COMMERCIAL ORGANIC ANALYSIS

VOLUME II.—PART II

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Commercial Organic Analysis

AUTHORIZED EDITIONS.

A Treatise on the Properties, Proximate Analytical Examination and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of Impurities, Adulterations and Products of Decomposition, &c. Revised and Enlarged. By ALFRED ALLEN, F.C.S., Public Analyst for the West Riding of Yorkshire; Past President Society of Public Analysts of England, &c.

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COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE ANALYTICAL EXAMINATION OF THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANUFACTURES, MEDICINE, &c.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

BY

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PUBLIC ANALYST FOR THE WEST RIDING OF YORKSHIRE, THE CITY OF SHEFFIELD, ETC.

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WITH REVISIONS AND ADDITIONS BY THE AUTHOR AND

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VOLUME II—PART II

HYDROCARBONS, PETROLEUM AND COAL-TAR PRODUCTS, ASPHALT, PHENOLS AND CREOSOTES.

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REVISER'S NOTE TO THIRD EDITION.

The present volume completes the revision of volume II of the second edition of "Commercial Organic Analysis" except the section relating to essential oils. The two parts now issued include over seven hundred pages; the same text in the former edition covered about five hundred and twenty-five pages, from which it will be seen that a large amount of matter has been added.

Much of the text of the present volume has been revised by Mr. Allen. The first half of the work, up to about page 150, was so far advanced at the time of his visit to the United States that only limited corrections could be made, but the remaining portion received much attention at his hands, especially the section on "Phenols."

The revision has been extensive; the text has been largely rewritten. The principal additions and changes are: systematic arrangements of hydrocarbons according to the modern system, including application of the nomenclature of the Geneva convention; summaries of the technology of acetylene, coke-oven tars, and asphalt; testing of petroleum, lubricating-oils, and coal-tar products; and special tests for many benzene derivatives now used as drugs, food-preservatives, or disinfectants. The section of asphalt has been increased more than three-fold. Mr. Allen has added largely to the analytic data concerning phenol, phenolic disinfecting agents, and wood-tar creosote.

The reviser has added as an appendix a detailed description of new extracting and drying apparatus, and has calculated tables of comparison of Beaumé degrees and specific gravities (lighter than water); also for comparison of thermometric degrees F. and C.

Original references have been consulted wherever possible, in which work the extensive libraries of the Franklin Institute and Philadelphia College of Pharmacy have been available. The index has been much enlarged.

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HYDROCARBONS.

PHENOLS.

ERRATA.

Page 57, in foot-note, for "water" read "winter."
Page 76, line six from bottom, for "fluorescent" read "fluorescence."

The following corrections for preceding volumes are to be noted in addition to those given on page x of Volume II, Part 1:

VOLUME I.

Page 155, fifth line from bottom, for "= 67·5" read "— 67·5." Last line, for "improper" read "imperfect."

Page 174, line fourteen from bottom, for "Reitman" read "Reitmair." Line nine from bottom, insert after "over" the following, as a new sentence: "The receiver is changed and the operation continued so long as alcohol distils."

VOLUME II.—PART 1.

Page 94, the specific gravity of linseed oil at 100° C. is 0·8809.

Page 144, line seven, insert "direct" after "by." Line four from bottom, for "115" read "125."

Page 165, omit the sentence beginning on line five.

Page 193, in table, the figure for cottonseed stearin should be + 25-

HYDROCARBONS.

The term hydrocarbon is a convenient designation for all compounds containing only hydrogen and carbon. It has been applied in physiologic literature to the fats and fixed oils, and, still more objectionably, to the carbohydrates; but this erroneous and confusing use is no longer observed in standard text-books.

The number of known hydrocarbons is very large, and theory indicates the possibility of many others. They are conveniently divided into two groups according to an assumed arrangement of the carbon atoms: the open-chain, fatty, or aliphatic series, and the closed-chain, cyclic, or aromatic series. Each of these series may be divided into numerous sub-groups according to simple arithmetical relations in their formulæ. The most important relation is that termed *homologous*, which refers to a constant difference of CH_2 or some multiple thereof. The members of any given homologous series may therefore be represented by a general formula, and this is often used as a designation of the series. Instances of isomerism are numerous.

The open-chain hydrocarbons are found in many natural products, such as petroleum, mineral naphtha, natural gas, and bitumens, and also in the more volatile portions of the products of destructive distillation. The closed-chain hydrocarbons are represented in the less volatile portion of the products of destructive distillation, especially of bituminous coal at a high temperature. A distinct and well-marked group includes the substances known as "essential" or "volatile" oils, which give the odors to many plants, especially species of *Rosaceæ*, *Rutaceæ*, *Labiatæ*, and *Coniferæ*. The camphors and resins are oxidised products of these bodies. Solid hydrocarbons occur very rarely in plants.

As produced both in nature and artificially, the hydrocarbons often occur as intimate mixtures of many allied bodies very difficult to separate. The methods practically used for this purpose will be described later. Some of the hydrocarbons have common names derived from their properties, source, mode of production, etc., but as it is desirable to have a systematic nomenclature, the following table gives some of the members of the more important series and a system of prefixes and affixes by which the composition of any member is at once indicated. The principle upon which nomenclature is based is evident from the examples given:

GENERAL FORMULÆ:	C_nH_{2n+2}	C_nH_{2n+1}	C_nH_{2n}	C_nH_{2n-1}	C_nH_{2n-2}
	Methane. CH_4	Methyl. CH_3	Methene, or Methylene. CH_2	Methenyl. CH	
	Ethane. C_2H_6	Ethyl. C_2H_5	Ethene, or Ethylene. C_2H_4	Ethenyl. C_2H_3	Ethine, or Ethenylene. C_2H_2
	Tritane, or Propane. C_3H_8	Trityl, or Propyl. C_3H_7	Tritene, or Propylene. C_3H_6	Tritenyl. C_3H_5	Tritine. C_3H_4
	Tetrane, or Butane. C_4H_{10}	Tetryl, or Butyl. C_4H_9	Tetrene, or Butylene. C_4H_8	Tetrenyl. C_4H_7	Tetrine. C_4H_6

The syllable " alk " is used as a general designation, modified by the special terminations. Thus, homologues of CH_4 are called "alkanes," those of CH_3, are "alkyls."

It will be noted that all the members of the methene series have the same percentage composition, the ratio of the weight of the carbon to that of the hydrogen being always 12 to 2. Some of the open-chain series of less importance will be noted later.

The nomenclature of the closed-chain series is less systematic. The following are some of the important members:

	BENZENES.	NAPHTHALENES.	ANTHRACENES.	TERPENES.
GENERAL FORMULÆ:	C_nH_{2n-6}	C_nH_{2n-12}	C_nH_{2n-18}	C_nH_{2n-4}
	Benzene. C_6H_6	Naphthalene. $C_{10}H_8$	Anthracene. $C_{14}H_{10}$	Pinene. $C_{10}H_{16}$
	Toluene. C_7H_8	Methyl-naphthalene. $C_{11}H_{10}$	Methyl-anthracene. $C_{15}H_{12}$	
	Xylene. C_8H_{10}		Retene. $C_{18}H_{18}$	

SYNOPSIS OF SERIES OF HYDROCARBONS.

For the empirical and assumed structural formulæ of these bodies see the specific descriptions.

a. OPEN-CHAIN, FATTY, OR ALIPHATIC SERIES.

GENERAL FORMULA.	NAME.	IMPORTANT MEMBERS.	CHIEF SOURCES.
C_nH_{2n+2}.	Methanes, paraffins.	Marsh gas, paraffin.	Petroleum, ozokerite, natural gas, coal gas.
C_nH_{2n}.	Ethenes, olefins.	Ethene (ethylene).	Petroleum, coal gas and shale gas.
C_nH_{2n-2}.	Ethines, acetylenes, Di-ethenes, allenes.	Acetylene.	Coal gas. Ethine by action of water on calcium carbide.
	Olefinoid terpenes.	Isoprene, myrcene, linaloolene.	Essential oils.

b. CLOSED-CHAIN, AROMATIC, OR CYCLIC SERIES.

GENERAL FORMULA.	NAME.	IMPORTANT MEMBERS.	CHIEF SOURCES.
C_nH_{2n}.	Naphthenes, Paraffenes.	Octonaphthene.	Russian petroleum.
C_nH_{2n-2}.	Naphthylenes.	Menthene.	Essential oils.
C_nH_{2n-4}.	Terpenes.	Pinene, camphene.	Essential oils.
C_nH_{2n-6}.	Benzenes.	Benzene, toluene.	Coal-tar.
C_nH_{2n-8}.		Phenyl-ethene.	Storax.
C_nH_{2n-10}.		Phenyl-ethine.	Synthetic.
C_nH_{2n-12}.	Naphthalenes.	Naphthalene.	Coal-tar.
C_nH_{2n-14}.	Diphenyls.	Diphenyl.	“
C_nH_{2n-16}.	Diphenylenes, Dibenzyls.	Fluorene, Stilbene.	“
C_nH_{2n-18}.	Anthracenes.	Anthracene, retene.	“
C_nH_{2n-20}.		Fluoranthene.	“
C_nH_{2n-22}.		Pyrene.	“
C_nH_{2n-24}.		Chrysene.	“
C_nH_{2n-26}.		Dinaphthyl.	“
C_nH_{2n-28}.			
C_nH_{2n-30}.	Picenes.	Picene, Benzerythrene.	Lignite tar, California petroleum, coal-tar.

Methanes, Paraffins, C_nH_{2n+2}.

Methane, marsh gas, CH_4, is produced in the decomposition of vegetable matter under restricted access of oxygen. It occurs in large amount in the emanations from marshes and shallow pools, in the atmosphere of mines, and in natural gas and common illuminating gas. It does not need special consideration here.

The liquid homologues of methane are found in petroleum, and the highest members are substances known as *ozokerite, hatchettite, mineral tallow, mineral wax, cerasin,* and *paraffin wax.*

The term "*paraffin*" (*parum affinis,* little affinity) was applied to some of the solid homologues on account of their indifference to chemical agents. All the members of the methane series are saturated hydrocarbons, and therefore show no tendency to combine with other bodies. All above *tritane,* C_3H_8, are capable of isomeric modification, the isomers having different boiling points and specific gravities, and yielding different products on oxidation. Pentane contains 83·33 per cent. of carbon, and the proportion rises very gradually with the number of carbon atoms; paraffin of the composition $C_{25}H_{52}$ containing 85·23 per cent. of carbon.

The methanes containing a small number of carbon atoms are gaseous at ordinary temperatures; the intermediate ones are liquid, their viscosity, specific gravity, and boiling point rising with each increment in the number of carbon atoms. $C_{20}H_{42}$ and the higher homologues are solids.

The following synopsis of the important data in regard to all isomeric forms from tritane to hexane, and of the normal forms from heptane upward, is taken from Richter's *Organic Chemistry:*

		Structural Formula.	Boiling point at less than 760 mm. (°C).
C_3H_8	Tritane	$CH_3 . CH_2 . CH_3$	— 45°
C_4H_{10}	Normal tetrane	$CH_3 . CH_2 . CH_2 . CH_3$	+ 1°
	Trimethyl Methane	$CH_3.CH(CH_3)_2$	— 17°
C_5H_{12}	Normal Pentane	$CH_3.(CH_2)_3.CH_3$	+ 38°
	Dimethyl-ethyl Methane	$CH_3.CH_2.CH(CH_3)_2$	+ 30°
	Tetramethyl Methane	$C(CH_3)_4$	+ 10°
C_6H_{14}	Normal Hexane	$CH_3(CH_2)_4CH_3$	+ 71°
	Methyl diethyl Methane	$CH_3(C_2H_5)_2CH$	+ 64°
	Dimethylpropyl Methane	$CH_3.CH_2.CH_2.CH(CH_3)_2$	+ 62°
	Di-isopropyl	$(CH_3)_2.CH.CH.(CH_3)_2$	+ 58°
	Trimethyl ethyl Methane	$CH_3.CH_2.C(CH_3)_3$	+ 43—48°

		Melting Point.		B.P.	Sp. Gr.	
Heptane,	C_7H_{16}	. . .		98.4°	0.7006(0°)	
Octane,	C_8H_{18}	. . .		125.5°	0.7188(0°)	
Nonane,	C_9H_{20}	— 51°		149.5°	0.7330(0°)	
Decane,	$C_{10}H_{22}$	— 32°	Under 760 mm. pressure.	173°	0.7456(0°)	
Undecane,	$C_{11}H_{24}$	— 26.5°		194.5°	0.7745	at their m. p.
Dodecane,	$C_{12}H_{26}$	— 12°		214°	0.773	
Tridecane,	$C_{13}H_{28}$	— 6.2°		234°	0.775	
Tetradecane,	$C_{14}H_{30}$	+ 5.5°		252.5°	0.775	
Pentadecane,	$C_{15}H_{32}$	+ 10°		270.5°	0.775	
Hexadecane,	$C_{16}H_{34}$	+ 18°		287.5°	0.775	
Heptadecane,	$C_{17}H_{36}$	+ 22.5°		303°	0.776	
Octadecane,	$C_{18}H_{38}$	+ 28°		317°	0.776	
Nonadecane,	$C_{19}H_{40}$	+ 32°		330°	0.777	
Eicosane,	$C_{20}H_{42}$	+ 36.7°	Under 15 mm. pressure.	205°	0.777	
Heneicosane,	$C_{21}H_{44}$	+ 40.4°		215°	0.778	
Docosane,	$C_{22}H_{46}$	+ 44.4°		224.5°	0.778	
Tricosane,	$C_{23}H_{48}$	+ 47.7°		234°	0.778	
Tetracosane,	$C_{24}H_{50}$	+ 51.1°		243°	0.778	
Heptacosane,	$C_{27}H_{56}$	+ 59.5°		270°	0.779	
Hentriacontane,	$C_{31}H_{64}$	+ 68.1°		302°	0.780	
Dotriacontane,	$C_{32}H_{66}$	+ 70.0°		310°	0.781	
Pentatriacontane,	$C_{35}H_{72}$	+ 74.7°		331°	0.781	
Dimyricyl,	$C_{60}H_{122}$	+ 102°		. . .	. . .	

The methanes are unaffected by chlorine or bromine in the dark—a character which distinguishes them from hydrocarbon of the ethene and ethine (acetylene) series. In sunlight, hydrochloric or hydrobromic acid and *chloro-* or *bromo-substitution* products are formed. The action takes place more readily at the boiling point than in the cold. Cold heptane readily absorbs chlorine in diffused daylight, becoming yellow. The liquid suddenly becomes very hot, and evolves torrents of hydrochloric acid. From this point it remains colorless, absorbs the chlorine quietly, and evolves hydrochloric acid continuously. In presence of a little iodine the action continues in the dark, but secondary products are readily formed.

The substitution-products obtained by the action of chlorine or bromine reproduce the original methanes under the influence of nascent hydrogen, and are converted into the corresponding alcohols on treatment with alkalies. Iodine has no direct action on paraffins, but substitution-products containing iodine can be obtained by indirect means. Thus, tri-iodomethane, or *iodoform*, CHI_3, is a product of the simultaneous action of iodine and an alkali on various organic bodies, such as alcohol or acetone. Concentrated sulphuric acid has but little action on the methanes. The lower homologues are unaffected by nitric acid, though interesting nitro-substitution-compounds ("nitro-paraffins") may be obtained indirectly. The higher members are not affected by even the strongest nitric acid in the cold, but solid paraffin is attacked by hot nitric acid even when dilute, and is acted on by chromic acid mixed with sulphuric acid.

Ethane occurs in admixture with methane in coal-gas, fire-damp, and the gases from petroleum wells.

Propane (*tritane*) and *butane* (*tetrane*) are found in considerable amount in petroleum gas. The latter paraffin forms the greater part of the product known as "*cymogene*." "Gasolene" is a far more volatile product, scarcely obtainable.

Pentane occurs, together with *isopentane*, in the most volatile portions of petroleum spirit, and in the products of the distillation of cannel coal and bituminous shale. Mixtures of pentane and air are used for producing standard flames for photometric purposes.

Hexane, *heptane*, and *octane* constitute the greater part of the liquid known in commerce as *petroleum naphtha* or "benzoline." Normal heptane exists in a state of approximate purity in the liquid obtained by distilling the terebinthinous exudation of *Pinus sabiniata*.

The higher paraffins require no separate description.

DETECTION AND DETERMINATION OF PARAFFINS.

Paraffins in the vaporous or gaseous state can be separated from hydrocarbons of the ethene and ethine (acetylene) series by treatment in the dark with excess of bromine. The paraffins remain unaffected, while the admixtures are converted into liquid bromine compounds. The same principle is also applicable to liquid mixture of paraffins and olefins. The unchanged paraffins may be separated from the olefin bromides by distillation in a vacuum.

When paraffins are heated with bromine and water for some time in sunlight, they are converted into bromo-substitution-compounds, half the bromine which enters into reaction being afterwards found as hydrobromic acid. This reaction is peculiar to paraffins, and may, under favorable circumstances, be employed for their recognition and quantitative determination.

Liquid paraffins may also be separated from hydrocarbons of other series by treating the mixture first with sulphuric acid, as long as the acid becomes colored, and then with fuming nitric acid, avoiding rise of temperature. Other bodies are oxidised, or converted into nitro-compounds which remain dissolved by the acids or are much less volatile than the unaltered paraffins. After washing with water, drying over caustic potash, and rectification over sodium, a distillate of pure paraffins is obtained. A practical use of this principle is sometimes made in analysis.

R. Höland (*Abst. J. S. C. I.*, 1894, 286) obtained good results in the analysis of mixtures of brown-coal tar containing known amounts of methanes by dissolving 20 grm. of the substance in 100 c.c. of absolute alcohol, cooling the solution for two hours in ice, and collecting the separated solid by filtering through a double filter. If the amount of paraffin is less than 20 per cent., it is advisable to concentrate the oil by distillation.

Ethenes, Methenes. *Olefins.* C_nH_{2n}.

Ethene, ethylene, or *olefiant gas,* C_2H_4, is the lowest known member. The first three members are gaseous at ordinary temperatures. The liquid olefins are oily bodies, lighter than water, and insoluble in it, but miscible with ether, chloroform, carbon disulphide, benzene, and fixed and volatile oils. They are not readily affected by dilute acids or alkalies, but are far more susceptible of chemical change than the corresponding paraffins. By the action of nascent hydrogen the olefins are converted into the corresponding *paraffins.*

By treatment with hydrochloric, hydrobromic, or hydriodic acid in saturated aqueous solution, the olefins are converted with more or less facility into the corresponding derivative of the methyl series. Thus *tetrene,* C_4H_8, when heated with hydriodic acid, forms *isotetryl iodide,* C_4H_9I. The reaction occurs most readily with hydriodic acid, and least so with hydrochloric acid.

The olefins form with hypochlorous and hypobromous acids, monochlorinated alcohols (*e. g.*, $C_2H_4 + HClO = C_2H_4ClOH$), which are converted into alcohols of the methyl series by nascent hydrogen.

By treatment with chlorine, bromine, or iodine, even in the dark, the olefins are immediately converted with evolution of heat into additive-compounds containing two atoms of the halogen. This important reaction is common to the whole series. These compounds are oily liquids, in each case of higher boiling point than the original olefin. The reaction is of value for the detection and estimation of olefins in presence of other hydrocarbons. By treating the bromides with silver or potassium acetate, *olefin acetates* are formed, which on distillation with an alkali yield the corresponding *glycols.*

By treatment of the lower olefins with sulphuric acid, *esters of the methyl series* are produced with more or less facility. Thus, by the action of sulphuric acid on ethene, *ethylsulphuric acid,* $C_2H_5.HSO_4$, is formed. These compounds, on distillation with water, yield alcohols. *Sulphonic acids* are also formed by treating the higher olefins with sulphuric acid, but the reaction is complicated by oxidation of the olefins, and by their tendency to become polymerised. The formation of polymers occurs to a considerable extent when shale oil is treated with sulphuric acid of 1·70 specific gravity. Acid of 1·845 specific gravity acts as a powerful oxidising agent, at the same time partially converting the oil into crystallisable sulphonates soluble in cold water, but decomposed on heating.

By treatment with fuming nitric acid, olefins suffer oxidation with more or less facility, forming in some cases unstable *nitro-compounds.* The reaction with nitric acid may be employed for separating olefins from paraffins.

Olefins are oxidised by potassium permanganate or chromic acid to glycols, which may be subsequently converted into acids. Thus, ethene yields ethene-glycol, $C_2H_4(HO)_2$, and then formic and oxalic acids.

Determination of Olefins.

The only method practically available for the direct and accurate determination of olefins, when in admixture with hydrocarbons of other series, is based on the facility with which they unite with the halogens, especially bromine, or on their absorption by fuming sulphuric acid.

For the estimation of the *gaseous olefins,* as existing in coal-gas, a known measure of the gas is introduced into a graduated Cooper's tube, care being taken that the water which is displaced has been previously saturated with gas of the same quality. Bromine is then dropped into the water which remains in the curved part of the tube, the tube closed with a stopper or the thumb, and the contents well agitated. On opening the tube under water, the diminution of the volume of the gas will indicate that olefins have been absorbed, and, on observing the water, oily globules of $C_2H_4Br_2$ will be perceived. These should be red or yellow in color; if colorless, more bromine must be added and the agitation repeated.

The tube being again opened under water, a small piece of caustic soda is added to absorb free bromine, and the tube agitated once more. The tube is then immersed in a cistern having glass sides, so that the volume of the residual gas can be read off when the water in the cistern is on the same level with that in the tube. The loss of volume, duly corrected, if necessary, for temperature, &c., gives the hydrocarbons absorbable by bromine.

Satisfactory determinations of olefins can be made by means of Hempel's gas-burette or Lunge's nitrometer. Hempel (*Methods of Gas Anal.*) states that the sulphuric acid method is the most accurate.

When the proportion of olefins is small, a known measure of the gas can be caused to bubble through a solution of bromine in carbon disulphide.

For the determination of the olefins in *liquid hydrocarbons* the bromine-reaction is still available, but the method of operating must be modified. The following modification of the process of Mills and Snodgrass (Vol. II, Part 1, p. 63) has been extensively employed in the author's laboratory and found very useful for the examination of commercial products from shale and petroleum. An approximately decinormal solution of bromine is made by dissolving 2 c.c. of bromine in 750 c.c. of recently distilled carbon disulphide. This solution, which keeps well in the dark, is rendered perfectly anhydrous by the addition of some lumps of dry calcium chloride. An accurately weighed or measured quantity of the dry hydrocarbon, weighing between 0·3 and 1·0 gram, or a measure of a solution of the oil in carbon disulphide containing a known weight of the hydrocarbon, is then placed in a perfectly dry stoppered flask or separator, the solution diluted, if necessary, with carbon disulphide (kept over calcium chloride) to about 25 c.c., and then 25 c.c. of the carbon disulphide solution of bromine added. The flask is then closed, and the contents agitated. If the liquid is distinctly red, sufficient bromine has probably been added, but should the solution be nearly or quite decolorised, a further addition of a known measure of the bromine solution should be made without delay. The flask is then at once placed in the dark and kept there for a quarter of an hour, when an excess of an aqueous solution of potassium iodide is poured in, the contents agitated, the flask removed to a light place, and the solution titrated with a decinormal solution of sodium thiosulphate, 24·8 grams of crystallised salt per litre). The end of the reaction is indicated by the decolorisation of the carbon disulphide, and is rendered sharper by adding a few drops of starch solution towards the end of the titration.

Twenty-five c.c. of the carbon disulphide solution of bromine is then placed in a similar flask, potassium iodide solution added, and the titration with thiosulphate conducted as before. The difference between the volume of standard thiosulphate now required and that previously employed for the titration in presence of the hydrocarbon is the measure of thiosulphate corresponding to the bromine which has combined with the unsaturated hydrocarbons present. One c.c. of decinormal thiosulphate corresponds to 0·008 gram of bromine. The bromine solution keeps for a considerable time without change, and hence the verification of its strength is only occasionally necessary.

It is absolutely necessary not to expose the hydrocarbon to the action of bromine in presence of strong light. Even a very moderately diffused daylight is prejudicial, but gaslight has no sensible effect. Fifteen minutes should be allowed for the completion of the reaction. If much exceeded, secondary reactions are liable to occur, which give results in excess of the truth, more or less hydrobromic acid being usually produced, the amount increasing with the time allowed for the reaction. On the other hand, the reaction with bromine is sometimes not completed immediately. McArthur (*J. S. C. I.*, 1888, 65) points out that moisture must be rigorously excluded, the bromine added must be twice the quantity required for absorption (ascertained by a preliminary experiment), and the oil solution must be diluted with carbon disulphide to three times the volume of the bromine solution that is to be added.

The foregoing process gives tolerably concordant results, and has been adopted by the author in place of a method described by himself, in which the bromine was employed in aqueous solution. In its simplest form this process is conducted exactly in the manner of that just described, except that approximately decinormal aqueous bromine is used, instead of a carbon disulphide solution of that element, and the potassium iodide solution is added directly after the oil has been thoroughly shaken up with the bromine water. If the bromine compounds formed are viscous and adhere strongly to the sides of the flask, so as to hinder the action of the bromine water, a few centimeters of carbon disulphide may be added, by which the oils will be dissolved, and may be brought in contact with the bromine water by agitating. This method gives fairly constant results, but they do not represent simply the bromine assimilated by the unsaturated hydrocarbon, &c., of the sample, as oxidation also occurs to a very sensible extent. The results yielded are therefore in excess of those obtained by the carbon disulphide process, but they are fairly comparative, and for works-assays of shale and petroleum products the method will be found of service.

Owing to the complex character of commercial hydrocarbons, a determination of the amount of bromine combining with them does not give the means of calculating the percentage of olefins present. If, however, a fraction of constant boiling point be prepared and its vapor-density ascertained, its mean combining weight could be deduced, and a determination of its power of assimilating bromine would give a means of obtaining a close approximation to the proportion of olefins contained in the fraction. This suggested method assumes that the fraction consists essentially of paraffins and olefins. Any admixture of hydrocarbons of other series would further complicate the problem.

On this account it is preferable in practice to express the results of titrations as bromine-absorptions; that is, in grams of bromine assimilated by 100 grams of the oil. If a known measure of the sample has been employed, the number of grams of bromine taken up by 100 c.c. must be divided by the density of the sample to ascertain the bromine assimilated by 100 grams.

It must be borne in mind that, besides olefins, many other substances, both hydrocarbons and oxygenated bodies, assimilate bromine, and hence the "bromine-absorption" of a complex mixture arises from several sources. Nor does the bromine assimilated by bodies other than olefins bear a constant relation to their molecular weight. Thus the hydrocarbons of the acetylene (ethine) series absorb either Br_2 or Br_4, and the latter proportion is also assimilated by terpenes. Oleic acid reacts with Br_2, linolic acid with Br_4, and phenol with Br_6, a bromo-substitution-product being formed in the last case. The results yielded by these bodies are described in the sections on oleic acid, turpentine oil, phenol, &c.; and determinations of the bromine-absorptions of shale and petroleum products, rosin oil, and resins will also be found duly recorded.

It is possible to determine the iodine-absorption of hydrocarbons by Hübl's method, which gives results comparable with those obtained by bromine if the former be multiplied by the factor 0·63.

The process is not well adapted for the examination of hydrocarbons, as the reaction may not be complete in less than twenty-four hours.

Ethines, Acetylenes, C_nH_{2n-2}.

The substances corresponding to this general formula may be based upon two structurally different arrangements. In one form it is assumed that one triple linking exists; in the other, that a double union occurs twice, thus:

$HC\equiv C—CH_3$	$H_2C=C=CH_2$
Tritine (allylene).	Isotritine (isoallylene).

These structural differences are indicated by the difference in deportment with chemical agents. Those having the triple union are considered the true acetylenes. They form silver and copper compounds; the others do not. The higher members are readily polymerised with sulphuric acid of 1·7 sp. gr. With bromine they form $C_nH_{2n}\ {}_2Br_2$ and $C_nH_{2n-2}Br_4$.

The formation of a copper compound is one of the important properties of ethines. To prepare this a solution of ammonio-cuprous oxide should be made by treating copper-turnings in a separator with strong ammonia in presence of a limited quantity of air, until the blue liquid first formed has become colorless. The reagent is then run from the tap into a U-tube fitted with a tube bent twice at right angles, the open end of which dips under water, so as to prevent contact of air. On passing a gas through the cuprous solution, a yellow or red precipitate will be produced if ethines be present. If the precipitate be filtered from the liquid and treated with strong hydrochloric acid, the ethine will be liberated. This reaction furnishes a means of isolating acetylene and its homologues in a condition of purity. On treating the cuprous compound with ammonium hydroxide and zinc, the corresponding olefin will be produced, and may be identified by the proportion of bromine with which it unites.

The silver-derivatives of the ethines may be obtained by substituting an ammoniacal solution of silver nitrate for the cuprous solution. A solution prepared by dissolving cuprous or silver chloride in ammonium hydroxide *absorbs* ethines, but some of the hydrocarbons are not *precipitated* by such a reagent, owing to their metallic derivatives being soluble in ammonium hydroxide containing ammonium chloride.

By passing coal-gas through a cuprous solution, a copious copper-red precipitate is readily produced, the probable formula of which is $C_2H_2Cu_2O$. By passing a current of hydrogen through warm coal-tar naphtha, shale naphtha, or "first runnings," and then through the cuprous reagent, a yellow precipitate, consisting chiefly of the cuprous compounds of tetrine and pentine, is formed. It must be borne in mind that the house-gas supplied in American cities is largely, often entirely, the so-called water-gas, consisting of carbon monoxide and hydrogen, enriched with petroleum products.

ACETYLENE, C_2H_2, has come into prominence lately as an illuminating agent. It may be prepared in various ways, but the only one of moment is the action of water on calcium carbide, by which calcium hydroxide and acetylene are the only products. Acetylene is a colorless gas with a faint ethereal odor. It is usually regarded as highly poisonous, but several investigators deny this. As prepared from commercial calcium carbide it is quite impure, and the disagreeable odor and poisonous action attributed to the acetylene itself are due to the impurities, especially hydrogen phosphides and sulphur compounds. The statement that acetylene causes the odor and annoyance developed by the imperfect combustion of illuminating gas, as when a Bunsen burner "strikes back," is, therefore, not correct. The following data concerning the manufacture and properties of commercial acetylene are mostly taken from a paper by H. Fowler:[1]

One pound of pure calcium carbide will require 0·562 lb. of water and yield 1·156 of slaked lime and 0·4064 of acetylene, equal to 5·5857 cu. ft. at 0° C. and 760 mm. The yield of good commercial carbide is about 5 cubic feet per pound. Water dissolves about 1·1 times its volume, but a saturated solution of common salt dissolves only about 0·05 volumes. Alcohol dissolves about 6 volumes and paraffin about 2·5; acetone dissolves a large amount. Since the density of acetylene is nearly that of air, it diffuses slowly, hence the danger of formation of explosive mixtures in the neighborhood of a leak. The most violent explosion is produced by a mixture containing 8·37 per cent. by volume of the gas. Acetylene is liquefied at 0° C. by a pressure of 21·5 atmos-

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[1] *Proc. of the (British) Institute of Civil Engineers*, No. 3093, Mar. 1898.

pheres; at 20° C. by a pressure of 42·8 atmospheres. The critical temperature is 37·05° C. at 68 atmospheres.

Liquid acetylene has a sp. gr. of 0·4, and is highly expansible. It is liable to explosive dissociation. The conditions under which this occurs have been extensively studied. Berthelot and Vielle placed 18 grm. of acetylene in a small flask and fired the mass by means of a wire rendered incandescent by an electric current. The pressure rose to 5638 atmospheres, and the carbon was left as a lump with brilliant surface and conchoidal fracture. Explosion may also be brought about by fulminating powder, and even by friction. The presence of spontaneously inflammable hydrogen phosphide (PH_2) is said to have been the cause of at least one explosion. To remove this objectionable ingredient, Pictet uses a washing solution of strong calcium chloride, and then a lead salt at —16° C., but even this treatment may not remove all the phosphorus. The following are analyses of ordinary acetylene:

	FOWLER.	OUTON.
Acetylene, ...	95·6	98·74
Hydrogen sulphide, ...	trace	1·03
Hydrogen phosphides, ...	0·038	0·23
Ammonia, ...	0·03	——

According to Chevastelon (*Abst., J.S. C. I.*, 1897, 828), acetylene can be determined by titrating the free nitric acid produced by the action of the gas on a solution of silver nitrate. The reaction is represented as follows:

$$C_2H_2 + 3AgNO_3 = C_2Ag_2NO_3 + 2HNO_3.$$

The mixture must not contain any gases which react with nitric acid or which are themselves acid in character. The only data necessary for the calculation are the volume, temperature, and pressure of the gas, and the final volume and acidity of the liquid. The operation may be performed in a Raoult eudiometer, 20 c.c. of a ten per cent. solution of silver nitrate sufficing for a 60 c.c. eudiometer, distilled water being afterward run in until the pressure is equalised.

The most serious impurity of acetylene, as prepared by the action of water on commercial calcium carbide, is hydrogen phosphide, which, like ammonia, appears to favor the formation of the explosive copper acetylide, and, if present in notable quantity, may render the gas spontaneously inflammable. The hydrogen phosphide may be determined by passing the gas, as it is liberated, through a solution of sodium hypochlorite, and precipitating the phosphoric acid formed by means of magnesia mixture. If care be taken that all the reagents are free from sulphates, the hydrogen sulphide in the acetylene may be determined by acidifying the filtrate from the magnesium precipitate and adding barium chloride. It should be observed that the amount of hydrogen sulphide in different specimens of acetylene yielded by the same calcium carbide varies considerably, according to the conditions obtaining at the time of preparation. Moreover, the whole of the sulphur in the gas does not exist as hydrogen sulphide.

P. Wolff (*Chem. Zeit.*, xxii, 281) states that the tendency of acetylene to produce soot can only be avoided by the use of special burners, and that the employment of hypochlorites for removal of hydrogen phosphides, as recommended by Lunge and Cedercreutz, will involve danger when notable amounts of ammonia are present in consequence of the formation of nitrogen chloride. The ammonia should be first removed by thorough washing. Chlorine and moisture may be removed by subsequent treatment with lime. Acetylene thus purified has a faint ethereal odor, and does not attack copper or copper alloys. The stains on copper fittings when common acetylene is used are due to copper phosphide.

Lewes (*J. Gas Lighting*, Nov. 30, 1897) states that acetylene is much safer when diluted with other combustible gases. The best diluent is a mixture of 30 per cent. methane with hydrogen, carbon monoxide, or both. This diluting gas when mixed with ten per cent. of acetylene is a convenient substitute for coal-gas.

Hempel and Kahl (*Zeit. f. Ang. Chem.*, 1898, 53) suggest a volumetric method for determining hydrogen phosphide in acetylene. A solution of 15·6 grams of copper sulphate ($CuSO_4$, $5H_2O$) in 100 c.c. of water, to which were added 5 c.c. of dilute sulphuric acid (1 volume of concentrated acid to 4 volumes of water), was found to be the best absorbent. One c.c. of the solution absorbed 8·8 c.c. of hydrogen phosphide and 0·2 c.c. of acetylene from 100 c.c. of each gas. In the presence of mercury and excess of the solution of copper sulphate, the diminution of volume resulting from the absorption of hydrogen phosphide exactly corresponded to four times the volume present. Hydrogen phosphide produced by heating an alcoholic solution of caustic potash with ordinary phosphorus was mixed in various known proportions with nitrogen, and the phosphide determined. The mean value was 52·4 per cent., and mixtures of known volumes of this mixture and acetylene were examined by agitating it for three minutes, in a pipette sealed with mercury, with 3 c.c. of the copper sulphate solution. It was assumed that the hydrogen phosphide amounted to one-fourth of the diminution of volume. The test analyses were satisfactory.

Detection of Acetylene in Cases of Poisoning.—D. Vitali (*Abst. Analyst*, 1898, 11) recommends the following method: A sample of blood is mixed with 5 or 8 per cent. of pure dry acetone, placed in a retort, and distilled into an empty condenser and a set of absorbing bulbs containing more acetone. The retort is heated on a water-bath, the condenser and bulbs kept cold in ice. The acetone passes over, carrying the acetylene with it, and the latter may be identified by its characteristic reactions. Hydrogen sulphide and phosphide, which often occur in the crude gas, also dissolve in the acetone, and can be sought for therein.

Calcium carbide is prepared by the action of an electric current upon a mixture of quicklime and carbon (coke or anthracite coal). Pure calcium carbide is brown, but the commercial form is a hard, grayish, slag-like mass, which, when exposed to the air, usually emits an odor of hydrogen phosphide, and slowly crumbles to a dry powder. It is often irregular in quality. A considerable proportion of free carbon may often be observed in it, and great care must be taken in sampling. Water acts violently on calcium carbide, but a strong aqueous solution of zinc chloride acts much more slowly. Calcium carbide may be used for the detection and estimation of water in alcohol, since absolute alcohol is without action upon it.

A method for the assay of calcium carbide has been published by Lunge and Cedercreutz (*Abst. J.S. C.I.*, 1897, 1046). One hundred grams of the material should be used. The apparatus is a gas holder having a capacity of forty liters. A saturated solution of common salt should be employed as a seal. In exact work this must be previously saturated with acetylene. If plain water be used as a seal, a correction must be made for the acetylene absorbed. The reaction is most conveniently carried out in an apparatus arranged to cause the carbide to fall into the salt solution by degrees, but the reverse process may be employed.

Two samples of calcium carbide examined by Lunge and Cedercreutz evolved, as the mean of several tests, 0·1435 grm. (94·1 c.c.)

and 0·338 grm. (222 c.c.) of hydrogen phosphide per kilogram of carbide respectively.

Separation of Various Hydrocarbons.

The separation of individual hydrocarbons from complex mixtures is often effected by processes of fractional distillation, fusion, &c. Basic substances may be removed by agitation with diluted sulphuric acid, and phenoloid and acid bodies by treatment with caustic soda. The residual hydrocarbons, even when of perfectly constant boiling and melting points, often contain, however, several isomeric hydrocarbons of the same series, as well as members of several isologous series.

The analysis of mixtures of *hydrocarbons of different series* is usually difficult, especially when their fusing and boiling points are approximately the same, in which case the methods of fractional fusion and distillation are not available. The following principles may be successfully applied to the analysis of complex mixtures which have been previously treated by fractional distillation, &c., so as to reduce them to approximately parallel products:

The hydrocarbons of the *methane series* are not acted on by bromine in the dark or in diffused daylight; but the hydrocarbons of most other series form compounds having higher boiling points than the original bodies. Hence the paraffins may be separated from the resultant bromo-compounds by fractional distillation, preferably conducted under reduced pressure, or in a current of steam. The *olefins* form dibromides, from which, as also from the bromides of other series, the original hydrocarbons may be regenerated by warming with alcohol and a copper-zinc couple.

By treatment with bromine and water in sunlight, the paraffins are converted into monobromo-substitution-products, the aqueous liquid containing an amount of bromine, in the form of hydrobromic acid, equal to that which has entered into the hydrocarbon. By separating the aqueous liquid, removing free bromine by agitating with shale naphtha, and estimating the hydrobromic acid formed, a determination can be made of the amount which has combined with the paraffins present.

By treatment at 100° C. with concentrated sulphuric acid of 1·845 specific gravity, all hydrocarbons except those of the paraffin series are oxidised, polymerised, or converted into sulphonic acids. On adding water or solution of sodium hydroxide, separating the residual oil from the aqueous liquid, and distilling the former, the unchanged paraffins will pass over, while the polymerised olefins, terpenes, &c., will not distil until a much higher temperature is reached. From the aqueous liquid, acidulated if necessary, many of the hydrocarbons which form soluble sulphonic acids (*e. g.*, benzene, toluene, &c.) may be recovered by distillation with steam. In many cases it is better not to employ very concentrated sulphuric acid, but to treat the hydrocarbons repeatedly with a mixture of 2 measures of strong acid (sp. gr., 1·845) to 1 measure of water until no further action takes place, and then with a stronger acid (4 acid : 1 water).

All hydrocarbons except those of the paraffin series are readily attacked by warm nitric acid of 1·45 specific gravity. In some cases nitro-compounds are formed, while in others products of oxidation result. The nitro-compounds distil at a higher temperature than the hydrocarbons from which they are derived.

Acetylene and some other hydrocarbons of that and the next series form metallic compounds on treatment with an ammoniacal solution of cuprous chloride, or of silver nitrate. These derivatives are solid bodies, insoluble in water, but decomposed by hydrochloric acid with liberation of the original hydrocarbon.

The hydrocarbons of the naphthalene series and many of the subsequent series form with picric acid and other nitro-compounds characteristic crystalline compounds, which may be decomposed by alkalies with formation of the original hydrocarbons.

Destructive Distillation.

Non-volatile organic substances heated without access of free oxygen undergo complex decomposition, by which volatile products escape and a residue of carbon, more or less pure, is left. If the body consists only of carbon, hydrogen, and oxygen, the last two elements are found in the distilled portions, together with the greater part of the carbon. Sulphur and nitrogen are also principally converted into volatile compounds. Slow heating will sometimes produce volatilization with little or no change. The nature and proportions of the bodies obtained will be dependent on the character of the substance distilled, the temperature of the retort, and other conditions. When the heat is moderate, methanes are chiefly produced; but as the higher members of this series readily split up into lower members and ethenes, the latter bodies are nearly always present. By further degradation ethines are formed, whilst benzene and its homologues contain a still smaller proportion of hydrogen.

When the temperature is high, hydrogen, ethine, benzene, and naphthalene are the chief unoxygenated products. Thus, *coal* being distilled at a high temperature for the manufacture of coal-gas, the condensable hydrocarbons consist chiefly of benzene and its homologues, and naphthalene. At a somewhat lower temperature the hydrogen and acetylene disappear, together with most of the naphthalene, while chrysene and a larger proportion of benzene are formed.

At a dull red heat, such as is employed for the distillation of bituminous shale, the liquid products are wholly free from benzene and naphthalene, whilst little or no hydrogen or acetylene is present in the gases. On the other hand, the distillate is rich in methanes and ethenes, with some anthracene and chrysene; the oxygenised and nitrogenised products consist chiefly of substances of the formula $C_nH_{2n-7}OH$, and other phenoloid bodies, and bases of the formula $C_nH_{2n-5}N$ (pyridine bases), although the corresponding series, C_nH_{2n-6},—*i. e.*, benzene and its homologues,—is almost wholly absent.

When *wood* is subjected to dry distillation, the volatile products are practically free from compounds of nitrogen and sulphur. The watery portion of the distillate from wood, peat, and lignite has an *acid* reaction, owing to the presence of acetic acid. In other respects the products of the distillation of wood, as ordinarily conducted, are a mixture of low- and high-temperature products.

When the temperature of the distillation is low, a large yield of liquid products is usually obtained, together with a small yield of gas of high illuminating power. At a high temperature a maximum production of gas of low illuminating power results, while the proportion of liquid products is small. The higher the temperature of the retort, the larger the percentage of solid carbonaceous residue (coke or charcoal) left in it.

The three cases afforded in practice by the treatment of coal, shale, and wood may be regarded as typical of the changes attending the destructive distillation of organic substances, though others, such as bone, rosin, and oil, yield special products of some practical interest. Too much stress cannot be laid on the fact that the nature of the products depends not only on the nature of the substance treated, but also on the circumstances under which the operation is conducted with regard to temperature and other conditions.

The following table indicates the general nature of the more prominent volatile organic products of the dry distillation of coal (for the manufacture of illuminating gas), bituminous shale, and wood, *as the processes are carried on in practice.* To facilitate comparison, the leading constituents of American petroleum are shown in juxtaposition:

ORGANIC PRODUCTS.	COAL.	BITUMINOUS SHALE.	WOOD.	PETROLEUM.
Hydrogen,	Large,	Traces,	Large,	Present.
Gaseous Hydrocarbons.				
Methanes,	Large,	Large,	Large,	Present.
Ethenes,	Large,	Large,	Considerable,	Present.
Ethine,	Present,	None.	. . .	. . .
Liquid and Solid Hydrocarbons.				
Liquid methanes,	Small,	Large,	Absent,	Very large.
Solid paraffins,	Traces,	Considerable,	Present,	Moderate.
Liquid ethenes,	Small,	Very large,	. . .	Considerable.
Liquid pseudolefins,	. . .	. . .	. . .	Present.
Liquid acetylenes (ethines),	Present,	Present.	. . .	. . .
Benzenes,	Large,	Trace,	Moderate,	Present.
Naphthalene,	Large,	None,	Moderate,	None.
Anthracene,	Moderate,	Trace,	. . .	Present.
Chrysene,	Moderate,	Considerable,	Present,	Present.
Oxygenated Bodies.				
Acetic acid,	Present,	Present,	Large.	. . .
Methyl alcohol,	None,	. .	Considerable.	. . .
Phenols,	Large,	Considerable,	Moderate.	. . .
Oxyphenols (creosote),	. . .	Large,	Large.	. . .
Nitrogenised Bodies.				
Ammonia,	Considerable,	Considerable,	None.	. . .
Aniline bases,	Present,	None.	. . .	. . .
Pyridine bases,	Considerable,	Considerable.	. . .	. . .
Acridine,	Present.	. . .	. . .	. . .
Carbazol,	Present.	. . .	. . .	. . .
Sulphur Compounds,	Present,	Present,	None,	Present.

It will be seen from this table that the products of the distillation of each of the raw materials contain certain characteristic bodies. Thus, oxygenated products are found most largely in the products of the distillation of wood; paraffins are *especially* characteristic of petroleum; olefins, and, to a lesser extent, paraffins, of the distillation of shale; whilst coal tar, as obtained in the manufacturing of illuminating gas, is remarkable for the comparatively large proportion of benzene and naphthalene contained in it.

TARS.

By the destructive distillation of organic bodies and bituminous minerals three classes of products are generally obtained—namely, gas, watery liquid, and a viscid, dark-colored oil or tar. The methods of assaying the gaseous products do not come within the scope of this work. The watery liquid from wood, peat, and lignite is acid, and its examination is described in Volume I. The watery liquid from the distillation of coal, shale, and bones is strongly alkaline, the first of these constituting the "ammoniacal liquor" of the gas-works.

TAR is a brown or black viscid, oily liquid, of a more or less characteristic odor, according to its origin. The composition of tar varies widely according to its source and the conditions of distillation. Wood, peat, and lignite tars are acid; coal, bituminous shale, and bone tars are alkaline. On repeatedly agitating the tar with water, the soluble matters to which the acid or alkaline reaction was due may be more or less completely removed.

All tars consist largely of hydrocarbons, but oxygenised and nitrogenised bodies are sometimes present in considerable proportion. All tar, being of very complex composition, and consisting in the main of volatile bodies, the most instructive method of examining it consists in subjecting it to careful distillation, collecting apart the distillates obtained at different temperatures, and subsequently fractionating these products with the view of effecting a more perfect proximate analysis of the material. Toward the end of the distillation the tar remaining in the retort becomes more and more viscous, and if allowed to cool, sets to a solid, brittle, jet-black mass known as *pitch*. If the distillation be pushed further, *coke* is obtained.

Tar frequently contains a considerable proportion of water which should be separated as far as possible before distillation. This is best effected by giving the mass an occasional gyratory motion, and removing each quantity of water by decantation as it separates. Water causes tar to froth during distillation.

For the method of conducting the distillation, no general instructions can be given; much depends on the character of the tar, the information desired, the scale on which the operation is to be conducted, and other conditions. The process should be conducted in the simplest suitable apparatus, and the distillate collected in a very moderate number of fractions, all refinements of fractional distillation being reserved for the treatment of the products first obtained. In the first distillations the more volatile constituents are retained in the retort by those of higher boiling point, and it is only after being separated tolerably perfectly from these that they distil at temperatures approximating to their true boiling points.

The separation by fractional distillation having been carried out as far as appears desirable, a further proximate analysis of the different fractions may be made into basic, acid, and indifferent bodies. Thus, by agitating one of the fractions with dilute sulphuric acid, any basic bodies (*e. g.*, ammonia, methylamine, pyridine, acridine, &c.) will be dissolved in the acid liquid, and can be recovered by appropriate means. On agitating the residual oil with sodium hydroxide solution, first dilute, and then somewhat concentrated, any organic acids, phenols, or phenoloid bodies will be dissolved, and can be recovered by separating the alkaline liquid and adding a slight excess of dilute sulphuric acid. The neutral bodies which have not undergone solution either by the treatment with acid or with alkali consist essentially of hydrocarbons. Particular processes are suitable for special purposes. Thus, benzene may be crystallised out by subjecting the more volatile fraction of coal-tar naphtha to a freezing mixture; naphthalene readily separates from oils containing it, especially after removal of the phenols by caustic soda; while the presence of anthracene can be inferred from the formation of anthraquinone by the oxidation of a certain high-boiling fraction of the tar. The hydrocarbons of the different series may be successfully differentiated in many cases by their behavior with reagents, especially with bromine, nitric acid, and strong sulphuric acid, in the manner indicated on page 22.

The following sections contain detailed descriptions of the characters and methods of examining tar from bituminous shale and coal. Tars of some other origins are also briefly described.

Shale Tar. Crude Shale Oil.

The crude oily liquid obtained in the south of Scotland by the destructive distillation of bituminous shale is an olive-green, strongly-smelling, viscous liquid. The specific gravity of the product from the old form of retorts is 0·890 to 0·894, and from the new kind 0·865 to 0·870. The composition of shale oil has not been so thoroughly investigated as that of coal tar, but it has been proved to be of extremely complex nature, the following being among the more characteristic and important substances hitherto recognised in it:

Hydrocarbons of the Methane series; most of the members from C_4H_{10} to $C_{30}H_{62}$ being probably present.

Hydrocarbons of the Ethene series; most of the members from C_4H_8 to $C_{20}H_{40}$ being probably present.

Hydrocarbons of the Allylene (isoethine) series; e. g., C_6H_{10}, C_7H_{12}, and C_8H_{14}.

Hydrocarbons of the Benzene series; present only in minute amount, and probably often wholly absent.

Only traces of naphthalene and anthracene are found in shale tar, but notable quantities of pyrene and chrysene occur.

Nitrogenised bodies. Shale tar contains ammonia, a considerable proportion of pyrroline, and members of the pyridine series (especially coridine, rubidine, and viridine), but neither aniline nor any of its homologues has been detected.

Oxygenated bodies. Besides traces of acids of the acetic series, shale tar contains a notable proportion of phenols and oxyphenols analogous to those present in wood tar. Thymols and analogous bodies have been found in the fraction distilling between 215° and 290°.

Sulphur compounds exist in shale tar, but their exact nature has not been ascertained. Shales containing much sulphur give little paraffin wax on distillation, and a low yield of other products.

The method of treating shale tar on a large scale differs in different works, but consists essentially in repeated fractional distillations, alternated by treatment of the several fractions with sulphuric acid and sodium hydroxide, and sometimes sodium carbonate, together with refrigeration of the high-boiling fractions to cause the crystallisation of solid paraffin. This is separated from the adhering oil by pressure, and the crude paraffin scale which results is purified by appropriate methods.

ASSAY OF CRUDE SHALE OIL.

The examination of crude shale oil is frequently required, in order to ascertain the proportions of naphtha, burning oil, lubricating oil, and "scale" or crude paraffin wax it is likely to yield on a large scale. The assay is best made by treating a known quantity of the oil as nearly as possible in the same manner as that employed in the manufacturing process. For the following description the author is indebted to Mr. R. Tervet:

All statements of quantities refer to measures, and the paraffin scale is similarly expressed, the volume being calculated from the weight. When not otherwise described, the term "acid" signifies sulphuric acid of 1·85 specific gravity, and the term "soda" a solution of sodium hydroxide of the specific gravity stated in the appended parenthesis. The percentage proportions of acid and soda prescribed refer to 100 measures of the fraction to be treated, and not to 100 parts of the crude oil.

A. 1000 c.c. of the crude oil should be employed for the assay. The specific gravity should be noted, also the specific gravity and volume of the various products at each stage of the process. The oil is distilled to dryness with the aid of a current of steam, the distillate being collected in a capacious separator. The residue consists of *coke.*

B. The distillate or "once-run oil" is warmed to about 40° C. by immersing the separator in warm water. Any water which separates is tapped off, and the oil is treated with 5 per cent. by measure of sulphuric acid (sp. gr., 1·70) and agitated for not less than ten minutes, immersing the separator in water at about 35° C. to prevent any notable rise of temperature. After standing at this temperature for half an hour, the "acid tar" will have separated, and may be run off.

C. The acid-washed oil is next washed with 16 to 20 c.c. of soda (sp. gr., 1·30), and again kept warm for half an hour to allow the "soda tar" to separate, when it is run off.

D. The *once-purified oil* is then measured and its density observed. It is next transferred to a clean still, and again distilled to dryness, but the distillate is collected in two or more fractions, according to circumstances. These are (E) naphtha, (F) light oil, (G) heavy oil, and (H) still-bottoms. For the first product, only yielded at this stage by certain crude oils, the receiver should be changed when the distillate has a density of 0·780. The process is then continued until a drop of the distillate, caught on a well-cooled spatula as it falls from the neck of the retort, shows signs of solidifying, when the receiver is changed. The product to this point is (F) "crude light oil." Toward the end of the distillation for heavy oil a thick viscid product of a brown or yellow color is sometimes obtained, containing a large proportion of chrysene. When this product (H) appears, the receiver should be changed, for if allowed to get into the heavy oil it would prevent the paraffin scale from crystallising properly, and would effectually prevent the oil from being separated from the scale by pressure. The best plan is to add these objectionable *still residues* to the crude light oil (F), where it will be again treated with acid and alkali, which removes the chrysene, and the intermixed heavy oil will go back to the main quantity.

I. The *crude light oil* (F) from the last distillation is agitated with 2 per cent. of strong sulphuric acid, the acid separated, the oil washed with excess of soda (sp. gr. 1·36), and the alkaline solution separated. The mixture should not be warmed to promote the separation of the acid; the operation should be conducted at the ordinary temperature.

J. The washed light oil, after observing its measure and density, is distilled to dryness, the distillate being collected in three fractions, as before—namely, naphtha (up to sp. gr. 0·750) (K), light oil (M), and heavy oil. The last product should be added to G.

K. The *naphtha* may either be added to that obtained at a previous stage (E), and the density and total measure of the product observed; or, if not in large quantity, it may be added to the light oil.

O. The light oil, or *crude burning oil* (M), from the redistillation of K, after being mixed with any fractions obtained by redistilling the heavy oil, is washed with 2 per cent. of acid (sp. gr. 1·845) without warming and then agitated with excess of dilute soda (sp. gr., 1·020), when its specific gravity and volume are recorded as the yield of *finished burning oil* (P).

Q. The *crude heavy oil* (G), together with the fraction (N) obtained by redistilling the light oil, should next be poured into a flat-bottomed capsule or plate, and allowed to cool very slowly, in order that the crystals of paraffin may have time to develop. It is then further cooled to a temperature not above —3° C., and preferably as low as —12° C. The cooled cake is next wrapped up in a closely woven linen cloth, which has been previously saturated with lubricating oil. A gentle pressure is then applied until the bulk of the oil has drained out, after which the pressure should be increased until no more oil can be obtained. The *paraffin scale* (R) is then detached from the cloth and weighed.

S. The "*blue oil*" separated by pressure from the paraffin scale is washed first with 3 per cent. of strong acid, then with excess of soda (sp. gr., 1·33), measured and distilled to dryness, the products being burning oil (U), intermediate oil (V), and unfinished lubricating oil (W). The first of these is added to M for further purification.

V. The *intermediate oil* produced in the last process may either be added to the unfinished burning oil (O), or may, if thought requisite, be purified by washing in succession with 2½ per cent. of concentrated sulphuric acid and excess of weak soda (sp. gr., 1·020), when the measure gives the yield of *finished intermediate oil*, having a density of about 0·850.

W. The *unfinished lubricating oil* is similarly purified by treatment with 3 per cent. of sulphuric acid (sp. gr., 1·845) and excess of soda (sp. gr., 1·020), when the gravity and volume are noted as those of the *finished lubricating oil.*

The tabular arrangement on page 43 shows the process in a concise form, together with the densities and volumes of the products actually obtained in the assay of a sample of crude shale oil.

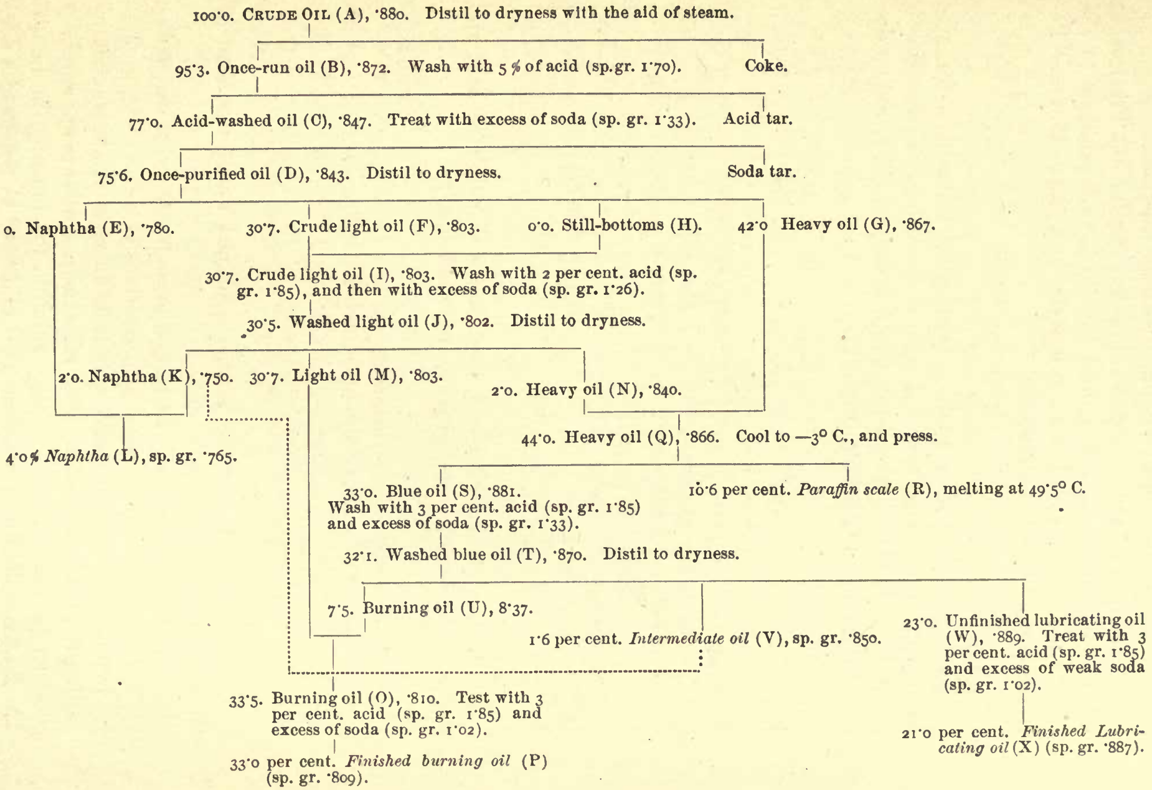
Thus the finished products from the sample examined were:

PRODUCT.	PER CENT.; BY MEASURE.	SPECIFIC GRAVITY.	MELTING POINT.
Naphtha,	4·0	·765	. .
Burning oil,	33·0	·809	. .
Intermediate oil,	1·6	·850	. .
Lubricating oil,	21·0	·887	. .
Paraffin scale,	10·6	. .	49·5
Total,	70·2		

If the naphtha obtained at the second stage (K) and the intermediate oil (V) were added to the burning oil, the volume of this would be increased to 36·6 per cent., without sensible alteration, while the yield of naphtha would be only 2 per cent. of 0·780 specific gravity. This is an unusually high figure for naphtha, 0·730 being about the average.

