molecular weight of 183, a value that would agree with experiment if it were assumed that the decomposition is not quite complete. Since phosphorus halogenonitrides with less than three phosphorus atoms are not known, it is desirable that the decomposition reaction be studied further.

Phosphorus bromonitrides having the formulas $(PNBr_2)_3$ and $(PNBr_2)_n$ are also known. Their preparation parallels that of the chloronitrides; phosphorus pentabromide is treated with ammonia [Besson, *Compt. rend.*, **143**, 37 (1906)]. Efforts to prepare the chloronitrides of antimony and tin have not been successful.

Hydrazine, N_2H_4

Hydroxylamine may be regarded as a hydroxy derivative of ammonia, and hydrazine in turn may be looked upon as an amide of ammonia.

H_2NH	H_2NOH	H_2NNH_2
Ammonia	Hydroxylamine	Hydrazine

The $—NH_2$ group plays the same role, as it frequently does in other compounds, in hydrazine as the —OH group does in hydroxylamine. The fact that the two nitrogens are bonded to each other suggests also an analogy with hydrogen peroxide,

$$HO—OH \qquad H_2N—NH_2$$

and, indeed, the properties of hydrazine parallel those of hydrogen peroxide in several respects.

Hydrazine appears in small amounts as a reduction product in a number of reactions involving nitrates, nitrites, and other nitrogen compounds. The method of preparation now used depends, however, on the oxidation of ammonia in alkaline solution by hypochlorite [discovered by Raschig, *Ber.*, **40**, 4588 (1907)]. In order that the yield be appreciable, it is necessary that the reaction mixture contain glue or gelatine, the function of which has not been definitely established. The first step in the reaction is thought to be the formation of chloramine, NH_2Cl,

$$NH_3 + ClO^- = NH_2Cl + OH^-$$

then

$$NH_2Cl + NH_3 = N_2H_4 + HCl$$

That the glue or gelatine does not form a compound with chloramine is shown by the fact that the distribution ratio between ether and water or water containing glue and ammonia is the same [Joyner, *J. Chem. Soc.*, **123**, 1114 (1923)].

$R = \frac{NH_2Cl \text{ (ether layer)}}{NH_2Cl \text{ (aqueous layer)}}$	Aqueous Layer
1.4	Water at 0°
1.5	Glue soln. at 0°
1.3	Water at −8°
1.3	2 n NH_3 at −8°
1.4	2 n NH_3 + glue at −8°

It is still possible for glue or gelatine to act catalytically without at the same time forming with NH_2Cl a compound present at detectable concentrations.

The effect of the glue or gelatine and the relative concentrations of ammonia and hypochlorite on the yield has been determined carefully by Joyner (*loc. cit.*); representative data are shown in the following table.

TABLE 26

THE EFFECT OF CATALYST AND CONCENTRATIONS ON THE YIELD OF HYDRAZINE

10 cc 3.95 n NaClO + 1 cc 10% glue soln. mixed with varying amounts of 7.95 n NH_4OH, and the mixture diluted to 100 cc and heated at 80–90°.			Mixture 0.4 n in NH_4OH and 0.01 m in NaClO heated to 80–90°.	
Moles NH_4OH in 100 cc	Mole Ratio (NH_3/NaClO)	Per Cent Yield Based on NaClO	Milligrams Gelatine per 100 cc Mixture	Per Cent Yield Based on NaClO
0.0397	2.02	5.7	0	2.0
.0795	4.04	18	1.9	8.8
.1590	8.08	32	2.9	18.2
.3925	20.2	52	3.9	25.4
.7155	36.4	63	10.9	39.0
1.510	76.8	75	30.9	48.3
			100.9	51.0

The presence of NH_4^+ greatly decreases the yield; for best results, the solution should be alkaline with NaOH. Ordinarily one prepares the mixture by passing the proper amount of chlorine into a sodium hydroxide solution and then adding the most effective amount of strong ammonia solution and some glue or gelatine. The resulting mixture is heated to 80–90° for from one-half to one hour; it is then cooled and neutralized with sulfuric acid. $N_2H_6SO_4$ crystallizes out, since it is not very soluble in water and is less so in solutions containing sulfate ion.

