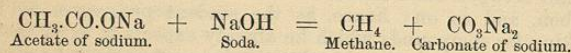


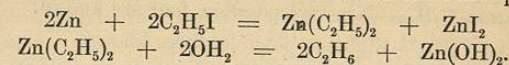
THE PARAFFIN SERIES OF HYDROCARBONS.

METHANE, Marsh gas, Light carburetted hydrogen, Hydride of methyl, Fire damp, CH_4 .—This gaseous hydrocarbon occurs naturally in coal-mines and in the mud-volcanoes of the Crimea, and is constantly rising in bubbles to the surface of stagnant pools in marshy places. It is a non-luminous constituent of ordinary coal gas. It is inodorous and colorless. It may be produced by acting on iodide of methyl with zinc on which copper has been deposited, but is best obtained by heating a mixture of 2 parts of dry acetate of sodium, 3 of lime, and 2 of caustic soda, or, better, potash.



Two Notes on the Notation of the Foregoing and Similar Formulae and on the Constitution of Salts.—(a) Soda, NaHO , contains bivalent oxygen, univalent sodium, and univalent hydrogen. The chemical power of the oxygen atom is double that of either of the other atoms, a relationship perhaps better realized if the symbol for the oxygen be placed between those of hydrogen and sodium, NaOH or HONa . So HOK , HOH , etc. The student must expect to find the symbols of a formula placed where apparently they will best reflect our knowledge of the structure of the molecule pictured. (b) Acetic acid, $\text{C}_2\text{H}_4\text{O}_2$, by action of chlorine (presented as PCl_3) loses hydroxyl, OH , and yields chloride of acetyl, $\text{C}_2\text{H}_3\text{OCl}$. Hence acetic acid would seem in constitution to be hydrate of acetyl, $\text{C}_2\text{H}_3\text{O.OH}$; especially when we find that the chloride of acetyl by reaction with water, HOH , yields again acetic acid (and HCl). Sodium will only displace one atom of hydrogen from water, yielding HONa ; and will only displace one atom of hydrogen from acetic acid, yielding acetate of sodium, $\text{C}_2\text{H}_3\text{OONa}$. Further, chlorine will not displace more than one portion or atom of hydroxyl, OH , from acetic acid. So that three atoms of the hydrogen in acetic acid apparently perform different functions to those of the fourth atom; and, apparently, the two atoms of oxygen perform different functions. Hence our necessity for separating in the formula the letters representing those atoms, $\text{C}_2\text{H}_3\text{O.OH}$. Once more, acetates may be formed from two different methyl compounds: acetate of sodium by the direct combination of methide of sodium, CH_3Na , and carbonic acid gas, CO_2 , giving CH_3COONa ; and acetate of ammonium by the combination of methyl cyanide, CH_3CN , with water (2HOH), yielding $\text{CH}_3\text{CO.ONH}_4$. From these and other facts and modes of reasoning arises our justification—from them, indeed, comes the necessity—for thus extending the formulae for acetates. Less extended formulae are of course correct and even occasionally more useful: $\text{C}_2\text{H}_4\text{O}_2$, $\text{C}_2\text{H}_3\text{O}_2\text{H}$, $\text{C}_2\text{H}_3\text{O.OH}$, $\text{CH}_3\text{CO.OH}$ form an illustration of a set of formulae for a substance either member of which set may be used according to circumstances. (See also pp. 285 and 298.)

ETHANE, C_2H_6 , Dimethyl, Hydride of Ethyl.—This is one of the constituents of crude petroleum. It also results on heating iodide of ethyl with granulated zinc or zinc covered with copper, and then adding water to the iodide of zinc and ethide of zinc first produced.

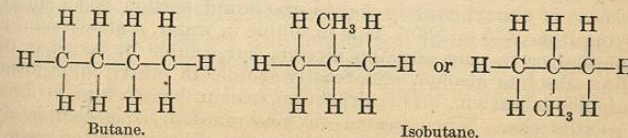


Ethane is sometimes regarded as dimethyl or methyl-methane, CH_3CH_3 ; that is to say, as being derived from methane by the substitution of an atom of hydrogen in methane, CH_4 , by methyl, CH_3 ; its properties, however, are not those of a radical. It is also considered to be hydride of ethyl, $\text{C}_2\text{H}_5\text{H}$; its properties, however, are not those of such a substance. The other hydrocarbons of the paraffin series are also similarly regarded as containing radicals. Such views of constitution are useful, as enabling composition to be remembered and relationships to be realized, especially if their hypothetical character be fully recognized; but these hydrocarbons are apparently single homogeneous substances, and whatever other views of their constitution be held, this last should be dominant.

PROPANE, methyl ethyl, C_3H_8 .—This gas, like methane, occurs dissolved in the Pennsylvanian petroleum springs.

TETRANE OR BUTANE, C_4H_{10} .—Two varieties exist—normal butane or diethyl, $\text{C}_2\text{H}_5\text{C}_2\text{H}_5$, found in petroleum, and iso-butane or trimethyl methane, $\text{CH}(\text{CH}_3)_3$, formed by artificial means.