The method of assay described represents closely the process of treating shale oil adopted in practice, though differences in detail will be observed.

Instead of the foregoing method, it is sometimes sufficient to make a fractional distillation of the sample, collecting the distillate in


100·0. Crude Oil (A), ·880. Distil to dryness with the aid of steam.
95·3. Once-run oil (B), ·872. Wash with 5 % of acid (sp.gr. 1·70).
Coke.
77·0. Acid-washed oil (C), ·847. Treat with excess of soda (sp. gr. 1·33).
Acid tar.
75·6. Once-purified oil (D), ·843. Distil to dryness.
Soda tar.
0. Naphtha (E), ·780.
30·7. Crude light oil (F), ·803.
0·0. Still-bottoms (H).
42·0 Heavy oil (G), ·867.
30·7. Crude light oil (I), ·803. Wash with 2 per cent. acid (sp. gr. 1·85), and then with excess of soda (sp. gr. 1·26).
30·5. Washed light oil (J), ·802. Distil to dryness.
2·0. Naphtha (K), ·750.
30·7. Light oil (M), ·803.
2·0. Heavy oil (N), ·840.
4·0 % Naphtha (L), sp. gr. ·765.
44·0. Heavy oil (Q), ·866. Cool to —3° C., and press.
33·0. Blue oil (S), ·881. Wash with 3 per cent. acid (sp. gr. 1·85) and excess of soda (sp. gr. 1·33).
10·6 per cent. Paraffin scale (R), melting at 49·5° C.
32·1. Washed blue oil (T), ·870. Distil to dryness.
7·5. Burning oil (U), 8·37.
1·6 per cent. Intermediate oil (V), sp. gr. ·850.
23·0. Unfinished lubricating oil (W), ·889. Treat with 3 per cent. acid (sp. gr. 1·85) and excess of weak soda (sp. gr. 1·02).
33·5. Burning oil (O), ·810. Test with 3 per cent. acid (sp. gr. 1·85) and excess of soda (sp. gr. 1·02).
33·0 per cent. Finished burning oil (P) (sp. gr. ·809).
21·0 per cent. Finished Lubricating oil (X) (sp. gr. ·887).

portions of 5 per cent. each, and noting the density of each fraction and the solidifying point of the high-boiling fractions.

The methods of examining the naphtha, burning oil, lubricating oil, and paraffin scale which form the proximate products of the distillation of crude shale oil are described in the section on "Petroleum and Shale Oil Products."

BLAST-FURNACE TAR.

The tar produced by cooling waste-gases from blast furnaces consuming bituminous coal has been examined by Watson Smith (*J. S. C. I.*, 1883). The sample had a density of ·954, and on distillation gave the following results:

	PERCENTAGE OF PRODUCTS.	SPECIFIC GRAVITY.
Distillate below 230° C., . . .	Water, 30·6 by volume.	1·007
	Oil, 2·9 ,,	·889
,, from 230° to 300°, .	7·0 ,,	·971
,, from 300° till oils solidify, . .	13·0 ,,	·994
,, solidifying on cooling, or soft paraffin scale, .	16·7 ,,	·987
Coke, ...	21·5 by weight.	...
Loss, ...	5·5 ,,	...

On further fractionation and treatment with sulphuric acid and caustic soda the following products were obtained:

	PER CENT. BY VOLUME.
Tar bases, soluble in sulphuric acid, ...	10·6
Phenols and tar-acids, soluble in sodium hydroxide, ...	5·6
Neutral oils, ...	18·2
Soft paraffin scale, ...	5·7

(Yielding solid paraffin, 0·54 per cent.)

The phenoloid bodies are further described under the head of "Blast Furnace Creosote."

Of the neutral oils, only an insignificant fraction distilled below 180° C. The density of successive fractions rose from ·858 to ·980. No naphthalene could be separated from an appropriate fraction by cooling it with ice and salt. The intermediate oils are not specially good as lubricants, nor are they suitable for burning in lamps. The fractions distilling between 250° and 350° C. possessed a deep green fluorescence, and closely resembled heavy lubricating oil from shale. On treating the soft paraffin scale with glacial acetic and chromic acids, solid paraffin was obtained, and a large proportion of a pitchy deposit was formed, but no anthraquinone, produced by the oxidation of anthracene, could be detected.

TAR FROM JAMESON COKE-OVENS.

In the recovery of secondary products from coking coal according to the Jameson process, a tar is obtained which in its leading features resembles the blast-furnace tar and shale oil just described. The neutral oils have very little viscosity, and are unfit for burning in lamps. Toluene and xylene are present in trifling proportion. No naphthalene or anthracene appears to be present, but a notable quantity of paraffin wax is obtainable. The phenoloid bodies exist in considerable proportion. They contain little or no phenol.

TAR FROM SIMON-CARVÈS COKE-OVENS.

This tar is the product of the distillation of coal at a high temperature, and hence approaches in composition the tar obtained in the manufacture of illuminating gas from Newcastle coal. The proportion of benzene and toluene is low, probably owing to imperfect condensation, but the tar is very rich in naphthalene and anthracene, though the proportion of intermediate and anthracene oils is very small (Watson Smith, *J. S. C. I.*, 1883, 500).

The utilization of coke-oven products has become an important industry. A plant is in operation at Halifax, N. S., supplying illuminating gas as well as tar products, and a large plant is being constructed near Boston, Mass., U. S. A. The plants used in these cases are termed Otto-Hoffmann ovens. H. O. Hofman (*Tech. Quar.*, Dec., 1898) gives the following data from the results at Halifax:

	FIXED CARBON.	VOL. WATER.	ASH.	SULPHUR AND OXYGEN.	NITROGEN.
Coal, per cent., .	59·56	34·60	5·84	13·80	1·51
Coke, ,, .	69·82	1·27	8·91	(Phosphorus, 0·0041)	

The yield of the various products was, in per cent.:

COKE.	TAR.	GAS.	GAS LIQUOR.	AMMONIA.
71·13	3·38	16·43	8·17 (by difference)	0·34

Hydrogen sulphide in gas, . . . 0·048
Carbon disulphide ,, ,, . . . 0·007

The gas amounted to 10,390 cu. ft. per long ton; sp. gr., 0·466. The results of fractional distillation of different samples of the tar are shown in comparison with average German gas-house tar:

	° C.	OTTO-HOFFMANN TAR.		AV. GER. GAS-HOUSE TAR.	
Light oils, . . .	80–170	3·7	6·55	3·0	2·5
Middle ,, . . .	170–230	9·8	10·54	2·5	2·5
Heavy ,, . . .	230–270	12·0	7·62	33·5	25·0
Anthracene, over	270	4·3	44·35	10·5	10·0
Pitch, ...		67·0	30·55	45·4	60·00

Hofman also gives a comparative table of the more detailed fractionation of the coke-oven tar in comparison with gas-house tar:

	OTTO-HOFFMANN.	AV. GER. GAS-HOUSE TAR.
Water, ...	2·9	2·2
Light oils, burning at 200° C., .	4·0	3·4
Aniline benzols, ...	0·92	1·1
Solvent naphtha, ...	0·2	0·32
Creosote oils, ...	8·6	14·5
Crude naphthalene, ...	7·4	27·3
Pure anthracene, ...	0·6	0·7
Pitch, ...	58·4	44·4

Wood Tar.

The products of the destructive distillation of wood are very numerous, and vary much with the nature of the wood and the temperature at which the process is conducted. But under all circumstances the volatile products are characterized by the large proportion of oxygenised products contained in them, and by the small proportion of sulphur and nitrogen compounds. Among the gaseous products are carbon dioxide, carbon monoxide, hydrogen, and some methane. The aqueous portion of the liquid distillate, known as *crude pyroligneous acid,* usually forms from 28 to 50 per cent. of the weight of wood distilled, and contains chiefly acetic acid, methyl alcohol, allyl alcohol, and acetone, with many other bodies in smaller proportion.

The "tar," or oily portion of the crude distillate from wood, averages from 7 to 10 per cent., and is a complex mixture of various liquids holding solid matters in solution. On distillation between 70° and 250° C., Russian wood tar yields oils of a density ranging from 0·841 to 0·877, and leaves a residue of *pitch,* consisting of solid paraffin, various resinous matters, pyrene, chrysene, and other hydrocarbons of high boiling point.

On redistillation the tar-oils yield the following products:

Below 100° C.; fatty acids, sylvane (C_5H_6O), methyl alcohol, benzene.
Between 100° and 150°; benzene homologues.
Between 150° and 200°; benzene homologues, phenols, and oxyphenols.
Between 200° and 250°; phenols and oxyphenols, lignoceric acid ($C_{24}H_{48}O_2$), naphthalene, retene, paraffin wax.

The lower paraffins appear to be absent from the tar, but the permanent gases produced by the distillation of the wood contain methane. If the oils of wood tar are exposed to a high temperature, they are partially converted into heavy gaseous hydrocarbons. "Wood-gas" is manufactured in this manner, and contains, when purified:

Hydrogen,	48·7 to 18·7
Methane,	35·3 to 9·4
Ethene and its homologues,	10·6 to 6·5
Carbon monoxide,	61·8 to 22·3

Eighty per cent. of the more volatile portion of Swedish wood tar consists of a mixture of two terpenes: australene, boiling at 155°; and sylvestrene, boiling at about 175°. The most important product from wood-tar is the mixture of phenoloid bodies known as creosote, the method of examining and the nature of which are described later.

STOCKHOLM TAR, used in shipbuilding, is the product of a rude distillation of the resinous wood of the pine. It contains much resin and turpentine, and has applications for which the tar obtained in the manufacture of pyroligneous acid cannot be substituted. It has a density of 1·04, and on standing usually deposits a granular, crystalline matter consisting mainly of *pyrocatechol*. Water agitated with the tar acquires a light brown color and sharp, bitterish, taste. The aqueous liquid is colored transiently green by ferric chloride, owing to the pyrocatechol; lime water acquires a permanent brownish-red color. When Stockholm tar is heated, water, acetic acid, and impure turpentine oil are volatilised and ordinary *pitch* remains.

Coal Tar.

Coal tar, as obtained as a by-product in the manufacture of illuminating gas, is a black viscid fluid of complex composition and characteristic disagreeable odor. The specific gravity ranges from

1·10 to 1·20, being usually between 1·12 and 1·15. It usually contains some ammoniacal liquor, and some of the constituents of the illuminating gas.

The first treatment of coal tar on a large scale consists in distilling it and collecting the distillate in three or four fractions. The temperatures at which the receivers are changed differ considerably in the practice of different works, and hence the products are far from being identical. The following table represents three methods of fractionation which are largely employed:

A.		B.		C.	
Product.	Distilling Point ° C.	Product.	Distilling Point ° C.	Product.	Distilling Point ° C.
Crude naphtha, or light oils, . .	0 to 170	First runnings, or first light oils, ...	0 to 110	Light naphtha, . .	0 to 110
Heavy oils, dead oils, or creosote oils, ...	170 to 270	Second light oils,	110 to 210	Light oil, ...	110 to 170
		Carbolic oils, . .	210 to 240	Carbolic oils, . . .	170 to 225
		Creosote oils, . .	240 to 270	Creosote oils, .	225 to 270
Anthracene oils,	above 270	Anthracene oils,	above 270	Anthracene oils, .	270 to 360
Pitch, ...	. . .	Pitch, ...	. . .	Pitch, ...	. . .

The arrangement on page 50, taken with certain alterations from a table published by E. J. Mills, shows the general method of treating coal tar in works employing method C of original fractionation.

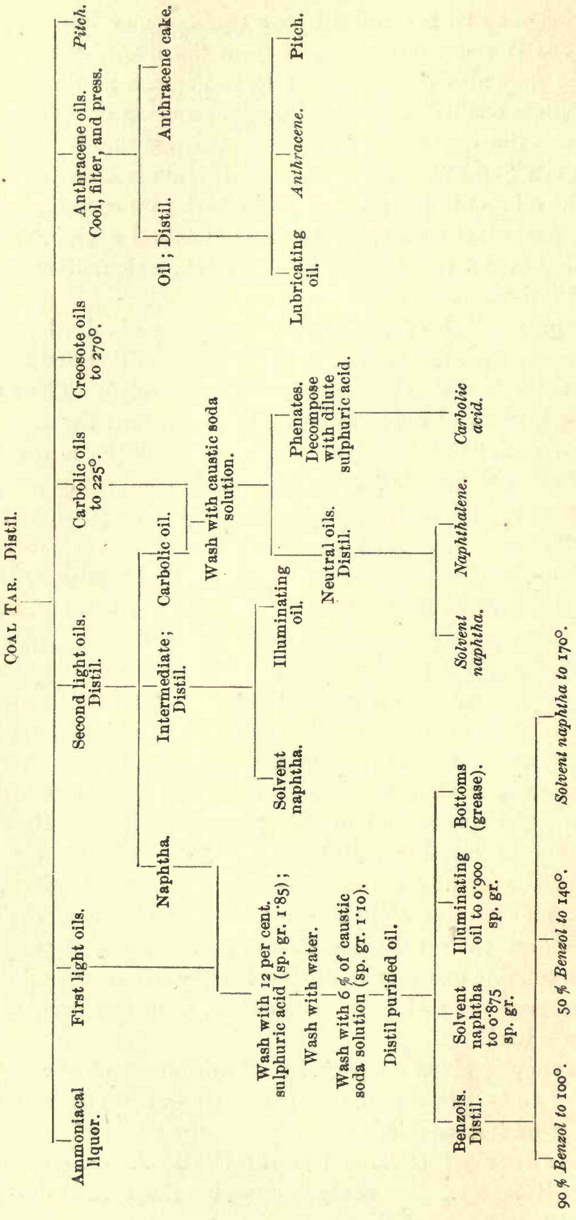
During the first part of the process permanent gases are given off, while the fluid distillate consists of ammoniacal water and the most volatile constituents of the tar proper, together with sensible traces of less volatile bodies, carried over mechanically or volatilised in company with the steam, &c. The ammoniacal liquor forms a lower layer which can be readily separated from the first light oils. The point when the shoot should be changed is indicated pretty accurately by a "break" or comparative cessation of distillation, together with a peculiar noise known as "the rattles." On further heating the distillation recommences, and the second light oils come over regularly. The point for again changing the shoot is, in some works, that at which a sample of the distillate sinks in water, while in other cases the solidification of the distillate on cooling, from the crystallisation of naphthalene, is the indication relied on. At a higher temperature a distillate is again obtained, which remains liquid on cooling. The commencement of the anthracene oil period may be ascertained by a thermometer immersed in the *vapor*, but is commonly deduced from the quantity of the distillate. It may also be considered to commence at the point when the distillate again deposits solid matter on being completely cooled. Sometimes the anthracene oils are subdivided into first and second "green oils" and "red oil." The distillation is sometimes stopped when the oil sets to the consistence of butter on cooling, but is now usually pushed as far as possible short of actual coking, the residue remaining in the retort consisting of pitch, which, after cooling, is run out into tanks.

The proportions of the various products obtained necessarily vary largely with the character of the tar distilled and the details of the mode in which the operation is conducted. These differ in different works and in the same works at different times.

If the coal be distilled at a low temperature, a considerable amount of methanes and other open-chain compounds are formed; distillation at high temperature increases the proportion of closed-chain hydrocarbons. At high temperature, however, much carbon is deposited in the free state by contact of the distilling substances with the hot walls of the retort. The resulting gas is, therefore, lighter than that produced at a low temperature. This fact is practically applied in filling large balloons. When possible, the engineer works a bench of retorts at a high temperature, and thus obtains a gaseous mixture containing more methane and free hydrogen, and hence of greater lifting power, than a gas from a lower heat. For yields of English tars, see pages 53 and 54.

The general composition of the various fractions obtained by the distillation of coal-tar will be regulated chiefly by the boiling points of the leading constituents, but the vapor-densities, vapor-tensions, and relative abundance of the constituents of the tar also largely affect their behavior in the still. Thus, naphthalene is found in notable quantity in all the fractions from second light oils to anthracene oil, and is even deposited from the purified illuminating gas itself.

The synopsis given on page 51 of substances obtained from or presumed to be present in coal-tar is transcribed from Lunge's "*Coal-tar and Ammonia*," and supplemented by reference to data from Richter's "*Organic Chemistry*" (3d Amer. edition, translated by Smith). For analytic data, see the special descriptions.


Coal Tar. Distil.
Ammoniacal liquor.
First light oils.
Second light oils. Distil.
Carbolic oils to 225°.
Creosote oils to 270°.
Anthracene oils. Cool, filter, and press.
Pitch.
Naphtha.
Intermediate; Distil.
Carbolic oil.
Oil; Distil.
Anthracene cake.
Wash with caustic soda solution.
Wash with 12 per cent. sulphuric acid (sp. gr. 1·85);
Wash with water.
Wash with 6 % of caustic soda solution (sp. gr. 1·10).
Distil purified oil.
Solvent naphtha.
Illuminating oil.
Neutral oils. Distil.
Phenates. Decompose with dilute sulphuric acid.
Lubricating oil.
Anthracene.
Pitch.
Benzols. Distil.
Solvent naphtha to 0·875 sp. gr.
Illuminating oil to 0·900 sp. gr.
Bottoms (grease).
Solvent naphtha.
Naphthalene.
Carbolic acid.
90 % Benzol to 100°.
50 % Benzol to 140°.
Solvent naphtha to 170°.

Constituents of Coal-tar.

I. Hydrocarbons.

a. Methanes, CH_4 to $C_{27}H_{56}$.
b. Ethenes, C_2H_4 to C_7H_{14}.
c. Ethines (Acetylenes), C_2H_2 to C_6H_{10} ; $C_{10}H_{20}$; $C_{14}H_{24}$; $C_{16}H_{28}$.
d. Tetrones, C_9H_{14}.
e. Benzenes, C_6H_6 to $C_{10}H_{14}$.
  Benzene hydrides, C_6H_{12} to C_8H_{14}. Naphthenes.
f. Naphthalenes, $C_{10}H_8$ to $C_{12}H_{12}$.
  Naphthalene hydrides, $C_{10}H_{10}$; $C_{10}H_{12}$.
g. Acenaphthenes, $C_{12}H_{10}$. Acenaphthene hydrides, $C_{12}H_{12}$.
  Diphenyl, $C_{12}H_{10}$. Fluorene, $C_{13}H_{10}$.
h. Anthracene, $C_{14}H_{10}$ to $C_{16}H_{14}$; $C_{18}H_{18}$.
  Anthracene hydrides, $C_{14}H_{12}$; $C_{14}H_{16}$.
i. Phenanthrene, $C_{14}H_{10}$.
j. Fluoranthrene, $C_{12}H_{10}$.
k. Pyrene, $C_{16}H_{10}$.
l. Chrysene, $C_{18}H_{12}$.
m. Picene, $C_{22}H_{14}$.
n. Benzerythrene, $C_{24}H_{18}$.

II. Oxyhydrocarbons.

a. Water.
b. Methyl hydroxide.
c. Ethyl hydroxide.
d. Acetone.
e. Acetic acid.
f. Benzoic acid.
g. Phenol.
h. Cresols.
i. Xylols.
j. Naphthols.
k. Pyrocresols.
l. Rosolic acid.

III. Compounds Containing Sulphur.

a. Hydrogen sulphide.
b. Ammonium sulphide.
c. Ammonium thiocyanate.
d. Sulphur dioxide.
e. Carbon disulphide.
f. Carbon oxysulphide.
g. Mercaptans.
h. Thiophens, C_4H_4S to C_6H_8S.

IV. Nitrogenous Bodies.

a. Amine, NH_3.
b. Ammonium compounds.
c. Amines.
d. Anilines.
e. Pyridines, C_5H_5N to $C_{12}H_{19}N$.
f. Quinolines, C_9H_7N to $C_{11}H_{11}N$.
g. Acridine.
h. Pyrrol.
i. Methyl cyanid and isocyanid.
j. Carbazol ; phenylnaphthyl carbazol.

Assay of Coal Tar.

The assay of coal tar is usually limited to a laboratory operation, in which the various fractions are collected as nearly as possible under the same conditions as those which pertain to the large scale, though the details will necessarily vary with circumstances. With practice, good results are obtained with as small a quantity as 10 ounces of the tar, the yields corresponding closely with those given on a large scale; but the chief value of such laboratory operations is for *comparing* different samples of tar. The following mode of operation is that recommended by B. Nickels, to whom the author is indebted for the communication of a number of valuable facts and methods connected with coal-tar products: 250 c.c. or 10 ounces measure of the tar is placed in a retort which it only one-third fills, so as not to spoil the distillate if there is much frothing during distillation. The retort should be supported on a cup-shaped piece of coarse wire-gauze, placed in an aperture in a sheet-iron plate. Over the retort is placed a dome, made by removing the bottom from a tin can or bottle and cutting out a piece of the side to allow the neck of the retort to pass through. This contrivance confines the heat, and prevents the distillate or heavy vapor from falling back; indeed, without some such arrangement a satisfactory assay of coal tar in glass is nearly impossible. The products obtained by the distillation are: (1) ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) anthracene oils; and (5) pitch. In obtaining these fractions, the character of the distillate is amply sufficient to indicate the point at which the receiver should be changed. No thermometer is necessary, nor need any condensing arrangement be attached to the retort. A powerful bunsen should be used, as toward the close of the operation it is necessary to maintain the wire-gauze at a red heat. The ammoniacal liquor and naphtha are collected together in a graduated cylinder, which is changed as soon as a drop of the distillate sinks when collected in a test-tube of water. After standing, to allow perfect separation of the *ammoniacal liquor* and *light oils*, the volume of each is observed, and, if desired, the strength of the former can be ascertained in the usual way by distillation with lime and titration of the distillate. The quantity of light oils is too small for further fractionation.

The next fraction of the distillate consists of *creosote oil.* At first it will contain much naphthalene, and will probably solidify in white crystals on cooling, but afterward a more fluid distillate is obtained. At a still later stage a drop of the distillate collected on a cold steel spatula will be found to deposit amorphous solid matter of a yellow or greenish-yellow color; the receiver is now again changed, the fraction measured, and, if desired, assayed for carbolic acid and naphthalene, as described in the section on "Creosote Oils." With many tars this fraction is semi-solid, and must be measured whilst quite warm.

The next fraction of the distillate is rich in anthracene, and not unfrequently condenses in the neck of the retort as a yellow, waxy substance, which may be melted out by the local application of a small bunsen flame.

The collection of *anthracene oil* is complete when no more distillate can be obtained, and the pitch intumesces and gives off heavy yellow fumes. The distilled fraction is then measured and cooled thoroughly, and the resultant pasty mass pressed between folds of blotting-paper, weighed, and assayed for real anthracene by the anthraquinone test. The result is calculated into *crude anthracene* at 30 per cent., a standard which is generally adopted by manufacturers.

When the distillation for anthracene oil is complete, the retort may be allowed to cool, and when almost cold its body should be plunged into cold water. This produces a rapid surface-cooling and shrinking of the pitch from the glass; the latter may then be broken and removed by gentle tapping, leaving the cake of *pitch* clean and ready for weighing.

The following figures, communicated by B. Nickels, show the results obtained by the assay of four representative samples of London tar. The apparent excess is due to the tar having been measured and the pitch weighed:

	A.	B.	C.	D.
Ammoniacal water, ...	2·5	3·7	8·0	5·0
Total light oils, ...	2·5	3·4	0·5	3·2
Carbolic and creosote oils, . .	21·3	17·0	23·0	20·0
Anthracene oils, ...	17·0	17·0	13·0	13·0
Pitch (grm. per 100 c.c.), . .	59·4	60·0	58·0	62·0
	102·6	101·1	102·2	103·2
Pressed anthracene, ...	4·0	...	1·15	...
Containing real anthracene,	13·4%	...	25·68%	
=30% crude anthracene in tar,	1·8	1·47	1·3	1·12

The following table shows the mean composition of the foregoing samples in juxtaposition with the general yield of English country tar:

	London.		Country.	
Ammoniacal water,	4·5	per cent.	4	per cent.
Total light oils,	2·4	,,	3	,,
Carbolic and creosote oils,	20·3	,,	22	,,
Anthracene oils,	15·0	,,	4	,,
Pitch (grm. per 100 c.c.),	59·9	,,	67	,,
	102·1	,,	100	,,

The methods of examining the fractions obtained in the first distillation of coal tar will be described in the sections on "Commercial Benzols," "Naphthalene," "Anthracene," and "Creosote Oils."

Coal-tar Pitch.

This is the residue remaining in the still after the first distillation of coal tar, and usually amounts to about two-thirds of the weight of tar operated on. Its physical characters depend somewhat on the kind of coal distilled and the point at which the distillation was arrested. Thus, soft pitch is obtained if the process is stopped when the oils distilling have a density of about 1·090, and hard pitch if it is continued until the specific gravity of the products distilling reaches 1·120. In order to obtain a large yield of anthracene, the distillation is often pushed as far as possible, and the residual hard pitch diluted with a certain proportion of creosote oil or anthracene oil, whereby a product of any requisite softness can be obtained. A compounded pitch of this sort will yield a notable quantity of liquid oils when distilled, and, possibly, naphthalene, which last is much objected to.

Soft pitch can be easily kneaded between the teeth, but moderately hard pitch with difficulty only, while hard pitch crushes to powder. Soft pitch is blacker and more lustrous than hard pitch, which often has a grayish tint and is somewhat porous. In the latter case it is partly coked, and is unfit for making patent fuel, for which pitch of but moderate hardness is preferred. The specific gravity of hard pitch ranges from 1·275 to 1·300.

Soft pitch	softens	at 40° C.,	and melts	at about	60°.
Moderately hard	,,	at 60°	,,	,,	80°.
Hard	,,	at 80°	,,	,,	120°.

Contract-notes for pitch intended for exportation to the Continent often stipulate that a sample is to "twist fairly after immersion for two minutes in water at 60° C., but not under 55° C.;

must contain at least 53 per cent. of volatile organic matter; and must be free from any extraneous matter, such as sand or grit."

The twisting point and melting point of pitch are ascertained by F. G. Holmes by fixing several pieces of the sample (about ½ inch cube) on wires, by heating the ends of the wires sufficiently to press them into the pitch, and suspending them, side by side with a thermometer, in a beaker containing 500 c.c. of water, which is heated at the rate of about 5° C. per minute. The pitch is taken out from time to time, and the twisting point taken as the temperature at which the fragment can be fairly twisted round several times. The melting point is the temperature at which the pitch melts off the wire, avoiding premature dropping.

The proportion of volatile organic matter in pitch ranges from 47 to 64 per cent. It is determined by gradually heating 1 grm. of the carefully sampled and powdered pitch in a platinum crucible until distillation ceases. The operation should occupy about fifteen minutes, and must not be hurried, or the pitch may swell up and even boil over the sides of the crucible, leaving a very porous residue. A cover with a small aperture in the centre is then placed on the crucible, which is placed in a crucible-jacket and further heated for ten minutes over a powerful bunsen, and finally for ten minutes over a blast-flame. The residual *coke*, which should be dense and graphitoidal, is then weighed, and the volatile organic matter calculated from the loss. With care and attention to details the test gives constant results, but otherwise very discordant figures may be obtained. The coke may be burned and the proportion of ash ascertained if the presence of *sand* or *grit* is suspected.

According to Habets, the ultimate percentage composition of good, hard coal-tar pitch is 75·32 of carbon, 8·19 of hydrogen, 16·06 of oxygen, and 0·43 of ash. Small proportions of nitrogen and sulphur are also present. The proximate composition of coal-tar pitch is very imperfectly understood. It always contains some of the high-boiling hydrocarbons of coal-tar, such as anthracene, phenanthrene, pyrene, chrysene, &c., together with "bitumene," and probably free carbon.[1] The form in which the oxygen exists is not known.

[1] When pitch which remained after all oils of a density up to 1·120 had distilled over was treated successively with cold benzene, carbon disulphide, boiling benzene, and boiling alcohol, Behrens obtained 23·54 per cent. of a black powder resembling anthracite, and containing 91 to 92 per cent. of carbon, 3·1 of hydrogen, and 0·4 to 0·9 of ash.

Coal-tar pitch is wholly insoluble in water, but soluble to a greater or less extent in alcohol, and more completely in benzene and carbon disulphide. In cold petroleum spirit it is but little soluble, but by boiling solvent it is somewhat more acted on, though the greater part remains undissolved. This behavior distinguishes coal-tar pitch from *wood pitch* and *natural asphalt*, for which it is sometimes substituted without acknowledgment. Methods of distinguishing coal-tar pitch from these materials are given later.

The determination of *anthracene* in coal-tar pitch is described later.

BITUMENS.

Mineral products consisting essentially of a complex mixture of hydrocarbons are found in numerous localities, and under very varied circumstances. These products, of which petroleum may be regarded as a type, occur in all parts of the world, and, like coal, are not confined to any one geological formation.

The natural hydrocarbons present every variety of aggregation, from the state of gas, as evolved from coal and petroleum, through the conditions of a thin mobile liquid like the naphtha of Persia, the viscous tar of Rangoon, the elaterite or mineral rubber of Derbyshire, the wax-like ozokerite of Galicia, to the brittle, pitch-like asphalt of Trinidad.

The origin of the bitumens or mineral hydrocarbons is, in many cases, obscure. The subject has been treated in an able and exhaustive report by S. F. Peckham,[1] and has been discussed by many writers. Products more or less similar to petroleum and asphalt have been obtained by distilling complex animal and vegetable matter out of contact of air. All the evidence tends to show that the natural bitumens are derived from various sources. Peckham has reviewed the question (*Amer. Jour. Sci.*, Nov., 1894) and reiterated his earlier statement. In mineralogy the term bitumen includes all natural substances which contain notable propor-

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[1] *Report on the Production, Technology, and Uses of Petroleum and its Products*, to the Hon. C. W. Seton, Department of the Interior, U. S. America. Peckham (*Report*, page 67) concludes that all bitumens have, in their present condition, originally been derived from animal or vegetable remains, but that the manner of their derivation has not been uniform.

tions of hydrocarbons. Peckham proposes the following classification:

Solid,	Asphalt.
Semi-solid,	Maltha.
Liquid,	Petroleum.
Gaseous,	Natural gas.

The consideration of the different varieties of coal is beyond the scope of this treatise.

Petroleum. Rock Oil. Mineral Oil. Coal Oil.

French—Pétrole. *German*—Steinöl. *Spanish*—Petrólea.

Petroleum is a natural oily liquid occurring in the earth at very varied depths, and in a great many localities. It is not confined to any particular geological formation. Thus, the petroleum of the great Pennsylvania field is derived from the Devonian and Carboniferous limestone formations, while that of California and Russia is found in tertiary rocks. Petroleum may not be indigenous to the strata in which it is found; in some instances it has undergone distillation. Brannt (*Petroleum and its Products*) limits the terms "rock oil" and "naphtha" to those hydrocarbons which are clear and nearly colorless in their natural condition.

Petroleum is now obtained on a considerable scale in the Caucasus, on the shores of the Caspian Sea, and smaller quantities are produced in Canada, Galicia, Hanover, and other localities, but the largest quantity is obtained from the United States. The last source so overshadows all others, from a commercial point of view, that the following description applies chiefly to that product:

Crude natural petroleum is an oily liquid, varying in density from ·73 to ·97, the Pennsylvania product ranging between ·79 and ·83. It has a characteristic odor, sometimes, but by no means invariably, disagreeable; its color varies from straw-yellow to brownish black. Its coefficient of expansion varies considerably with its specific gravity, as is shown by the following table:[1]

SPECIFIC GRAVITY AT 15° C.	EXPANSION-COEFFICIENT FOR 1° C.
Under ·700	·00090
·700 to ·750	·00085
·750 to ·800	·00080
·800 to ·815	·00070
over ·815	·00065

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[1] On a stock of 1,000,000 barrels of petroleum, the shrinkage in ~~water~~ winter amounts to 7000 to 10,000 barrels.

Petroleum is insoluble in water, and but slightly soluble in alcohol, but it is miscible in all proportions with chloroform, ether, carbon disulphide, and hydrocarbons. It mixes readily with ordinary fixed oils, castor oil being an exception (Vol. II., Part I, page 158). All varieties are combustible, burning with a luminous, more or less smoky, flame.

CHEMICAL COMPOSITION OF PETROLEUM.

Chemically, crude petroleum consists of a mixture of a considerable number of hydrocarbons with small quantities of sulphuretted, nitrogenised, and oxygenised bodies.

The nitrogen in crude petroleums and paraffin oil is given thus by **Beilby** (*J. S. C. I.*, 1891, 120):

Scotch shale oil from retorts,	1·160	per cent.
,, petroleum or ozokerite,	0·296	,,
American petroleum residuum,	0·080	,,
Baku ,, ,,	0·050	,,
,, ,,	0·050	,,
Galician ozokerite,	0·188	,,
Scotch basic tar,	3·900	,,
American residuum tar,	0·716	,,
Scotch crude still coke,	3·200	,,
American crude still coke,	0·375	,,

According to **Kast** and **Lagai** (*Ding. Poly. Jour.*, 1892, 284, 69), all crude petroleums, except that from Tegernsee, contain sulphur in amounts varying from 0·136 to 1·87 per cent. **Mabery** and **Smith** have investigated the nature of the sulphur compounds, and find that they are in the form of alkali sulphides; thiophenes and mercaptans are absent.

Petroleum is variable in composition, and more or less volatile and mobile according to its content of bitumen and solid bodies. In general, it contains about 85 per cent. of carbon and 15 of hydrogen, but its elementary composition gives no idea of the variety of hydrocarbons contained in it. In brief, the constituents of petroleum present the following varieties of character:

(*a*) Their volatility is very different, for they extend from gases of very low boiling points to solids which boil at high temperatures (370° and 450° C.).

(*b*) The volatility of the constituents is usually inversely as their specific gravity, the lightest oils being the most volatile.

(*c*) The inflammability is a function of the volatility, the more volatile constituents taking fire on approach of a flame at ordinary temperatures, while the denser and less volatile oils require to be heated considerably before they can be inflamed or made to give off inflammable vapors.

The hydrocarbons of petroleum belong to several series, the methanes largely predominating in American petroleum, while members of other series are present in relatively large amount in the petroleum of other regions.

Pennsylvania petroleum has been most completely studied. A complete series of methanes, from CH_4 to $C_{16}H_{34}$, has been obtained from it; and the solid members, $C_{25}H_{52}$, $C_{27}H_{56}$, and $C_{30}H_{62}$, are also present, especially in the oils from the Bradford district. Isomethanes, as well as the normal forms, exist in American petroleum. The paraffins from CH_4 to C_4H_{10} are gaseous at ordinary temperatures, and hence escape in admixture with hydrogen from petroleum wells, or when the petroleum is stored or gently heated. The members from C_5H_{12} to $C_{15}H_{32}$ constitute the greater part of the liquid portion of American petroleum, one of the most characteristic constituents being hexane. The olefins from $C_{10}H_{20}$ to $C_{12}H_{24}$ have been isolated by Warren from American petroleum, and doubtless other of the higher members of the series are present. Gaseous olefins also occur. Naphthenes similar to those characteristic of Russian petroleum are also present. Benzene and its homologues exist in traces in American petroleum, and among the less volatile constituents anthracene, chrysene, pyrene, fluoranthrene, and thallene exist in small quantity.

Natural gas from the Pennsylvania wells has been found to contain from 40 to 94 per cent. of methane, CH_4, with smaller proportions of hydrogen and ethane, CH_6, and traces of higher homologues. Small proportions of olefins are also present. On the other hand, the liquid obtained by J. J. Coleman, by the action of cold and pressure on the gases produced in the distillation of bituminous shale, consisted chiefly of tetrene, C_4H_8, pentene, C_5H_{10}, and hexene, C_6H_{12}. Natural gas is employed for manufacturing and household purposes in many of the Middle and Western States of the United States. F. C. Phillips[1] has found from one to nearly three per cent. of nitrogen in natural gas.

Canadian petroleum contains various hydrocarbons of the paraffin

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[1] *Proc. Engin. Soc. Western Pennsylvania*, Dec., 1898.

and olefin series, and is richer in aromatic compounds and poorer in gaseous paraffins than the Pennsylvanian product. It contains a notable quantity of sulphur compounds and traces of benzene and nitrogenous basic oils. It yields about 3 per cent. of solid paraffin.

Californian petroleum contains, as far as known, benzene hydrides, naphthenes, benzenes, sulphur compounds, with a notable amount of the esters of nitrogenous basic oils.

Ohio petroleum is intermediate in properties between Caucasian and Pennsylvanian oils, and contains the following: Methane, two tetranes, pentane, isopentane, hexanes, heptanes, octane, nonane. These form less than ten per cent. of the oil. The crude oil contains a large amount of sulphur compounds. Aromatic hydrocarbons are present in very small amount. The sulphur compounds have a tendency to collect in the higher fractions.

Russian petroleum has acquired considerable commercial importance. It is chiefly obtained in the neighborhood of Baku on the Caspian Sea, but is also found in other parts of the Caucasus. A fraction of given boiling point has a higher density than a similar fraction of American petroleum or Scotch shale oil, and the viscosity is more readily decreased by heat. It usually yields no solid paraffin.

This petroleum is scientifically interesting from its peculiar composition. Beilstein and Kurbatow could not obtain any products of constant boiling points, even after nine distillations, nor were they able to extract any benzenoid hydrocarbons by treatment with fuming nitric acid nor any olefins with bromine. Their researches, as extended by Schützenberger and Ionine, and by Markownikoff and Oglobini, have shown that Caucasian petroleum consists chiefly of a mixture of naphthenes, having the general formula C_nH_{2n}. These are isomeric with the ethenes, and with the benzene hexahydrides (so-called paraffenes, $C_nH_{2n-6}H_6$), obtained synthetically by Wreden. With the exception of the hydrocarbon $C_{13}H_{26}$, all the naphthenes from C_8H_{16} to $C_{15}H_{30}$ have been separated from Caucasian petroleum. They boil at somewhat lower temperatures than the isomeric ethenes and the normal methanes containing the same number of carbon atoms, and at approximately the same temperatures as the synthetically prepared paraffenes; but the densities of the Caucasian hydrocarbons are notably greater than those of the isologous paraffins from American petroleum. Thus, while normal octane, C_8H_{18}, boils at 124° C. and has a density of ·7188 at

0°, octonaphthene, C_8H_{16}, boils at 119° and has a density of ·7714. Similarly, $C_{12}H_{26}$ boils at 202° and has a density of ·7655, while $C_{12}H_{24}$ boils at 196° and has a density of ·8027 at 17°.

The naphthenes do not form nitro-derivatives, and resemble the methanes in not yielding additive compounds and in being convertible into chlorinated derivatives from which alcohols are obtainable. When oxidised, the naphthenes form oxidation-products, or are converted into higher isologues.

The higher boiling portions of Caucasian petroleum probably contain hydrocarbons of the ethene and higher series, while 10 per cent. of the petroleum consists of benzenoid hydrocarbons belonging to known series, and also a series of hydrocarbons isomeric with styrolene and its isologues. These compounds form brominated derivatives, but no additive compounds; their benzenoid character is exhibited in the formation of nitro- and sulpho-derivatives.[1] The petroleum also contains neutral and acid oxygenated bodies. A petroleum examined by Markownikoff yielded a fraction boiling between 220° and 230° C., which contained 5·25 per cent. of oxygen.

The investigation of Russian petroleum is very difficult, owing to the facility with which the constituents break up into other bodies on distillation, especially during the latter part of the process. When passed through an iron tube heated to bright redness, Caucasian petroleum yields an abundant deposit of carbon, which soon chokes the tube, the metal itself being strongly corroded. The volatile products consist largely of benzene and its homologues, with naphthalene and anthracene. This reaction has been utilized for the production of benzene and anthracene from Russian petroleum.

Galician petroleum, according to Lachowicz, contains a number of paraffins and also aromatic hydrocarbons. Pawlewski found in a petroleum from Kleczany about 2 per cent. of aromatic hydro-

[1] A petroleum from near Tiflis, examined by Beilstein and Kurbatow (*Jour. Chem. Soc.*, xl. 1020), yielded a fraction of lower boiling point containing the paraffins C_4H_{10} to C_7H_{16}, with a little benzene and toluene. By treating the fraction of a Caucasian petroleum boiling between 180° and 200° with fuming sulphuric acid, Markownikoff and Oglobini found that various sulphonic acids were formed, while the hydrocarbons of the formula C_nH_{2n} were left unchanged. Isomerides of cymene, metamethyl-propylbenzene, and probably durene, were present. The 240° to 250° fraction contained a modification of propylnaphthalene ($C_{13}H_{14}$), then $C_{12}H_{14}$ and $C_{11}H_{14}$ (the last probably belonging to the cinnamene series), and finally $C_{15}H_{30}$ (? $C_{15}H_{10}$).

carbons, consisting chiefly of benzene and paraxylene. The fraction boiling between 97° and 100° C. consists chiefly of heptane with some toluene hexhydride, but the presence of oxylene hexhydride was not established. The first six fractions obtained by distilling the crude petroleum on the large scale are not acted on by bromine, but the seventh and higher fractions absorb bromine with evolution of heat. Hence it is probable that ethenes do not pre-exist in the petroleum, but are formed during the distillation by the decomposition of paraffins. Hell and Meidinger have isolated from Wallachian petroleum an acid forming alkali-salts resembling soft soap. Other homologous acids are probably present.

Hanoverian petroleum, according to C. Engler, contains hydrocarbons both of the paraffin and olefin series, besides notable quantities of aromatic hydrocarbons (*e. g.*, pseudocumene, mesitylene, and probably hexahydrometaxylene). Sulphur compounds are also present.

Rangoon tar is a heavy variety of petroleum, of a semi-solid consistency, owing to the presence of about 40 per cent. of solid paraffin. By fractional distillation, Warren and Storer proved the presence of the paraffins from C_7H_{16} to C_9H_{20}, ethenes from C_9H_{18} to $C_{13}H_{26}$, besides xylene, cumene, and naphthalene.

The composition of petroleums from other sources has been but imperfectly ascertained. The behavior of some of them on distillation is described later.

The method of treating crude petroleum for the manufacture of commercial products varies considerably with the character of the crude article and the practice of the works, but it is always essentially a process of fractional distillation, sometimes supplemented by a decomposing action in the still, induced by the injection of superheated steam. The character and proportion of the various products obtained depend largely on the nature and source of the oil and the details of the mode of treatment, which is capable of considerable variation in detail. As a rule, the lighter and more volatile portions are fractionated into a number of products, known commercially as cymogene, rhigolene, gasolene, naphtha, and benzine or benzolene; but in many cases the proximate separation of the products of the distillation of crude petroleum is less complete, only three principal products being made—namely, naphtha, kerosene, and lubricating oil. By the present system of manufacture, "cracking" of the heavier oils (see under "Kerosene"), about

75 per cent. of burning oil, flashing at 68° F. by Abel's test, may be obtained from crude American petroleum. The yield of higher class oils (such as would pass English inspection) is proportionately smaller, and of "water-white oil" only from 12 to 20 per cent. is obtained. The proportion of naphtha obtainable from American oil varies from 9 to 18 per cent., according to the age of the oil-producing territory.

Caucasian petroleum yields very different proportions, the proportion of burning oil flashing at 32° C. and of 0·821 specific gravity being only about 27 per cent.; but a much larger percentage of oil of lower flashing point or higher specific gravity can be obtained. B. Redwood (*J. S. C. I.*, 1884, 74), who gives the above figures, also states that the Caspian Company manufactures three qualities of the burning oil, of the following characters:

QUALITY.	SPECIFIC GRAVITY.	FLASH POINT; C.	YIELD PER CENT.
1	·815	30°	20
2	·820	25°	33
3	·821 to ·822	22°	38

The following table of products from 100 gallons of Russian petroleum is from information furnished by the Ragosine Company.

PRODUCTS.	SPECIFIC GRAVITY.	GALLONS.
"Benzin,"	·725	1
"Gasolene" or heavy benzin,	·775	3
Kerosene,	·822	27
Pyronaphtha (flash-point 132° C., open test),	·858	12
Lubricating oil,	·890–·905	27
Cylinder oil,	·915	5
Vaseline (not a direct product),	·925	1
Residuum and loss,	. .	24
		100

The heavier lubricating oils or "oleonaphthas" of the Ragosine Company range in density from ·905 to ·920, and have low freezing points.

The fractions of the crude petroleum obtained by distillation are purified by treatment with a limited quantity of strong sulphuric acid, and then washed with caustic soda, and finally with water. In some works they are then redistilled over caustic soda. In Canada the burning oil is treated with a solution of litharge in caustic soda, to remove sulphur-compounds.

The following is an outline of the usual process of petroleum distillation as conducted in America: The oil is heated in large stills holding from 600 to 1200 barrels. The more volatile portions soon come over; they are either burnt or condensed by artificial cold and pressure. The liquids thus obtained are known as "cymogene" and "rhigolene." After these, products condensible by cold water are obtained, the first portions having a density of ·636, the product becoming heavier as the distillation proceeds. (The distillate obtained in this part of the operation is usually again distilled, when it yields "gasolene," "naphtha," and "benzin.") When the liquid passing over acquires a density of ·725 to ·750,—according to the works' custom,—the stream is diverted from the "naphtha" tank to the "kerosene" receiver, where it is collected until its gravity reaches ·840 to ·845. The residue is then transferred to other stills, and generally to other works, where it is distilled to dryness to obtain lubricating oils and paraffin. The residue in the still is combustible with difficulty, but is used as fuel. If the operation be arrested before actual coking occurs, the residue has the characters of thick tar. The purification and fractionation of the first products are conducted in much the same manner as with shale oil.

On the Caspian Sea the distillation of the petroleum is conducted as a continuous process, a stream of oil flowing through the entire series of twenty-five stills. This method is peculiarly suited for the treatment of Russian petroleum, since it yields comparatively little burning oil, and the residue is almost as fluid as the crude oil. The distillate is collected in three fractions: light benzin (·754), heavy benzin or "gasolene" (·787), and kerosene (·820 to ·830). The residue has a density of ·903, and yields on distillation about 30 per cent. of lubricating oil and 15 of "solar oil" (sp. gr. ·860, flashing point 105° C.), the remainder being commonly used as fuel. Attempts have been made to employ *astatki* (residuum) for the production of benzols and anthracene by subjecting it to a full red heat. Baku petroleum contains little or no solid hydrocarbons, but the oil obtained on the other side of the Caspian yields as much as 6 per cent.

ASSAY OF CRUDE PETROLEUM.

According to a definition adopted by the New York Produce Exchange in 1879, "crude petroleum shall be understood to be pure natural oil, neither steamed nor treated, free from water, sediment, or any adulteration, of the gravity of 43° to 48° Beaumé" (= ·8092 to ·7865 specific gravity). The usual range in the specific gravity of the New York crude oil is between ·790 and ·800. Each parcel is usually a mixed product from a number of wells.

The *water* and *sediment* are usually determined by mixing the sample with an equal quantity of petroleum spirit, free from water, and keeping the mixture at 49° C. (= 120° F.) in a graduated glass vessel for at least six hours, after which the liquid is allowed to cool and settle for a period of not less than two hours for light grade oils, increasing to eighteen hours for the heaviest qualities.

Besides this test and the determination of the specific gravity, the ordinary characters relied on as commercial tests of the quality of crude American petroleum are: Its specific gravity, its odor and color, its feel when rubbed between the fingers, and the percentage of naphtha yielded on fractional distillation.[1] The crude oil of the New York market will generally furnish from 12 to 15 per cent. of naphtha of ·700 specific gravity, and the proportion should not exceed 17 per cent. It will yield, in addition, from 9 to 12 per cent. of benzin of ·730 gravity and about 60 per cent. of burning oil at ·795 specific gravity. The residue contains a quantity of dry paraffin scale equal to about 2½ per cent. of the crude oil.[2]

For the assay of crude petroleum by distillation 250 or 500 c.c. should be employed, and the operation conducted in a retort furnished with a good condensing arrangement, in the same manner as

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[1] Crude American petroleum was formerly frequently adulterated with petroleum spirit. As this was less valuable than the heavier and less volatile kerosene oil, it not infrequently found its way back to the wells, to be repumped as crude petroleum, or was even directly added to the latter in the tanks. The difference in the commercial value of the products is not now sufficiently great to afford much inducement to continue this practice, which, however, has extended to Baku. Excess of the lighter oils reduces the density of the oil, and causes it to give off inflammable vapor at a lower temperature, while the percentage of naphtha yielded on distillation is increased. Hence the best petroleums give only a moderate percentage of naphtha.

[2] The density of the first ninety fractions, of 1 per cent. each, obtained by distilling the average petroleum oil of the New York market, has been determined by Bourgongnon. The following table shows the density of every tenth fraction obtained, the original oil having a specific gravity of ·7982 at 15° C.:

	SPECIFIC GRAVITY.
First Fraction,	·679
Tenth ,,	·705
Twentieth ,,	·728
Thirtieth ,,	·750
Fortieth ,,	·765
Fiftieth Fraction,	·777
Sixtieth ,,	·790
Seventieth ,,	·815
Eightieth ,,	·829
Ninetieth ,,	·825

The products yielded by the distillation of the same crude oil were: Naphtha at ·700, 17 per cent.; benzin at ·730, 9 per cent.; burning oil at ·783, 64 per cent.; residue and loss, 10 per cent.; and the residue contained about one-fourth of its weight of solid paraffin. The results obtained by the distillation of petroleum on a laboratory scale are not strictly identical with those yielded in practice, as a large proportion of the heavier fractions are often "cracked" into burning oil. Thus the Standard Oil Company, at its New Jersey works, obtains from 6 to 15 per cent. of naphtha, from 75 to 80 per cent. of burning oil of two qualities, and a residue of 8 to 10 per cent., which by subsequent distillation yields lubricating oil.

is directed for the examination of "Commercial Benzols." The cylinders in which the distillates are collected should be surrounded with water kept constantly at 15° C. A small hydrometer contained in the cylinder in use will indicate when the thoroughly mixed fraction acquires the standard density, at which point the flame is withdrawn from the retort, the condenser allowed to drain, and the volume of the distillate carefully observed. By employing a thermometer-plummet (Vol. II, part I, p. 28) instead of the hydrometer, more accurate results are obtainable, and the distillation can be conducted on a smaller quantity of petroleum.

Some useful hints on the assay of crude petroleum have been published by Nawratil, who has examined a number of Galician petroleums. He distils 500 c.c. in a glass retort. The distillate collected below 150° C. is regarded as light oils or naphtha, that from 150° to 300° as burning oil, and that from 300° to 400° as heavy oils. The densities of the original samples (18) ranged from ·902 (Harklowa) to ·799 (Kenczany), and the proportions of the several fractions showed similar variations. The light oils varied from 43·5 to 3·4 per cent., the 150° to 300° fraction from 45·4 to 29·2, and the heavy oils from 56·7 to 22·8 per cent.

To extract solid paraffin from crude petroleum, Sadtler mixes the oil with several times its volume of ether, and places the liquid in a freezing mixture, when "almost all the dissolved paraffin will separate, and can be filtered off."

The *flashing point* of petroleum is an indication of considerable importance, but is more especially connected with the examination of refined petroleum or kerosene, under which head the subject is fully discussed.

Determination of Sulphur.—Brannt ("Petroleum and its Products," p. 26) gives the following method: Heat 0·5 gram of the sample with about 20 to 25 c.c. of concentrated nitric acid to about 170° C. The resulting product is freed from the greater part of the nitric acid, diluted with water and precipitated in the usual way. For other methods see under "Asphalt."

Ozokerite.

This substance, known also as cerasin, cerite, or mineral wax, usually occurs in the neighborhood of petroleum springs, and in association with bituminous sandstone, clay-schist, gypsum, and common salt. Though not very abundant, ozokerite occurs in many parts of the globe, the most remarkable and best-known deposit being that in the miocene rocks of Galicia, on the slopes of the Carpathian Mountains, and also on the Wallachian side of the range. It is also worked on the island of Tscheleken in the Caspian and at Swatoi-Astrow, near Apsheron, where a variety called *neftgil* is found. It exists also in Turkestan, and a valuable deposit has been found in Utah. Its commercial interest is chiefly as a source of cerasin, though liquid hydrocarbons are also obtained by the distillation of the inferior kinds.

According to Brannt ("Petroleum and Its Products," 400) Sauerlandt has found ozokerite to contain:

Volatile hydrocarbons.
Paraffins melting at from 60° to 70° C.
$\left.\begin{array}{l}\text{Waxy resins,}\\ \text{Bituminous resins,}\end{array}\right\}$ Oxygenated.
Coke.

Crude ozokerite varies much in appearance. The finest varieties are transparent, of a pure yellow or greenish color, and can easily be kneaded between the fingers. Crude Galician ozokerite is a scaly or waxy substance, with a resinous fracture. It is usually brittle, but as hard as beeswax. It becomes negatively electric by friction and exhales an aromatic odor. According to Lach (*Chem. Zeit.*, 13, 831), the so-called ozokerite from Colorado does not yield cerasin, but is suitable for paraffin making. It begins to distil at 360° C., and yields 90 per cent. paraffin and oil and about 5 per cent. of residuum. Caucasian ozokerite yields about 58 per cent. of a second quality cerasin.

Inferior kinds of Galician ozokerite are black and soft, or hard, with a fibrous structure and conchoidal fracture, varying in color from yellow ("butter-stone") to black. Some pieces are as hard as gypsum, and are dichroic, the transmitted light being a pure yellow, and the reflected dark green. The melting point is very variable, ranging from 58° to 100° C. The raw ozokerite occurring on the island of Tscheleken, in the Caspian Sea, is a brownish-black sticky mass, almost entirely soluble in boiling benzene. On extracting it with ether, the oily portion and coloring matter are dissolved, leaving a hard residue. On boiling this with acetic ether, the paraffin is dissolved, and by repeated treatment with animal charcoal, &c., may be obtained in lustrous crystals, melting constantly at 79° C., and containing 85·10 of carbon and 14·57 of hydrogen (Beilstein and Wiegand, *J. C. S.*, xliv. 1073).

Ozokerite is separated from the gangue by being melted, and, after being pressed, is treated with alkali and filtered through fine animal charcoal. Frequently both acid and alkali are used in the purification of ozokerite; fuller's earth and magnesium silicate have been substituted for the charcoal. The charcoal used is preferably the fine carbonaceous residue produced in the manufacture of potassium ferrocyanide. The purification of ozokerite with sulphuric acid is attended with considerable loss, owing to the action of the acid on the oxygenated bodies present. Peritz obtained from 75 to 82 per cent. of crystallised paraffin from Boryslaw ozokerite, and 9 to 13 per cent. of light oils. Ozokerite refined in England yields nearly 70 per cent. of white paraffin. The purified substance constitutes *cerasin*, which name should be confined to the solid paraffin obtained without distillation. Inferior ozokerite is usually distilled with superheated steam, when it yields paraffin wax, lubricating oil, naphtha. Galician ozokerite yields on distillation about 25 per cent. of petroleum, 21 of lubricating oil, and 36 of solid paraffin. A higher yield might doubtless be obtained by improved manipulation. B. Redwood (*J. Soc. Arts*, xxxiv. 886) gives the products as 5 per cent. of gaseous hydrocarbons, 3 per cent. of naphtha, 6 of semi-solid "ozokerin," 12 of soft paraffin (melting at 44° to 46° C.), distilled ozokerite (melting at 61° C.), and a black waxy residue. The following are the products obtained by the distillation of Caspian ozokerite (*neft-gil*), according to Grabowski:—2 to 8 per cent. of benzin, 15 to 20 per cent. of naphtha, 15 to 20 per cent. of heavy oils, 36 to 50 per cent. of solid paraffin, and 10 to 20 per cent. of coke.

Sometimes the products are less carefully differentiated, the chief being:

30 to 40	per cent.	of benzin of 0·73 specific gravity, and
50 to 76	,,	of solid paraffin melting at from 60° to 70° C.

The crude ozokerite is worked up for cerasin, paraffin being extracted from the residue, which then forms "ozokerite pitch." In distilling for paraffin, a burning oil comes over at 150° C., the fraction 200°–300° C. consisting of a mixture of heavy oil and paraffin, and being worked up for the latter or for vaseline, whilst the chief yield of paraffin comes from the fraction 300°–350° C. The average yield of the various distillation products is, at Boryslaw: Light oil (up to 150° C.), 6 per cent.; heavy oil (150°–300° C.), 32 per cent.; paraffin, about 55 per cent.

