

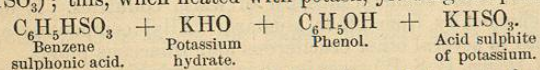
QUESTIONS AND EXERCISES.

724. Give an outline of the relations between alcohols and acids.
 725. Give a general method of preparing the primary alcohols of the ethylic series.
 726. Name the source of methylic alcohol.
 727. What is "methylated spirit"?
 728. Describe the method by which methylated spirit is detected in a tincture.
 729. How can artificial ethylic alcohol be prepared?
 730. Write a few sentences on the formation, purification, and concentration of alcohol, and explain the difference between rectified spirit, proof spirit, and absolute alcohol.
 731. What quantity of water must be added to one gallon of spirit of wine 56 degrees over-proof to convert it into proof spirit?
 732. To what volume must 5 pints of spirit of wine of 53 degrees over-proof be diluted before it becomes proof spirit?
Ans. 7 pints 13 ounces.
 733. State the specific gravity of proof spirit.
 734. State the proportion of alcohol commonly present in malt liquors, light wines, port and sherry, and "spirits," and state the extent to which spirits may be diluted without "adulteration."
 735. Enumerate the characters of alcohol.
 736. Whence is brandy obtained? and to what are due its color and flavor?
 737. Describe the official process for the preparation of ether, giving equations.
 738. Offer a physical explanation of the mode of producing local anaesthesia.
 739. How is commercial ether purified?
 740. Is "amylic alcohol" a simple or complex body?
 741. How is allylic alcohol prepared? In what relation does allylic alcohol stand to oil of mustard and oil of garlic?

Alcohols of the $C_nH_{2n-1}OH$ Series. Phenols and Benzylic Alcohols.

Carbolic Acid.

*Phenol, Phenic Alcohol, Phenic Acid, or Carbolic Acid** (C_6H_5OH) may be artificially obtained by heating benzene with sulphuric acid, which forms benzene (page 446) sulphonic acid ($C_6H_5HSO_3$); this, when heated with potash, yielding the phenol:—



Commercially, carbolic acid is obtained from that part of coal tar boiling between 180° and 190° C. When purified it is a colorless†

* Ordinary carbolic acid is a mixture of phenol, cresol, and other homologues.

† Phenol soon assumes a pink color, probably owing to the formation of aurin ($C_{19}H_{14}O_3$) or rosolic acid ($C_{20}H_{16}O_3$) by absorption of carbonic acid and oxygen.

crystalline body (*Acidum Carbolicum*, U. S. P.). A crystalline, so-called hydrous acid ($C_6H_5OH.H_2O$) may also be obtained.

At temperatures above 95° F. ordinary carbolic acid is an oily liquid. It is only slightly soluble in water, but readily dissolved by alcohol, ether, and glycerin (*Glycerinum Acidi Carbolici*, B. P.). In odor, taste, and solubility (and in appearance when liquefied by heat or by the addition of 5 to 10 per cent. of water) it resembles creasote, a wood-tar product for which carbolic acid has been substituted. Besides phenol (C_6H_5OH), coal-tar oil contains *cresol*, cresylic acid (C_7H_7OH), or ($C_6H_4CH_3OH$), the alcohol of toluene, while wood-tar oil furnishes *guaiacol* ($C_7H_7O_2$), boiling-point 200° C.—also a product of the destructive distillation of guaiacum resin—and *creasol* ($C_8H_{10}O_2$) or creasote. Certain coloring-matters may be obtained by the oxidation of carbolic acid; ammonia or, still better, phenyl-ammonia (aniline or phenylamine) mixed with it, and then a small quantity of solution of a hypochlorite, gives a blue liquid. No very satisfactory chemical method can be found for distinguishing creasote from carbolic acid, as creasote contains phenol, the chief difference consisting in the fact that the former boils only at 370° F., while the latter readily dries up at 212° . Some other physical differences exist: thus, carbolic acid does not affect a ray of polarized light; creasote twists it slightly to the right. Carbolic acid is either solid or may be solidified by cooling; creasote is not solidified by the cold produced by a mixture of hydrochloric acid and sulphate of sodium. Creasote from coal (impure or crude carbolic acid) gives a jelly when shaken with albumen or with collodion; creasote from wood (*Creasotum*, U. S. P.) is scarcely affected, especially if quite free from even all natural traces of carbolic acid. Coal creasote is soluble in solution of potash and in the strongest solution of ammonia (Read), wood creasote scarcely soluble. The coal product is soluble in twenty volumes of water, and a neutral solution of ferric chloride strikes a more or less permanent green or blue color with the liquid; wood creasote is less soluble (*Aqua Creasoti*, U. S. P., is said to contain 1 in 129), and not permanently colored blue by ferric chloride. An alcoholic solution of the coal oil is colored brown by ferric chloride; a similar solution of true creasote green. A dilute solution of creasote, such as creasote-water, is not affected by agitation with spirit of nitrous ether, while a similar solution of phenol becomes red. A few drops of the spirit of nitrous ether are placed in a test-tube, then about a drachm of the aqueous fluid and an equal volume of sulphuric acid are poured down the sides of the tube. A pink or red color results if phenol be present, especially after standing aside a short time (Eykmán; MacEwan). A solution of carbolic acid gives with excess of bromine-water an insoluble white precipitate of tribromo-phenol, $C_6H_2Br_3OH$. This reaction is useful in quantitative estimations of carbolic acid. According to Mr. Thomas Morson, pure creasote is unaffected when mixed with an equal volume of commercial glycerin, while carbolic acid is miscible in all proportions, and will carry into solution even a considerable quantity of creasote.

