The Journal of the
American Chemical Society
with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 46 OCTOBER, 1924 No. 10

SYSTEMS OF ACIDS, BASES AND SALTS

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RECEIVED JULY 25, 1924 PUBLISHED OCTOBER 4, 1924

In the years following "*la révolution chimique*" the view prevailed among chemists that all acids, bases and salts owe their characteristic properties to the presence of oxygen. It is the present purpose to show that not only oxygen, but also sulfur, nitrogen, the halogens, and to a recognizable extent even carbon, are acid, base and salt-forming elements in the original Lavoisian sense.

An adequate basis for the ready grasp of what is meant by a system of bases, acids and salts is afforded by a brief presentation of what may be called the water system.

The Water System of Acids, Bases and Salts

Every one recognizes that in an entirely reasonable sense the ordinary oxygen bases, acids and salts may be looked upon as derivatives of water. A molecule of a typical base, such as potassium hydroxide, is accordingly assumed to be a molecule of water in which one hydrogen atom is replaced by a strongly electropositive potassium atom. An acid is similarly an hydroxide or a partially dehydrated hydroxide of an electronegative element, while a salt is a mixed oxide, or in other words, a derivative of water in which part of the hydrogen is replaced by a metal or an electropositive group while the place of another portion of the hydrogen is taken by a negative element or radical. Bases react with acids, with especial facility in solution in water, to form salts, as represented for example by the familiar equation, $KOH + HONO_2 = KONO_2 + H_2O$.

For present purposes such derivatives of water will be referred to as aquo bases, aquo acids and aquo salts, respectively. The above equation may therefore be read as representing the action of an aquo base, potas-

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[1] Presidential address, American Chemical Society, 1923.

sium hydroxide, on aquonitric acid to form potassium aquonitrate and water.

The Hydrogen Sulfide System of Acids, Bases and Salts

With this brief sketch of a water system of compounds in mind and at the same time recalling the contiguous positions of oxygen and sulfur in the sixth group of the periodic system of the elements one is led to inquire concerning the formulation of an analogous hydrogen sulfide system. As a matter of fact many sulfur compounds are known which may be looked upon as the bases, acids and salts of such a system.

Potassium sulfhydroxide is a thio base, while trithiocarbonic acid and carbon disulfide are the sulfur analogs of aquocarbonic acid and carbonic anhydride, respectively. Just as potassium hydroxide, an aquo base, acts on aquocarbonic acid and on carbonic anhydride to form potassium aquocarbonate and water, so potassium sulfhydroxide, the thio base, acts on thiocarbonic acid, a carbonic acid of the hydrogen sulfide system, and on carbon disulfide to form a potassium thiocarbonate and hydrogen sulfide as represented by the equations, $2KSH + CS(SH)_2 = (KS)_2CS + 2H_2S$, $2KSH + CS_2 = (KS)_2CS + H_2S$.

The student of qualitative analysis is familiar with the action of potassium hydrosulfide on arsenic sulfide in accordance with the equation $6KSH + As_2S_5 = K_3AsS_5 + 3H_2S$, which may be read as representing the action of a thio base on arsenic sulfide, a compound related to thio-arsenic acid as arsenic anhydride is related to aquo-arsenic acid to form potassium thio-arsenate.

A system of compounds is therefore known in which sulfur occupies a position strictly analogous to that which oxygen occupies in the water system; or in other words just as the ordinary oxygen bases, acids and salts have been assumed to belong to a water system so the corresponding sulfur compounds may be said to constitute a hydrogen sulfide system.

It might be expected that for every known aquo base, acid and salt an analogous thio base, acid and salt might be prepared. As a matter of fact, however, the number of known thio compounds, excepting perhaps the sulfides which are the analogs of the oxides, is far below the number of known aquo compounds, and this undoubtedly for the reason that the great majority of soluble compounds belonging to the hydrogen sulfide system undergo hydrolysis in the presence of water. Water is therefore not a suitable solvent in which to carry out the reactions necessary for the preparation of bases, acids and salts belonging to the hydrogen sulfide system.

In view of the results obtained by the use of liquid ammonia as a solvent in the development of the ammonia system of compounds and just as water is the solvent in which by far the greater portion of investigations on the aquo compounds have been accomplished so one might expect to achieve results by the use of liquid hydrogen sulfide as a solvent in which to study the compounds of the hydrogen sulfide system. Unfortunately, however, for the prospect of the further development of this system by this means stands the fact that liquid hydrogen sulfide is a non-electrolytic solvent. Certain halogen compounds of the non-metals together with a considerable variety of organic compounds dissolve readily enough in liquid hydrogen sulfide but no typical salt-like substances are soluble in it.

The Ammonia System of Bases, Acids and Salts

Like water and hydrofluoric acid, at the same time, strikingly unlike hydrogen sulfide, hydrochloric acid, phosphine and methane, ammonia is an excellent ionizing solvent. Indeed in all those properties which give to water its unique position among solvents liquid ammonia shows a most striking similarity to water. Excepting water itself, it is, so to speak, by far the most water-like substance known. Approaching water as it does in its general properties, one might expect to find many resemblances between derivatives of ammonia and the analogous water compounds and, indeed, many such resemblances have long been recognized. More specifically one might expect to find that compounds formally related to ammonia as the aquo bases, acids and salts are related to water possess the properties, respectively, of bases, acids and salts, and thus constitute an ammonia system of compounds analogous to the water and hydrogen sulfide systems to which brief attention has just been given. Many such basic, acidic and salt-like compounds derived from ammonia have long been known though an adequate recognition of their real nature as bases, acids and salts of an ammonia system has awaited a study of their reactions in liquid ammonia solutions.

