temperature is in good agreement with the equation of van't Hoff.

A simple equation is given from which the equilibrium constant at any temperature may be calculated.

The value thus calculated for 1537° agrees with the results of Löwenstein on the dissociation of water and hydrochloric acid at that temperature.

From the equilibrium constant of the Deacon reaction at 25°, and the experiments of Dolazalek, the electromotive force of the hydrogen-oxygen cell at 25° is calculated to be 1.207 volts, while the value obtained by an entirely different method in a previous paper was 1.217±0.010 volts.

The conclusion of the previous paper, that the value at present accepted for the electromotive force is one-tenth of a volt too low, is thus fully corroborated.

LIQUID METHYLAMINE AS A SOLVENT, AND A STUDY OF ITS CHEMICAL REACTIVITY.

By H. D. Gibbs.

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Since Franklin[1] and his co-workers have shown, in an extended series of investigations, that liquid ammonia shows many analogies to water, both as a solvent and in its reactions, liquid methylamine would naturally be expected to show the same analogies to methyl alcohol. As $H.NH_2$ is to $H.OH$ so is CH_3NH_2 to $CH_3.OH$. Owing to its intermediate position in the group $H.NH_2$, $H.OH$, $CH_3.NH_2$, $CH_3.OH$, one would expect methylamine to possess the property of existing in compounds as methylamine of crystallization to a degree corresponding to that of the other members of the group. The compounds in which water is known to be a constituent as water of crystallization are too numerous for mention; ammonia is a constituent of a large number of known compounds as ammonia of crystallization, and methyl alcohol possesses the property of uniting with many compounds as alcohol of crystallization. Among the latter which are mentioned in the literature are:

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[1] Franklin and Kraus: Am. Ch. J. 20, 820 and 836; 21, 1 and 8; 23, 277; 24, 83; Franklin and Stafford: Ibid. 28, 83; Franklin and Cady: This Journal, 26, 499; Franklin and Kraus: Ibid. 27, 191; Franklin: Ibid. 27, 802.

$LiCl.3CH_3OH$;[1] $MgCl_2.6CH_3OH$;[1] $CaCl_2.4CH_3OH$;[2] $BaO.2CH_3OH$;[3] $3BaO.4CH_3OH$;[4] $SbCl_5.CH_3OH$;[5] $CuSO_4.CH_3OH$;[6] $5NaOH.6CH_3OH$;[7] $3KOH.5CH_3OH$;[8] $CH_3OH.H_2O$;[9] $CH_3ONa.CH_3OH$;[10] and various methyl alcohol addition products of $SnCl_4$, $FeCl_3$, $SbCl_5$, BF_3, SiF_4 described by Kuhlmann.[11] From these analogies it would be expected that many compounds, both organic and inorganic, containing methylamine of crystallization, can be prepared and experimentation has upheld this theory.

With these considerations in view, a study of the solubilities of a number of compounds in liquid methylamine, together with some of the reactions involved and qualitative measurements of the electrical conductivity of the solutions, has been undertaken. The results of quantitative conductivity measurements together with a description of the apparatus employed and a further study of some of the reactions which have not as yet been investigated will be described in later papers.

The liquid methylamine[12] employed in these investigations was the same as that used in the boiling-point determinations[13] and the same steel cylinder was used as a container. This steel cylinder is of about 500 cc. capacity and is fitted with an outlet tube and a tightly fitting needle valve. Methylamine, stored in sealed glass cylinders, is distilled into the steel cylinder, the connections being made by means of lead tubing of 0.5 cm. diameter attached to the glass with sealing-wax and to the steel cylinder by soldering to a steel screw connection made tight with lead washers. The glass tubes of about 100 cc. capacity containing the methylamine are cooled in a Dewar test-tube of liquid

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[1] Simon: J. pr. Chem. [2] 20, 374.

[2] Kane: Ann. 19, 168.

[3] Dumas and Peligot: Ibid. 15, 10.

[4] Forcrand: Bull. soc. chim. 46, 337.

[5] Williams: Jsb. 1876, 332.

[6] Forcrand: Bull. soc. chim. 46, 61.

[7] Forcrand: Ann. chim. phys. [6] 11, 462.

[8] Göttig: Ber. 21, 1835.

[9] Forcrand: Ann. chim. phys. [6] 27, 547.

[10] Ibid. [6] 11, 455.

[11] Ann. 33, 208.

[12] Obtained from Kahlbaum through the kinduess of the trustees of the Bache Fund, to whom acknowledgments are due.

[13] Gibbs: This Journal, 27, 851.

ammonia and one end is drawn down in the blast flame to about the size of the lead tubing so that when inserted into the lead tubing a snug fit is afforded. A minimum surface of the sealing-wax is thus exposed to the methylamine whose solvent action upon the wax is quite rapid. The steel cylinder is cooled in ice water, the valve opened and the glass tube of methylamine warmed in the air and finally in warm water, thus causing the methylamine to distil into the steel cylinder from which it can be conveniently redistilled into any form of apparatus and in any quantity desired.

The solubilities, qualitative measurements of the electrical conductivity of solutions of various substances in methylamine and the reactions which often take place were studied in closed tubes, the most convenient form of which is shown in Fig. 1.

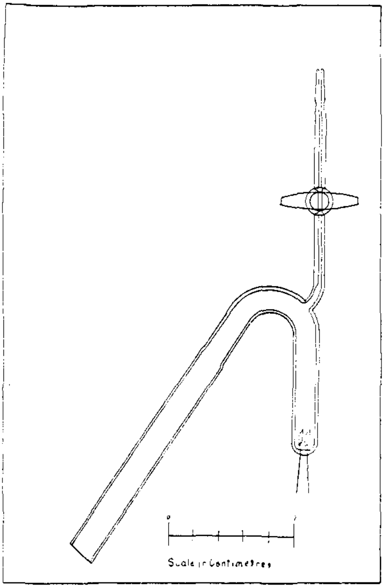

Fig. 1.

Platinum electrodes, sealed into one arm of the tube, are connected to the measuring apparatus by dipping the short platinum wires into mercury terminals. Solids are introduced into the other arm and sealed in. The tube, after exhaustion with the mercury pump is ready to be connected, by means of lead tubing and sealing-wax, to the methylamine cylinder and the liquid distilled in. In order to permit of quantitative determinations, the tube is weighed after each of the operations described. Methylamine is first condensed in that arm of the tube which contains the electrodes (by cooling the arm in liquid ammonia) so that the electrical conductivity of the liquid can be measured. If any appreciable conductivity is shown, owing to the introduction of impurities, the determination is discontinued and the process repeated with a clean tube and fresh substance. The methylamine is brought in contact with the solid by slowly inverting the tube. If solution is effected, the conductivity is measured after pouring the solution back into the arm containing the electrodes. In the investigation of liquids and gases the tube is first sealed and exhausted and the liquid or gas introduced through the stop-cock. The Kohlrausch form of apparatus with bridge and telephone is employed for the measurements.