Turning back to the highly extended formulae for methane, ethane, propane, and butane given on p. 389, the reader will see why there should only be one ethane or propane, while two butanes are possible. We can but replace one of the atoms of hydrogen, H , in methane, CH_4 , to form ethane, CH_3CH_3 , and it matters not which; hence only ethane (one ethane) can result. In ethane, CH_3CH_3 , if an atom of hydrogen be displaced by methyl, CH_3 , it can but be a hydrogen atom of one of the two methyl groups (CH_3CH_3), and it matters not which. But in propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, a CH_2 group exists, as well as CH_3 groups. Now CH_2 is a different group to CH_3 ; hence if we displace one of its two atoms of hydrogen (it matters not which) by methyl to get butane, we should expect to get a butane of different properties to the butane obtained by displacing one of the atoms of hydrogen in the methyl groups by methyl; and two butanes, and two only, do actually exist. Normal butane may be thus formulated, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, while iso-butane would be either $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$, or a practically identical formula, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$.



PENTANE, C_5H_{12} .—Three varieties are possible, and three only.

three are known, and three only; the second, or *isoamylic hydride*, yielding the ordinary Amylic Alcohol and Valerianic Acid.

HEXANES, C_6H_{12} .—Five are possible, five are known.

HEPTANES, C_7H_{16} .—Nine are possible, four are known.

OCTANES, C_8H_{18} .—Eighteen possible, three known.

NONANE, C_9H_{20} ; DECANE, $C_{10}H_{22}$; and paraffin hydrocarbons up to HEXDECANE, $C_{16}H_{34}$, as well as derivatives of far higher members of the paraffin series of hydrocarbons, are known.

Benzin, Petroleum Ether, Petroleum Benzin, Paraffin Oil, Paraffin— $C_{10}H_{12}$, $C_{12}H_{14}$ —and Homologous Compounds.

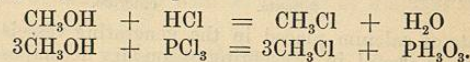
Benzin, U. S. P. (*pentane*, C_5H_{12} , *hexane*, C_6H_{14}), known also as *benzoline* and *petroleum spirit*, "the purified distillate from American petroleum, consisting of the hydrocarbons of the marsh gas series, a transparent, colorless, diffusive liquid, of a strong, characteristic odor, slightly resembling that of petroleum, but much less disagreeable; neutral in reaction; insoluble in water, soluble in about 6 parts of alcohol, and readily in ether, chloroform, benzol, and fixed volatile oils. Boiling-point, 50° to 60° C. (122 to 140° F.). Specific gravity, about 0.670 to 0.675." (Benzine or benzol is quite a different fluid; *vide* Index.)

Paraffin Oil, the *Paraffinum Liquidum* of the German Pharmacopoeia, is a mixture of the higher fluid members of the paraffin series of hydrocarbons, a clear oily liquid obtained from petroleum after distilling off the lower-boiling portions. Specific gravity, not below 0.840. Boiling-point, not below 360° C. (680° F.). Digested and agitated with warm sulphuric acid for a day or two, the oil is not colored and the acid only tinged brown; metallic sodium under similar conditions is not tarnished; alcohol boiled with the oil should not become acid. *Petrolatum*, U. S. P., *Soft Paraffin* (*Paraffinum Molle*, B. P.), officially termed *Unguentum Paraffini* in Germany and *Pétroléine* in France, and known in commerce by various fanciful names, is a semi-solid mixture of paraffins, usually obtained by purifying the less volatile portions of petroleum. It has a melting-point about 40° C. to 51° C. (104° F. to 125° F.), the first constituting the softer, and the second the firmer, variety. It is "a yellowish or yellow, fat-like mass, transparent in thin layers, more or less fluorescent, especially when melted, completely amorphous, tasteless, and odorless, or giving off, at most, only a faint petroleum odor when heated, and having a neutral reaction. When gently heated, until the mass is almost entirely melted, the liquid portion has a sp. gr. varying from .835 to .860. It is insoluble in water, scarcely soluble in alcohol or in cold absolute alcohol, but soluble in 64 parts of boiling absolute alcohol, and readily soluble in ether, chloroform, disulphide of carbon, oil of turpentine, benzin, benzol, and in fixed or volatile oils. When heated on platinum-foil, it is completely volatilized without emitting the acrid vapors of boiling fat or resin." *Hard Paraffin* (*Paraffinum Durum*, B. P.), commonly termed *paraf-*

fin wax or simply *paraffin*, is "a mixture of several of the harder members of the paraffin series of hydrocarbons; usually obtained by distillation from shale, separation of the liquid oils by refrigeration, and purification of the solid product. It is colorless, semi-transparent, crystalline, inodorous, and tasteless; slightly greasy to the touch. Specific gravity, 0.82 to 0.94. Insoluble in water, slightly soluble in absolute alcohol, freely soluble in ether. It melts at 110° to 145° F. (43.3° to 62.8° C.), and burns with a bright flame, leaving no residue."