A less convenient method for preparing hydrazine, but one which is of chemical interest, is that of Divers and Haga [*J. Chem. Soc.*, **69**, 1610

(1896)]. The salt $K_2[(NO)_2SO_3]$ is first prepared by passing nitric oxide into a solution of K_2SO_3 made alkaline with KOH. After recrystallizing the $K_2[(NO)_2SO_3]$ from hot water, a solution of it is reduced with sodium amalgam. The reactions are

$$2K^+ + SO_3^= + 2NO = K_2[(NO)_2SO_3]$$

and

$$(NO)_2SO_3^= + 6Na + 5H_2O = N_2H_4 + SO_4^= + 6Na^+ + 6OH^-$$

It is necessary to acidify the mixture after the reduction is complete, since the oxygen of the air slowly oxidizes the hydrazine to nitrogen and ammonia in alkaline solution.

From the hydrazine bisulfate obtained by the above methods of preparation, it is possible to prepare the monohydrate, $N_2H_4{\cdot}H_2O$ or N_2H_5OH, and anhydrous hydrazine itself, N_2H_4. The hydrate is prepared by distilling a mixture of KOH (100 g), water (250 g) and $N_2H_6SO_4$ (100 g) in a silver still. (The hydrate, like ammonium hydroxide, attacks glass slowly.) [Curtius and Schultz, *J. prakt. Chem.*, **123,** 1114 (1923).] Alternatively the hydrazine bisulfate can be converted to the bromide N_2H_5Br and this salt treated with KOH solution and alcohol; the KBr precipitates out, and the solution is subjected to distillation to remove the alcohol. The residue consists of a solution of hydrazine hydrate, and the hydrate is isolated by fractional distillation at 125 mm pressure [Lobry de Bruyn, *Rec. trav. chim.*, **18,** 297 (1899)].

Hydrazine hydrate, $N_2H_4{\cdot}H_2O$, is a colorless, fuming liquid (density = 1.0305 at 21°) which boils at 118.5° and at low temperatures solidifies to a colorless solid melting at −40°. Since the vapor, and doubtless the liquid also, dissociates reversibly into N_2H_4 and H_2O, it is not possible to say that the liquid is a pure substance. A mixture of 58.5% N_2H_4 and 41.5% H_2O has a higher boiling point than mixtures containing more or less hydrazine. The molecular weight from the vapor density of $N_2H_4{\cdot}H_2O$ at 98.8° and 366 mm is 31.6, and at 138° and 744.1 mm it is just one-half the formula weight. This shows that there is appreciable dissociation at 98.8° and 366 mm according to the equation

$$N_2H_4{\cdot}H_2O(g) = N_2H_4(g) + H_2O(g)$$

and at 138° and 744.1 mm the dissociation is effectively complete [Scott, *J. Chem. Soc.*, **85,** 913 (1904)]. The known vapor density data are not sufficient to permit of the calculation of thermodynamic quantities; since these calculations would be of interest, it is desirable to have careful measurements at more frequent temperature intervals, from, say, 90° to 130°. Such measurements might serve to throw more definite light on the nature of the bond between N_2H_4 and H_2O. Presumably the hydrate is $H_2N{-}NH_3OH$, since, as will be discussed below, in aqueous solution it has basic properties. The heats of formation of hydrazine hydrate and of anhydrous hydrazine are given in Table 27 [Hughes, Corruccini, and Gilbert, *J. Am. Chem. Soc.*, **61**, 2639 (1939)].