Crystallization of the compounds in solution is often effected by cooling the reaction tube in liquid ammonia. The excess of the solvent is in many cases easily and completely removed by spontaneous evaporation on opening the stop-cock. In other cases exhaustion with the mercury pump is necessary to remove traces which are mechanically held. Other substances break down under reduced pressure and give up methylamine which was held in chemical combination. This is especially noticeable in the case of certain aromatic hydroxyl compounds which not only unite with one molecule of methylamine for each hydroxyl group, but also crystallize with additional amounts of methylamine varying with the temperature and pressure. The temperature at which the substances under investigation and the methylamine are brought in contact is frequently an important factor in the character of the reaction. In the majority of the cases investigated the methylamine and other reacting substances were at the room temperature when brought in contact with each other. In many cases the rise of temperature caused by the reaction was sufficient to produce complicated and secondary changes which were not investigated. Quinone and the aldehydes, picric acid and other nitro derivatives are notable examples, and it is very probable that the reactions with these substances will be much simplified if carried on in the cold. Resorcinol and quinol undergo complicated reactions with methylamine if contact occurs at the room temperature, while if the arm of the tube which contains the hydroxyl compound is cooled in liquid ammonia and the methylamine condensed therein, the reactions are quantitative and unaccompanied by the production of by-products.

The gain in weight of the reaction tube will in most cases, except when volatile products are formed as a result of the reaction, show the amount of methylamine which has entered into reaction. It is to be expected that this method of investigation will often give unsatisfactory quantitative results owing to impurities which may be present in the reacting substances and to the fact that in many cases the last traces of methylamine which are mechanically held are difficult of removal, and also it must be remembered that some of the 'reaction products break down slowly, constantly losing weight and giving up methylamine or other volatile products, and in other cases the reactions are evidently not quantitative. The amounts of methylamine of crystallization are in many cases difficult of determination by analytical methods for the crystals usually have low melting-points, effloresce at low temperatures and comparatively high pressures, and are difficult to obtain uncontaminated by the mother-liquors from which they are crystallized. No attempts to determine the composition of the crystalline compounds thus obtained, have been made by physicochemical methods. Therefore, the amount of methylamine of crystallization in combination, as determined from analytical data, can not in some cases be considered as definitely fixed.

The behavior of the substances under investigation was in each case studied as fully as circumstances at the time seemed to warrant. Some of the observed reactions have been carefully studied, the products recrystallized from other solvents and analyzed. In many instances, however, this has not been attempted, the reactions being manifestly complicated, leading too far afield, and perhaps better attempted as a separate piece of research.

EXPERIMENTAL PART.

The Hydrocarbons.—All of the hydrocarbons investigated are soluble in liquid methylamine, the solutions are colorless and practically non-conductors of the electric current.[1] At the temperatures to which the solutions were subjected, namely from the room temperature to that of liquid ammonia (about 20° to about —33°), no evidence of a reaction was apparent.

Acetylene was found to be very soluble. Measured volumes of the gas were conducted into weighed quantities of methylamine. In one case 0.3584 gram of methylamine absorbed 18 cc. of acetylene. Normal pentane, toluene and metaxylene were found to be miscible in every proportion which was tried. Paraffin, triphenylmethane, diphenyl, naphthalene, anthracene and phenanthrene are all very soluble and crystallize readily from the solutions, no methylamine of crystallization being held in any case.

THE HYDROXYL COMPOUNDS.

Methyl alcohol is miscible in all proportions, the solution is colorless and conducts the electric current to some extent. As the alcohol is an electrolytic solvent it is possible that the conductivity is due to the dissociation of the methylamine. There is no evidence of reaction.

Isopropyl alcohol is miscible in all proportions, the solution is colorless and is practically a non-conductor of the electric current. There is no evidence of a reaction.

Tertiary butyl alcohol in the solid state dissolves very slowly. Upon raising the temperature above the melting-point of the alcohol (23.5°) the two liquids are found to be miscible in all proportions. The solid alcohol separates slowly when the concentrated solution is cooled. The solutions are colorless and practically non-conductors of the electric current. There is no evidence of a reaction.

Cetyl alcohol is very soluble, the solution is colorless and practically a non-conductor of the electric current. The alcohol can be crystallized from the solution. There is no evidence of a reaction.

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[1] An arbitrary scale for expressing the results of the conductivity measurements was adopted.

Resistance less than 100 ohms	very good conductor.
From 100 ohms to 200 ohms	good conductor.
From 200 ohms to 500 ohms	fair conductor.
From 500 ohms to 2000 ohms	poor conductor.
From 2000 ohms to 5000 ohms	very poor conductor.
Above 5000 ohms	practically a non-conductor.

The solutions measured were usually quite concentrated and the cell employed was of about unit resistance capacity.

Glycerol is very soluble with marked rise of temperature. The solution is colorless and a fairly good conductor of the electric current. There is some evidence of a reaction taking place between the two liquids, although no reaction products were isolated. It is possible that the glycerol contained a little water but the assumption is not necessary to explain the conductivity, for both glycerol and methylamine are electrolytic solvents.

*Hydroxylamine hydrochloride** is very soluble but was not further investigated.

Phenol is very soluble with a slight rise of temperature. The colorless solution which is formed is a good conductor of the electric current. Upon cooling the solution, by means of liquid ammonia, there is slowly formed a fine crop of beautiful colorless crystals. These were purified by allowing the internal pressure to force the mother-liquor out through the stop-cock, after which they were melted, the solution cooled and the crystals allowed to again slowly form and the mother-liquor again removed. By repeating this operation a number of times a crop of crystals was obtained melting from 8.5° to 9.0°. The methylamine in these crystals was obtained by distillation with caustic potash, collecting the evolved gas in standard hydrochloric acid solution and titrating with standard ammonia solution, using methyl-orange as an indicator.

0.4054 gram substance gave 0.1480 gram methylamine.

$C_6H_5.ONH_3.CH_3.CH_3NH_2$, calculated CH_3NH_2 39.79, found 36.57.

*Orthonitrophenol** is very soluble, producing a yellow solution which was not further investigated. The ammonia compound $NH_4O.C_6H_4NO_2$ is described by Merz and Ris,[1] and its electrical conductivity in liquid ammonia solution has been investigated by Franklin and Kraus.[2]

Picric acid is very soluble with marked rise of temperature. The orange-red solution which is formed is a good conductor of the electric current. Upon expelling the excess of methylamine the solid, as it dries, changes from a deep red to a yellow-orange color. This compound is somewhat soluble in alcohol and very soluble in warm water. The aqueous solution deposits yellow

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* All compounds marked with a star were investigated by Professor E. C. Franklin, and the results here recorded are taken from his unpublished notes.

[1] Ber. 19, 1752.

[2] Am. Ch. J. 23, 295.

crystals on cooling. These crystals were washed with alcohol and dried in a vacuum desiccator. They are not exploded by friction or shock. On heating they gradually turn red at 186° and at 195° decompose, turning black without melting. The reaction products are under further investigation. An addition product, $C_6H_2(NO_2)_3OH.NH_2CH_3$ has previously been prepared from aqueous, alcoholic or chloroformic solutions.[1]

Thymol is very soluble with a slight rise of temperature. The colorless solution which is formed is a fairly good conductor of the electric current. Upon removing the excess of methylamine with the mercury pump, a process which requires about six hours, some colorless crystals were formed upon cooling the thick viscous solution with liquid ammonia. The melting-point of these crystals is about 25°. Attempts to determine their composition gave no satisfactory results.

