

“On some Properties of Anhydrous Liquefied Ammonia.” By
G. GORE, F.R.S. Received May 15, 1872*.

To examine the general solvent properties of anhydrous liquefied ammonia, and to detect any manifest chemical reactions between it and various substances, I employed precisely the same kind of method as that I used in examining liquid cyanogen (see *Proc. Roy. Soc.* vol. xx. p. 67).

It was desirable in these experiments not to use flint-glass tubes, because the tenacity of that substance is so feeble the tubes burst by the pressure of the gutta-percha stoppers; when such tubes were employed, the mouths of them had to be closed by fusion. The tubes require to be somewhat stronger than those used with liquid cyanogen, because the pressure exerted by the vapour is so much greater. The length of the horizontal portion of the tubes was $7\frac{1}{2}$ inches; by having this part of the tube very much longer, a much lower degree of heat is necessary in the experiments, and a greater quantity of the liquid may be obtained.

To procure the anhydrous liquid, chloride of calcium was heated to redness, reduced to fine powder, and perfectly saturated with well-dried ammonia in a current of that vapour, the flask containing the powder being immersed in broken ice during the latter part of the process, and occasionally shaken to prevent formation of lumps. During this process the powder evolved much heat and swelled considerably. Every precaution was taken to prevent the powder absorbing moisture from the atmosphere.

The temperature employed to expel the vapour from the salt, with tubes of the dimensions given, was much below that of visible redness. On allowing the tubes to become quite cold, the vapour was reabsorbed and the liquid disappeared; the pressure having also ceased, enabled the stopper to be removed and the products further examined. By this means some of the tubes could also be employed for fresh substances.

250 substances, including solids and liquids, and a great variety of simple and compound bodies, were subjected to the action of the liquefied vapour. Except when otherwise stated, the substances were in nearly all cases as free from moisture as it was convenient to obtain them; nevertheless in some instances the effects were evidently due in a slight degree to traces of water. The substances were also generally very pure, many of them having been carefully prepared by myself. The following is a statement of the results:—

Water mixed perfectly with the liquid. After the reabsorption of the ammonia by the chloride of calcium and the tube had become perfectly cold, the water had become about twice its original bulk by retention of ammonia.

Iodine first liquefied to the appearance of thin treacle, then entirely dissolved to a clear and slightly yellow liquid. On evaporation of the

* Read June 20, 1872. See abstract, vol. xx. p. 441.

ammonia, reddish-black crystals separated, apparently consisting of unaltered iodine. I did not examine whether the residue contained any of the explosive compound, "iodide of nitrogen." Iodic acid did not dissolve or show any change in the liquid.

Wood-charcoal, also Brodie's intumescent graphite, did not dissolve or change. C_2Cl_2 would not mix with the ammonia; but a little of it dissolved, and the ammonia became slightly brown. Liquid C_2Cl_4 mixed perfectly, and after the evaporation of the ammonia it was left behind. Solid C_2Cl_6 did not dissolve or suffer any change. Liquid CCl_4 behaved like C_2Cl_4 . Solid CBr_4 * dissolved rapidly and very copiously, and did not recrystallize until nearly all the liquid had evaporated.

Boron crystals, boracic anhydride, silicon crystals, and precipitated silica were all unaffected.

Sulphur dissolved sparingly, and formed a deeply coloured purplish-red solution, and on evaporation of the liquid a yellow film of it was left. Liquid chloride of sulphur became dark red and solid in the gas, and purple in the liquid, apparently with chemical action; a portion of the solid dissolved and formed a deeply purple liquid, on evaporation of which the red solid was left behind. Bisulphide of carbon became yellow and opaque in the gas, and changed in the liquid to a yellow bulky solid. Selenium was unaffected. Selenious acid prevented the formation of the liquid, probably by uniting with the ammonia, but did not enlarge in bulk, or show any visible change. Bright tellurium was unaffected.

Red phosphorus showed no change. White phosphorus dissolved to a yellow liquid, and separated again on evaporation of the ammonia. Phosphoric anhydride contracted in bulk in the gas, dissolved but very slightly in the liquid, and exhibited no other change. Glacial phosphoric acid was not visibly affected. Terchloride of phosphorus produced strong chemical action, and formed a colourless bulky solid. Pentachloride of phosphorus dissolved freely, and crystals formed on evaporation of the liquid.