ASSAY OF CRUDE OZOKERITE.

According to B. Lach (*Chem. Zeit.*, 1885, 905), for the valuation of crude ozokerite 100 grammes of the sample should be treated with 20 grammes of fuming sulphuric acid in a tared basin. The mixture is heated to 170° to 180° C., and continuously stirred till all sulphur dioxide has escaped. On reweighing the basin, the loss is said to represent the volatile constituents—namely, *petroleum* and *water*. No allowance appears to be made for the loss due to the formation of sulphur dioxide and possible volatilisation of sulphuric anhydride. Probably a better plan would be to dilute the mixture, and separate and weigh the paraffin. Lach further directs that another quantity of 100 grammes of the sample should be treated with 10 grammes of the carbonaceous residue from the manufacture of potassium ferrocyanide, which has been previously dried at 140°. A tenth part of the mixture (11 grammes) is then weighed into a tared paper thimble, and extracted with petroleum spirit, boiling between 60° and 80° C. The wax is estimated from the loss, or recovered by evaporating the solvent.

REFINED OZOKERITE or CERASIN usually melts between 61° and 78° C., is quite odorless and colorless, and has a waxy section. A variety manufactured in Frankfort-on-the-Oder is said to melt at 83°, and to be so hard as scarcely to yield to the finger nail. Cerasin possesses the general characters of paraffin wax. The commercial samples are sometimes artificially colored.

Cerasin may be distinguished from bleached beeswax by its lower specific gravity and by its resistance to alcoholic potash, no trace of saponifiable matter being present. In admixture with beeswax, cerasin may be detected and approximately determined by the methods given in Vol. II., part 1, p. 224.

Ozokerite vaseline is obtained by allowing melted ozokerite to pass through 12 to 15 filters of animal charcoal, or through double that number if a perfectly colorless product be required. The mass is then treated, for 3 to 4 hours, with superheated steam (250° C.). About 25 to 30 per cent. of product is obtained.

Asphalt. Asphaltum. Mineral Pitch.

German—Erdpech. *French*—Asphalte. *Spanish*—Asfalto.

Under the term asphalt is included a considerable number of natural products, consisting largely of compounds of carbon and hydrogen mixed with substances containing oxygen, nitrogen, and sulphur, also some mineral matter. A portion of this mineral matter sometimes exists in combination with the oxidized or sulphurized substances, forming compounds analogous to those produced by resins. Such compounds may dissolve in the liquids employed for the fractionation of the asphalt in analysis, and thus error arise from computing the loss by solution as due entirely to bituminous matter.

Deposits of asphalt occur in all parts of the world; each locality yields a material more or less distinct in character. Of late years much attention has been paid to the analysis of asphalt, especially in the United States, owing to the discovery of new and important local deposits and the extensive introduction of asphalt-paving in American cities. This paving is often merely an asphaltic mixture, inferior to the rock-asphalts employed in Europe. Even mixtures of coal-tar pitch, and petroleum residuum without true asphalt have been used.

Natural asphalts exhibit wide differences in composition. Some forms (rock-asphalts) consist of limestones or sandstones saturated with bituminous matter. In other cases but little mineral matter is present, and in still other cases the mineral matter is abundant, but is simply mixed with the bituminous material and does not produce a rock-asphalt.

Blake (*Trans. Amer. Inst. Min. Engin.*, 1889–90, 563) gives the following list of the principal localities of the several types of asphalt:

Mixed with calcium carbonate,	Seyssel; Val de Travers; Lobsann; Illinois.
,, ,, sandstone,	California; Kentucky; Utah.
,, ,, earthy matter (clay),	Trinidad; Venezuela; Cuba; California; Utah.
Bituminous schists,	Canada; Kentucky; California; West Virginia.

Some asphalts, such as Trinidad and Bermudez, are submitted to a refining process before being marketed. This consists in heating the crude material in large kettles to not over 200° C., by which much water and some volatile matters are removed, portions of the earthy materials, principally clay and sand, allowed to settle, and some of the non-bituminous organic substances collect as a scum and may be removed. Petroleum residuum may be added during this operation, which will, of course, increase the amount of bituminous matter, especially that soluble in petroleum spirit, and produce a strongly fluorescent solution.

Although asphalts have been used for a long period in engineering work, the first scientific investigation seems to have been made by Boussingault,[1] who, in 1836, examined a viscous material from Pechelbronn. He tried several solvents, but relied more upon a process of distillation in an oil bath, by which he obtained a liquid to which he gave the name "pétrolène." He assigned to this a composition of $C_{80}H_{64}$ $(C = 6)$, pointing out that it was isomeric with oil of turpentine. The non-volatile portion he designated "asphaltène," and assigned to it the formula $C_{80}H_{64}O_6$ $(C = 6, O = 8)$, but recognized that oxidation had occurred during the distillation, and that therefore the proportion of asphaltène obtained was in excess of the true amount. From an ultimate analysis of the material, he computed that the proportions of pétrolène and asphaltène were about 85·4 and 14·8, respectively. Heal so made a brief examination of the asphalt of Coxitambo.

Boussingault's methods are not now used, but, by a curious misapplication, the terms petrolene and asphaltene have been applied to the products obtained by the use of solvents. Efforts have been made to establish standards for judging of the value of an asphalt for engineering uses by means of these methods. Carbon disulphide is sometimes used to determine the total bitumen, all organic matter left undissolved being regarded as non-bituminous. For the fractionation of the bituminous matter, petroleum spirit, ethyl ether, acetone, boiling oil of turpentine, chloroform, and benzene have been employed. Usually the portion soluble in petroleum spirit, ether, or acetone is called petrolene, and that insoluble in either of these liquids, but dissolved by boiling turpentine and cold chloroform, is designated as asphaltene. The organic matter insoluble in any of these solvents, and also in carbon disulphide, is considered as non-bituminous, and is thought to be objectionable if

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[1] *Ann. d. Chim.*, 64 (1837), 141; also *Compt. Rend.*, Meeting of Sept. 16, 1836.

present in notable proportion, rendering the paving mixtures liable to rot in the gutters. It has also been stated that clay will tend to produce disintegration. Many engineers have adopted or accepted limits of the proportion of petrolene to asphaltene in asphalts intended for paving purposes. Thus, Tillson[1] accepts any refined asphalt that contains from 50 to 60 per cent. of bitumen of which not more than 25 to 30 per cent. is asphaltene. This does not apply to rock-asphalts, which may contain less than 10 per cent. of bitumen. Petrolene is regarded as acting as a solvent on the asphaltene.

The calcareous asphalts have a deep brown or black color, and break without any sign of cleavage, the fracture being earthy and very similar to chocolate both in color and appearance. When long exposed to the air, the surface acquires the appearance of ordinary limestone, but on fracturing the specimen the interior will be found unchanged. The proportion of bitumen cannot be judged from the appearance.

The average specific gravity of rock-asphalt is about 2·23. It is very hard and sonorous when cold, and may be broken with a hammer. In summer it is softened by blows to a kind of paste, and at 50° to 60° falls to powder. Some rock-asphalts, such as that of Lobsann, contain a volatile oil which renders them greasy. This oil may be removed by distillation, after which the asphalt is fit for use.

Good rock-asphalt has a fine and homogeneous grain, and no particle of white limestone is visible. The rock is often streaked, while other samples contain crystals of calcite of considerable size, but impregnated with bitumen like the matrix, which is an important characteristic. Bad qualities are imperfectly impregnated, or contain so small a proportion of bitumen as to render it difficult to work them. The presence of clay spoils the homogeneous nature of the asphalt, and causes fissures.

When intended to be used for paving, the Val de Travers, Seyssel, and other rock-asphalts are often melted with a certain proportion of rich native asphalt, such as Trinidad pitch, the product being called " mastic." The mastic is often mixed with a further proportion of bitumen, residuum, shale oil, and mineral matter.

Composition of Rock-Asphalts.—The following data are compiled

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[1] *Trans. Amer. Soc. Civ. Engin.*, 1897, 214.

from various sources, as indicated. The detailed statement of the mineral ingredients is given somewhat vaguely in some of the reports, but the principal ingredients will serve for comparison. The loss at or about 100° C. is designated by some analysts as water, but it may include bituminous matters:

Source.	Loss at 90° C.	Soluble in Carbon Disulphide.	Calcium Carbonate.	Magnesium Carbonate.	Sand or Clay.	Sulphur.	Authority.
Ragusa, ...	...	9·72	88·75	...	...	...	Tillson.[1]
Seyssel, ...	...	8·15	91·70	...	...	...	,,
,, ...	1·90	8·00	89·55	0·10	0·25	...	Orton.[2]
Val de Travers, .	...	7·20	...	...	...	...	Tillson.[1]
,, .	...	12·00	...	...	...	...	,,
,, .	0·50	10·10	87·95	0·30	...	...	Orton.[2]
Limmer, . . .	...	14·30	67·00	...	17·52	...	Sadtler.[3]
,, . . .	...	8·26	56·50	27·01	4·98	...	Orton.[2]
Vorwohle, . . .	...	5·37	90·80	...	2·55	...	Sadtler.[3]
Lobsann, . . .	3·40	11·90	69·00	0·30	3·05	5·00[6]	Orton.[1]
Forens, ...	0·20	2·25	97·00	0·70	...	...	,,
California, . . .	2·50	20·20	3·00	...	74·00	...	Hilgard.[4]
,, . . .	0·33	15·13	...	...	83·40[7]	...	Linton.[5]
Kentucky, . . .	...	5·76	...	...	94·22[7]	...	,,
Turrelite (Texas), . . .	...	12·05	87·94[7]	...	...	...	,,

Composition of Soft Asphalts.—The natural asphalts other than the true rock-asphalts show great differences in composition, both as regards the proximate constituents and the nature and amount of mineral matter. The following table includes the more important forms. The total bituminous matter has usually been estimated by solution in carbon disulphide, or by successive extraction with petroleum spirit, boiling turpentine, and chloroform. The mineral matter is mostly a ferruginous clay. The ash, obtained by burning a known weight of the asphalt, does not represent exactly the mineral matter in the original material, but the differ-

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[1] *Trans. Amer. Soc. Civ. Engin.*, 1897. [2] Rep. to Geol. Survey of Ky. (data from German sources). [3] *Ind. Org. Chem.* [4] Ann. Rep. State Mineral. of Calif., 1890; average of fourteen samples. [5] *J. A. C. S.*, 1894 and 1896. [6] Present as iron sulphide. [7] Total mineral matter; the details of composition are not given, except that Turrelite is stated to consist largely of sea-shells cemented into a mass by the bitumen.

ence is not important, as at present the details of its composition have no practical value:

SOURCE.	SOLUBLE IN CARBON DISULPHIDE.	MINERAL MATTERS.	NON-BITUMINOUS ORGANIC MATTER.	AUTHORITY.
Trinidad—Lake, . .	54·25	36·51	9·24	Richardson.[1]
,, ,, . .	52·97	36·10	10·96	Linton.[2]
,, Land, . .	54·03	36·49	9·48	Richardson.
,, ,, . .	52.27	37·73	10·01	,,
,, ,, . .	52·57	35·88	11·52	Linton.[2]
Grahamite, Va., . .	100·00	...	...	,,
Bermudez, ...	94·75	3·65	1·60	Richardson.[1]
,, ...	98·52	0·50	0·98	,,
,, ...	91·88	1·67	6·45	,,
California maltha, .	98.26	1·74	...	Tillson.[3]
,, Kern Co., .	93·20	5·77	0·54	,,
Gilsonite, Utah, . .	100·00	0·10	...	Day.[4]

ADULTERATIONS OF ASPHALT AND ASPHALTIC MIXTURES.

Pure asphalt is much employed in the manufacture of black varnishes and japans, and for other similar purposes. It is not unfrequently mixed with or substituted by *coal-tar pitch* and other artificial products, which render it quite unfit for some of its most important uses.

Asphalt for varnish-making should be entirely (or with the exception of 4 or 5 per cent. of earthy matters) soluble in carbon disulphide, chloroform, high-boiling coal-tar naphtha, and oil of turpentine. It is also said to be insoluble in alcohol or a mixture of equal parts of alcohol and chloroform. It should break with a conchoidal fracture and brilliant resinous lustre, the streak and powder being of a bright brown. Asphalt should not flow or lose shape like wood-tar pitch when left on a plane surface, and an angular fragment or chip should retain its shape and the sharpness of its angles in boiling water, and only begin to melt at about 150° C. Asphalt adulterated with coal-tar pitch has a much less brilliant fracture-surface, and an adamantine or metallic rather than a resinous lustre. When fused at as low a temperature as possible, the adulterated asphalt has a granular pasty appearance

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[1] Contrib. from Lab. of Barber Asphalt Paving Co., No. 1 (1898). [2] *J. S. C. I.*, 1896, 275. [3] *Trans. Amer. Soc. Civ. Engin.*, 1897. [4] *Jour. Frank. Inst.*, Sept., 1895.

and feel, instead of being smooth and homogeneous, and will not draw out into even and transparent brown threads like pure asphalt.[1]

The following figures, due to E. Davies (*Pharm. Jour.*, [3], XIV. 394), show the behavior of certain natural asphalts, rock-asphalts, and their substitutes, with petroleum spirit. The proportions of sulphur and mineral matter are also recorded.

For these analyses, 5 grm. of the finely-divided sample were digested for one hour with 50 c.c. of petroleum spirit of 0·70 specific gravity, and the mixture frequently agitated. The liquid was then boiled for a short time, decanted, and the residue boiled with another quantity of 25 c.c. of petroleum spirit. This treatment was repeated eight or ten times, till the exhaustion was complete.

Material.	Ash.	Action of Petroleum Spirit.		Proportion Soluble for 100 of Organic Matter.	Sulphur.	
		Soluble.	Insoluble.		Per 100 of Material.	Per 100 of Organic Matter.
Val de Travers asphalt,	90·24	9·76	none	100·00	·41	4·20
Fine Syrian asphalt, .	·68	48·16	51·16	48·49	6·13	6·19
Low Syrian asphalt, .	2·64	49·68	47·68	51·02	5·65	5·80
Trinidad pitch, . . .	37·76	36·24	26·00	58·22	3·47	5·58
—	—	—	—	—	—	—
American asphalt, . .	·60	65·64	33·70	66·03	·62	...
American asphalt, . .	·26	63·62	36·12	63·78	·85	...
Stearin pitch, . . .	5·50	71·05	23·45	75·18	·04	...
Stockholm pitch, . .	·84	91·46	7·70	92·23	·01	...
Rosin pitch, ...	·58	86·94	12·48	87·45	·26	...
Coal-tar pitch, . . .	·20	24·44	75·36	24·29	·69	...
Coal-tar pitch, . . .	1·06	18·70	80·74	18·90	·41	...
Coal-tar pitch, . . .	·48	15·86	83·66	15·94	·59	...

Of these samples, those of American asphalt were evidently manufactured and not natural products. They were probably petroleum pitch, and were black, brittle substances, having a conchoidal fracture and black streak. They differed from stearin pitch in their brittleness and the proportion of sulphur. The Stockholm pitch was black, too soft to powder, and very easily

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[1] The characters of asphalt fitted for varnish-making given in the text are taken from Spon's *Encyclopædia*. They apply to refined asphalt.

soluble in petroleum spirit. The rosin pitch had a conchoidal fracture, and gave a brown powder. The different proportions of matter soluble in petroleum spirit present in the samples of coal-tar pitch were no doubt due to the extent to which the respective distillations had been carried.

The following results have been obtained by A. E. Jordan in the author's laboratory, by the analysis of typical specimens of pitch:

MATERIAL.	ASH.	ORGANIC MATTER.		ACTION OF PETROLEUM SPIRIT.		
		Volatile.	Non-volatile.	Soluble.	Insoluble.	Percentage of Organic Matter Soluble.
Asphalt (origin unknown), ...	·60	80·79	18·61	47·63	51·77	47·91
Trinidad pitch, . . .	5·48	76·75	17·77	74·23	20·29	78·53
—	—	—	—	—	—	—
Petroleum pitch, . .	none	50·43	49·57	36·16	63·84	36·16
Shale-oil pitch, . . .	·25	66·40	33·35	63·62	36·13	68·77
Coal-tar pitch, . . .	·15	49·33	50·52	18·56	81·29	18·58
Bone pitch (inferior),	·33	56·15	43·52	29·96	69·71	30·05

From a general consideration of the figures, it is apparent that Val de Travers asphalt yields the whole of its organic matter to petroleum spirit, and the other mineral pitches not sensibly less than one-half, but the soluble portion of coal-tar pitch does not exceed 25 per cent. Coal-tar pitch is only partially soluble in carbon disulphide, but a larger proportion dissolves than in petroleum spirit. The other varieties of manufactured pitch are not produced in sufficiently large amount to make their substitution for mineral pitch for paving a very important consideration.

For the distinction between natural asphalt and coal-tar pitch reliance has sometimes been placed on the fluorescence of the petroleum-spirit solution when coal-tar products are present, but some crude asphalts also produce fluorescent and refined asphalt may contain petroleum residuum. Durand-Claye suggested the following test: The sample is digested in carbon disulphide, filtered, the filtrate evaporated to dryness, and the residue heated until it is hard and brittle after cooling: About 0·1 grm. is shaken for a few minutes with 5 c.c. of fuming sulphuric acid in a stoppered tube, the mixture allowed to stand for twenty-four hours, and then 10 c.c. of water added, drop by drop, with constant stirring, after which the liquid is filtered through paper. Natural bitumens will give a colorless or faintly colored solution, but coal-tar pitch will give a dark brown. If the conditions of the test are uniform, approximate quantitative comparison of samples may be made. The following comparisons were made in the author's laboratory:

Rock asphalt,	Faintly colored.
Trinidad asphalt,	Slight brown.
Petroleum pitch,	No color.
Shale-oil ,,	Hair brown.
Coal-tar ,,	Very dark brown.
Bone pitch,	,, ,, ,,

Asphalt-paving Mixtures.—Many asphalts are unsuited for use in street-paving unless mixed with tempering materials. Practice, in American cities especially, has led to the selection of special proportions of petroleum residuum, sand, or stone-dust, and pulverized limestone. As a guide to the composition of these mixtures the official specifications of two large cities and some engineering notes are given. The Philadelphia specifications are in part based on the results of an examination made a few years ago,[1] but agree in the main with those of most American cities. The Washington specifications are more scientific.

Philadelphia, 1894.—If natural rock-asphalt is used for the wearing surface, it shall be natural bituminous limestone rock: From the Sicilian mines at Ragusa or the Catania mines, equal in quality and composition to that mined by the United Limmer and Vorwohle Rock Asphalt Company, Limited. From the Swiss mines of Val de Travers, equal in quality and composition to that mined by the Neuchatel Rock Asphalt Company, Limited. From the French mines at Seyssel, equal in quality and composition to that mined by Compagnie Générale des Asphalte de France in the proportions of four parts of the Sicilian Rock to one of the Seyssel or Vorwohle Rock.

If refined asphalt is used for the wearing surface, it shall be composed of the best quality of refined Trinidad or Bermudez asphalt, obtained from the so-called pitch or asphalt lake on the Island of Trinidad or from Bermudez, South America, or other asphalt which in quality and durability shall be equal to the standard of the Lake Trinidad or Bermudez, heavy petroleum residuum oil, fine sand, fine stone-dust, fine powder of calcium carbonate. The asphalt must be refined and as far as possible freed from

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[1] Report of experts (Sadtler, Leffmann, and Lewis) selected by Citizens' Municipal Association and the Trades' League of Philadelphia, 1894.

organic and mineral matter and volatile oil, and should contain at least sixty per cent. of bituminous matter soluble in carbon disulphide; the residuum oil must be free from coke and other impurities, of a specific gravity of eighteen or twenty-two Baumé, and withstand a fire test of 250° F. The refined asphalt and residuum oil will be mixed in the following proportions by weight: asphalt 100, petroleum 16 to 22.

The asphaltic cement made in the manner above described will be mixed with other materials in the following proportion by weight—viz.:

Asphaltic cement,	13 to 16
Sand,	58 to 63
Stone-dust,	23 to 28
Pulverized limestone,	5 to 3

Washington, D. C., 1898.—When the refined asphalt is not of proper consistency, the cement may be prepared by tempering the asphalt with heavy petroleum oil or other softening agent. The oil used shall be a petroleum oil from which the lighter portions have been removed without cracking until the residuum has the following characters:

Flash-point, taken in a New York State closed oil-tester, not less than 300° F. Distillate, at 400° F. for 30 hours, less than 10 per cent.

The distillate should be made with about 50 grm. of the oil in a small glass retort provided with a thermometer and packed entirely in asbestos. The residue after distilling must be fluid at 75° F. and not coarsely crystalline on cooling.

The proportions of asphalt cement and other material will depend on its various conditions, but the proportion of bituminous matter soluble in carbon disulphide shall not exceed the limits of 9 to 13 per cent.

The following formula has been used by engineers for paving mixtures containing Bermudez asphalt:

Asphaltic cement (Ref. Berm. Asp., 100; Residuum, 11),	10·05
Sand,	74·85
Pulverized calcium carbonate,	15·00

R. B. Stanton (*Trans. Amer. Soc. Civ. Engin.*, 1896, 73) used for reservoir-lining in California 4 parts best refined California asphalt and 1 part crude petroleum without sand; he also used broken stone, 2 inches and under, including all fine material. Trautwine employed at Philadelphia, for reservoir lining, 4 parts of Bermudez asphalt and 1 part of a liquid California asphalt.

Bowen's tester for ascertaining hardness of paving mixtures consists of a needle suspended on a lever arm connected with a thread that moves a pointer on a dial. The depth to which the needle sinks will depend on the hardness of the asphalt. The apparatus is much used, but two machines will give concordant results only when constructed and operated exactly alike. Dow has devised a more elaborate apparatus, in which a needle penetrates by a direct weight without friction.

Analytical Methods for Asphalts.—It has been noted above that much difference is shown in the practice of different analysts in examining natural asphalts. Sometimes determinations have been of volatile matter, fixed carbon, ash, and sulphur—figures which are applicable to fuels, but throw no practical light on the value of the asphalt for the uses made of it.

It is not possible to decide at the present time as to the preferable method of analysis, and therefore several of the best known will be given. Most of these involve extraction by simple solvents, and, as the original papers show, separating funnels, flasks, or beakers have been much employed, but the Soxhlet extractor is often more convenient. The sample may be mixed with fine sand or fine asbestos, placed in a plaited filter made of hardened paper and tied with a wire. This is put into a Schleicher and Schüll paper thimble, which is set in the Soxhlet tube, supported by a short, wide glass tube about 2 cm. long (a piece of a test-tube will serve). The thimble should stand at such a height that its top is just *below* the level of the turn of the siphon; the edge of the filter must not project above the top. A Gooch crucible is set snugly into the thimble so that the top of crucible is *above* the turn of the siphon. By this arrangement all the porous materials are bathed in the solvent and no fine particles can float out of the filter. It is easy to arrange the apparatus so that the drops from the condensing-tube fall directly into the filter and escape through the paper.

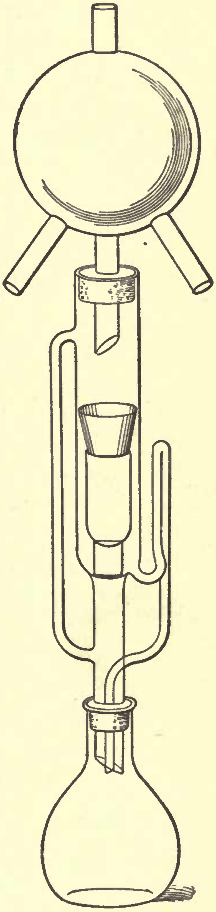
Fig. 1.

Figure 1 shows the arrangement. The condensing apparatus is a double ball, the outer surface nickel-plated. The space between the two balls receives the vapor of the solvent and communicates with the vertical tubes at the top and bottom; the inclined tubes communicate with the inner cavity and carry the cooling water, the direction being indicated by an inwardly-pointing arrow. (For other forms of extracting apparatus see Appendix.)

In these operations the portions extracted by solvents are usually estimated by loss in weight suffered by the sample, and it has been assumed by many analysts that the solvents will take up only bituminous matters, but it is now known that notable amounts of mineral matters may also be removed. Richardson asserts that these are mostly not in solution, but in suspension in such fine division that they will pass through any filter, and will not subside on long standing, but may be almost entirely removed by long whirling in a high-speed centrifuge. It is probable that proper fractionation cannot be made except by distillation in a non-oxidizing atmosphere. There is a limit, however, to the extent to which the distillation method can be used, even in an inactive atmosphere, for the so-called "cracking" of the hydrocarbons may occur, by which simpler and more volatile bodies may be formed from the less volatile ingredients.

Water.—The water in asphalt samples being hygroscopic, the proportion will be influenced by the condition of the atmosphere. Samples should be dried to constant weight at a temperature not above 50° C. Linton has shown that the loss of weight at or near 100° C. will include volatile hydrocarbons. Richardson dries samples over sulphuric acid at low pressure, but Peckham considers this unnecessary. (For drying apparatus see Appendix.)

Non-bituminous Organic Matter and Ash.—As noted above, the organic matter not soluble in the various solvents used for fractionating the asphalt is noted as "non-bituminous organic matter" or by some similar descriptive term. It is estimated by difference; the total residue left after the various solvents have exhausted their action is dried, weighed, ignited until all carbon has disappeared, and weighed again. The loss of weight is considered to be non-bituminous matter. It is obvious that if the original matter contained notable amounts of carbonates, the total loss will include the carbon dioxide that has escaped. To correct this, the ash may be recarbonated by allowing it to remain some hours in contact with a solution of carbon dioxide in water, or by heating it with ammonium carbonate solution, evaporating, and heating gently. Ash may, of course, be determined directly, without extraction. This will give a more accurate result in some cases in consequence of the solubility of some of the mineral material in the solvents used. The detailed examination of the ash is conducted according to the usual methods for clay, limestone, or sandstone as the case may be.

Sulphur.—Richardson recommends Mabery's method—combustion in a current of oxygen and absorption of the sulphur dioxide by standard alkali. Day[1] found considerable difficulty in determining sulphur in a specimen of Utah gilsonite, owing to the liability of sulphur compounds to distil before oxidation. He finally succeeded by oxidizing the material in an open vessel with strong nitric acid by aid of heat. In time the material dissolves completely to a dark red liquid. When this condition is reached, the solution should be poured into cold water, by which a reddish-brown precipitate is formed, which contains all but traces of the sulphur. This mass is well washed, and the sulphur determined by Eschka's method.

E. H. Hodgson[2] has made tests of several methods for determining sulphur in asphalts, and finds that Carius' method—oxidation by fuming nitric acid—gives the best results, but is tedious and liable to explosion. This process is thus described: The tubes used were made of heavy glass. Two determinations were made on each sample, one with one gram of material and one with half a gram. The sample is placed at the bottom of the tube and 15 c.c. of fuming nitric acid (sp. gr. 1·60) poured on. The open end is then drawn out fine, but not sealed, and the tube heated for about six hours in water kept at from 80° to 90° C. Five c.c. more of acid are added, the tube is sealed, and heated in a guarded oven (on account of danger of explosion) at 150° C. for from four to five hours. Allow the tube to cool, open, reseal, and heat again for from two to four hours at a temperature of 180° to 200° C. Cool, open, and remove the liquid to a beaker of 250 c.c. capacity; dilute with water, filter, and wash. If the residue contains anything but sand it is saved and treated separately. The filtrate is evaporated to dryness on the water-bath, adding a piece of sodium hydroxide. The nitrates are completely decomposed by repeatedly evaporating the solution with hydrochloric acid and the silica rendered insoluble by heating to 110° C. in an air-bath. The mass is cooled, 2 or 3 c.c. of hydrochloric acid added, then 100 c.c. of water, the mixture stirred, filtered, the filter well washed, and the filtrate diluted to 200 c.c., heated to boiling, and 20 c.c. of a 20 per cent. solution of

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[1] *J. Frank. Inst.*, Vol. 140 (1895), 221.

[2] *J. A. C. S.*, 1898, 882.

barium chloride added from a burette at the rate of about one drop each second, stirring all the time. When the chloride is added, boil for about ten minutes and allow to stand twenty-four hours. Filter, wash with hot water, dry, ignite, cool, moisten with sulphuric acid, re-ignite, cool, and weigh.

Eschka's method is next in accuracy to that with fuming nitric acid, and is carried out as follows:

One gram of the finely ground material is intimately mixed with one gram of calcined magnesium oxide and a half gram of mixed potassium and sodium carbonates added. The mass is thoroughly mixed and heated to dull redness in a platinum or porcelain crucible, with constant stirring, until it is converted into a dull yellow ash. The crucible is cooled and about a gram of finely powdered ammonium nitrate added and well mixed. The heat is again raised to dull redness and continued until all the ammonium nitrate is decomposed. The mass is cooled, extracted with hot water, filtered, the filter well washed, the filtrate and washings acidulated with hydrochloric acid, and precipitated with barium chloride in the manner described under Carius' method.

The methods employing sodium dioxide or nitrates are apt to be too low.

Fractionation of Asphalts; Determination of So-called Petrolene and Asphaltene.—The results obtained by the following processes are more or less arbitrary, and cannot be regarded as true proximate analyses; but it must be borne in mind that engineers have reached certain opinions as to qualities of asphalts for special purposes, and have interpreted the analytic data in accordance with these practical results; hence in examining newly-discovered asphalts it may be necessary to use the older methods, even if improved processes should also be employed.

Richardson's Method[1].—For Trinidad asphalt, separate weighed portions of the sample dried in vacuum over sulphuric acid are extracted in Erlenmeyer flasks, provided with reversed condensers, the solvents being kept boiling for the first portions about ten or fifteen minutes, the later extractions much longer. Between each addition of fresh solvent the liquid is decanted through an asbestos filter made in a Gooch crucible. The extraction is repeated until a fresh portion of solvent is no longer appreciably

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[1] Contrib. fr. Lab. Barber Asphalt Paving Co., No. 1 (1898). Amended by private communication (April 10, 1899) to American reviser.

colored. When carbon disulphide is used, the whole of the filtrate is collected and burned in a platinum basin, the residual bituminous matter ashed and weighed. This weight is deducted from the loss which the original material has suffered by the extraction. The petroleum spirit filtrate is not regarded as containing an appreciable amount of mineral matter, and hence is not further treated. The undissolved material from either extraction is weighed and the loss counted as bituminous matter dissolved, subject to the correction already noted in the case of the carbon disulphide. The petroleum spirit used should have a specific gravity of about 0·650. All solvents should be free from water.

The Gooch crucibles are more convenient if made broader and shallower than the usual form.

Bermudez asphalt requires a somewhat different method, owing to its sticky nature, which prevents drying of it by powdering and exposing to the air. The samples may be heated to the softening point, but some volatile matter other than water will be lost.

Linton's Method.[1]—The dried sample is weighed on a tared filter, which is then placed in a separator-funnel, 50 c.c. of petroleum spirit poured on, allowed to remain a few minutes, and then drawn off; more of the spirit is then added and also soon drawn off. It is necessary that the first portions of solvent should not become highly charged with soluble matters, since these may be precipitated as the liquid runs out of the funnel. When the mass is nearly exhausted, the later portions of solvent may be left for some hours in contact with the sample. The extraction must be carried on until the solvent ceases to be colored. The filter and its contents are dried in a steam-bath and weighed; the loss of weight represents that portion of the asphalt commonly designated as petrolene.

The filter and contents are placed in the separator-funnel, enough boiling oil of turpentine added to cover them, and the mixture allowed to stand for some hours or overnight. The process must be repeated with fresh portions of boiling oil of turpentine until the filtrate is colorless. The mass is now treated with chloroform sufficient to cover it, and at least an hour allowed for solution. Washing with chloroform is continued until it passes through colorless. The residue is dried and weighed; the loss is designated asphaltene. The filter and contents are burned in a platinum crucible, and if the sample originally contained a notable amount of

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[1] *J. A. C. S.*, 1894, 820; 1896, 276.

calcium carbonate the residue should be re-carbonated before weighing.

Sadtler's Method.[1]—An asbestos filter is made in a weighed Gooch crucible and dried. About 10 grm. of fine white sand, previously ignited and cooled, are added, a piece of stout platinum wire 7 or 8 cm. long is placed in the crucible, and the whole dried to constant weight at 100°. One to 2 grm. of the sample in fine powder are added, gently mixed with the upper portion of the sand layer with the aid of the platinum wire, care being taken not to disturb the asbestos filter. If the sample be a liquid bitumen, it is gently mixed with the sand layer after slightly softening with aid of the drying oven. The weight of the whole is accurately taken, and then dried at 100° to a constant weight in an air-bath or water-oven, cooled in a desiccator, and weighed. The crucible and contents are placed in a continuous extraction apparatus formed by placing a small conical percolator within a larger one, the inner one being held in position by a perforated cork. The crucible is placed in the inner percolator; the outer one is connected with a flask containing pure acetone, and with an upright condenser. The flask is heated by a water- or sand-bath. Acetone is first used and the operation continued until the loss on continuing the extraction for two hours does not exceed 2 mm. The loss of weight computed on the weight after drying is designated petrolene. The extraction is then continued with chloroform, and the additional loss is designated asphaltene. The duration of the total extraction varies with different samples, but usually twelve hours for the acetone and eight hours for the chloroform will suffice. The loss of weight should be taken every four hours at first, and then every two hours until the extraction is complete, the crucible and contents being dried at 100° each time and cooled in a desiccator. The final residue in the crucible is considered to represent the non-bituminous organic and mineral matter. It is ignited after placing the cap on the bottom of the crucible and weighed; the loss is designated non-bituminous matter, the residue mineral matter or ash.

Endemann's Method.[2]—Crude or very rich asphalts are subjected to a preliminary treatment strictly similar to that employed in refining on the large scale—to wit: Not less than 200 grm. should be put into a vessel with straight, perpendicular

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[1] *J. Frank. Inst.*, vol. 140 (1895), 385.

[2] *J. S. C. I.*, 1896, 874.

sides, about half as wide as deep, and of such capacity that the amount of sample used does not more than half fill it. It is stirred, if possible, during the heating. The end temperature should be from 175° to 235° C., according to the application to be made of the asphalt. The loss should be noted, and called light petrolene and water. Endemann does not state how long the heating is to be continued. If it be not desirable to promote uniformity by stirring and much mineral matter subside, the ratio thus removed should be ascertained by determinations of the mineral matter in both the crude and laboratory-refined, under proper consideration of the concentration of the material during the process. After ascertaining the loss due to refining, some of the material is poured out, cooled quickly, and analyses made as follows:

Five grm. of the refined asphalt (or more, if much mineral matter be present) are treated with chloroform, and the residue is collected on a weighed filter and treated in the ordinary way—for example, as described by Linton. The chloroform solution is distilled from a weighed flask, and the residue dried at 120° C. for half an hour. In order that this residue may be collected in a small flask, it is proposed to allow the solution to flow in through a funnel with stopcock, as the distillation proceeds.

About 0·2 to 0·5 grm. of the residue are placed in a porcelain boat and maintained at 250° C. in a current of carbon dioxide for twelve hours. The mass should be spread over as large a surface as possible. The tube containing the boat is closed at the end with an asbestos stopper. The loss of weight is assigned as petrolene; the residue is not a pure bitumen, but contains, as Endemann has shown, a notable amount of mineral matter, which passes into the chloroform solution, in consequence of existing in some form of combination with the oxidised portion of the bitumen. The residue must be burned off, therefore, and weighed when the loss is assigned as asphaltene.

Comparison of Methods.—It is obvious that these methods will not give strictly comparable results on even the same specimens, and that the designation of particular fractions as petrolene or asphaltene, without indicating the method of extraction, may be misleading. Endemann's method reverses the ratio between petrolene and asphaltene as given by the other methods. In accordance with the results by extraction with solvents, engineers have regarded 30 per cent. of asphaltene calculated on the total bitumen as the highest permissible limit for paving asphalt, but Endemann's figures make the asphaltene the more abundant ingredient.

Endemann states that he has found that the asphaltenes obtained by his process from Mexican and Trinidad asphalts are identical, and that by dividing by three the figure for petrolene as given in analysis by the extraction method, and adding the difference between the two figures to the asphaltene, an approximation may be obtained to the results of his method. This recalculation is adapted only to paving-asphalts. A table giving some recalculations of analytical data according to this rule is given later.

Peckham[1] has compared the results of the application of Linton's and Sadtler's methods to identical samples, and finds considerable differences. He gives the following figures. The exact nature of the sample marked "épurée" is not stated, but it is not the ordinary refined asphalt.

Linton's Method:

	TRINIDAD ASPHALT.	
	Crude.	Épurée.
Soluble in petroleum spirit, ...	33·73	33·62
,, ,, boiling oil of turpentine,	10·51	15·57
,, ,, chloroform, ...	8·12	2·67
Total bituminous matter, ...	52·36	51·86
Organic matter not bitumen, . . .	10·85	10·15
Mineral matter, ...	36·72	37·97

Sadtler's Method:

	Crude.	Épurée.
Soluble in acetone, ...	28·18	26·31
,, ,, chloroform, ...	27·00	29·17
Total bituminous matter, ...	55·18	55·48
Organic matter not bitumen, . . .	9·83	9·60
Mineral matter, ...	34·98	34·92

A sample of very dry Egyptian asphalt and one from the Athasbasca River region were selected as representing the ex-

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[1] *J. Frank. Inst.*, 1896.

tremes of variation in composition, and the solubilities in petroleum spirit and acetone compared, as follows:

	EGYPTIAN.	ATHASBASCA.
Per cent. soluble in acetone,	8·68	24·33
,, ,, ,, ,, petroleum spirit,	38·03	73·86

Acetone should not be substituted for petroleum spirit unless notice is given in the report of analysis.

Sadtler furnishes the following figures obtained by the acetone method, but gives no comparative analyses. It is to be noted that the Trinidad and Bermudez samples were the commercially refined.

	TRINIDAD.	BERMUDEZ.	ALCATRAZ (liquid).
Soluble in acetone,	46·40	66·47	89·21
,, ,, chloroform,	15·14	29·66	9·39
Organic matter not bitumen,	3·02	1·76	trace.
Mineral matter,	35·44	2·11	1·40

Ultimate Composition of Asphalts.—The ultimate composition of an asphalt will, as a rule, be of little value in determining its application in engineering or industrial operations. The amount of sulphur and nitrogen may be of some moment. The former is regarded by Richardson as influencing materially the hardness of the asphalt by inducing polymerization, but this view has not been accepted by all experts in this field. The oxidation of the sulphur, which is probably mostly present in combination with hydrocarbons, in forms analogous to the mercaptans, may produce acids which will injure the asphalt proper or the paving mixtures made with it. Nitrogen is usually present in small amount, and, in part at least, in the form of pyridine derivatives. The following figures are taken from results given by Richardson,[1] who gives all the elements present in the bituminous matter, but only the sulphur and nitrogen are here transcribed. In each case the percentage is calculated upon the extracted bitumen. Oxygen, according to Richardson, is not present in the bituminous matter of asphalts, except in traces. It is found in notable amount in the non-bituminous organic matter.

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[1] Contributions from Laboratory of Barber Asphalt Paving Co., No. 1, 1898.

	N.	S.
Nevada,	1·30	9·76
Texas, Uvalde Co.,	0·28	9·60
Italy, Ancona,	1·40	9·39
Egypt,	0·19	8·52
Cuba, Bejucal,	0·09	8·28
California, Waldorf,	0·35	6·47
Trinidad, Lake,	0·81	6·16
,, Land,	0·45	4·98
Bermudez, hard,	0·75	3·93
Sicily, rock asphalt,	0·33	3·69
Bermudez (maltha),		5·87
Montana (maltha),		3·92
Mexico,		1·48
California, Alcatraz (maltha),	1·21	1·32
Gilsonite, Utah,	0·79	1·79
Albertite, New Brunswick,	0·42	1·20

Bromine and Iodine Absorption.—Endemann obtained the following figures for iodine absorption. No hydriodic acid was formed, hence the iodine all formed additive compounds:

	TRINIDAD.		MEXICAN.
	Land.	Lake.	
Iodine, per cent., in twenty hours,	20·32	19·04	21·90

Richardson gives numerous observations of bromine absorptions. The following percentages are taken from his tables:

	BROMINE ABSORBED.	HYDROBROMIC ACID FORMED.
Trinidad, pure bitumen,	30·42	12·19
Crude Bermudez, various samples,	29·71	19·25
	32·69	18·89
	20·83	12·44
California (maltha),	23·73	15·31
Alcatraz (liquid),	29·31	19·85

Nature of the Hydrocarbons in Asphalt.—Richardson has studied the hydrocarbons in Trinidad and Bermudez asphalts by fractional distillations, under conditions which reduce to a minimum the liability to cracking. The lighter oils seem not to contain methanes, ethenes, ethines, or naphthenes, but to belong to a dicyclic series.

Artificial Asphalts.—Many attempts have been made to employ the pitches and residuums from coal-oil and coal-tar as substitutes for asphalt. Some of these paving mixtures have been laid extensively in American cities, but have almost always been unsatisfactory. A few special forms of substitute asphalts deserve notice.

"Pittsburg flux" is produced by heating coal-oil residuum with sulphur; much of the latter is converted into hydrogen sulphide and escapes, but a notable amount is retained. A tough and sticky mass is produced, which melts only at a high temperature. It differs, however, from true asphalt in several important particulars.

"Sludge asphalt" is made from the sludge-tar of the petroleum refinery by the use of sulphur, and resembles asphalt more closely than does "Pittsburg flux."

"Byerlyte" is made from the heavy petroleum oil left after the burning oil has distilled. This is heated gently for five or six days, a current of air being passed through continuously. It contains, of course, no sulphur, but the quantity of oxygen is not large.[1]

According to Sabin[2] these substitute asphalts have both advantages and disadvantages as compared with the natural material. The substitute materials resist the action of sodium hydroxide. They can be mixed with rosin and some mineral oils, but not with vegetable oils.

The following figures for nitrogen and sulphur in these products are given by Richardson:

	N.	S.
Pittsburg flux, ...	2·38	4·10
Sludge asphalt, ...	0·00	4·87

Linton[3] made analyses by her method (see p. 83) of several artificial asphalts of the type of Pittsburg flux, and obtained the following results:

	Soluble in Petroleum Spirit.	Soluble in Chloroform and Turpentine.	Organic Matter Not Soluble.
From California, "Grade B," . .	64·5	21·25	13·7
,, ,, "Grade D," . .	63·5	30·00	6·1
Dubb's artificial asphalt, ...	66·8	32·00	1·3

Recalculation of Asphalt Analyses by Endemann's Rule.—For purposes of comparison some reported analyses by the extraction method have been recalculated, so as to show the approximate

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[1] Mabery, *J. A. C. S.*, 1896, 282.

[2] *J. A. C. S.*, 1896, 283.

[3] *J. A. C. S.*, 1894, 821.

yield of petrolene and asphaltene by Endemann's method (see rule on p. 86).

	PETROLENE.	ASPHALTENE.	CALCULATED FROM DATA GIVEN BY
Mexican, refined,	29·04	68·27	Endemann.
Trinidad, ,,	15·5	46·1	Sadtler.
,, ,,	13·0	42·6	Tillson.
,, crude, Lake,	11·7	41·0	Peckham (average).
,, ,, hard,	11·1	40·6	,, ,,
,, épurée,	11·2	37·9	,,
,, crude, Lake,	11·8	40·2	Linton.
Turrellite (Texas),	2·9	9·1	,,
Seyssel,	2·5	9·3	,,
Bermudez, crude,	24·8	74·7	Richardson.
,, ,,	21·6	69·0	,,
,, refined,	22·1	73·9	Sadtler.
Alcatraz, liquid,	29·7	69·8	,,

By actual comparative analysis Endemann obtained, from a sample of refined Mexican asphalt, 87·12 per cent. of petrolene by solution in petroleum spirit, and 26·51 per cent. by distillation. This latter figure is not materially different from that obtained by calculation, according to his rule.

PETROLEUM AND SHALE PRODUCTS.

The parallel products obtained by the distillation of crude petroleum and the oil or tar from bituminous shale (p. 38) present a marked similarity in general character, though differing notably in certain respects. As a rule, the treatment of petroleum is a much simpler operation than the manufacture of marketable products from crude shale oil, but, broadly speaking, the same method of treatment is applied to both of the raw materials. The process employed consists essentially in fractional distillation, and treatment of the separate fractions successively with sulphuric acid and caustic soda, to remove bodies of acid and basic character and to destroy the less stable hydrocarbons. The less volatile portions deposit paraffin wax on cooling. The following table shows in parallel columns the character and quantities of the products obtained in first-class works from crude American petroleum of 0·800 specific gravity and Scotch shale oil produced at the works of the Broxburn Oil Company:

PRODUCTS.	FROM PETROLEUM.		FROM SHALE OIL.	
	Specific Gravity.	Percentage.	Specific Gravity.	Percentage.
Cymogene and Rhigolene, ...	·590 to ·625	very small	...	very small
Gasolene, ...	·636 to ·657	1·0 to 1·5	·730	5
"C" Naphtha ("benzin-naphtha"),	·700	10		
"B" Naphtha, ...	·714 to ·718	2·5		
"A" Naphtha ("benzin"), ...	·725 to ·737	2·0 to 2·5		
Kerosene or burning oil, ...	·802	50 to 55	·800 to ·810	37
Lubricating oil, ...	·875	17·5	·885	17
Paraffin wax, ...	...	2	...	13
Coke, gas, and loss, ...	...	8 to 10	...	28

The yield of burning oil from any sample of petroleum may be increased nearly twenty per cent. with corresponding diminution of heavier products by a modification of the distillation by which the hydrocarbons of higher boiling points are changed by dissociation or, perhaps, in some cases, polymerization, into bodies of lower boiling points. This process, technically known as "cracking," was discovered by accident in an American refinery about forty years ago, and is now generally adopted since an increase in the burning oil is the most valuable result to the refiner. The chemistry involved in the change is not thoroughly understood. It is carried out in practice by arranging the distilling apparatus so that the hydrocarbons are condensed and fall back in drops upon the much hotter body of the liquid in the still. By this action the condensed oils become overheated and changed. Burning oils obtained by this method are different from, and somewhat inferior to, those produced by normal distillations, but the process, as noted above, is very much in vogue.

The Abruzzo bitumen is said to yield on distillation:

	PER CENT.	SPECIFIC GRAVITY.	FLASHING POINT. °C.
Burning oil, ...	15	·850	54·5°
Intermediate, ...	33	·945 (?)	121·1°
Lubricant, ...	16½	·990 (?)	157·2°

The products from Russian petroleum are very different in both density and percentage from those yielded by the American oil (see pp. 60, 63). Rangoon tar of 0·885 specific gravity gives, on an average, the following proportions of refined products: Burning oil (sp. gr. 0·832), 30 per cent.; lubricating oil (sp. gr. 0·901), 51 per cent.; and paraffin scale (melting at 51·4° C.), 10·7 per cent.

The products obtained by the distillation of ozokerite have already been described (p. 68).

The number of products into which the more volatile portions of shale oil and petroleum are fractionated varies considerably according to the practice of the works, but gasolene and the more volatile products are obtainable from shale oil equally with petroleum. The only commercial product obtainable from petroleum having no analogue amongst the products from shale oil is the substance known as vaseline. Sadtler (*Ind. Org. Chem.*) quotes the following table from *Wagner's Jahresbericht*, 1886, for the percentage yields of petroleum distillation on the large scale:

Crude Oil.	Benzin and Volatile Oils.	1st Quality Burn. Oil.	2nd Quality Burn. Oil.	Residuum.
Pennsylvania, ...	10 to 20	60 to 75		5 to 60
Galicia, ...	3 to 6	55 to 65		30 to 40
Alsace, ...	...	35 to 45		55 to 60
Roumania, ...	4	60 to 70		25 to 35
Baku (Bibi-Eibat), ...	10·5	40	13·5	36
,, (Balakhan), ...	5 to 6	27 to 33	5·6	50 to 60

The more volatile products from petroleum are briefly described on page 96. The similar fractions from shale oil closely resemble the petroleum products in their physical characters, but they contain a much larger proportion of ethenes. This chemical distinction has been traced by the author in each of the parallel products from American petroleum and shale oil, and is the cause of some curious differences in the behavior of these substances as solvents and with chemical reagents.

Engles and Jezioranski have examined oil from Pennsylvania, Galicia, Sumatra, Baku (Bibi-Eibat), and Pechelbronn. They consider that the fractions boiling below 200° C. consist mainly of methanes, except with the Baku oil; the portions boiling above 200° C. contain ethenes (olefins).

The following table gives a general idea of the chemical composition of the leading commercial hydrocarbon products derived from bituminous shale and American petroleum. Of course, the quantitative composition is liable to considerable variation, and hence must not be interpreted too strictly. The general and analytical characters of the products named in the table are described in the succeeding sections. The hydrocarbons from distillation of coal do not admit of parallel comparison with those from petroleum and shale.

PRODUCT.	BITUMINOUS SHALE.	AMERICAN PETROLEUM.
Naphtha, ...	At least 50 to 60 per cent. of heptene and homologues. The remainder as methanes. No trace of benzenes.	At least 75 per cent. of heptane, and homologues. The remainder apparently ethenes, with distinct traces of benzenes.
Kerosene, or burning oil, ...	50 to 80 per cent. or more of the higher ethenes. The remainder methanes.	50 to 80 per cent. of higher members of the methane series. The remainder chiefly ethenes.
Lubricating oil, .	Chiefly ethenes, with some polymerised members of the ethines.	A large proportion of higher ethenes, but less than in corresponding shale product.
Vaseline, ...	No such product.	Chiefly higher (iso-?) methanes of low melting point.
Paraffin, ...	Methanes.	Methanes.

From this table it will be seen that while the methanes are conspicuous in American petroleum, shale products are remarkable for their richness in ethenes. In consequence of this peculiarity of constitution, concentrated nitric and concentrated sulphuric acid act far more vigorously on shale products than on the parallel products from petroleum, and the proportion of methanes given in the above table really represents the percentage by measure of hydrocarbons which withstand a consecutive treatment with nitric acid of 1·45 specific gravity, concentrated sulphuric acid, fuming sulphuric acid, and caustic soda. Russian petroleum behaves with reagents much like American petroleum, but consists largely of cyclic hydrocarbons (naphthenes). (See p. 60.)

A much more satisfactory method, and one which gives fairly constant results, is based on the fact that methanes and naphthenes do not react with bromine, whilst the hydrocarbons of most other series take it up freely, forming additive or substitution products (p. 24).

The following table shows the results obtained by the author as to the action of bromine on various representative commercial products from shale, and American and Russian petroleum. The shale products were furnished by Mr. R. Tervet; those derived from American petroleum (with the exception of the gasolene and vaseline) were furnished by Mr. J. Merrill, of Boston, Mass.; and the Russian petroleum products by Messrs. Ragosine & Co. The solution of bromine in dry carbon disulphide was allowed to act on the dry oil for from 15 to 30 minutes in the dark, when potassium iodide was added and the liquid titrated with decinormal thiosulphate. After titration the solution was filtered, and the aqueous liquid titrated with standard caustic alkali and litmus. From the amount used, the proportion of hydrobromic acid formed was ascertained, and from this the bromine existing in that form was calculated.

From these results it will be seen that there is in every case a marked difference between the proportion of bromine assimilated by any of the shale products and the quantity which combines with the parallel product from American petroleum, especially in the lighter fractions. It is evident, however, that the results must not be interpreted too strictly, for an oil which was obtained by "cracking" would be richer in ethenes, and hence would show a higher bromine-absorption than one of another kind.

The results yielded by the products from Russian petroleum are still more striking, though other samples of kerosene have shown higher absorptions (*e. g.*, 15 per cent.) than those given in the table.

The following determinations by Mills and Snodgrass were made by the process described in Vol. II., part 1, page 63.

PRODUCT.	SPECIFIC GRAVITY.	BROMINE-ABSORPTION.
Lubricating shale oil, ...	·860	22·2
,, ,, ,, ...	·870	20·6
,, ,, ,, ...	·890	12·6
,, ,, ,, ...	·900	11·7

DESCRIPTION OF SUBSTANCE.	SPECIFIC GRAVITY AT 15·5° C.	GRAMS OF BROMINE REACTING WITH 100 GRAMS OF SAMPLE.	BROMINE AS HBr PER 100 GRAMS OF SAMPLE.
GASOLENES—			
From shale, ...	·665	62·2	1·1
From American petroleum, .	·650	17·9	3·1
NAPHTHAS—			
Shale naphtha, ...	·720	67·2	4·0
C. naphtha from American petroleum, ...	·706	18·3	...
BURNING OILS—			
From shale, ...	·813	51·3	3·0
From American petroleum, .	·800	34·8	...
From Russian petroleum, . .	·821	2·0	0·1
INTERMEDIATE OILS—			
From shale, ...	·850	48·2	...
"Mineral sperm oil" (American petroleum), ...	·847	32·3	...
"Pyronaphtha" (Russ. petr.),	·868	1·9	0·1
LUBRICATING OILS—			
From shale, ...	·890	25·6	5·8
Cylinder oil (from shale), . .	·890	11·0	...
From American petroleum (heavy spindle oil), ...	·900	11·7	...
From Russian petroleum, . .	·904	4·9	0·8
"Champion oil" (Amer. petr.),	·911	9·9	0·8
Cylinder oil (Russian petr.), .	·909	5·8	0·6
VASELINES—			
From American petroleum (Chesebrough Co.), ...	·856	11·3	1·8
From Russian petroleum, . .	...	1·7	0·3
PARAFFIN WAXES—			
From shale (m. p. 52°), . . .	...	1·7	0·5
From petroleum (m. p. 54°), .	...	0·9	0·2

These results are interesting as showing the diminution of the bromine-absorption with the increase in the density of the oil, and presumably with the mean molecular weight of its constituents.

Mineral Naphtha. Petroleum Spirit. Shale Naphtha.

These names are employed to signify generally the more volatile fractions obtained by the distillation of petroleum or shale oil. By some manufacturers the products from American petroleum are further divided into fractions distinguished in following table. B. Redwood gives the following classification of the more volatile portions of American petroleum: 0·637, rhigolene or cymogene for surgical purposes; 0·642 to 0·648, gasolene for air-gas machines; 0·680, boulevard gas fluid for street naphtha lamps; 0·690 to 0·707, prime city naphtha (benzolin) for sponge-lamps, &c.; 0·729, benzin, for oil cloth and varnish making.

	COMMERCIAL NAME.	DEGREES BAUMÉ.	SPECIFIC GRAVITY.	COMPOSITION.
	Cymogene, ...	108	0·588	Consists chiefly of tetrane, C_4H_{10}.
Petroleum ether,	Rhigolene, ...	94 to 92	0·625 to 0·631	Consists chiefly of pentane and isopentane, C_5H_{12}.
	Gasolene (Canadol), .	95 to 80	0·622 to 0·666	Consists chiefly of hexane, C_6H_{14}, and isohexane.
Petroleum spirit or Benzolin,	C. naphtha, . . . Benzin-naphtha, .	76 to 70	0·680 to 0·700	
	B. naphtha, ...	66 to 65	0·714 to 0·718	
	A. naphtha, . . . Benzin, ...	59 to 58	0·740 to 0·745	

The term ligroïn is sometimes used to indicate a petroleum-product boiling between 70° and 120° C., and having a density between ·685 and ·690. All the products from Russian petroleum are of greater specific gravity than the parallel products from the American oil.

A rule of the New York Produce Exchange defines petroleum naphtha as "water-white and sweet, and from 68° to 73° Baumé" (= 0·707 to 0·690 sp. gr.).

The employment of the terms "benzolin," "benzine," and "benzin" to denote the more volatile fractions obtained on distilling petroleum or shale oil has caused great confusion between the products so called and benzene, C_6H_6, the leading constituent of coal-tar naphtha. This confusion has been increased by the intentional substitution, partial or complete, of one product for the other. Methods for distinguishing petroleum spirit from coal-tar naphtha and for analysing mixtures of the two are described later.

PETROLEUM SPIRIT (which would be preferably called "light petroleum") consists of a mixture of homologous hydrocarbons of the methane series, with smaller quantities of isomethanes, methanes, &c., and traces of cyclic hydrocarbons. The relative proportions of the several constituents vary according to the boiling point and density of the sample, pentane and hexane being the chief constituents of the lighter and more volatile fractions, such as gasolene, while heptane is the leading constituent of the denser kinds, such as commercial benzolin, in which octane and even higher homologues are also present. Petroleum spirit is a thin, colorless liquid, having, when refined, a peculiar but not unpleasant odor. It gives off inflammable vapor at ordinary temperatures, and rapidly evaporates. It is said to absorb oxygen from the air. It is insoluble in water, but dissolves in about six parts of rectified spirit. It has considerable solvent properties. The lighter forms especially dissolve caoutchouc, asphalt, and, with less facility, colophony, mastic, and dammar resin. The heavier form (sp. gr. 0·745) is said not to dissolve resins. Petroleum spirit dissolves, in all proportions, the fixed oils of almond, olive, rape, linseed, croton, cod-liver, palm, cocoanut, theobroma, and lard. It does not dissolve castor oil, but the latter liquid dissolves its own volume of petroleum spirit (Vol. II., part 1, p. 158). Petroleum spirit also dissolves naphthalene, paraffin, wax, and many similar bodies, and is miscible in all proportions with pentyl alcohol, ether, chloroform, benzene, oil of turpentine, creosote, and cresols, but not with phenol.

The "benzin" of the United States Pharmacopeia is the portion of the purified distillate from American petroleum, having a density between 0·670 and 0·675, and boiling between 50° and 60° C.

The "petroleumbenzin" of the German Pharmacopeia is the colorless, non-fluorescent portions of petroleum, having a specific gravity of 0·640 to 0·670, and distilling almost entirely between 55° and 75° C. On adding 2 c. c. of this liquid to a cold mixture of 1 c. c. of sulphuric acid and 4 c. c. of fuming nitric acid and shaking, no appreciable color and no odor of bitter almonds should be produced.

The British Pharmacopeia (1898) defines "petroleum spirit" to be a derivative of petroleum, boiling between 50° and 60° C., and with a specific gravity between 0·670 to 0·700.