α-Naphthol is very soluble with rise of temperature. The colorless solution is a good conductor of the electric current. The uncombined methylamine is removed by spontaneous evaporation, leaving a thick liquid which solidifies to a mass of colorless crystals on cooling. Melting-point about 37°.

0.2360 gram of α-naphthol retains 0.1042 gram of methylamine.

$C_{10}H_7.ONH_3CH_3.CH_3NH_2$, calculated CH_3NH_2 30.14 per cent., found 30.60.

This compound gives up a portion of its methylamine under diminished pressure, loses its crystalline form and becomes a white amorphous solid.

0.2360 gram of α-naphthol retains 0.0504 gram of methylamine.

$C_{10}H_7.ONH_3CH_3$, calculated CH_3NH_2 17.74 per cent., found 17.60.

β-Naphthol is very soluble with rise of temperature. The solution which is formed is of a light yellow color, probably due to impurities, and is a good conductor of the electric current. The spontaneous evaporation of the uncombined methylamine leaves a viscous liquid in which no crystals could be induced to grow. At this point, 0.1682 gram of β-naphthol retains 0.0656 gram of methylamine.

$C_{10}H_7.ONH_3CH_3.CH_3NH_2$, calculated CH_3NH_2 30.14 per cent., found 28.05.

Upon diminishing the pressure this liquid gives up methylamine

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[1] Delépine: Ann. chim. phys. [7], 8, 461; Ristenpart: Ber. 29, 2530.

readily until a second comparatively stable condition is reached. At this point still no crystals were obtained.

0.1682 gram β-naphthol retains 0.0337 gram of methylamine.

$C_{10}H_7.ONH_3CH_3$, calculated CH_3NH_2 17.74 per cent., found 16.7.

It is, of course, possible that the two conditions described do not represent definite compounds. It is probable, however, that crystallization may be effected by means other than those tried. Compounds with aniline, $C_6H_5NH_2.C_{10}H_7.OH$, and other allied substances have been produced.[1] Friedländer and Zakrzewski[2] have found that β-naphthylamine is produced on heating β-naphthol with ammonia.

Quinol is very soluble with a marked rise of temperature. The solution which is formed is a good conductor of the electric current. When methylamine and quinol react at room temperature the heat developed is sufficient to produce secondary reactions. When the quinol is cooled by immersing the reaction tube in liquid ammonia and the methylamine condensed upon the cold substance the reaction is not accompanied by the formation of secondary products. In the former case the solution is reddish brown, in the latter light pink. From the light pink solution on cooling there is obtained a beautiful crop of pink crystals. The color is probably not that of the pure compound.

0.6022 gram of quinol retains 1.4843 grams of methylamine.

$C_6H_4.(ONH_3CH_3)_2.6CH_3NH_2$, calculated CH_3NH_2 69.3 per cent., found 71.1.

These crystals melt considerably below the room temperature. When the methylamine is allowed to escape from this liquid another crop of pink crystals separates out.

0.6022 gram of quinol retains 0.3456 gram of methylamine.

$C_6H_4.(ONH_3CH_3)_2$, calculated CH_3NH_2 36.09 per cent., found 36.4.

These are comparatively stable at room temperature and atmospheric pressure but when the pressure is slightly reduced by suction of the water pump they slowly effloresce. The corresponding aniline addition product $C_6H_4(OH)_2.(C_6H_5.NH_2)_2$ has been prepared by Hebebrand.[3] With the mercury pump these crystals break down into a white solid.

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[1] Dyson: J. Chem. Soc. 43, 469.

[2] Ber. 27, 763.

[3] Ibid. 15, 1973.

0.6022 gram of quinol retains at good vacuum 0.1672 gram methylamine.

$C_6H_4.OH.ONH_3CH_3$, calculated CH_3NH_2 22.02 per cent., found 21.7.

This compound without further purification melts at 105°, assuming a brilliant red color in melting; on cooling, it solidifies into a brilliant red crystalline mass. The compound is very soluble in water, the solution being a good conductor of the electric current. An aqueous solution of quinol is a very poor conductor. The compound is almost insoluble in ether while quinol is soluble. Methylamine is given off upon boiling the aqueous solution with potassium hydroxide solution.

Resorcinol behaves in a manner analogous to quinol. It is very soluble with rise of temperature, the solution is a good conductor of the electric current, and the reacting substances must be strongly cooled in order to prevent the formation of secondary products. The solution is light green in color and separates light green crystals on cooling.

0.6755 gram of resorcinol crystallized with 0.8945 gram of methylamine.

$C_6H_4.(ONH_3CH_3)_2.3CH_3NH_2$, calculated CH_3NH_2 58.5 per cent., found 57.

From other experimental data it seems probable that a compound with a larger amount of methylamine of crystallization is capable of existence. As the methylamine is allowed to escape from the melted crystals, another crop of beautiful light green crystals is formed. These are quite stable at atmospheric pressure and room temperature but not as stable as the corresponding quinol compound.

0.6755 gram of resorcinol retains 0.3542 gram of methylamine.

$C_6H_4(ONH_3CH_3)_2$, calculated CH_3NH_2 36.09 per cent., found 34.3.

These crystals give up more methylamine with the mercury pump, producing a white amorphous solid.

0.6755 gram of resorcinol retains at good vacuum 0.1807 gram of methylamine.

$C_6H_4OH.ONH_3CH_3$, calculated CH_3NH_2 22.02 per cent., found 21.1.

This compound without further purification melts at 95° to a red liquid which solidifies to brilliant red crystals on cooling.

Methylamine is given off on boiling with caustic potash solution. The corresponding ammonia compound$C_6H_4.OH.ONH_4$, has been previously prepared by passing dry ammonia gas into a solution of resorcinol in dry ether.[1]

Pyrogallol is very soluble, the solution being a good conductor of the electric current. When the excess of methylamine is allowed to escape at room temperature the product assumes a constant weight but remains a viscous liquid, resisting all attempts to induce crystallization.

0.1608 gram pyrogallol retains 0.1135 gram of methylamine.

$C_6H_3(ONH_3CH_3)_3$, calculated CH_3NH_2 42.52 per cent., found 41.4.

Upon exhaustion with the water pump the substance quickly gives up methylamine and assumes the solid state and practically constant weight.

0.1608 gram of pyrogallol retains 0.0763 gram of methylamine.

$C_6H_3.OH.(ONH_3CH_3)_2$, calculated CH_3NH_2 33.02 per cent., found 32.2.

With the mercury pump the compound gives up an additional very small amount of methylamine, the stable form evidently being that in which two molecules of methylamine are in combination with one of pyrogallol. This compound is very soluble in water and on contact with the oxygen of the air is at once darkened in a manner characteristic of an alkaline solution of pyrogallol. An ammonia compound, $C_6H_3(OH)_2.ONH_4$, has been prepared by passing dry ammonia gas into a solution of pyrogallol in dry ether.[2]

Phenolphthalein is very soluble, the resulting solution being of a faint pink color and a fair conductor of the electric current. If all traces of moisture are absent from the methylamine and the phenolphthalein, the solution will in all probability be without color. Upon the removal of the excess of methylamine a viscous mass is first formed from which no crystals were induced to grow, and with the mercury pump this dried to a white solid.