Metallic arsenic was unaffected. Arsenious anhydride enlarged somewhat in bulk, but did not dissolve. Arsenic-acid crystals dissolved to a very minute extent only. Terchloride of arsenic was converted into a white solid with manifest chemical action. Teriodide of arsenic became white and swelled considerably. Realgar became yellow, and partly dissolved to a yellow solution, which on evaporation left an orange-yellow residue. Orpiment turned dark brown in the gas, and dissolved slightly in the liquid, producing a faintly yellow solution, which left a yellow film on evaporation.

Metallic antimony, sesquioxide of antimony, and antimonious acid were not visibly affected. Hydrated antimonious acid was slightly dissolved. Fused fluoride of antimony swelled very greatly in the liquid, but did not dissolve; it retained its enlarged bulk after evaporation of all the

* Given to me by the discoverers, Messrs. Groves and Bolas.

ammonia. Crystalline hydrated terchloride of antimony swelled considerably, but did not dissolve. Oxychloride of antimony was not visibly affected. Terbromide of antimony dissolved freely. Oxybromide of antimony was very slightly dissolved. Teriodide of antimony became yellow with apparent chemical action, and a portion dissolved and formed a dense layer beneath the colourless liquid ammonia. Black and red sesquisulphides of antimony were not visibly affected, but each imparted a faint purplish-blue colour to the liquid. Orange sulphide of antimony dissolved to some extent, forming an opaque brownish-green solution, and separated again on evaporation of the liquid. Vanadic acid and nitride of vanadium produced no visible effect*. "Molybdenum" (in the state of a fine black powder) imparted a weak cobalt-blue colour to the liquid, but did not visibly diminish in bulk. Molybdic acid became quite white, but did not dissolve. Native sulphide of molybdenum, "tungsten" (in the state of a black powder), and tungstic acid produced no visible effect.

Metallic bismuth, hydrated oxide of bismuth, and fluoride of bismuth were not visibly affected. Chloride of bismuth (not anhydrous) swelled greatly, and dissolved rather freely, but partly returned to its original bulk after the liquid had evaporated. Carbonate of bismuth and sulphide of bismuth were not visibly altered.

Metallic osmium was not visibly affected. Osmic acid was chemically altered, and produced first a yellow, then a red, and finally a brownish-black opaque mixture, consisting of solid particles suspended in a comparatively colourless liquid: on evaporation of the liquid, the solid substance remained behind. Black oxide of iridium, also scales of osmiridium, produced no visible effect. Metallic palladium was not affected. Bichloride of palladium became white, and enlarged in bulk, and slightly dissolved to a clear yellow liquid; the residue remained white and of enlarged bulk after evaporation of the liquid. Sulphide of palladium was unaffected. Black oxide of platinum was not visibly affected. Bichloride of platinum became nearly white, and slightly dissolved, forming a slightly yellow solution. Tetrachloride of platinum behaved like the bichloride. Tetraiodide of platinum turned red, dissolved freely to a reddish-yellow liquid, crystallized in red needles on evaporation of the solution, and finally left a black residue. Terchloride of gold was decomposed, and the product very slightly dissolved.

Bright silver was unaffected. Oxide of silver swelled considerably, but did not dissolve; it contracted again after evaporation of the liquid. Peroxide of silver (formed by electrolysis of a pure solution of argentic fluoride with platinum electrodes) became brown, and made the liquid slightly yellow, but did not visibly alter in bulk. Argentic nitrate dissolved freely, and on evaporation of the liquid long crystalline needles separated. Brown argentic fluoride swelled a little, became somewhat

* Given to me by Dr. Roscoe.

white, dissolved sparingly, and separated in needles on evaporation. Chloride of silver in powder swelled considerably, but did not dissolve; it remained enlarged in bulk after evaporation of the liquid. Fused argentic bromide lost its transparency, swelled and became white, dissolved slightly, and crystallized on evaporation. Argentic iodide dissolved rapidly and freely, and formed a dense colourless solution which mixed with the excess of liquefied ammonia; colourless crystals separated, but not until nearly all the liquid had evaporated: this salt is extremely soluble in the liquid. Argentic iodate showed no effect. Carbonate of silver turned dark brown and swelled considerably, but did not dissolve, and on evaporation of the liquid returned to its original volume and colour. Argentic sulphate swelled greatly, and disintegrated to a fine white powder, which returned partly to its original bulk after evaporation of all the liquid. Phosphate of silver and argentic arseniate were nearly insoluble, and suffered no chemical change. Vanadate of silver was insoluble.