Compounds which are related to ammonia as the metallic hydroxides are related to water are the bases of the ammonia system. They may appropriately be called ammono bases. Potassium amide, KNH_2, and lead imide, PbNH, for example, are ammono bases while the metallic nitrides are basic nitrides corresponding to the basic oxides of the water system. Amides of the electronegative elements, together with their partially de-ammonated products, are the acids of the ammonia system, that is to say they are ammono acids, while the final de-ammonation products as analogs of the acid oxides or acid anhydrides are acid nitrides or, as they may be fittingly called, acid anammonides. As examples of typical ammono acids the carbonic acids of the ammonia system together with the corresponding acids of the water and hydrogen sulfide systems are given herewith.

$$C(OH)_4 \longrightarrow OC(OH)_2 \longrightarrow CO_2$$
$$C(SH)_2 \longrightarrow SC(SH)_2 \longrightarrow CS_2$$
$$C(NH_2)_4 \longrightarrow HNC(NH_2)_2 \longrightarrow NCNH_2 \longrightarrow (NC)_2NH \longrightarrow C_3N_4$$

The orthocarbonic acids are represented as undergoing desolvation, the first to aquocarbonic acid and carbonic anhydride, the second, to the sulfur analog of carbonic acid and carbon disulfide, the third, successively through the ammonocarbonic acids, guanidine, cyanamide and dicyanimide, finally to carbonic anammonide.

Proceeding now on the assumption that the formal relations thus developed are real, that the metallic amides in fact are ammono bases and that guanidine, cyanamide and dicyanimide are ammonocarbonic acids, then these compounds in solution in liquid ammonia must react with ammono bases and with the more electropositive metals to form ammonocarbonates. Three experimentally established reactions, represented by the equations, $2KNH_2 + H_5CN_3 = K_2H_3CN_3 + 2NH_3$, $AgNH_2 + HC_2N_3 = AgC_2N_3 + NH_3$, $Mg + H_2CN_2 = MgCN_2 + H_2$, show these assumptions to be justified.

Furthermore, ammono bases and ammono acids in solution in liquid ammonia must bring about the same reciprocal color changes in indicators that are so familiar a characteristic of the action of aquo bases and acids in aqueous solutions. A few moments may be taken to describe a striking experiment illustrative of this statement.

A liquid ammonia solution of phenolphthalein contained in the middle branch of a three-legged reaction tube[2] is quite as colorless as a neutral aqueous solution of the same indicator. A single drop of a solution of potassium amide poured from a second leg of the reaction tube into the phenolphthalein solution develops instantly the red color characteristic of aqueous alkaline solutions of phenolphthalein. Addition of dicyanimide solution from the third leg of the reaction tube to the red solution, discharges the color just as sharply as an ordinary acid in water solution destroys the color of an alkaline aqueous solution of the indicator.

Finally, it has been shown that potassium amide, cyanamide and dicyanimide as well as the salts resulting from the interaction of potassium amide with these ammono acids form electrically conducting solutions when dissolved in liquid ammonia, just as is familiarly known to be the case with the corresponding aquo compounds in water solutions.

The existence of an ammonia or nitrogen system of bases, acids and salts thus definitely established, we may proceed to a consideration of a limited number of particularly interesting bases and acids belonging to this system.

Ammono Bases.—In so far as concerns the ammono bases it will be sufficient for present purposes to show by a few examples that ammono bases and basic nitrides may be prepared by reactions in liquid ammonia which are strictly analogous to the familiar reactions whereby metallic hydroxides and oxides are precipitated from water solutions.

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[2] In effect three test-tubes.

Metallic potassium reacts with ammonia to form potassium amide precisely as it acts on water to form potassium hydroxide, excepting that the former reaction is extremely sluggish whereas the latter is very energetic. Both reactions liberate hydrogen. The parallel reactions are represented by the equations, $K + H_2O = KOH + H$, and $K + NH_3 = KNH_2 + H$.

Just as potassium hydroxide acts on metallic salts in solution in water to form metallic hydroxides, or oxides as the case may be, so potassium amide added to liquid ammonia solutions of the salts of heavy metals gives, in certain instances, precipitates of the amides, in others of the imides and in still others of the nitrides. Typical reactions representing the formation of silver amide, lead imide and mercuric nitride, respectively, are shown by the equations, $AgNO_3 + KNH_2 = AgNH_2 + KNO_3$; $PbI_2 + 2KNH_2 = PbNH + PbI_2 + NH_3$; $3HgBr_2 + 6KNH_2 = Hg_3N_2 + 6KBr + 4NH_3$.

Ammono Acids.—Acids derived from the elements of the third periodic group so far as at present known are the amide and imide of boron, $B(NH_2)_3$ and $B_2(NH)_3$, and aluminum imide-amide, $HN{=}Al{=}NH_2$, of which last the sodium and potassium salts have been obtained beautifully crystallized and of sharply definite composition.