Carbolic acid and alkalis yield *carbulates* or *phenylates*, as

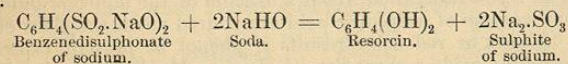
$C_6H_5OK.C_6H_5ONa$. Alcoholic solutions of the latter and of mercuric chloride yield yellow crystalline mercuric phenylate, or *phenolmercury*, $(C_6H_5O)_2Hg$.

Carbolic acid is a powerful *antiseptic* (*ἀντί, anti*, against, and *σῆπω, sēpō*, I putrefy). In large doses it is poisonous, *antidotes* being a mixture of olive oil and castor oil, freely administered, or a mixture of slaked lime, with about three times its weight of sugar rubbed together with a little water. Carbolic acid is soluble in oil of vitriol, *sulphocarboic acid*, phenol sulphonic acid $(C_6H_4(OH)SO_3H)$, or *sulphophenic acid* being formed. On diluting and mixing with oxides, hydrates, or carbonates *sulphocarbonates* are formed. The formula of *sulphocarbonate of sodium* is $NaC_6H_5SO_3.2H_2O$, or $C_6H_4(OH)SO_3.Na.2H_2O$. It is obtained by saturating sulphocarboic acid by carbonate of barium, and decomposing the resulting soluble sulphocarbonate of barium, $(C_6H_4OHSO_3)_2Ba$, by carbonate of sodium until a precipitate of carbonate of barium ceases to form. The filtrate on evaporation yields colorless, neutral, prismatic crystals of the salt (*Sodii Sulphocarbonas*, U. S. P.). *Sulphocarbonate of zinc*, $(C_6H_4OHSO_3)_2Zn.H_2O$ (*Zinci Sulphocarbonas*, B. P.), may be obtained by saturating sulphocarboic acid with oxide of zinc, $(C_6H_4(OH)SO_3)_2Zn$.

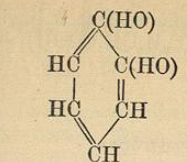
Trinitro-phenol $(C_6H_2(NO_2)_3OH)$ is formed on slowly dropping carbolic acid into fuming nitric acid; it is the yellow dye known as *carbazotic acid* or *picric acid*; most of the picrates are explosive by percussion.

Both carbolic acid and benzene are secondary products, obtained in the manufacture of coal gas; hence, indeed, the word *phenic*, and thence *phenyl* (from *φαῖνω, phainō*, I light, in allusion to the use of coal gas).

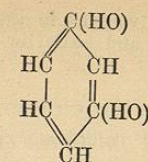
Constitution of Phenol.—Phenol (C_6H_5OH) may be regarded as benzene (C_6H_6) , in which one atom of hydrogen (H) is displaced by hydroxyl (OH). When two atoms of hydrogen in benzene are displaced by two of hydroxyl, *resorcin* $(C_6H_4(OH)_2)$ results, a colorless, crystalline antiseptic having many advantages over carbolic acid in surgical operations. Its name was given in allusion to its original source, resin, and to certain similarities with orcin. It occurs in white flat prisms readily soluble in most liquids. It may be made by passing benzol vapor into hot sulphuric acid, and heating the product (benzenedisulphonic acid, $C_6H_4(SO_2.OH)_2$) with excess of soda.



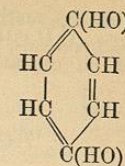
Resorcin is one of a group of three metameric dihydroxyl-benzenes. Their chemical relationships warrant the conclusion (on the atomic theory) that the cause of their differences in properties is a difference of position of the two atoms of hydroxyl in the molecule, these being, respectively, next to each other, separated by one atom (of CH) and by two atoms (of CH) (see Constitution of Benzene, p. 434), thus:



Ortho-dihydroxylbenzene (pyrocatechin).

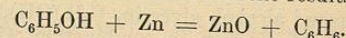


Meta-dihydroxylbenzene (resorcin).



Para-dihydroxylbenzene (hydroquinone).

By heating phenol with zinc dust benzene results,—



Salicylic acid is now made from phenol. (*Vide Salicylic Acid*.)

Cresol or *Tolyl Alcohol*, $C_6H_4OH.CH_3$, one of the alcohols of toluene, $C_6H_5CH_3$, is always found with crude phenol; artificially it may be made in the same manner as phenol, by acting on toluene with sulphuric acid and heating the resulting sulphonic acid $(C_6H_4(SO_3H)CH_3)$ with potash. With ferric chloride it gives a brown coloration.