TABLE 27
THE HEATS OF FORMATION OF HYDRAZINE AND ITS HYDRATE

Compound	$\Delta H^\circ_{298.1}$ (cal/mole)
$N_2H_4(g)$	22,250
$N_2H_4(l)$	12,050
$N_2H_4H_2O(l)$	10,300
$N_2H_4(aq.)$	8,160

Hydrazine hydrate attacks cork, rubber, and, more slowly, glass. The bottles of the commercial product (concentrated aqueous solutions) frequently contain gelatinous precipitates of silica or silica hydrates. In the presence of air, slow oxidation to nitrogen, ammonia, and water takes place. Spontaneous decomposition into nitrogen, hydrogen, and ammonia appears to take place to some extent also; this decomposition is accelerated by the presence of spongy platinum [Tantar, *Z. phys. Chem.*, **40**, 475 (1904)].

Anhydrous hydrazine, N_2H_4, is prepared by dehydrating the hydrate with barium oxide, BaO. The dehydration with solid sodium hydroxide does not appear to be effective enough to obtain a pure product. In one method 100 cc of $N_2H_4 \cdot H_2O$ and 530 g of crushed BaO are heated together for one to three hours under a reflux condenser and in an atmosphere of nitrogen or hydrogen [Hale and Shetterly, *J. Am. Chem. Soc.*, **33**, 1071 (1911)]. The resulting liquid is fractionally distilled at low pressures (2–30 mm) in an atmosphere of hydrogen.

Another method for obtaining anhydrous hydrazine directly from the more common hydrazine bisulfate has been suggested by Browne and investigated by Friedrichs [*J. Am. Chem. Soc.*, **35**, 244 (1913)]. Advantage is taken of the reversibility of the reaction,

$$N_2H_6SO_4(s) + 2NH_3(l) = (NH_4)_2SO_4(s) + N_2H_4 \text{ [in } NH_3(l)\text{]}$$

and the process consists in the continuous extraction of only the hydrazine bisulfate with liquid ammonia at its boiling temperature, the ammonium sulfate being insoluble in this solvent [Franklin and Kraus, *Am. Chem. J.*, **20**, 820 (1898)]; the hydrazine is freed from ammonia by simple evaporation. This method appears adaptable to large-scale operations.

Anhydrous hydrazine is a colorless, fuming liquid which boils at 113.5°; at low temperatures it is a colorless solid melting at 1.8°. The liquid density is 1.0258 g/cc at 0° and 1.0114 g/cc at 15°. The vapor pressures are known, for the most part, only at and above the normal boiling point; these are 71 mm at 56°, 1.0 atm at 113.5°, 5 atm at 170° 56 atm at 300°, and 145 atm at 380°. The vapor has been shown to be monomeric [Giguère and Rundle, *J. Am. Chem. Soc.*, **63**, 1135 (1941)]. The critical temperature is 380°. These data give some indication of the relative inertness toward decomposition of anhydrous hydrazine, namely, that even at rather high temperatures it shows no tendency to decompose, although thermodynamically it is doubtless unstable with respect to decomposition into nitrogen, hydrogen, and ammonia, $2N_2H_4(g) = 2NH_3 + N_2 + H_2$. The dielectric constant of the liquid is 53 at 22°.

Anhydrous hydrazine burns in air and reacts violently with chlorine, bromine, and iodine. It also reacts in a lively fashion with $SOCl_2$ to yield $(H_2N_2H)_2SO$, a white solid, and N_2H_5Cl. With SO_2 the acid-like compound $HO_2SNHNHSO_2H$ results, of which two barium salts are known, namely, $Ba(O_2SNHNHSO_2)$ and $Ba_2(O_2SN_2SO_2)$. When vapors of SO_3 are allowed to react with anhydrous N_2H_4, a hydrazine sulfonic acid forms, $N_2H_3SO_3H$, and the latter with potassium nitrite yields KN_3SO_3 and water.