Petroleum spirit is liable to contain impurities, which unfit it for certain uses. If of good quality, it will leave no odor when evaporated on the hand, and when evaporated in a porcelain basin heated over boiling water, will leave no oily residue of *heavy hydrocarbons.* Boiled for a few minutes with alcohol and a few drops of ammonia, a brown coloration produced on subsequently adding silver nitrate solution indicates *sulphur compounds,* which render the sample unfit for use as a turpentine substitute, as it will be liable to discolor white paints. When petroleum spirit is agitated with warm water, the water after separation should be perfectly neutral in reaction, and should give no cloud with barium chloride (absence of *sulphuric acid* and *sulphonates*).

Water cannot exist in notable quantity in petroleum spirit without rendering the liquid milky. If present to an extent sufficient to be thus visible, the liquid is rendered unfit for burning in sponge lamps,[1] &c. The water may be removed by prolonged subsidence,

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[1] The influence of small amounts of water and heavy oils on the burning of petroleum is indicated by the following results obtained in the author's laboratory. The samples were sold under the inappropriate name of "gasolene," and were intended for safety lamps. Sample A burnt well, and was of satisfactory quality. B gave a very small flame, which went out entirely in about half an hour.

	A.	B.
Appearance,	Clear.	Very milky.
Specific gravity at 15·5° C.,	0·7038	0·7015
Distillate below 60° ,,	3·0 per cent.	4·1 per cent.
,, 70° ,,	17·5 ,,	18·7 ,,
,, 80° ,,	37·9 ,,	43·2 ,,
,, 90° ,,	60·7 ,,	56·0 ,,
,, 100° ,,	75·3 ,,	74·8 ,,
Tailings,	24·7 ,,	25·2 ,,
,, specific gravity,	0·7150	0·7272

On further distilling the tailings to 150°, A left a residue equal to 2·4 per cent. of or more rapidly and perfectly by agitating the sample with a little dry plaster of Paris.

	PETROLEUM SPIRIT.	SHALE NAPHTHA.	COAL-TAR NAPHTHA.
Chemical Composition.	Contains at least 75 per cent. of methanes, principally heptane, the remainder apparently ethenes, with traces of benzenes.	Contains at least 40 to 50 per cent. of ethenes, principally heptene; the remainder methanes. No trace of benzenes.	Consists almost wholly of benzenes. A small percentage of open-chain hydrocarbons in some samples.
Specific gravity at 15° C., ...	0·700	0·718	0·876
Chiefly distils between, ...	65° and 100° C.	65° and 100° C.	80° and 120° C.
Solvent action on coal-tar pitch.	Very slight action; liquid but slightly colored even after prolonged contact.	Behaves similarly to petroleum spirit.	Readily dissolves pitch, forming a deep brown solution.
Behavior on shaking three measures of the sample at 20° C. with one measure of fused crystals of absolute phenol.	No apparent solution; the liquids are not miscible, but set to a mass of crystals when cooled slightly below 0° C.	The liquids form a homogeneous mixture, often setting to a mass of crystals at 18° to 20° C.	The liquids form a homogeneous mixture.
Reaction with bromine in the cold.	Combines with 10 to 20 per cent. of its weight of bromine.	Combines with upwards of 60 per cent. of its weight of bromine.	Reacts slowly with a considerable proportion of bromine.

the sample, of 0·784 specific gravity; B left 3·2 per cent. of 0·798 specific gravity. On heating these residues to 100° for some time, that from A entirely volatilised, while B left a viscid liquid resembling lubricating oil. On treating the plugs of cotton-wool which formed the extremity of the wicks with water, the solution from B gave a very distinct precipitate with barium chloride, and a little water agitated with the original oil acquired a distinct acid reaction.

Shale Naphtha, which is the lighter and more volatile portion of the oil obtained by the distillation of bituminous shale, is a product very similar to petroleum spirit in most of its properties and uses. The author has found, however, that the shale naphtha presents certain differences, which are due to a much larger proportion of ethenes than exist in petroleum naphtha. The table on p. 99 exhibits concisely these differences, and compares the characters of a sample of coal-tar naphtha with specimens of similar products from shale and American petroleum. Variation in minor details will be met with in different samples from similar sources.

Mineral Burning Oil. Kerosene. Coal oil.

Under these names, and others more fanciful and less appropriate, are classed the fractions of petroleum and shale oil which are suited for burning with a wick. The petroleum product is often broadly described as "refined petroleum," and that from shale oil as "paraffin oil," but the latter name is often popularly applied to the similar oil from petroleum. The name "kerosene" is a contraction of *keroselain*, or "wax oil," and was originally a trademark adopted for a certain patented fraction of coal oil. The term has now been adopted as the most convenient to apply to mineral burning oils generally.

Kerosene is a colorless or yellowish oily liquid, often possessing a well-marked blue fluorescence. It has a characteristic taste and smell which it imparts to water, though practically insoluble in that liquid. It is only moderately soluble in alcohol, but is miscible in all proportions with ether, chloroform, benzene, petroleum spirit, volatile oil, and fixed oils, with the exception of castor oil. It dissolves phosphorus, sulphur, iodine, camphor, many resins, waxes, fats, and softens india-rubber to a glairy varnish.

The commercial varieties of mineral burning oil are very numerous, and hence the physical characters are not very constant.

The specific gravity of ordinary American kerosene is about 0·790 to 0·800, the parallel product from shale oil being 0·800, and from Russian (Baku) petroleum 0·822. Burning oils of higher densities are also largely manufactured, and are well adapted for special purposes.

The following are the characters and special applications of certain other varieties of mineral burning oils:

Colzarine Oil.—Specific gravity about 0·838; fire-test 250° F. Quite odorless, pale amber; specially intended for burning in "moderator" and "carcel lamps."

Cazeline Oil.—Specific gravity 0·805; fire-test 144° F. Limpid, with scarcely a trace of color, and very light odor.

Mineral Sperm Oil.—Specific gravity 0.829 to 0·847. Abel flash-point 240° F.; fire-test about 300° F. Specially adapted for lighthouse and locomotive lights. Its use is compulsory on some of the American railroads, and it is also extensively employed on board ship. "Mineral colza oil" and "mineral seal oil" are similar products.

Belmontine Oil.—Obtained by distillation of Rangoon tar or Burmese petroleum with superheated steam. Specific gravity 0·847; fire-test 134° F. Though heavy, the oil has but little viscosity, and will rise through a long wick. The flame is very white, and of high illuminating power.

Pyronaphtha is a product from Russian petroleum somewhat similar to mineral sperm oil. It has a density of 0·858 to 0·869, a fire-test of 265° F., and a flash point by the Abel test of 205° to 250° F. (See also p. 110.)

Solar oil is a name commonly applied in Russia to an intermediate oil of about 0·860 specific gravity, and flashing at about 220° F. by the Abel-test.

Various fanciful names have been given to petroleum and shale products employed for illuminating purposes. It is often pretended that some process has been used to remove dangerously inflammable constituents. All such products come under the legal definition of "petroleum" (see p. 104), and the "flashing point" is a satisfactory test of their nature.

The photogene oil from shale resembles refined petroleum in all essential physical respects; but, when examined by the bromine process (p. 24), the shale product is found to contain a smaller percentage of methanes and more ethenes than is the case with petroleum. Some samples of shale photogene contain only 5 or 6 per cent. of methanes. The author has frequently found that when three measures of petroleum kerosene were shaken with one of fused crystals of absolute phenol, the latter gradually assumed a dark violet, and ultimately a black, color, but the reaction is not invariably produced; and no such reaction was observed to occur with burning oil from shale. The mixture of petroleum kerosene and phenol becomes turbid at 42° to 49° C., but the shale oil mixture remains clear till the temperature has fallen to about 25° C.

ASSAY OF MINERAL BURNING OIL OR KEROSENE.

Good kerosene should be water-white or light yellow, with or without blue fluorescence. A decided yellow often indicates imperfect purification, or the presence of heavy oils. If kept in clear glass bottles, exposed to light, it often acquires a yellow color, becomes ozonised, and bleaches the cork. Kerosene so changed will not burn well. The odor should be faint and not disagreeable. When agitated with an equal volume of sulphuric acid of 1·53 specific gravity, the color ought to become lighter rather than darker. The specific gravity is rarely less than 0·795, except in certain water-white oils, or *ordinarily* above 0·810 in the case of American, or 0·823 in the case of Russian oil, but kerosene from different sources, and intended for different special purposes (see preceding page), varies considerably in this respect, and hence the indication afforded by the density must not be interpreted too strictly. The absence of an objectionable proportion of very volatile constituents or "naphtha," as indicated by the flashing point, and the absence of a large proportion of "tailings" or heavy oil, as indicated by fractional distillation, are the most important characters in judging of the quality of a sample of kerosene. The rules of the New York Produce Exchange provide that refined petroleum or kerosene for contract purposes shall be standard white or better, with a burning test of 110° F. (equivalent to 70° Abel-test) or upwards, and specific gravity not below 44° Baumé (0·804).

The committee appointed by the Baku Section of the Russian Technical Society to examine the new petroleum testing regulations formulated by the Government, have reported that sulphuric acid of the prescribed density (1·53) is unsuitable for testing petroleum, the color of the acid extract being irregular, and not sufficiently decisive in gradation. On the other hand, sulphuric acid of 1·73 sp. gr. being found to give concordant results with all grades of petroleum and at all temperatures between 16° and 32° C., it is recommended that this strength of acid should be used in the proportion of 40 parts by volume to 100 of oil, the mixture being shaken up in a stoppered glass vessel for two minutes, and the acid layer removed and compared with normal solutions of Bismarck brown. The standard solutions are ten in number, and are graduated so that the highest (No. 1) contains 0·0005 per cent. of coloring matter, and the darkest (No. 10) 0·005 per cent., the intermediate shades differing from one another by 0·0005 per cent. The degree to which the oil has been refined is expressed by the number of the solution corresponding to the color of the acid extract, and the maximum effect in the case of ordinary petroleum distillate is found to be produced by the use of 0·75 per cent. of sulphuric acid (sp. gr. 1·843). Since few commercial petroleums examined fell below the limits 1 to 8, the latter shade is recommended as the outside limit for merchantable petroleum.[1]

Flashing Point of Kerosene Oil.—Cold kerosene oil of good quality will not take fire when a light is applied, nor will the supernatant vapor inflame. The temperature at which a sample of petroleum oil commences to give off sensible quantities of inflammable vapor is technically called its "flashing point." Clearly the lower the temperature at which an oil "flashes," the more dangerous it must be in transportation, storage, and use. The "flash-point," or temperature of ignition of the vapor, is greatly reduced by a small admixture of naphtha. Dr. B. W. White found that when a kerosene oil having a flashing point of 113° F. (= 45° C.) by the open test was mixed with 1 per cent. of naphtha, it flashed at 103° F., with 2 per cent. at 92°, with 5 at 83°, with 10 at 59°, and with 20 at 40° F. On addition of 20 per cent. of naphtha, the oil itself burned at a temperature of 50° F. The "burning point," "fire-test"—*i. e.*, temperature at which the oil permanently inflames—is sometimes taken as a test of quality, but is not reliable, since oils, when spilled, will ignite instantly on approach of a flame, when heated only a degree or two above their flashing point, even although the burning point is considerably higher. An oil flashing at 73° F. by the Abel close test, or at 100° F. by the old open test, will generally show about 120° F. by the American "fire-test," or determination of the temperature of permanent ignition. Experiment shows that an oil flashing at 86° by the open test, and burning at 107° F., can be made to flash at 37·7° C. by removing 6 or 7 per cent. distillation, though such treatment does not improve the oil in other respects.

Boverton Redwood (*Petroleum and its Products*, Vol. II., p. 510) gives a series of experiments to determine the proportion of air and vapors of light petroleums required to produce dangerous explosions. The apparatus consisted of a glass cylinder or churn, capable of being rotated at right angles to its longitudinal axis, an arrangement for displacing a known volume of the gaseous contents of the churn by admission of the required volume of the liquid under examination, and an explosion chamber. In performing the test, a quantity of the liquid was poured into the churn, which was rotated for a time. After relieving the pressure by permitting a portion of the gaseous contents of the churn to pass into

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[1] *J. S. C. I.*, 1896, 678.

the displacing arrangement, a known volume of the mixture, called air-gas, was driven into the explosion chamber; the contents of this were mixed and a flame applied to a vent.

Petroleum spirit, sp. gr. 0·639, produced a violently explosive mixture when 4 per cent. of air-gas was introduced into the explosion chamber. With a spirit of 0·680 sp. gr., the explosion was violent when the percentage of air-gas reached 7·5. With a spirit of 0·700 sp. gr., a violent explosion was produced by a mixture containing 5 per cent. of the air-gas. With the vapor obtained from crude American petroleum, over 20 per cent. of the air-gas was required for violent explosion.

According to the Petroleum Act of 1871, "the term 'petroleum' includes any rock oil, Rangoon oil, Burmah oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any products of petroleum or any of the above-mentioned oils; and the term 'petroleum to which this Act applies' means such of the petroleum so defined as, when tested in manner set forth in Schedule I. to this Act, gives off an inflammable vapor at a temperature of less than one hundred degrees of Fahrenheit's thermometer." Petroleum, within the meaning of the Act, is only allowed to be kept and sold under certain restrictions, which vary to a certain extent according to a discretionary power exercised by the local authorities, any breach of the provisions of the Act being punishable by heavy fines.

The Act prescribed a test, known as the open test, by which the flash-point was to be determined. The close test was made compulsory and the open test was abolished by the Act of 1879, but the restrictive legislation prescribed by the Act of 1871 with regard to petroleum with a flash-point under 100° was applied to petroleum with a flash-point under 73° F. All petroleum with a flash-point above 73° F. was thus, contrary to the 1871 Act, freed from legislative restrictions. The purpose of a bill now (1899) pending in Parliament is to substitute the accurate or close test for the inaccurate or open test in the Act of 1871, and to restore the 100° flash-point prescribed by that Act.

The open test for determining the flashing and firing point was originally performed by heating the oil in a hemispherical porcelain filled to within about half an inch of the brim, the bulb of a thermometer being immersed in the liquid. A lighted taper was passed at intervals across the oil on a level with the brim of the dish and the degree noted at which a flash was produced. The fire-test was determined in a similar manner. The method was quite inaccurate, and not materially improved by the use of Tagliabue's open tester, which has been adopted as the legal instrument in many localities. This consists of a small, rather deep glass cup resting in a water-bath, supported by a metal case and heated by a lamp below; a thermometer is immersed in the oil which nearly fills the cup, and the testing is performed as with the older method. The quantity of oil is too small and the open vessel causes loss of vapor. To obviate this, various closed testers have been constructed and stirrers have been added so as to secure the rapid mingling of the oil and consequent thorough heating. One of the most elaborate of these forms is the Pensky-Martens' tester. The forms about to be described in some detail are regarded as satisfactory by many experts and have been extensively employed.

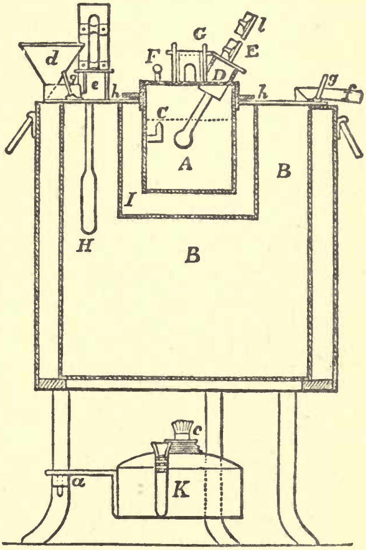

FIG. 2.

Abel's closed oil tester: The apparatus devised by Sir Frederick Abel is shown in figure 2, and the following description, abridged from Schedule I. of the Petroleum Amendment Act, 1879, sufficiently indicates the method of using it.

The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

The heating apparatus is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F. (neither more nor less).

The test-lamp is prepared for use by fitting it with a piece of flat-plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter; and this size of flame, which is represented by the projecting white bead (F) on the cover of the oil-cup, is readily maintained by simple manipulation from time to time with a small wire trimmer. When gas is available, it may be advantageously used instead of the little oil lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

The water-bath (B) having been raised to the proper temperature (130° F.), the oil to be tested is introduced into the petroleum cup (A) (2 inches high by $2\frac{2}{10}$ in internal diameter, and made of gun metal or brass tinned inside). The oil must be poured in slowly until the level of the liquid just reaches the point of the gauge (C), which is fixed at exactly $1\frac{1}{2}$ inches from the bottom of the cup. (In pouring in the oil to be tested, great care should be taken not to splash it against the sides of the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceed 65°, the samples to be tested should be cooled down to about 60° F.) The lid (D) of the cup, with the slide closed, is then put on, and the cup is placed in the bath or heating vessel. The thermometer (E) in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position, which is adjusted to $1\frac{1}{2}$ inches below the centre of the lid, is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

The test-lamp is then placed in position upon the lid of the cup, the lead-line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° F., the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree F., in the following manner: The slide is slowly drawn open while a pendulum 24 inches in length performs three oscillations, and is closed during the fourth oscillation. (It is obvious that a metronome would be more convenient. Some method of marking time is necessary.) In moving the slide so as to uncover the holes, the oscillating lamp (G) is caught by a pin fixed in the slide and tilted so as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position. The temperature at which the vapor of the oil gives a blue flash in applying the test-flame is noted as the flashing point of the sample. To determine the flashing point of burning oils of very low volatility, the air-chamber which surrounds the lamp is filled with cold water to a depth of 1½ inches, and the heating vessel or water-bath is filled as usual, but with cold water instead of water at 130° F.; the heating lamp under the apparatus, and kept there during the entire operation. If a very heavy oil is being tested, the operation may be begun with the water heated to 120° F.

The results of this method are satisfactory. The flashing of the vapor occurs at a temperature much lower than was the case with the old apparatus for the open test.

The flashing point of a sample of kerosene, as determined by Abel's apparatus, has been found to be sensibly lower in India and the tropics than when the same oil is tested in temperate climates. A sample which, under ordinary circumstances, flashed at 73° F., had a flash-point of 66° when examined in a tropical region. The difference is due to the fact that at a high atmospheric temperature the more volatile hydrocarbons are less readily held in solution in the oil, and the least agitation, such as is involved in pouring the oil into the cup, determines their vaporisation. To obtain concordant results in hot countries Abel and Redwood recommend that the operator should commence to apply the test-flame at a much lower temperature (56° F.) than that prescribed in the Act, which is when the oil in the cup has acquired a temperature of 66° F. This modification causes the removal of the superincumbent vapors in quantities too small to flash, by currents of air set up by each application of the gas flame. Even with this modification of the test, a sample which flashes at 73° in England will flash at about 70° F. in India. It is evident that the causes which lead to errors in India will have a tendency to affect the test in temperate countries, and to render the flash-point of the same oil lower in summer than in winter, but this tendency can be counteracted by bringing the sample to be tested to 56° F. before commencing the operation. Changes in barometric pressure also affect the flash-point of kerosene, a fall of one inch of the mercury in the barometer lowering the flash-point of an oil by about 1° C.

S. Gray (*J. S. C. I.*, 1891, 348) has described a stirrer attachment to the Abel cup, by which it is claimed that the results are more correct, are independent of its manner and rate of heating. The apparatus consists of two sets of vanes—one in the oil and the other in the vapor-space—with beveled gearing, or arranged that it may be easily put in or out of gear and the lighting attachment brought into action. There are three orifices—one central for the test-light, the others for admission of air. The change from stirring to testing, and *vice versâ*, can be made promptly. The Pensky modification is also the introduction of a stirrer. Martens has still further improved the apparatus.

New York State Closed Oil-tester.—As a result of investigations, Elliott devised a form of tester which has been highly approved. It consists of a copper cup holding about 300 c.c. immersed in water, which can be heated by a small flame. The cup is covered by a convex clock-glass, which is perforated in the centre to permit the passage of a thermometer, and has a notch at the edge for insertion of the testing flame. The official directions are: Fill the water-bath with cold water up to the mark, place the oil-cup in it, and pour in enough oil to fill the cup up to the flange that joins the cup with the vapor-chamber above. The oil must not flow over the flange. Air-bubbles may be removed by means of dry paper. The glass cover is then put on, and the thermometer placed so that its bulb is just covered by the oil. A swell flame must be used for heating, so that the rise in temperature should be about two degrees per minute, never over three degrees. For the igniting flame a gas-jet one-quarter of an inch in length is employed. When gas is not at hand, a piece of waxed linen twine may be used. The flame should be small. Testing should begin when the oil reaches the temperature of 29·3° C. (85° F.). The torch is inserted through the testing notch at such an angle as to well avoid contact with the glass, and to a distance about midway between the surface of the oil and the under surface of the cover. Its movement must be steady, uniform, swift, and without pause, and should be repeated at every 1° C. or 2° F.; increase until the thermometer marks 35° C. (95° F.), when the heating flame should be shut off and the testing made at each 0·5° C. or 1° F. until 37·5° C. or 100° F. is reached. After this the heating flame may be again started if necessary, and the testing continued for each 1° C. or 2° F. as at first. The appearance of a slight bluish flame indicates that the flashing point has been reached. In every case the temperature of the oil should be noted *before* the testing flame is introduced. This flame must not touch the oil. The water-bath must be refilled with cold water, and the oil-cup well cleaned for each test. This tester is largely used in many laboratories and designated in many official specifications. Engler's tester, which is used in Germany, employs an electric spark from a small induction coil to fire the petroleum vapor in a chamber which has two metal shutters, which are lifted by an explosion as soon as the atmosphere through which the spark is passing becomes sufficiently charged with vapor.

In Germany the minimum flash-point is fixed at 21° C., and an allowance of 1·62° F. is made for a variation of 1 inch in the barometric pressure.

In Russia the legal flash-point for sale or exportation is 28° C. For testing up to 85° C., the Abel-Pensky apparatus is prescribed. When the oil flashes below 60°, the oil-cup is to be inserted direct into the water-bath, the temperature of the latter being about as high again as the expected flashing point, so that when this is beyond 50°, the water must be boiling. For oils flashing between 60° and 85° the space between the oil-cup and the water-bath must be filled with a heavy mineral oil (specific gravity over 0·900), and the water maintained at about 15° above the flashing point anticipated. A preliminary test having been made, the test-flame is first applied and the temperature is 5° below the flashing point thereby ascertained. Only when the oil flashes between 27° and 29° is a correction for atmospheric pressure to be made. For all heavy burning and lubricating oils and residuum flashing above 85° C., the Pensky-Martens instrument is necessary.

In France and Switzerland the limit is fixed at 35° C., and in Austria and some of the United States at 37·5° C.

On *fractional distillation*, mineral burning oils should not give a high percentage below 150° C., and, on the other hand, should not have a large proportion of "tailings" or heavy oil, distilling above 300° C. By judicious manipulation of a mixture of naphtha and heavy oil, kerosene may be sophisticated without altering the specific gravity and without reducing the flash-point so as to excite suspicion. Such an oil will not be satisfactory, as the more volatile portions will be consumed first, the heavy viscous portions remaining to clog the wick.

J. Biel recommends that the fractional distillation of mineral burning oils should be conducted on 250 grm. of the sample, in a glass flask of 500 c.c. capacity. This is wrapped round tightly with thin brass gauze or glass wool, to protect it from too rapid changes of temperature, and is connected by a Glinsky's dephlegmator (Vol. I. p. 32) with a Liebig's condenser. The thermometer is fixed in the dephlegmator so that the bulb may be on a level with the exit-tube. At the commencement, the flame under the flask should not be larger than is requisite to drive over the light oils, which are collected as long as any notable quantity (more than 10 drops per minute) of oil distils at 150°. The flame is then enlarged, and the "normal petroleum" distilling between 150° and 270° C. is next driven over, the receiver being changed when no appreciable quantity distils when the thermometer is maintained at the latter temperature. Biel weighs the distillates, and ascertains the amount of the residue or "tailings" by noting the difference between the weight of the flask and dephlegmator on the completion of the distillation and again after cleaning. It is evident that the method of measurement commonly employed in practical examinations of volatile oil is equally available.

The following results obtained by Biel by the foregoing process are interesting as showing the behavior of typical samples of Russian oils:

	KEROSENE.			PYRONAPHTHA.	
	A.	B.	C.	D.	E.
Specific gravity, ...	0·820	0·820	0·835	0·857	0·867
Flash-point; ° C., . . .	52·5	35·0	44·5	7·5	94·0
——		Percentage.			
Light oils (below 150°),	0·8	10·0	6·0	0·0	0·0
Normal oils (150° to 270°),	92·0	76·5	63·5	44·5	30·5
Heavy oils (tailings), . .	7·2	13·5	30·5	55·5	69·5

Biel has also placed on record the following figures obtained by the distillation of certain burning oils in a glass retort with a thermometer immersed in the oil:

	"STANDARD," Imp. Ref'g Co.	PRATT'S ASTRAL OIL.	BAKU. No. 1.	BAKU. No. 2.
Original oil; specific gravity, .	0·795	0·783	0·803	0·822
,, ,, flash-point; ° C., .	26·0	48·0	26·0	30·0
——		Percentage.		
Light oils (below 150°), . . .	14·4	2·2	33·5	12·8
Normal oil (150° to 270°), . .	45·9	87·8	66·5	78·3
Heavy oils (tailings), ...	39·7	10·0	0·0	8·4

The "Standard" sample oil was decidedly inferior in quality, and had probably been produced by "cracking" the heavy residue from which the normal burning oil had been partially removed. It must not, however, be assumed that all oils produced by cracking are of the same unequal character.

Beilstein[1] states that the rule for Russian petroleum is that an oil to be considered safe should yield less than five (5) per cent. of "light oils," and less than fifteen (15) per cent. of "heavy oils." With American petroleum, the "heavy oils" should not exceed fifteen (15) per cent. (See also description of Regnault's apparatus, under "Benzene.")

As already stated, Russian kerosene is usually of distinctly higher density than that from American petroleum. Russian petroleum gives much the smaller yield of burning oil, but the product is more nearly homogeneous, the hydrocarbons composing it not differing widely in specific gravity, boiling point, and other characteristics. This peculiarity is well shown by the following figures obtained by B. Redwood by fractionally distilling samples of kerosene made from Baku and American petroleum. A measured quantity of the liquid was distilled, and the density of each fraction of 10 per cent. was observed:

	Russian Kerosene. Spec. Grav.	American Kerosene. Spec. Grav.
Kerosene.	0·822	0·803
First fraction,	0·783	0·748
Second ,,	0·796	0·759
Third ,,	0·803	0·778
Fourth ,,	0·814	0·792
Fifth ,,	0·827	0·802
Sixth ,,	0·831	0·812
Seventh ,,	0·837	0·822
Eighth ,,	0·838	0·831
Ninth ,,	0·846	0·838
Tenth ,, (residue),	0·864	0·849

In Russian kerosene there is less difference between the specific gravity of the lightest and heaviest fractions than in American oil.

A test of kerosenes by burning them in similar lamps and noting the rates of consumption and the comparative intensities of the light yielded, is often capable of giving valuable information. Much depends on the character of the wick used, all oils burning far more satisfactorily and safely with an American wick of long staple cotton loosely woven, than with the comparatively hard, tightly-woven wick often employed in Great Britain. Kerosenes containing a large proportion of light oils give a better light, but

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[1] *Zeit. Anal. Chem.*, 1883, 14.

burn faster than others, while the presence of heavy oils retards the consumption and seriously diminishes the light yielded. Care must be taken not to form too hasty an opinion on the oils tested, as a kerosene containing excess of both light and heavy oils, or in technical phrase consisting largely of "mixed tops and bottoms," may give a good light at first, but after some time the flame will greatly diminish in size and luminosity, and in extreme cases the wick becomes so clogged and charred as to cause extinction. Russian kerosene does not give so much light as American, but, on the other hand, there is considerably less diminution as the level of the oil falls in the reservoir.

The *color* of kerosene is a character to which attention should be paid. Frequently, it is sufficient to compare the color of the sample with that of a standard specimen, the two oils being contained in bottles of the same size. A preferable plan is one proposed by B. Redwood. He places the oils to be compared in two glass cylinders, such as are used for measuring water, and holds these above a mirror in such a position that the images of the bottoms of the cylinders are presented side by side. In this way it is easy to make an accurate comparison of the reflected disks, which are, of course, tinted in proportion to the color of the liquids. With a fluorescent liquid like kerosene, Redwood finds this plan preferable to looking down on the oils while the cylinders are placed on a white surface. A chromometer devised by R. P. Wilson, in which the kerosene is compared with disks of colored glass of standard tints, has been adopted by the Petroleum Association.

The glass disks for Wilson's chromometer are issued by the Petroleum Association of London (85, Gracechurch Street), and the instruments are all precisely alike in construction, so that the testing of the color of petroleum, wherever these chromometers are used, is placed on a uniform basis. In a German form of the instrument devised by Stammer, the column of oil can be adjusted in length until its color is identical with that of the standard, by which means results of considerable precision are obtainable. Lovibond's tintometer is an elaborate instrument adapted for analysis, measuring, and recording of colors. (For a discussion of its uses and of a proposed improvement by H. R. Proctor, see *J. S. C. I.*, 1895, 123.)

The following grades of color are recognised in the trade: Superfine white, standard white, prime white, water white, and good merchantable.

In some cases a diminution of light may be due to the presence of mineral ingredients—*i. e.*, compounds of calcium or magnesium. These may be detected by reducing a moderate amount of the oil to ash, dissolving the residue in hydrochloric acid, and applying the usual precipitation tests.

Sulphur compounds exercise an injurious effect upon the illuminating power of kerosene. Specimens containing large proportions of ethenes, as do those obtained by cracking, are apt to contain sulphonates. These may be detected by a method given in connection with the examination of lubricating oils. For the detection of ordinary sulphur compounds the oil should be heated to boiling for some time with a fragment of sodium, in a flask furnished with an inverted condenser. After cooling, water is added drop by drop to the contents of the flask till the sodium is oxidised. More water is then added, the aqueous liquid separated, and the solution tested with a drop of sodium nitroprusside, which will produce a fine violet-blue coloration if the sample contained sulphur. The quantity of sulphur can be ascertained by several analytic methods (see pp. 66 and 81) or by burning a known weight of the oil in a standard gas-testing apparatus and precipitating the acid condensed with the water, as barium sulphate. Sulphur is a highly objectionable ingredient, owing to the formation of corrosive and poisonous bodies when the oil is burned.

An annoying turbidity sometimes develops in refined oil. It has been ascribed to various causes, such as the size used on the inside of the casks, but, according to Vieth (*Ding. Poly. Jour.*, 277, 571; *J. S. C. I.*, 1891, 39), the usual cause is the failure to remove all the sulphonic acids formed during the treatment of the oil with sulphuric acid in the refining process. The turbidity often appears in the dark and disappears when the sample is exposed to light and air. The only means of preventing it appears to be by treating the fresh distillate with about one per cent. of sodium hydroxide solution of 1·3 sp. gr., separating the solution, treating the oil with sulphuric acid, washing thoroughly, again treating with sodium hydroxide, and repeating the process until the oil is no longer affected by the alkali. All the alkali must be washed out before the oil is marketed.

For distinguishing between the products of Russian and American petroleum, and for detecting admixtures of crude with refined oil, Riche and Halphen[1] have devised a test depending on the

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[1] *Jour. Pharm. et Chim.*, xxx (1894), 289; abst. *J. S. C. I.* 1895, 190.

proportion of a special solvent required to form a clear solution with a definite weight of the sample. The solvent is a mixture of equal parts of anhydrous chloroform and 93 per cent. alcohol. The quantity of oil taken is 4 grm. in each case. Reference must be made to the original paper for the tables showing the comparative results with mixtures of known composition. Redwood states that the method is satisfactory if the strength of the alcohol be rigidly adhered to.

LUBRICATING OILS.[1]

Lubrication has for its object the reduction of friction between moving surfaces. In the sliding friction of solids the magnitude of the resistance is, up to the point of abrasion, dependent on the character of the surfaces, and proportional to the force with which they are pressed together, though when the pressure is very low, the resistance may be principally due to the adhesion, in the case of lubricated surfaces. In fluid friction, on the other hand, the resistance is proportional to the area and velocity of the surface exhibiting it, and to the density and viscosity of the liquid. In the practical application of lubricants to the rubbing surfaces of machinery in motion, the friction is usually compounded of the friction of solids and of fluids in proportions varying in each case. In cases, however, in which it is practicable to float the moving part in the lubricant, fluid friction alone is concerned; while in the case of slowly-moving heavy machinery, the resistance is chiefly due to the friction of solids.

In theoretically perfect lubrication the resistance would be independent of the pressure. The more viscous the lubricant, the greater the pressure which can be sustained without squeezing out the film of lubricant from between the moving surfaces; but *unnecessarily* high viscosity creates unnecessary fluid friction, and the viscosity of the lubricant should therefore be proportional to the pressure. In other words, the lubricant should have just sufficient "body" or viscosity to keep the moving surfaces apart, under the maximum pressure. Hence for heavy machinery a highly viscous or even solid

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[1] In the second edition of this work the subject of lubricants was treated partly under fats and partly under hydrocarbons. In the present edition these articles have been combined.

lubricant must be employed, and oils are not unfrequently wholly or partially replaced by graphite, steatite, sulphur, or soft metal. In some cases the viscosity of the oil is increased by an admixture of soap or by adding alkali.[1] For delicate movements, such as exist in clocks and watches and light and fast-running machinery, the thinnest oils are suitable.

A thick oil takes a greater power to drive, and develops a higher temperature than an oil of low viscosity; and, as a rule, the lubricant should be as thin as is consistent with the weight of the machinery and the temperature to which the oil will be subjected. With ample driving power a moderately thick oil may be used for heavy machinery, particularly if the temperature be high, but if the driving power be inadequate, it may be necessary to use a thinner oil.

Although the foregoing is the main principle governing the choice of lubricants, the degree of viscosity required is also dependent on the fit of the bearing surfaces and upon the character of the motion, and these conditions vary largely in each case. It is very difficult to predict the behavior of a particular oil in practice from its trial in a mechanical testing machine. On this account, as also from the more efficient of them necessitating the use of steam-power, the ingenious machines devised for testing lubricating oils have not fully justified the anticipations of their inventors. The only rational plan of applying such tests is to use a series of standard spindles for testing spindle oils, standard bearings for axle-lubricants, and so on for other oils. This requirement is practically prohibitory of the use of mechanical testers in an ordinary laboratory, and it is fortunate that a close relationship exists between the viscosity of an oil and its characters as a lubricant. In other words, if a given oil is satisfactory under known conditions of fit, pressure, speed, and temperature, it may be predicted with tolerable cer-

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[1] The following table shows the composition of three mixtures used for lubricating the axles of railway carriages:

	English.		German.
	Summer.	Winter.	
Tallow,	504	420	246
Palm oil,	280	280	98
Rape oil,	. .	. .	11
Sperm oil,	22	35	. .
Caustic soda,	120	126	52
Water,	1370	1524	593

Rosin grease is a mixture of similar consistency, largely employed for lubricating the wheels of carts and colliery trucks.

tainty that another oil of the same nature, having a similar viscosity, will yield equally good results.

The characters which should be taken into consideration in forming an opinion on the suitability of a lubricating oil for a particular class of work are:

1. The viscosity or "body" of the oil at the temperature at which it is to be used.
2. The temperature at which the oil thickens or actually solidifies.
3. The flashing point, or temperature at which the oil gives off inflammable vapor in notable quantity.
4. The volatility or loss in weight which the oil suffers on exposure in a thin film to an elevated temperature.
5. The "gumming" character, or tendency of the oil to become oxidised.
6. The proportion in which the fatty and hydrocarbon oils of a mixture are present.
7. The proportion and nature of the free acid, if any, in the oil.
8. The tendency of the oil to act on metals.
9. The presence of mineral matters, such as the bases of soaps.

Viscosimetry.

As already stated, the viscosity or "body" of an oil is the most important criterion of its suitability as a lubricant under certain conditions, and hence great interest attaches to its satisfactory determination. It has acquired greater importance of late years, owing to the rapidly increasing employment of mineral lubricating oils as substitutes for the fatty oils formerly used. Thus, different specimens of any given fixed oil, such as sperm oil or rape oil, vary in viscosity only within comparatively narrow limits at a given temperature, and hence an engineer accustomed to use a given fixed oil would, in purchasing such oil, derive little advantage from a knowledge of the viscosity of a particular sample of such oil. On the other hand, mineral lubricating oils may be manufactured of any required viscosity within comparatively wide limits, and hence it is very important that an engineer should be able to ascertain whether further supplies of this class of lubricant are of a viscosity similar to that of batches of oil previously employed.

It was formerly assumed that the viscosity of an oil bears a tolerably definite relation to its specific gravity, but the fact that this is an error is now generally recognised.

Krause observed the following rates of flow at 15° C. for four varieties of mineral oil of identical specific gravity (0·883):

Saxony oil (paraffin),	170 seconds.	American,	550 seconds.
Oelheim,	355 ,,	Scotch,	585 ,,

Temperature has much influence on the viscosity of oils, and is greatest in those which are solid or partly so at ordinary temperatures. The thicker animal oils containing much stearin are most sensitive to an increase of temperature. Many mineral oils, however, though fluid at ordinary temperatures, decrease in viscosity so rapidly when heated as to have quite different characters at high temperatures. This fact must be kept in mind when an oil is to be used in an engine cylinder or under similar conditions. As the temperature of a given friction surface is liable to vary considerably, preference should be given to an oil which shows the least variation in viscosity within the limits of temperature to which it is likely to be subjected.

The following figures by J. Veitch-Wilson show the decrease in viscosity by rise of temperature of certain typical fatty lubricating oils:

Oil.	Number of Seconds Required.		
	At 15·5° C.	At 49° C.	At 82° C.
Sperm,	47	30·5	25·75
Olive,	92	37·75	28·25
Lard,	96	38	28·5
Rape,	108	41·25	30
Neatsfoot,	112	40·25	29·25
Tallow (oil),	143	37	25
Engine tallow,	Solid	41	26·5

The following are figures obtained in the author's laboratory:

Oil.	Sp. Gr. At 15·5° C.	Number of Seconds Required.		
		At 15·5° C.	At 50° C.	At 100° C.
Sperm,	881	80	47	38
Seal (pale),	924	131	56	43
Northern whale,	931	186	65	46
Menhaden,	932	172	40	. .
Sesame,	921	168	64	50
Arachis,	922	180	64	. .
Cottonseed (refined),	925	180	62	40
Nigerseed,	927	176	59	43
Olive,	916	187	62	43
Rape,	915	261	80	45
Castor,	965	2420	330	60

Boverton Redwood (*J. S. C. I.*, 1886, 128) has determined by his standard viscosimeter (p. 120) the comparative rates of flow of a number of oils for every rise of 10° F. The following figures are the number of seconds required for 50 c.c. of each oil to flow through an orifice out of which an equal measure of water at 60° F. ran in 25·5 seconds:

TEMPERATURE; ° F.	REFINED RAPE OIL.	BEEF TALLOW.	SPERM OIL.	NEATSFOOT OIL.	AMERICAN MINERAL OIL, SP. GR. = ·885.	AMERICAN MINERAL OIL, SP. GR. = ·913.	AMERICAN MINERAL OIL, SP. GR. = ·923.	RUSSIAN MINERAL OIL, SP. GR. = ·909.	RUSSIAN MINERAL OIL, SP. GR. = ·915.	RUSSIAN MINERAL OIL. SEMI-SOLID.
50	712·5	. .	. .	620	145	425	1030	2040	2520	. .
60	540	. .	177	470	105	295·5	680	1235	1980	. .
70	405	. .	137	366	90	225	485	820	1320	. .
80	326	. .	113	280	73	171	375	580	900	. .
90	260	. .	96	219	63·5	136	262	426	640	. .
100	213·5	. .	80·5	175	54	111	200	315	440	1015
110	169	. .	70·5	147·5	50	89·5	153	226	335	739·5
120	147	. .	60·5	126	47	78	126	174	245	531
130	123·5	. .	57	112	44·75	63·5	101	135·5	185	398·5
140	105·5	. .	51	88·5	41	58	82	116	145	317·5
150	95·5	. .	49	75·5	37·5	52	70·5	95	115	250
160	85	. .	47·5	70	. .	46	63·5	83·5	93·5	200
170	76	. .	46	62	. .	. .	58	70·5	77·5	161
180	69	. .	44·5	56·5	. .	. .	52·5	61·5	67·5	134·5
190	64·5	. .	43	53	. .	. .	47	56·5	61	115·5
200	58·5	54·5	42	50·5	. .	. .	42	48	54	99
210	54	. .	41	48·5	. .	. .	40	. .	. .	85
220	54	. .	39	47	. .	. .	38	. .	. .	77
230	47·5	. .	37	46	. .	. .	. .	. .	. .	70·5
240	45·5	. .	36	44·5	. .	. .	. .	. .	. .	64·5
250	43·5	40	35	44	. .	. .	. .	. .	. .	59
260	Viscosity slightly above the average.	. .	34	43·5	. .	. .	. .	. .	. .	54
270		. .	33	43	. .	. .	. .	. .	. .	48·5
280		. .	32	41·5	. .	. .	. .	. .	. .	46·5
290		. .	31	41	. .	. .	. .	. .	. .	46
300		. .	30	38	. .	. .	. .	. .	. .	42·5

On examining the results recorded in the foregoing table, it will be observed that sperm oil is remarkable for the comparatively slight reduction in its viscosity caused by increase of temperature, a property to which the value of this oil as a lubricant for use under very varied conditions is probably due. The Russian mineral oils lose their viscosity with an increase of temperature more rapidly than American oils of the same specific gravity, but in both classes the reduction is most rapid in the case of the most viscous oils, and, as the Russian oils have a higher viscosity than the American, a more rapid reduction in the former case might be anticipated.

The elementary form of apparatus for determining viscosities consists of a pipette drawn out to a narrow orifice at the lower end. The tube is supported in a vertical position and filled with the oil to a certain mark, the orifice being closed by the finger. The oil is then allowed to flow out till a lower mark is reached, or till a definite measure has been received in a graduated vessel, the number of seconds required being noted.

The viscosity of oils being affected to an important extent by very slight variations of temperature, it is very desirable to surround the viscosity-tube with an outer tube or cylinder containing water at the desired temperature; for high temperatures a less volatile liquid than water might be substituted.

It is desirable in all cases to compare a sample of oil with others of known quality and origin, as the viscosity-figures obtained by the use of one apparatus of the above kind are not directly comparable with, or even capable of strict conversion into, those yielded by others.

The viscosities are often stated as the number of seconds required to run through a certain orifice at a given temperature, and to render such figures comparative, they have usually been referred to rape oil as a standard. As, however, different samples of rape oil differ sensibly in viscosity, the results obtained by different observers have, for this and other reasons, not been capable of accurate comparison.

If, however, a defined and constant apparatus be employed, it becomes a simple matter to refer different samples to a standard. Water possesses too little viscosity to make it a desirable liquid with which to compare lubricating oils. Glycerol can be diluted with water to any required viscosity, and the specific gravity of the standard liquid being once ascertained, a fresh standard can always be prepared at will. It is evident, however, that if the viscosity of rape oil be determined by the careful testing of a number of specimens, the average can be regarded as the viscosity of a standard rape oil, and if a constant apparatus be employed, the results can always be expressed in terms of such standard. Redwood has determined the viscosity of a considerable number of samples of genuine rape oil, and finds that the average time required for 50 c.c. of the oil at 15·5° C. to flow out of a Redwood's viscosimeter is 535 seconds, water under similar circumstances running out in 25·5 seconds. Taking, therefore, the viscosity of standard rape oil at 100, the viscosity of any other oil of the same density will be found by multiplying by 100 the time in seconds required for 50 c.c. to flow through the orifice, and dividing the product by 535. If the density of the sample be different from that of rape oil, the figure thus obtained should be multiplied by the specific gravity of the sample at the temperature of the experiment, and divided by 915 (the specific gravity of refined rape oil at 155° C.). The rule is expressed by the following equation:

$$\frac{\text{Seconds of flow} \times 100 \times \text{sp. gr. of sample}}{489525} = \text{Viscosity.}^{1}$$

Redwood's Viscosimeter.—Boverton Redwood devised an instrument (Fig. 3) which is capable of being standardized, and has been much used. The viscosity tube (A) is made of copper thickly electroplated, and is 3½ inches high by 1⅞ inches internal diameter. In practice it is filled until the surface of the liquid just touches the point of a bent wire soldered to the side of the tube. The orifice is a hole of a definite size drilled in agate (C), but glass might doubtless be substituted without affecting the accuracy of the indications. The friction of the flowing oil against the sides of a long tubular orifice notably affects the indications of the instrument, and hence the tubular portion of the orifice is made as short as practicable. The upper surface of the agate is cup-shaped, so as to fit the bulb of the thermometer (D), which may be used as a plug, but the instrument is also supplied with a spherical plug of electroplated copper attached to a wire. The viscosity tube is surrounded by a cylindrical reservoir of copper (E), which can be filled with water or other fluid and readily brought to and maintained at any desired temperature. For temperatures below 100° C., water is most convenient; above that temperature, paraffin or

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[1] For Poiseuille's formula for calculating the *absolute viscosity* of liquids, see *J. S. C. I.*, 1886, 148.

mineral lubricating oil of high boiling point may be used. The fluid in the reservoir may be heated by a gas-flame placed under

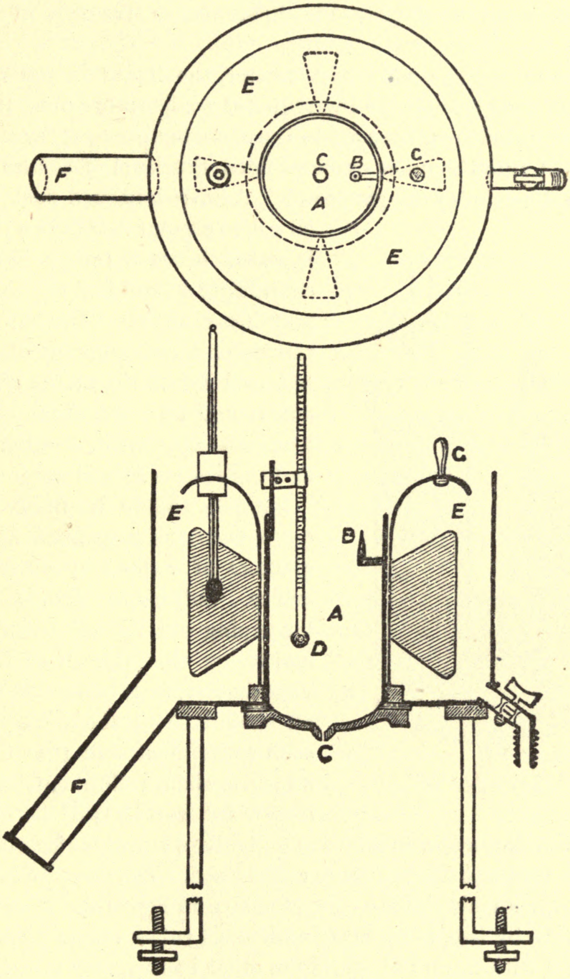

FIG. 3.

the projecting portion (F), and can be agitated by gently moving the inclined paddles by means of the handle (H). When the temperature employed is considerably above that of the laboratory, the agitator should be kept in gentle motion throughout the experiment. Care must also be taken that the temperature of the oil in the inner cylinder is maintained constant, as a difference of 1° or less will make an appreciable difference in the rate of flow of some oils.

In using Redwood's viscosimeter, the liquid in the reservoir should first be brought to the required temperature, and the oil to be tested, previously brought to the same temperature, should then be poured into the inner cylinder until the level of the liquid just reaches the point of the gauge (B). A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball-valve is raised, and the number of seconds required for 50 c.c. of the oil to flow out is noted in the usual way. At least two experiments should be made, and the results should agree closely.

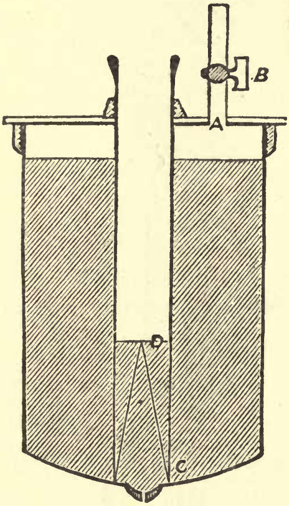

FIG. 4.

Samples should be filtered if not quite clear, as suspended matter or globules of water may obstruct the orifice. Soft paper should be used for wiping out the oil-cylinder. In employing this or similar forms of viscosimeter, it is essential that the oil should be at the same height in each experiment, and that the same measure should flow out, otherwise discordant results will be obtained. The author has made an addition to the Redwood's viscosimeter by which a constant head of oil is maintained. The oil-cylinder is provided with an air-tight cover, as shown in figure 4. The cover is perforated by two holes fitted with short tubes, one of which (A) is furnished with a tap (B), while the other has another tube screwing air-tight into it. This tube (C) is prolonged on two sides in contact with the agate-orifice, while the angles of the inverted V-shaped slits cut on each side terminate at D, exactly 1½ inches higher. The cylinder is filled with oil before commencing an experiment, the tap (B) closed, and the orifice opened till the oil sinks to the level of

D in the inner tube. Air then bubbles regularly in at D, and when this is noted, the oil is collected in a graduated cylinder. Any volume from 10 to 50 c.c. may be allowed to run out, as the oil gradually falls in the upper part of the cylinder, but is maintained constantly at the level D. Experiments made in the author's laboratory prove the flow to be extremely regular; and the modification has the additional advantage of allowing the viscosity to be determined from the flow of a very moderate measure of oil, whereas if 50 c.c. be the volume collected, the observation sometimes becomes tedious. The results obtained by comparative testing by the closed and open apparatus agree.

Engler's viscosimeter consists of an accurately made brass oil-vessel 106 mm. internal diameter, 80 mm. deep at the side, and 48 mm. at the center, the bottom being a flat cone. A slightly conical lid, fitting snugly like a saucepan-lid, closes the vessel. The inner surface of the oil-vessel is gilded. In the center of the bottom is a platinum outflow-tube 20 mm. long, with a slightly conical caliber 2·9 mm. at the top, 2·8 mm. at the lower end. This tube can be closed by a pointed rod of hard wood. The level to which to fill the oil (240 c.c. are used) is indicated by three small pointed projections on the side of the oil-vessel. A thermometer passing through a hole in the lid dips into the oil. The oil-vessel is surrounded by an oil-bath 130 mm. in diameter, 58 mm. high at the sides, and 68 mm. at the center, at which latter point the lower end of the outflow-pipe passes through by a tight joint. The top of this bath is on a level with the top of the oil-vessel. The bath is not covered; a thermometer dips into the oil. The whole apparatus is securely supported and heated by a ring burner. A flask marked at 200 c.c. and 240 c.c. is placed precisely below the outflow-tube. To secure uniformity and obtain comparable data standardized instruments must be employed, for the construction of which Engler has arranged with Desaga, of Heidelberg. Full directions for use are furnished with each apparatus. This viscosimeter is much used in Germany, especially in the railway service.

Allen's Viscosimeter.—Figure 5 shows a form of instrument that the author has used for a number of years with satisfactory results. A 25 c.c. pipette is cut off at the lower extremity and the orifice carefully contracted, by heating, to a diameter of 0·03 inch. By this means a tapering extremity is avoided. The pipette is filled from below by suction to a definite point marked on the upper stem, and the oil allowed to flow out until the level reaches another marked on the lower stem. The time required for the flow between these is noted. The level of the oil in the upper stem may be adjusted and the flow started as required by the clip on the rubber tube attached to the upper part of the pipette. The apparatus is seen to be arranged so that the oil may be heated to any temperature. A coil of block-tin pipe is heated by the burner, and the contained liquid circulates constantly through the outer cylinder. The glass stirrer with ring-shaped terminal can be used to effect thorough admixture. A short glass tube is attached to the nose of the pipette by a caoutchouc stopper. This permits the nose to be kept within the limits of the cylinder, and hence at the same tem-

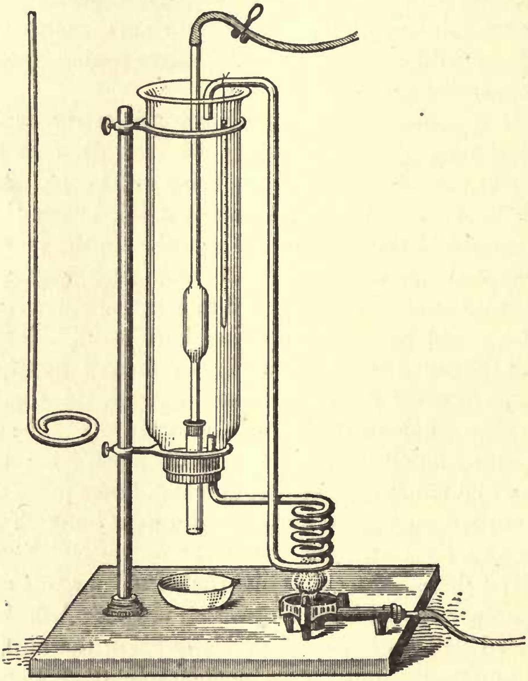

FIG. 5.

perature as that of the body of the oil. The following data have been obtained, the time being given in seconds:

°C.	Refined Rape Oil.	Olive Oil.
15·5, ...	154	144
50·0, ...	53	50·5
90·0, ...	41	40

Torsion Viscosimeter.[1]—This instrument, shown in figure 6, depends on the principle of the torsion balance. It was devised by O. S. Doolittle for use in the laboratory of the Philadelphia and Reading Railroad Company. It has been found very satisfactory, and has been much used in American laboratories.

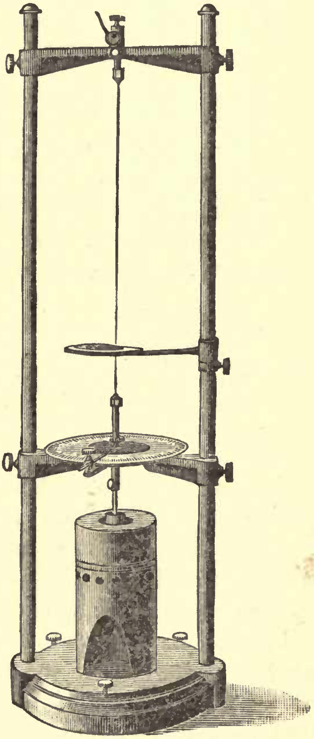

FIG. 6.

A steel wire is suspended from a firm support and fastened to a stem which passes through a graduated horizontal disk, thus allowing the torsion to be exactly measured. The disk is adjusted so that the index points to zero, showing that there is no torsion in the wire. A cylinder, 2 inches long by 1½ inches in diameter, having a slender stem by which to suspend it, is then immersed in the oil and fastened by a thumb-screw. The oil is surrounded by a bath of water or paraffin, according to the temperature at which the observation is to be made. This temperature being observed while the disk is resting on its supports, the wire is twisted 360° by means of the knob at the top. The disk being released, the cylinder rotates in the oil by reason of the torsion of the wire. The action is analogous to that of the pendulum. If there were

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[1] *J. A. C. S.*, 1883, 173, 454. The cut was loaned by Bullock & Crenshaw, of Philadelphia.

no resistance to be overcome, the disk would revolve to zero, and the momentum thus acquired would carry it again to 360°. In reality, the resistance of the oil to rotation causes the revolution to fall short of 360° in proportion to the viscosity of the liquid. The retardation thus produced is a delicate measure of the viscosity.

There are a number of ways in which this retardation may be read, but the simplest is the number of degrees retardation between the first and second complete arcs covered by the rotating pendulum. For example, suppose the wire be twisted 360° and the disk released so that rotation begins. In order to obtain an absolute reading which shall be independent of any slight error in adjustment, the start from 360° is ignored, and the first reading taken at the end of the first swing. The next reading, which is on the other side of the *O* point, is also ignored, as it belongs in common to both arcs. The third reading is taken, which will be at the end of the second complete arc and on the same side of the *O* point as the first reading. The difference between these two readings will be the number of degrees retardation caused by the viscosity of the oil. Suppose the readings are as follows:

First reading,	. . . . right hand	355·6°
Second ,,	. . . . left hand—ignore	
Third ,,	. . . . right hand	338·2°
		17·4° retardation.

In order to secure freedom from error, we make two tests—one by rotating the milled head to the right and the other to the left. If the instrument is in exact adjustment, these two results will be the same; but if it is slightly out, the mean of the two readings will be the correct reading.

In order to overcome the variations in different instruments, each one is standardized against pure cane-sugar solutions, and the viscosity is expressed in the number of grams of pure cane sugar contained in 100 c.c. of the syrup at 60° F., which will give the retardation designated at 80° F. These readings are obtained by making a number of solutions containing known amounts of pure cane sugar, and determining the retardation of each. A curve is then marked out on a piece of plotting-paper, the number of grams of sugar in 100 c.c. of the different syrups representing the abscissas, and the degrees of retardation the ordinates. This curve enables us to interpolate the value of each degree of retardation in terms of pure cane sugar, and in this way a table of viscosities is drawn up and furnished with each instrument. This table renders the results obtained by the different instruments strictly comparable.

One advantage of the torsion viscosimeter is that the observations are independent of the specific gravity of the liquid, which is not the case with instruments depending on flow. Doolittle, in fact, found that liquids of the same viscosity, but different gravities, gave markedly different results with Saybolt's viscosimeter. Tables showing comparisons between viscosities determined by the Saybolt and Doolittle apparatus are furnished by the makers of the latter form.

Among other advantages, the instrument permits of the taking of viscosities at high temperatures without the inconveniences of handling the hot liquid. This is an important point, as the results obtained below 100° C. are often so much changed at higher temperatures that the relative viscosities of two oils compared at 100° C. may be reversed when compared at 175° C. (See p. 117.) By means of a paraffin bath these high temperatures can be easily employed in this instrument.

When an oil has been tested, it is only necessary to remove and wipe off the cylinder, when it is ready for another test. The data are also independent of any moderate amount of dirt in the oil.

