$ or $\text{CuSO}_4.3\text{H}_2\text{NCN}$.
5. The hydrochloride, $\text{H}_2\text{NCN}.\text{HCl}$, is produced when dry hydrogen chloride is passed into cyanamide at a temperature of 55°C .
6. Potassium phosphate causes cyanamide to polymerize to dicyandiamide.
7. Cyanamide may be kept at a temperature of 55°C . for six hours without appreciable polymerization.
8. Salts dissolved in cyanamide form solutions which are fair conductors of electricity.

VI. SUMMARY

1. In this investigation the solubilities of 75 different compounds in cyanamide have been determined.
2. In general, the inorganic compounds that were found to be soluble in cyanamide are very soluble in water.
3. The organic acids, alcohols, and esters tested were found to be soluble in cyanamide.
4. Cyanamide reacts with antimony chloride, anhydrous cupric sulfate, and dry hydrogen chloride to form compounds.
 - a. The compound formed with antimony chloride is believed to have the composition, $\text{Sb}(\text{HN.CN})_2.\text{HCl}$. It is stable under room conditions.
 - b. The green solvated compound formed when cupric sulfate is added to cyanamide was found to be very hygroscopic and could be dried only in a vacuum desiccator. Its composition can be represented by the formula, $\text{CuSO}_4.2\text{H}_2\text{NCN}$ or $\text{CuSO}_4.3\text{H}_2\text{NCN}$.
 - c. Hydrogen chloride reacts with cyanamide to form the hydrochloride, $\text{H}_2\text{N.CN.HCl}$. The white crystalline substance is stable.
5. Potassium phosphate caused cyanamide to polymerize. This was indicated by the form of the conductivity curve

and by the analysis of the crystalline compound obtained when the phosphate was added to cyanamide. The analysis designated the polymer, dicyandiamide.

6. In carrying out the conductivity determinations, cyanamide was kept in a state of fusion for six hours without appreciable polymerization. This was indicated by no apparent lack of solubility in ether.

7. Salt solutions with cyanamide as the solvent were found to be conductors of electricity. For every dilution tested, the solution showed an increase in specific conductivity over that of the pure solvent. In the case of potassium iodide, the solution showed an increase in equivalent conductivity with progressive dilution. Other series of solutions, except potassium phosphate, gave an initial rise and then a decrease in equivalent conductivity.

8. In plotting the dilution against the equivalent conductance of salts in cyanamide, the curves obtained are irregular. It can be shown that potassium phosphate causes polymerization of cyanamide. Other salts must have the same effect. This subject needs further study.

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