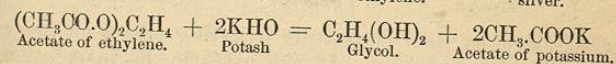
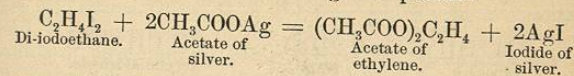
Benzyl Alcohol, *Phenylcarbinol*, $C_6H_5CH_2OH$, is isomeric with cresol, but having the hydroxyl group replaced in the methane nucleus, and not in the benzene nucleus of toluene. Having the CH_2OH group, on oxidation it yields benzoic aldehyde, C_6H_5COH (oil of bitter almonds), and benzoic acid, C_6H_5COOH .

b. Dihydroxyl Derivatives of Hydrocarbons.

Dihydric Alcohols—Glycols— $C_nH_{2n}(OH)_2$ Series.—Glycols may be viewed as dihydroxyl derivatives of the paraffins, the alcohols of the ethylic series being mono-derivatives:



They are prepared by acting on di-iodo-derivatives of the paraffins by acetate of silver, and then treating with potash:



The glycols yield very interesting results on oxidation, forming two sets of acids, the lactic and the succinic series.

Aromatic Glycols, $C_nH_{2n-2}(OH)_2$, and *Saligenin Alcohols*.—For the dihydric alcohols of benzene—namely, resorcin, pyrocatechin, and hydroquinone—see Phenol. *Toluene Dihydric Alcohols*.—*Orcin*, $C_6H_3(OH)_2CH_3$. This is found in lichens. *Hydroxybenzyl Alcohol*, salicylic alcohol, saligenol, saligenin, $C_6H_4OH.CH_2OH$. This is obtained from the salicin of willow-bark. Having the hydroxyl

group in the methane as well as in the benzene nucleus, salicylic aldehyde ($C_6H_4OH.COH$) and salicylic acid ($C_6H_4OH.COOH$) are formed on oxidation.

c. *Trihydroxyl Derivatives of Hydrocarbons.*

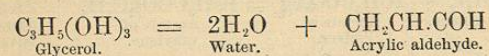
Trihydric Alcohols.— $C_nH_{2n+1}(OH)_3$ Series—*Glycerol*.

Glycerin.

Glycerol,* propenyl alcohol, glycerin, $C_3H_5(OH)_3$. The propenyl (glycyl or glyceryl) of glycerin, in combination with many of the acidulous radicals of the acids, oleic, palmitic, stearic, etc., forms most of the solid fats and oils. When these latter substances are heated with metallic hydrates (even with water—hydrate of hydrogen—at a temperature of 500° to 600° F.), double decomposition occurs, oleate, palmitate, or stearate of the metal is formed, and glycerol (propenylhydrate) is set free. Hence glycerin is a by-product in the manufacture of soap, hard candles, and lead plaster. (*Vide Index*.)

Properties.—Glycerin is viscid when pure, specific gravity not below 1.25, U. S. P., has a sweet taste, and is soluble in water or alcohol in all proportions. It has remarkable powers as a solvent, is a valuable antiseptic even when diluted with 10 parts of water, and is useful as an emollient. In vacuo it may be distilled unchanged, but under ordinary atmospheric pressure it is decomposed by heat, especially if distillation be attempted in a flask or retort. In a shallow open vessel heat readily vaporizes it. From damp air glycerin absorbs moisture slowly, but in considerable proportions. Perfectly pure and anhydrous glycerin, at a few degrees below the freezing-point of water, sometimes solidifies to a mass of crystals.

Tests.—Heat one or two drops of glycerin in a test-tube, alone or with strong sulphuric acid, acid sulphate of potassium, or other salt powerfully absorbent of water; vapors of acrolein, acrylic aldehyde (from *acer*, sharp, and *oleum*, oil), are evolved—



—recognized by their powerfully irritating effects on the eyes and respiratory passages. If the glycerin be in solution, it must be evaporated as low as possible before applying this test.

Add a few drops of the fluid suspected to contain the glycerin to a little powdered borax; stir well together; dip the

* It will be noticed that all the alcohols have the termination *-ol*—carbinol, glycol, glycerol, saliginol, pyrogallol.

looped end of a platinum wire into the mixture, and expose to an air-gas flame; a deep-green color is produced (Senier and Lowe).

The glycerin liberates boric acid, and it is the latter which colors the flame. Ammoniacal salts, which similarly affect borax, must first be got rid of by boiling with solution of carbonate of sodium. Liquids containing much indefinite organic matter must sometimes be evaporated to dryness, the residue extracted by alcohol, and the latter tested for the glycerin. To detect traces, liquids must be concentrated.

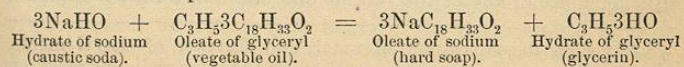
Glycerin, by action of very strong nitric acid, yields *nitroglycerin*, a compound containing, in place of three atoms of hydrogen of the glycerin, three of NO_2 . It is highly explosive, a very small quantity being liable to explode during preparation, and to do great harm. 75 parts of nitroglycerin, absorbed by 25 of porous silica, yield a pasty mass more convenient to handle than nitroglycerin itself; it is used for blasting under the name of *dynamite*. Tablets of chocolate, weighing $2\frac{1}{2}$ grains and containing $\frac{1}{100}$ grain of nitroglycerin, constitute the *Tabellæ Nitroglycerini*, B. P.