Saybolt's viscosimeter is much used in the United States. It is made in three forms, adapted for testing different grades of oils. One form consists of an outer vessel serving as a bath, and inner tube to carry the oil. In each of these there is a glass window, that the time when the level of the oil reaches a certain point can be readily observed.

At the top of the oil-tube there is a series of holes which open into a trough, so that the tube can not be filled above the line of these holes; hence the same amount is used each time. For higher temperatures an apparatus is used without windows, the oil being allowed to flow into a flask marked at a definite volume.

Many other forms of viscosimeter have been devised or proposed. Most of them are based on the rate of flow under the influence of gravity, and hence are different only in details from the Redwood, Engler, and Saybolt instruments. Traube[1] has suggested a

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[1] *J. S. C. I.*, 1887, 414.

form in which the oil is forced by pressure through pipettes, the caliber of which differs according to the oil to be tested. Wright and Gill have expressed favorable opinions of this instrument, but it has not come into general use. Several forms have been constructed in which a vane is rotated in the oil, but with such apparatus it is very difficult to obtain uniform results. It is probable that the torsion instrument comes more nearly to the conditions of practice than any form.[1]

THE SOLIDIFYING POINT of a lubricating oil can be determined as described in Vol. II., part 1, page 36. It is a character of such obvious importance in judging of the suitability of a lubricating oil for a particular purpose that nothing need be said of it here except that, as a rule, an oil is required to remain liquid at the temperature at which it is employed.

THE FLASHING POINT, or temperature at which an oil gives off a notable quantity of *inflammable vapor*, may be determined by the methods given on pages 104 to 109. The flashing and boiling points of the fatty oils are so high as to be beyond the temperature to which they are subjected in use; but with hydrocarbons the point becomes important. In the case of oils employed for engine cylinders, the flashing point should certainly not be lower than 200° C., nor the boiling point below 260° C. The importance of a high flashing point is twofold in such cases. There is less chance of inflammation, and the india-rubber packing of the cylinders is less liable to be injured.

THE LOSS BY HEATING the oil is also an indication of the presence of volatile constituents, which may cause a serious increase in the amount of oil consumed in practice. To observe the behavior of the oil, a known weight should be placed in a watch-glass, wide beaker, or flat porcelain dish, and kept for twenty-four or forty-eight hours in an air-bath at a temperature similar to that to which it will be exposed in practice, and the residual oil weighed. Gill heats the oil for eight hours, and regards a loss of over four per cent. as sufficient to condemn the oil.

THE OXIDISABILITY OR DRYING CHARACTER of an oil is likewise indicated by the test last described, the increase in the weight of different samples when exposed under the same conditions being

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[1] In a private communication (April 3, 1899) to the American reviser, Mr. Doolittle states that large experience with the instrument in comparison with other viscosimeters has confirmed the value of it.

a measure of their tendency to oxidise. The method of making the test may be varied (see Vol. II., part 1, p. 68), but comparison between different oils is difficult unless the mode of operating has been identical. "Gumming," or tendency to dry, if existing to any notable extent, renders an oil unfit for use as a lubricator. The hydrocarbon and terrestrial animal oils are practically free from drying tendencies; but "fish" oils are less perfect in this respect, with the exception of sperm and bottlenose oils, which have peculiarities which distinguish them from all others (see Vol. II., part 1, p. 204). The vegetable oils differ greatly in their drying properties, but even the so-called non-drying oils, like rape and olive (see Vol. II., part 1, p. 138), are not wholly free from a tendency to thicken. An admixture of hydrocarbon oil notably reduces the tendency of a vegetable oil to thicken, and correspondingly diminishes its liability to generate sufficient heat to cause spontaneous combustion. On the other hand, the presence of resin causes a notable increase in the gumming tendency of an oil.

For determining the gumming quality of lubricating oils, A. Bach[1] uses the following method, slightly modified from that of Fresenius:

The oil is heated for ten hours with oxygen in a sealed tube (about 100 to 125 c.c. capacity) in an air-bath; the point of the tube is then broken under a measured volume of water, and from the difference in volume the absorption is calculated. The presence of excess of oxygen after the completion of the experiment should be proved with a glowing splinter of wood. The following absorptions were obtained, 1 grm. of oil being taken in each case:

	Oxygen Absorbed.
Mineral oils,	0·1 to 0·7
,, ,, (0·865),	4·8
Lubricating grease,	21·8
Cod oil (0·963),	76·3
Rosin oil,	181·0
Olive oil,	144·0
Rape oil,	166·0
Cotton-seed oil,	111·0
Mineral oil (0·865) with 10 per cent. cod oil,	9·4
Oleo-naphtha ,, ,,	8·6

Rosin oil or vegetable oils in admixture with mineral oils can thus be detected on account of the low oxygen-absorption of the

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[1] *Chem. Zeit.*, **13**, 905.

latter. Further, the oil has only a slight or no acid reaction in the case of mineral oil, and a strongly acid reaction in that of rosin oil.

THE FREE ACID of an oil and its tendency to *act on metals* are characters which are closely related. A perfectly neutral oil has no action on metals at ordinary temperatures, and experiment shows that the corrosive action increases in direct proportion with the quantity of free acid present (Vol. II., part 1, p. 126).

Many cases of so-called "clogging" or "gumming" of oils, commonly attributed to oxidation, are really due to the action of the free acids on the metal bearings of the machinery, with consequent production of soaps. The corrosion of bearings by oils has not received the attention it deserves, as the wear and tear of the metal and the thickening of the oil have been attributed to other causes. Liquid oils appear to corrode metals very evenly, so that the effect is not readily observed, but with solid fats it is very different.

Although *when freshly manufactured* an oil may be free from any trace of acid, it is not unlikely to acquire a very sensible acidity in time. This is true of many animal and vegetable oils, which have a tendency to become acid by keeping, through a partial splitting up of the fats into glycerol and free fatty acids. Hydrocarbons are free from this tendency, but it must be remembered that a hydrocarbon which has been over-refined by means of sulphuric acid may develop serious acidity by keeping or by exposure to heat.

The presence or formation of free acid in an oil being the chief if not the only cause of its tendency to act on metals, the results published by various observers, showing the amounts of iron and copper dissolved in equal times by different oils, have no interest or meaning apart from the particular samples of oils examined, the action on the metals being simply a function of the free acid the oils happened to contain.

Although, at the time of using, an oil may be wholly free from acid reaction, it may, if of animal or vegetable origin, readily become acid, and hence corrode the metallic surfaces it is employed to lubricate. This is notably the case when the oil is exposed to the action of high-pressure steam, as under such conditions all the fatty oils suffer decomposition more or less readily, with formation of free fatty acids and glycerol.

The free fatty acids formed by the hydrolysis of the oil readily act on the metal of the cylinder and produce an iron soap which clogs up the machinery in a very troublesome manner. It is a curious fact that the soaps of iron and other of the heavy metals (especially the oleates) are soluble in hydrocarbons, though insoluble in water, the reverse being the case with the soaps of the alkali-metals. As a consequence of this the iron soap produced in engine cylinders lubricated with tallow, castor oil, or other fatty oils, becomes dissolved out whenever a change is made to a mineral lubricating oil. This fact is well known to engineers, but it has often been wrongly attributed to an abundant production of "gummy matter" by the mineral oil itself.

In consequence of their tendency to become decomposed by high-pressure steam, fatty oils are unsuited for use in engine cylinders, at any rate in an unmixed state, and in many instances they may be wholly replaced with advantage by mineral oils of low volatility and high viscosity.

In some cases it is found difficult to obtain mineral oil having a sufficiently high viscosity at the temperature at which it is intended to be employed, and an addition of castor oil is consequently made. There then arises the practical inconvenience that mineral and castor oil are mutually soluble only to a very limited extent, but by addition of some other oil, such as tallow oil, perfect union can be effected. The "blown oils" now extensively manufactured as substitutes for castor oil are readily miscible with mineral oil.

A mixture of mineral oil with fatty oil, when used in an engine cylinder, appears to exert a less corrosive action on metals than might be anticipated from the proportion of fatty oil in the mixture, the mineral oil appearing to prevent the decomposing action of the steam on the fatty oil.

It is evident from the foregoing considerations that, in making an examination of a lubricating oil, its tendency to act on metals should be tested as far as possible under the circumstances and at the temperature of its use in practice. Thus, not only should the nature and proportion of free acid present in the original oil be ascertained, as described in Vol. II., part 1, p. 104, but in some cases this determination should be supplemented by a titration of the oil after it has been exposed to a high temperature in contact with water. Fifty grams of the oil and an equal measure of water should be heated in a closed bottle immersed in boiling water. The contents are frequently agitated, and after six or eight hours the bottle is opened and the oil and water are separated. They are then titrated separately with decinormal alkali and phenolphthaleïn (Vol. II., part 1, p. 104). The acidity of the aqueous liquid will generally be due to *free sulphuric acid,* produced by the decomposition of sulphonates in the original oil, and if found in notable quantity, proves the oil to be of an objectionable character. The acidity of the oily stratum will represent the fatty acids formed by the action of the water, *plus* the fatty acids previously present, which latter can be ascertained by titrating the original oil. In the case of cylinder oils, it may sometimes be desirable to heat the oil and water in a sealed tube contained in a bath of boiling saturated solution of calcium chloride, which will give a temperature corresponding to an internal pressure of 10 atmospheres, or about 150 lbs. per square inch, but in most cases a temperature of 100° C. will suffice.

Useful results can be obtained by exposing, to the air, samples of lubricating oil in flat porcelain dishes. Bronze coins, or coils of copper or iron wire, are partially immersed in the oils. When copper is employed, in the course of a day or two many samples of oil acquire a bright green color from dissolved copper oleate, but in other cases the extent of the action is much disguised by the brown color of the oil. If the oil be transferred to a separator (Vol. II., part 1, p. 113), and shaken with ether and dilute sulphuric acid, the dissolved metals pass into the acid liquid. On separating this from the ethereal layer and adding excess of ammonium hydroxide, the depth of the blue coloration produced is a fairly accurate measure of the action of the oil on the copper. If iron wire has been employed, the depth of the red coloration produced by adding a thiocyanate instead of ammonium hydroxide, will serve to indicate the extent of the action. The method, which is due to Archbutt, is capable of being applied quantitatively, and gives useful comparative results when employed under constant conditions.

In some cases useful results are obtainable by exposing oils in contact with metals at an elevated temperature, and then ascertaining the extent of the action as just described.

W. Fox (*Analyst,* 1883, 116) considers that the value of a lubricating oil is inversely as its tendency to absorb oxygen when heated to 100° C. in contact with a metal, such as finely-divided lead. His figures show, however, that the drying tendency of the oil employed is the chief factor concerned, though the amount of oxygen absorbed is not an accurate criterion of this property.

MINERAL MATTERS can be detected in the residue left on igniting the oil. *Free alkali* can be determined by titrating the oil in presence of alcohol with standard acid and phenolphthaleïn, and that existing as *soap* by using methyl-orange as an indicator. *Aluminum palmitate* and *oleate* are now added to mineral oils to increase viscosity. Various soaps, especially those of aluminum, are added to lubricants to increase the viscosity. A mixture of mineral oil with about 10 per cent. of aluminum soap is sold largely under the misleading name "gelatin."

For the detection of these Schweitzer and Lungwitz[1] have devised the following test: About 0.5 c.c. of the sample are dissolved in 5 c.c. of petroleum spirit (boiling below 75° C.), anhydrous ether or absolute alcohol, and mixed with 1 c.c. of a saturated solution of metaphosphoric acid in absolute alcohol or anhydrous ether. In the presence of potassium, sodium magnesium, or aluminum a precipitate is formed. The reaction depends on the fact that, while metaphosphoric acid is soluble in absolute alcohol or ether, most of its salts are insoluble. The reagent may be prepared by shaking the powdered metaphosphoric acid with absolute alcohol, allowing the mixture to stand until clear, and pouring off the solution. It must be kept tightly stoppered.

Calcium oleate is not infrequently added to mineral lubricating oils.

Mineral Lubricating Oil.

The products classed under this title are obtained chiefly from two sources—namely, the less volatile fluid portions of petroleum and the less volatile fluid portions of the oil produced by the distillation of bituminous shale. In the case of petroleum the lubricating oil has not always undergone distillation, but is obtained from the residues by treatment with charcoal and other purifying agents. Such oils, often called "natural oils," or "reduced oils," are preferable as lubricants to those which have undergone distillation.

The lubricating oil obtained from either American petroleum or shale has essentially the same chemical composition. It consists largely of the higher ethenes, with, in the case of the shale product,

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[1] *J. S. C. I.*, 1894, 1178.

small amounts of polymerised ethines, and possibly also terpenes. Small proportions of solid methanes are often present in solution, but higher members of the series peculiar to Caucasian petroleum (p. 63) are probably present in large amount.

Mineral lubricating oils are called by various trade-names, such as "oleonaphtha," "valvoline," "vulcan oil," "globe oil," &c. In color they range from pale yellow through all shades of red, brown, green, and blue, to black. The better qualities have very little taste and no marked odor, either at the ordinary temperature or when heated.

Mineral lubricating oils have specific gravities ranging from 0·850 to 0·925, the most usual figures being between 0·880 and 0·910. An oil of sp. gr. 0·940 has been prepared from Brazilian petroleum. They are not optically active, but usually exhibit a strongly marked blue or green fluorescence, a characteristic in their detection. The method of applying the test is described Vol. II., part 1, p. 111.

The fluorescence or "bloom" of mineral lubricating oil may sometimes be destroyed by exposure to light, but more rapidly and certainly by subjecting it to a process of limited oxidation by treatment with nitric acid. Turmeric, α-nitronaphthalene, and picric acid also obscure the fluorescence. Dinitrotoluene is much used in the proportion of four pounds to the ton of oil. There are, however, varieties of mineral lubricating oil wholly non-fluorescent, and in which the property cannot be developed by any known treatment. These oils, if derived from shale, usually deposit solid paraffin on cooling to about —8° C. They distil without decomposition, are unaffected by alkalies, and behave in the ordinary manner with sulphuric acid.

Mineral lubricating oil is not acted on by alkali, a fact on which is founded the process of detecting and estimating it when mixed with fat oils. (See Vol. II., part 1, p. 113.)

When treated with bromine, mineral lubricating oils absorb a proportion of bromine which is of some value in forming an opinion as to the origin and constitution of the oil. (See p. 25.)

An English patent has been granted for a mixture of soap, turpentine, and mineral oil of high boiling point. It is claimed that by this means a much larger proportion of paraffin oil can be added to soap than when turpentine is not used.

EXAMINATION OF MINERAL LUBRICATING OILS.

In determining the general character of hydrocarbon lubricating oils, as also their suitability for special purposes, the properties to be taken into account are the same as those which are important in the case of lubricating oils of animal or vegetable origin, but the following additional characters may be noted:

a. Color is of little importance except for the fine kinds of oil. A well-marked fluorescence is an ordinary characteristic of mineral oils, but is in no respect a test of quality. Turbidity may be due to water in suspension, in which case the oil usually froths on heating, or it may be caused by the presence of solid hydrocarbons which dissolve on warming the oil. Other *solid matters* may be separated by diluting the oil with ether or petroleum spirit, filtering, washing the residue with ether, drying it gently, and weighing.

b. The smell should be very slight, even on warming. A marked odor indicates an imperfectly refined oil, or the presence of objectionable volatile compounds which will lower the flash-point of the oil and increase its waste in use.

c. The specific gravity may vary within wide limits. As a rule, the greater the specific gravity of an oil, the higher will be its flash-point and viscosity; but there are many exceptions. Lubricating oils from Russian petroleum have a higher viscosity than the products of similar density from American petroleum and shale oil. In the case of oils completely fluid at the ordinary temperature, the specific gravity may be determined by any of the usual methods. The density of the thicker and semi-solid oils is best ascertained by filling a specific gravity bottle to the brim with the warm oil. When it has cooled to a temperature of 15·5° C., the stopper is inserted, and worked to and fro until it is forced home, the excess of oil gradually escaping through the perforation in the stopper, when the bottle may be wiped and weighed.

d. On exposure to cold the oil should assume the consistency of a jelly or ointment, and the temperature at which it undergoes this change should not be inconsistent with the conditions under which it is to be used. The test is commonly applied by slowly cooling a sample in a tube about 1⅝ inches in diameter, and noting the temperature at which the oil no longer flows on inclining the tube, or that at which separation of solid paraffin begins. The lubricating oil from Baku petroleum bears exposure to a very low temperature (—20° F. in some cases) without becoming solidified or even depositing any paraffin. This peculiarity may be employed to distinguish Russian from American products.

e. The flash-point (p. 104) of a lubricating oil should be fairly high. A low flash-point indicates the presence of volatile constituents which will produce an odor, cause waste, and may possibly be dangerous. A high flash-point is often rigidly insisted on in the case of oils to be used in cotton mills or engine cylinders. The flashing points of the pale Scotch oils from shale range from 130° to 180° C., and of the darker oils and greases from 180° to 230°. These oils usually become viscous about 0° C. The pale oils from American petroleum manufactured by the Thompson and Bedford Company flash from 166° to 230° C., the specific gravity ranging from 0·885 to 0·920. The black oils flash at temperatures ranging from 180° to 204° C., according as the melting point varies from —10° to —1° C.

The flash-point of lubricating oils is best observed by the Abel apparatus, but the water-bath must be removed and the intermediate air-bath filled with olive oil or melted paraffin wax. The apparatus is then heated on a sand-bath, and the flash-point of the oil observed in the usual way. The New York State tester is also used. Some operators use the open test.

f. On heating a mineral lubricating oil in a platinum capsule, it should volatilise without the production of any very pungent odor; and if the vapors be allowed to ignite and the flame be then blown out, no smell of resin or acroleïn (from fixed oils) should be observable. Spindle oil should not lose more than 5 per cent. of its weight when absorbed by filter-paper and exposed to 60° C. for twelve hours. (See also p. 128.)

g. On ignition, a mineral lubricating oil should leave no inorganic residue, or merely an insignificant trace (less than 0·05 per cent.). Certain oils, which have been treated with *soda*, leave a very sensible quantity of ash of marked alkaline reaction to litmus. The same result would be obtained if the oil contained a *soap* of an *alkali-metal*, but soap is neutral to an alcoholic solution of phenolpthaleïn (Vol. II., part 1, p. 292). A more usual addition, however, is *aluminum palmitate* or *oleate*, which is added to lubricating oils to increase the viscosity. It often separates from the mineral oil after a time, especially in contact with water. If such oil be heated, it foams violently. Aluminum oleate can be detected as noted on page 133.

h. The oil should be agitated in a test-tube with an equal measure of boiling water, and the tube then kept in the water-oven until separation occurs. The formation of a granular white layer at the junction of the two liquids indicates the presence of *resin.* If the liquid assume a milky-white appearance, the oil has been insufficiently washed after the final treatment with soda. *Alkali* is often purposely left in an oil with the view of increasing its "body" or viscosity. This is effected by blowing air through the imperfectly washed oil. As the moisture is got rid of, the oil takes up the soda, while remaining perfectly transparent. Such oil is very prone to oxidise, and becomes turbid on exposure to air from absorption of moisture. It is also liable to change in color. If a mineral oil be boiled in a large excess of water for three or four hours, the oil will be practically unaltered in color if of first-rate quality.

i. If the oil be agitated with an equal measure of caustic soda solution of 1·36 specific gravity, and the tube kept at about 55° C. until the liquids have separated, a precipitation of *tarry matter* indicates that the oil has previously been insufficiently treated with soda, and hence is liable to deteriorate in color. A first-rate oil gives no trace of tarry matter when submitted to this test. The formation of a white emulsion with the alkali is due to an admixture of some *fatty oil*, *fatty acid*, or *resin.* A diminution in the bulk of the oil indicates the presence of *phenoloid bodies*, which may be determined by a quantitative application of the test.

k. Fatty oils may be detected and determined with considerable accuracy by saponifying the oil and extracting the aqueous solution of the soap with ether, as described in Vol. II., part 1, p. 113.

l. When 10 c.c. mineral lubricating oil are shaken with 4 c.c. of sulphuric acid of 1·73 specific gravity at 15·5° C. for two minutes, it will remain unchanged or acquire simply a yellow tint if of good quality, but if the sample be imperfectly refined, or if *coal-tar oil* be present, more or less browning will ensue. On treatment with concentrated sulphuric acid, in the manner described in Vol. II., part 1, page 76, lubricating oils from shale and petroleum at first develop a trifling degree of heat (3° to 4° C.), though on continued stirring a very decided increase of temperature is sometimes observed. *Rosin oil* usually causes a rapid rise of 18° to 22° C., and with *coal-tar oil* the action is still more marked. *Fatty oils* rarely give a less rise than 40° C.

m. If 10 c.c. of the oil be mixed with an equal measure of fuming nitric acid of 1·45 specific gravity, but little rise of temperature will occur with good mineral oil or shale lubricating oil, but great heat is produced by coal-tar oil. Rosin oil mixes quietly with the acid, and then suddenly evolves much heat. Methods for detecting adulteration with rosin oil are described under that head.

Deblooming Agents.—As a general preliminary test, Holde[1] advises the following: The clear oil is boiled for from one to two minutes in a test-tube with about 3 c.c. of concentrated alcoholic solution of potassium hydroxide. Oils containing nitro-compounds become blood-red or violet-red, and on warming the upper part of the tube where there are adhering drops of the alkaline solution, just above the main bulk of the liquid, these drops become at once reddish-violet. Holde has never observed the latter reaction with any oils not containing nitro-derivatives, but some fatty oils will produce on long heating a yellowish-red or blood-red in the body of the liquid, although the usual color is a merely brownish.

For the detection of α-nitronaphthalene used as a deblooming agent, N. Leonard[2] has devised the following method, depending upon the production of α-amidonaphthalene, which has a characteristic disgusting odor, similar to that of a decayed tooth.

A small quantity of the oil is gently warmed with zinc dust and dilute hydrochloric acid, and the mixture shaken from time to time. If α-nitronaphthalene be present, the odor of the amido-derivative will be noted. When the reduction is complete, the acid water is withdrawn by a separator funnel. A portion of this liquid, neutralised by ammonium hydroxide, will give, with ferric chloride, a blue precipitate, becoming purple. The remainder of the solution may be rendered alkaline with sodium hydroxide and extracted with ether, the ether evaporated, the residue dissolved in a little alcohol, and to this solution a drop of a solution of sodium nitrite, acidified with acetic acid, is added. A yellow is produced, which is changed to crimson by hydrochloric acid.

Mineral oils are sometimes adulterated with caoutchouc. For the detection of this, Holde[3] advises the following data in addition to the usual tests: Ascertain the solubility by shaking one

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[1] *J. S. C. I.*, 1894, 906.

[2] *Chem. News*, **68** (1893), 297.

[3] *J. S. C. I.*, 1891, 390.

volume of the oil with two volumes of alcohol, benzene, or ether; precipitate the caoutchouc by treating the oil with a mixture of three parts ether and four parts alcohol. The precipitate is filtered out, washed, dried, and weighed.

The following methods for the examination of heavy mineral oil have been formulated by the Scottish Mineral Oil Association (*J. S. C. I.*, 1891, 346):

Flashing Point.—The oil-cup and cover of the ordinary "Abel" flash-point apparatus is to be employed. The cup is filled with oil in the usual manner, and the rate of heating is to be such that at least fifteen minutes are taken in raising the temperature of the oil to 300° F. In the event, however, of a dispute arising as to the correct flashing point of a heavy mineral oil, the question is to be decided by means of the "Pensky-Martens" apparatus.

Viscosity.—The "Redwood" viscometer is that which is to be employed in the determination of the viscosity of mineral oils. Ordinary results are to be expressed—as the time, in seconds, which 50 c.c. of the oil take to flow through the orifice at a temperature of 70° F.

Setting Point.—This is determined in the following manner: Into a test-tube having a diameter of about 1¼ inches the oil to be tested is added to the depth of about 2 inches, the tube is then immersed in a freezing mixture, the oil being slowly stirred with a thermometer until it has cooled down considerably below the temperature at which solid paraffin first appears; the tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil, until two experiments give concordant results, the temperature so found being the setting point.

Vaseline. Petroleum Jelly. Soft Paraffin.

Vaseline consists of those portions of petroleum which are soft or pasty at ordinary temperatures. It is taken from petroleum or ozokerite stills after the greater part of the oil has volatilised. The crystallisable paraffin is more or less removed, and the residue purified without distillation, treatment with sulphuric acid and superheated steam and filtration through animal charcoal being the usual methods employed. An English patent was taken out in 1847 by C. B. Mansfield for a process for deodorising or decolorising petroleum sediment by means of animal charcoal.

Vaseline is now extensively used as a lubricant and to protect iron and steel goods from rust. It has been much used as a valuable basis for ointments. It varies somewhat in its physical characters according to its origin and quality. It is ordinarily a colorless or pale yellow, translucent, fluorescent semi-solid. The commoner kinds used for lubricating have a dark greenish or brownish color. It is free from taste and smell. Under the microscope crystals are sometimes visible which become more numerous on cooling.

The commercial varieties may be classed under two heads: (1) those which, like the product from American petroleum, are obtained as a ready-formed mixture of hydrocarbons of gelatinous consistence; and (2) those made by directly mixing solid paraffin of low melting point with heavy lubricating oil. The latter kind are less homogeneous and are liable to deposit crystals of paraffin on keeping, and hence are not so suited for the preparation of ointments as the American article.

Vaseline usually melts between 40° and 50° C. At the boiling point of water, compared with water at 15·5° C., the specific gravity of vaseline ranges between 0·803 and 0·855, figures which present a striking contrast to those representing the specific gravity of paraffin and ozokerite under the same circumstances (0·748 to 0·757). It is insoluble in water. Cold alcohol of 98 per cent. dissolves a small amount; in hot alcohol it dissolves freely to a clear solution, from which it separates in flakes on cooling.

Vaseline consists chiefly of methanes, the iso-forms from $C_{16}H_{34}$ to $C_{20}H_{42}$ being apparently most abundant. A notable proportion of ethenes is also present.

The following figures show the specific gravity and bromine-absorption of samples of vaseline and allied products examined in the author's laboratory. The density determinations at 99° C. were made with a plummet and Westphal balance, and the bromine-absorptions as on page 24:

DESCRIPTION.	SPECIFIC GRAVITY.		BROMINE-ABSORPTION.	
	Solid; at 15·5° C.	Melted; at 99° C.	Total.	Br. as HBr.
White pomade vaseline (Chesebrough Co.),	0·856	0·8036	11·3	1.8
Yellow vaseline (maker unknown),	0·870	0·8140	1·1	0.0
Yellow vaseline (maker unknown),	0·873	0·8172	7·2	1·1
White pomade ozokerine (J. C. & J. Field),		0·8110	1·1	0·3
Yellow pomade ozokerine (J. C. & J. Field),	0·909	0·8547	8·5	1·2
White cerasin mixture,		0·8228	1·7	0.3
Petroleum jelly (Grindley & Co.),	0·896	0·8421	2·9	0·7
Vaseline tallow,	0·884	0·8374	10·2	1·7
Petrolina (Binghamton Oil Co.),		0·8145	7·9	1·3

In warm ether, American vaseline dissolves freely to a clear solution exhibiting a strong blue fluorescence, and the liquid remains clear, or becomes at most only slightly turbid on cooling. German vaseline, on the contrary, is said to form a thick solution and give a considerable deposit on cooling. Russian vaseline is stated to dissolve completely in warm ether, and give a clear solution which becomes turbid on cooling.

Vaseline is readily soluble in chloroform, benzene, carbon disulphide, and turpentine. From these and its ethereal solution alcohol precipitates it. Vaseline is miscible in all proportions with fixed and volatile oils. With glycerol it forms an intimate mixture which separates into its constituents when warmed, the melted vaseline floating on the glycerol. Treatment with water also removes the glycerol.

Vaseline is neutral in reaction, and but little affected by chemical reagents. It is not saponified or otherwise acted on by alkalies, and is unaffected by hydrochloric or dilute nitric acid. Boiling sulphuric acid of 1·60 and boiling nitric acid of 1·18 specific gravity are said not to alter it; but fuming nitric acid colors it yellowish-red and sulphuric acid of 1·820 specific gravity greyish-black, the acid itself acquiring a yellowish-brown color. Some samples blacken on treatment with cold concentrated sulphuric acid, a reaction which indicates the presence of bodies other than paraffins. It does not oxidise or turn rancid on exposure to air. Vaseline intended for pharmaceutic use should be refined with the aid of acid.

Good vaseline should be completely volatile when heated in platinum, without giving any smell of burning fat (acroleïn) or rosin. When agitated with twice its measure of strong alcohol it should remain practically undissolved. The spirit should not acquire an acid or alkaline reaction, and should not give any noticeable precipitate on dilution with water. When agitated with cold concentrated sulphuric acid diluted with one-ninth of its weight of water, vaseline gives no marked increase of temperature, and ought not to become very strongly colored. When subjected to the saponification process employed for the determination of hydrocarbons in fixed oils, vaseline should yield to the ether an amount of unsaponifiable matter almost equal to the original weight of vaseline used for the experiment; while, on the other hand, the aqueous liquid separated from the ethereal layer should yield no notable precipitate on being acidulated.

The United States Pharmacopeia has introduced, under the title "Petrolatum," a preparation equivalent to vaseline. It is defined as follows in the current (1890) issue: "A mixture of hydrocarbons, chiefly of the marsh-gas series, obtained by distilling off the lighter and more volatile portions from petroleum and purifying the residue when it has reached the desired melting point. A fat-like mass of about the consistency of an ointment, varying from white to yellowish or yellow, more or less fluorescent when yellow, especially after being melted, transparent in thin layers, completely amorphous and without odor and taste, or giving off when heated a faint odor of petroleum."

The British Pharmacopeia (1898) recognizes "Paraffinum molle" and "Paraffinum liquidum." The former should melt at from 35·5° to 38·9° C., have at its melting point a specific gravity of from 0·840 to 0·870, give off no unpleasant odor when heated to 48·9° C., and be freely soluble in ether, chloroform, and benzene. The latter should boil at not below 360° C. and have a specific gravity of from 0·885 to 0·890.

The German Pharmacopeia recognizes "Paraffinum liquidum" and "Paraffinum solidum." The former should have a specific gravity not less than 0·880 and should boil above 360° C. The latter should melt at from 74° to 80° C.

Mixtures of the intermediate members of the petroleum derivatives of such composition as to remain liquid at common temperatures and practically free from odor are now familiar commercial articles. One of these preparations is commercially known as "glycoline." Among the uses which may be made of it in the laboratory is the preservation of specimens of sodium and potassium, which keep bright much longer in this liquid than in ordinary kerosene.

"Ozokerine," "fossiline," "chrysine," "cosmoline," "saxolene," "geoline," "petrolina," "vaseline tallow," &c., are trade-names of articles of the vaseline class.

Paraffin. Paraffin Wax. Solid Paraffin.

Paraffin is found native in the coal-measures and other bituminous strata, constituting the minerals known as fossil wax, hatchettin, ozokerite, &c. It exists also in solution in many kinds of petroleum, and is obtainable therefrom by distilling off the more volatile portions and exposing the remainder to a low temperature. Solid paraffin may be obtained in a similar manner from the tars of wood, cannel coal, and bituminous shale, and is now manufactured on an enormous scale from the last source. (See p. 38.)

Paraffin is a white or bluish-white, waxy solid, without taste or smell. Its density and melting point vary with its composition, and the same is true of its boiling point, which is very high. Exposure to continued heat, aided by pressure, resolves paraffin into liquid hydrocarbons (p. 91), and the same result is partially obtained by distillation. By merely raising the temperature to 370° C. it undergoes decomposition, with separation of carbon and formation of permanent gas, liquid products, and a paraffin of lower melting point. It contains about 85 per cent. of carbon and 15 per cent. of hydrogen.

The specific gravity of paraffin increases with its melting point, as is shown by the following results attained by Galletly from Boghead coal products:

Specific Gravities.	Melting Points.	
0·8236	32·0° C.	89·6° F.
0·8480	39·0 ,,	102·2 ,,
0·8520	40·5 ,,	104·9 ,,
0·9090	[1] 53·3 ,,	128·0 ,,
0·9110	[1] 53·3 ,,	128·0 ,,
0·9243	58·0 ,,	136·4 ,,
0·9248	59·0 ,,	138·2 ,,
0·9400	80·0 ,,	176·0 ,,

G. Beilby (*J. C. S.*, xliii. 388) has given the following data

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[1] These temperatures are correctly quoted.

respecting the specific gravity of a sample of shale-oil paraffin melting at 38° C.:

	SPECIFIC GRAVITY.
In the solid state, at 21° C.,	0·8740
Dissolved in ·885 paraffin oil, at 21° C.,	0·7950
In the melted state (calculated to 21° C.),	0·7956

From this it appears that paraffin in solution has practically the same density as when in the molten state. This result is comparable with one obtained by the author, who found that spirit of camphor has a volume equal to the sum of the volumes of the camphor and alcohol used in preparing it.

The data in the following table, obtained in the author's laboratory, show the relations between the solidifying point of paraffin wax and its density in the solid and liquid state. The determinations of specific gravity of solid samples were in most cases made as described in Vol. II., part 1, p. 220, but, on repetition, the figures obtained were not very concordant. The density at 99° was determined by the plummet (Vol. II., part 1, p. 29), and the solidifying point was ascertained by method *d* (Vol. II., part 1, p. 37).

ORIGIN OF SAMPLE.	SPECIFIC GRAVITY.		SOLIDIFYING POINT ; ° C.
	Solid, at 15·5° C.	Liquid, at 99° C.	
1. Shale oil,	0·8666	0·7481	44·0
2. ,,	0·8961	0·7494	47·0
3. ,,	0·9000	0·7517	52·0
4. ,,	0·9111	0·7572	58·5
——	. .	. .	. .
5. American petroleum,	0·9083	0·7535	53·8
6. Ozokerite,	.	0·7531	61·5
7. Rangoon tar,	0·8831	0·7571	49·0

From these figures it appears that, except in the case of the refined ozokerite, there is a regular increase in the density with a rise in the melting point, as was observed by Galletly. There is a striking contrast between the densities of the waxes in the molten state at 99° and the densities of the same samples when solid, the range in the latter case being, for the shale products, five times as great as in the former. In other words, the density of paraffin wax is far more constant when melted than in the solid state. It also appears that paraffin is much less dense in the melted state than the oil from which it crystallises on cooling, a sample of which had a specific gravity of 0·843 at 99°. Vaseline also is considerably denser than paraffin.

Paraffin melting from 32° to 43° C. exhibits a well-defined crystalline fracture; from 43° to 50° C. the crystals become much smaller and less marked, and from 50° C. upwards the fracture is very close and fine in the grain. Paraffin that melts at 65° C. presents, on fracture, brilliant, white, acicular crystals having a silky lustre, and that melting at 77° C. closely resembles bleached beeswax, but the fracture is not conchoidal.

When paraffin is kept for some time under gentle pressure, the temperature being somewhat below its melting point, a molecular change occurs and the substance becomes transparent. A sudden change of temperature or a sharp blow or knock causes the mass to return to its original state, but it may be annealed by slow cooling.

Paraffin becomes plastic at a temperature considerably below its melting point, a fact which is disadvantageous when it is employed for making candles, but which is to a great extent obviated by a small admixture of stearic acid, wax, or other foreign body.

Mixtures of paraffins of different fusing points melt at a temperature which is the mean of the melting points of the constituent hydrocarbons; but the products obtained by melting together paraffin wax and stearic or palmitic acid, beeswax, &c., always have a melting point *lower* than the mean of those of their constituents. This is well shown by the following table from Vincent's *Manufacturing Chemistry*, the results recorded being obtained from mixtures of the Musselburgh Company's stearic acid, melting at 130° F., with various proportions of three varieties of Young's paraffin:

STEARIC ACID.	PARAFFIN.	MELTING POINT OF MIXTURE. PARAFFIN MELTING AT		
		120° F.	126° F.	127° F.
55	45	114	113·5	115·5
60	40	119	116	118
65	35	121	118	120
70	30	122·5	122·5	122
75	25	124·5	124	124
80	20	125·25	125·5	125·5
85	15	126	127	127
90	10	127·5	128	129·5
95	5	128·5	129	130

When two pieces of paraffin are sharply struck together, a metallic ring is heard, the sound being sharper the higher the melting point of the paraffin.

Paraffin is completely insoluble both in hot and cold water. It is insoluble in rectified spirit, and but sparingly soluble in boiling absolute alcohol, the dissolved portion separating again on cooling. It dissolves readily in ether, is very soluble in petroleum spirit, shale naphtha, kerosene and benzene, cold essential oils, and warm fixed oils, and does not again separate from the last named on cooling. Hence it is miscible with all kinds of vegetable and animal oils and fats. It differs from these in its indifference to alkalies, and cannot be saponified. If, however, the soap be made from a mixture containing carnaüba wax as well as paraffin, the latter is completely dissolved by the alkali, a fact which is said to be attributable to its solubility in the myricyl alcohol, $C_{30}H_{61}.OH$, which is a constituent of the carnaüba wax.

Paraffin burns with a very bright but not smoky flame, and hence is much employed for making candles and tapers. *Paraffin candles* usually contain from 5 to 15 per cent. of stearic acid. The presence of the admixture may be detected by adding a little powdered fuchsine to the sample and keeping it at 100° C. for some time. If pure, the melted paraffin will remain uncolored, but with 2 per cent. of stearic acid a pink color is produced, and if as much as 5 per cent. be present, the whole mass becomes crimson. Colored candles are made by dissolving the fuchsine or other coloring matter in stearic acid or beeswax, and adding the product to the paraffin until the desired tint is obtained.

Boiled with concentrated nitric acid, paraffin is oxidised, with formation of various products, of which the most characteristic are succinic acid, $C_4H_6O_5$, and cerotic acid, $C_{27}H_{54}O_2$, the production of the latter of which points to the presence of the hydrocarbon, $C_{27}H_{56}$, in the original substance. Cerotic acid was also the chief product obtained by Gill and Meusel by the oxidation of a paraffin, melting at 56° C., by means of chromic acid mixture.

Paraffin is also violently oxidised by permanganate of potassium mixed with sulphuric acid and heated. Concentrated sulphuric acid attacks it at high temperatures, and the more readily, the higher the melting point of the sample.

When heated with sulphur, paraffin is decomposed, with evolution of hydrogen sulphide and separation of carbon.

Other chemical characteristics of paraffin, and methods for separating it from *hydrocarbons* of other series are given on page 22 *et seq.*

For the quantitative analysis of mixtures of paraffin with *fatty acids* or *fats*, the process described in Vol. II., part 1, page 112, is suitable. The detection and determination of paraffin in *beeswax* can be effected as described in Vol. II., part 1, page 224.

PARAFFIN SCALE. Crude Paraffin.

"Scale" is the technical name for the crude paraffin deposited by cooling the oils holding it in solution. The lower the temperature employed for refrigeration, the lower the melting point of the paraffin deposited.

In the practical assay of paraffin scale, methods must be employed which are acceptable under reasonable conditions by all interested parties. The following are the methods adopted by the Scottish Mineral Oil Association and certain representative purchasers:[1]

Sampling.

The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, waggon, or bing.

Preservation of Samples.

Immediately after the sample has been drawn it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

Determination of Oil.

(*a*) *Press.*—No special form of press is recommended for general adoption, but it must have some arrangement for indicating the pressure applied. The cup, in which the scale is placed during the application of pressure, should have an area of 20 square inches.

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[1] *J. S. C. I.*, 1891, 342.

(*b*) *Preparation of Sample.*—A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool over night to a temperature of 60° F. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(*c*) *Quantity and Conditions.*—The quantity of scale to be used in the determination of oil is to be 250 grains, which may, however, be reduced to 150 grains in the event of the scale containing much oil (over 7 per cent.). With "soft" scale the smaller quantity should be taken.

(*d*) The temperature of the scale and the press is to be 60° F.

(*e*) The scale is to remain under pressure for fifteen minutes.

(*f*) Fine linen pressing cloths and a number of layers of filter-paper sufficient to absorb all the oil are to be used. The exterior papers must not be soiled by oil.

(*g*) The maximum pressure is to be 10 cwt. per square inch, and the working pressure 9 cwt. per square inch.

Determination of Water.

The amount of water present in paraffin-scale may be determined by either of the following processes:

(*a*) *Distillation from a Copper Flask.*—From 1 to 2 lb. of the scale are heated in a conical copper flask of about the following dimensions: 27·5 cm. (11 inches) high over all, 20 cm. (8 inches) diameter at the base, and 0·4 cm. (1·5 inches) at the neck. The bottom of the flask is slightly concave downwards. This is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasoline or naphtha and added to the principal quantity.

(*b*) *Price's Company's Method.*—Five hundred grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 230° F., until bubbles cease to be given off: the loss is then determined.

Five hundred grains of the *same scale*, which has been freed of its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way, to a similar temperature for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment; the remainder is taken as the quantity of water present.

Determination of Dirt.

The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale, and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried, and weighed. When available, the quantity of scale to be used in the determination of the percentage of dirt should not be less than 7000 grains.

Calculation of Results.

As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

Determination of the Melting (Setting) Point of Solid Paraffin.

This is to be determined by what is known as the "English" test—*i.e.*, a test-tube about 1 inch in diameter is filled to the depth of about 2 inches with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

What is technically known in England as the "melting point" of paraffin scale is in reality the solidifying point, and can be ascertained by method *d*, Vol. II., part 1, p. 37.

Boverton Redwood[1] has devised a special machine for testing paraffin scale, and the greater part of that imported from America is sold on the results of the assay by Redwood's test. The apparatus consists of a press furnished with a gauge for indicating the pressure applied. The test is, of course, a purely arbitrary one, depending upon (*a*) temperature, (*b*) amount of pressure applied, (*c*) length of time during which the pressure is continued, and (*d*) quantity of scale operated upon in relation to the diameter of the press-cake. The operation is conducted at 60° F., which temperature must be closely adhered to. The quantity of scale operated upon is 500 grains, and the pressure is applied for

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[1] *J. S. C. I.*, 1884, 430.

five minutes. The gauge of the press indicates from 1 to 10 tons, and the working pressure is 9 tons on the whole surface of the press cake of 5⅝ inches diameter, equal to about 7 cwt. per square inch. The sample is placed between two circular pieces of filter-cloth in a turned iron cup into which the ram of the press fits, and a sufficient number of circular pieces of filtering paper are placed above and beneath the cloth to absorb the expressed oil. The press cake is carefully removed from the cloth at the expiration of five minutes, and the loss in weight noted. The proportion of oil in American scale usually ranges between 1 and 12 per cent. Much depends upon the proper drawing and averaging of the samples of scale. A good plan is to sample one cask in twenty by taking out a core with a sampling iron driven into the centre of the cask, and then mix the sample by passing it through a small hand sausage-machine.

In America the paraffin scale is melted over a water-bath in a hemispherical tinned iron or glass dish, 3 or 4 inches in diameter. The dish is then placed on a stand where slow cooling can take place, in a room at a temperature of about 60° F., and a thermometer, with a spherical bulb half an inch in diameter, is suspended over the centre of the dish so that seven-eighths of the bulb is immersed in the paraffin. The surface of the melted scale is then carefully watched, and the temperature noted at which a "spider" extends from the edge of the liquid to the bulb of the thermometer. The "spider" or network makes its appearance before there is any uniform film over the surface, and is not readily observable unless the observer be suitably placed in relation to the source of light. Redwood, to whose published papers and private communications the author is indebted for much information on the subject of petroleum-products, states that the results of the American test are from 2·5° to 3·0° F. higher than those obtained by the English test.

According to Lewkowitsch,[1] the German method of determining the solidifying point of paraffin-scale is as follows: A small beaker, 7 cm. high and 4 cm. in diameter, is filled with water and warmed to about 70° C. A piece of the sample large enough to form a globule 6 mm. in diameter is dropped on the water. A standard thermometer is immersed in the water so that its bulb is entirely submerged, and liquid allowed to cool slowly. The temperature at which a film is noticed on the paraffin globule is taken as the solidifying point.

[1] *Chem. Anal. Oils, Fats, and Waxes*, 762.

Petroleum Residuum.

In some works the distillation of petroleum is carried to actual coking, and in others so far as to produce a kind of pitch. In other cases the process is stopped at an earlier stage, and the "petroleum residuum" obtained is separately treated.

Besides methanes and ethenes, the residues from American petroleum contain notable quantities of cyclic hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogene, and pyrene have been recognised, as also a hydrocarbon called thallene. From the residue from California petroleum the hydrocarbon picene, $C_{22}H_{14}$, has been isolated. When treated with strong sulphuric acid it yields a sulphonic acid, which dissolves in water with fine blue-green fluorescence.

For the assay of petroleum residues a method may be used similar to that employed for the examination of crude shale oil (page 39). That is, 500 c.c. should be distilled, the distillate washed with acid and soda, and the purified product again distilled, when it will yield *burning oil*, heavy oil containing paraffin, and "grease" which should be separately cooled and pressed. The oil separated from the *scale* is again treated with acid and soda, when it forms *finished lubricating oil.* A sample of residue examined by R. Tervet yielded: burning oil, 5·5; lubricating oil, 50·6; and paraffin scale, 5·8 per cent.

Petroleum residues often contain a considerable proportion of *water*, which cannot be separated by simply heating the substance. The residue should be treated with a large excess of petroleum spirit and the water allowed to settle out, any *gritty matter* being separated by filtration. In the United States, petroleum residuum is largely used in the preparation of asphalt-paving mixtures. (See page 77.)

CYCLIC HYDROCARBONS FROM COAL-TAR.

The tar obtained as a by-product in the manufacture of illuminating gas from bituminous coal was at one time a source of much annoyance to the gas-engineer, since no convenient disposition or use of it could be made. At the present day, however, it constitutes a valuable material, chiefly owing to the fact that it is rich in cyclic hydrocarbons, from which a long line of synthetic products of great practical value may be produced. Russian petroleum residuum has also been used as a source of cyclic hydrocarbons, but the present indications are that before long the utilization of the by-products of coke-ovens will afford the most economic and abundant supply of these bodies.

Tars from various kinds of coal, and even from the same kind under varying methods of operating, will obviously differ in composition, but will always be mixtures of many more or less analogous bodies. A synopsis of the more important of these is given on page 51. The preliminary step in the separation of the different constituents is by fractional distillation. The table on the following page shows the general character of this distribution as ordinarily carried out; more detailed information is given in connection with the description of the characteristic and important ingredients in each fraction.

The most important constituents of coal-tar may, from the standpoint of the analyst, be arranged in three groups, as derivatives of *Benzene*, *Naphthalene*, and *Anthracene*. Each of these forms the starting point of a homologous series, and of an extensive and complex series of derivatives.

COMPOSITION OF THE PRINCIPAL FRACTIONS OF COAL-TAR.

Crude naphtha. Light oils.	**Dead oils. Creasote oils.**	**Green or Anthracene oils.**	**Pitch.**
(Specific gravity less than 1.000.)	(Specific gravity more than 1.000.)		
Distilling below 180° C.	Distilling between 180° C. and 270° C.	Distilling above 270° C. Methyl-naphthalene.	
Methanes (paraffins). Tetrane to decane.	Phenol.	Phenanthrene. Anthracene.	
Ethenes (olefins). Pentene to heptene.	Methylphenols (cresols).	Pyrene. Chrysene.	
Ethines (acetylenes).	Naphthalenes. Naphthaline hydrides.	Benzerythrene. Solid paraffin.	
Benzenes. Benzene to durene.	Anilines. Leucolines.	Benzonitrile. Carbazol.	
Benzene hexhydrides.	Pyridines.	Acridine.	
Naphthalene hydrides.	Quinolines.		
Phenol (carbolic acid).			
Methylphenols (cresols).			
Pyridines.			
Sulphur compounds (thiophenes).			
Amine derivatives.			

BENZENE AND DERIVATIVES.

The following is a synopsis of the empirical and rational formulæ, conventional and systematic names of some of the known members of the series. Isomerism does not occur in the first two forms:

Empirical Formula.	Rational Formula.	Conventional Name.	Systematic Name.
C_6H_6		Benzene	
C_7H_8	$C_6H_5CH_3$	Toluene	Methylbenzene.
C_8H_{10}	$C_6H_5C_2H_5$		Ethylbenzene.
	$C_6H_4(CH_3)_2$	Xylenes	Dimethylbenzenes.
C_9H_{12}	$C_6H_3(CH_3)_3$	Mesitylene	Trimethylbenzenes.
		Pseudocumene	
		Hemimellithene	
	$C_6H_5C_3H_7$	Cumene	Isopropylbenzene.
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$	Durene	Tetramethylbenzenes.
		Isodurene	
		Prehnitene	
	$C_6H_4(CH_3)(C_3H_7)$	Cymene	Methylpropylbenzene.
$C_{11}H_{16}$	$C_6H(CH_3)_5$		Pentamethylbenzene.
$C_{12}H_{18}$	$C_6(CH_3)_6$		Hexamethylbenzene.

The homologues of benzene prominently occurring in coal-tar are bodies in which one or more of the atoms of hydrogen of benzene are replaced by methyl, CH_3. Meta-derivatives are more abundant than either ortho- or para-derivatives. Higher homologues than tetramethylbenzene are rare, if occurring at all.

The members of the benzene series present very close resemblances both in their physical and chemical characters, and hence, with the exceptions specified below, the description given of benzene on page 157 *et seq.* may be regarded as of general applicability to the others.

Benzene, C_6H_6.

This substance was discovered by Faraday in the liquid obtained by compressing coal-gas, and subsequently prepared by Mitscherlich by distilling calcium benzoate.[1] The chemistry of benzene has become of immense importance, and research has been materially aided by the general acceptance of Kekulé's

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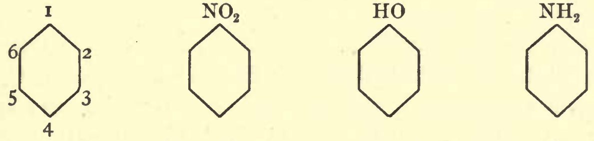
[1] Mansfield, a pupil of A. W. Hofmann, first obtained benzene in practicable quantity from coal-tar. He lost his life by an accident that occurred while preparing a sample for exhibition at the Paris Exposition of 1854.

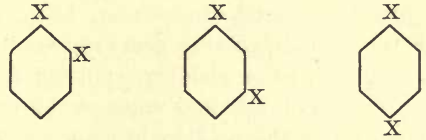
theory of the benzene-ring—namely, that the carbon atoms are arranged in a closed chain, so that six valencies are latent, twelve are concerned in forming the chain, and the remaining six are saturated by the hydrogen. Various suggestions have been made as to the distribution of the latent valencies, but the subject does not need elaborate consideration here. The play of affinities cannot be shown without the use of stereochemical formulæ. For convenience the benzene molecule is represented by a hexagon, which, if unmodified, stands for C_6H_6. When any sign is attached without a connecting line to any angle of the hexagon, it indicates that the body represented is substituted for the hydrogen at that point. To assist in the nomenclature of the benzene derivatives the hexagon is "oriented"—that is, the angles are numbered, the figures 1 to 6 being used, arranged in the direction of the figures of a clock.



Orientation. Nitrobenzene. Hydroxybenzene. Amidobenzene.

Mono-substitution Compounds.

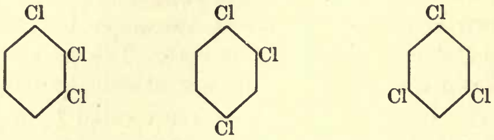
When only one hydrogen atom is replaced in a given molecule the position is unimportant, but when more than one is replaced isomeric forms are always produced. Many of these have been obtained. When two hydrogen atoms are replaced by the same or different radicals, three isomeric forms are possible. Representing the substituting radicals by X, the following formulæ will show the forms and names:



1-2 (ortho) 1-3 (meta) 1-4 (para)

Di-substitution Compounds.

The numerical system 1-2, 1-3, 1-4 is to be preferred to that by prefixes, as the latter becomes complicated and difficult to under-stand with the complex derivatives. The replacement of three hydrogen atoms by the same substances also gives rise to three forms, thus:



1-2-3 1-2-4 1-3-5

Trichlorbenzenes.

These tri-substitution compounds have been called, respectively, *consecutive* or *adjacent*, *asymmetrical*, and *symmetrical.*

When three hydrogen atoms are substituted by *different* radicles the number of possible isomeric forms is much increased. Further details will be given in connection with the description of special substances.

The additive-compounds are formed not only with chlorine and bromine, but also with hydrogen. Benzene hexhydride, $C_6H_6H_6$, is isomeric with hexene. The following table shows the specific gravity and boiling points of some of the hexhydrides:

FORMULA.	BOILING POINT; ° C.	SPECIFIC GRAVITY.		
C_6H_{12}	69	0·760 at 0° C.	—	
C_7H_{14}	97	0·772 ,,	0·758 at 20°	Compared with water at 0° C.
C_8H_{16}	118	0·781 ,,	0·765 at 20°	
C_9H_{18}	135–138	0·790 (?) ,,	—	
$C_{10}H_{20}$	153–158	0·802 ,,	0·788 at 23°	

For this series the term "paraffene" has been suggested, in allusion to its analogy to the true paraffins. The paraffenes behave in many respects like saturated hydrocarbons, being incapable of forming additive-compounds, offering great resistance to the action of oxidising agents, and, when yielding, splitting up completely, with formation of carbon dioxide and water as the chief products. They are not acted on in the cold by bromine, fuming sulphuric acid, nor nitric acid of sp. gr. 1·4; but fuming nitric acid, or a mixture of nitric and sulphuric acids, converts them into the nitro-derivatives of the benzene hydrocarbons. The paraffenes are either isomeric or identical with the naphthenes which have been found largely in Caucasian petroleum, and which are present also in American petroleum (see page 60).

The light oil from coal-tar, known as commercial "benzol," consists chiefly of a mixture of benzene and its homologues in variable proportions. The method of assay is described on page 180 *et seq.* The characters of benzene and its immediate homologues are described in separate sections.

The term benzol is one frequently applied to the hydrocarbon benzene, but when used at all it should be strictly limited in its application to the mixture of homologous hydrocarbons obtained from light coal-tar oil, of which benzene, C_6H_6, is the most important constituent.

Benzene is produced by a great number of reactions, and also results from the heating of various hydrocarbons and other organic bodies. It occurs in certain petroleums.

In practice, benzene is obtained from the portion of coal-tar which distils below 100° C., technically known as "light oils." To prepare pure benzene, the oil is agitated successively with dilute sulphuric acid, water, and milk of lime or caustic soda solution. It is next digested, at 100° C., with 5 per cent. by measure of concentrated sulphuric acid for several hours, in order to separate thiophene and the hydrocarbons of the ethene and ethine series, and this treatment is continued as long as fresh quantities of acid continue to blacken it. The purified product is then separated and fractionally distilled, the portion which passes over below 90° C. being collected separately. This is cooled by a freezing mixture, when the benzene crystallises out, and is separated from the more fusible hydrocarbons by draining on a vacuum-filter. If a pure product be required, the benzene is melted and recrystallised several times, the mother-liquor being separated as before.

Pure benzene is a colorless, very limpid, highly refractive liquid, of a peculiar and somewhat agreeable odor. When subjected to a freezing mixture it solidifies to a brilliant white mass of fern-like tufts, which melts at 5·5°, and boils without decomposition at 80·5°, emitting a highly inflammable vapor, which burns with a luminous and very smoky flame. Benzene is practically insoluble in, though communicating its odor to, water, but is miscible (apparently in all proportions) with alcohol, pentyl alcohol, ether, chloroform, petroleum spirit, turpentine, absolute phenol and fixed and volatile oils.

Hot benzene dissolves sulphur, phosphorus, and iodine. It is an excellent solvent for gutta-percha and india-rubber, and which are left unaltered on evaporation. It also dissolves waxes, fats, and fatty acids.

The following are determinations of the specific gravity of benzene:

Source of Benzene.	Density.	Temperature; ° C.	Observer.
...	0·8991	0	Kopp.
...	0·8957	0	Warren.
...	0·8820	15	,,
Benzoic acid, ...	0·9002	0	Adrieenz.
,, ...	0·8846	15	,,
,, ...	0·8689	30	,,
,, ...	0·8133	80	,,
Coal-tar, ...	0·9012	0	,,
,, ...	0·8850	15	Nickels.

Benzene may be heated to 400° C. in a sealed tube without change; but when passed through a tube heated to a bright redness it yields hydrogen, together with diphenyl, $C_{12}H_{10}$, and other hydrocarbons. Benzene is not acted on by distilling it with metallic sodium. Caustic alkalies have no effect on it. It dissolves entirely when heated to 100° C. for some hours with four or five times its volume of concentrated sulphuric acid. The resulting liquid contains benzenesulphonic acid, $C_6H_5HSO_3$, and is colorless if pure benzene be employed. At very high temperatures, or when fuming sulphuric acid is employed, benzenedisulphonic acids are produced. Under the influence of oxidising agents benzene yields a number of interesting products, according to the treatment to which it is subjected. Thus:

a. By the action of chromic oxychloride on a solution of benzene in glacial acetic acid, trichloroquinone, $C_6HCl_3O_2$, is formed.

b. By the action of manganese dioxide and concentrated sulphuric acid, benzene yields carbon dioxide, formic acid, and water, together with small quantities of benzoic, phthalic, and terephthalic acids.

c. By the action of concentrated nitric acid, benzene is readily converted into nitrobenzene, $C_6H_5NO_2$; and by the continued action of the acid, especially if hot or mixed with sulphuric acid, dinitrobenzene, $C_6H_4(NO_2)_2$, is produced.

By the action of chlorine or bromine in the dark or diffused light, benzene is converted into chlorinated or brominated derivatives, in some cases five out of the six atoms of hydrogen being replaced. In direct sunlight, chlorine and bromine form additive-compounds with benzene, of which benzene hexchloride, $C_6H_6Cl_6$, is a type. Iodine alone has no action on benzene, but when a mixture of benzene with iodine and iodic acid is heated iodobenzenes are formed.

By prolonged treatment with hydriodic acid, under high pressure, benzene is converted into benzene hexhydride, C_6H_{12}, a body isomeric with hexene.

SEPARATION AND RECOGNITION OF BENZENE.