Mercury was unaffected. Yellow mercuric oxide, also red-brown mercuric oxide (both obtained by precipitation), did not dissolve or alter. Mercurous nitrate turned black in the gas, and dissolved to some extent in the liquid; the residue left after evaporation of the liquid was a blackish-grey powder, apparently consisting of minute particles of metallic mercury. Mercurous chloride became brown in the gas, and dissolved copiously to a dense solution in the liquid; but its solution would not mix with the excess of liquefied ammonia: by evaporation of the ammonia it was left in a crystalline state. Mercuric chloride dissolved freely, forming a colourless dense solution, which would not mix or dissolve in the slightest degree in the excess of liquid: by evaporation the excess of liquid separated first, then that containing the chloride, and left the salt in a crystalline state. Mercuric bromide fell to powder with apparent chemical action, and dissolved to a small extent. Scarlet mercuric iodide first became yellow, then dark brown, and dissolved freely: on evaporation of the liquid, the salt separated in a crystalline state. Mercuric sulphide was unaffected. Anhydrous mercuric sulphate was very little affected. Hydrated mercuric sulphate swelled greatly, imparted a violet colour to the liquid, and partly returned to its former bulk after evaporation of the ammonia.

Copper lost its brightness, and imparted a slightly brown colour to the ammonia: when nearly all the liquid had evaporated, the residuary portion was deep blue in colour. Copper filings produced no additional effect. Suboxide of copper was nearly insoluble, and but little affected. Protoxide of copper was also insoluble and unaffected. White anhydrous cupric fluoride became deep blue in colour, but imparted scarcely any colour to the liquid. Anhydrous cupric chloride became deep blue, swelled greatly, did not dissolve nor impart colour to the liquid. Cuprous iodide (not perfectly anhydrous) became partly green, and imparted a

faint blue colour to the liquid, but did not otherwise dissolve. Cupric carbonate produced no effect. Cupric sulphide was superficially changed to a deep blue colour. White anhydrous cupric sulphate turned deep blue and swelled greatly, but did not impart any colour to the liquid; it remained enlarged in bulk after evaporation of the ammonia. Cupric phosphate produced no visible effect.

Nickel filings were unaffected. Anhydrous oxide of nickel and hydrated oxide of nickel were also unaffected. Fluoride of nickel suffered no great visible change, and did not dissolve. Nearly anhydrous chloride of nickel swelled and became of a purplish-blue colour, but did not dissolve: after evaporation of the liquid, the salt remained enlarged in bulk.

Oxide of cobalt, also fluoride of cobalt, was unaffected. Anhydrous chloride of cobalt swelled to about ten times its original volume and fell to powder, but was quite insoluble; it partly contracted in bulk again on evaporation of the ammonia. Carbonate of cobalt was unaffected. Sulphate of cobalt (not perfectly anhydrous) swelled, but did not dissolve; it remained expanded after evaporation of the liquid.

Electro-deposited iron was unaffected. Anhydrous persulphate of iron absorbed much of the liquid, swelled considerably, and showed signs of decomposition, but did not dissolve; it remained enlarged in bulk after evaporation of the liquid.

Metallic manganese, fluoride of manganese, chloride of manganese, and manganic sulphate were all unaffected.

Chromic acid turned yellow, absorbed ammonia, swelled greatly, dissolved slightly, forming a yellow solution, and retained its enlarged bulk after evaporation of the liquid. Solid green fluoride of chromium was not affected. Violet chloride of chromium swelled considerably and dissolved slightly, forming a purplish solution; it did not contract to its original bulk after evaporation of the liquid. Chromate of silver turned bright yellow at its edges, and nearly black in its mass, but did not dissolve. Chromate of copper was not dissolved, but was converted externally into a substance having the colour of sesquioxide of chromium. Metallic aluminium was unaffected. Yellow oxide of uranium and nitrate of uranium produced but little effect. Fluoride of uranium was slightly dissolved, forming a yellowish solution.