One of the remarkable properties of anhydrous hydrazine is its ability to dissolve sulfur. [See Ephraim and Piotrowsky, *Ber.*, **44**, 386 (1911), and adjoining articles These papers report several interesting reactions of N_2H_4.] The sulfur dissolves freely in the hydrazine (100 cc of N_2H_4 dissolves some 54 g of S at room temperature) to give a dark-red solution. The solutions are not completely stable, since a slow reaction, $3N_2H_4 + 2S = N_2 + 2N_2H_4H_2S$, takes place. The reaction decreases in rapidity with time, but after about twenty-four hours it is nearly complete; the color of the solution changes during the reaction period from dark red to a light yellow of low intensity. H_2S dissolves freely in N_2H_4 (l). Some ammonia is also formed in the sulfur solutions. These colored sulfur solutions may be used for the volumetric estimation of zinc or cadmium salts dissolved in hydrazine; ZnS and CdS are precipitated, and the disappearance of the color indicates the end point [Welsh and Broderson, *J. Am. Chem. Soc.*, **37**, 825 (1915)]. It must be presumed that the reactions involved are somewhat as follows:

$$N_2H_4 + S = S \text{ (in } N_2H_4) \tag{1}$$
$$3N_2H_4 + 2S = 2N_2H_4H_2S + N_2 \tag{2}$$
$$N_2H_4H_2S + CdI_2 = N_2H_4{\cdot}2HI + CdS \tag{3}$$

The rate of reaction (2) is apparently increased in some way as a result of reaction (3) taking place, since (2) is somewhat slow. Reaction (1) is doubtless not so simple as written, the true condition being probably represented by an equilibrium between hydrazine sulfide or polysulfide and a sulfur-nitrogen compound. In this connection, the solution of sulfur in liquid ammonia should be compared.

Iodine dissolves freely in hydrazine with vigorous or explosive reaction.

Metallic sodium reacts with anhydrous hydrazine at a moderate rate if the surface exposed is small, but it may react violently otherwise, to give a yellow solid or, with excess hydrazine, yellow solutions. The solid, NaN_2H_3, is soluble in hydrazine to give solutions that conduct electric current; the solid sometimes explodes violently. Sodium amide reacts with anhydrous hydrazine to form the same compound and ammonia. The reactions are [Welsh, *J. Am. Chem. Soc.*, **37,** 497 (1915)]

$$Na + N_2H_4 = NaN_2H_3 + \tfrac{1}{2}H_2$$
$$NaNH_2 + N_2H_4 = NaN_2H_3 + NH_3$$

The analogy between the group of compounds NaOH, $NaNH_2$, and NaN_2H_3 will be noted at once. The fact that one of the ammonia hydrogens has been replaced by $—NH_2$ in forming N_2H_4 does not completely inhibit the acid character of the remaining hydrogens.

From what has been said, anhydrous hydrazine has properties that recall those of liquid water, pure H_2O_2, and liquid ammonia. The acid constituent in the aqueous system is H^+ or H_3O^+, in the liquid ammonia system it is NH_4^+, and in the hydrazine system it would be $N_2H_5^+$. $N_2H_3^-$ would correspond to OH^-, and there is little doubt but that hydrazine solutions of N_2H_5Cl and NaN_2H_3 would, when mixed, react according to the equation

$$Na^+ + N_2H_3^- + N_2H_5^+ + Cl^- = Na^+ + Cl^- + 2N_2H_4$$

Because of the comparative difficulty of the experiments in the anhydrous hydrazine system, the detailed chemistry of neutralization, hydrazinolysis, and so on, has not been fully investigated. A few reactions of $N_2H_5^+$ in anhydrous hydrazine on metals have received attention; Cu, Sn, Al, and Zn are not appreciably attacked by such solutions. Magnesium and calcium, on the other hand, are readily attacked if $N_2H_5^+$ is present, but they suffer little or no dissolution in contact with anhydrous hydrazine alone. Accordingly, the reactivity of $N_2H_5^+$ in $N_2H_4(l)$ toward metals is much less than that of H_3O^+ in $H_2O(l)$ [see, for example, Welsh and Broderson, *J. Am. Chem. Soc.*, **37,** 825 (1915)].