When in a pure state and in tolerable quantity, benzene is readily recognisable by its smell, specific gravity, and boiling point. The chemical tests capable of ready application are few, the most satisfactory being the formation of nitrobenzene with nitric acid, followed by the action of reducing agents on the nitro-compound, and recognition of the aniline so formed.

This test is only applicable to benzene in approximate purity, or at least free from certain admixtures. With complex mixtures one or all of the following means must be adopted to separate the benzene from interfering bodies:

1. The liquid should be agitated with solution of caustic soda, and separated from the aqueous layer. This treatment removes phenols and other bodies of an acid character.

2. The purified oily liquid should be separated from non-volatile matters by distillation in a small retort or flask furnished with a thermometer and good condensing arrangement. The portion passing over between 65° and 100° C. will contain any benzene which may be present, and should be collected separately and treated as follows:

3. The fraction passing over between 65° and 100° C. is shaken with a small quantity of cold concentrated sulphuric acid, and the treatment repeated, if necessary, with successive small portions of acid till no further blackening ensues. Thiophene and members of the ethene and ethine series are thus removed. If at this point the liquid be warmed with excess of concentrated sulphuric acid, the acid liquid separated, heated to from 180° to 200° C., and a current of steam passed through it, all benzene and homologues which had dissolved as sulphonic acids will be recovered nearly pure.

4. The purified oil is separated from the acid and washed by agitation with dilute caustic soda solution.

5. The product of the last operation should next be redistilled in an apparatus provided with a dephlegmator, and the fraction passing over between 78° and 84° C. collected separately, and, if thought desirable, again fractionated, the portion distilling between 80° and 82° being collected separately. The product will consist of benzene, probably mixed with more or less of other bodies having approximately the same boiling point, those most likely to be present being thiophene, carbon disulphide, toluene, and benzene hexhydride.

6. The first of these may be removed by treatment with aluminum chloride (see page 165), and the second by alcoholic potash (see page 180), while the remaining bodies may be further separated by again fractionally distilling, and remain liquid on exposure to 0° C., at which temperature benzene solidifies.

When present in but small proportion in a mixture of volatile bodies the foregoing process wholly fails to isolate the benzene present, and in many other cases it is unnecessary to obtain the hydrocarbon in a state of absolute purity in order to demonstrate its existence. As a rule, it is sufficient to treat the partially purified substance resulting from process 4 for nitrobenzene as described below.

The benzene, having been concentrated and obtained more or less pure in the manner above described, is next treated with about twice its measure of fuming nitric acid of 1·50 specific gravity. The operation is conducted in a small flask or retort furnished with an inverted condenser. If a vigorous action occur, no extraneous heat need be applied; but if the reaction be sluggish, the liquid should be well agitated and moderately heated for a few minutes. The flask is then cooled and the contents transferred to a tapped separator. If separation into distinct strata occur, *all except the top stratum*[1] are run off, while still warm, through the tap into a quantity of cold water. If this liquid remain clear, no nitrobenzene has been formed, and consequently benzene was not present.

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[1] In the case of mixtures of petroleum spirit and benzene, three layers are formed, the uppermost consisting of unaltered paraffins, the middle one of nitrobenzene, and the lowest of a solution of nitrobenzene in nitric acid. If the proportion of benzene in the mixture be moderate, the nitro-compound produced remains wholly in solution in the nitric acid until the latter is diluted.

In presence of a considerable quantity of benzene, separation of yellow, oily nitrobenzene will occur at the bottom of the water, and a marked odor of bitter almonds will be perceived. With smaller quantities, the nitrobenzene will form a finely divided precipitate, which will collect after some hours at the bottom of the vessel. The liquid is passed through a wet filter, washed with cold water, and the nitrobenzene collected is dissolved by dropping alcohol on the filter. The alcoholic solution thus obtained is then treated with zinc and hydrochloric acid, in the manner described on page 167, and the resultant *aniline* detected by bleaching-powder.

For the determination of benzene in complex mixtures, the only available method is to separate fixed matters, purify by treating with acid and alkali, as already described, then to remove any carbon disulphide by alcoholic potash (see page 180 *et seq.*), and subsequently to carefully fractionate the purified hydrocarbons in a bulb-apparatus, as directed. The product may then be converted into nitrobenzene as described on pages 162 and 183, the latter body being dissolved in strong sulphuric acid and any residual hydrocarbons deducted from the apparent benzene previously found.

For the determination of benzene and its homologues in the liquid obtained by compressing the gaseous hydrocarbons obtained by subjecting petroleum to a red heat, as in the Pintsch system of lighting railway carriages, C. G. Williams rejects the portion distilling below 65·5° C., and treats the remainder with its own measure of commercial nitric acid, previously diluted with an equal bulk of water. On distilling the mixture at 100° C., the benzene and its homologues readily come over, while the olefins are converted into compounds, which remain in the still.

COMMERCIAL BENZENE.

The benzene of commerce varies in purity from an article containing only insignificant proportions of other bodies to the "90," "50," and "30" per cent. benzols of the tar distiller. The composition and methods of assaying these products are described in a subsequent section (page 180 *et seq.*). Commercial benzol, when sold retail, is sometimes entirely replaced by petroleum spirit. Shale naphtha may also be substituted. These products are readily distinguished from the coal-tar product by the tests described on page 99.

Benzene is now manufactured of such purity that from 95 to 98 per cent. will distil within 1° C. of the theoretical boiling point. The assay of such products is conducted by more rigid methods than those employed for ordinary benzols. Thus, the distillation is conducted on 100 c.c., which is fractionated in a flask with side-tube, the bulb of the thermometer being adjusted so as to be just below the tubulure.

In some cases, and in conformity with Continental contracts, commercial benzene is subjected to the following special tests:—(*a*) 1 c.c. of the sample is agitated with 20 c.c. of pure concentrated sulphuric acid in a small stoppered bottle, and allowed to stand some hours. The colorisation at the end of this time should be very slight, never exceeding a pale straw-yellow. (*b*) 10 c.c. of the sample is agitated in a stoppered bottle with successive small quantities of saturated bromine-water until a yellow tint is obtained, which persists for some minutes. Not more than 0·5 c.c. of bromine-water should be required to produce this result.

For the purpose of determining the available benzene in a mixture, G. Lunge[1] recommends the *nitrofication test*, which depends on the production of nitrobenzene. He describes it as follows: 100 c.c. of the sample are placed in a 500 c.c. flask provided with a cork carrying two tubes, as shown in Fig. 7. A mixture of 150 grm. of nitric acid (sp. gr. 1·4), and 180 to 200 grm. of sulphuric acid (sp. gr. 1·84) is prepared and allowed to cool. Portions of this mixture are placed in the stoppered tube and allowed to flow drop by drop into the benzene, shaking well between each addition. If the temperature rises, the flask must be cooled by immersion in water. When addition of acid ceases to produce rise of temperature, the flask should be heated gently for an hour or two, during which time it will be an advantage to connect *b* with a reflux condenser. Allow the mixture to settle, and separate the layers by a stoppered funnel. Most of the crude nitrobenzene is in the upper layer. The lower (acid) layer should be diluted with several times its bulk of water and allowed to stand for a few hours. Any oily liquid separating should be added to the nitrobenzene. Wash the latter with water several times, then with a very dilute solution of

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[1] "Coal Tar and Ammonia," p. 484.

sodium hydroxide, and once again with water. Care should be taken that none of the product is lost in these washings. The washed nitrobenzene is then allowed to settle, carefully separated, redistilled in a fractionating flask until a temperature of 150° C. is reached, and the distillate once more nitrated, using a large excess of the acid mixture. Any material remaining undissolved may be regarded as non-nitrofiable hydrocarbons. 157·6 parts of nitrobenzene correspond to 100 parts of benzene.

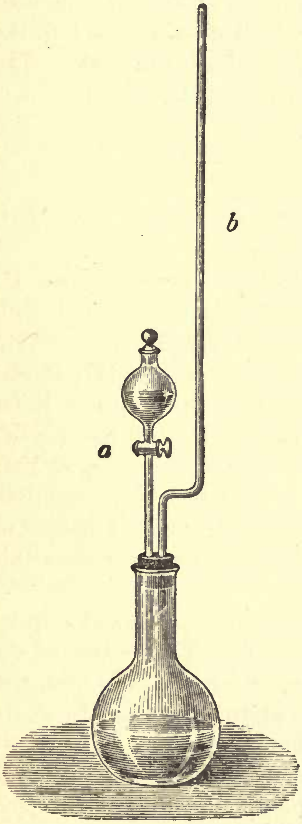

FIG. 7.

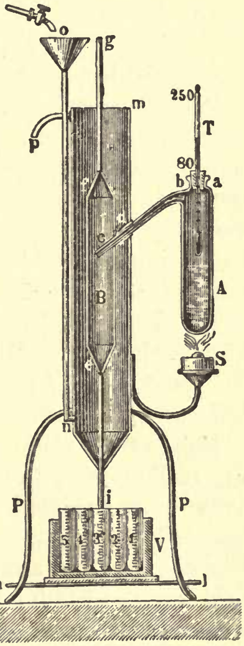

FIG. 8.

For testing crude benzene by fractional distillation the methods described on page 185 may be employed. The French Government has adopted an apparatus devised by Regnault, which is shown in Fig. 8. A is a cylindrical copper retort, of not less than 300 c.c. capacity, connected with a condenser, as shown. Cold water flows in at o. Five glass receivers marked in cubic centimeters are provided. 100 c.c. of the sample are placed in the retort, and the thermometer fixed so that the bulb does not dip into the oil and the mark of 80° C. comes just above the cork. The receivers are changed at 100°, 120°, 140°, 160°, and 180° C.

THIOPHENE, C_4H_4S.

This body is present to the extent of 0·5 per cent. or more in all commercial benzene prepared from coal-tar.

Pure thiophene is a colorless, mobile liquid, boiling at 84° C., and having a density of 1·07 at 15° C. It is not miscible with water, and is not attacked by alkalies or alkali-metals. With concentrated sulphuric acid it forms a sulphonic acid, and is oxidised very rapidly by nitric acid. Mono- and dinitrothiophene have, however, been obtained, and may be present in the best commercial nitrobenzols. Bromine forms monobromthiophene, boiling at 150° and having a density of 1·652 at 23°; or by a larger quantity into dibromthiophene, $C_4H_2Br_2S$, which is a colorless liquid boiling at 211° and of 2·147 specific gravity at 23°. In its reactions this body closely resembles thiophene.

Many of the color-reactions of commercial benzene and toluene are really due to the presence of thiophene. This is true of the brown color produced on agitation with strong sulphuric acid, and especially the reaction observed by Laubenheimer. To apply this test, a dilute solution of phenanthraquinone in glacial acetic acid is treated with a few drops of the liquid to be examined, the mixture well cooled, and concentrated sulphuric acid then added drop by drop, the resulting solution after a few minutes being treated with water. A coloring matter separates, which, on agitation with chloroform, dissolves to a fine green liquid. Another highly characteristic reaction is the deep blue indophenin produced on agitating thiophene with isatin and strong sulphuric acid. When the proportion of thiophene is large, a dirty brown is produced. If the mixture be warmed, the same reaction is produced by many of the derivatives of thiophene, including dibromthiophene, thiophene-sulphonic acid, $C_4H_3S.SO_3H$, and thiophenic acid, $C_4H_3S.COOH$. The purple reaction of dinitrobenzene with alcohol and potassium hydroxide is due to the presence of nitro- or dinitrothiophene.

For the removal of thiophene from benzene, Haller and Michel[1] employ aluminum chloride. One per cent. is sufficient when the sample contains but little thiophene; but when the proportion is greater, four or five per cent. may be needed. The aluminum chloride is agitated with the benzene and then allowed to stand, when a viscous, reddish product collects at the bottom. The benzene may be distilled off at once, or after separation from this liquid.

Estimation of Thiophene in Benzene.[2]—2 c.c. of the sample are placed in a 60 c.c. stoppered flask with 30 c.c. of methyl alcohol, free from acetone, and 10 c.c. of mercuric sulphate solution. The flask is closed and the mixture allowed to stand for about twenty minutes. An insoluble compound, $2HgO, HgSO_4, C_4H_4S$, is formed, and is removed by filtration. 21 c.c. of the filtrate (0·1 c.c. of the sample) are placed in a liter flask with 350 c.c. of water, 15 c.c. of ammonium hydroxide solution, 10 c.c. decinormal potassium cyanide solution, and five or six drops of a 20 per cent. solution of potassium iodide, and the whole well shaken. If not perfectly clear, a gentle heat may be applied, and then, after cooling, decinormal silver nitrate is added until a permanent turbidity results. The amount of thiophene (x) can be calculated by the formula:

$$x = 2{\cdot}8\,(n - 0{\cdot}3)\,;$$

in which n equals the number of cubic centimeters silver nitrate solution used.

Methylthiophene or *thiotolene*, C_5H_6S, is contained in impure toluene, from which it is isolated with difficulty as a colorless liquid boiling at 113° C. *Dimethylthiophene*, or *thioxene*, C_6H_8S, is also present in coal-tar naphtha.

NITROBENZENE, $C_6H_5NO_2$.

Nitrobenzene, sometimes called "nitrobenzol," is a product of the action of nitric acid on benzene, $C_6H_6 + HNO_3 = C_6H_5NO_2 +$

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[1] *Bull. Soc. Chim.*, 1896, 1065; abst. *J. S. C. I.*, 1896, 706.

[2] Denigès, *Bull. Soc. Chim.*, 1896, 1064; abst. *Analyst*, 1896, 297.

H_2O. The acid should not be of lower specific gravity than 1·45; on the large scale it is employed in admixture with sulphuric acid. Great heat is evolved, and more or less red fumes are produced. When the action is over, the product may be poured into water, when the nitrobenzene sinks to the bottom as a yellow oil.

Pure nitrobenzene is a pale-yellow liquid, having an odor resembling that of the essential oil of bitter almonds or benzaldehyde, C_7H_6O, but differs from that body in many respects besides chemical composition. Its odor has led to its extensive use as a scenting and flavoring agent under the name of "Essence of Mirbane." It is nearly insoluble in water, but dissolves in nitric acid, being reprecipitated on dilution. It is readily soluble in alcohol, and is miscible in all proportions with ether, benzene, and oils, and has great stability, being unaffected by chlorine or bromine even at the boiling point, unless iodine or antimonic chloride be simultaneously present.

Great discrepancies are found in text-books as to the physical constants of nitrobenzene. **Friswell**[1] points out that **Schultz** (in 1882) gave the specific gravity as 1·2002 at 0° C., and 1·1866 at 14·4° C., and, later, 1·208 at 15° C.; while he puts the fusion point at 3°. **Beilstein** gives the same figures, quoting **Mitscherlich** as his authority.

With regard to boiling points, **Gmelin**, quoting **Mitscherlich**, gives 213°; **Schultz** gives 210°, and, later, 206° to 207° C.; while **Beilstein**, on the authority of **Städeler**, gives 205° at 730 mm. **Friswell** found solid and liquid nitrobenzene to have the specific gravity as under, compared with water at 4° C.:

	° C.	SPECIFIC GRAVITY.
Solid,	1·5	1·3440
Liquid,	3·8	1·2220
Liquid,	13·0	1·2160
Liquid,	28·0	1·1931

The boiling point (corrected) was 209° C; the melting and solidifying points, 5° C.

The vapor of nitrobenzene is distinctly colored, closely resembling that of chlorine. This is easily visible in a depth of five centimeters, and is strongly marked in a depth of ten centimeters. When light is transmitted through the vapor, no bands of absorp-

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[1] *Jour. Chem. Soc.*, 1897, 147.

tion are produced in the visible spectrum. The violet and the blue are absorbed, but less strongly than with the fluid.

By treatment with a mixture of sulphuric acid and the strongest nitric acid, nitrobenzene is converted into a mixture of the three isomeric dinitrobenzenes, $C_6H_4(NO_2)_2$. These form pale-yellow crystals.

Nitrobenzene is scarcely affected by aqueous alkalies, even when boiling, but is converted by alcoholic potash into a mixture of azobenzene, $(C_6H_5)_2N_2$, and azoxybenzene, $(C_6H_5N)_2O$.

Under the influence of reducing agents, *e. g.*, hydrogen sulphide, zinc and hydrochloric acid, or acetic acid and iron filings, nitrobenzene is converted into aniline, $C_6H_5.H_2N$, the production of which affords one of the most delicate and characteristic tests for nitrobenzene. The alcoholic solution of the nitrobenzene should be mixed with hydrochloric acid and boiled for some time with metallic zinc. The liquid is next diluted, neutralised with caustic soda, and a clear solution of bleaching powder cautiously added. A blue or purple coloration, often appearing somewhat slowly, and gradually changing to brown, will be produced if aniline, resulting from the reduction of nitrobenzene, be present. According to Balls, magnesium ribbon, with the addition of a few drops of solution of platinum chloride, rapidly and completely reduces nitrobenzene in alcoholic solution to aniline, giving a solution which can be at once decanted and tested with bleaching powder.

The following methods of detecting small quantities of nitrobenzene are due to Jacquemin. A single drop of nitrobenzene dissolved in 20 c.c. of alcohol is stated to suffice for all three tests:

a. The liquid is treated with zinc and sulphuric acid to reduce the nitrobenzene to aniline. The liquid is treated with excess of sodium carbonate and filtered; to the filtrate one drop of carbolic acid is added, and then some sodium hypochlorite, when a brown coloration, rapidly changing to blue, due to formation of sodium erythrophenate, indicates the presence of nitrobenzene.

b. The liquid is treated with some lead dioxide. If excess of the oxide be used, a rose tint, changing to brown, is developed, but otherwise the rose color changes to blue. The reaction is said to be very delicate.

c. A crystal of potassium chlorate is added to the liquid, and a drop of concentrated sulphuric acid allowed to run down the side of the tube, when a violet coloration is produced.

Toxicological Detection of Nitrobenzene.—The symptoms produced by nitrobenzene, when taken either in the liquid or the gaseous state, show that it is an active poison of a peculiarly insidious nature. For the most part its action is that of a powerful narcotic, and, as a rule, it produces but little local irritation of the stomach or bowels. The first symptoms are usually headache and drowsiness, followed by flushing of the face, difficult breathing, irregular pulse, dilation of the pupils, more or less loss of voluntary power, and sometimes convulsions. On attempting to walk, the poisoned person will sometimes reel as if drunk, and the breath will smell of nitrobenzene. These symptoms are followed by coma, which may come on slowly, but is more frequently sudden, increasing in intensity until death ensues in five or six hours from the commencement of the symptoms. When the stage of coma is reached there is but little chance of preventing a fatal termination of the case. On the whole, the symptoms of poisoning by nitrobenzene simulate those of apoplexy; but the strong and persistent odor and the intense salivation it is apt to produce sufficiently distinguish it from the latter affection.

The vapor may prove injurious even when largely diluted with air.

The *post-mortem* appearance of the stomach is normal, but the smell of the poison will usually be perceptible, unless death has ensued by inhalation of the vapor. The brain is always congested, and the blood everywhere black and thick, but fluid, the heart being full of dark, treacly blood. There is usually well-marked and long-continued rigidity. In cases of delayed death, nitrobenzene may not be found as such on analysis, owing to its reduction to aniline, which will be met with in the brain and urine. In many cases a distinct color will be observed on the skin, at least in some parts.

The poisonous effects of nitrobenzene are identical with those of aniline, and are most probably due to the reduction of the nitrobenzene to that substance in the body.

For the detection of nitrobenzene, the portions of the body to be examined should be reduced to fragments and acidulated with dilute sulphuric acid. The liquid is distilled, and the distillate examined from time to time, with the view of detecting the presence of any unchanged nitrobenzene. Then treat the contents of the retort with rectified spirit of wine, and filter. Precipitate the filtrate with excess of basic lead acetate, and again filter. Remove any lead from the liquid by adding a slight excess of sodium sulphate. Evaporate the filtered liquid nearly to dryness, and render the solution alkaline with sodium carbonate. Then agitate with ether to dissolve the aniline, run off the aqueous liquid, and agitate the ethereal solution with a little very dilute sulphuric acid. Separate this acid layer, which will contain any aniline as sulphate, concentrate by evaporation at a low temperature, and test for aniline by bleaching powder solution as described on page 167.

Commercial Nitrobenzol.—The products obtained on a large scale by the action of nitric acid on commercial benzols (pages 162 and 183) vary in composition with the character of the benzols employed in their manufacture, but are often exceedingly complex, containing simultaneously several isomeric varieties of the different mono- and dinitro-derivatives of the benzene series of hydrocarbons, which diminish in volatility and fusibility with the number of atoms of carbon or molecules of NO_2 contained in them. By the action of reducing agents the various nitro-compounds yield aniline and other bases, the constitution of which depends on that of the nitro-compounds from which they are derived. Some of these yield coloring matters materially differing in shade or brilliancy from those given by purer products.

The presence of hydrocarbons in nitrobenzol may be detected by dissolving 30 c.c. of the sample in 70 c.c. of concentrated sulphuric acid, in which it ought to be entirely soluble.

Commercial nitrobenzene and dinitrobenzene commonly contain the nitro-derivatives of thiophene. These impurities may be detected by dissolving the sample in alcohol, and adding a single drop of aqueous potash, when a deep-red solution is obtained, a thin layer appearing violet. An excess of alkali destroys the color, but it may be restored by cautious neutralisation.

The specific gravity of nitrobenzol made from 90 per cent. benzene should be 1·186, and from 30 to 40 per cent. benzol 1·175 to 1·190.

Toluene. Methylbenzene, $C_7H_8 = C_6H_5CH_3$.

Toluene, formerly called "toluol,"—a name which should be applied only to the impure commercial substance,—is obtainable by various synthetical methods, is a product of the dry distillation of tolu-balsam and many other resins, and is present to a considerable extent in coal-tar naphtha. It closely resembles benzene. The chief points of difference are:

1. The *odor*, which is distinct from that of benzene.

2. The *specific gravity*, 0·881 at 0°, 0·871 at 15° C.

3. The *boiling point*, 111° C., is considerably higher than that of benzene.

4. The *solidifying point*, toluene remaining liquid even at —20° C., while benzene is solid at 0°.

By the action of concentrated nitric acid, toluene is converted into one or more nitrotoluenes, or dinitrotoluenes; but when boiled with dilute nitric acid it is oxidised with formation of benzoic acid and other products. Commercial nitrotoluol has a specific gravity of 1·167. Pure orthonitrotoluene has a gravity of 1·162, metanitrotoluene being 1·168. Paranitrotoluene is solid at ordinary temperatures. Dinitrotoluene is used for deblooming oils.

When treated with excess of hot concentrated sulphuric acid, toluene forms two isomeric toluenesulphonic acids, $C_7H_7HSO_3$. On heating the liquid to about 160° C., and passing a current of steam, these compounds are decomposed and the toluene distils over almost without loss.

COMMERCIAL TOLUENE.

Toluene constitutes the greater part of "50 per cent. benzol" (page 178), and also occurs to a considerable extent in "90 per cent. benzol."

Toluene occurs in an approximately pure state in commercial "toluol," which is now manufactured on a large scale. When fractionated in the manner described on page 185, commercial toluols should give the first drop at 110° to 111°, and 90 per cent. of distillate below 120° C.

An almost pure toluene is now made commercially, which distils wholly within a degree or two of 110° C.

Xylenes. Dimethylbenzenes. $C_8H_{10} = C_6H_5.(CH_3)_2$.

All three forms of xylene (see page 172) occur in coal-tar; the isomeric body, ethylbenzene, $C_6H_5(C_2H_5)$, has also been found by some investigators.

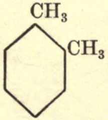
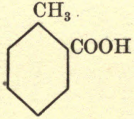
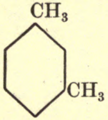
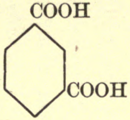
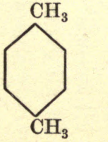
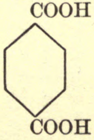
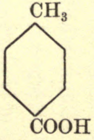
The isomeric xylenes present a close general resemblance to benzene and toluene, but are distinguished by their higher boiling points, lower specific gravity, and the greater facility with which they are oxidised and are converted into sulphonic acids.

The different behavior of the isomeric xylenes with reagents has some practical interest as affording a means of examining the nature of—

COMMERCIAL XYLENE or XYLOL, which is now manufactured on a considerable scale for the preparation of cumidine (by heating the monomethyl-metaxylidine hydrochloride with methyl alcohol) and of azo-coloring matters (scarlets, oranges, &c.). Commercial xylene is obtained by the fractional distillation of coal-tar naphtha. It varies greatly in purity, giving 90 to 95 per cent. within a range of 2° to 6° C. from the first drop over. The distilling points may range from 136° to 138° C.; 136° to 140° C.; 136° to 142° C.; 138° to 140° C.; or 138° to 142° C., according to the stipulations of the contract-note. In some cases the contract-note stipulates that 90 per cent. of the sample of xylene shall distil within a range of 1° C., and this behavior is very strictly enforced.

Besides varying proportions of the three xylenes, the properties of which have already been described, commercial xylol contains more or less of the lower and higher homologues (methylbenzene, 1-3-4- and 1-3-5-trimethylbenzenes), together with a notable proportion of paraffins, and probably ethylbenzene and ethenylbenzene and hydrocarbons of other series. The hydrocarbons of the ethene and ethine series are not improbably present in the fraction of crude naphtha from which commercial xylene is prepared, but they either suffer absorption by the sulphuric acid used for the purification, or are thereby polymerised so as to remain in the retort when the purified substance is redistilled. Orthoxylene also undergoes absorption by the sulphuric acid employed, and hence the refined product contains a comparatively small proportion of this hydrocarbon, the same reaction having prevented its recognition in coal-tar until recently. Thioxene, or dimethylthiophene, C_6H_8S, if present, will also be absorbed by treatment with sulphuric acid. On the other hand, metaxylene hexhydrides and homologues behave in all essential respects like paraffins.

Of all these constituents of commercial xylene, the *metaxylene* is the only one of value, even its two isomers being useless. If the metaxylene contain even a few units per cent. of orthoxylene, on converting it into the nitro-derivative, and this into xylidine, tarry matters are formed which are a serious inconvenience in practice.

NAME.	SOLIDIFYING POINT (DEGREES CENTIGRADE).	BOILING POINT (DEGREES CENTIGRADE).	(For preparation of reagents, see opposite page.) RESULTS OF ACTION OF			
			DILUTED SULPHURIC ACID.	CHROMIC ACID MIXTURE.	DILUTED NITRIC ACID.	COLD MIXTURE OF NITRIC AND SULPHURIC ACIDS.
Orthoxylene 1-2-dimethylbenzene. 	Below —22	142 to 143	Easily soluble.	Entirely decomposed.	Orthotoluic acid 	Liquid products.
Metaxylene 1-3-dimethylbenzene. 	...	137 to 140	Soluble.	With difficulty, Isophthalic acid 	With difficulty, Isophthalic acid	Trinitrometaxylene, $C_6H(NO_2)_3$-$(CH_3)_2$.
Paraxylene 1-4-dimethylbenzene. 	15	136 to 137	Insoluble.	Teraphthalic acid 	Paratoluic acid 	Trinitroparaxylene, $C_6H(NO_2)_3$-$(CH_3)_2$.

The table on page 172 shows some points of difference between the xylenes. The reagents named are prepared as follows:

Chromic Acid Mixture.—A solution of 8 grams of potassium dichromate in a mixture of 10 grams of sulphuric acid and 90 c.c. of water.

Diluted Nitric Acid.—Nitric acid (sp. gr. 1·4), diluted with twice its volume of water.

Nitric sulphuric Acid Mixture.—Equal measures of fuming nitric acid (sp. gr. 1·5) and concentrated sulphuric acid are mixed and allowed to cool.

The first two reagents are applied by boiling the hydrocarbon with excess under an inverted condenser for several hours. For oxidation of metaxylene a temperature of 150° C. is desirable.

The nitric-sulphuric acid mixture is used cold, the hydrocarbon being gradually added and the product allowed to stand some hours. It is then poured into an excess of water, the liquid passed through a wet filter, the separated nitro-derivatives recrystallised from boiling alcohol and examined under the microscope.

The following method for the assay of commercial xylene is due to J. M. Crafts:[1]

A weighed amount of the sample (10 to 20 grams) is poured on 2·5 times its weight of concentrated sulphuric acid in a tube of hard glass. The depth of the xylene layer in millimeters is noted, the tube is sealed and heated to 120° C., with occasional violent shaking. The tube is allowed to cool, opened, three or four measures of a mixture of equal parts of hydrochloric acid and water added, the mixture shaken well and allowed to stand for an hour at room temperature. An insoluble layer of saturated hydrocarbons is formed. This is measured and separated in a separator-funnel, the solvent acid returned to the tube, which is resealed and heated to 122° C. for twenty hours. By this treatment 97 per cent. of the 1-3-xylene forms a layer, which can be measured, and after separation distilled and weighed. A small amount of impurity is removed by distillation. The 1-2- and 1-4 xylenesulphonic acids undergo but little decomposition at 122° C., but at 175° C. the hydrocarbons are regenerated. If these be dissolved in three parts of concentrated sulphuric acid, the solution cooled, and one part of concentrated hydrochloric acid added, 1-4-xylenesulphonic acid is thrown down in crystals, which should be collected on an asbestos

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[1] *Compt. Rend.*, **114** (1892), 1110. Abst. *J. S. C. I.*, 1892, 849.

filter, washed with concentrated hydrochloric acid until the washings no longer react with barium chloride, and the precipitate allowed to dry in the air to constant weight. The crystals have the composition $(C_8H_9SO_3H)_2 + 3H_2O$; the weight multiplied by 0·4977 gives the xylene. For direct estimation of 1-2-xylene, Levinstein[1] advises the following method: 100 c.c. of the sample are shaken thoroughly with 120 c.c. cold concentrated sulphuric acid until no further solution of hydrocarbons occurs. It is best to cool the mixture. The 1-2- and 1-3-xylenes are converted into sulphonic acids, but the 1-4-xylene is unaffected and separates unchanged. The acid liquid containing the two sulphonic acids is then separated, and these converted into their calcium and then into their sodium salts. On concentrating the solution of the latter, sodium 1-2-xylenesulphonate will crystallise in large, flat prisms, while the 1-3-salt remains in solution. The mother-liquor should be further concentrated, when a second crop of crystals will be obtained. Both crops are purified by resolution and recrystallisation. The indistinct crystals of the 1-3-form are readily distinguished from the large, well-defined crystals of the 1-2-salt from English crude xylols. That from Scotch products crystallises far less readily, probably owing to an admixture of some foreign sulphonate. Crystallised sodium 1-2-xylenesulphonate contains $C_6H_3(CH_3)_2NaSO_3 + 5H_2O$. It is dried by pressure between folds of filter-paper, and then over sulphuric acid, when it can be weighed, if desired. The xylene can be regenerated by adding excess of sulphuric acid and distilling in a current of steam at 120° to 150° C.

It might be preferable to saturate the acid liquid with barium hydroxide solution, filter from the sulphate, and crystallise the sulphonates from the filtrate. Barium 1-2-xylenesulphonate crystallises in large, nacreous laminæ, requiring 3 parts of boiling water or 18 parts of cold water for solution.

Samples 2 and 5 were analysed independently by the same methods by A. Rademacher, with the following results:

NUMBER.	1-2-XYLENE.	1-3-XYLENE.	1-4-XYLENE.	PARAFFINS.
2	14·5	81	3	1·5
5	3	87 86·5	4·5	8 6

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[1] *J. S. C. I.*, 1884, 77.

The following figures were obtained by Levinstein, but partly by methods different from those above described :

No.	Origin of Sample.	Sp. Gr. at 19° C.	Distilling Degrees ; °C.	Percentage of			
				1-2 xylene.	1-3 xylene.	1-4 xylene.	Paraffins.
1	From Manchester tar, ...	0·8629	134–140	4	87	6	3
2	From English tar,	0·8660	138–141	15	79	3	3
3	From Scotch tar, .	0·8574	134–140	12	72	8	8
4	From mixed English and Scotch tars, ...	0·8605	134–141	3	81	10	6
5	From mixed English and Scotch tars, ...	. . .	140–141	5	86	3	6
6	Unknown, ...	. . .	139–141	15	70	5	10
7	Pure metaxylene isolated by dilute nitric acid, &c., .	0·8668	142–143	0	100	0	0

Coal-tar Naphtha.

In the first distillation of coal tar two fractions are obtained, known respectively as "first light oils" and "second light oils." Sometimes they are not collected separately, in which case the fraction is known as "crude naphtha" or "light oil." Good "first light oils" or "first runnings" ought, on redistillation, to yield 10 per cent. below 100° C., and an average of 78 per cent. below 170° C. On again distilling the fraction collected under 130° C. fully 25 per cent. should come over under 100°. "Second light oils" should have a density of about 0·975. It yields but little distillate below 120° C., and about 30 per cent. below 170° C.

Crude Coal-tar Naphtha is a more or less fluorescent liquid, of a dark coffee color and disagreeable odor. It has a density of 0·840 to 0·940, or even higher, and evolves ammonia abundantly on distillation. It is an extremely complex product, as will be seen on reference to the table on pages 51 and 153. Many or all of the bodies boiling below about 220° C. are sometimes present simultaneously. The specific gravity of crude naphthas of London make usually ranges between 0·883 and 0·888, and that of Scotch naphthas from

0·868 to 0·876, but the density is sometimes considerably outside these limits.

Crude naphtha is usually submitted to redistillation without previous chemical treatment, the resultant products being "once-run naphtha" and "last runnings."[1] By some distillers an intermediate product is obtained, termed "medium naphtha." It is the fraction of the crude naphtha which on redistillation passes over between 160° and 180° C. Benzene can be isolated in small quantity even from this fraction by the use of a dephlegmating arrangement.

Once-run Naphtha is a fluid of a more or less amber-yellow color, and a specific gravity ranging from 0·886 to 0·892. The method of assaying once-run naphtha by distillation is described on page 185 *et seq.*

Before redistilling once-run naphtha on a large scale it is purified by treatment with sulphuric acid of 1·845 specific gravity. This removes the bases, hydrocarbons of the ethene and ethine series, and some of the higher homologues of benzene. A subsequent treatment with lime or sodium hydroxide eliminates the phenols and any other bodies of acid character. The oil is then washed with water and again distilled.

Once-run naphtha is the starting point from which the manufacturer derives, by fractional distillation, the following products: 90 per cent. benzol; 50 and 90 per cent. benzol (called "$\frac{50}{90}$ benzol"); 30 per cent. benzol; solvent naphtha; burning naphtha; and a further quantity of last runnings. Each of these products has distinctive characters by which it is known and recognised commercially. In addition, benzene, toluene, and xylene are now manufactured on the commercial scale in a condition of high purity.

Burning Naphtha is a product similar to "last runnings," but results from a second distillation. It should have a specific gravity of 0·880 to 0·887, and should give 20 to 30 per cent. over at 150° C., and 90 at 170° C.

Solvent Naphtha is so called from its wide application as a

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[1] "Last runnings" are highly charged with naphthalene, and find an application as a common burning oil in street vapor-lamps. A sample examined by B. Nickels gave, on fractional distillation, 10 per cent. at 142°; 20 at 146°; 30 at 151°; 40 at 157°; 50 at 164°; 60 at 170°; 70 at 179°; 80 at 191°; and 90 at 209° C. When 70 per cent. had passed over, naphthalene appeared in quantity. By repeated fractioning, evidence of the presence of toluene and xylene was obtained.

solvent for india-rubber in the manufacture of waterproof articles. It is also used for washing crude anthracene. It gives from 8 to 30 per cent. of distillate below 130° C., and about 90 below 160° C. The specific gravity should not exceed 0·875. Solvent naphtha has a complex and variable composition, but consists chiefly of isomeric xylenes and cumenes, with a notable proportion of paraffins, and sometimes several units per cent. of naphthalene, the last constituent being considered very objectionable. Formerly, solvent naphtha comprised the whole of the fraction from the redistillation of once-run naphtha passing over above the benzols and below 160° C., but when a demand arose for xylene as a separate product, much of it was removed, with the result of rendering the residual solvent naphtha less suitable for its intended purpose.

CARBURRETING NAPHTHA is a product consisting chiefly of xylenes. It is usually specified as giving at least 70 per cent. of distillate at 130° C. and 90 at 150° C., the specific gravity ranging from 0·850 to 0·870.

COMMERCIAL BENZOLS. In commerce, the term "benzol" is applied generically to the more volatile portions of redistilled coal-tar naphtha. It is a convenient name to indicate this more or less complex liquid, consisting chiefly of benzene and its homologues; while the use of the term "benzene" should be restricted to the definite hydrocarbon of the formula C_6H_6.

Commercial benzols consist essentially of mixtures of very variable proportions of benzene and its homologues, together with: smaller percentages of carbon disulphide; certain light hydrocarbons technically known as "petroleum," and which are incapable of nitrofication, consisting largely of pentene; thiophene and its homologues; traces of water; acetylene, and probably homologues; and impurities of an indefinite nature.

The light hydrocarbons diminish the yield of coloring matter from the aniline made from the benzols containing them, and, if present in considerable proportion, render the process of nitrofication irregular and even dangerous. Carbon disulphide is a somewhat troublesome impurity, and is difficult to get rid of by ordinary means.

The details of the method of effecting the assay of benzols are given on page 180 *et seq.* According to the behavior of the sample when distilled, it is classed as 90 per cent. benzol, 50 per cent. benzol, or 30 per cent. benzol.

90 per cent. Benzol is a product of which 90 per cent. by volume distils before the thermometer rises above 100° C. A good sample should not begin to distil *under* 80° C., and should not yield more than 20 to 30 per cent. at 85° C., or much more than 90 per cent. at 100° C. It should wholly distil below 120° C. An excessive distillate—*e.g.*, 35 to 40 per cent. at 85° C.—indicates a larger proportion of carbon disulphide or light hydrocarbons than is desirable. The actual percentage composition of a 90 per cent. benzol of good quality is about 70 of benzene, 24 of toluene (including a little xylene), and 4 to 6 of carbon disulphide and light hydrocarbons. The proportion of real benzene may fall as low as 60 or rise as high as 75 per cent. 90 per cent. benzol should be colorless ("water-white"), and free from opalescence.

The specific gravity of English 90 per cent. benzols ranges from 0·880 to 0·888 at 15·5° C., but the figure is no indication of the quality of a sample, owing to the presence of carbon disulphide and light hydrocarbons, which, from their high volatility, become concentrated in this class of benzol. Since carbon disulphide has a specific gravity of 1·27, and the light hydrocarbons ("petroleum") average 0·860, the two may in certain proportions exactly compensate and be without effect on the specific gravity of the product. Watson Smith examined a 90 per cent. benzol which had a specific gravity of 0·900, and contained 6 per cent. of carbon disulphide. After removing this impurity the specific gravity of the benzol fell to 0·880.

Scotch 90 per cent. benzols contain but little carbon disulphide, but a considerable proportion (7 to 8 per cent.) of light hydrocarbons; hence the specific gravity is often as low as 0·870 or even less. The first 20 per cent. distilled from such a sample may have a density of 0·866; while the residual 80 per cent. will be as dense as 0·872. The low density of the first fraction here distinctly indicates "petroleum," and not carbon disulphide, as the predominant impurity. By eliminating the carbon disulphide from 90 per cent. benzol in the manner described on page 180, the anomaly in the specific gravity almost disappears, and the interpretation of the results of the fractional distillation becomes much simpler.

50 per cent. benzol, often called 50/90 benzol, is a product of which 50 per cent. by volume distils over at a temperature not exceeding 100° C., and 40 per cent. more (making 90 in all) below 120° C. It should wholly distil below 130° C. The density of English

50 per cent. benzol is about 0·878 to 0·880, and of Scotch 0·867 to 0·872. This class of benzol is nearly free from carbon disulphide, and contains comparatively little of the light hydrocarbons, while the proportion of toluene and xylene is, of course, larger than in 90 per cent. benzol. 50/90 benzol is employed for producing the heavy aniline used for preparing rosaniline or magenta.

In the case of a benzol of intermediate character, the proportions of 90 and 50 per cent. benzol to which it corresponds may be found by the following rule: Deduct 50 from the percentage-volume of the sample distilling below 100° C., and multiply the difference by 2·5. The product gives the percentage of 90 per cent. benzol in the sample, the difference between this and 100 being the proportion of 50 per cent. benzol. Thus, a benzol giving 64 per cent. over below 100° C. corresponds to a mixture of 35 parts of 90 per cent. benzol with 65 parts of 50/90 benzol; for:

$$64 - 50 = 14\ ;\ 14 \times 2{\cdot}5 = 35\ ;\ \text{and}\ 100 - 35 = 65.$$

For English benzols the rule is accurate to 1 per cent.

30 per cent. benzol is a product of which 30 per cent. distils below 100° C., about 60 per cent. more passing over between 100° and 120° C. It consists chiefly of toluene and xylene, with smaller proportions of benzene, cumene, &c. The specific gravity should be about 0·875.

For the manufacture of aniline-red, magenta, or fuchsine, a benzol is required which will yield (by nitrofication and subsequent reduction) an aniline oil of which three-fourths distils between 180° and 190° C., and the remainder between 190° and 215° C. Such an aniline oil is producible from a benzol of which three-fourths passes over between 80° and 100° C., and the rest between 100° and 130° C. For the manufacture of methyl-violet, on the contrary, an aniline as free as possible from higher homologues is required, and this must be made from a benzol which almost wholly distils below 83° or 84° C. For xylidine-red an aniline oil derived from benzols boiling above 115° or 120° C. is required, but it is often found preferable to prepare this by fractionating an ordinary aniline oil rather than to employ a benzol of specially high boiling point for the purpose. The commercially pure xylene and toluene now extensively manufactured have, to a great extent, replaced the high-boiling "benzols" formerly employed.

The "Benzol" of the British Pharmacopeia (1898) is defined as a mixture of about 70 per cent. of benzene and 20 to 30 per cent. of toluene, having a specific gravity of from 0·880 to 0·888. It should begin to distil at 80° C.; 90 per cent. should pass over below 100° C. and should wholly distil below 120° C.

Assay of Commercial Benzols and Naphthas.

The observations of importance in judging of the quality of a commercial benzol or naphtha are, in addition to the appearance and smell of the sample: its specific gravity; its behavior with concentrated sulphuric acid; the proportion of carbon disulphide; the proportion of the light hydrocarbons, technically known as "petroleum"; the proportion of nitrofiable hydrocarbons; and its behavior on fractional distillation. In the case of commercial xylols, the proportion of metaxylene should be ascertained in the manner directed on pages 173 and 174.

Commercial 90 per cent. benzol should not be diminished in volume by more than ½ per cent. when agitated with 5 per cent. by measure of cold concentrated sulphuric acid. For a more stringent test, applicable to commercially pure benzene, see page 162.

Water, if present in such quantity as to render the sample turbid, must be got rid of prior to any further process of assay. This may be done sufficiently perfectly by passing the liquid through a dry filter. A complete elimination of the water may be easily effected by agitating the sample with a little recently gently ignited plaster of Paris, and filtering. The dehydration is almost instantaneous. If a known weight of plaster be employed, and it be afterwards washed with a little gasolene, dried at a gentle heat, and reweighed, a determination of the amount of the water may be readily effected.

Carbon disulphide often exists in very sensible quantity in crude and once-run naphtha, and in 90 per cent. benzol. From the less volatile classes of benzol it is usually absent. Its presence is important only in 90 per cent. benzol. Carbon disulphide may be eliminated from benzol, and its amount determined with a near approach to accuracy, by the following method devised by B. Nickels:[1] 100 c.c. measure of the sample of benzol (preferably dehydrated with plaster of Paris, as above described) is treated with a solution of 1 grm. of potassium hydroxide in the smallest

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[1] *Chem. News*, **43** (1881), 148, 250 and **52** (1885) 170.

possible quantity (about 20 c.c.) of hot absolute alcohol, and the mixture agitated thoroughly. If carbon disulphide be present, a yellow color is usually developed, and the mixture becomes pasty from the formation and separation of potassium xanthate in crystals of a characteristic silky appearance. The mixture is shaken at intervals during half an hour, and is then passed through a dry filter. The adhering benzol is separated as far as possible from the precipitated xanthate by carefully folding the filter and pressing it against the sides of the funnel by means of a spatula. The filtrate is agitated in a cylindrical separator with its own volume of warm water, which removes the excess of alcohol and a little dissolved xanthate. If the purified benzol is to be submitted to distillation, it is preferable to operate on at least 200 c.c. of the sample, and treat it a second time with the alcoholic solution of potassium hydroxide, before treating it with water. The aqueous liquid is run off, and the benzol again agitated with its own measure of cold water, after the removal of which it may be dehydrated with plaster, and then further examined by fractional distillation.

The potassium xanthate collected on the filter is washed with a little ether, dried at 100° C., and weighed. Preferably, it is dissolved in alcohol, the washings from the treated benzol added, and the united solution obtained rendered slightly acid with acetic acid. On adding a solution of copper sulphate, a brownish precipitate of cupric xanthate is formed, rapidly changing to bright yellow cuprous xanthate, $CuC_2H_5(CO)S_2$, insoluble in water and dilute acids. The cuprous xanthate may be collected on a filter, washed, ignited in the air, and weighed as CuO; or the cupric oxide may be ignited with sulphur in hydrogen, and thus converted into cuprous sulphide. The weight of CuO or Cu_2S obtained, divided by 0.523, gives that of the carbon disulphide in the sample operated upon.

Instead of weighing the cuprous xanthate, H. Macagno (Chem. News, 13 (1866), 138) titrates the acidulated solution of potassium xanthate with a solution of cupric sulphate containing 12·47 grm. of the crystallised salt per litre. The end of the reaction is indicated by the brown color produced when a drop of the liquid taken out with a glass rod is added to a drop of potassium ferrocyanide solution on a porcelain plate. 1 c.c. of the above cupric sulphate solution corresponds to 0·0076 grm. of carbon disulphide.[1]

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[1] Macagno's figures, both gravimetric and volumetric, correspond approximately

Holland and Phillips[1] have described a process of determining carbon disulphide in commercial benzols which is based on the reaction:

$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S.$$

The procedure is as follows: A piece of combustion-tube about 13 inches in length is sealed at one end and drawn out into a funnel at the other. An accurately measured volume of 2 c.c. of the sample is introduced, followed by 5 c.c. of a 24 per cent. ferric chloride solution and 10 c.c. of strong ammonium hydroxide solution. The tube is carefully sealed, well shaken, wrapped in a cloth, and heated in boiling water for about an hour. It is then cooled, opened, and the contents evaporated just to dryness in a flask. To the residue 20 c.c. of fuming nitric acid should be suddenly added, and the solution boiled nearly to dryness. A repetition of the treatment with nitric acid will be necessary if any sulphur remain unoxidised. Hydrochloric acid and water are next added, and the solution filtered. The filtrate is precipitated by barium chloride, when the weight of barium sulphate multiplied by 0·326 gives the carbon disulphide in the quantity taken. It is probable that other sulphur-compounds (*e. g.*, thiophene) are partially estimated as carbon disulphide by this process.

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to the ratio Cu : $2CS_2$. This ratio would be readily explicable if the reaction resulted in the formation of cupric xanthate, $(C_2H_5.O.CS.S)_2Cu$; but as the main product is cuprous xanthate, it follows that reduction of the copper occurs, and this must be accompanied with corresponding oxidation of a portion of the xanthate. According to H. Debus, the yellow precipitate is a compound of cupric xanthate with cuprous sulphide, but this is very improbable. The copper salt of the acid $C_2H_5.O.CO.SH$ is also said to be formed, together with other products. It is certain that the reaction is very complex and requires further investigation. Experiments made by A. R. Tankard have shown that the ratio Cu : $2CS_2$ is roughly correct, whether the determination be made by titrating with decinormal cupric sulphate or by weighing the cuprous sulphide left on igniting the precipitate with sulphur; provided that the copper solution is added immediately after acidulating the xanthate solution, since the free xanthic acid decomposes very rapidly. If the precipitation be conducted in alcoholic solution and the precipitate washed with alcohol, a substance is removed which otherwise remains in the precipitate. On diluting the filtrate with water, this body is thrown down in a state of very fine division. It appears to consist, in part at least, of sulphur. From the presence of this, and probably of other impurities in the precipitate, this should not be directly weighed. If precipitated from aqueous liquids, it contains the body above referred to, and if thrown down from alcoholic solution, it is contaminated with potassium sulphate, which might be removed by washing with water. The process is useful, but the results are not strictly accurate.—A. H. A.

[1] *J. S. C. I.*, 1884, 295.

The test-analyses made by this process were very fairly satisfactory. Holland and Phillips found the following proportions of carbon disulphide (c.c. per 100 c.c.) in commercial benzols:

	CS_2 PER CENT. BY VOLUME.
90 per cent. benzols from Lancashire tar, ...	1·62 ; 1·97 ; 1·93
50 per cent. benzols, ...	1·16 ; 0·82 ; 0·89
Toluols, ...	0·16 ; 0·17
Specially purified benzols, ...	0·19 ; 0·20
"Pure benzols" from retail shops, ...	0·72 ; 0·55 ; 0·68
Crude naphthas, ...	0·14 ; 0·21

The change in density which results from the elimination of the carbon disulphide from a benzol is very noticeable. Thus, in the case of a sample which would be conveniently classified as a "light 90 per cent." there will be an entire removal of the previous alliaceous odor; a diminution of density from 0·885 to 0·882 or 0·880, according to the amount of carbon disulphide which has been removed; and a disappearance of the abnormally large proportion of liquid distilling below 85° C., the reduction in this respect being from 30 per cent. or more down to 12 per cent.

The proportion of carbon disulphide eliminated by treatment with alcoholic potash has been proved by B. Nickels to be indicated with a considerable approach to accuracy by the reduction in the specific gravity of the sample, thus:

1 per cent.	by volume of carbon disulphide	raises the sp. gr.	by	0·0033
2	,,	,,		0·0065
3	,,	,,		0·0093

The specific gravity of benzol is not readily determined by the bottle, owing to its high coefficient of expansion. A delicate hydrometer may be used, but the Westphal balance is specially suitable for such determinations. As the specific gravity of hydrocarbons of the benzene series decreases with the increase in the number of carbon atoms and the boiling point rises, low volatility corresponds with a low specific gravity, though such samples are technically called "heavy benzols."

Instead of determining the light hydrocarbons, it is sometimes of interest to ascertain the proportion of true benzene and its homologues by converting them into nitro-compounds. To effect this, J. von Hohenhausen proceeds in the following manner: A mixture is made of 150 grm. of nitric acid of 1·40 specific gravity with 200 grm. of sulphuric acid of 1·845 specific gravity. When quite cold, this is gradually added through a tapped funnel to 100 grams of the sample of benzol contained in a 500 c.c. flask. The liquids are well mixed by agitating the flask between each addition, and cooled if they become warm. When the whole of the acid has been added and the contents of the flask have become cold, the nitrobenzene is separated from the acid, washed several times by agitation with a dilute solution of caustic soda, and subsequently with water, the latter allowed to separate completely, and the nitrobenzol produced weighed. A good quality of benzene should not get hot immediately a small portion of the acid is added to it. One hundred parts by weight of an English 90 per cent. benzol of fair average quality yield not less than 150 parts of well-washed nitrobenzene, while some Scotch benzenes do not give more than 135 parts. The nitrobenzene produced should be further examined by fractionally distilling it, when the last 2 per cent. in the retort should remain liquid after cooling. If 100 c.c. of the nitrobenzol be distilled (see page 185), and the first 30 c.c. of distillate be treated with 70 c.c. of concentrated sulphuric acid, the nitrobenzene and its homologues will dissolve in the acid, while all the non-nitrofied hydrocarbons will separate. This layer should be again treated with the mixture of sulphuric and nitric acids, when the presence of previously unchanged benzene will be indicated by a rise of temperature. The acid is tapped off, the residual hydrocarbons again treated with strong sulphuric acid, and their volume observed.

FRACTIONAL DISTILLATION OF BENZOLS AND NAPHTHAS.

A fractional distillation in some specified manner is a method of very general application for the commercial assay of benzols and allied products, and, if carefully conducted, and the results interpreted in connection with the specific gravity and chemical tests, the process affords very satisfactory indications. These indications, however, are of a purely arbitrary character, and, unless the prescribed conditions of manipulation be rigidly adhered to, great discrepancies result. Thus, the barometric pressure, the rapidity of the distillation, the size and shape of the retort, the position of the thermometer-bulb, and even its shape and length, are all more or less important factors in the result obtained. On this account it is usual in contract-notes to specify minutely the mode in which the test is to be made, and the slightest departure from the prescribed directions may invalidate the contract.

Ordinary Retort Test.—The following "mode of test" is taken *verbatim* from a form of contract-note largely employed in commercial benzol transactions: "A quantity of 100 c.c. to be distilled in a glass retort of a capacity of 200 c.c.; bulb of thermometer to be placed $\frac{3}{8}$ of an inch from bottom of retort; distillation to be made over a naked flame, and at such a speed that the distillate shall not pass over in a stream, but as quickly as it can drop in separate particles. Any deficiency in quantity arising from evaporation or other natural causes during the operation to be added to the product at each point, and proper allowance to be made (if necessary) for the observed reading of the barometer."

The proportion by volume of the sample which passes over below and at a given temperature is called the "strength" of the sample at that temperature. For crude naphtha it is usually sufficient to note the volume distilling below 120° C.; in the examination of once-run naphtha, an observation of the volume distilling below 160° C. is also made; in the case of 90 per cent. benzols the volumes distilled are noted at 84° or 85° C., and again at 100° C.; while with 50 and 30 per cent. benzols the temperatures noted are 100° and 120° C.

The very great majority of parcels of benzol and naphtha sold in this country are bought, or are supposed to be bought, on the above test; the results obtained by competent operators understanding the test agree closely, the variations rarely exceeding 1·5 per cent.

The following is the best mode of conducting the ordinary retort-test so as to ensure results which are constant, and which can be trusted to be as accurate as the process admits. The instructions given apply to the assay of a 90 per cent. benzol. The temperature to be observed must, of course, be modified according to the contract-note, or to the nature of the product under treatment:

100 c.c. of the sample are measured in an accurately graduated cylinder, and poured thence into a tubulated retort, of such a size as to be capable of containing 200 c.c. or 8 fluid ounces, when placed in the ordinary position for distillation. The retort should be previously rinsed with some of the sample to be tested, or a little may be distilled in it, and the residue carefully drained out. A delicate

thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be ⅜ of an inch distance from the bottom of the retort.[1] The neck of the retort is then inserted into the inner tube of a Liebig condenser, and pushed down as far as it will go. The condenser should be from 15 to 18 inches in length, and well supplied with cold water. The neck of the retort should not project too far into the condenser; if necessary, it should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, the tube of the condenser should be rinsed with a little of the sample, and allowed to drain, or some of the benzol may be sprayed through it. The graduated cylinder employed for measuring out the sample is next placed under the further end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner.[2] The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences, the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers a temperature of 85° C.[3] the flame is extinguished. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then relighted and the distillation continued till the thermometer rises to 100° C.,[3] when the gas is turned off as before, and

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[1] The thermometer should be 14 inches long; the bulb sufficiently small to ensure its remaining well immersed in the boiling liquid; the first marking or division at 70° C., which point should be well out of the tubulure of the retort; and the graduation should be continued up to 130° C. in benzol-testing. Instruments guaranteed to 0.1 degree, and constructed in the manner above detailed, are now obtainable.

[2] The burner should be furnished with an air-regulator working automatically with each movement of the tap, and should be surrounded with a cylinder to exclude currents of air. The lamp should be placed in a deep tin basin containing sand or sawdust, in order to absorb the benzol in the event of the retort cracking.

[3] It is found in practice that, if the light be turned out exactly when the thermometer registers the required temperature, the mercury subsequently rises to an extent varying from ½ to fully 1 degree. With a little experience with a thermometer the range of this "after-rise" will become known, and in subsequent operations the lamp should be turned out when the mercury is as much below the critical temperature as it is expected afterwards to rise about it. Thus, if the after-rise of a thermometer has

the volume of the distillate read off, after allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring cylinder. A deficiency from the 100 c.c. originally taken will generally be observed. This is the loss arising "from evaporation or other natural causes," referred to in the contract-note.

The difference between the collective volume after distillation and that of the original sample is to be added to the measure of the distillate collected at each temperature, and the corrected volumes reported as the "strength" of the benzol examined.

Thus, if by distilling 100 c.c. of a benzol there were obtained 20 c.c. at 85° and 90 c.c. at 100°, and the total liquid mixed after distillation measured 99 c.c., the difference between that and 100 c.c., *i. e.*, 1 c.c., must be added to the yields at 85° and 100° respectively, making the corrected figures 21 per cent. at 85° and 91 at 100° C. As a matter of fact, the loss of volume by distillation is due far more to expulsion of acetylene and other gases than to actual loss of benzol.

In benzol-testing it is very desirable to observe the barometric pressure before making an experiment, and to modify the manipulation accordingly. A difference of 1 inch in the height of the barometer makes a difference of about 1° C. in the boiling point of a benzol. Hence, if the barometer registers 29·5 inches instead of 30 inches, the gas should be extinguished so that the thermometer may show a mean temperature of 99·5° instead of 100°.

The foregoing method of testing benzols is admittedly crude and unscientific, but its indications are well understood; and for a time it sufficed for the technical examinations required. Now, however, that a demand has arisen for practically pure benzene, toluene, and xylene, the value of the crude products depends on their content of these hydrocarbons, and hence there is need to replace the test by others giving absolute results.

Modified Retort Test.—A preferable plan to observing the volume of distillate obtained at one or two temperatures only is to note the height of the thermometer at every 5 or 10 c.c. of liquid which passes over.