Paraffin resists all ordinary reagents (hence the original name *paraffin*, from *parum affinis*, without affinity), but may, by continued boiling with sulphuric acid and solution of bichromate of potassium, be oxidized to *cerotic acid*, $C_{27}H_{54}O_2$, and by continued digestion with nitric and sulphuric acids yields acids of the acetic series and *paraffinic acid*, $C_{24}H_{48}O_2$ (Pouchet).

SUBSTITUTION-PRODUCTS OF METHANE.—The paraffins all form substitution-derivatives with the halogens, chlorine acting energetically, bromine less so, and iodine scarcely at all. In the preparation of chlorine and bromine substitution-products by acting on the hydrocarbons the mono-derivatives are always mixed with the higher derivatives, even though the quantities are taken in relation to their combining proportions; thus, if methane and chlorine are mixed in the proportion of $CH_4 + Cl_2$, not only will *monochloromethane*, or *chloride of methyl*, CH_3Cl , be formed, but *dichloromethane*, CH_2Cl_2 , and *trichloromethane*, $CHCl_3$, with free hydrogen. The best method of obtaining the mono-derivatives is to act on the alcohols by haloid acids or by phosphorus compounds:—



Chloroform.

Trichloromethane, or *chloroform*, $CHCl_3$, may be made by acting on methane with chlorine, as already indicated,

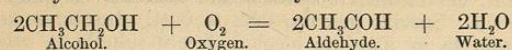


but on a larger scale by the official process, as follows:—

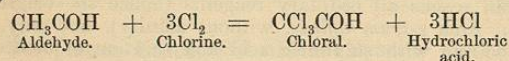
Process.—One fluidounce and a half of spirit and 24 of water are placed in a retort or flask of at least a quart capacity; 8 ounces of chlorinated lime and 4 of slaked lime are added, the vessel connected with a condenser, and the mixture heated until distillation commences, the source of heat then being withdrawn. The condensed liquid should fall into a small flask containing water, at the bottom of which about a drachm of chloroform will slowly collect.

Explanation of the Process.—Though there is some doubt as to the exact reaction, the following seems to be most probable. The

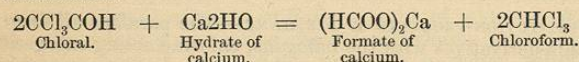
hypochlorite of calcium believed to be present in the chlorinated lime (see the remarks in connection with the latter, p. 112) readily yields up oxygen and chlorine to organic substances, the calcium being liberated as hydrate. The alcohol used in making chloroform is thus probably first reduced to aldehyde:—*



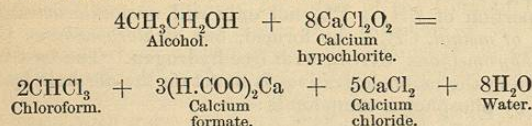
The action of chlorine on aldehyde then probably gives chloral (*chloraldehyde*):—



The hydrochloric acid being at once neutralized by some of the liberated hydrate of calcium to form chloride of calcium and water, more freed hydrate of calcium and chloral give formate of calcium and chloroform:—

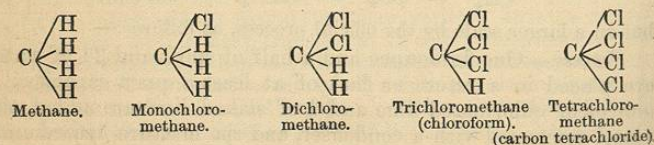


Or, neglecting the probable steps in the process, and regarding only the materials and the products, 4 molecules of alcohol and 8 of hypochlorite of calcium give 2 of chloroform, 3 of formate of calcium, 5 of chloride of calcium, and 8 of water, thus:—



The hydrate of calcium placed in the generating vessels is not essential, but is useful in preventing secondary decompositions, the hydrate of calcium obtainable from the reaction being insufficient for this purpose.

Chlorine converts chloroform into *tetrachloromethane* or *tetrachloride of carbon*, CCl_4 , completing the chlorine substitution-products of methane.



Chloroform is purified by shaking it with water, and then with pure sulphuric acid (containing no trace of nitric acid), which chars

* The special formulæ for alcohol, aldehyde, and formates used in the accompanying equations will be better understood when the constitution of alcohols and acids has been considered.

and removes hydrocarbons, etc., but does not affect chloroform. It is freed from any trace of acid by agitation with lime, and from moisture by solid chloride of calcium.