Ammonia dissolves to a smaller extent in $N_2H_4(l)$ than in water. At 0° the three-phase system $N_2H_4(s)$, NH_3 [in $N_2H_4(l)$], $NH_3(g)$ shows a partial pressure of NH_3 of 175 mm, and the liquid phase consists of 98% N_2H_4 and 2% NH_3 by weight [Friedrichs, *Z. anorg. Chem.*, **127,** 221 (1923)]. At lower temperatures the solubility of ammonia is greater.

The high dielectric constant, 53, of anhydrous hydrazine suggests that it might prove to be an ionizing solvent for polar substances. Not only do solutions of salts in it conduct the electric current, but many salts are readily soluble in anhydrous hydrazine, as the following table shows [Welsh and Broderson, *J. Am. Chem. Soc.*, **37**, 816 (1915); Walden and Hilgert, *Z. phys. Chem.*, **A 165**, 241 (1933)].

TABLE 28
APPROXIMATE SOLUBILITIES OF SALTS IN ANHYDROUS HYDRAZINE AT ROOM TEMPERATURE
(S, in grams/100 cc N_2H_4)

Salt	S	Salt	S	Salt	S
NH_4Cl	75[a]	$MgSO_4$	0	Na_2CO_3	0
As_2O_3	1	$NiCl_2$	8	$NaNO_3$	26.6
H_3BO_3	55	KCl	8.5	Na_2SO_4	0
$CdBr_2$	40	KBr	56.4	$ZnCl_2$	8
$CaCl_2$	16	KI	135.7	RbCl	5
$CrCl_3$	13[b]	$NaClO_3$	66		
LiCl	16	NaCl	12.2		

[a] NH_3 is evolved.
[b] Red solution (complex), and some gas forms.

A number of other salts dissolve with reaction. Thus $AgNO_3$ is reduced to metallic silver; $NaBrO_3$ is reduced with the formation of a yellow solution. Precipitates of unknown composition result with $CuCl_2$ (brown), $PbCl_2$ and $Pb(NO_3)_2$ (yellow), $HgI_2(Hg)$, and $MgCl_2$ (white, flocculent). The nature of the precipitates is not exactly known; presumably in those cases where reduction is not evident, they consist of nitrides or hydrazinides, M_4N_2.

Aqueous solutions of hydrazine

The aqueous solutions of hydrazine or hydrazine hydrate are weakly alkaline. The reaction with water is, like that of ammonia,

$$N_2H_4 + H_2O = N_2H_5OH$$

and to indicate the basic property

$$N_2H_5OH = N_2H_5^+ + OH^-$$

$$\frac{(N_2H_5^+)(OH^-)}{(N_2H_5OH)} = 8.5 \times 10^{-7} \text{ at } 25^\circ$$

The ionization constant for ammonium hydroxide is 1.65×10^{-5}; that is, at the same total concentration, the (OH^-) in ammonium hydroxide solutions is about twenty times that in a hydrazinium hydroxide solution. The substitution of an $-NH_2$ for $-H$ in NH_3 decreases its basic character [Schwarzenbach, *Helv. Chem. Acta*, **19**, 178 (1936)].

Although H_2N-NH_2 is probably not a symmetric molecule, it is to be expected that the dihydroxide, HOH_3N-NH_3OH, would form and that the substance would be diacidic. In fact, it is possible to prepare the dichloride, $N_2H_6Cl_2$, and the corresponding nitrate and sulfate by the addition of excess acid and subsequent recrystallization. The second OH^-, however, ionizes much less freely than does the first,

$$\frac{(N_2H_6^{++})(OH^-)}{(N_2H_6OH^+)} = 8.9 \times 10^{-16} \text{ at } 25^\circ$$

and, accordingly, aqueous solutions of $N_2H_6Cl_2$ or similar salts will show extensive hydrolysis and the solutions will be acid. When solutions of N_2H_4 in water are titrated electrometrically with strong acids, only one inflection point is observed, which is to be expected if the second ionization constant of $N_2H_6(OH)_2$ is as small as the value just given [Gilbert, *J. Am. Chem. Soc.*, **46,** 2648 (1924)]. The titration of hydrazine sulfate solutions, $N_2H_6SO_4$, with strong bases yields two inflection points, the first corresponding to the neutralization of the acid in $N_2H_5^+ + H^+ + SO_4^=$ and the second to the conversion of $N_2H_5^+$ to N_2H_5OH.