Besides glycerin itself (*Glycerinum*, U. S. P.), solutions or mixtures of starch and of yolk of egg and glycerin (*Glycerinum Amyli*, U. S. P., *Glycerinum Vitelli* or *Glyconin*, U. S. P.) are official.

FATTY BODIES.

Processes of Extraction.—Fixed oils and fats are extracted from animal and vegetable substances by pressure or straining with or without the aid of heat, or by digestion in solvents, as ether, etc., and evaporation of the solvent.

Constitution and General Relations.—Fixed oils and fats are, apparently, almost as simple in constitution as ordinary inorganic salts. Just as acetate of potassium ($KC_2H_3O_2$) is regarded as a compound of potassium (K) with the characteristic elements of all acetates ($C_2H_3O_2$), so soft soap is considered to be a compound of potassium (K) with the elements characteristic of all oleates ($C_{18}H_{33}O_2$), and hence is chemically termed oleate of potassium ($KC_{18}H_{33}O_2$). Olive oil (*Oleum Olivæ*, U. S. P.), from which soap is commonly prepared, is mainly oleate of the trivalent radical *glyceryl* (C_3H_5), the formula of pure fluid oil being $C_3H_5.3C_{18}H_{33}O_2$, and its name *oleine*. The formation of a soap therefore, on bringing together oil and a moist oxide or hydrate is a simple case of double decomposition (or, rather, metathesis), as seen already in connection with lead plaster (p. 245), or in the following equation relating to the formation of common hard soap:—



Berthelot has succeeded in preparing oil artificially from the oleate of hydrogen, or oleic acid, $HC_{18}H_{33}O_2$, and glycerin; and it is said to be identical with the pure oleine of olive and of other fixed

oils. Hard fats chiefly consist of *stearin*—that is, of tristearate of glyceryl ($C_3H_5C_{18}H_{35}O_2$). Mr. Wilson, of Price's Candle Company, obtains stearic and oleic acids and glycerin by simply passing steam, heated to 500° or 600° F., through melted fat. Both the glycerin and fat-acids distil over in the current of steam, the glycerin dissolving in the condensed water, the fat-acids floating on the aqueous liquids. From oleate of glyceryl and hydrate of hydrogen there result oleate of hydrogen and hydrate of glyceryl.* The oleic acid (*Acidum Oleicum*, U. S. P.) is separated by cooling and pressing the mixture. It is "a straw-colored liquid, nearly odorless and tasteless, and with not more than a very faint acid reaction. Unduly exposed to air, it becomes brown and decidedly acid. Specific gravity, 0.860 to 0.890. It is insoluble in water, but readily soluble in alcohol, chloroform, and ether. At 40° to 41° F. (4.5° to 5° C.) it becomes semi-solid, melting again at 56° to 60° F. (13.3° to 15.5° C.). It should be completely saponified, when warmed, with carbonate of potassium, and an aqueous solution of this salt, neutralized by acetic acid and treated with acetate of lead, should yield a precipitate which after washing with boiling water is almost entirely soluble in ether," showing the absence of any important quantity of stearic and palmitic acids, the lead stearate and palmitate being insoluble in ether.

In a mixture of oils and fats and free fatty acids the latter may be estimated by taking advantage of their solubility in spirit of wine, and the formation of a neutral soap, on shaking the spirituous solution with caustic soda, phenolphthalein being used as indicator. (See the section on the use of the caustic-soda solution in volumetric analysis.)

The author found (*Pharmaceutical Journal*, March, 1863) that oleic acid readily combines with alkaloids and most of the metallic oxides or hydrates, forming *oleates* which are soluble in fats. In this way active medicines may be administered internally in conjunction with oils or externally in the form of ointments (*Oleatum Hydrargyri*, U. S. P.; *Oleatum Veratrinae*, U. S. P.). Tichborne considers the formula of mercuric oleate to be $Hg(C_{18}H_{35}O_2)_2H_2O$.

Some fats, such as "suint" from sheep's wool, and unctuous matter from bristles, feathers, horn, and hair, generally yield, by saponification, etc. fatty acids, and, instead of glycerin, *cholesterin*, an alcoholoid crystalline substance (Lieblich). The "lanolin" of pharmacy is *cholesterin* fat which has absorbed a large volume of water.

As regards the conversion of oily substances into emulsions resembling the common natural emulsion, milk, Gregory states that three drachms of gum acacia in fine powder are necessary to emulsify one ounce of any of the volatile oils, and that a little less (about

* Any such decomposition of water and fixation of its elements, whether direct as above or indirect through the intermediate agency of saponification, is termed *hydrolysis* (*ὑδρόψις*, *hudōr*, water, *λύω*, *lío*, to decompose). The fixation of water without decomposition is termed *hydration*.

two drachms) will answer for the fixed oils and balsams. To this quantity of gum four drachms and a half of water must be added (no more and no less). Either the water or the oil may be added first to the gum, but it is the quickest to add the oil first and well triturate before adding the water.

Soaps.