Properties.—The sp. gr. of chloroform is at least 1.500, perhaps higher. It is liable to slowly decompose when exposed to air and light. To render it stable a minute amount (1 volume in 100, or less) of absolute alcohol is necessary; hence the specific gravity of medicinal chloroform is about 1.497 (1.485–1.490, *Chloroformum Purificatum*, U. S. P.). It readily and entirely volatilizes at common temperatures, having, to the last drop, its pleasant characteristic odor. It has a sweetish taste, is limpid, colorless, soluble in alcohol (1 to 9 gives *Spiritus Chloroformi*, U. S. P.) and ether, and slightly in water. Boils at 142° F. It burns with a sluggish, green, smoky flame. It should be neutral to test-paper, indicating absence of acid; give no precipitate with solution of nitrate of silver, indicating absence of ordinary chlorides; remain colorless when heated with potash, indicating absence of aldehyde; and give no more color than is producible by the absolute alcohol that is present to any sulphuric acid with which it may be shaken, even after the mixture has been set aside for half an hour, indicating absence of hydrocarbons, etc. Alcohol may be detected by the iodoform test (see Index), or by shaking with a little of the dye termed “Hofmann’s violet,” which gives the chloroform a purple tint if alcohol be present, but affords no color with pure chloroform. At the temperature of melting ice chloroform unites with water to form a crystalline compound, $\text{CHCl}_3 \cdot 18\text{H}_2\text{O}$.

Commercial Chloroform (*Chloroformum venale*, U. S. P.) should have a sp. gr. not lower than 1.470 at 15° C.

Aqua Chloroformi, B. P., Chloroform Water, is made by shaking 1 fluidrachm of chloroform with 25 ounces of distilled water till dissolved.

Iodoform.

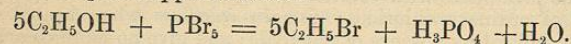
Tri-iodomethane, or *iodoform*, CHI_3 (*Iodoformum*, U. S. P.), analogous in constitution to chloroform, the iodine occupying the place of the chlorine, is made by mixing in a retort 1 part of alcohol, 2 parts of crystallized carbonate of sodium, and 10 parts of water; the whole being heated at about 150° F., and 1 part of iodine gradually added in small portions. When the fluid becomes colorless, it is poured into a beaker and allowed to settle. The iodoform is collected on a filter, washed thoroughly with water, and dried between filtering-paper. (This reaction forms a very delicate means of testing the presence of alcohol. *Vide* “Alcohol, test for,” in Index.)

Iodoform occurs as yellow, shining, six-sided scales. It is volatile at ordinary temperatures, almost insoluble in water, soluble in alcohol or ether. Warmed with an alcoholic solution of potash, formate and iodide of potassium are produced, $\text{CHI}_3 + 4\text{KOH} = \text{KCOOK} + 3\text{KI} + 2\text{H}_2\text{O}$; and the resulting fluid, heated with

a little nitric acid, yields free iodine, recognized by its color or by giving a blue color with starch. Sp. gr. 2.000.

Chloroform, iodoform, and bromoform may also be obtained on passing a current of electricity through hot strong alcohol containing chloride, iodide, or bromide of potassium respectively, carbonic anhydride being simultaneously supplied.

SUBSTITUTION-PRODUCTS OF ETHANE.—Ethane, like methane, yields substitution-derivatives. *Monobromethane, bromide of ethyl, ethylic bromide, or hydrobromic ether*, C_2H_5Br , may be prepared by gradually adding 4 parts of bromine to a mixture of 45 parts of ethylic alcohol and 4 of amorphous phosphorus contained in a flask fitted with an upright condenser, care being taken to keep the apparatus cool.



When all the bromine has been added, the mixture is poured into a retort and distilled over a water-bath, the resulting ethylic bromide freed from excess of bromine by washing with a small quantity of dilute soda or potash, then washed with water and rectified over calcium chloride and redistilled.

For its preparation on a large scale De Vrij's method is preferable, $C_2H_5HSO_4 + KBr = C_2H_5Br + KHSO_4$ (see *Pharm. Journ.*, Feb. 15, 1879), or the same method as modified by Green (*P. J.*, July 12, 1879), by Remington (*P. J.*, May 29, 1880), or by Wolff (*P. J.*, July 3, 1880).

Mon-iodoethane, iodide of ethyl, or ethylic iodide, C_2H_5I , may be made, like the bromide, by mixing 7 to 8 parts of amorphous phosphorus and 70 of absolute alcohol with 100 parts of iodine. The complete decomposition takes three or four hours, after which it may be treated as above. It should be kept in a dark place, as light favors decomposition and liberation of iodine.

The paraffins give rise to many substitution-derivatives by displacement of their hydrogen by compound acidulous radicals. The following, chiefly from ethane and pentane, are of pharmaceutical interest:—

Spirit of Nitrous Ether.

Nitrite of Ethyl, Nitrous Ether, $C_2H_5NO_2$.—A "spirit" probably containing nitrous ether was one of the earliest known medicinal compounds, its discovery being generally ascribed to Raymond Lully.

Process.—To a third of a test-tubeful of rectified spirit add about a tenth of its bulk of sulphuric acid, rather more of

nitric acid, and warm the mixture; as soon as ebullition commences the vapor of nitrous ether (with other substances) is evolved, recognized by its odor. A long bent tube, kept very cool, may be adapted by a perforated cork to the test-tube, and thus a little of the product be condensed and collected.