The important salts of hydrazine are the chloride, N_2H_5Cl, the nitrate, $N_2H_5NO_3$, and the bisulfate, $N_2H_5HSO_4$, of which the last is by far the most common and most readily prepared. The chloride is very soluble in water; it melts at 89° and decomposes at higher temperatures. The dichloride is more soluble than the chloride; it may be obtained as octahedral crystals. Hydrazine nitrate is also very soluble in water, 76.61 g being contained in 100 g of the saturated solution at 25°, but it is sparingly soluble in alcohol; it melts at 70.7° and decomposes fairly rapidly at 200°. The bisulfate, $N_2H_5HSO_4$, is much less soluble in water than the other inorganic salts; the solubility is depressed by the presence of sulfate ion, as the mass law would predict [Sommer and Weise, *Z. anorg. Chem.*, **94,** 51 (1916)].

TABLE 29
SOLUBILITY OF HYDRAZINE BISULFATE IN WATER
(*S* expressed in g/100 g water.)

t(°C)	*S*
20	2.861
25	3.415
40	5.249
60	9.077
80	14.39

The normal sulfate, $(N_2H_5)_2SO_4$, is much more soluble than the bisulfate; 100 g of water dissolves 202.2 g at 25°.

Hydrazine in aqueous solutions shows itself to be both an oxidizing and a reducing agent. With such reducing agents as Zn, Sn, Sn^{++}, and Ti^{+++} reduction to ammonia is observed, while with oxidizing agents the product is most frequently nitrogen, although in some cases ammonia and hydrazoic acid, HN_3, are also formed. In agreement with the asserted similarity of hydrazine to hydrogen peroxide, the oxidation to nitrogen is to be expected; thus

$$H_2O_2 + \text{Oxidizer} = 2H^+ + O_2 + \text{Reduced form of oxidizer}$$
$$N_2H_5^+ + \text{Oxidizer} = 5H^+ + N_2 + \text{Reduced form of oxidizer}$$

The oxidation reactions have been carefully studied by Bray and Cuy [*J. Am. Chem. Soc.*, **46**, 1796 (1924), *et ante*].

The reaction of $N_2H_5^+$ with chlorine or bromine proceeds rapidly and quantitatively in acid solutions.

$$N_2H_5^+ + 2Br_2 = N_2 + 5H^+ + 4Br^-$$

Hypochlorous acid in a buffer solution of NaH_2PO_4—Na_2HPO_4 (to prevent the decomposition of HClO into H_2O and Cl_2 and thus loss by volatilization) also rapidly oxidizes hydrazinium salts quantitatively to nitrogen. Pentavalent vanadium in acid solution, VO_2^+, rapidly oxidizes $N_2H_5^+$ principally to nitrogen, but the reaction is not quite quantitative, an error of ½% or more being possible. With dichromate in acid solution, nitrogen is the principal product; but some NH_4^+ and HN_3 are also observed; the dichromate reaction proceeds with a measurable rate which is first-order with respect to both dichromate and hydrazinium ions [Seubert and Carstens, *Z. anorg. Chem.*, **56**, 357 (1908)]. Ferricyanide ion reacts rapidly in alkaline solution with $N_2H_5^+$ to give nitrogen and ferrocyanide, but in acid solution the reaction is slow. In 0.3 n to 2 n acid solution iodate oxidizes $N_2H_5^+$ rapidly and quantitatively to nitrogen, but in alkaline solution the reaction is slow. The reaction with iodine is slow in acid but rapid in alkaline solution, a fact that is probably to be related to the concentration of hypoiodite, this being largest in alkaline solution. Unlike the cases just described, the oxidation of $N_2H_5^+$ by permanganate in acid solution, although rapid, is far from quantitative, the number of oxidation equivalents of permanganate required per mole of $N_2H_5^+$ varying from 1.4 to 1.7. This number would be 4.0 if only nitrogen were the oxidation product; in alkaline solution 3.9 equivalents are observed, and this suggests that in acid solution some intermediate oxidation state of manganese affects the course of the reaction. The observations of Cuy, Rosenberg, and Bray showed that manganic salts, Mn^{+++}, oxidize $N_2H_5^+$ mainly according to the equation