0.0854 gram of phenolphthalein retains 0.0160 gram of methylamine.

$C_6H_4C_2O_2(C_6H_4.ONH_3CH_3)_2$, calculated CH_3NH_2 16.3 per cent., found 15.79.

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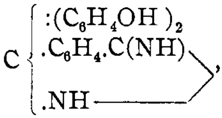
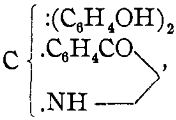
[1] Malin: Ann. 138, 80; Baker: Patentschrift des Deutschen Reiches, 40372; Friedländer's "Fortschritte der Theerfarbenfabrication," 1, 564.

[2] Luynes and Esperandien: Ann. Supplement, 6, 252.

The compound dissolves in water, giving a red solution. From previous considerations of the behavior of the hydroxyl ring compounds at ordinary temperatures and below, in the absence of water, it seems quite probable that the methylammonium salt of phenolphthalein is formed. Baeyer[1] has found that a solution of phenolphthalein in aqueous ammonia loses all of its ammonia on drying, while on heating in sealed tubes at 160° to 170° iminophenolphthalein,[2]  $C\left\{\begin{array}{l} :(C_6H_4OH)_2 \\ .C_6H_4.C(NH) \\ .NH \end{array}\right.$, is produced. H. Meyer,[3] by the action of ammonia solutions at about the same temperatures, obtained monoiminophenolphthalein,  $C\left\{\begin{array}{l} :(C_6H_4OH)_2 \\ .C_6H_4CO \\ .NH \end{array}\right.$, as the principal product. In both cases the hydroxyl group remains intact.

Alizarin turns a dark purple immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. When liquid methylamine is poured upon the crystals they turn a brilliant dark blue and dissolve, forming an intense purple solution which conducts the electric current to some extent. After the removal of the excess of methylamine by spontaneous evaporation under slightly reduced pressure a solid of a dark red-brown color remains.

0.1091 gram of alizarin retains 0.0286 gram of methylamine.

$C_6H_4.C_2O_2.C_6H_2(ONH_3CH_3)_2$, calculated CH_3NH_2 20.6 per cent., found 20.8.

This compound is extremely soluble in water, giving a purple-red solution. No attempt was made to prepare the compound containing one less molecule of methylamine, $C_6H_4.C_2O_2.C_6H_2OH.ONH_3CH_3$, by exhaustion with the mercury pump, but it seems quite probable from the results obtained with quinol and resorcinol that this compound can be obtained. It is probable that the ammonium salt, $C_{14}H_7O_4.NH_4$, has been prepared by Perkin,[4] although no analyses of the compound were made.

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[1] Ann. 204, 74.

[2] Baeyer and Burkhardt: Ber. 11, 2297; Ann. 204, 111.

[3] Monatsh. 20, 358.

[4] J. Chem. Soc. 75, 435.

THE ALDEHYDES.

Acetic aldehyde is readily miscible with violent rise of temperature and the discoloration of the liquid. The solution is a fair conductor of the electric current. No reaction products have been isolated.

Benzaldehyde is readily miscible with strong rise of temperature. The solution formed is a fairly good conductor of the electric current, due probably to the presence of benzoic acid. Upon distilling off the methylamine, by cooling one leg of the reaction tube in liquid ammonia, the conductivity of the solution rapidly decreases. When the two liquids are again mixed, the temperature again rises and the conductivity returns to the previous figure. After removing the excess of methylamine with the mercury pump and cooling the resulting liquid in liquid ammonia, colorless crystals form very slowly. The composition of the reaction products has not been determined.

Metanitrobenzaldehyde is readily soluble with slight rise of temperature. The resulting pink solution is a poor conductor of the electric current. On cooling the solution in liquid ammonia beautiful dark red crystals can be induced to grow. When the excess of methylamine is allowed to escape, the entire solution can be made to solidify into a mass of these crystals which melt quite sharply at —9.0°.

0.1890 gram metanitrobenzaldehyde retains 0.2439 gram of methylamine.

$C_6H_4.NO_2CHO.6CH_3NH_2$, calculated CH_3NH_2 55.24 per cent., found 56.3.

Upon exhausting the tube with the mercury pump, another crop of crystals is obtained. These are lighter in color, melt at about 47°, at which temperature they also undergo decomposition.

0.1890 gram metanitrobenzaldehyde retains 0.0422 gram of methylamine.

$C_6H_4.NO_2CHO.CH_3NH_2$, calculated CH_3NH_2 17.1 per cent., found 18.3.

There is some evidence of an intermediate product lying between the two described.

THE KETONES AND QUINONES.

Acetone is miscible in all proportions and the solution which is formed is to some extent a conductor of the electric current.

The conductivity, however, may be due to the dissociation of the methylamine in the acetone. The evidence of a reaction taking place between the two liquids when in contact for several hours, was very slight.

Götschmann[1] has obtained, by combination of acetone and methylamine on long standing, methyldiacetonamine, $CH_3.CO.CH_2C(CH_3)_2.NH(CH_3)$. The action of aniline upon acetone in sealed tubes has been studied by Pauly.[2]

Benzophenone is quite soluble and readily crystallizable unchanged from the solution, which is a very poor conductor of the electric current.

The action of ammonia upon benzophenone in sealed tubes has been studied by Pauly.[3]

Benzil is very soluble with marked rise of temperature. The solution which is formed is a poor conductor of the electric current. Upon the removal of the excess of methylamine a mass of poorly defined yellow crystals is formed which melt at about 23°. These do not give methylamine on boiling with potassium hydroxide solution.

0.2620 gram benzil gained 0.0674 gram in weight.

$(C_6H_5)_2(CO)_2.2CH_3NH_2$, calculated CH_3NH_2 20.46, found 22.4.

The reaction which takes place is probably deep-seated. Laurent[4] and others described complicated reactions corresponding to this in ammonia solutions.

Carbamide is very soluble without reaction. The compound is readily crystallizable unchanged from the solution, which is a poor conductor of the electric current.

Quinone reacts immediately on coming in contact with the vapors of methylamine, turning successively green, purple and black, with evolution of much heat. The solution is of a dark red color and is a fairly good conductor of the electric current. A study of the reaction products has not yet been attempted.

By action of dry ammonia in alcohol, ether and chloroform solutions, various products have been produced.[5] The action of some substituted ammonias with quinone and substitution prod-

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[1] Ann. 197, 38.

[2] Ibid. 187, 216.

[3] Loc. cit.

[4] J. pr. Chem. 35, 461; Henius: Ann. 228, 341; Pinner: Ber. 35, 4138.

[5] Waskresensky: Jsb. 26, 801; J. pr. Chem. 34, 251; Knapp and Schultz: Ann. 210, 178; Hebebrand and Zinke: Ber. 16, 1555.

ucts of quinone has also been investigated. By heating quinone with dimethylamine solution tetramethyldiaminoquinone is obtained,[1] $(N(CH_3)_2)_2C_6H_2O_2$.