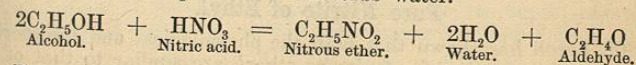
*The above process, conducted on a larger scale, with definite quantities of materials, temperature regulated by a thermometer, and a well-cooled condenser, etc. etc. (see p. 126), is the official process for the preparation of a concentrated solution of nitrous ether, etc., in spirit; diluted with nearly three times its bulk of rectified spirit, it forms the official variety of the "spirit of nitrous ether" (*Spiritus Ætheris Nitrosi*, U. S. P.) of pharmacy, containing about 5 per cent. of the crude ether.*

"Take of—

Nitric Acid 9 parts,
Sulphuric Acid 7 parts,
Alcohol,
Distilled water, each a sufficient quantity.

"Add 7 parts of sulphuric acid gradually to 31 parts of alcohol. When the mixture has cooled transfer it to a tubulated retort connected with a well-cooled condenser, to which a receiver, surrounded by broken ice, is connected air-tight, and which is further connected by means of a glass tube with a small vial containing water, the end of the tube dipping into the latter. Now add 9 parts of nitric acid to the contents of the retort, and, having introduced a thermometer through the tubulure, heat rapidly, by means of a water-bath, until strong reaction occurs and the temperature reaches $80^\circ C.$ ($176^\circ F.$). Continue the distillation at that temperature, and not exceeding $82^\circ C.$ ($180^\circ F.$), until reaction ceases. Disconnect the receiver, and immediately pour the distillate into a flask containing 16 parts of ice-cold distilled water. Close the flask and agitate the contents repeatedly, keeping down the temperature by immersing the flask occasionally in ice-water. Then separate the ethereal layer, and mix it immediately with 19 times its weight of alcohol. Keep the product in small glass-stoppered vials in a dark place, remote from lights or fire."

Disregarding other products, the following equation represents the chief decompositions that occur in the operation. The main point in the reaction is the reduction of the nitric to the nitrous radical by the hydrogen of some of the alcohol, which is thereby reduced to aldehyde. The sulphuric acid absorbs water.



Properties.—Spirit of Nitrous Ether is a "clear, mobile, volatile, and inflammable liquid, of a pale straw-color, inclining slightly to green, a fragrant ethereal odor free from pungency, and a sharp, burning taste. Sp. gr. 0.823 to 0.825. It slightly reddens litmus-

paper, but should not effervesce when a crystal of bicarbonate of potassium is dropped into it. When mixed with half its volume of solution of potassa, previously diluted with an equal volume of water, it assumes a yellow color, which slightly deepens, without becoming brown, in twelve hours. A portion of the spirit, in a test-tube half filled with it, plunged into water heated to 63° C. (145.4° F.), and held there until it has acquired that temperature, should boil distinctly on the addition of a few small pieces of glass."

The great tendency of aldehyde to become converted into acetic acid by the absorption of oxygen from the air renders Spirit of Nitrous Ether unstable, and pharmacists are obliged to neutralize such acid, generally by bicarbonate of potassium, before adding it to medicines containing iodides, etc.

"Test (U. S. P.).—If 10 gm. of spirit of nitrous ether be macerated with 1.5 gm. of potassa for twelve hours, with occasional agitation, the mixture then diluted in a beaker with an equal volume of water, and set aside until the odor of alcohol has disappeared, then slightly acidulated with diluted sulphuric acid, and a solution of 0.335 gm. of permanganate of potassium gradually added, the color of the whole of this solution should be discharged (presence of at least 4 per cent. of real ethyl nitrite)."

The nitrous radical may be detected by adding sulphate of iron and sulphuric acid to some of the spirit of nitrous ether, a brown or black compound being produced, already explained in connection with nitric acid.

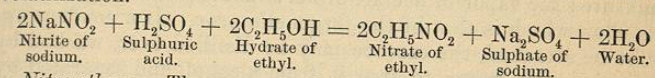
Official (B. P.) Test of Strength.—"Tested as described in the *Pharmaceutical Journ.*, 3d series, vol. xiii. p. 63 [Eykmán's test, $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 2\text{C}_2\text{H}_5\text{NO}_2 = \text{Fe}_2\text{SO}_4 + 2\text{C}_2\text{H}_5\text{HO} + 2\text{NO}$, a figure of the apparatus is given], or vol. xv. p. 101 [Dymond's modification of Eykmán's apparatus], or vol. xv. p. 673 [Allen's modification], it [the British preparation] should yield, at the ordinary temperature (60° F., 15.5° C.) and pressure (30 inches, or 760 millimetres of mercury), and when freshly prepared, seven times its volume of nitric oxide gas; and even after it has been kept some time and the vessel containing it has occasionally been opened, it should yield not much less than five times its volume of the gas." If the gas were yielded by nothing but nitrite of ethyl, the seven volumes would correspond to nearly 3 per cent. of that substance, and the five volumes to nearly 2 per cent. Simonson says the preparation official in the United States Pharmacopœia also contains from 2 to 3 per cent. of nitrite of ethyl.