Metallic thallium, peroxide of thallium, and fluoride of thallium were not visibly altered. Bright metallic lead and red oxide of lead were unaffected. Nitrate of lead dissolved, and was apparently partly decomposed; crystals separated on evaporation of the last portions only of the liquid. Fluoride of lead produced no effect. Chloride of lead swelled considerably, but did not dissolve; it did not diminish in bulk on evaporation of the liquid. Iodide of lead turned white, dissolved slightly, and colourless crystals were left on evaporation of the liquid. Iodate of lead produced no effect. Yellow chromate of lead behaved in all respects like the iodide.

Metallic tin, stannous oxide, and stannic oxide were not affected. Fused bichloride of tin was partly dissolved. Liquid tetrachloride of tin was first converted into a solid substance with strong chemical action; the solid then dissolved freely, and separated again on evaporation of the liquid. Metallic indium was unaffected.

Fluoride of cadmium was not affected. Chloride of cadmium swelled, but did not dissolve; it contracted again on evaporation of the liquid. Bromide of cadmium swelled somewhat, but did not dissolve. Iodide of cadmium swelled greatly, and absorbed a large quantity of ammonia, but did not dissolve; it remained enlarged in bulk after evaporation of the liquid. Carbonate of cadmium produced no effect. Sulphide of cadmium was not visibly affected, but it imparted to the liquid a faint cobalt-blue colour.

Fluoride of zinc produced no effect. Chloride of zinc fell to powder, swelled greatly, and did not contract after evaporation of the liquid; it did not dissolve. Bromide of zinc and iodide of zinc behaved like the chloride.

Nitrocyanide of titanium, black oxide of titanium, titanio acid, zirconium scales, oxide of zirconium, sulphate of thorium, glucina, chloride of glucinum, carbonate of glucinum, sulphate of glucinum, sulphate of lanthanum, and niobic acid produced no visible effect.

Oxide of cerium and fluoride of cerium were unaffected. Nitrate of cerium dissolved slightly. Chloride of cerium swelled slightly, but did not dissolve. Metallic magnesium was unaffected. Basic chloride of magnesium dissolved slightly.

Metallic calcium became covered with an insoluble white powder, but did not dissolve nor exhibit any other effect. Fused chloride of calcium fell to powder, swelled greatly, but did not dissolve. Bromide of calcium swelled a little, but did not dissolve. Metallic strontium behaved like calcium. Metallic barium lost its metallic appearance, but showed no signs of solution or other effect. Caustic anhydrous baryta was unaffected. Nitrate of barium dissolved freely, and crystallized on evaporation of the liquid. Chloride of barium swelled considerably, but did not dissolve; it remained enlarged in bulk after evaporation of the liquid. Baric sulphate was not visibly affected.

Metallic lithium produced strong action, and formed a deep indigo-blue coloured fluid: as the liquid evaporated the metal separated, and exhibited successive colours, first that of bronze, then of brass, and ultimately colourless and brilliant like silver. Metallic sodium swelled, and then behaved very much like lithium. Chloride of sodium dissolved sparingly, and did not enlarge in bulk. Metallic potassium behaved like lithium and sodium*. Nitrate of potassium was soluble, but not freely

* These results agree with those previously obtained by C. A. Seely (see 'Chemical News,' vol. xxiii. p. 169). Seely found lithium, sodium, potassium, and rubidium soluble, and mercury, copper, thallium, indium, aluminium, and magnesium insoluble in anhydrous liquid ammonia.

so. Fluoride of potassium was very slightly soluble. Chloride of potassium was not visibly affected. Potassic bromide dissolved sparingly, and crystallized on evaporation of the liquid. Iodide of potassium was freely soluble. Silico-fluoride of potassium was insoluble. Chloriridiate of potassium crystals were superficially changed to a brown colour, but did not dissolve. Permanganate of potassium dissolved very freely to a deep purple-red solution, and was left behind on evaporation of the liquid. Chromate of potassium dissolved to a minute extent. Potassic bichromate dissolved somewhat, and formed a yellow solution. Chrome-alum was only superficially changed. Fluozirconate of potassium was not visibly affected. Metallic rubidium behaved like sodium and potassium. Fluoride of rubidium was insoluble.