Anthraquinone is only slightly soluble with no evidence of reaction and the solution is practically a non-conductor of the electric current.

THE ACIDS.

Acetic acid is very soluble with strong rise of temperature. The colorless solution which is formed is a good conductor of the electric current. By cooling the solution beautiful colorless crystals which evidently contain some methylamine of crystallization are obtained. At atmospheric pressure they give up methylamine, forming methylammonium acetate which melts at about 80°. This salt is very soluble in water and the solution is a good conductor of the electric current

0.4050 gram acetic acid unites with 0.2091 gram of methylamine.

$CH_3COO.NH_3CH_3$, calculated CH_3NH_2 34.11, found 34.03.

On heating the methylammonium acetate above the melting-point in sealed tubes a reaction takes place, probably producing methylacetamide, $CH_3CO.NHCH_3$,[2] although the compound was not isolated.

Phenylacetic acid behaves in a manner very similar to acetic acid. It is very soluble with strong rise of temperature and the solution is a good conductor of the electric current. From this solution on cooling, beautiful crystals which evidently contain methylamine of crystallization, are obtained. They immediately lose their form upon release of the pressure and give up methylamine, forming methylammonium phenyl acetate.

0.2300 gram phenylacetic acid unites with 0.0545 gram methylamine.

$C_6H_5.CH_2COO.NH_3CH_3$, calculated CH_3NH_2 18.57, found 19.1.

This salt is very soluble in water and the solution is a good conductor of the electric current.

Beilstein gives no record of the ammonium salt or the methylammonium salt, but the amide $C_6H_5.CH_2CO.NH.CH_3$ has been prepared.[3]

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[1] Kehrmann: Ber. 23, 905; Mylius: Ibid. 18, 467.

[2] Prepared previously by Hofmann: Ber. 14, 2729; Franchimont: Rec. trav. chim. 2, 121.

[3] Ergänzungsb. II, 814 (1903).

Palmitic acid is very soluble and the solution is a fair conductor of the electric current.

0.1140 gram palmitic acid unites with 0.0136 gram methylamine.

$C_{15}H_{31}COO.NH_3CH_3$, calculated CH_3NH_2 10.81, found 10.66.

This salt melts at about the same temperature as palmitic acid, namely 62°, is quite soluble in water and is decomposed by caustic potash solution.

Succinic acid reacts immediately on contact with methylamine with evolution of much heat. The reaction products are insoluble in the liquid.

0.6207 gram succinic acid unites with 0.3290 gram of methylamine.

$C_2H_4(COONH_3CH_3)_2$, calculated CH_3NH_2 34.12, found 34.6.

The methylammonium succinate is very hygroscopic, begins to decompose at 130° and gradually assumes a quiet state of fusion at 150°. On cooling, the liquid solidifies to a mass of colorless crystals. The composition of this crystalline substance was not determined.

Methylsuccinimide has been prepared by Menschutkin[1] by the distillation of the salt of succinic acid and methylamine.

Tartaric acid (*d*) reacts immediately on contact with methylamine with the evolution of much heat. The reaction products are insoluble in the liquid.

0.8328 gram tartaric acid unites with 0.3474 gram of methylamine.

$C_2H_2(OH)_2(COONH_3CH_3)_2$, calculated CH_3NH_2 29.19, found 29.43.

The methylammonium tartrate melts, probably with decomposition, at about 148°. It is so very hygroscopic that the salt is soluble in the smallest amount of water and cannot be again dried in a vacuum desiccator over sulphuric acid. Methylamine bitartrate is described by A. Ladenburg[2] as melting and decomposing at 170° with the production of two stereoisomeric methyl tartrimides. The racemic variety was also prepared by Wende.[3]

Benzoic acid is very soluble with rise of temperature. The solution is a very good conductor of the electric current. Upon

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[1] Ann. 182, 92.

[2] Ber. 29, 2710.

[3] Ibid. 29, 2719.

removing the excess of methylamine with the mercury pump a white solid is obtained.

1. 0.3487 gram of benzoic acid unites with 0.0803 gram methylamine.

2. 0.5320 gram of benzoic acid unites with 0.1452 gram methylamine.

$C_6H_5.COO.NH_3CH_3$, calculated CH_3NH_2 20.27, found I, 18.7; II, 20.9.

The methylammonium benzoate is a very hygroscopic white solid, very soluble in methyl alcohol, ethyl alcohol and insoluble in ether. It is decomposed on heating at atmospheric pressure into benzoic acid and methylamine. Heated in a sealed tube it melts at 110–112°. The affinity for water is so great that the wet salt cannot be dried in a vacuum desiccator over sulphuric acid.

Methylbenzamide, $C_6H_5.CO.NH.CH_3$, has been prepared but not from methylammonium benzoate.[1]

Orthonitrobenzoic acid is very soluble with rise of temperature. The solution is a good conductor of the electric current. When the temperature of the reacting substances is allowed to rise it is quite probable that the nitro group also enters into the reaction. When the temperature is maintained at a low point only the carboxyl group reacts with the methylamine, forming the methylammonium salt. This salt crystallizes from the concentrated solution in beautiful pale yellow needles.

0.7460 gram of orthonitrobenzoic acid retains on the mercury pump 0.1420 gram of methylamine.

$C_6H_4.NO_2.COONH_3CH_3$, calculated CH_3NH_2 16.69, found 16.0.

These crystals are very soluble in water, methyl alcohol, ethyl alcohol and insoluble in ether. They can be crystallized readily from a mixture of alcohol and ether. Without further purification they melt from 128° to 129°.

Phthalic acid forms methylammonium phthalate upon contact with methylamine. The salt is insoluble in the liquid, very soluble in water, from which solvent it crystallizes in beautiful colorless crystals which decompose easily upon heating.

0.3535 gram of phthalic acid unites with 0.1446 gram of methylamine.

$C_6H_4.(COO.NH_3CH_3)_2$, calculated CH_3NH_2 27.2, found 29.0.

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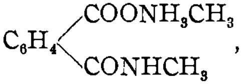
[1] Beilstein: 2, 1159 (1896).

Phthalic anhydride reacts with the production of much heat and the resulting compound is insoluble in the liquid.

0.2122 gram of phthalic anhydride retains 0.0855 gram of methylamine.



$C_6H_4\begin{cases}COONH_3CH_3\\CONHCH_3\end{cases}$, calculated CH_3NH_2 27.5, found 28.7.

The methylammonium methylphthalamate, which probably is produced, is very soluble in water and from the solution beautiful, colorless, transparent, star-shaped crystals slowly form.

Methylphthalimide,[1] $C_6H_4(CO)_2NCH_3$, has been prepared from phthalic anhydride and methylamine.

Uric acid reacts with methylamine and the product, a white powder, is insoluble in the liquid.

0.1354 gram uric acid combines with 0.0225 gram methylamine.

$C_5H_4N_4O_3.CH_3NH_2$, calculated CH_3NH_2 15.5, found 14.2.

The methylammonium urate is soluble in warm water and decomposes on heating without melting. The methylamine in combination was determined by distillation with caustic potash, the distillate collected in N/10 hydrochloric acid.