Acids derived from the fourth periodic group of elements are given in a table.

$C(NH_2)_4$	$HNC(NH_2)_2$	$NCNH_2$	$(NC)_2NH$	C_3N_4
$Si(NH_2)_4$	$HNSi(NH_2)_2$	$NSiNH_2$	$(NSi)_2NH$	Si_3N_4
$Ti(NH_2)_4$	......	$NTiNH_2$	......	Ti_3N_4
$Sn(NH_2)_4$	......	$NSnNH_2$	......	.....

All the compounds listed, excepting the ortho acids, are known either in the free state or in the form of salts.

The fifth group of elements furnishes one particularly interesting ammono acid, namely, Curtius' hydrazoic acid. This compound if assigned the formula, $H\text{-}N{=}N{\equiv}N$, is thereby represented as an acid related to ammonia as ordinary nitric acid is related to water as will be clear from a comparison of the formulas, $H\text{-}O\text{-}NO_2$ and $H\text{-}N{=}N{\equiv}N$, for just as aquonitric acid is ordinarily assumed to be built up of a pentavalent positive nitrogen atom with its five valences satisfied by two divalent oxygen atoms and a monovalent hydroxyl group, so in hydrazoic acid, as represented by the above formula, the five valences of a pentavalent positive nitrogen atom hold in combination one negative trivalent nitrogen atom and a negative divalent imido group. Or, as the formula of nitric acid is sometimes shown by assuming the acid to be a dehydration product of the unknown orthonitric acid, so the formula $H\text{-}N{=}N{\equiv}N$ may be deduced by assuming hydrazoic acid to be a de-ammonation product of the hypothetical ortho-ammononitric acid, as shown by the parallel schemes,

$$N(OH)_5 \longrightarrow ON(OH)_3 \longrightarrow O_2NOH$$

$$N(NH_2)_5 \longrightarrow HN{=}N(NH_2)_3 \longrightarrow N{\equiv}N(NH_2)_2 \longrightarrow N{\equiv}N{=}NH.$$

Obviously this formula represents hydrazoic acid as the ammonia analog of ordinary nitric acid. That the compound is in fact an ammononitric acid and that its salts are ammononitrates has been shown by a very considerable number of observations most important among which are perhaps the following. First, a mixture of hydrazoic acid and hydrochloric acid dissolves gold and platinum, and oxidizes ferrous iron to ferric iron. Second, a warm mixture of hydriodic acid and sodium azide evolves iodine and rapidly dissolves gold. Third, just as potassium nitrate is well recognized as an energetic oxidizing agent, so the potassium salt of hydrazoic acid has been found to be a nitridizing agent, for when added to fused potassium cyanide it nitridizes the latter salt to potassium cyanamide, a reaction which will be recurred to later. Fourth, and possibly most significant of all, it has been found that nitric acid in the form of its potassium salt in solution in liquid ammonia may be ammonolyzed to potassium azide, potassium ammononitrate, in accordance with the equation, $KONO_2 + 2NH_3 = K\text{-}N{=}N{\equiv}N + 3H_2O$.

Formally phospham, $H\text{-}N{=}P{\equiv}N$, arsenous amide, $As(NH_2)_3$, and imide, $As_2(NH)_3$, are further ammono acids derived from elements of the fifth periodic group. That phospham is in fact an ammonophosphoric acid is shown by its behavior toward sodium amide, and toward water in accordance with the equations: $H\text{-}N{=}P{\equiv}N + NaNH_2 = Na\text{-}N{=}P{\equiv}N + NH_3$; $H\text{-}N{=}P{\equiv}N + 4H_2O = H_3PO_4 + 2NH_3$. The first equation may be read as representing the action of an ammonophosphoric acid on the ammono base, sodium amide, to form sodium ammonophosphate and ammonia; the second, as representing the hydrolysis of an ammonophosphoric acid to an aquophosphoric acid.

Two compounds represented by the formulas, $Hg{=}N\text{-}S{\equiv}N.NH_3$, and $Pb{=}N\text{-}S_2{\equiv}N.NH_3$, are known which may be looked upon, respectively, as a mercury ammonosulfite and a lead ammonothiosulfate.

Concerning possible ammono acids derived from elements belonging to the seventh periodic group, it may be noted that chloro-amine is formally an ammonohypochlorous acid. While little is known concerning the properties of chloro-amine as an acid it must nevertheless be looked upon as a nitridizing agent, just as its analog, aquohypochlorous acid, is known to be an oxidizing agent, for by means of the former potassium cyanide, an ammonocarbonite of potassium, has been nitridized to the potassium ammonocarbonate of the formula, KC_2N_3.

Representatives of another class of ammono acids, the water analogs of which are theoretically impossible, are pyrrole, indole, carbazole, imidazole and purine, the formulas for which follow: $(C_4H_4)NH$, $(C_8H_6)NH$, $(C_{12}H_8)NH$, $(C_3H_3N)NH$, $(C_5H_3N_3)NH$.