Olive oil boiled with solution of potash yields potassium soap or *soft soap* (*Sapo Mollis*, B. P.; *Sapo Viridis*, U. S. P., or green soap); with soda, sodium soap, or *hard soap* (*Sapo*, U. S. P.), or *white castile soap*, as distinguished from the variety of hard castile or Marseilles soap, which is "mottled" by iron soap; mixed with ammonia, an ammonium soap (*Linimentum Ammoniae*, U. S. P.); and with lime-water, calcium soap (*Linimentum Calcis*, U. S. P.),—all oleates, chiefly, of the respective basylous radicals. Their mode of formation is indicated in the foregoing equation. The alkali soaps are soluble in alcohol, the others insoluble. A green soap much used on the continent of Europe, and indeed official in Germany (formerly as *Sapo Viridis*, now as *Sapo Kalinus Venalis*), is made by adding indigo to ordinary soft soap; the yellow color of the soap yielding with the indigo a greenish compound. The official characters of hard soap are—"grayish-white, dry, inodorous; horny and pulverizable when kept in dry warm air; easily moulded when heated; soluble in rectified spirit, leaving not more than 3 per cent. of insoluble matter, of which at least two-thirds are soluble in water. A 4 per cent. alcoholic solution should not gelatinize on cooling (abs. of animal fats); not imparting an oily stain to paper; incinerated, it yields an ash which does not deliquesce. And of soft soap: "yellowish-green, inodorous, of a gelatinous consistence; soluble in rectified spirit; not imparting an oily stain to paper; when dried yields nothing to benzol: incinerated, it yields an ash which is very deliquescent." Curd soap (*Sapo Animalis*, B. P.) is "a soap made with soda and a purified animal fat, consisting principally of stearin." It will, of course, chiefly contain stearate of sodium. In pharmacy it is often advantageously employed instead of the "hard soap."

The hard soap met with in trade is made from all varieties of oil, the commoner kinds being simply the product of the evaporated mixture of oil and alkali, while the better sorts have been separated from alkaline impurities and the glycerin by the addition of common salt to the liquors, which causes the precipitation of the pure soap as a curd. Potash soap is not so readily precipitable by salt. Saponification on the small scale is much facilitated by first well mixing the oil with 5 per cent. of sulphuric acid, and letting this mixture stand for twenty-four hours. The dark product is then readily soluble when boiled with soda, and the clear fluid yields a crust of white soap on cooling. If required quite free from alkali, the resulting soap is boiled with water until dissolved, salt added, and the whole cooled. A cake of pure soap results.

Yellow soap is a common, cheap soap, containing a good deal of

resin soap, resin consisting chiefly of acids—pinic, sylvic, pimaric, etc.—which readily unite with alkalies to form true soaps.

Saponification.—This term is now extended in chemistry so as to include any process analogous to the foregoing, any reaction in which an alkali decomposes any ethereal salt or alkyl salt.

Solid Fats.

1. *Lard* (*Adeps Preparatus*, U. S. P.) is the purified internal fat of the abdomen of the hog—the perfectly fresh *omentum* or *flare*, freely exposed to the air to dissipate animal odor, rubbed to break up the membranous vesicles, melted at about 130° F. (54.4° C.), and filtered through paper or flannel. *Lard Oil* (*Oleum Adipis*, U. S. P.), which is chiefly olein, is a “fixed oil expressed from lard at a low temperature.” Sp. gr. 0.900 to 0.920. 2. *Benzoated Lard* (*Adeps Benzoatus*, U. S. P.) is prepared lard heated over a water-bath with 2 per cent. of benzoin, which communicates an agreeable odor and prevents or retards rancidity. Purified lard is a mixture of oleine and stearin: *margarine*, the margarate of glyceryl, was formerly supposed to be a constituent of lard and other soft fats, but is now regarded as a mere mixture of *palmitine* (the chief fat of palm oil) and stearin. 3. *Suet*, the internal fat of the abdomen of the sheep, purified by melting and straining, forms the official *Serum*, U. S. P.; it is almost exclusively composed of stearin ($C_{18}H_{35}O_2$). 4. Expressed oil of *nutmeg* (*Oleum Myristice Expressum*, B. P.), commonly but erroneously termed *Oil of Mace*, is a mixture of a little volatile oil with much yellow and white fat; the latter is *myristin* or myristate of glyceryl ($C_{14}H_{27}O_2$). 5. Oil of *theobroma*, or *Cacao-butter* (*Oleum Theobromæ*, U. S. P.), chiefly stearin, but with one higher and some lower homologues (Heintz), is a solid product of the roasted and roughly crushed seeds or *cocoa-nibs* of the *Theobroma cacao*. They contain from one-fourth to one-half of this fat. (These also furnish when ground *flake cocoa*; or, when ground and much sweetened, *chocolate*; or, with farina and some sugar, *cocoa*; or, with a portion of the butter extracted, “*cocoatina*,” etc.). 6. *Cocoa-nut oil* or *butter*, a soft fat largely contained in the edible portion of the nut of *Cocos nucifera*, or common cocoanut of the shops, is a body containing glyceryl united with no less than six different univalent acidulous radicals—namely, the caproic ($C_6H_{11}O_2$), caprylic ($C_8H_{15}O_2$), rutic ($C_{10}H_{19}O_2$), lauric ($C_{12}H_{23}O_2$), myristic ($C_{14}H_{27}O_2$), and palmitic ($C_{16}H_{31}O_2$)—radicals which, like some from common resin, when united with sodium form a soap differing from ordinary hard soap (oleate of sodium) by being tolerably soluble in a solution of chloride of sodium; hence the use of cocoanut oil and resin in making *marine soap*, a soap which, for the reason just indicated, readily yields a lather in sea-water. 7. *Kokum Butter*, *Garcinia Oil*, or *Concrete Oil of Mangosteen*, a whitish or yellowish-white fat obtained from the seeds of *Garcinia indica* or *G. purpurea*, is composed of stearin, myristicine, and olein. It is recognized officially in the Pharmacopœia of India (*Garciniæ purpureæ Oleum*).