0.0919 gram methylammonium urate required 4.15 cc. acid to neutralize the distillate. This is equivalent to 14.03 per cent. of methylamine.

Hippuric acid is very soluble with slight rise of temperature. The solution is a good conductor of the electric current. As the excess of methylamine escapes, crystals of methylammonium hippurate are formed.

0.3341 gram of hippuric acid unites with 0.0564 gram methylamine.

$C_6H_5.CO.NHCH_2COONH_3CH_3$, calculated CH_3NH_2 14.7, found 14.4.

The salt is very soluble in cold water and the solution is a good conductor of the electric current.

THE HALOGEN SUBSTITUTION PRODUCTS.

Chloroform is miscible in all proportions and a reaction gradually sets in between the two liquids in the cold. The conductivity of the solution slowly increases as the reaction proceeds. At higher temperatures it is very probable that the reaction will be

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[1] Graebe and Pictet: Ann. 247, 302.

more rapid. On spontaneous evaporation of the solution on a watch-glass the isocyanide odor is very marked. A very hygroscopic residue remains which becomes crystalline on standing in a vacuum desiccator over sulphuric acid. These crystals are probably methylammonium chloride, for they decompose with caustic potash, giving the odor of methylamine and with silver nitrate show the presence of the chlorine ion. The most probable reaction is $CHCl_3 + CH_3NH_2 = CH_3NC + 3HCl$, the hydrochloric acid uniting with methylamine to produce methylammonium chloride.

Ethylene bromide is miscible but not in all proportions. A reaction slowly commences and becomes very violent unless the reaction tube is kept in a cooling mixture. The products are soluble in liquid methylamine and the solution is a very good conductor of the electric current. From the concentrated solution a mass of beautiful colorless crystals, resembling the cubical crystals of sodium chloride, is obtained on cooling. They are found to be extremely hygroscopic and cannot be recrystallized from aqueous solution. They are insoluble in dry ether and are purified by repeated washing with this solvent and drying with the mercury pump. During the washing, which is conducted in the reaction tube, all air must be excluded, for traces of moisture are sufficient to spoil the form of the beautiful crystals. The melting-point, 179°, is not as sharp as might be desired.

0.9052 gram of substance was dissolved in 200 cc. of water and aliquot parts taken for analysis. The base was set free with caustic potash solution and collected by distillation. The bromine was determined by precipitating and weighing as silver bromide.

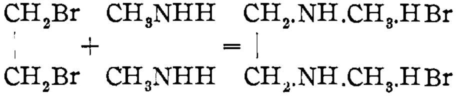
I. 1/10 of 0.9052 gram required 7.12 cc. N/10 hydrochloric acid.

II. 1/10 of 0.9052 gram required 7.14 cc. N/10 hydrochloric acid.

Calculated for $(CH_2.NH.CH_3HBr)_2$: Br, 63.91. Found: Br, 64.27 and 64.37.

Calculated for $(CH_2NH.CH_3HBr)_2$: $(CH_2.NH.CH_3)_2$, 35.26. Found: $(CH_2NH.CH_3)_2$, 34.68 and 34.78.

The reaction which takes place is probably best represented by the equation:



$$\begin{array}{l}CH_2Br \\ | \\ CH_2Br\end{array} + \begin{array}{l}CH_3NHH \\ \\ CH_3NHH\end{array} = \begin{array}{l}CH_2.NH.CH_3.HBr \\ | \\ CH_2.NH.CH_3.HBr\end{array}$$

(Ethylenedimethyldiamine hydrobromide.)

The hydrochloride of this base has been prepared by Schneider[1] by heating dimethylethylenedibenzenesulphamide with hydrochloric acid. He states the boiling-point of the base to be 119°, and the melting-point of the hydrochloride to be 235–236°.

Brombenzene is miscible and the solution is a non-conductor of the electric current. If any reaction takes place, it goes on so slowly, at room temperature and below, as to be imperceptible. The brombenzene can be separated unchanged by distilling off the methylamine.

Parabromacetanilide is very soluble without reaction and separates unchanged from the concentrated solution, which is a poor conductor of the electric current.

THE NITRO COMPOUNDS.

Nitromethane is miscible, a slight rise of temperature resulting. The solution is a fairly good conductor of the electric current. On cooling in liquid ammonia colorless crystals are formed. By blowing off the mother-liquor, melting the crystals and recrystallizing seven different times they melt quite sharply from —8.0° to —7.5°. Analysis was made by distilling with potassium hydroxide and collecting the distillate in N/10 hydrochloric acid.

0.5439 gram of substance gave 0.2050 gram of methylamine.

$CH_3NO_2.CH_3NH_2$, calculated CH_3NH_2 33.7, found 37.8.

It would be expected from this method of production that the crystals would be contaminated by some free methylamine.

Nitrobenzene is miscible, producing an intense dark red solution, with a slight rise of temperature. The solution is to a small extent a conductor of the electric current. In all probability no reaction takes place at the temperatures studied.

Metadinitrobenzene is very soluble. Immediately upon contact with methylamine vapor the compound turns a beautiful purple and as the solvent distils into the tube a brilliant, reddish purple solution is formed. The solution is a good conductor of the electric current. On concentrating the solution, crystals of metadinitrobenzene separate out and these resume their original color as the methylamine evaporates. There is no evidence of a

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[1] Ber. 28, 3072.

reaction. The brilliantly colored solution is in all probability due to dissociation in the electrolytic solvent.

The behavior of dinitrobenzene in liquid ammonia is somewhat analogous and has been studied by Franklin and Kraus.[1]

*Orthonitrotoluene** is very soluble. The solution is slightly yellow.

*Dinitrotoluene** (2-4) is very soluble. The solution is blue in color, greenish in thin layers.

Dinitraniline (1-2-4) is not affected by the methylamine vapor but in the liquid the crystals immediately turn a brilliant red and quickly go into solution. The brilliant red solution is a good conductor of the electric current. The original substance crystallized unchanged from the solution.

Trinitraniline (1-2-4-6) melts on contact with the vapor of methylamine with evolution of heat and formation of a dark red mass. The dark red solution which is formed is a good conductor of the electric current. From the concentrated solution, brilliant red crystals are formed. The reaction which evidently goes on has not been further investigated.

THE SUGARS.

Galactose is quite soluble, a slight rise of temperature resulting. The solution is a poor conductor of the electric current. Upon the removal of the excess of methylamine a viscous mass, which becomes solid on standing, results.

0.2440 gram galactose retains with the mercury pump at good vacuum 0.0775 gram of methylamine.

$C_5H_{11}O_5CHO.2CH_3NH_2$, calculated CH_3NH_2 25.3, found 24.1.

The reaction products have not been investigated.

Glucose behaves in a manner quite analogous to galactose; however, the viscous mass obtained after removal of the methylamine, crystallizes quite well on standing.

0.4520 gram of glucose retains on the mercury pump 0.1023 gram of methylamine.

$C_5H_{11}O_5CHO.2CH_3NH_2$(?), calculated CH_3NH_2 25.3, found 18.4.