Recalling the activating effect of the double bond on the strengths of acids, one might expect to find a similar activation of the imide hydrogen in such compounds as those formulated above. As a matter of fact the behavior of these substances in general and especially in liquid ammonia shows them to be ammono acids. Solutions of pyrrole, indole and carbazole in liquid ammonia act on sodium, potassium, magnesium and calcium with the evolution of hydrogen to form well crystallized salts and with the ammono bases, potassium amide and silver amide, to form the respective potassium and silver salts. Silver salts of imidazole and pyrazole are known. Fischer prepared a sodium and a zinc salt of purine.

This discussion of the ammono acids may be brought to a close with a brief consideration of hydrocyanic acid which, in so far as it may be represented by the formula HNC, is formally an ammonocarbonous acid, for obviously this formula represents the acid as ammonia in which two atoms of hydrogen are replaced by a negative divalent carbon atom.

Some of the most convincing experimental evidence in favor of the view that potassium cyanide is in fact an ammonocarbonite of potassium is briefly summarized in the table.

1. $KNC + KNN_2 = K_2CN_2 + N_2$
2. $KNC + 2C_2N_2 = KC_2N_3 + (C_3N_2)$
3. $2KNC + 2NH_2Cl = KC_2N_3 + KCl + NH_3.HCl$
4. $KNC + O = KNCO$
5. $K_2CN_2 + C = 2KNC$

When potassium azide is added to fused potassium ammonocarbonite the latter is nitridized as represented in Equation 1 to a potassium ammonocarbonate of the formula K_2CN_2. Equation 2 represents the nitridizing action of cyanogen on fused potassium cyanide to form an ammonocarbonate of the formula KC_2N_3, that is, the potassium salt of dicyanimide. Chloro-amine is formally a hypochlorous acid of the ammonia system. Its action as a nitridizing agent is shown in Equation 3. Equation 4 represents the familiar oxidation of potassium cyanide to potassium cyanate, that is, the oxidation of an ammonocarbonite to a mixed aquo-ammonocarbonate. Equation 5 represents the reduction of a potassium ammonocarbonate to potassium ammonocarbonite.

Amphoteric Amides and Imides.—Just as certain metallic hydroxides, such as those of zinc, lead and aluminum dissolve in aqueous solutions of potassium hydroxide to form potassium zincate, plumbite and aluminate, respectively, so zinc amide, lead imide and aluminum amide-imide are acted on by potassium amide in liquid ammonia solution to form the analogous ammono salts, potassium ammonozincate, ammonoplumbite and ammonoaluminate. It will be recalled that because of the hydrolyzing action of water on salts of weak acids, the preparation of alkali metal aluminates, zincates and plumbites is attended with serious manipulative difficulties. Pure specimens of the zincates have never been obtained. Plumbites are known only in solution.

In sharp contrast to the behavior of water solutions of the aquo salts it has been found that from liquid ammonia solutions the analogous ammono salts may be easily obtained beautifully crystallized and of sharply definite composition. It is a matter of much interest, furthermore, to observe that whereas, on the one hand, a very limited number of metallic hydroxides react after the manner of aluminum hydroxide with potassium hydroxide in aqueous solution, on the other, the number of metallic amides which react with potassium amide in liquid ammonia is very large. Not only have an ammonoaluminate, zincate and plumbite of potassium been prepared but the list of such compounds has been extended to include a cadmiate, a cuprite, argentate, manganite, thallite, nickelite, magnesiate, bariate, strontiate, calciate and even a sodiate and lithiate. The analogous aquo compounds are undoubtedly formed when metals or metallic oxides are dissolved in fused potassium hydroxide.

Ammonobasic Salts.—It is worth while to note in passing that a considerable number of ammono basic salts is known, especially interesting among which are the so-called infusible white precipitate and Nessler's precipitate, $HgNH_2Cl$ and Hg_2NI. Although in the past generally looked upon as ammonium salts in which hydrogen is replaced by divalent mercury, these two compounds are in fact ammonobasic salts formed by the ammonolytic action of ammonia on mercuric chloride and iodide, respectively, in accordance with the reversible equations: $HgCl_2 + 2NH_3 \rightleftharpoons NH_2HgCl + NH_4Cl$; and $2HgI_2 + 4NH_3 \rightleftharpoons Hg\text{-}N\text{-}Hg\text{-}I + 3NH_4I$.

The Hydrogen Fluoride System of Acids, Bases and Salts

That a considerable number of known compounds are related to hydrogen fluoride as, first, the aquo bases and basic oxides, second, the aquo acids and the acid anhydrides, and third, the aquo salts are respectively related to water will be clear from a consideration of the equations given in the table following.

1. $H_2O + SO_3 = H_2O.SO_3$
2. $2HF + SiF_4 = 2HF.SiF_4$
3. $K_2O + H_2O = K_2O.H_2O$
4. $KF + HF = KF.HF$
5. $K_2O + SO_3 = K_2O.SO_3$
6. $2KF + SiF_4 = 2KF.SiF_4$
7. $K_2O.H_2O + H_2O.SO_3 = K_2O.SO_3 + 2H_2O$
8. $2KF.HF + 2HF.SiF_4 = 2KF.SiF_4 + 4HF$