Bulb-Tube Test.—When there is no contract-note to describe, the

been found to be 1° C., the gas should be turned out when the instrument registers 84·5° instead of 85°, as it will subsequently rise to 85·5°, and hence 85° may be considered to be the mean reading.

mode of conducting the distillation, it is very much better to substitute for the simple retort a flask fitted with some form of dephlegmator. A very useful arrangement of this kind is that of Le Bel and Henninger, which consists of a number of bulbs, varying from two to six, blown upon a tube, which is fitted by means of a cork to an 8-oz. flask containing the liquid to be distilled. The upper end of the tube is furnished with a tubulure, which can be fitted by a cork to a Liebig condenser, and with an orifice into which a thermometer can be fitted so as to observe the temperature of the vapor which passes over. Each of the bulbs is connected with the one below by a small side-tube. In the constriction of each bulb is placed a little cup of platinum- or copper-gauze, of the size and shape of a small thimble. These cups are made by folding the gauze over the end of a stout glass rod. The ascending vapor condenses in the cups, and thus serves to wash the vapor subsequently formed as it bubbles through. When the liquid rises to a certain height in each bulb, it runs off by the side-tube, and ultimately finds its way back to the distilling flask, the flame under which is so regulated as to keep all the cups full and cause the distillate to fall in separate drops.

In the improved form of dephlegmator, devised by Glynsky, the wire-gauze is replaced by hollow balls of glass, introduced into the bulbs during manufacture.

Hempel substitutes for the more complex apparatus of Henninger and Glynsky a long glass tube arranged vertically and filled with solid glass beads. This simple arrangement is remarkably efficient.

By employing a dephlegmating apparatus, greatly improved results are obtainable, and a complex liquid may be fractionated at one operation into approximately pure constituents. Hence it is probable that the present empirical method of testing will ultimately be entirely superseded by the more rational process.[1] Almost absolutely pure benzene, toluene, and xylene are now articles of commerce, being produced on a large scale by a single apparatus based on the principle of the bulbed tube; and it will be necessary to ascertain the percentage composition of the benzols used in their

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[1] The use of a dephlegmator in fractionating benzols is universal in German laboratories, tubes having as many as twelve bulbs on the same stem being sometimes employed. 1000 c.c. is the quantity usually employed for this test, and the distillation is conducted in a copper vessel.

production. This is approximately possible by operating with the bulb-apparatus, especially if the carbon disulphide be previously removed, but it is wholly beyond the powers of the ordinary retort.[1]

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[1] The annexed figures are communicated by Mr. B. Nickels. Column A. represents the temperatures recorded by the thermometer when the *original* benzol was distilled in an 8-oz. retort in the ordinary way; B. shows the alteration produced *by removing the carbon disulphide* in the manner described on page 180; and C. shows the results obtained when the *purified* benzol was distilled in a three-bulbed apparatus instead of in a retort.

	A. COMMERCIAL 90 PER CENT. BENZOL IN 8-OZ. RETORT.	B. A., IN 8-OZ. RETORT, AFTER BEING PURIFIED FROM CS_2.	C. B., DISTILLED IN FLASK WITH THREE-BULB APPARATUS.
Specific gravity at 15·5° C., . .	0·884	0·881	0·881
First drop distilled at	79·5° C.	83·4° C.	. . .
5 per cent. over at	. . .	84·2	81·25° C.
10 ,, ,, ...	. . .	84·3	82·0
20 ,, ,, ...	. . .	85·0	82·8
25 ,, ,, ...	84·0	. . .	. . .
30 ,, ,, ...	85·0	85·8	83·0
40 ,, ,, ...	85·4	86·4	83·5
50 ,, ,, ...	86·4	87·1	84·7
60 ,, ,, ...	88·0	88·3	85·3
70 ,, ,, ...	90·0	90·0	86·5
80 ,, ,, ...	93·0	93·0	89·3
90 ,, ,, ...	100·0	100·0	100·0
95 ,, ,, ...	. . .	112·4	111·8

When the original sample A. was fractionated in the three-bulb apparatus at 45° C., it gave oily drops indicative of carbon disulphide; and these became more abundant at 60° C. At 70° C., 5½ per cent. had distilled, and the thermometer rose at once to 80° C. The process being stopped at this point, the contents of the flask were found to have decreased in density from 0·884 to 0·882, showing the removal of a substance heavier than benzene. That this was largely carbon disulphide is proved by the figures in column B., the complete removal of the impurity reducing the gravity and raising the boiling point. When the purified sample B. was fractionated by the three-bulb apparatus into 20, 70, and 10 per cent. portions, they showed a density of 0·883, 0·885, and 0·8715, respectively. Had carbon disulphide been present, the first fraction would have been denser instead of lighter than benzene (sp. gr. 0·885). Hence the first portion of the distillate must have contained light hydrocarbons ("petroleum"). By operating originally on 300 c.c. of the same sample, removing the carbon disulphide by alcoholic potash, and several times repeating the process of fractionating with the three-

If 400 or 500 c.c. of the sample of benzol be carefully purified from carbon disulphide by treatment with alcoholic potash and then fractionated with the aid of a 6-bulb tube, the light hydrocarbons can be concentrated in a comparatively small volume distilling between 60° and 70° C. The lightest of these impurities have a specific gravity of 0·760, and such a product is readily obtainable by again fractionating that first obtained. B. Nickels has pointed out that if 0·760 be taken as the mean specific gravity of the light *hydrocarbons*, the proportion of these present in commercial 90 per cent. benzol may be deduced with a considerable approach to accuracy from the specific gravity of the sample previously purified from carbon disulphide. Thus a mixture of 70 measures of pure benzene with 30 of pure toluene (which is the proportion in which they usually exist in 90 per cent. benzol) has a specific gravity of 0·8805, which would therefore be that of the sample purified from carbon disulphide if no light hydrocarbons were present. Each 1 per cent. of impurity of 0·760 specific gravity reduces the specific gravity of the mixture by about 0·0012. Thus the synthetic sample described on page 193, containing 8 per cent. of light hydrocarbons, had, after removal of the carbon disulphide, a specific gravity of 0·8710. (0·0012 × 8 = 0·0096; and 0·8805 — 0·0096 = 0·8709; or 0·8710 nearly.) *Thiophene* is not commonly present in benzol in sufficient proportion to affect the figures obtained as above; but if existing in quantity, as in some carbonisation benzols, it can be separated by agitating the purified sample with one-tenth of its measure of strong sulphuric acid before proceeding to fractionate.

The assay of *crude naphtha* by distillation is not infrequently limited to a determination of the volume-percentage obtained at a temperature not exceeding 120° C., the operation being conducted in an ordinary retort (page 185). The proportion of distillate

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bulb apparatus, Nickels obtained the following results as indicative of the proximate analysis of the benzol tested:

Carbon disulphide, removed by alcoholic potash, ...	1·5	per cent.
Light hydrocarbons, sp. gr. 0·860 (more or less non-nitrofiable; probably chiefly pentene and acetonitrile), ...	3·5	"
Benzene, specific gravity 0·885, and distilling wholly within a range of 2 degrees, ...	78·4	"
Toluene, specific gravity 0·8715, and distilling within 2 degrees, ...	16·6	"
	100·0	"

usually ranges from 15 to 35 per cent., according to the quality of the naphtha under examination. J. von Hohenhausen gives the following data as representing the distilling points of certain typical crude coal-tar naphthas:

Temperature; ° C.	Percentage of Distillate.		
	Wigan.	Yorkshire.	Scotland.
105	. .	4	. .
110	4	16	17
120	19	34	38
130	33	47	49
140	45	. .	58
150	55	. .	69

Once run naphtha may be similarly assayed. It usually yields from 40 to 60 per cent. of distillate below 120° C. when examined by the retort-method,[1] and an additional 32 to 36 per cent. between 120° and 160° C. These products, when mixed and redistilled, should yield from 19 to 26 per cent. over at 100° C. For technical purposes the results thus obtained are often sufficient, and their interpretation is well understood. London makes generally give a good yield of 90 per cent. benzol, while Midland products are preferable for 50/90 benzols. The results obtained by fractionally distilling a sample of very good once-run naphtha are given on page 192.

A careful inspection of these results shows that crude London naphthas give a low yield by the retort method at 120°, as compared with the yield by the bulb-tube at 100°; while country naphthas give a yield at 120°, by the retort, not much less than, and often considerably exceeding, the yield by the bulb-tube at 100°.

Crude naphthas of London make (*e.g.*, giving by retort method 17 per cent. at 100° and 35 at 120°) generally give a good yield of 90 per cent. benzol; on the other hand, Midland makes (*e.g.*, giving by retort 10 per cent. at 100° and 48 at 120°) are better for 50/90 benzols.

The following figures, communicated by B. Nickels, show the

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[1] A sample of genuine once-run naphtha yielding 50 per cent. over at 120°, when distilled in a retort at a rate of 120 drops per minute, should also yield 50 per cent. over below 100° when distilled with a bulb-tube at a rate of 100 drops per minute.

comparative behavior of typical samples of crude and once-run naphthas when distilled in an ordinary retort and in a flask furnished with a bulb-tube. The test may be made on 100 c.c.:

CHARACTER OF NAPHTHA.	BY RETORT METHOD.			BY BULB-TUBE METHOD.		
	Below 100° C.	From 100° to 120°.	From 120° to 170°.	Below 100° C.	From 100° to 120°.	From 120° to 160°.
CRUDE—						
London,	. .	12	. .	28	. .	. .
London,	. .	36	. .	41	. .	. .
London,	. .	8	. .	20	. .	. .
Plymouth,	. .	46	. .	45	. .	. .
Lancashire,	. .	20	. .	25	. .	. .
Cleckheaton,	3	44	. .	30	23	24
Derbyshire,	4	43	35	36	20	26
Scotch,	. .	28	. .	32	17	37
ONCE-RUN—						
London,	. .	45	. .	43	. .	. .
London,	. .	66	. .	52	. .	. .
Country,	. .	60	. .	45	. .	. .
Country,	. .	59	. .	41	. .	. .
Country,	. .	58	. .	42	. .	. .
Country,	. .	64	. .	46	. .	. .

G. E. Davis[1] recommends the following method for the valuation of crude coal-tar naphthas: 200 c.c. of the sample are well agitated for five minutes with 20 c.c. of strong sulphuric acid in a stoppered funnel of 300 c.c. capacity. The mixture is allowed to stand until the acid separates; this is run carefully so that no naphtha is lost. In some cases it is preferable to use two washings with successive portions of 10 c.c. of acid each. In either case the naphtha, after drawing off the acid as far as possible, is washed with two portions of water (30 c.c. each), then 30 c.c. of five per cent. sodium hydroxide solution added, and the naphtha again washed with water. The volume of residual naphtha is measured, and after separating it from the washing liquid it is ready for distillation. Davis recommends a 200 c.c. flask with a thermometer and a Le Bel-Henninger or Glinsky fractionating tube, connected with a Liebig condenser delivering into a graduated jar. It is obvious that other standard fractionating apparatus may be employed. The distillation should proceed so that a drop falls every two seconds, and be continued until the thermometer reaches

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[1] *J. S. C. I.*, 1885, 647.

120° C., when the receiver is changed and the distillate up to 170° C. collected. The first distillate consists almost wholly of benzene and toluene, the second portion is "solvent naphtha," the residuum "creasote oil."

The simultaneous presence of variable and unknown proportions of carbon disulphide and light hydrocarbons in benzol often completely masks the results of the fractional distillation, and hence B. Nickels strongly recommends that the fractionation should be conducted on a portion of the sample from which the carbon disulphide has been previously removed by treatment with alcoholic potash in the manner described on page 180. The proportion of carbon disulphide present can be determined by the xanthate formed, or may be deduced from the alteration in the specific gravity of the sample. B. Nickels prepared a mixture of the following composition, and subjected portions to fractional distillation with and without previous removal of carbon disulphide:

Pure benzene, . . .	sp. gr. 0·885,	63	per cent. by measure.
Pure toluene, .	sp. gr. 0·871,	27	,, ,,
Light hydrocarbons,	sp. gr. 0·760,	8	,, ,,
Carbon disulphide, .	sp. gr. 1·27,	2	,, ,,
		100	

Columns A. and B. show the results thus obtained. Column C. shows the behavior of a mixture of 70 measures of pure benzene with 30 of pure toluene, or, in other words, the mixture without either carbon disulphide or light hydrocarbons:

	A. ORIGINAL MIXTURE.	B. WITH CS_2 REMOVED.	C. BENZENE AND TOLUENE.
Specific gravity, . .	0·879	0·871	0·8805
First drop collected at	79·0°	82·5°	85·4°
5 per cent. ,,	. .	84·0	86·2
10 ,, ,,	. .	85·0	86·6
20 ,, ,,	84·0	86·2	87·2
30 ,, ,,	85·5	87·2	87·8
40 ,, ,,	87·2	88·2	88·8
50 ,, ,,	88·5	89·6	89·8
60 ,, ,,	90·4	91·2	91·4
70 ,, ,,	92·6	93·3	93·2
80 ,, ,,	95·6	96·7	96·2
88 ,, ,,	. .	100·0	. .
90 ,, ,,	100·0	. .	102·0

These results are very instructive when compared with the figures on page 192, obtained by B. Nickels from the fractionation of representative commercial samples of different classes of benzols and naphthas. It is interesting to observe the characters of the Scotch 90 per cent. benzol, which exhibits an abnormally low specific gravity owing to the presence of a notable proportion of light hydrocarbons.

From the results yielded by the distillation of the synthetical sample after removal of carbon disulphide (column B.) there is no indication of the presence of 8 per cent. of light hydrocarbons, though the low specific gravity of the sample would point to their presence. This character is disguised in the unpurified sample by the presence of the carbon disulphide. As stated on page 178, a good 90 per cent. benzol should not begin to distil below 80° C., and should not yield more than 20 to 30 per cent. of distillate below 85° C. The distilling point is now seldom below 85° C., and many 90 per cent. benzols are now rectified so as to give the first drop over at 83° to 84° C., and the disposition is to go still further, *i. e.*, to 85° C. This has not been done voluntarily by the manufacturer, but to meet the demands of continental buyers.

	GOOD 90 PER CENT. BENZOL.	GOOD 90 PER CENT. BENZOL.	SCOTCH 90 PER CENT. BENZOL.	50 PER CENT. BENZOL	30 PER CENT. BENZOL	SOLVENT NAPHTHA.	VERY GOOD ONCE-RUN NAPHTHA.
Specific gravity, .	0·8855	0·882	0·873	0 880	0·875	0·877	...
First drop collected at	82·5°	82°	...	...	...	...	...
10 per cent. ,,	84	83·25	84·5°	94°	97°	128·5°	96°
20 ,, ,,	84·75	84·5	85	95	98	130	99·5
30 ,, ,,	85·5	85	85·75	96·5	99·5	132·5	102
40 ,, ,,	86·25	85·75	86·5	98	101	135	107
50 ,, ,,	87·25	86·75	87·75	100	104	137	111
60 ,, ,,	88·5	88	89	102·5	106	140	119
70 ,, ,,	90·25	89·75	91·25	106	109·5	143·5	128
80 ,, ,,	93·25	92·5	94·75	110·5	113·5	148·5	145
90 ,, ,,	...	...	...	120	120	156	170
92 ,, ,,	100	100	100	...	...	...	...

J. von Hohenhausen gives the following data as typical of the behavior of good average commercial benzols on distillation in an 8-oz. retort:

	90 PER CENT. BENZOL.	50 PER CENT. BENZOL.	30 PER CENT. BENZOL.
Specific gravity, ...	0·882	0·878	0·875
Distillate at 85° C.	22 per cent.	...	...
,, 90	74 ,,	...	...
,, 95	87 ,,	18 per cent.	...
,, 98	...	40 ,,	21 per cent.
,, 100	90 ,,	50 ,,	30 ,,
,, 105	94 ,,	68 ,,	55 ,,
,, 110	98 ,,	79 ,,	73 ,,
,, 115	...	85 ,,	84 ,,
,, 120	...	90 ,,	90 ,,

G. Lunge (*Treatise on Coal Tar, &c.*, page 290) gives the following figures as his own experience of the behavior of commercial benzol and coal-tar naphthas when distilled from a fractionating flask with side-tube, the thermometer-bulb being just immersed in the liquid at the commencement of the distillation:

DEGREES C.	90 PER CENT. BENZOL.	50 PER CENT. BENZOL.	TOLUOL.	CARBURETTING NAPHTHA.	SOLVENT NAPHTHA	BURNING NAPHTHA
Boiling point	82	88	100	108	110	138
at 88	30	...	...	...	...	...
,, 93	65	13	...	...	...	...
,, 100	90	54	...	...	...	...
,, 110	...	74	56	1	...	...
,, 120	...	90	90	35	17	...
,, 130	...	...	...	71	57	...
,, 138	...	...	...	84	71	...
,, 149	...	...	...	97	90	30
,, 160	...	...	...	...	...	71·5
,, 171	...	...	...	...	...	85

A good knowledge of the composition of crude naphtha may be obtained by distilling 500 c.c. in a retort and collecting the distillate in two portions. The fraction passing over below 160° represents the yield of *once-run naphtha*, and that distilling between 160° and 180° C. the yield of *medium naphtha*. These distillates may then be further fractionated by means of a bulb-tube. The fraction of once-run naphtha which on redistillation with a bulb-tube passes over below 100° represents *90 per cent. benzol;* from 100° to 120°, *toluol,* commencing to distil at 108° to 110°, and giving 88 to 90 per cent. over at 120°; and from 120° to 160°, *solvent naphtha.* The use of the bulb-tube for fractionating naphthas has now become general. The indications obtained when once-run naphthas are assayed in the laboratory by this method agree fairly well with the actual yields given on a practical scale, at any rate for 90 per cent. benzol and toluol, the determination of solvent naphtha being but rough. The following are results actually obtained:

Laboratory.

Distillate below 100° C. = 30 per cent.
,, between 100° and 120° = 15 ,,
,, ,, 120° and 160° = 20 ,,

Works.

90 per cent. benzol = 31 to 32 per cent.
,, toluol = 14 to 16 ,,
Solvent naphtha = 12 to 15 ,,

The foregoing test may be satisfactorily made on 100 c.c. of the once-run naphtha, but it is preferable to operate on such a quantity as will yield at least 100 c.c. of distillate below 100°, so that this fraction can be proved by a subsequent test to have the actual characters of a 90 per cent. benzol. A rule is given on page 179 by which the proportion of 90 per cent. benzol in a higher boiling product can be deduced.

If a fractionating bulb-tube be not at hand, an assay of crude naphtha for the yield of 90 per cent. benzol can still be made tolerably satisfactorily by the following process:—Distil 500 c.c. of the sample in a glass retort, and collect separately the portion passing over below 180° C. This fraction, representing *once-run naphtha,* is then redistilled up to 120°, and the distillate again distilled up to 105° C., when the fraction which passes over below this temperature should have the characters of "90 per cent. benzol." This, however, should be proved to be the case, when the measure obtained indicates the yield from 500 c.c. of the crude naphtha. If once-run naphtha is to be examined, the first distillation up to 180° C. should be omitted.

For the *detection of benzene in petroleum spirit* and *vice versâ*

Holde[1] utilizes the difference of solvent action of the two liquids upon a specially prepared asphalt. This is obtained by extracting a Syrian asphalt with petroleum spirit of the highest obtainable gravity until only a faint yellow is imparted to the solvent. This operation can be conveniently carried on in the usual continuous-extraction apparatus. A little of the extracted material is placed in a filter, and some of the liquid to be tested poured on it. The presence of not less than 5 per cent. of benzene in a light petroleum of sp. gr. from 0·64 to 0·70, or of not less than 10 per cent. in a light petroleum boiling below 35° C. is shown by a color imparted to the fluid. Conversely, any considerable amount of petroleum spirit may be detected in benzene (see page 98).

For the quantitative separation of benzenes from petroleum spirit Henriques[2] employs the following process: 5 c.c. of the sample are introduced into a 25 c.c. glass-stoppered cylinder graduated to 0·2 c.c., mixed with 10 c.c. of sulphuric acid, to which 1 grm. (5 per cent.) of sulphuric anhydride has been added and shaken until no more of the sample is dissolved. The benzenes are sulphonated and dissolved by the acid, while the petroleum products are but little affected and float on the acid mixture.

NAPHTHALENE AND ITS DERIVATIVES.

Among the products of the dry distillation of organic substances certain closely-associated bodies occur, of which naphthalene itself is the best known and most characteristic, but homologues and additive hydrogen compounds are also present.

Naphthalene. Naphthalin. $C_{10}H_8$.

Naphthalene is present most abundantly in products resulting from destructive distillation of organic bodies at a high temperature. Hence it occurs largely in the tar produced in the distillation of coal for the manufacture of illuminating gas, the usual proportion being 5 to 10 per cent. It is said to be wholly absent from the products of the distillation of bituminous shale when conducted in the ordinary manner, being in this product replaced by paraffin.

Pure naphthalene, obtained by sublimation, or by the cooling of

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[1] Abst. *Analyst*, 1896, 69.

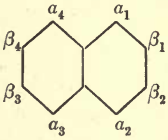
[2] *Chem. Zeit.*, 1895, 958; Abst. *J. S. C. I.*, 1895, 604.

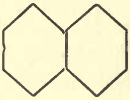
its boiling saturated solutions, forms in colorless rhombic plates of silvery lustre. It possesses a characteristic odor, which may be overcome by the addition of a small proportion of oil of bergamot. Its taste is biting and somewhat aromatic. It melts at 79° C., and boils at 216° to 218° C., but evaporates copiously with the vapor of boiling water, and volatilises sensibly even at ordinary temperatures. It inflames easily, and burns with a luminous but smoky flame.

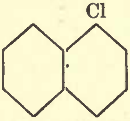
Solid naphthalene has a specific gravity of 1·158. In a molten state, at 79·2° C., its specific gravity is 0·978. Melted naphthalene dissolves sulphur, phosphorus, iodine, indigo, &c.

Naphthalene is insoluble in cold, and but faintly soluble in hot water, insoluble in alkaline or dilute acid liquids, but dissolves readily in alcohol, wood-spirit, ether, chloroform, carbon disulphide, benzene, petroleum spirit, and fixed and volatile oils. It is also slightly soluble in concentrated acetic acid, and readily in phenol and the cresols.

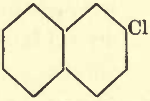
Naphthalene is assumed to consist of two symmetrically combined benzene nuclei. A study of its derivatives has shown that the substitution of even a single atom of hydrogen gives rise to *two* isomeric forms; these are distinguished by the letters α and β. The complete ring-symbol for naphthalene is—



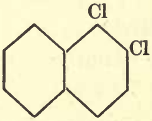
Each of the positions designated by the same letter is of equal value when but one hydrogen atom is substituted. The derivatives are formulated by the system employed in the case of benzene. The symbol  stands for $C_{10}H_8$; substitutions are indicated by the affixing proper formula to the point in the ring at which the substitution is assumed to exist—



α-chlor-naphthalene.



β-chlor-naphthalene.



$\alpha'\beta'$-chlor-naphthalene

The inferences as to the number of isomerides are fully borne out by research. The relation and number of the α- and β-positions have also been amply demonstrated, but it is not necessary to enter into these questions further in this work.

Nitric acid converts naphthalene into nitronaphthalene, $C_{10}H_7NO_2$, or dinitronaphthalene, $C_{10}H_6(NO_2)_2$, according to the strength of the acid employed.

Chromic acid and certain other oxidising agents convert naphthalene into naphthalquinone, $C_{10}H_8O_2$, which by further treatment is converted into phthalic acid, $C_8H_6O_4$.

Concentrated sulphuric acid converts naphthalene into isomeric naphthalenesulphonic acids, the exact natures of which vary with the temperature and proportions of materials employed. They serve for the preparation of the corresponding naphthols, $C_{10}H_7OH$ (page 201).

Chlorine and bromine act on naphthalene with formation of various chloro- and bromo-substitution-products.

For the *detection* of naphthalene, the substance should be distilled, and the fraction passing over between 210° and 225° C. treated with fuming nitric acid, the product poured into water, and the precipitate washed and heated with a boiling solution of equal parts of potassium hydroxide and sulphide; a purple coloration will be produced if naphthalene were present.

COMMERCIAL NAPHTHALENE.

Naphthalene is contained largely in the less volatile portions of coal-tar naphtha, in the crude carbolic acid and "creosote oils" which subsequently distil, and in the semi-fluid "anthracene oils" obtained at a still higher temperature. It is said to be wholly absent from the products of the distillation of bituminous shale. By cooling the portion of the coal-tar distillate which passes over about 200° C., naphthalene is frequently deposited in such quantities as to render the product semi-solid. It may be separated by pressure from the liquid oils, and purified by heating strongly with 5 to 10 per cent. of concentrated sulphuric acid, washing thoroughly with water, and subliming the product.

Naphthalene is now prepared commercially of high purity, as colorless crystals which distil wholly within a very few degrees of the boiling point of pure naphthalene, and giving no pink color with sulphuric acid. Besides this nearly pure product, which, when remelted and cast into moulds, is employed in "albocarbon" lamps, and (under the name "coal-tar camphor") for protecting furs and woolens from moths, naphthalene occurs in commerce as an impure, coarsely crystalline substance of rank odor, technically known as crude naphthalene or "naphthalene salts."

The methods of testing naphthalene "salts" are of a very simple character, the following being those most commonly employed:—25 grm. weight of the sample is wrapped up in several layers of coarse filter-paper, so as to form a flat, thin cake. This is placed between two iron plates and strongly pressed in a vice, as long as any oil is expressed. The usual proportion of oil eliminated varies from 6 to 16 and occasionally to 20 per cent. of the sample; but 13 per cent. is the maximum proportion which should be present.

The "salts" freed from oil in the above-described manner may then be further examined by distilling 10 grm. in a small retort as described on page 185. A good sample of pressed salts should give nothing over below 210°, and should yield 90 per cent. of distillate before the temperature of the contents of the retort rises above 225° C.

The sublimed naphthalene of commerce contains from 70 to 99 per cent. of the pure substance. The finer qualities form colorless crystals, but the inferior grades have a fawn or brown color. A good test for the purity of sublimed naphthalene is to warm the sample in a test-tube with a little pure concentrated sulphuric acid. Pure naphthalene produces a colorless solution, but a decided pinkish tint is observed if as little as 1 per cent. of impurity is present. The coloration becomes deeper pink, or even brown, with a greater proportion of foreign matters.

Naphthalene Oils.

This name, as also that of "creosote oil," is applied to the fraction of coal-tar distilling between 200° and 280° or 300° C. Its composition is very imperfectly understood, but besides phenols and phenoloïd bodies, and a variety of bases, it is apparently largely composed of naphthalene and certain hydrides and homologues of that body, the following of which have been described as being present.

NAPHTHALENE DIHYDRIDE, $C_{10}H_8H_2$, is a viscid liquid of strong, disagreeable smell, boiling at 200° to 210° C. It is powerfully acted on by bromine, and is soluble in cold fuming nitric acid.

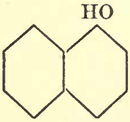
Naphthalene Tetrahydride, $C_{10}H_8H_4$, resembles the dihydride, but boils at 190° C.

α- and β- Methylnaphthalene, $C_{10}H_7CH_3$, occur in the fraction of coal-tar distilling between 220° and 270°. At the ordinary temperature the α-variety forms a colorless liquid of blue fluorescence and pleasant aromatic odor. It has a density of 1·0042 at 22° C., distils in a current of open steam, and crystallises at —18° to a hard mass. α-methylnaphthalene is miscible in all proportions with alcohol, ether, glacial acetic acid, carbon disulphide, and benzene. It is readily attacked by oxidising agents. β-methylnaphthalene crystallises like naphthalene in large white plates, melts at 32·5°, and boils at 141–142° C.

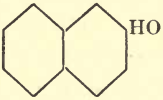
Dimethylnaphthalenes, $C_{10}H_6(CH_3)_2$. According to Emmert and Reingruber,[1] the fraction of coal-tar boiling between 252° and 270°—after removing basic, oxygenated, and crystallisable bodies—apparently consists of a mixture of several isomeric dimethylnaphthalenes, the separation of which has hitherto proved unmanageable. These bodies are said to constitute the major portion of coal-tar creosote oils.

The assay of naphthalene oils is described in the section on "Creosote Oils."

Naphthols. Naphthyl Alcohols. Hydroxynaphthalenes. $C_{10}H_7OH$.



α-naphthol.



β-naphthol.

By the action of concentrated sulphuric acid, naphthalene yields two isomeric sulphonic acids of the formula $C_{10}H_7SO_3H$. At moderate temperatures (*e.g.*, 80° to 100° C.) the α-modification is the chief product, but at 160–170° C. β-naphthalenemonosulphonic acid predominates. On diluting the solution with water, saturating it with lead carbonate, and filtering from the insoluble lead sulphate and excess of lead carbonate, the lead salts of the two sulphonic acids are obtained in solution. They may be separated by concen-

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[1] *Annalen,* 211 (1882), 365.

tration and crystallisation, lead α-naphthalenesulphonate forming shining laminæ soluble in 27 parts of cold water or 11 of alcohol, while the β-derivative crystallises in scales or crusts which require 115 parts of cold water or 305 of alcohol for solution. When either of these lead salts is fused with excess of caustic potash, a substitution of OH for SO_3H occurs, with formation of the variety of naphthol corresponding to the sulphonate employed. On dissolving the fused mass in water, and treating the filtered solution with hydrochloric acid, the naphthol is precipitated, and may be purified by crystallisation from hot water, followed by sublimation.

I. Levinstein[1] has patented a process for manufacture of the naphthols by heating naphthalenesulphonic acids with sodium hydroxide very gradually until the mixture forms two layers. The upper, consisting of sodium naphtholate, is decanted and decomposed by acid.

α-Naphthol may be obtained by heating α-amidonaphthalene sulphate to 200° C. with five times its weight of water. The naphthol separates as a cake when the mass is cooled, and may be purified by redistillation.[2] It is not stated whether β-naphthol can be obtained by the analogous method.

The isomeric naphthols have been isolated by Schulze from the "green oils" left after the filtration of the anthracene from a high-boiling fraction of coal-tar.[3] They closely resemble phenol in their general chemical properties, and bear to naphthalene the same relation that phenol bears to benzene. They are colorless, crystalline bodies, melting and distilling unchanged. They are sparingly soluble in hot and nearly insoluble in cold water, but dissolve readily in alcohol, ether, chloroform, and benzene; also in solutions of caustic alkalies, forming with these unstable compounds which are decomposed when the solutions are evaporated. By the action of carbon dioxide on their sodium-derivatives, the sodium salts of hydroxy-acids are formed, in a manner analogous to the production of salicylic acid from phenol.

On warming with concentrated sulphuric acid, the naphthols are dissolved and converted into sulphonic acids, $C_{10}H_6(OH)SO_3H$. Both the naphthols yield interesting nitro-derivatives, but these are more conveniently prepared by indirect methods (see Vol. III, Part 1).

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[1] Eng. Pat. 2300, 1883; also *J. S. C. I.*, 1885, 478.

[2] Eng. Pat. 14301, 1892; also *J. S. C. I.*, 1893, 672.

[3] *Annalen*, 227 (1885), 143.

The analytical examination of the naphthols has become of importance in view of their value as antiseptics, disinfectants, and therapeutic agents. β-naphthol is now almost exclusively used, being regarded as the less toxic form. It is now readily obtainable in a high degree of purity. Many tests have been devised for distinguishing between the two naphthols and for detecting one in the presence of the other. The following table summarises the more trustworthy of these:

	α-NAPHTHOL.	β-NAPHTHOL.
Odor.	Faint, resembling phenol.	Almost odorless.
Crystalline form.	Monoclinic needles.	Rhombic plates.
Melting point, ° C.	94	122
Boiling point, ° C.	286. Readily distils with open steam.	286. Scarcely distils with open steam.
Effect of light.	Becomes dusky red.	Darkens but little.
Ferric chloride in aqueous solution.	Red, turning to violet.	Pale green.
Bleaching powder in aqueous solution.	Dark violet, changing to reddish-brown.	Pale yellow.
0·1 grm. of sample, 1 drop of strong solution of sucrose, 5 c.c. of water *underlaid* with about 3 c.c. of strong sulphuric acid (U. S. P. test).	Crimson ring at contact line, subsequently turning deep blue in upper part.	Yellowish brown at contact line.
Azo-reaction. 1c.c. of acid solution of sulphanilic acid (sulphanilic acid, 0·5 grm.; acetic acid [30 per cent.], 150 c.c.). Freshly prepared, very dilute solution of sodium nitrite, a few drops added at time of making test. The colors develop slowly.	Orange red.	Yellow.
A few drops of a solution of 1 grm. of potassium dichromate and 1 grm. of nitric acid in 100 c.c. of distilled water, added to a solution of the sample in water or very dilute alcohol.	Black precipitate.	No precipitate.

The azo-reaction is delicate, showing the presence of 0·1 per cent. of α-naphthol. In the medicinal and sanitary uses of β-naphthol so small a percentage is probably without significance. The color tests become more delicate and positive if comparisons are made with samples of pure β-naphthol.

The U. S. Pharmacopeia requires that β-naphthol shall dissolve in 50 parts of ammonium hydroxide solution (sp. gr. 0·960) (proving absence of naphthalene), and the solution should not have a deeper tint than pale yellow.

Hydronaphthol.—Under this name a preparation, said to be obtained from β naphthol, has been exploited as superior to either of the naphthols. The process of manufacture has not been made known. Merck states that the substance is an impure β-naphthol.

For the quantitative estimation of α naphthol in presence of large proportions of β-naphthol, J. Prochazka and H. N. Herman[1] have devised the following process, depending on the greater facility with which α-naphthol combines with diazo-bodies:

27·5 grm. of 90 per cent. of sodium naphthionate are dissolved in 185 c.c. of water. 6·2 c.c. of sulphuric acid (sp. gr. 1·835) are diluted with 180 c.c. of water and the mixture run slowly into the naphthionate solution, which is continuously stirred to secure a uniform paste. The mixture is cooled to below 5° C., and a 10 per cent. solution of sodium nitrite, containing 7 grm. of the commercial 98 per cent. product, added slowly, stirring constantly. The resulting paste, made up to 750 c.c., is now ready for use.

For the test, 15 grm. of the sample, 200 grm. of a 25 per cent. solution of sodium hydroxide solution, and 140 c.c. of a 10 per cent. solution of sodium carbonate are heated together until the β-naphthol is dissolved. The solution is cooled to below 5° C. and made up to 250 c.c. The diazo-compound as prepared is run slowly and carefully into this solution of the sample, which is continually stirred. If the β naphthol is pure, the resulting azo-compound will precipitate completely in the shape of a fine crystalline powder, and hardly any color will pass into solution, while the first portions of the diazo-compound are being added. On the contrary, if α-naphthol is present, a colored solution will be formed. As little as 0·1 per cent. can be detected. If the rest of the diazo-compound be added, the presence of the α-naphthol compound is obscured by the formation of a thick color paste. However, by boiling the product the

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[1] *J. S. C. I.*, 1897, 894.

paste is made to settle as a layer of fine crystals, and the supernatant liquid is more or less colored with the α-naphthol compound. The following short method may be used:—Instead of combining the whole of the β-naphthol, only a part—say, 5 per cent. of the whole—is combined with diazo-compound. The diazo-paste prepared as above is well shaken and 37·5 c.c. run into the β-naphthol solution of the same quantity as above, and with the same precautions as already described. It is then not necessary to boil the product, as the insoluble color formed settles readily, and by dipping strips of filtering paper into the supernatant liquid, and comparing the tint with that obtained similarly from mixtures of pure β-naphthol with a known percentage of α-naphthol, a fairly accurate idea of the amount of α-naphthol present can be obtained. The method can be further simplified by using color solutions of known strength and same shade as that of the above colored filtrate, for the purpose of comparison. With proper caution the method can be successfully applied to less than 1 grm.

For distinguishing between *naphthalene*, *α-naphthol*, and *β-naphthol*, L. Reuter[1] utilizes the difference of action of chloral hydrate and zinc. 0·1 grm. of the sample is mixed with 2·5 grm. of fused chloral hydrate and warmed for ten minutes. A similar experiment is performed with addition of 5 drops of strong hydrochloric acid, and also with the same amount of acid and a piece of zinc.

	NAPHTHALENE.	α-NAPHTHOL.	β-NAPHTHOL.
Chloral hydrate.	Colorless.	Intensely ruby-red, transparent, not fluorescent.	Pure blue, transparent, not fluorescent.
Chloral hydrate, and acid.	Very slight pink.	Intensely dark greenish-blue, not transparent.	Intensely yellow, transparent.
Chloral hydrate, acid and zinc.	Violet, passing into brown.	A dark violet-blue. (Water gives a violet flocculent precipitate.) Alcoholic solution, reddish-violet with a violet fluorescence.	Dark brown. (Water throws down a greasy body.) Alcoholic solution, yellow with a blue fluorescence.

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[1] *Pharm. Zeit.*, 1891, 289. Abst. *J. S. C. I.*, 1891, 799.

Detection of β-Naphthol in Foods.—The marked antiseptic qualities of β-naphthol render it suitable for use as a food-preservative, but it has not been largely employed. For its detection in ordinary foods, the American Association of Official Agricultural Chemists suggests the following procedure, which covers also the detection of several similar antiseptics.[1]

Two hundred grm. of the sample are acidified with dilute sulphuric acid, distilled with open steam, and the first 200 c.c. of the distillate extracted in a separating funnel with about 20 c.c. of chloroform. After being run off, the chloroform is rendered slightly alkaline with potassium hydroxide and heated for a few minutes almost to boiling. Color changes occur as follows, if an antiseptic of the phenol class is present:

Phenol, ...	Light red, to brown, to yellow, to colorless.
1-2-Cresol, ...	Lilac with tinge of orange.
β-naphthol, ...	Deep blue, to green, to brown.
Salol, ...	Light red.

Abrastol and *asaprol* are commercial names of calcium β-naphthol-α-monosulphonate, $C_{10}H_6HOSO_3Ca$. It is freely soluble in water and has active antiseptic qualities. It is stated that it has been used as a food preservative. The following method for its detection, ascribed to Bellier, is quoted in the report of the A. O. A. C.[1]

Fifty c.c. of the sample are made alkaline with a few drops of ammonium hydroxide and gently shaken for a few minutes with 10 c.c. of amyl alcohol; ethyl alcohol may be added if an emulsion be formed. The alcoholic liquid is decanted, filtered if necessary, and evaporated to dryness, the residue thoroughly moistened with 2 c.c. of a mixture of equal parts of water and strong nitric acid, heated on the water-bath until half the water is evaporated, and transferred to a test-tube with the addition of 1 c.c. of water. About 0·2 grm. of ferrous sulphate are now added and then ammonium hydroxide drop by drop with constant shaking, until in excess. If the resulting precipitate be reddish, it is redissolved by a few drops of sulphuric acid, and the ferrous sulphate and ammonium hydroxide added as before. As soon as a dark or greenish precipitate is obtained, 5 c.c. of ethyl alcohol are added, the precipitate dissolved by sulphuric acid, the fluid well shaken and

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[1] *Proc. Fourteenth Ann. Conv.* (1897) *A. O. A. C., Bull.* 51, *U. S. Dept. of Agric.*

filtered. The presence of 0·01 grm. of the antiseptic will be indicated by the red color of the solution. If not present, the solution will be light yellow or colorless. Fatty matters should be melted, extracted with hot 20 per cent. ethyl alcohol, the filtered liquid evaporated to dryness, and the residue treated as above.

If salicylic acid be present in the sample, the above process will yield a solution of a deeper orange than with asaprol; moreover, the solution will give the violet color with ferric chloride, while asaprol gives a blue color, discharged by heating. Natural coloring-matters are not extracted from the alkaline liquid by amyl alcohol; coal-tar colors may be removed by evaporating to dryness with immersed clean white wool, adding acetic acid or ammonium hydroxide according to the color present. From the residue, water will extract only the asaprol.

Determination of β-naphthol[1]*:* 3 grm. of the sample are dissolved in a solution of not less than 3·5 grm. of sodium hydroxide ($= C_{10}H_7HO + 4NaHO$), and the solution diluted to an exact volume, not less than 250 c.c. Ten c.c. of the solution are placed in a small flask, heated to 55° C., and decinormal iodine solution added until the liquid shows a yellow color, indicating excess of iodine. On shaking, a dirty green precipitate may be produced. The liquid is cooled, acidified with sulphuric acid, diluted to 250 c.c., and an aliquot portion titrated with decinormal sodium thiosulphate to ascertain the excess of iodine. The figure for the iodine actually used, calculated to the whole amount taken, and multiplied by 0·3784, will give the amount of β naphthol present.

Nitronaphthalenes.—The manufacture of nitronaphthalenes is of importance, as their presence in nitroglycerin renders the latter practically non-sensitive to concussion, and even a small admixture prevents dynamite from freezing. Nitronaphthalenes are said to possess the property of rendering dynamite "fumeless," but this has not yet been definitely decided. They considerably increase the solvent action of nitroglycerin on nitrocellulose.[2]

When used in conjunction with nitroglycerin, the melting-point of nitronaphthalene is of minor importance, but it is desirable to have as high a degree of nitration as possible, since this will retard the momentum of the explosion. When used with solid explosives, such

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[1] *Pharm. Jour.* and *Trans.*, XXI. (1890–91), 1053.

[2] W. H. Krug and J. E. Blomen, *J. A. C. S.*, 1897, 532.

as picric acid, the melting-point must obviously be below the point of decomposition of the explosive agent. When it is desired to use a higher nitronaphthalene in this connection, it may be accomplished by adding a small amount of mononitronaphthalene, as the latter acts as a solvent of the higher nitro-derivatives, and they together will dissolve picric acid, nitrocellulose, and the like.

The nitro-derivatives of naphthalene are generally obtained either by the action of nitric acid alone or mixtures of nitric and sulphuric acids on naphthalene, or, for the highest nitro-derivatives, by renitration of the lower compounds. It is best to nitrate with a mixture of nitric and sulphuric acids, using about three times as much acid (specific gravity 1·3) as naphthalene. The amount of sulphuric acid to be used will vary with the degree of nitration desired, and ranges from 4 : 1 (nitric : sulphuric) for low melting-points to 3 : 2 for the higher derivatives.

ANTHRACENE AND ITS ASSOCIATES.

In the distillation of coal-tar, the fraction passing over above the temperature of 270° C. is a heavy, greenish or reddish, oily liquid known as anthracene oil, which usually amounts to about one-sixth of the entire distillate. On cooling completely, a granular, crystalline deposit is formed, which consists chiefly of a mixture of various solid hydrocarbons, of which anthracene is the most important and characteristic. The deposit is freed as much as possible from the adherent oil by filtration, pressure, or other mechanical means. Formerly it was sold in a pasty state, but the purification is now carried further. To obtain a superior product it is desirable to use powerful hydraulic pressure, and to press the crude anthracene, first cold and then hot, by which means a 30 to 40 per cent. cake may be obtained without washing. The anthracene may be further purified by treatment, after crushing, with coal-tar naphtha boiling between 120° and 190° C., which, in some cases, is subsequently washed out by petroleum spirit boiling between 70° and 90° C.[1] Anthracene and the other chief constituents of the

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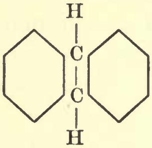
[1] The solvent is recovered by distillation. The residue consists largely of phenanthrene and liquid oils of unknown nature. Hitherto its only application has been for making lamp-black.

product thus obtained are described in the following sections. The assay of the crude anthracene is described on page 229, *et seq.*

Anthracene. $C_{14}H_{10}$ =



Anthracene is formed in a variety of reactions taking place at high temperatures. It is a characteristic constituent of coal-tar from the manufacture of illuminating gas, and is also found in the tar produced by condensing the gas from Simon-Carvès coke-ovens, and in the tar obtained in the manufacture of gas by exposing petroleum to a high temperature. Anthracene is now manufactured on a large scale from the high-boiling fractions of these tars (see above). It is contained in notable quantity in coal-tar pitch, and hence the distillation of this product has been carried as far as actual coking in order to obtain the greatest possible yield of anthracene, but the product was so impure, and is refined with such difficulty, that the manufacture from this source has been abandoned.

When quite pure, anthracene crystallises in colorless rhomboidal plates or shining scales, which exhibit a fine violet fluorescence. It melts at 213° C., sublimes at about the same temperature in micaceous scales, and distils almost unchanged at about 360° C.[1] It may be distilled nearly unchanged in admixture with caustic potash, and Perkin recommends this as the only method by which crude anthracene can be purified on the large scale.

Anthracene is insoluble in water, and in dilute acid and alkaline solutions. In cold alcohol chemically pure anthracene dissolves to the extent of 0·6 per cent., while benzene dissolves 0·9, and carbon disulphide 1·7 per cent. of anthracene.

If picric acid be added to a solution of anthracene in boiling benzene, a compound having the formula $C_{14}H_{10},C_6H_2(NO_2)_3OH$ is formed. On cooling, this so-called picrate separates in ruby-red needles, which melt at 170° C., and are soluble in a small proportion of alcohol with red color, but on adding more alcohol the compound

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[1] Nearly pure anthracene may be obtained by melting a partially purified sample in a retort and passing a strong current of air through it, when the anthracene is carried off and deposited in brilliant flakes.

undergoes decomposition and the liquid is decolorised. The crystals are also decomposed by water.

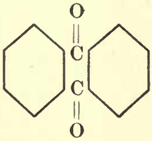
Hot dilute nitric acid converts anthracene into a mixture of anthraquinone with dinitranthraquinone, $C_{14}H_6(NO_2)_2O_2$. The latter body crystallises in microscopic quadratic plates, and, according to Fritzsche, forms compounds with all the solid hydrocarbons associated with anthracene in coal-tar. With anthracene itself, Fritzsche's reagent gives shining, rhomboidal, purple plates, which appear blue if the hydrocarbon be not quite pure; and if too impure, the reaction fails altogether.

On gently heating, concentrated sulphuric acid dissolves anthracene with greenish color, and at a higher temperature forms anthracene sulphonic acids. Fuming sulphuric acid acts violently on anthracene.

By the action of bromine or chlorine, anthracene is converted into various bromo- and chloro-derivatives. On treating dibromanthracene, $C_{14}H_8Br_2$, with oxidising agents, it is converted into dibromanthraquinone, $C_{14}H_6Br_2O_2$, and this, when heated with caustic potash, yields dioxyanthraquinone or alizarin, $C_{14}H_6(OH)_2O_2$. Similarly, by treatment with chlorine, anthracene is converted into the theoretical weight of dichloranthracene, $C_{14}H_8Cl_2$, a lemon-yellow crystalline substance resembling picric acid. The reaction forms an important step in the manufacture of artificial alizarin.

By exposing purified anthracene suspended in benzene or xylene to the action of direct sunlight for several weeks a modification, commonly called *paranthracene*, is obtained, but which Orndorff and Cameron[1] find to have the formula $C_{28}H_{20}$, and propose the name *dianthracene*. It has a specific gravity of 1·265 $\left(\frac{27^\circ\text{ C.}}{4^\circ\text{ C.}}\right)$. It melts at 244° C. It differs from anthracene in many points. It is not soluble in benzene, is not attacked by ordinary nitric acid or bromine, and does not combine with picric acid. It is converted into anthraquinone by chromic acid or warm fuming nitric acid.

ANTHRAQUINONE. $C_{14}H_8O_2 =$



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[1] *Amer. Chem. Jour.*, 1895, 658.

Anthraquinone has the constitution of a diphenylene-diketone. It is produced by the action of oxidising agents on anthracene. Chromic acid is the best oxidiser for the purpose; with nitric acid, nitranthraquinone is apt to be produced. The details of the process are given on page 229, *et seq.*

As usually prepared, anthraquinone appears as a felted mass of delicate crystalline needles of a yellowish or pale buff color, but when purified by sublimation, it is obtained in long, delicate, lemon-yellow needles, or golden-yellow prisms. When pure, it melts at 277° C., and boils at a temperature between the points of ebullition of mercury and sulphur.

Anthraquinone is neutral in reaction, and insoluble in water and in dilute acid and alkaline liquids. It is sparingly soluble in alcohol and ether; more soluble in hot benzene. It is very stable, resisting the action of many reagents. It is not affected by hot hydrochloric acid, or by boiling with solution of potassium hydroxide or calcium hydroxide. It dissolves in hot nitric acid of 1·4 specific gravity, and is deposited in crystals on cooling,—a more complete separation occurring when the acid is diluted.

In concentrated sulphuric acid at 100° C. anthraquinone dissolves unchanged, and on exposing the solution to a moist atmosphere, is gradually redeposited in crystals, or may be obtained in a more finely-divided state by pouring the acid into water. Solution in sulphuric acid is employed for purifying commercial athraquinone. When strongly heated with concentrated sulphuric acid, or more easily if fuming acid be used, anthraquinone is converted into a mixture of anthraquinonemonosulphonic and anthraquinone-disulphonic acid. These bodies are also obtained by the action of sulphuric acid on dichloranthracene, $C_{14}H_8Cl_2$, and play an important part in the manufacture of artificial alizarin. The proportion of the two sulphonic acids formed depends on that of the sulphuric acid employed. On nearly neutralising the product with caustic soda, sparingly soluble sodium anthraquinonemonosulphonate separates, and may be obtained in brilliant pearly scales by pressure and recrystallisation. Heated with sodium hydroxide and potassium chlorate it yields pure alizarin.

When fused with potassium hydroxide, anthraquinone yields potassium benzoate, and, when ignited with or distilled over soda-lime, benzene is formed.

By the action of certain reducing agents, such as sodium amalgam, or sodium hydroxide solution and zinc-dust, anthraquinone is converted into hydranthraquinone, $C_{14}H_{10}O_2$. This reaction has been applied by A. Claus as an extremely delicate means of detecting anthraquinone, and hence anthracene. A few particles should be placed in a test-tube with some sodium amalgam, covered with ether free from water and alcohol, and the whole well shaken together. On adding a drop of water a splendid red color appears, but is destroyed by shaking in contact with air, reappearing on standing. If absolute alcohol be substituted for the ether, the color produced is dark green, turned to red by a trace of water, and destroyed by shaking with air.

The marked characters and stability of anthraquinone render it the most convenient body into which to convert anthracene for the purpose of determining it. The best method of effecting this is described on page 230.

ANTHRACENE DIHYDRIDE, $C_{14}H_{12}=C_{14}H_{10}.H_2$, occurs in coal-tar. It crystallises in colorless plates resembling naphthalene, fuses at 106°, and distils unchanged at 305° C. It has a peculiar odor, sublimes at the temperature of boiling water, and distils readily with the vapor of water or alcohol. Anthracene dihydride is insoluble in water, but is readily soluble in alcohol, ether, or benzene, the solutions exhibiting a blue flourescence, which is not shown by the solid substance. It is said not to yield a compound with picric acid.

ANTHRACENE HEXHYDRIDE, $C_{14}H_{16}=C_{14}H_{10}H_6$, occurs in coal-tar with the dihydride, which it closely resembles. It melts at 63° and boils at 290°.

METHYLANTHRACENE, $C_{15}H_{12}=C_{14}H_9(CH_3)$, occurs in small quantities in coal-tar, and is produced by the reduction of chrysophanic acid and other bodies. It resembles anthracene, crystallises from hot alcohol in thin, pale yellow, bright scales, and sublimes in greenish scales. It melts at a temperature variously stated at 200° to 210° C., is sparingly soluble in alcohol, ether, and glacial acetic acid, but readily in benzene, chloroform, and carbon disulphide. It forms a picric acid compound similar to that of anthracene, and is dissolved by concentrated nitric or sulphuric acid, especially if hot.

DIMETHYLANTHRACENE, $C_{16}H_{14}=C_{14}H_8(CH_3)_2$, resembles the last compound, melts at 224° to 225° C. and is supposed, though not proved, to exist in coal-tar.

Constituents of Crude Anthracene.

The crude commercial anthracene, obtained from coal-tar in the manner described in outline on page 208, is an extremely complex mixture of hydrocarbons and other organic compounds, some of which have been but very imperfectly studied. The tables on pages 214 and 215 give a synopsis of the principal hydrocarbons occurring in crude anthracene:[1]

Besides the bodies classified in the foregoing table, and methyl-anthracene and the hydrogen additive-compounds of anthracene already described, crude anthracene is apt to contain other hydrocarbons of which but little is known. A solid paraffin is present in considerable quantity in the crude anthracene made from the tar of cannel coal.

Crude commercial anthracene also contains liquid hydrocarbons of high boiling point and almost unknown composition; the phenols corresponding to anthracene, phenanthrene, and probably to other hydrocarbons; and the nitrogenised bodies carbazol, imido-phenyl-naphthyl, and acridine.

The following is a more detailed description of the principal bodies occurring in association with anthracene in the crude commercial product. Some of their important reactions are described on page 221 *et seq.*:

NAPHTHALENE, $C_{10}H_8$, has already been fully described (page 197). It can be separated from crude anthracene with tolerable facility, as it is taken up by solvents more readily than are the associated hydrocarbons, and has a lower melting and boiling point.

DIPHENYL, $C_{12}H_{10}$, dissolves readily in alcohol and ether, and crystallises from its solutions in large, colorless scales. It may be isolated from the indifferent oils of the fraction of coal-tar boiling between 240° C. and 300° C. by treating them with warm sulphuric acid, separating the resultant mono- and dimethylnaphthalene-sulphonates, and cooling the undissolved oil to —15° C., when the diphenyl separates out.

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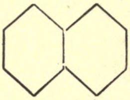
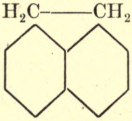
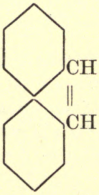
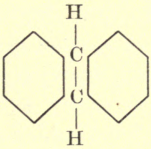
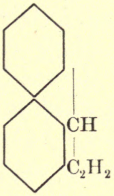
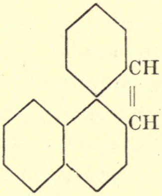
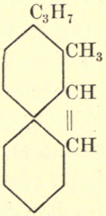
[1] The structural formulæ have been compiled principally from the last (8th) German edition of Richter's *Organic Chemistry*, which gives for retene merely the general structure, as a methyltritylphenanthrene. In the formula for retene, given in the table, the assignment of the alkyls to particular points is merely provisional.

Name.	Empirical Formula.	Structural Formula.	Melting Point. ° C.	Boiling Point. ° C.
Naphthalene, ...	$C_{10}H_8$		79	218
Diphenyl, ...	$C_{12}H_{10}$		71	254
Acenaphthene, ...	$C_{12}H_{10}$		95	277
Fluorene (diphenylmethane), .	$C_{13}H_{10}$		113	295
Phenanthrene, ...	$C_{14}H_{10}$		99	340

NAME.	EMPIRICAL FORMULA.	STRUCTURAL FORMULA.	MELTING POINT. ° C.	BOILING POINT. ° C.
Anthracene, ...	$C_{14}H_{10}$		213	36
Fluoranthrene, ...	$C_{15}H_{10}$		109	...
Pyrene, ...	$C_{16}H_{10}$		148	371
Chrysene, ...	$C_{18}H_{12}$		250	436
Retene (methylisopropylphenanthrene), ... (See note, page 213.)	$C_{18}H_{18}$		98	390

Acenaphthene, $C_{12}H_{10}$, is metameric with diphenyl. It occurs chiefly in the fraction of coal-tar distilling between 270° C. and 300° C., and crystallises from the 280° C. to 290° C. fraction on cooling. It may be purified by crystallisation from hot aclohol or coal-tar naphtha, followed by careful sublimation. From alcohol it crystallises in long, colorless, lustrous needles, and from heavy tar oil in hard, brittle crystals. Acenaphthene has an odor like that of naphthalene, is readily acted on by bromine, forms a sulphonic acid all the salts of which are readily soluble, and yields a nitro-compound with nitric acid.

Acenaphthene Dihydride, $C_{12}H_{10}H_2$, is stated to occur in coal-tar and to boil at 260° C.

Fluorene, $C_{13}H_{10}$, is contained in the fraction of coal-tar boiling between 290° C. and 350° C., and particularly in the 295–310° C. fraction, from which it may be isolated by repeated crystallisation from alcohol. Fluorene forms colorless, fluorescent scales, easily soluble in hot alcohol and in benzene, ether, and carbon disulphide. It yields dirivatives with bromine and nitric acid.

Phenanthrene, $C_{14}H_{10}$, is metameric with anthracene, and occurs in the crude substance in very considerable proportion. It may be separated from anthracene by fractional distillation, followed by repeated crystallisation from alcohol, in which liquid it is much more soluble than anthracene, and hence becomes concentrated in the mother-liquors. The fusing point of phenanthrene is much lower than that of anthracene, but it sublimes less readily than the latter hydrocarbon, though its boiling point is lower. It is also distinguished from anthracene by its behavior with picric acid, with antimony and bismuth chlorides (pages 222, 225), and with chromic acid. Phenanthrene forms a sulphonic acid when heated to 100° C. with concentrated sulphuric acid, and with nitric acid yields a nitro-compound. Its behavior with chromic acid is described on page 226.

Pseudophenanthrene, $C_{16}H_{12}$, occurs in small quantity in the portion of crude anthracene soluble in acetic ether. It forms large, white, glistening plates, exhibiting no fluorescence, and melting at 150° C. This last character distinguishes it from phenanthrene and similar hydrocarbons, as does the fact that the picrate separates on mixing cold saturated alcoholic solutions of the hydrocarbon and picric acid. It is also characterised by the properties of the product formed on oxidising it with chromic acid.

Fluoranthrene, or **Idryl**, $C_{15}H_{10}$, occurs in the highest-boiling fractions of coal-tar, and is best separated from the accompanying pyrene by repeated crystallisations of its picric acid compound from alcohol. Fluoranthrene crystallises from dilute alcohol in large shining plates, from strong alcohol in needles. It dissolves in concentrated sulphuric acid, on gently warming, with greenish-blue coloration, changing at a higher temperature to blue, and at length turning brown.

Pyrene, $C_{16}H_{10}$, is contained in the fractions of the oils of coal-tar and crude anthracene boiling above 360° C. On extracting these with carbon disulphide, evaporating the filtered solution to dryness, dissolving the residue in hot alcohol, and adding an alcoholic solution of picric acid, the picrate separates on cooling. The compound should be recrystallised several times from alcohol, decomposed by ammonia, and the separated hydrocarbon recrystallised from alcohol. It forms colorless, tabular crystals.