The reaction products have not been investigated.

Sucrose is quite soluble, a slight rise of temperature resulting. The solution is to a slight extent a conductor of the electric current. There is some evidence of a reaction but the question has not been sufficiently investigated.

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[1] Loc. cit.

MISCELLANEOUS COMPOUNDS.

Acetamide is very soluble without reaction. From the solution, which is a fairly good conductor of the electric current, the compound is readily crystallizable.

Phenylhdyrazine is miscible in all proportions and there is no evidence of a reaction. The solution is to some extent a conductor of the electric current.

Amyl formate is miscible in all proportions. The sample employed was evidently contaminated with a small amount of formic acid and therefore no definite conclusions can be drawn as to the conductivity of the solution.

Pyridine is miscible in all proportions without reaction. The solution is a non-conductor of the electric current.

Azobenzene is very soluble. From the brilliant red solution, which is a non-conductor of the electric current, the azobenzene crystallizes beautifully. There is no evidence of a reaction.

Diphenylketoxime dissolves almost immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. The solution is to a small extent a conductor of the electric current. The more dilute solutions seem to be better conductors than the concentrated. From the concentrated solution beautiful colorless crystals are obtained.

0.5246 gram diphenylketoxime retains with the mercury pump at good vacuum 0.0850 gram of methylamine.

$(C_6H_5)_2CNOH.CH_3NH_2$, calculated CH_3NH_2 13.62, found 13.94.

This compound decomposes a few degrees below 140°, giving off methylamine and leaving the oxime which melts at 140°. A further study of the composition of the compound was not made.

Benzenesulphimide is very soluble with reaction. The resulting solution is a good conductor of the electric current. On the removal of the excess of methylamine on the mercury pump only a semi-solid mass results, from which no crystals are obtained. The reaction was not further studied.

Metanitrobenzenesulphonamide is quite soluble and the colorless solution is a good conductor of the electric current.

DYES.

Gallein turns a brilliant blue immediately upon contact with methylamine vapor, a strong rise of temperature resulting. The reaction products are only slightly soluble in the liquid, producing a bluish purple solution which is a poor conductor of the electric current. Upon removal of the excess of methylamine with the mercury pump 0.2891 gram of gallein holds 0.0814 gram of methylamine.

$C_{20}H_{12}O_7.3CH_3NH_2$, calculated CH_3NH_2 20.5, found 21.7.

The resulting solid is, by reflected light, a very dark purple.

It is evident that the carboxyl group will unite with one molecule of methylamine, and, judging from the behavior of other hydroxyl ring compounds such as phenol, quinol, resorcinol and pyrogallol, when two hydroxyl groups are united to the same ring only one uniting with methylamine to form a stable compound, a second molecule of methylamine is accounted for by combination with the ring holding the two hydroxyl groups. The third molecule can easily be held by the hydroxyl group or the quinone oxygen of the other ring as both have been found to be reactive. The reaction products, have, however, not been investigated in order to verify this theory.

Coerulein is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a poor conductor of the electric current.

0.1635 gram of coerulein retains with the mercury pump 0.0272 gram of methylamine.

$C_{20}H_{10}O_6.2CH_3.NH_2$, calculated CH_3NH_2 15.2, found 14.8.

The resulting solid is, by reflected light, a very dark green. The arguments used in the case of gallein concerning the character of the reaction, hold equally well here.

Dichlorgallein turns a brilliant blue immediately upon contact with methylamine vapor. The brilliant blue solution which is formed with the liquid is a very poor conductor of the electric current. The reaction which takes place is more complicated than the reaction between methylamine and gallein. The product which holds about 23 per cent. methylamine has not been investigated.

Tetrachlorgallein[1] turns a brilliant blue immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. The reaction products, which are only slightly soluble

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[1] My thanks are due to Professor William R. Orndorff, of Cornell University, for the samples of gallein, coerulein, dichlorgallein and tetrachlorgallein, which are the same as those employed by Orndorff and Brewer in their investigation of the constitution of these compounds. Am. Ch. J. **26**, 97.

in liquid methylamine, form a blue solution which is a poor conductor of the electric current. The reaction product holds over 25 per cent. of methylamine, is very soluble in water and does not contain the chlorine ion. No further study of the reaction has been made.

Indigo is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a good conductor of the electric current. There is no evidence of a reaction, for the indigo separates unchanged from the concentrated solution.

Methyl orange is to a small extent soluble. The resulting deep red solution is a moderately good conductor of the electric current. There is no evidence of a reaction as the original substance separates unchanged upon opening the reaction tube and allowing the methylamine to escape.

Rosaniline turns a dirty brown color immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. This compound is very soluble in the liquid and the resulting dirty brown solution is to a slight extent a conductor of the electric current.

INORGANIC COMPOUNDS.

The solubilities of a number of inorganic compounds have been investigated by Franklin[1] but the reactions which occur in many cases have been investigated in only a few instances. For the most part the sulphates of the metals are insoluble in liquid methylamine, while the nitrates and the halogen salts are about equally divided.

*Aluminum chloride** is insoluble.

*Arsenious iodide** is very soluble.

*Ammonium chloride** is very soluble.

*Bismuth nitrate** is insoluble.

*Bismuth chloride** is very soluble with the separation of a white mass. Probably a basic salt analogous to Franklin's ammono basic salts[2] is formed.

*Boric acid** is slightly soluble with slow reaction, producing an amorphous mass which is presumably the methylammonium salt.

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[1] All of the data on the inorganic compounds, with the exception of silver nitrate, methyl mercuric chloride, mercuric cyanide, mercuric chloride, mercurous chloride and mercuric iodide, have been taken from his unpublished notes.

[2] This Journal, 27, 826.

*Cadmium iodide** unites with methylamine to form a bulky, white mass which is insoluble, or only slightly soluble in the liquid.

0.1096 gram of cadmium iodide unites with 0.0369 gram of methylamine.

$CdI_2.4CH_3NH_2$, calculated CH_3NH_2 25.31, found 25.26.

*Calcium chloride** unites with methylamine, forming a bulky mass which is insoluble.

*Cuprous chloride** reacts, producing an unpromising mass which was not investigated.

*Cupric sulphate** forms an intensely blue mass which is insoluble.

*Chromic chloride** is slightly soluble, forming with an excess of the solvent a purple mass which is an addition product.

*Iodic acid** is insoluble.

*Lithium chloride** is very soluble, forming a viscous solution which solidifies to a crystalline mass on cooling.

*Lithium nitrate** is very soluble. On standing, the contents of the tube solidify to a crystalline mass.

*Lead nitrate** forms a bulky addition product with the evolution of heat.

Mercuric chloride unites with the solvent with evolution of heat and the formation of a white addition product which is only slightly soluble in the liquid. The solution is a poor conductor of the electric current.

Mercurous chloride blackens in the methylamine and a mass of crystals separates out on cooling.

Methyl mercuric chloride is quite soluble at room temperature but on cooling crystals separate out, the solution almost completely solidifying. The solution is a very good conductor of the electric current.

Mercuric cyanide is very soluble with evolution of heat. The colorless solution which is formed is a fair conductor of the electric current. On cooling, crystals are formed in the solution.