Just as sulfur trioxide and water unite to form an acid of the water system, namely, sulfuric acid, so the compound formed by the union of silicon fluoride with hydrogen fluoride may be looked upon as an acid of a hydrogen fluoride system. Silicon fluoride is obviously an acid anhydride-like compound related to hydrofluosilicic acid as sulfur trioxide is related to sulfuric acid, the former being an acid fluoride, the latter an acid oxide. Hydrogen fluoride and potassium fluoride react in accordance with Equation 4 to form potassium acid fluoride, just as water and potassium oxide unite with each other to form the hydrated potassium oxide or potassium hydroxide. Potassium acid fluoride thus appears formally to be a base of a hydrogen fluoride system while potassium fluoride is a basic fluoride, just as potassium oxide is a basic oxide. Furthermore, as potassium oxide unites directly with sulfuric anhydride to form potassium sulfate, so the basic fluoride, KF, by direct union with the acid fluoride, SiF_4, forms the well-known salt, potassium fluosilicate, as represented by Equation 6. Finally, just as potassium hydroxide reacts with sulfuric acid to form potassium sulfate and water as represented in Equation 7, so the last equation must be looked upon as representing the action of a fluoro base on a fluoro acid to form a fluoro salt with the elimination of the water analog, hydrogen fluoride.

Reactions analogous to the action of aquo bases on aquo acids, as represented by the last of the equations given above, are not numerously known. Certain familiar reactions such, for example, as that between chloroplatinic acid and potassium chloride to form potassium chloroplatinate are analogous to the action of aquo acids on basic oxides as will be clear from the equations,

$$2HCl.PtCl_4 + 2KCl = 2KCl.PtCl_4 + 2HCl$$
$$H_2O.SO_3 + K_2O = K_2O.SO_3 + H_2O$$

Very much more generally halogeno salts are formed by the direct union of the basic halide with the acid halide, reactions which clearly are entirely analogous to those involved in the union of basic oxides with acid anhydrides to form aquo salts.

Methano or Carbono Acids, Bases and Salts

While the generally non-polar nature of carbon would not lead one to expect it to function as fluorine, oxygen and nitrogen do in the formation of bases, acids and salts, nevertheless the existence of such compounds as sodium methyl and zinc methyl, which formally are related to methane as sodium hydroxide and zinc hydroxide are related to water, on the one hand, and the ready replacement of hydrogen in acetylene and a few other hydrocarbons by metals, on the other, makes it worth while to inquire whether the formulation of a methano system of bases, acids and salts will be a procedure of any significance. It is clear that formally a methano base must be a derivative of methane in which one, two or three of the hydrogen atoms are replaced by a positive metal. Sodium methyl, zinc dimethyl, and methyl magnesium bromide, the latter of course only in so far as the alkyl metal part of the molecule is concerned, are therefore methano bases.

Such compounds as nitromethane and tricyanomethane are methane in which hydrogen is replaced by negative groups and may therefore be looked upon as methano acids. As a matter of fact, hydrogen in these compounds is labile and easily replaceable by metals. They are certainly acids. Metallic derivatives of nitromethane and cyanomethane, however, are not unequivocally methano salts and this for the reason that they contain respectively the strongly polar elements, oxygen and nitrogen. The sodium salt of nitromethane is undoubtedly to be represented by the formula $CH_2{=}NOONa$, while analogously the salt of tricyanomethane probably has the constitution represented by the formula $(NC)_2{=}C{=}C{=}NNa$. The former formula represents sodium nitromethane as an aquo salt; according to the latter formula sodium tricyanomethane is an ammono salt. To the extent to which these two salts are tautomeric substances they may be looked upon, the one as an aquo methano acid, the other as an ammono methano acid. In consequence of the tendency of acids such as these to act as aquo acids or ammono acids instead of as methano acids all groups containing strongly polar elements, such as oxygen, sulfur, nitrogen or the halogens, must be eliminated from consideration as negative radicals which, substituted in methane, are to form methano acids. This necessity practically reduces the choice of negative groups to hydrocarbon radicals.

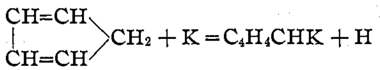
Now, a considerable number of hydrocarbons is known which readily form metallic derivatives, among them triphenylmethane and acetylene. Three phenyl groups replacing three hydrogen atoms in methane results in the formation of a compound with recognizable acid properties. Acetylene may be looked upon as marsh gas in which three hydrogen atoms are replaced by the negative CH group. It is therefore a methano acid.

Pyrrole, indole and carbazole, as has already been shown, are ammono acids. Derivatives of ammonia as these compounds are, it is certainly significant that cyclopentadiene, indene and fluorene—which may be looked upon, respectively, as derivatives of methane in the same sense that pyrrole, indole and carbazole are derivatives of ammonia—are compounds in which hydrogen of the methylene groups is replaceable by metals.

Cyclopentadiene, indene and fluorene, represented by the formulas, $(C_4H_4)CH_2$, $(C_8H_6)CH_2$, and $(C_{12}H_8)CH_2$, are therefore methano acids.