Butter commonly yields 87½ per cent. of fat acids by saponification and decomposition of the soap by acid. Other animal fats, with which butter is likely to be adulterated, yield about 95½. Hence the percentage of fat acids, and, especially, volatile acids, insoluble acids, and soluble acids, yielded by a suspected sample of butter indicates purity or the opposite. Occasionally, however, a sample of genuine butter may not conform to the figures; hence they cannot be relied on to show extent of sophistication.

Fixed Oils.

Fixed and Volatile Oils are naturally distinguished by their behavior when heated; they also generally differ in chemical constitution—a fixed oil being, apparently, a combination of a basylous with an acidulous radical, as already stated, while a volatile oil is more commonly a neutral or normal hydrocarbon or the same oxidized.

Drying and Non-drying Oils.—Among fixed oils, most of which are oleate with a little palmitate and stearate of glyceryl, a few, such—as (1) *Linseed oil* (*Oleum Lini*, U. S. P., contained in *Linum*, U. S. P., *Linseed* or *Flaxseed*, the ground residue of which “should yield, when extracted with disulphide of carbon, not less than 25 per cent. of fixed oil,” is *linseed meal*), and (2) *Cod-liver oil* (*Oleum Morrhue*, U. S. P.), and to some extent *castor* and *croton*—are known as *drying oils*, from the readiness with which they absorb oxygen and become hardened to a resin. Linseed commonly contains 37 or 38 per cent. of oil; 25 to 27 per cent. is obtained by submitting the ground seeds to hydraulic pressure, 10 or 12 per cent. remaining in the residual oil cake. *Boiled oil* is linseed oil which has been boiled with oxide of lead. This treatment increases the already great tendency of linseed oil to resinify, forming *linoxyn*, $C_{32}H_{54}O_{11}$, on exposure to air. The drying oils appear to contain linolein, an oily body distinct from olein. Cod-liver oil contains a trace of iodine; a little choline also and other bases, Gautier and Mourgues having recently isolated *asellin*, $C_{25}H_{32}N_4$, and *morrhaine*, $C_{19}H_{27}N_3$. Among the *non-drying oils* are the following: (3) *Almond oil* (*Oleum Amygdalæ Expressum*, U. S. P.), indifferently yielded by the bitter (*Amygdalæ Amara*, U. S. P.) or sweet seed (*Amygdalæ Dulcis*, U. S. P.) to the extent of 45 and 50 per cent. respectively. (3a) *Cotton-seed oil* (*Oleum Gossypii Seminis*, U. S. P.) contains olein and some palmitin. Sp. gr. 0.920 to 0.930. It should not be permanently colored dirty yellow by sulphuric acid. (4) *Croton oil* (*Oleum Crotonis*, B. P., and *Oleum Tiglii*, U. S. P.). Geuther states that no such acid as crotonic is obtainable from croton oil, but acetic, butyric, valerianic, and higher members of the oleic series, together with *tiglic acid*, $HC_5H_7O_2$. H. Senier states that alcohol separates croton oil into a vesicating portion which is soluble, and a powerful purgative portion which is insoluble. Kobert says that free crotonoleic acid is both the vesicant and the purgative. (5) *Lycopodium* (U. S. P.), a yellow powder composed of the spores of the common Club-Moss (*Lycopodium clavatum*), contains a large proportion of a very fluid fixed oil; also an alkaloid (Büdeker), $C_{32}H_{52}N_2O_3$. (6) *Olive oil*