Nitrate of ammonium dissolved very freely. Chloride of ammonium also dissolved very freely, and did not crystallize until nearly all the liquid had evaporated. Carbonate of ammonium, ammonium vanadate, and ammonium metavanadate produced no visible effect.

Uric acid and paracyanogen were unaffected. Argentic cyanide dissolved very freely and rapidly, and crystallized in scales on evaporation of the liquid. Cyanide of mercury dissolved freely, and crystallized only on evaporation of the last portions of the liquid. Cupric cyanide turned deep blue, and dissolved to some extent. Cupric ferrocyanide was converted into a dark green solid. Cyanide of zinc was very little affected. Potassic cyanide was insoluble. Potassic sulphocyanide dissolved to some extent. Ferrocyanide of potassium produced no effect. Fusel-oil, ether, alcohol, aldehyde, and chloroform mixed freely and perfectly. Alloxan became of a deep purple-red colour, and dissolved freely, and left a purple-red solid after evaporation of the liquid. Succinic acid was insoluble. Indigo dissolved sparingly, and formed a reddish-brown solution. Sulphate of quinine dissolved to some extent. Gutta percha imparted a brown colour to the liquid, and a sticky residue was left on evaporation. Paraffin, anthracene, and naphthalin were not visibly affected. Amylene would not mix with the liquid. Mesitylene behaved similarly. Starch swelled and mixed as it does with water, but did not form a clear solution. Glycerine mixed perfectly. White sugar dissolved freely, and left a gummy residue on evaporation of the liquid. Isinglass rapidly became semifluid. Camphor dissolved copiously, and crystallized when the liquid evaporated. Gum-copal dissolved only to a minute extent. Gun-cotton dissolved sparingly, and the solution left a film on evaporation. Bengal silk was quite insoluble.

A few experiments were made for the purpose of examining the chemical properties of the solution of potassium by placing other substances inside the tubes with that metal, and then distilling the ammonia into contact with them. C_2Cl_6 prevented the production of the blue colour. C_2Cl_4 produced chemical action, and prevented the blue colour; the residue was a white solid, exhibiting no signs of free carbon. CBr_4

caused strong chemical action, sparks and flashes of light, the formation of a colourless salt, and prevented the blue colour, and finally produced a violent detonation, by which the whole of the tube was shattered to small particles. Anhydrous carbonate of sodium caused the blue colour first produced to gradually disappear; the residue was quite colourless, and entirely soluble in water. Anhydrous formiate of soda produced similar effects. Crystals of oxalate of ammonia produced chemical action, destroyed the blue colour first produced, and left a colourless residue which contained no free carbon. Sesquioxide of chromium did not prevent the blue colour, nor show any signs of reduction or other chemical change. Sesquioxide of uranium prevented the permanency of the blue colour.

I have not specially classified the results of these experiments, but may remark that the only elementary substances soluble in anhydrous ammonia are the alkali metals proper, also iodine (bromine was not tried), sulphur, and phosphorus. The more commonly soluble inorganic salts are nitrates, chlorides, bromides, and iodides; whilst oxides, fluorides, carbonates, sulphides, and sulphates were very generally insoluble. Many saline substances, especially certain chlorides, bromides, iodides, and sulphates, absorbed ammonia copiously, and swelled greatly, but did not dissolve. The behaviour of the chlorides of mercury was peculiar.

In many of these experiments chemical changes took place, and new products were formed; but I did not analyze those products, because that was not my object: these chemical reactions offer a field for future investigators. The sulphides of antimony and cadmium, and the sulphates of mercury and manganese, imparted a purple tint to the liquid; sulphur behaved similarly.

February 6, 1873.

Sir GEORGE BIDDELL AIRY, K.C.B., President, in the Chair.

The Right Hon. Hugh Culling Eardley Childers was admitted into the Society.

The following communications were read:—

- I. “On the Osteology of the *Hyopotamidæ*.” By Dr. W. KOWALEVSKY. Communicated by Prof. HUXLEY, Sec. R.S. Received December 19, 1872.

(Abstract.)

The paper laid before the Society is intended to fill a certain deficiency in our knowledge of the extinct creation by giving a complete osteology of a family of Paridigitate Ungulata, which, by the completeness of its skeleton, unreduced number of digits, and rich development in generic