In accord with the assumption that acetylene, triphenylmethane, cyclopentadiene, indene and fluorene are methano acids and that zinc methyl and Grignard's reagent are methano bases, are the known reactions represented by the equations,

$$HC{\equiv}CH + 2Na = NaC{\equiv}CNa + H$$



$$\left.\begin{matrix} CH{=}CH \\ | \\ CH{=}CH \end{matrix}\right\rangle CH_2 + K = C_4H_4CHK + H$$

$$(C_6H_5)_3CH + K = (C_6H_5)_3CK + H$$

$$HC{\equiv}CH + Zn(C_2H_5)_2 = ZnC_2 + 2C_2H_6$$

$$CH_3C{\equiv}CH + C_2H_5MgBr = CH_3C{\equiv}CMgBr + C_2H_6$$

$$HC{\equiv}CH + 2NaNH_2 = NaC{\equiv}CNa + 2NH_3$$

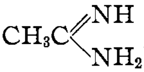
$$C_8H_6CH_2 + NaNH_2 = C_8H_2CHNa + NH_3$$

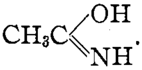
which may be said to represent the action of methano acids on metals, methano bases and ammono bases, respectively.

Methano bases react with acids in general and of course are vigorously hydrolyzed by water, ammonolyzed by ammonia and in general solvolyzed by any solvolyzing agent.

The relationships thus indicated are interesting and possibly of some significance, but at the same time the formulation of a system of bases, acids and salts derived from such an unwater-like compound as methane is probably pushing the principle of analogy rather too far.

Mixed Compounds. Acids Derived Simultaneously from Water and Ammonia

The numerous known acid amides and imides are to be looked upon as acids belonging at the same time to both the water and the ammonia systems and consequently may be fittingly called mixed aquo ammono acids. Acetic acid, CH_3COOH, a derivative of water, is an aquo acetic acid, aceto-amidine,  $CH_3C\begin{matrix}\nearrow NH \\ \searrow NH_2\end{matrix}$, the analogous derivative of ammonia, is an ammono-acetic acid, while aceto-amide, CH_3CONH_2, is a mixed aquo-ammono-acetic acid.

In the past the acid amides and imides have been discussed as ammono acids and indeed the familiar formula, CH_3CONH_2, represents a compound in which one hydrogen atom of an ammonia molecule is replaced by the negative acetyl group and so formulated acetamide is of course represented as an ammono acid; but as is well known the properties of acetamide are quite as well represented by the formula,  $CH_3C\begin{matrix}\nearrow OH \\ \searrow NH\end{matrix}$. In other words, acetamide is a tautomeric substance to which a unique formula cannot be assigned. The acid hydrogen atoms are labile and cannot be said to be fixed in any specific position. Acetamide as well as the acid amides and acid imides in general are therefore mixed aquo ammono acids.

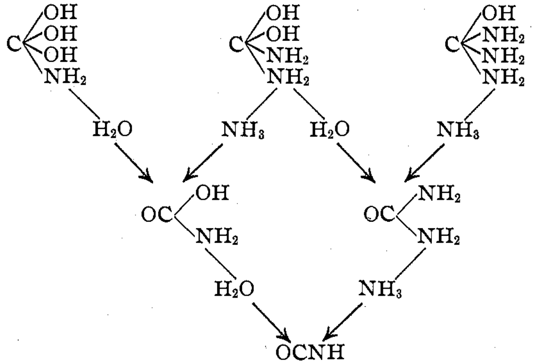
The acid properties of many acid amides and imides have long been recognized to the extent at least that they are capable of forming metallic derivatives.

In solution in liquid ammonia the amides of the fatty acids, benzamide, benzenesulfonamide, etc., have been found to react with ammono bases to form salts with all the facility which characterizes salt formation in water solutions. Typical reactions are represented by the equations,

$$CH_3CONH_2 + AgNH_2 = CH_3CONHAg + NH_3$$
$$C_6H_5CONH_2 + KNH_2 = C_6H_5CONHK + NH_3$$
$$C_6H_5CONH_2 + 2KNH_2 = C_6H_5CONK_2 + 2NH_3$$
$$3C_6H_5SO_2NH_2 + Tl_3N = 3C_6H_5SO_2NHTl + NH_3$$
$$CH_3C_6H_4SO_2NH_2 + CuNH_2 = CH_3C_6H_4SO_2NHCu + NH_3$$
$$CH_3CONHC_6H_5 + AgNH_2 = CH_3CONAgC_6H_5 + NH_3$$

The acid imides containing, as they do, two acidifying groups in the molecule as contrasted with one in the acid amides are frequently acids of sufficient strength to form metallic salts even in the presence of water as witness, for example, the formation of phthalimide potassium by the action of potassium hydroxide on phthalimide in aqueous alcoholic solutions. Tri-acetamide is a representative organic acid anhydride-acid anammonide.

Aquo-ammonocarbonic Acids.—Proceeding to a consideration of the important mixed aquo-ammonocarbonic acids it will be clear that as the formulas $C(OH)_4$ and $C(NH_2)_4$ represent, respectively, the ortho aquo- and ortho-ammonocarbonic acids, so the three intermediate formulas given in the table are purely hypothetical formulas for mixed aquo-ammonocarbonic acids.