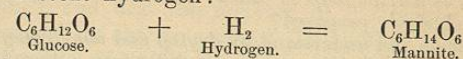
(*Oleum Olivæ*, U. S. P.), already noticed (p. 461). "If 1 gm. of olive oil be agitated in a test-tube with 2 gm. of a cold mixture prepared from equal volumes of strong sulphuric acid and of nitric acid of sp. gr. 1.185; and the mixture be set aside for half an hour, the supernatant oily layer should not have a darker tint than yellowish; nor should a green or red layer separate on standing if 1 gm. of the oil be shaken for a few seconds with 1 gm. of a cold mixture of sulphuric acid (sp. gr. 1.830) and nitric acid (sp. gr. 1.250), and 1 gm. of disulphide of carbon; and if 5 drops of the oil are let fall upon a thin layer of sulphuric acid in a flat-bottomed capsule, no brown-red or dark-brown zone should be developed within three minutes at the line of contact of the two liquids (abs. of appreciable quantities of other fixed oils of similar physical properties)." — U. S. P. (7) *Castor oil* (*Oleum Ricini*, U. S. P.), chiefly a *ricinoleate of glyceryl* ($C_3H_5 \cdot 3C_{18}H_{33}O_2$) or *ricinolein*, a slightly oxidized olein, soluble, unlike most fixed oils, in alcohol and in glacial acetic acid. Castor-oil seeds were stated, by Tuson, to contain an alkaloid, *ricinine*. Beck has recently confirmed Tuson, giving as the formula $C_{24}H_{42}N_2O_3$. It possesses no purgative property. (8) *Oil of Male Fern*, a vermifuge obtained by exhausting the rhizome (*Aspidium*, U. S. P.) with ether and removing the ether by evaporation—a dark-colored oil containing a little volatile oil and some resin, and officially termed an *oleoresin* (*Oleoresina Aspidii*, U. S. P.). Its chief active constituent appears to be *filicic acid*, $C_{14}H_{18}O_5$. (9) *Fixed oil of Mustard*, a bland, inodorous, yellow or amber oil, yielding by saponification and action of sulphuric acid, glycerin, oleic acid, and *erucic acid* ($HC_{22}H_{41}O_2$) (Darby). (10) *Arachis oil* (*Oleum Arachis*, P. I.) is found to the extent of 40 or 50 per cent. in the seeds of *Arachis hypogæa* (P. I.), the Ground-nut or Earth-nut (so called because the pod of the herb in the growth of its stalk downward is forced beneath the surface of the ground, and there ripens). It is chiefly olein, but contains hypogæin, palmitin, and arachin. The oil is largely used in India in the place of olive oil, and is becoming much employed in Europe, especially for soap-making. (11) *Sesame oil*, or oil of *sesamum* (*Oleum Sesami*, U. S. P.) (Gingelly, Teal, or Benné Oil), from the seeds of *Sesamum indicum*, is also largely used in Europe. It has most of the characters of the best olive oil. (12) *Shark-liver oil*, from *Squalus carcharis* (*Oleum Squalæ*, P. I.), is used to some extent as a substitute for cod-liver oil in India.

Trihydric Alcohols of the $C_nH_{2n+3}(OH)_3$ series.
Pyrogallol or *Pyrogalllic Acid*.—Trihydroxybenzene, $C_6H_3(OH)_3$.
 (Vide Index.)

d. Other Polyhydroxyl Derivatives of Hydrocarbons.

Only one *tetrahydric alcohol* is known—namely, *Erythrite* or *Lichen Sugar*, $C_4H_8(OH)_4$, found in *Protococcus Vulgaris*, *Rocella Tinctoria*, and *R. fuci formes*. *Quercite*, the sugar of acorns, is *Penthydric*; *Mannite* is *hexahydric*.

Hexahydric Alcohols.—*Mannite*, $C_6H_8(OH)_6$.—Boil manna with 15 or 16 parts of alcohol, filter, and set aside; mannite separates in colorless shining crystals or acicular masses to the extent of from 90 to 80 per cent. of the manna. It is closely related to the sugars, glucose becoming mannite by action of nascent hydrogen:



Indeed, glucose itself is probably an alcohol of another radical (C_6H_8)⁶OH. Mannite does not undergo vinous fermentation in contact with yeast. With nitric acid it forms an explosive body, *nitromannite*, $C_6H_8(NO_3)_6$.

Manna, U. S. P., is a concrete saccharine exudation obtained by making transverse incisions in the stems of cultivated trees of *Fraxinus Ornus*. It occurs in stalactitic pieces, varying in length and thickness, flattened or somewhat concave on their inner surface, and of a pale yellowish-brown color and nearly white externally. This manna, which is known as *flake manna*, is crisp, brittle, porous, crystalline in structure, and readily soluble in about six parts of water. Odor faint, resembling honey; taste sweet and honey-like, combined with a slight acidity and bitterness. It contains about 10 per cent. of moisture. Mannite is also met with in celery, onions, asparagus, certain fungi and sea-weeds, occurs in the exudations of apple and pear trees, and is produced during the viscous fermentation of sugar.

Dulcitol, isomeric with mannite, is formed by the action of nascent hydrogen on inverted milk-sugar. It differs from mannite by oxidizing to mucic acid, $C_6H_{10}O_8$, when treated with nitric acid.

QUESTIONS AND EXERCISES.

742. State the composition of phenol; how is it artificially and commercially prepared?
743. State the character by which carbolic acid is distinguished from creasote.
744. Give the formulæ and systematic names for picric acid, carbolate of sodium, and resorcin.
745. Give names for the bodies having the formulæ $C_6H_4OH.CH_3$ and $C_6H_5CH_2OH$.
746. What are glycols? how prepared?
747. Give formula and mention the chief properties of glycerin.
748. What is the specific gravity of glycerin?
749. By what test is glycerin recognized?
750. Enumerate some official preparations in which glycerin is employed as a solvent.
751. Give a sketch of the general chemistry of fixed oils, fats, and soaps.