(For the detection of methyl alcohol in spirit of nitrous ether, *vide* "Methylated Sweet Spirit of Nitre" in Index.)

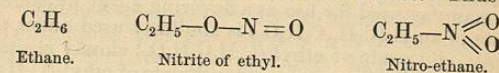
Pure Nitrite of Ethyl.

Dr. Leech has shown that both the physiological and the therapeutic actions of "spirit of nitrous ether" are similar to that of a solution of nitrite of ethyl of similar strength. The latter solution was prepared for Dr. Leech, in the Research Laboratory of the Pharmaceutical Society of Great Britain, by Hare's process of mixing nitrite of potassium, sulphuric acid, and alcohol at a low tempera-

ture. The nitrite of ethyl then separates as a pale-yellow layer. It may be washed rapidly with a little water, and dried with anhydrous carbonate of potassium. It is decomposed by prolonged contact with water; hence Dunstan recommends the use in medicine of a solution of two parts of the ether in absolute alcohol containing, as previously suggested by Williams, 5 per cent. of glycerin, and that it be dispensed and used from small bottles to avoid loss by volatilization.



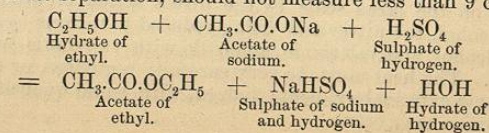
Nitro-ethane.—There are two derivatives of ethane, having similar composition, but differing very much in properties—namely, *nitrite of ethyl* ($\text{C}_2\text{H}_5\text{NO}_2$), which boils at 63.5° F. (17.5° C.) and has a sp. gr. of 0.900 (at 0° C.; water = 1; 0.917 to 0.920, Dunstan and Dymond); and *nitro-ethane* ($\text{C}_2\text{H}_5\text{NO}_2$), which boils at about 235° F. (nearly 113° C.) and has a sp. gr. of 1.058. The former is easily decomposed, the latter stable. The official spirit of nitrous ether contains nitrite of ethyl. Possibly the nitrite of ethyl contains the nitrogen in the trivalent or unsaturated condition, while in the nitro-ethane it is in the quinivalent or saturated state. Thus:—



Acetic Ether, or Acetate of Ethyl.

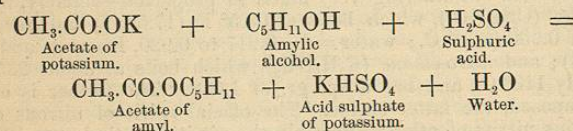
Acetate of Ethyl, or *Acetic Ether*, $\text{CH}_3\text{CO.OCC}_2\text{H}_5$ or $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$.—To a little dried acetate of sodium in a test-tube add a small quantity of rectified spirit of wine and some sulphuric acid, and, adapting a long bent tube in the usual manner, heat the test-tube and so distil over acetic ether; which may be collected in another test-tube kept cool by partial immersion in cold water.

The official proportions (*Ether Aceticus*, B. P.) are: rectified spirit, 32½ fluidounces; sulphuric acid, 32½ fluidounces; acetate of sodium, 40 ounces; carbonate of potassium, freshly dried, 6 ounces. It is purified from any water by shaking in a bottle with fused chloride of calcium, and after twenty-four hours rectifying. It is a colorless liquid with an agreeable ethereal odor. *Ether Aceticus*, U. S. P., has the specific gravity 0.889 to 0.897. Boiling-point, about 76° C. (168° F.). Soluble in all proportions in rectified spirit and in ether. When 10 c.c. are agitated with an equal volume of water, in a graduated test-tube, the upper, ethereal layer, after its separation, should not measure less than 9 c.c.



Acetate of Amyl, $\text{CH}_3\text{CO.OC}_5\text{H}_{11}$ or $\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$.—(Fousel oil, or ordinary amylic alcohol, is a mixture of two or more alcohols derived from pentane, but the derivatives may be simply termed amyl compounds; *vide* Pentylic or Amylic Alcohol.)

To a small quantity of amylic alcohol in a test-tube add some acetate of potassium and a little sulphuric acid, and warm the mixture; the vapor of acetate of amyl is evolved, recognized by its odor, which is that of the jargonelle pear. If a condensing-tube be attached, the essence may be distilled over, washed by agitation with water, to free it from alcohol, and separated by a pipette:



Fruit-Essences.—Acetate of amyl, prepared with the proper equivalent proportions of constituents, as indicated by the above equation, is largely manufactured for use as a flavoring agent by confectioners. Valerianate of amyl ($\text{C}_5\text{H}_{11}\text{C}_5\text{H}_9\text{O}_2$) is similarly used under the name of apple-oil. Butyrate of ethyl ($\text{C}_4\text{H}_9\text{C}_2\text{H}_5\text{O}_2$) closely resembles the odor and flavor of the pine-apple; cenanthyate of ethyl ($\text{C}_7\text{H}_{15}\text{C}_2\text{H}_5\text{O}_2$) recalls greengage; pelargonate of ethyl ($\text{C}_9\text{H}_{17}\text{C}_2\text{H}_5\text{O}_2$) quince; suberate of ethyl ($\text{C}_{10}\text{H}_{19}\text{C}_2\text{H}_5\text{O}_2$), mulberry; sebacate of ethyl ($\text{C}_{12}\text{H}_{25}\text{C}_2\text{H}_5\text{O}_2$), melon. Salicylic aldehyde, salicyl or salicylous acid, $\text{C}_6\text{H}_4\text{OH.CO.H}$, is the essential oil of meadow-sweet (*Spiraea ulmaria*), and may be prepared artificially by the oxidation of salicin (*vide* Index, "Salicin"). Acid salicylate of methyl ($\text{CH}_3\text{HC}_7\text{H}_3\text{O}_2$) or gaultheric acid forms the chief part of the essential oil of winter-green (*Gaultheria procumbens*, the fresh leaves of which yield about 0.4 per cent. of oil). Oil of sweet birch (*Betula lenta*) is salicylate of methyl. The latter may also be prepared artificially from salicin and by heating chloroform and sodium phenol. Salicylic acid ($\text{C}_6\text{H}_4\text{OH.CO.OH}$) can easily be obtained from the salicylate of methyl, but more cheaply from carbolic acid.

By mixing ethereal salts with each other and with essential oils in various proportions the odor and flavor of nearly every fruit may be fairly imitated. (For a set of formulæ of fruit-essences see *Pharmaceutical Journal*, May 17, 1879.)

Nitrite of Amyl.

Nitrite of Amyl (*Amyl Nitris*, U. S. P.) ($\text{C}_5\text{H}_{11}\text{NO}_2$).—This may be prepared on the large scale by the direct action of nitric acid on amylic alcohol, the nitric acid being reduced to nitrous by a portion of the alcohol, and valerianic aldehyde with valerianic acid being produced. The heat must be very carefully regulated, or the action may become extremely violent; indeed, with small quantities a violent explosion may occur.

For experimental purposes it is preferable to pass nitrous gases, generated by the action of nitric acid on white arsenic or on starch, into the amylic alcohol (kept cool by standing the vessel in cold water) until the alcohol is saturated. The product is shaken with an aqueous solution of hydrate or carbonate of potassium, to remove free acids, and the oily liquid then separated is distilled, the portion distilling between 205° and 212° F. being amyl nitrite.

The official nitrite of amyl is a yellowish ethereal liquid; sp. gr. of liquid 0.874, of vapor 4.03; boiling-point, about 96° C. (205° F.); soluble in spirit of wine, insoluble in water; converted by fused caustic potash into valerianate of potassium; exposed to the air, it yields amylic alcohol. If of good quality (for physiological purposes, although perhaps not chemically pure), about 70 per cent. will distil between 194° and 212° F. (90° to 100° C.), the bulb of the thermometer being in the vapor and not touching the residual fluid.

The official and commercial varieties of "nitrite of amyl" are well known to be only *chiefly* real nitrite of amyl. The staff of the Research Laboratory of the Pharmaceutical Society of Great Britain have recently shown that the fluid may contain the nitrites of both alpha-amyl and beta-amyl, nitrite of iso-butyl and nitrite of propyl, and have furnished specimens of these substances to Professor Cash, who is investigating their physiological and therapeutic properties. These nitrites are of course derived from the hydrates (see pp. 443 and 444) in the amylic alcohol.

Nitropentane ($\text{C}_5\text{H}_{11}\text{NO}_2$) is another derivative of pentane, similar to nitrite of amyl in composition, but differing much in properties. It is obtained by reaction of iodide of amyl on nitrite of silver. It boils at 300° to 320° F. The remarks made respecting the two similar derivatives of ethane (p. 469) may be applied to those of pentane.

QUESTIONS AND EXERCISES.

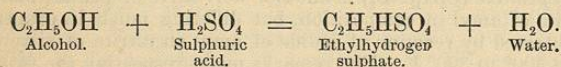
680. How would you prepare methane and ethane? Give formulæ.
681. Give details of the production of chloroform from alcohol, tracing the various steps by equations.
682. Give the formulæ and state the constitution of the various chlorine derivatives of methane.
683. How is chloroform purified?
684. State the characters of pure chloroform.
685. Explain the official process for the preparation of nitrous ether.
686. Give the properties of nitrous ether as compared with nitro-ethane.
687. By what official method is the strength of spirit of nitrous ether to be estimated?
688. How is iodide of ethyl made?
689. Mention the systematic names of several artificial fruit-essences.
690. What is the formula of nitrate of amyl? and how is it prepared?

THE OLEFINE SERIES OF HYDROCARBONS.