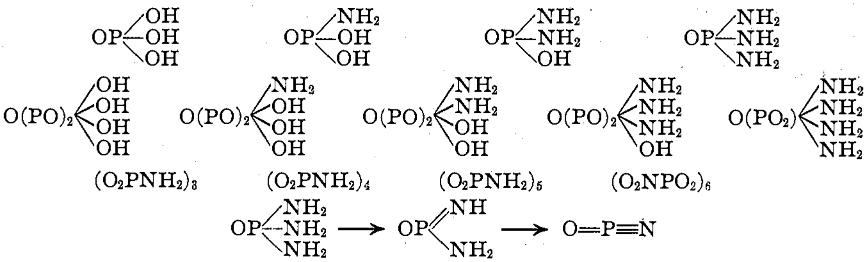
Since dehydration (or loss of water) and de-ammonation (loss of ammonia) are strictly analogous phenomena, it is obvious that the elimination of the elements of water or ammonia or of both water and ammonia from the respective mixed aquo-ammonocarbonic acid formulas will yield formulas which will be recognized as those of carbamic acid, urea and cyanic acid.

It thus becomes clear that carbamic acid, urea and cyanic acid are to be looked upon as mixed aquo-ammonocarbonic acids. In support of this view are the following experimentally established facts. First, carbamic acid and cyanic acid are familiarly known to form salts. In liquid ammonia solution carbamic acid reacts with an excess of potassium amide to form a dipotassium salt. Second, urea, although too weak an acid to form salts in the presence of water, reacts in liquid ammonia solution with potassium amide to form a mono- and a dipotassium salt, and also with metallic magnesium to form a magnesium salt. Third, all three aquo-ammonocarbonic acids, when heated in water, on the one hand, are hydrolyzed to carbon dioxide and ammonia; when heated with liquid ammonia, on the other, they are ammonolyzed to guanidine. Finally, when fused with an excess of sodium amide all three mixed acids are converted into the sodium ammonocarbonate, sodium cyanamide.

Cyanic acid, carbamic acid and urea are three of the simplest and best known members of a large group of aquo-ammonocarbonic acids. Even the names of others must be omitted here.

Aquo-ammononitric Acid.—An important compound which is to be looked upon as a mixed aquo-ammononitric acid is Lachman's nitramide. Its acid properties are shown by the formation of a mercury and an ammonium salt and by the fact that its solutions in liquid ammonia, as well as in water, are good conductors of electricity. Its ready decomposition to form nitrous oxide and water is to be interpreted as the dehydration of the mixed aquo-ammono acid to form a mixed acid anhydride-acid anammonide as represented by the equation, $O_2N\text{-}NH_2 = N\equiv N{=}O + H_2O$.

Mixed Aquo-ammonophosphoric Acid.—A surprisingly large number of amides of the phosphoric acids is known, some in the form of the free acids and their salts, others in the form of salts only. It will be sufficient for present purposes to note first, that a silver salt of the mixed acid of the formula, $(H_2N)_2P(OH)_3$, is known, that mixed orthophosphoric acids—orthophosphoric acid being $OP(OH)_3$ and not $P(OH)_5$—are recorded in the literature in which successively one, two and three hydroxyl groups are replaced by amido groups, that mixed acids are known in which one, two, three and four of the hydroxyl groups in pyrophosphoric acid are replaced by amido groups, that just as metaphosphoric acid is reported to exist in polymeric modifications, so the mixed aquo-ammono acid has been obtained in the trimeric, tetra-, penta- and hexameric forms. Finally, the aquo-ammonophosphoric acids of the respective formulas, $OP(NH_2)_3$, and $OP(NH)(NH_2)$, have been de-ammonated to the mixed acid anhydride-acid anammonide of the formula, $N\equiv P{=}O$. The foregoing statements are summarized as follows.



$$OP{<}\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix} \qquad OP{<}\begin{smallmatrix}NH_2\\OH\\OH\end{smallmatrix} \qquad OP{<}\begin{smallmatrix}NH_2\\NH_2\\OH\end{smallmatrix} \qquad OP{<}\begin{smallmatrix}NH_2\\NH_2\\NH_2\end{smallmatrix}$$

$$O(PO)_2{<}\begin{smallmatrix}OH\\OH\\OH\\OH\end{smallmatrix} \quad O(PO)_2{<}\begin{smallmatrix}NH_2\\OH\\OH\\OH\end{smallmatrix} \quad O(PO)_2{<}\begin{smallmatrix}NH_2\\NH_2\\OH\\OH\end{smallmatrix} \quad O(PO)_2{<}\begin{smallmatrix}NH_2\\NH_2\\NH_2\\OH\end{smallmatrix} \quad O(PO_2){<}\begin{smallmatrix}NH_2\\NH_2\\NH_2\\NH_2\end{smallmatrix}$$

$$(O_2PNH_2)_3 \qquad (O_2PNH_2)_4 \qquad (O_2PNH_2)_5 \qquad (O_2NPO_2)_6$$

$$OP{<}\begin{smallmatrix}NH_2\\NH_2\\NH_2\end{smallmatrix} \longrightarrow OP{\lessgtr}\begin{smallmatrix}NH\\NH_2\end{smallmatrix} \longrightarrow O{=}P{\equiv}N$$

Mixed Aquo-ammonosulfuric Acids.—Of mixed acids derived from elements of the sixth periodic group three aquo-ammonosulfuric acids, one mixed chromic acid and one mixed molybdic acid may be noted as follows: imidosulfuric acid, $HN(SO_2OH)_2$, sulfamide, $SO_2(NH_2)_2$, imidosulfamide, $HN(SO_2NH_2)_2$, amidochromic acid, H_2NCrO_2OH, and amidomolybdic acid, H_2NMoO_2OH.