$$Mn^{+++} + N_2H_5^+ = NH_4^+ + \tfrac{1}{2}N_2 + Mn^{++} + H^+$$

in acetic acid solution. If the direct reaction with permanganate is

$$4MnO_4^- + 5N_2H_5^+ + 7H^+ = 5N_2 + 4Mn^{++} + 16H_2O$$

and if for every mole of MnO_4^- reacting in this way one mole reacts with Mn^{++} to form Mn^{+++}, and if this in turn oxidizes hydrazine as indicated, then 1.6 equivalents of MnO_4^- per mole of hydrazine would be required. This conclusion is in fair agreement with the number of equivalents observed; namely, 1.4–1.7. In this case the net reaction would be

$$8MnO_4^- + 25N_2H_5^+ + 19H^+ = 20NH_4^+ + 15N_2 + 32H_2O + 8Mn^{++}$$

Hydrazinium salts act as reducing agents toward many other oxidizing agents, the products being principally nitrogen together with some ammonia and hydrazoic acid in a few cases. Ammoniacal silver solutions give silver mirrors, and Fehling's solution ($CuSO_4 + KOH +$ tartrate) is reduced to cuprous oxide. Of special interest is the effect of oxygen on alkaline solutions of N_2H_5OH. It was once supposed that spontaneous decomposition of the hydrazinium hydroxide into nitrogen and ammonia took place, but more careful observations show that in the absence of oxygen the solutions do not change in strength. With oxygen of the air, a 0.05 m solution of N_2H_5OH in 0.5 n OH^- may be oxidized to the extent of 1% in five minutes and 20% in 16 hours. A neutral, 0.015 m N_2H_5OH solution loses, by atmospheric oxidation, about 8% of its strength in 48 hours.

Of interest is the catalyzed reaction of $N_2H_5^+$ with chlorate in acid solution. With chlorate alone, the reaction is extremely slow, if it takes place at all. On the addition of a small amount of osmium salt, the evolution of nitrogen sets in slowly at first and then proceeds more rapidly until one of the reactants is used up. The mechanism of the reaction is not known; some unpublished results indicate that osmium acts by being oxidized to OsO_4 by chlorate, the tetroxide then reacting with the hydrazine. That this is not the complete explanation is indicated by the autocatalytic nature of the reaction.

We may conclude our discussion of hydrazine by calling attention once more to its twofold character. First, it acts as both a reducing and an oxidizing agent; second, its structure, because it is a derivative of ammonia, is such that its physical and chemical properties are intermediate between those of ammonia and its analogue, water. Efforts to prepare further derivatives such as $NH(NH_2)_2$ and $N(NH_2)_3$ do not appear to have been successful. (Judging from the properties of NH_3 and N_2H_4, $NH(NH_2)_2$ would be a liquid of high dielectric constant.)

The geometrical structure of hydrazine has not been established; it would be of interest to know whether or not the $—NH_2$ groups rotate freely about the nitrogen—nitrogen bond. Electron-diffraction experiments show the N—N distance to be 1.47 Å, but the bond angles, H—N—N, are not known [Schomaker and Giguère, unpublished results]. According to our current ideas, the two nitrogens are bonded together through an electron pair; and since the hydrogens are bound to the nitrogens in the same manner, each nitrogen would have a valence of three.

Hydrazoic Acid, HN_3

So far we have discussed a number of compounds which were regarded as derivatives of ammonia, but when we consider hydrazoic acid, HN_3, it soon becomes apparent that it cannot be so derived directly from