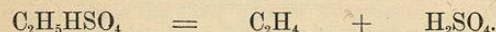
The Olefine Series of Hydrocarbons consists of *unsaturated* hydrocarbons having the general formula C_nH_{2n} . *Ethylene*, C_2H_4 ; *Propylene*, C_3H_6 ; *Butylene*, C_4H_8 ; *Amylene*, C_6H_{10} ; *Hexylene*, C_6H_{12} ; and *Heptylene*, C_7H_{14} , are well known.

Ethylene, *Olefiant Gas*, or *Heavy Carburetted Hydrogen*, C_2H_4 , is the first of this series. It is formed in the destructive distillation of coal, and is the chief illuminating constituent of coal gas. Coal gas consists of 30 to 40 per cent. of methane, 40 to 50 per cent. of hydrogen, and from 5 to 7 per cent. of ethylene and its homologues. Hydrocarbons, normally fluid, but kept in the vaporous condition by the diluents, also contribute materially to the illuminating power of gas. The impurities are nitrogen, air, carbolic acid, bisulphide of carbon, CS_2 , and some badly smelling sulphur compounds. Upward of one hundred and fifty distinct chemical substances have been obtained from the solid, liquid, and gaseous products of the destructive distillation of coal.

Preparation.—Ethylene may be prepared by dropping alcohol into a large retort or flask containing 10 ounces of sulphuric acid and 3 ounces of water heated to 160° – 165° C. The gas is washed in cold water and a solution of soda, to free it from ether, alcohol, and sulphurous acid:—



The product, when further heated, yields ethylene,—

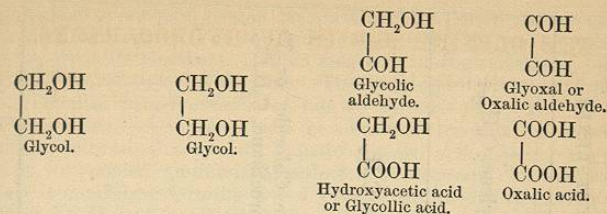


If the ethylene be passed into bromine under water until all the bromine disappears, *ethylene dibromide*, $C_2H_4Br_2$, or *dibrom-ethane*, will be formed.

Properties.—A colorless, odorless, condensable gas, burning with a luminous flame.

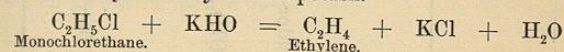
Ethylene Sulphate, $C_2H_4SO_4$, is probably contained in the *Spiritus Aetheris Compositus*, U. S. P., a solution of 3 parts of *etheral oil* in 30 of stronger ether and 67 of alcohol. The so-called *etheral oil* or heavy oil of wine is obtained by digesting spirit of wine and sulphuric acid together, then distilling, removing any acid from the distillate by washing with lime-water, and exposing the *etheral fluid* to the air to facilitate escape of the more volatile fluids. The product is a mixture consisting probably of ethylene sulphate, ethyl sulphate, ether, dissolved ethylene, and other bodies.

Glycols.—The olefines form dihydric alcohols or glycols (named from glycol, the first member of the series), and these give two sets of aldehydes and acids. Thus,—

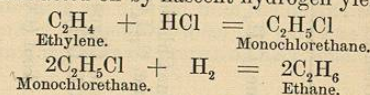


RELATION OF PARAFFINS TO OLEFINES.

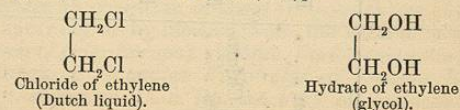
1st. The paraffins may be converted into olefines either by acting on an alcohol of the paraffin series by sulphuric acid, or by acting on a monochloro-paraffin by caustic potash.



Inversely, the olefines may be converted into paraffins. By combining an olefine with hydrochloric acid a monochloro-paraffin results, which when acted on by nascent hydrogen yields a paraffin.



2d. The bromine, chlorine, and iodine additive derivatives of the olefines are either identical or isomeric with the substitution-derivatives of the paraffins. Thus, $C_2H_4Cl_2$ is either dichlorethane or ethylene chloride; and the additive derivatives with the acids, such as hydrochloric, produce mono-substitution-derivatives of the paraffins. In the case of the chloride, however, $C_2H_4Cl_2$, it has a different boiling-point and specific gravity according as it is prepared from ethylene and chlorine (*chloride of ethylene*, alpha-dichlorethane, or the old "Dutch liquid"), or from monochlorethane (chloride of ethyl) and chlorine (chloride of monochlorethyl, beta-dichlorethane, or *chloride of ethylidene*). The former may be represented by the formula $CH_2Cl.CH_2Cl$, and the latter as $CH_3.CHCl_2$. It is the former also which yields glycol (by reaction of the chloride with silver acetate, and of the resulting ethylene acetate with an alkaline hydrate), hence the formula of the glycol also must be $CH_2OH.CH_2OH$, and not $CH_3.CH(OH)_2$:—



THE ACETYLENE SERIES OF HYDROCARBONS.

The acetylene series, C_nH_{2n-2} , are characterized by forming metallic substitution-derivatives. *Acetylene* itself, C_2H_2 , is formed during