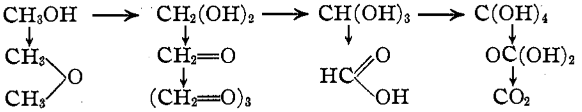
A tripotassium salt of imidosulfuric acid is known, as are also the ammonium, potassium and silver salts of imidosulfamide. A mono- and a dipotassium salt of sulfamide have been made by the action of potassium amide on sulfamide in liquid ammonia solution. Similarly in liquid ammonia solution a tripotassium salt of amidochromic acid has been made. Salts of trimeric sulfimide, a much stronger acid, are also known.

Further Mixed Acids.—Benzenesulfonenitramide, nitro-urea, nitroguanidine, acetylurea, malonylurea, uric acid and other similar compounds are mixed aquo-ammono acids and at the same time are mixed compounds in a sense theoretically impossible of realization among the aquo acids, for obviously the substitution of a second negative group in a molecule of water results not in the formation of an acid but of an acid anhydride. Four typical representatives of this class of compounds are benzenesulfonenitramide, $C_6H_5SO_2NHNO_2$, nitroguanidine, $NH_2C(NH)NHNO_2$, acetylurea, $CH_3CONHCONH_2$, and barbituric acid, $CH_2(CONH)_2CO$.

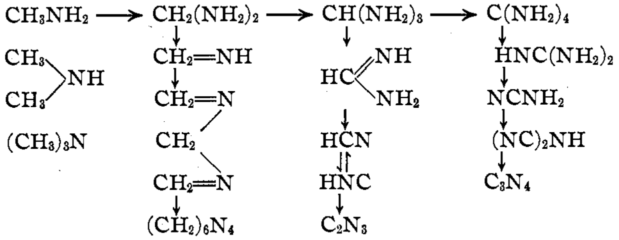
Benzenesulfonenitramide is an aquo-ammonobenzenesulfonic acid and at the same time an aquo-ammononitric acid. It may be looked upon as a derivative of ammonia, of which one hydrogen atom is replaced by the negative benzenesulfonyl group and a second by the nitro group. It is an acid of sufficient strength to form salts in aqueous solution. Nitroguanidine is a mixed ammonocarbonic acid–aquo-ammononitric acid. Acetylurea is aquo-ammono-acetic acid–aquo-ammonocarbonic acid. Barbituric acid is an aquo-ammonocarbonic acid–aquo-ammonomalonic acid.

Finally and very briefly, it seems important to show that just as the ordinary alcohols, ethers, aldehydes, ketones, etc., as oxygen compounds may be included with the aquo bases, acids and salts in a water system of compounds, so a very large number of nitrogen compounds may be looked upon as analogous members of an ammonia system. With an inspection of the following table the very remarkable analogies between the compounds of the water system, on the one hand, and the ammonia system, on the other, become at once obvious.

DERIVATIVES OF WATER



DERIVATIVES OF AMMONIA



Methylamine and dimethylamine are the analogs of methyl alcohol which, moreover, they resemble in many of their chemical and physical properties. Trimethylamine is formally, as well as in its general behavior, an ammono methyl ether. Methylenediamine like methylene glycol, and ortho-ammonoformic acid like ortho-aquoformic acid are known only in the form of their alkyl derivatives. The ammonia analog of orthocarbonic acid is not known either in the free state or in the form of its esters.

Methylene-imine is a representative of a class of substances unknown in the water system. Formally, it is a mixed alcohol aldehyde (or acid aldehyde) of the ammonia system. It is not known in the free state. Alkyl and especially aryl derivatives have been prepared in large numbers and are known as Schiff's bases which possess conspicuous aldehydic properties. Nor has monomolecular ammonoformaldehyde been prepared. When aquoformaldehyde is ammonolyzed to ammonoformaldehyde the latter immediately polymerizes to hexamethylenetetramine which is a dimeric modification of ammonoformaldehyde. Formamidine is an ammonoformic acid. Hydrocyanic acid shows the properties simultaneously of an acid anammonide, of an ammono aldehyde and of an ammonocarbonous acid. The compounds represented by the formulas given in the last column have already been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE ELECTRIC MOMENTS OF TYPICAL ORGANIC MOLECULES

BY CHARLES P. SMYTH

RECEIVED MAY 3, 1924 PUBLISHED OCTOBER 4, 1924

The electric moment of a molecule is a fundamental property dependent upon the arrangement of the electric charges within the molecule.[1] If we adopt the view that the average position of an electron in an orbit may be treated as the actual position of the electron in the molecule of which it is a part, it becomes possible to calculate the location of the centers of gravity of the electrons and of the positive charges in the molecule in much the same way that the center of gravity of a system of rigid bodies is located. When these two centers of gravity do not coincide, the molecule may be regarded as containing an electric doublet the moment of which is equal to the product of the distance between the two centers of gravity and the total electric charge of either sign in the molecule. The method of calculation has been explained in a recent paper.[2]

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[1] Compare Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Company, **1923**, p. 56.

[2] Smyth, *Phil. Mag.*, **47,** 530 (1924).