Mercuric iodide is very soluble. The colorless solution which is formed is a very good conductor of the electric current. An addition product, $HgI_2.XCH_3NH_2$, crystallizes out as a white solid on cooling. Composition not determined.

*Mercurous nitrate** blackens on contact with the liquid and goes into solution.

Potassium bromide, chlorate* and chromate** are insoluble.

*Potassium permanganate** is very soluble.

Silver nitrate is extremely soluble with considerable rise of temperature. There is at first a blackening of the silver nitrate, and fine black particles are seen suspended in the liquid. These disappear as the concentration decreases, the liquid becoming clear and colorless. The colorless solution which is formed is an excellent conductor of the electric current. When the excess of methylamine is allowed to escape upon opening the stop-cock, a heavy viscous liquid results. Upon cooling this liquid it completely solidifies to a mass of colorless needle crystals which melt at about the temperature of the room.

0.9005 gram of silver nitrate crystallizes with 0.6283 gram of methylamine.

$AgNO_3.4CH_3NH_2$, calculated CH_3NH_2 42.2, found 41.1.

When the pressure is reduced, these crystals immediately lose their form, giving up methylamine and turning green in color. When the vacuum is fairly good with the mercury pump there still remains held 0.3704 gram of methylamine.

$AgNO_3.2CH_3NH_2$, calculated CH_3NH_2 26.8, found 29.1.

This substance upon standing continues to give up methylamine. Under the microscope it is seen to have a crystalline structure, the crystals being of a green color or contaminated by impurities which give them the green cast. The crystals are decomposed by water, going partially into solution and leaving a dark brown residue which is soluble in ammonia solution. The crystals are soluble in potassium cyanide solution, insoluble in dry ether and quite soluble in absolute alcohol. On heating they fuse and then explode, giving the isocyanide odor very strongly and leaving a residue of metallic silver.

*Silver sulphate** is insoluble.

*Sodium nitrate** is very soluble.

*Sodium sulphite** is insoluble.

*Sodium thiosulphate** reacts with the solvent.

*Tetramethylammonium iodide** is insoluble.

*Thallium chloride** is insoluble.

SUMMARY.

Liquid methylamine has been found to be a remarkably good solvent for organic compounds, exceeding liquid ammonia and

perhaps exceeding methyl alcohol,[1] while for inorganic compounds it is not as good a solvent as liquid ammonia, far inferior to water and ranking perhaps closer to methyl alcohol. It is extremely reactive with both organic and inorganic compounds, in this respect, probably, exceeding the most reactive of the other three solvents mentioned, namely liquid ammonia.[2]

Next to its wide solvent action the most striking property of liquid methylamine is its remarkable power of uniting with many compounds, both organic and inorganic as methylamine of crystallization. Among those mentioned in the literature are: $LiCl.CH_3NH_2$;[3] $LiCl.2CH_3NH_2$;[3] $LiCl.3CH_3NH_2$;[3] $LiCl.4CH_3NH_2$;[4] $ZrCl_4.4CH_3NH_2$;[5] $ThCl_4.4CH_3NH_2$;[5] $PbCl_4.4CH_3NH_2$;[5] $AgCl.CH_3NH_2$;[6] $AgBr.CH_3NH_2$;[6] $AgI.CH_3NH_2$;[6] $2AgI.CH_3NH_2$;[6] $CH_3NH_2.H_2O$;[7] and $C_6H_2(NO_2)_3.OH.CH_3NH_2$.[8]

Addition products other than those already described in the literature, which in all probability contain methylamine of crystallization, have been prepared from phenol, quinol, resorcinol, α-naphthol, β-naphthol (?), metanitrobenzaldehyde, galactose (?), acetic acid, phenylacetic acid, diphenyl ketoxime, nitromethane, bismuth chloride, cadmium iodide, calcium chloride, cuprous chloride (?), cupric sulphate (?), chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercuric chloride, mercurous chloride (?), methyl mercuric chloride, mercuric cyanide (?), mercuric iodide and silver nitrate.

This work was commenced at Stanford University at the suggestion of Professor E. C. Franklin, and carried to its present state of completion under his kindly advice, direction and assis-

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[1] Liquid methylamine probably does not exceed liquid ammonia as a solvent for organic compounds to the same extent as methyl alcohol exceeds water for the same purpose.

[2] This has often been observed in the case of aqueous and alcoholic solution of ammonia and methylamine. Lassar-Cohn, "Applications of Some General Organic Reactions," page 36. Laubenheimer: Ber. 11, 1155; A. Hempel: J. pr. Chem. [2] 41, 161; Kehrmann and Messinger: Ibid. [2] 46, 565; Bettenhausen-Marquardt, Schulz, Patentschrift des Deutschen Reiches, 72, 253; Paal and Sprenger: Ber. 30, 62; Ristenpart: Ibid. 29, 2526.

[3] Bonnefoi: Compt. rend. 127, 516.

[4] Ibid. 124, 771.

[5] Matthews: This Journal, 20, 826.

[6] Jarry: Compt. rend. 124, 964; Ann. chim. phys. [7] 17, 376.

[7] Henry: Private paper; Beilstein: Ergänzungsb. 1, 596.

[8] Delépine: Ann. chim. phys. [7], 8, 461.

tance. I am grateful to him for the many favors shown me. The manuscript was in process of preparation at the time of the San Francisco fire, and a small portion of the work cannot be chronicled here, owing to the destruction of the notes. As opportunity offers, the research will be extended.

FOOD LABORATORY OF THE
SAN FRANCISCO HEALTH COMMISSION,
May 15, 1906.

[CONTRIBUTION FROM THE COMMITTEE ON PURITY OF REAGENTS, NO. 1.]

SOME SOURCES OF IMPURITIES IN C. P. CHEMICALS.[1]

BY J. W. SCHADE.

Received June 30, 1906.

THE elimination of impurities in chemically pure chemicals has long been the desire of chemists; but owing to a seeming indifference on their part, the manufacturers have not exerted themselves to make their products better than they deemed absolutely necessary to meet the demands. During the past year or two much increased interest has been manifested in the movement to secure the best grade of laboratory reagents consistent with economy in manufacture. To ask for a reagent "absolutely pure" is to ask, in most cases, for the impossible in economical manufacture. The object of this paper is to present some sources of impurities in chemical reagents and to point out that there are limits of purity obtainable by manufacturers.

With few exceptions all reagents are shipped in glass containers. The dry salts probably do not take up impurities from the bottles, but acids and ammonia after standing in containers for a few days are contaminated with impurities from the glass. These impurities may be one or more of the following: iron, potassium, sodium, silica, calcium and from bottles of Jena or "Nonsol" glass, zinc. In the case of ammonia, silica is the principal impurity from the glass; in the case of acids, iron. The latter is due mainly to the fact that small chips of iron oxide flake from the blowpipes used by the glassblowers and although acid is allowed to stand in the bottles before they are washed for use, there are undoubtedly minute particles that escape immediate solution. Acids shipped in carboys having glass covers secured by zinc rings are liable to contamination from the zinc, owing to the

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[1] Read at the Ithaca Meeting of the American Chemical Society.