752. What is the difference between hard and soft soap?
 753. Which soaps are official?
 754. Name the source of lard, and state how "Prepared Lard" is obtained.
 755. Mention the chief constituent of suet.
 756. Whence is cacao-butter obtained?
 757. Why is *marine soap* so called? and from what fatty matter is it almost exclusively prepared?
 758. What do you understand by *drying* and *non-drying* oils?
 759. In what respects does castor oil differ from other oils?
 760. How is oil of male fern (*Ex. Filicis Liquidum*) prepared?
 761. Under what head do the following fall: pyrogallol (*Pyrogallic acid*), erythrite, mannite, and dulcite?
 762. Describe the source and characters of manna.

CARBOHYDRATES.

The carbohydrates may be placed in three classes:—

- | | |
|--|--|
| 1. $C_6H_{12}O_6$, Glucoses | { Glucose or Dextrose or Grape-Sugar.
Lævulose or Inverted Sugar. |
| 2. $C_{12}H_{22}O_{11}$, Saccharoses
or Saccharons | { Cane-Sugar or Sucrose.
Maltose.
Lactose or Milk-Sugar. |
| 3. $C_6H_{10}O_5$, Amyloses or
Amyloids | { Dextrin.
Starch.
Cellulose. |

Glucoses, $C_6H_{12}O_6$.

Dextrose or *Grape-Sugar* or *Glucose* (from $\gamma\lambda\upsilon\kappa\epsilon$, *glucūs*, sweet) is often seen in the crystallized state in dried grapes or raisins and other fruits; it is also the variety of sugar met with in diabetic urine. Its crystalline character is quite distinct from that of cane-sugar, the latter forming large four- or six-sided rhomboidal prisms, while grape-sugar occurs in masses of small cubes or square plates. Grape-sugar is also less soluble in water, but more soluble in alcohol than cane-sugar.

According to Fresenius, the percentage proportion of saccharine matter in the dried fig is 60 to 70, grape 10 to 20, cherry 11, mulberry 9, currant 6, whortleberry 6, strawberry 6, raspberry 4 (*Rubus Idæus*, U. S. P.).

Lævulose is lævogyrate, while sucrose and glucose possess right-handed rotation; the latter twist a ray of polarized light from left to right to an extent dependent on the amount of sugar present—a fact easy of application in estimating the amount of sugar in syrups or in diabetic urine.

Inverted Sugar or *Lævulose* is uncrystallizable. It is found in the grape, fig (*Ficus*, U. S. P.), cherry, and gooseberry; both grape-sugar and inverted sugar in the strawberry, peach, plum, etc. Fruit-sugar reduces cupric salts and ammonio-nitrate of silver.

Artificial Formation of Grape-Sugar from Cane-Sugar—Tests for Sugar.—Dissolve a grain or two of common cane-sugar in water. To a portion of this solution placed in a test-tube add more water, two or three drops of solution of sulphate of copper, a considerable quantity of solution of potash or soda (enough to turn the color of the liquid from a light to a dark blue), and heat the mixture to the boiling-point; no obvious immediate change occurs. To another portion of the syrup add a drop of sulphuric acid and boil for ten or twenty minutes, then add the copper solution and alkali, and heat as before; a yellowish-red precipitate of cuprous oxide (Cu_2O) falls. This test is exceedingly delicate.

The above reaction is due to the conversion of the *cane-sugar* ($C_{12}H_{22}O_{11}$) into *inverted sugar* or *lævulose*, $C_6H_{12}O_6$ (so called because its solution causes left-handed rotation of a ray of polarized light, cane-sugar having an opposite effect), and *grape-sugar*, $C_6H_{12}O_6 \cdot H_2O$, by the influence of the sulphuric acid, and to the reducing action of the inverted sugar and grape-sugar on the cupric solution. The formation of a precipitate immediately, without the action of acid, shows the presence of the latter sugars—its formation only after ebullition with acid indicating, in the absence of starch or dextrin, cane-sugar. In this reduction process the sugar is oxidized and broken up into several substances, but the exact nature of the reaction has not been ascertained.

Dextrin also reduces the copper salt to suboxide, unless its solution is cold and very dilute. It does not, however, so act on a solution of cupric acetate acidified with acetic acid, while glucose produces with this liquid the usual red cuprous precipitate (Barfoed).

Sugar from Starch.—Boil starch with a little water and a drop of sulphuric acid, as for dextrin, but continue the ebullition for several minutes; on testing a portion of the cooled liquid with iodine, and another portion with the heated alkaline solution of a copper salt, as described on page 547, it will be found that the starch has nearly all become converted into a sugar—dextrose. Maltose is also formed at first, but by the continued action of the acid is changed to dextrose. When made on a large scale, a warm ($131^\circ F.$) mixture of starch and water of the consistence of cream is slowly poured into a boiling solution of one part of sulphuric acid in one hundred of water, the whole boiled for some time, the acid neutralized by chalk, the mixture filtered, the liquid evaporated to a thick syrup, and set aside; in a few days it crystallizes to a granular mass resembling honey. In this operation a small quantity of dextrin remains with the glucose, but if the process be conducted under pressure, conversion, according to Manbré, is complete. Sugar made from the starch of rice, maize, etc. is