Retene, $C_{18}H_{18}$, occurs in thin, unctuous scales in fossil pine-stems, in beds of peat and lignite; and is also produced in the dry distillation of very resinous fir and pine wood. It forms shining scales. Retene volatilises readily at 100° and slowly at the ordinary temperature, but is devoid of smell. It sinks in cold water and floats on boiling water.

Chrysene, $C_{18}H_{12}$, is contained in the fraction of coal-tar which distils immediately before the occurrence of coking, when it is obtained in admixture with pyrene as a dry powder or yellow mass. On extracting this with carbon disulphide chrysene remains, and may be purified by crystallisation from hot glacial acetic acid or heavy tar oil. Turpentine oil also dissolves it, but in carbon disulphide it is nearly insoluble. Chrysene forms brilliant scales, which when pure are colorless, but which are commonly obtained yellow, owing to the presence of chrysogene as a persistent impurity. Chrysene boils at about the same temperature as sulphur, with partial decomposition. It forms compounds with picric acid and dinitro-anthraquinone, yields nitro-compounds with nitric acid, and dissolves in hot, concentrated sulphuric acid with purple color.

Chrysogene is the body which imparts to impure chrysene its yellow color. Its formula has not been established. It is isolated from crude chrysene by frequent crystallisation from coal-tar naphtha, and washing with ether and alcohol. Chrysogene crystallises from boiling alcohol in yellow, cohering scales, which if very thin are pink, with a gold-green reflection. It dissolves in 2500 of cold or 500 parts of boiling benzene, and in 10,000 of cold or 2000 of boiling glacial acetic acid. The presence of $\frac{1}{3000}$ part of chrysogene colors naphthalene and other hydrocarbons an intense yellow. Its solutions are rapidly decolorised on exposure to sunlight. Chrysogene fuses at 280–290° C. with partial decomposition, and dissolves without visible change in concentrated sulphuric acid.

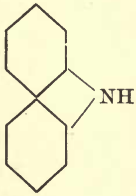
Benzerythrene, or **Triphenylbenzene**, $C_{24}H_{18}=C_6H_3(C_6H_5)_3$. This hydrocarbon forms the very last product obtained in the distillation of coal-tar pitch, and may thus be separated without difficulty. After nearly all the other bodies have passed over, the benzerythrene appears as a vapor easily condensing to a bright-red powder, which, however, contains much chrysene and other bodies troublesome to separate. When pure, it forms white, shining scales which melt at 307° C., and are but sparingly soluble in alcohol, or even in boiling glacial acetic acid, but are more soluble in hot benzene. In strong sulphuric acid benzerythrene dissolves with green color. The symmetric form has been obtained artificially.

Picene, or Parachrysene, $C_{22}H_{14}$, resembles chrysene, but is still less acted on by solvents. Its best solvent is high-boiling coal-tar naphtha. Picene melts at an exceptionally high temperature (330–345°), and boils at 518–520° C.

Paraffins, C_nH_{2n+2}. In the crude anthracene from the tar of cannel coal, such as is produced in Scotch and north-country gasworks, a solid paraffin is present in considerable quantity and is a highly objectionable impurity, as it greatly reduces the value of the product and even renders some batches wholly unmarketable.

Carbazol. Imido-diphenyl. Diphenylene-imide.

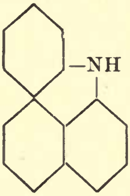
$C_{12}H_9N =$



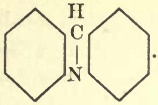
Carbazol often occurs in crude washed anthracene to the extent of 10 or 12 per cent. It is best isolated from the residue left in the retort after purifying crude anthracene by distillation with caustic potash. It exists in this as a potassium-derivative, $C_{12}H_8NK$, which is decomposed by water with formation of caustic potash and regeneration of the carbazol. Carbazol fuses at 238° C., sublimes readily, and boils at about 355° C. It forms colorless, crystalline, fluorescent scales or plates, which resemble anthracene. It is insoluble in water, and but little dissolved by cold alcohol, ether, chloroform, or benzene, but more readily by these solvents when hot (page 221). It has no basic properties like acridine and forms no salts with acids, but substitution-products with potassium and with acetyl exist. Its characters are very similar to those of the hydrocarbons with which it is associated. Carbazol forms a compound with picric acid, and with nitric acid yields nitro-compounds. In pure cold sulphuric acid it dissolves with yellow color, but in presence of the most minute trace of nitric acid, chlorine, chromic acid, or other oxidising agent, an intense green coloration is produced. It is employed for the preparation of several dye-stuffs. S. C. Hooker has suggested its use as a colorimetric test for nitrates in water.

IMIDO-PHENYLNAPHTHYL. Phenylnaphthylamine.

$C_{16}H_{11}N =$



This body is obtained by subliming the residue remaining after distilling crude anthracene. It crystallises in greenish or golden-yellow metallic-looking plates, melts when pure at 330° C., and boils at a higher temperature than sulphur. It is but little soluble in alcohol, benzene, toluene, or glacial acetic acid, even when boiling, and with difficulty in high boiling coal-tar naphtha. It is more soluble in hot aniline. Both in the solid state and when dissolved in benzene it is remarkable for its greenish fluorescence and banded, fluorescent spectrum, and broad and well-defined absorption-bands. In the benzene solution, two are seen between F and G, and another slightly more refrangible than G. When the substance is examined in the solid state, the bands are nearer the red end of the spectrum.

Acridine, $C_{13}H_9N$ = 

. Acridine is a basic body which may be isolated by agitating crude anthracene with dilute sulphuric acid, precipitating the solution with potassium chromate, purifying the acridine chromate by recrystallisation, precipitating the base by ammonia, and recrystallising it from hot water. The hydrochloride, which forms golden or brownish-yellow scales, may also be employed for the purification of the base. Acridine forms colorless or brownish-yellow, rhombic prisms. It melts at 110° C., sublimes in broad needles at about 100° C., boils unchanged at 360°, and distils with the vapor of water. It is slightly soluble in cold, but more readily in boiling water, and is readily dissolved by alcohol, ether, carbon disulphide, benzene, &c. Acridine exhibits a feeble alkaline reaction, and combines with acids to form a series of yellow salts, all of which are crystallisable and most of them easily soluble. They suffer decomposition when boiled with a large quantity of water. In dilute solution acridine salts exhibit a strong blue fluorescence, which is green with more concentrated solutions, and disappears if they are very strong. With strong nitric acid acridine forms nitro-compounds. Sulphuric acid has no action except at a very high temperature, and caustic potash does not react below 280° C. By oxidising agents acridine is unaffected. Its most characteristic property is an irritating effect on the skin and mucous membrane. Violent sneezing and coughing are produced on inhaling the smallest particle of the dust or vapor, and even very dilute solutions of its salts cause acute stinging when applied to the skin or tongue. It has been used as an insecticide, and compositions containing it have been used for coating the bottoms of vessels. The preservative properties of coal-tar creosote oil may be in part due to acridine.

Acridine Picrate, $C_{13}H_9N,C_6H_3(NO_2)_3O$, is a canary-yellow crystalline salt, which is also wholly insoluble in cold, and is partially decomposed by boiling, water. It melts at 208° C., and is but slightly dissolved by alcohol or benzene, even when boiling.

For a more extended account of acridine salts see Vol. III., part 2, p. 125.

Detection and Separation of Anthracene and its Associates.

The reactions of anthracene itself have already been detailed (page 209). The recognition and separation of the various constituents of crude commercial anthracene are attended with great difficulties. Fractional fusion and distillation are processes suggested by the tables on pages 214, 215, and the employment of suitable solvents and fractional crystallisation therefrom are methods often referred to in the foregoing description of the constituents of crude anthracene. Other useful processes and tests are based on the properties of their compounds with picric acid, on their reactions with concentrated sulphuric acid and with the fused chlorides of bismuth and antimony, and on the nature of the oxidation-products yielded on treating the solutions in glacial acetic acid with chromic acid.

BEHAVIOR OF SOLID HYDROCARBONS WITH SOLVENTS.

The following table, due to G. von Bechi, shows the behavior of anthracene and its associates with solvents. The sign ∞ signifies that the substance dissolves in all proportions:

	100 PARTS OF TOLUENE DISSOLVE		100 PARTS OF ABSOLUTE ALCOHOL DISSOLVE	
	At 15° C.	At 100° C.	At 15° C.	At 78° C.
Naphthalene, ...	31·94	∞	5·29	∞
Phenanthrene, ...	33·02	∞	2·62	10·08
Anthracene, ...	0·92	12·94	0·076	0·83
Pyrene, ...	16·54	Very soluble.	1·37	3·08
Chrysene, ...	0·24	5·39	0·097	0·17
Anthraquinone, . . .	0·19	2·56	0·05	2·25
Carbazol, ...	0·55	5·46	0·92	3·88
Imidophenylnaphthyl,	Scarcely soluble.	0·39–0·57	Scarcely soluble.	0·25

Figures showing the behavior of anthracene itself with some solvents are given on page 209. The comparatively slight solubility of anthracene in alcohol, carbon disulphide, and petroleum spirit was formerly applied to the assay of the commercial substance.

The following data are due to W. H. Perkin:

	100 Parts of Petroleum Spirit Boiling between 70° and 100° C. Dissolve	100 Parts of Coal-tar Naphtha Boiling between 80° and 100° C. Dissolve
Phenanthrene, ...	3·207	21·94
Anthracene, ...	0·115	0·976
Dichloranthracene, . .	0·137	0·52
Anthraquinone, . . .	0·013	0·166
Carbazol, ...	0·016	0·51

A process has been given by Zeidler[1] for the further separation by solvents of such of the constituents of crude anthracene as are dissolved by acetic ether.

Compounds of Solid Hydrocarbons with Picric Acid.

Most of the constituents of crude anthracene form characteristic crystalline compounds with picric acid, which have the general formula $MC_6H_3(NO_2)_3O$, in which M represents a molecule of the hydrocarbon. In some instances this reaction affords a valuable means of recognising the hydrocarbon. These so-called "picrates" are usually decomposed by water or alkaline solutions, and in some cases even by alcohol. To produce them a saturated solution of the hydrocarbon in hot benzene should be mixed with an approximately equivalent quantity of picric acid, also dissolved to saturation in hot benzene, and the mixed solution then allowed to cool. In other cases alcohol may be substituted for the benzene; for the detection of naphthalene, cold alcoholic solutions should be employed. The following is a description of the compounds of picric acid with the more important substances of this class:

Naphthalene is the only solid hydrocarbon, except pyrene and pseudophenanthrene, giving a precipitate when its cold alcoholic solution is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of yellow needles, melting at 149° C.

Diphenyl forms no definite crystalline compound.

Acenaphthene.—The compound forms orange-yellow needles on cooling the boiling alcoholic solution.

Fluorene.—The compound crystallises from benzene in slender red needles, melting at 81° C.

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[1] *J. S. C. I.*, 1882, 98.

Phenanthrene.—The compound crystallises from benzene in yellow needles, melting at 145° C. and soluble in hot alcohol without decomposition.

Pseudophenanthrene.—The compound forms readily on mixing saturated cold alcoholic solutions of hydrocarbon and picric acid. It crystallises in light-red needles, melting at 147° C.

Anthracene.—The compound is deposited from solution in hot benzene in ruby-red crystals, very soluble with red color in a little alcohol, the solution being decolorised and compound decomposed on adding more alcohol.

Fluoranthrene.—The compound forms reddish-yellow needles, melting at 182° C., difficultly soluble in cold alcohol, and decomposed by boiling with water.

Pyrene.—The compound is deposited from hot alcohol as a red crystalline precipitate or long dark-red needles, melting at 222° C., nearly insoluble in cold alcohol, but very soluble in benzene and decomposed slowly by boiling with water.

Retene.—The compound forms orange-yellow needles, readily soluble in alcohol.

Chrysene.—The compound crystallises from benzene in orange needles. It is decomposed by cold alcohol.

Benzerythrene.—The compound is deposited from very concentrated, hot alcoholic solutions in brownish-yellow flocks.

Carbazol.—The compound forms large red prisms, fusing at 182° C.

Acridine forms a true *picrate* (see page 220).

The reaction with picric acid has been made the basis of a method of estimating several of these hydrocarbons and their derivatives.[1] If substances that form insoluble compounds with picric acid be digested on the water-bath with a measured quantity of an aqueous solution of picric acid, nearly saturated at ordinary temperatures,—about $\frac{n}{20}$,—the original substance gradually disappears, and in its place an equivalent quantity of the picric acid compound separates quantitatively, either at once or on cooling. The amount of picric acid in the original solution and in an aliquot portion of the filtrate from the molecular compound can be determined by titration with barium hydroxide (using lacmoid as indicator), and the quantity of picric acid contained in the precipitate calculated.

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[1] F. W. Küster, *Ber.*, 1894, 1101; Abst. *J. S. C. I.*, 1894, 844.

The digestion on the water-bath must take place in hermetically closed vessels. The substance to be determined, together with the measured volume of picric acid of known strength in excess, is placed in a flask, which must be nearly filled with the solution. The flask is closed with a good india-rubber stopper, through which passes a tube about 7 cm. long. The tube is sealed up at the lower end, and about 1·5 cm. above the sealed end a small hole is blown in the side. When the side hole is just below the stopper, the air in the flask may be pumped out; then, on withdrawing the tube until the sealed end is flush with the under side of the stopper, the flask, having a vacuum in the upper part, may be disconnected from the pump and safely heated in the water-bath. The flask must be heated until the reaction is complete (2 hours—2 days), and frequently shaken during cooling, in order to wash down any material which may have sublimed into the upper part of the flask. After standing for a few hours, the picric acid in the filtrate is determined by titration. Test analyses show that the method is exact, except in the case of β-naphthol, with which a correction must be introduced owing to the solubility of the molecular compound. For every 100 c.c. of picric acid solution, 0·0075 grm. of β-naphthol remain unprecipitated.

REACTIONS OF SOLID HYDROCARBONS WITH METALLIC CHLORIDES.

Watson Smith has proposed to employ fused antimonous chloride and bismuthous chloride as reagents for the discrimination of solid hydrocarbons. For this purpose a small quantity of the crystallised chloride is placed in a small porcelain crucible and melted, and then further heated over a small flame. A small particle of the hydrocarbon to be tested is next placed on the side of the crucible, which is then so inclined that the melted chloride comes in contact with it. Fusion follows, accompanied in many cases by a coloration. On restoring the crucible to a vertical position, the colored spot elongates and forms a colored streak. Tested in this way, the hydrocarbons give the reactions shown in the following table:

HYDROCARBON.	REACTION WITH ANTIMONOUS CHLORIDE.	REACTION WITH BISMUTHOUS CHLORIDE.
Naphthalene, pure.	No coloration. During cooling, characteristic rhombic tables form in the fused chloride.	No coloration. During cooling, yellow, transparent needles separate.
Naphthalene, impure.	More or less carmine coloration.	More or less orange coloration.
Diphenyl.	No coloration.	No reaction.
Phenanthrene.	Difficultly soluble. Faint greenish coloration.	Brown or greenish brown.
Anthracene.	Traces even give a yellowish-green color. Colorless needles formed during cooling.	Purple-black coloration; very characteristic.
Dinaphthyls.	No coloration.	No reaction.
Pyrene.	Same as phenanthrene.	. .
Chrysene.	Traces even produce golden-yellow color.	. .
Stilbene.	At 40° C. smallest trace gives orange color, destroyed at higher temperature.	. .
β-Phenylnaphthalene.	No reaction.	. .
Triphenylmethane.	No reaction. Greenish color with excess.	. .

BEHAVIOR OF SOLID HYDROCARBONS WITH CHROMIC ACID.

When treated with oxidising agents, anthracene and many of the bodies occurring in association with it yield characteristic oxidation products. The best method of obtaining these bodies is to act on the hydrocarbons by a solution of chromic acid in glacial acetic acid. When the object is to obtain the immediate products of the oxidation, the treatment should be of limited duration and the oxidising agent should be employed in theoretical quantity or very moderate excess, but otherwise the process should be conducted as described on page 229. The following is an epitomised account of the products obtained by the action of chromic acid in acetic solution on the principal constituents of crude anthracene:

Naphthalene is apt to be completely oxidised to carbon dioxide and water, but by careful treatment may be converted into naphthalquinone, $C_{10}H_6O_2$, and ultimately into phthalic acid, $C_8H_6O_2$.

Acenaphthene is oxidised to naphthalic acid, $C_{12}H_8O_4$.

Diphenyl yields benzoic acid, $C_7H_6O_2$.

Fluorene is oxidised to diphenylene-ketone, $C_{13}H_8O$, which is volatile in a current of steam, and is deposited in crystals from its solution in alcohol.

Phenanthrene is transformed by the chromic acid mixture into phenanthraquinone, $C_{14}H_8O_2$, and this is ultimately converted into diphenic acid, which is susceptible of still further oxidation. Phenanthraquinone crystallises in dark orange-yellow prisms, melting at 198° C. It is sparingly soluble in hot water, but dissolves freely in benzene and acetic acid. Ignited with soda-lime it yields diphenyl, $(C_6H_5)_2$, in almost the theoretical proportion, whereas anthraquinone gives benzene when similarly treated. The two bodies also differ in their behavior with the acid sulphites of the alkali-metals, with which anthraquinone does not combine. Phenanthraquinone, when warmed with solution of sodium hydrogen sulphite, is dissolved and may be reprecipitated by mixing the filtered liquid with hydrochloric acid. This reaction may be used for the detection of phenanthrene. The hydrocarbon is oxidised by warm chromic acid mixture, the oxidation-product treated with alkali, and then warmed with the sulphite solution. Pyrenequinone gives a similar reaction.

If a few drops of *commercial* toluene be added to a dilute solution of phenanthraquinone in glacial acetic acid, and, after thoroughly cooling, concentrated sulphuric acid be then added, drop by drop, and the resultant solution treated with water after a few minutes, a coloring matter separates out which is dissolved with splendid violet-blue coloration on agitation with ether. This reaction depends on the presence of methylthiophene (thiotolene), C_5H_6S, in the toluene used (see page 165).

Pseudophenanthrene yields a yellow quinone, fusing at 170° and soluble with facility in alcohol and cold benzene.

Anthracene is converted by the chromic acid treatment into anthraquinone, $C_{14}H_8O_2$, which is an exceedingly stable body, resisting further action to a remarkable degree. Its properties have already been fully described (see page 209).

Methylanthracene is converted into soluble anthraquinone-carboxylic acid, $C_{14}H_7O_2 . COOH$.

Fluoranthrene is converted by the chromic acid mixture into fluoranthraquinone, $C_{15}H_8O_2$, and an acid soluble in alkaline liquids.

Pyrene yields pyrenequinone, $C_{16}H_8O_2$, which forms reddish crystals. It yields finally, and with some difficulty, products soluble in alkali.

Retene forms retenequinone, $C_{18}H_{16}O_2$, and other products. Retenequinone is a brick-red powder, crystallising from alcohol in orange-red needles, melting at 197° C. It can be further oxidised only with great difficulty, and is insoluble in cold and dilute soda, but is dissolved by hot concentrated alkalies.

Chrysene yields chrysoquinone, $C_{18}H_{10}O_2$, and is afterwards converted, with some difficulty, into phthalic acid, $C_8H_6O_2$. Chrysoquinone has a deep-red color, melts at 235° C., and dissolves in strong sulphuric acid with deep indigo-blue coloration.

Benzerythrene yields soluble products under the chromic acid treatment.

Chrysogene, said to exist in considerable quantity in certain kinds of anthracene (see page 217), is alleged to be completely and readily converted into soluble products by the chromic acid mixture. This is doubtful, for—

Imidophenylnaphthyl (described on page 219), yields a quinone of the formula $C_{16}H_9N_2O_2$, which forms reddish-yellow needles and obstinately resists further oxidation. It appears always to be produced by the oxidation of anthracenes which give banded absorption-spectra of the nature described on page 219, and leads to excessive estimates of the yield of real anthracene. The quinone is destroyed by prolonged treatment with fuming sulphuric acid at 100° C.

The *paraffin* in crude anthracene is practically unaltered by treatment with the chromic acid mixture.

A dark-green *hydrocarbon*, fusing at 271° C., is occasionally present in anthracene. It is soluble with difficulty in glacial acetic acid, and should, if present, be separated as far as possible by this solvent before employing the chromic acid mixture, as its oxidation is very difficult to effect.

Assay of Crude Anthracene.

Commercial crude anthracene is a green or brownish-green friable mass or crystalline powder. It contains a very variable percentage of real anthracene, the usual proportion being from 30 to 40 per cent., though formerly 15 per cent. was common, and special makes now assay over 80 per cent. It cannot be too strongly insisted on that the true value of a sample of crude anthracene is dependent not merely on the proportion of real anthracene contained in it, but also on its comparative freedom from objectionable impurities.

The *paraffin* existing in Scotch and north-country anthracenes has a high melting point, and little solubility in either petroleum or coal-tar naphtha. It dissolves in the hot liquids, but is almost entirely deposited on cooling. A small percentage of this paraffin greatly impedes the subsequent treatment of the anthracene, and, being a very stable substance, it passes through most of the processes unchanged. Experience has proved that in the operation of oxidising anthracene on a large scale, by treatment with potassium bichromate and dilute sulphuric acid, all other admixtures may be dealt with and to a great extent removed, but paraffin resists the oxidising action, melts, and retards the operation to a hopeless extent. Hence a search for this objectionable impurity should never be omitted, unless it be known to a certainty that bituminous shale or cannel coal has had no share in the production of the sample. It may be detected and determined in crude anthracene in the following manner: 10 grm. of the sample is treated with 108 c.c. of strong sulphuric acid. The mixture is heated on a water-bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obtained is cautiously poured into 500 c.c. of water contained in a tall beaker. After being thoroughly stirred the liquid is allowed to cool, when any paraffin will rise to the surface, and, having solidified, can be removed, washed with a little cold water, dried between blotting paper, and weighed. From 2 to 5 per cent. is the quantity commonly present in Scotch anthracenes.

Hensler and Herde[1] employ the following method for estimating the paraffin in crude anthracene: Two grm. of the sample

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[1] *Zeit. f. Ang. Chem.*, 1895, 283; Abst. *J. S. C. I.*, 1895, 828.

are weighed into a 150-c.c. flask, and fuming nitric acid added slowly,—at first, drop by drop,—the flask being kept cooled by ice-water. After the mass has been completely digested with the acid the flask is warmed on the water-bath until the undissolved material melts. The mixture is allowed to cool, filtered through asbestos, the filter washed thoroughly with fuming nitric acid, and then with water until a drop of the filtrate gives no turbidity with water. The filter is washed with alcohol and subsequently by warm ether to dissolve the paraffin. The alcohól filtrate is evaporated in a weighed dish, the ether solution added and evaporated, the residue dried for thirty minutes at 105° to 110° C. and weighed.

According to B. Nickels, samples of crude anthracene containing *imidophenylnaphthyl* (page 219) show the highly characteristic absorption-spectrum of this body; two broad, well-defined black bands between F and G and another slightly more refrangible than G. Samples exhibiting these bands are purified with some difficulty, and yield by oxidation an impure anthraquinone containing many amorphous particles. For observing the spectrum of the sample, about 0·25 grm. should be dissolved in 6 c.c. of warm benzene, the liquid passed through a dry filter, and observed with a spectroscope. A micro-spectroscope or a direct-vision pocket spectroscope will suffice. The intensity of the absorption-bands is an approximate measure of the objectionable impurities of the sample.

ANTHRAQUINONE TEST.—For the *quantitative* assay of commercial anthracene the most satisfactory method is that based on the formation of anthraquinone by the action of chromic acid. This is a characteristic, insoluble body, not liable to further change, while nearly all the associates of anthracene are, by the same treatment, either completely oxidised or else converted into products readily removed by water or dilute alkali (see page 225).

This method was first proposed by E. Lück, and, with suitable modifications, affords a very satisfactory solution of a difficult problem. The following mode of operating is essentially that of Meister, Lucius, and Brüning, with some precautions and modifications recommended by G. E. and T. H. Davis, who verified the accuracy of the method by operating on pure anthracene and impure samples of known composition. The test is commercially known as "Meister, Lucius and Brüning's anthraquinone test, with appendix." One grm. of the carefully sampled specimen is placed in a flask of 500 c.c. capacity. 45 c.c. of the very strongest glacial acetic acid is then added, and an inverted condenser or long glass tube adapted to the flask. The liquid is then brought to the boiling point, and, while boiling, the chromic acid is added to it gradually, drop by drop, by means of a tapped funnel passing through the india-rubber stopper of the flask, or inserted in the top of the vertical condenser (fig. 9). The chromic acid solution is prepared by dissolving 15 grm. of crystallised chromic anhydride (perfectly free from lead salts and insoluble matter generally) in 10 c.c. of water and 10 c.c. of glacial acetic acid. The addition of the oxidising agent should occupy two hours, and the contents of the flask should be kept in continued ebullition for two hours longer, four hours in all being necessary to ensure complete oxidation of the impurities. The flask is then left at rest for twelve hours, when the contents should be diluted with 400 c.c. of cold water and allowed to rest another three hours. The precipitated anthraquinone is then filtered off and well washed with cold water. It is next washed on the filter with a boiling-hot 1 per cent. solution of caustic soda, and again thoroughly washed with boiling water, about 300 c.c. being employed. The anthraquinone, which should exhibit no alkaline reaction, is then rinsed from the filter into a small dish by means of a jet of water, the water evaporated off, and the residue dried at 100° C. and weighed.

FIG. 9.

The anthraquinone obtained in the foregoing manner is rarely sufficiently pure to allow of the percentage of real anthracene in the sample being at once calculated from its weight. Several methods have been proposed for the further purification of the crude product, but the following improved "appendix" by Meister, Lucius, and Brüning, commercially known as the "sulphuric acid test of October, 1876," is now universally employed. The crude anthraquinone is mixed in the dish in which it was weighed, with ten times its weight of fuming sulphuric acid having a specific gravity of 1·880 at 60° F., and the whole heated to 100° C. on a water-bath for ten minutes. The solution obtained is next left in a damp place for twelve hours to absorb water. 200 c.c. of cold water are then added, the precipitated anthraquinone collected on a filter, and washed free from acid with cold water, then with about 100 c.c. of boiling sodium hydroxide solution (1 per cent.), and finally with about 400 c.c. of boiling water. The character of the quinone is an indication of its purity, a deep yellow or orange tint indicating the presence of phenanthrene- or chrysene-quinone. The latter body is also recognised by the production of an indigo-blue coloration on adding the sulphuric acid. With impure anthraquinones both the acid filtrate and the alkaline washings are deeply colored,—brown, purplish, and bluish tints being the most common.

The greater part of the moist anthraquinone is then transferred to a flat platinum or porcelain dish by means of a spatula, the remaining portion being rinsed off the filter into the dish by means of a fine jet of water. The water is then evaporated off at 100°, and the residue weighed. An alternative method is to dry the anthraquinone on the filter, and then remove it. To avoid loss, the stained portion of the filter may be cut small and heated in a test-tube with about one c.c. of benzene. The resultant solution is poured off into a small dish, and the residue obtained by its evaporation added to the main quantity of anthraquinone. The difference in the result caused by the benzene treatment often amounts to 0·2 per cent. of the crude anthracene, owing to the loss in the other methods by imperfect removal from the filter. Hence, when the analyst is not limited by the conditions of the contract-note, treatment of the filter with benzene should not be neglected. Either of the foregoing methods of treatment is preferable to weighing the anthraquinone on the filter, which is apt to be altered in weight by the reagents employed, though this source of error may be to a great extent avoided by using a double filter, the apex of the outer one being cut off. The weights of the two filters are accurately adjusted before use by trimming with a pair of scissors, and on weighing the anthraquinone, the outer filter is used as a counterpoise to the inner.

H. Bassett[1] has proposed the following modification of this method: After the washing of the anthraquinone collected on the filter, it is dried in the water-oven and then transferred to a flask of the usual size, with a short and wide neck, using a small wash-bottle containing 45 c.c. of glacial acetic acid to rinse the filter-paper and funnel. (The hardened filter-paper now furnished would probably serve well.) 10 c.c. of pure nitric acid (sp. gr., 1·4) and

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[1] *Chem. News*, **73** (1896), 178; Abst. *J. S. C. I.*, 1896, 385.

2·5 c.c. of chromic acid solution are added, and the mixture boiled for an hour, using a reflex condenser. The flask is allowed to stand overnight, then diluted to 400 c.c., filtered, washed with water, and then with boiling solution of sodium hydroxide as above. Bassett[1] states that samples of chromic anhydride often contain considerable sulphuric acid, but this does not interfere seriously with the test.

The weight of anthraquinone thus obtained ought not to be regarded as representing that of the pure product, as it usually contains extraneous matters, such as *sand*, and frequently *chromium*. Some anthracenes yield anthraquinones which carry much chromium sesquioxide. Hence the dish should be gradually heated so as to completely sublime the anthraquinone, and the residue obtained deducted from the weight previously found. This corrected weight of the anthraquinone, multiplied by the factor 0·856, gives the real anthracene in the weight of the sample employed.

The *anthraquinone* obtained by the above process should be crystallised, and of a uniform pale-yellow color. The purer it is, the paler the color. Certain strange quinones are apt to be present in some cases, and are recognisable by the modified form of the crystals and the color of the product. Phenanthraquinone is orange, and chrysene-quinone deep red. Continued treatment with the chromic acid mixture removes all these bodies, but does not affect the quinone, $C_{16}H_9NO_2$, produced by the oxidation of imido-phenylnaphthyl referred to on pages 219 and 229 as giving a characteristic absorption-spectrum. This body, unlike the quinones from phenanthrene, chrysene, &c., tends to prevent the crystallisation of the anthraquinone, and is one of the sources of the so-called "amorphous particles" which are frequently present in sufficient quantity to obliterate all trace of crystallisation in the oxidised product. This troublesome impurity may, however, be destroyed by a somewhat longer-continued heating with sulphuric acid in the manner already described, and hence this supplementary treatment should never be omitted in the case of samples which originally showed absorption-bands, or which have produced crude anthraquinones of unhealthy appearance.

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[1] *Chem. News*, **71** (1895), 202.

DETERMINATION OF ANTHRACENE IN TAR AND PITCH.

For the determination of anthracene in coal-tar, C. Nicol[1] distils 20 grm. in a small luted retort, and the vapors are received in a U-tube, kept at 200° C. by being immersed in a bath of hot paraffin. The more volatile products are not condensed, but the anthracene and other hydrocarbons of high boiling point collect in the U-tube. Care must be taken to prevent bumping, and the condensation of the distillate on the neck and sides of the retort. When the contents of the retort become coked, the process is stopped and the neck is cut off, pounded, and the powder added to the distillate. The whole is then dissolved in glacial acetic acid, and subjected to oxidation with the chromic acid mixture in the manner already described. Watson Smith considers 20 grm. far too small a quantity. He operates on at least a litre, and rejects the portion distilling just before coking, as it contains much resinous matter of an objectionable kind, and would not in practice be treated for anthracene. The anthracene oil is well mixed and an aliquot part oxidised.

In some cases it is preferable to reject the fraction distilling between 200° and 250° C., as it contains little or no anthracene, and in tars rich in naphthalene is so large in quantity as materially to impede the subsequent treatment. The anthracene may be further concentrated by cooling the heavy oils to a low temperature, filtering, and pressing the deposit of solid hydrocarbons between folds of filter-paper. The crude anthracene thus obtained is then oxidised to anthraquinone in the usual way. Ordinary gas-works coal-tar contains from 0·3 to 0·5 per cent. of real anthracene, but from the tar obtained from Simon-Carvès coke-ovens, Watson Smith obtained 0·73 per cent. of anthracene, and A. H. Elliott found as much as 2·63 per cent. in the tar produced in the manufacture of water-gas from petroleum naphtha.

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[1] *Ztschr. anal. Chem.*, 1875, 318; Abst. *J. Chem. Soc.*, **30** (1876), 553.

PHENOLS.

The bodies termed phenols are intermediate in character between acids and the true aromatic alcohols, of which benzyl alcohol is the type.

The MONOHYDRIC PHENOLS have the general formula $C_nH_{2n-7}OH$. Of these, phenol and cresol are described in the following sections. Thymol, $C_{10}H_{13}OH$, which is a higher homologue of these bodies, will be considered in connection with the essential oils. The naphthols, $C_{10}H_7OH$, which are closely related to the monatomic phenols, are described on page 201.

The DIHYDRIC PHENOLS or HYDROXYPHENOLS, $C_nH_{2n-8}.(OH)_2$, are described on page 265. Catechol (or pyrocatechin), resorcinol, and quinol (or hydroquinone) are isomeric bodies of the formula $C_6H_4(OH)_2$. Orcinol, or orcin, $C_7H_6(OH)_2$, obtained from various lichens, is a phenol homologous with resorcinol.

The TRIHYDRIC PHENOLS or DIHYDROXYPHENOLS are represented by pyrogallol and phloroglucol, $C_6H_3(OH)_3$.

Certain ethers of catechol and pyrogallol are described in the section on "Wood-tar Creosote" (page 277), in which liquid they are present in large proportion.

MONOHYDRIC PHENOLS. $C_nH_{2n-7}OH$.

The monohydric phenols form a homologous series, of which phenol proper, or carbolic acid, is the first member, and the cresols form the next homologue.

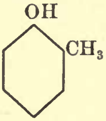
Of the higher members of the series, some exist in the tars produced by the distillation of coal and wood (*e. g.*, xylenols); others in certain natural essential oils (*e. g.*, thymol); while others again have hitherto been obtained by synthetical reactions only. The higher monohydric phenols present a close resemblance to phenol in their general characteristics. They may be distilled without decomposition, are but slightly soluble in water, but dissolve readily in aqueous alkalies, alcohol, and ether.

The monohydric phenols may be regarded as being formed from benzene and its homologues by the substitution of a molecule of hydroxyl for an atom of hydrogen in the principal chain. All but the lowest term are susceptible of isomeric modifications, according to the relative positions of the hydroxyl and other substituted radicals in the benzene nucleus.

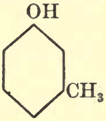
The difference in structure between the monohydric phenols and the true aromatic alcohols, typified by benzyl alcohol, is shown by the following example, all four bodies having the empirical formula C_7H_8O:—

VARIETIES OF CRESOL OR METHYL-PHENOL.

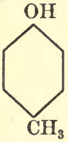
Orthocresol (1-2)



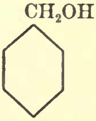
Metacresol (1-3)



Paracresol (1-4).



BENZYL ALCOHOL OR PHENYL-CARBINOL.



The *monohydric phenols* are distinguished from the *alcohols of the benzyl series* by the following reactions:—

a. Hydrochloric acid is without action on the phenols, but (*e. g.*) converts benzyl alcohol into benzyl chloride, $C_6H_5CH_2Cl$.

b. Phenol readily dissolves in concentrated sulphuric acid to form phenolsulphonic acids, while benzyl alcohol is resinified by similar treatment.

c. On treatment with oxidising agents the phenols yield quinones, but benzyl alcohol yields benzoic acid.

d. Nitric acid converts the phenols into well-characterised nitro-derivatives of acid character, but benzyl alcohol is oxidised by the same reagent to benzoic aldehyde and benzoic acid.

e. The phenols dissolve in solutions of alkalies to form compounds in which they play the part of an acid. The acid character is less marked in the higher members of the series, but the chloro- and nitro-derivatives have strongly acid properties, not only dissolving in solutions of alkaline hydroxides, but decomposing carbonates with effervescence and forming definite and stable salts.

f. Ferric chloride produces a characteristic blue or violet color with many of the phenols and their derivatives.

g. On adding hydrochloric acid to the aqueous solution of a phenol, immersing a slip of pine-wood and allowing it to dry, a blue color is developed.

h. The phenols react immediately with excess of bromine water to form bromo-derivatives (usually containing Br_3), which are usually white or yellowish, and are insoluble or nearly insoluble bodies.

The reactions of the phenols of service for their recognition are described more in detail on page 241.

Phenol. Carbolic Acid. Phenic Acid. Phenyl Alcohol. Hydroxybenzene. C_6H_5OH.

Phenol is a product of putrefaction, and is formed in various analytical and synthetical reactions, but the principal source of commercial interest is the fraction of coal-tar distilling between 150° and 200° C. On treating this with caustic soda, phenol and its homologues are dissolved, together with a certain amount of naphthalene and other indifferent bodies. These are partially precipitated on diluting the alkaline liquid, and become further oxidised on exposing the solution to the air. On treating the liquid with an excess of sulphuric acid the liberated phenols form an oily layer, which is separated from the aqueous liquid. From the crude material so obtained, pure phenol is obtained by fractional neutralisation, the homologues having less defined acid properties. On again liberating the phenol from its sodium compound a product is obtained which is fractionally distilled. The portion passing over within a few degrees of 182° C. is subjected to a freezing mixture, when crystals of phenol form, which are separated from the liquid by a centrifugal machine. The product may be further purified by a repetition of the process.

For the synthetic preparation of phenol several methods may be employed, two of which are of sufficient importance to be briefly described.[1] The first, or sulphonate method, is similar to that used in preparing the naphthols. Pure benzene, free from thiophene, is placed with about five times its weight of strongest commercial sulphuric acid in closed cast-iron pots. While the mixture is slowly stirred the vessel is gently heated with steam in such a manner that the vapors of benzene which pass over into the cooler are continually returned to the kettle. After a number of hours the reaction is finished, and the benzene not acted on is

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[1] H. W. Jayne, *Amer. Jour. Pharm.*, 1891; Abst. *J. S. C. I.*, 1892, 264.

collected as it flows from the cooler. The crude benzenesulphonic acid formed, mixed with the excess of sulphuric acid, is allowed to cool, and then diluted with water in a lead-lined tank. Slaked lime is added to the hot solution in sufficient quantity to render it faintly alkaline, and the calcium sulphate formed separated by means of a filter-press. The clear liquor containing calcium benzenesulphonate is treated with sufficient sodium carbonate to precipitate all the calcium as carbonate, and the filtered liquid is evaporated to dryness, leaving the sulphonate as a white powder. Sodium hydroxide is then melted in a cast-iron kettle, and small portions of the dry sodium benzenesulphonate, prepared as above, are gradually added, the whole being kept in quiet fusion for some time. The melt now contains sodium phenate, sodium sulphite, and the excess of sodium hydroxide:

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O.$$

It is ladled from the kettle into pans and allowed to cool, broken up, dissolved in water, and the solution acidified with sulphuric or hydrochloric acid. The phenol thus liberated separates from the concentrated salt solution, and is distilled.

In melting the sodium benzenesulphonate with sodium hydroxide it is necessary, in order to obtain a good yield, to use a very large excess of the latter. A better yield is obtained with potassium hydroxide.

It has been proposed to treat the melt, after dissolving in water, with carbon dioxide, which would liberate the phenol equally as well as a stronger acid, and in addition would form sodium or potassium carbonate, which, together with the sulphite already present, could be converted into the hydroxide by treating with lime, and this used for a second operation.

The second method is much simpler. A pure aniline oil, preferably that grade called "aniline for blue," is dissolved in water in a lead-lined tank covered with a hood, and provided with stirrers and leaden steam-coils. The solution is acidulated very strongly with sulphuric acid, and to the hot liquid a solution of commercial sodium nitrite is gradually added, when phenol is at once formed.

In this reaction the sodium nitrite in contact with the acid solution liberates nitrous acid, which forms diazobenzene sulphate with the aniline sulphate:

$$(C_6H_5NH_2)_2H_2SO_4 + 2HNO_2 = (C_6H_5N_2)_2SO_4 + 4H_2O;$$

but, as the solution is hot, the diazo-compound at once decomposes, with the formation of phenol and evolution of nitrogen:

$$(C_6H_5N_2)_2SO_4 + 2H_2O = 2C_6H_5OH + H_2SO_4 + 4N.$$

Pure phenol may be prepared by heating crystallised salicylic acid, either alone or mixed with pounded glass or lime, strongly and rapidly in a glass retort. Phenol passes over into the receiver, and crystallises almost to the last drop.

Pure phenol is a colorless solid, crystallising in long needles and melting at 42·2° C. to a colorless, limpid fluid, slightly heavier than water, which boils at 182° C. and distils without decomposition. Specimens having a lower melting point than 42° C. contain cresols or water. The taste of phenol is biting, but at the same time sweet. The odor is usually strong and characteristic, but both smell and taste are much less marked in pure specimens than in the crude article.

The crystals of phenol readily absorb water from the air, whereby the fusing point is lowered, owing to the formation of a *hydrate*, of the formula $2C_6H_6O + H_2O$. This hydrate contains 8·74 per cent. of water and melts at 17·2° C. It forms large, six-sided prisms, which in very moist air absorb still more water, forming a product which is fluid at ordinary temperatures.

When cold water is gradually added to absolute phenol as long as it continues to be dissolved, a liquid is obtained which contains about 73 per cent. of phenol and 27 of water. This approximately agrees with the composition of a hydrate of the formula $C_6H_6O + 2H_2O$; but the fact is probably merely a coincidence, as the proportion of water depends greatly on the temperature, and the liquid gives up its phenol to benzene, and deposits crystals of the hydrate melting at 17·2° C. when subjected to a freezing mixture.

The liquid hydrate dissolves in about 11·1 times its measure of cold water. This corresponds to a solubility of 1 part by weight in 10·7 for the absolute acid, the saturated solution containing 8·56 per cent. of real phenol. In hot water phenol is much more soluble, and is miscible in all proportions at about 70° C.; but in water saturated with sodium chloride or sulphate it is but slightly soluble. *Anhydrous* phenol is miscible in all proportions with alcohol, glacial acetic acid, glycerol, ether, benzene, carbon disulphide, and chloroform. When *aqueous* phenol is shaken with excess of any one of the last four solvents, the phenol dissolves and the contained water is separated. According to Staveley, absolute phenol is soluble in petroleum spirit, but is separated by water. This separation is prevented by the presence of from 20 to 25 per cent. of benzene.

The above statements as to the solubility of phenol are the result of the author's own experience. The solubility is often misstated, partly owing to the use of an acid containing cresol, and partly from a confusion between the absolute and the hydrated acid.

Phenol coagulates albumin, is a powerful antiseptic, acts as a caustic on the skin, and is powerfully *poisonous.* Its local action is much influenced by the solvent; it is stated that the solution in pure glycerol or absolute alcohol is scarcely caustic. Strong phenol dissolves gelatin completely, but coagulates it when added to its aqueous solution. Indigo-blue (indigotin) is soluble in hot phenol and may be obtained in crystals on cooling the liquid.

By the action of fused sodium hydroxide on phenol, phloroglucol, catechol, and resorcinol are formed, together with other products.

Phenol is converted by the action of chlorine and bromine into chloro- and bromo-derivatives (page 244). Nitric acid acts on it with formation of nitrophenols. Concentrated sulphuric acid converts phenol into phenolsulphonic acids. Hydrogen dioxide converts phenol into catechol, hydroquinone, and quinone.

Moist phenol turns red; the color has been ascribed to various impurities—*e. g.,* thiophene. Kohn and Fryer[1] have carefully investigated the subject and state that the change is due to the oxidation of the phenol itself, dependent, in part at least, on the absorption of water. A well-known German house advertises a pure phenol, "guaranteed not to redden under the usual precautions of keeping," but the precautions are not stated.

According to J. Walter,[2] ferrous salts increase the liability of phenol to turn red, the iron in ordinary bottles being sufficient to cause contamination. Walter states that a sample of phenol that began to redden in ten days in a bottle made of glass containing iron, remained colorless for several months in a bottle of the same kind of glass that had been coated on the inside with paraffin.

PHENATES.

Although its aqueous solution does not redden litmus, phenol is much more soluble in weak alkaline solutions than in pure water.

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[1] *J. S. C. I.,* 1893, 107.

[2] *Chem. Zeit. Rep.,* 1899, 47.

With equivalent amounts of the strong bases it forms compounds which are difficult to obtain in a definite form. The potassium and sodium compounds are readily soluble in water, and the solutions are not decomposed on dilution. *Potassium phenate*, C_6H_5OK, obtained by heating phenol with potassium or potassium hydroxide, crystallizes in slender white needles soluble in ether. De Forcrand[1] proposes to distinguish two series of derivatives—namely, "true phenates," corresponding to the general formula C_6H_5HO,MHO, and phenoxides, C_6H_5MO, the bodies of the latter class being capable of assimilating water so as to become metameric with the phenates.

PHENOL ETHERS.

On heating potassium phenate with alkyl iodides, ethers are produced. *Methyl phenate*, or anisoïl, $C_6H_5OCH_3$, is a mobile liquid of pleasant, aromatic odor, having a density of 0·991 and distilling unchanged at 152°. It dissolves in strong sulphuric acid to form methylphenolsulphonic acid, and with bromine yields substitution-products. Ethyl phenate and amyl phenate resemble the methylic ether.

PHENOL ESTERS.

Besides the foregoing bodies, which are of the type of the mixed ethers, many phenol esters are known, but have little practical importance. The production of phenol orthoxalate has been observed to occur in the manufacture of aurin; phenyl salicylate constitutes the antiseptic known commercially as "salol."

Béhal and Choay[2] have prepared the *benzoates* of various phenols, and recommend the method for their differentiation. With the exception of the orthocresyl compound, the benzoates are all crystalline solids, insoluble in water but very soluble in most organic solvents. They are prepared by the action of benzoic chloride on a solution of the phenol dissolved in excess of sodium hydroxide. The table on next page shows the melting and boiling points of the phenols and their benzoates, as recorded by Béhal and Choay, whose figures in some cases differ considerably from those of previous observers.

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[1] Abst. *J. S. C. I.*, 1893, 618.

[2] *Comp. rend.*, **118** (1894), 1211; Abst. *J. C. S.*, 1894, 449.

FORMULA.	COMPOUND.	PHENOL.		BENZOATE.	
		M. P. °C.	B. P. °C.	M. P. °C.	B. P. °C.
$C_6H_5.OH$	Phenol,	42·5–43	178·5	69	298–299
C_6H_4MeOH	Orthocresol,	30	178·5	liquid	307
	Metacresol,	4	200	54	313–314
	Paracresol,	36·5	199	71·5	315·5–316
$C_6H_3Me_2OH$	Orthoxylenol (1 : 2 : 3),	73	212–213	58	326–327
	Orthoxylenol (1 : 2 : 4),	65	222	58·5	333
	Metaxylenol (1 : 3 : 4)	25	208–209	38·5	321
	Para-xylenol,	75	208–209	61	318–319
C_6H_4EtOH	Ortho-ethylphenol,	liquid	202–203	38	314–315
	Meta-ethylphenol,	—4	214	52	322–325
	Para-ethylphenol,	45–46	218·5–219	59–60	328

1 : 3 : 5-metaxylyl benzoate melted at 24° and boiled at 326°. 1 : 2 : 3-metaxylenol could not be obtained. Parethylphenol is identical with the body sometimes called *a*-ethylphenol.

DETECTION AND DETERMINATION OF PHENOL.

The following reactions are in most cases common to phenol and the cresols. They do not require that the substance should be in a concentrated state, but are applicable to the aqueous solution. Many of them have been verified by the author. Various other reactions are described in the sections on "Cresylic Acid" and "Creosote."

a. When a drop of a dilute aqueous solution of phenol is added to a few drops of a solution of 1 grm. of molybdic anhydride in 10 c.c. of concentrated sulphuric acid, contained in a porcelain crucible, a yellowish-brown spot is produced, which rapidly changes to purple, the latter tint being tolerably permanent. Warming the mixture to about 50° C. greatly assists the reaction, but a higher temperature must be avoided. As this test depends on the deoxidation of the molybdic anhydride, many substances interfere with it.

b. Ferric chloride (avoiding excess) gives a fine violet color, by which 1 part of phenol in 3000 of water can be detected. Many allied bodies give a similar reaction (see pages 266, 288). The presence of common salt, nitre, or boric acid is unobjectionable, but the reaction is hindered by most mineral and organic acids, acetates, borax, sodium phosphate, glycerol, alcohol, amyl alcohol, and ether.

c. If an aqueous solution of phenol be gently warmed with ammonia and a solution of sodium hypochlorite (avoiding excess), a deep-blue color is obtained, which is permanent, but turns to red on addition of acids. Solutions containing 1 part of phenol in 5000 of water react well when 20 c.c. are employed. Much smaller quantities give the reaction after a time.

A modified, and in some respects preferable, method of performing the test is to add to 50 c.c. of the aqueous liquid to be tested 5 c.c. of a mixture of one measure of ammonium hydroxide of 0·880 specific gravity with nine measures of water, and then drop in fresh and dilute bromine-water very slowly, avoiding excess. The presence of phenol will be indicated by the production of a fine blue tint, which is very permanent. A still better plan is to expose the ammoniacal liquid to the vapor of bromine, avoiding excess of the latter.

d. According to E. Jacquemin, if to a neutral solution of phenol a minute quantity of aniline be first added, and then a solution of sodium hypochlorite be dropped in, the reagent produces yellow striæ, which change to a greenish blue. The reaction is said to be very delicate.

e. If 20 c.c. of a dilute phenol solution be boiled with 5 or 10 drops of Millon's reagent (prepared by dissolving mercury in an equal weight of fuming nitric acid, boiling, and diluting the solution with two measures of water), and nitric acid added drop by drop to the hot solution, until the precipitate is redissolved, the mixture assumes a fine blood-red color, which is permanent for several days. The reaction is exceedingly delicate, but is not peculiar to phenol.[1]

E. Hoffmann modifies this test by pouring 2 or 3 c.c. of the liquid supposed to contain phenol on to the surface of an equal measure of strong sulphuric acid, so as not to cause the liquids to become mixed. A few granules of potassium nitrite are then dropped in, when each particle will produce violet streaks if even a very minute quantity of carbolic acid be present.

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[1] E. Ackermann (*Rev. Chim. Ind.*, 1895, p. 322) obtained the following results when 0·01 grm. of the phenoloïd substance was acted on by about 20 drops of Millon's reagent: Beechwood creosote gave a reddish-brown coloration in the cold, the color remaining unaltered after 15 minutes' standing. On heating, the color changed to brownish-black. Creosol and guaiacol both gave a red coloration in the cold, changing to reddish-brown after 15 minutes. On heating, the color became brownish-black. Resorcinol gave an orange coloration in the cold, unchanged after 15 minutes, but changed to deep-red on heating. α-Naphthol gave an immediate red coloration in the cold, and β-naphthol gave a brown coloration on heating. Proteids, some morphine compounds, and various other substances also give with this reagent colorations which are often very similar to those given by phenoloids.

Liebermann has observed that strong sulphuric acid to which a 6 per cent. solution of potassium nitrite has been added gives a brown coloration, changing to green and blue when gently warmed with phenol or its allies.

f. The phenols give characteristic color-reactions with chloroform and alkali. The phenol is dissolved in chloroform, a small piece of potassium hydroxide added, and the solution boiled. The characteristic coloration is quickly developed. Reducing and oxidising agents affect the reaction, alcohol sometimes accelerates and sometimes hinders it, ether nearly always impedes it. In aqueous solutions the reaction is less sharp; in this case it is best to shake up with chloroform and proceed with the decanted chloroform as usual, or to extract with ether, boil the ether off, and dissolve the residue in chloroform. When testing for phenols in complex liquids, such as blood or the contents of a stomach, it is best to acidulate and distil in a current of steam. The distillate may then be examined as above.

The results of the test with some members of the phenol group are given on page 206. The following additional data relate to the behavior of substances not likely to be found in food or beverages when subjected to the foregoing test:[1]

Metacresol.—As with orthocresol, but a more marked orange shade.

Thymol.—Fine red coloration verging on purple, with a violet tinge, which is accentuated by the addition of a little alcohol or ether, and soon disappears. Limit of sensitiveness, 1:20,000.

Guaiacol.—Cherry-red coloration with a blue tinge, changing to violet-blue. Limit of sensitiveness, 1:100,000.

Resorcinol.—On warming gently, a cherry-red deposit on the potash and a brownish-yellow coloration of the chloroform; the chloroform ultimately takes up the color, which is fairly stable. Limit of sensitiveness, 1:500,000.

Quinol.—Bluish-green coloration, soon disappearing. Limit of sensitiveness, 1: 20,000.

Pyrogallol.—A reddish-brown coloration in the cold, which on warming takes on a green tinge, and on boiling soon disappears. Limit of sensitiveness, 1:300,000.

Betol.—Bluish-green coloration like β-naphthol. In this last case it is best to boil with a little potassium hydroxide, before

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[1] Abst. *J. S. C. I.*, 1890, 974.

adding the chloroform in order to saponify the ester. The colors then obtained are very characteristic.

g. Reaction of Phenol with Bromine.—When bromine water is added in moderate excess to an aqueous solution of phenol, a snow-white crystalline precipitate is formed, which readily collects into flocks on agitation, and appears under the microscope in the form of fine stellated needles. In presence of much cresylic acid or of certain other phenols the precipitate loses its crystalline character, and may even assume the form of yellow or reddish oily globules. In extremely dilute solutions the precipitate is only produced slowly; but in twenty-four hours a solution containing $\frac{1}{60000}$ of phenol gives the reaction.

The reaction with bromine was employed by Landolt to demonstrate the effect of a gas-works on the water of the neighboring wells; but the production of a white or yellowish precipitate with bromine-water is by no means conclusive evidence of the presence of carbolic acid, a similar reaction being produced by homologues of carbolic acid (*e. g.*, cresylic acid, thymol), besides other phenoloid bodies (*e. g.*, guaiacol, orcinol, pyrogallol, phloroglucol), salicylic acid, aniline, and various alkaloids.

On gradually adding bromine to a moderately concentrated solution of pure phenol, in a proportion not exceeding that necessary for the reaction $C_6H_5OH + Br_2 = C_6H_4BrOH + HBr$, a white turbidity is produced owing to the formation of the sparingly soluble *monobromophenol* (14:1000). If the solution be dilute, no actual precipitation occurs at this stage. On adding more bromine-water, a formation of *dibromophenol*, $C_6H_3Br_2.OH$, takes place, but often no further precipitation occurs until the bromine added exceeds the proportion:—$C_6H_5OHBr_4$. On further addition of bromine a very bulky precipitate is produced, and when the proportion of phenol is to that of the bromine as C_6H_5OH to Br_6, the whole is separated as the almost insoluble (1:14,300) and characteristic *tribromophenol*, $C_6H_2Br_3OH$. By the action of excess of bromine the hydrogen of the hydroxyl is replaced, in addition to three atoms of the phenylic hydrogen, the reaction being:—$C_6H_5OH + Br_8 = C_6H_2Br_3OBr + 4HBr$. This body, tribromophenol bromide, crystallises in scales, is gradually decomposed by water, and reacts with potassium iodide in acid solution according to the equation:

$$C_6H_2Br_3OBr + 2KI + 2HCl = C_6H_2Br_3OH + 2KCl + 2HBr + I_2.$$

Neither the free iodine nor an excess of potassium iodide has any effect on the tribromophenol. Hence, if it be desired to determine the amount of phenol in an aqueous liquid, it may be effected by adding bromine-water in excess, followed by potassium iodide, and then titrating back with a standard solution of sodium thiosulphate in the usual manner. By operating in this way, it is a matter of indifference whether $C_6H_2Br_3OH$ or $C_6H_2Br_3OBr$ be first formed, as by the subsequent treatment with potassium iodide the latter body is converted into the former.[1]

The formation of tribromophenol as a means of determining phenol was first suggested by Landolt, who operated gravimetrically. The method was greatly improved by Koppeschaar, who devised a volumetric process. This method has been modified by various chemists with more or less advantage. With this process it often happens that the liquid, after being decolorized by thiosulphate,

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[1] TRIBROMOPHENOL. $C_6H_2Br_3OH$. This body has a very peculiar and persistent odor, melts at 92° C., and readily volatilises. It is almost insoluble in water and dilute acid liquids, but is readily soluble in ether, chloroform, carbon disulphide, etc. It dissolves in absolute alcohol, but is precipitated from the solution by a very small quantity of water.

Tribromophenol has marked acid properties. It dissolves in the fixed alkalies and in ammonia, and the latter solution yields on evaporation sparingly soluble crystalline needles of ammonium tribromophenate, $NH_4OC_6H_2Br_3$, and from this other tribromophenates may be obtained by double decomposition. The metallic solutions must be perfectly neutral, or a flocculent precipitate of tribromophenol will be obtained. The silver salt forms an orange-yellow flocculent precipitate, the cupric salt is reddish brown and flocculent, and the lead salt white. The nickel salt is insoluble and dark red, but no precipitate is obtained with solutions of cobalt.

The author has investigated the reactions of the *tribromophenates* with a view of finding a means of estimating phenol and cresol in mixtures of the two, but has met with only very partial success, partly owing to the difficulty of preparing a soluble salt of tribromocresol. The following differences were observed in the reactions with neutral solutions of metallic salts of ammonium tribromophenate and sodium tribromocresolate from coal-tar cresol:

WITH SOLUTION OF	PHENOL-DERIVATIVE.	CRESOL-DERIVATIVE.
Silver nitrate.	Orange-yellow, flocculent.	Cream colored, flocculent.
Nickel sulphate.	Dark-red, dissolved on boiling.	Dark red, not dissolved on boiling.
Cobalt nitrate.	No precipitate.	Light brown, flocculent.
Calcium chloride.	No precipitate.	White, flocculent.
Barium chloride.	White, crystalline, readily soluble in hot alcohol.	White, flocculent, not readily dissolved by hot alcohol.
Magnesium sulphate.	No precipitate.	White, flocculent.

acquires a blue color on standing. This is said to be caused by bromine (or iodine?) being retained by the oily tribromocresol, and only slowly dissolving in the supernatant fluid. To overcome the difficulty L. de Koningh recommends that the liquid should be poured off and the insoluble matter dissolved in a little alcohol; a 20 per cent. solution of potassium iodide and some starch are then added, and the titration continued.

A very simple means of determining carbolic acid in soap by direct titration with bromine water is given in Volume II, part 1, page 281, but the process there described is not adapted to yield results of more than approximate accuracy. Very good results are obtainable by the wet bromine process of determining olefins described on page 24. In some cases it is preferable to substitute for the bromine-water a standard solution of sodium bromate of known strength. A known quantity of the sample to be examined (containing from 0·2 to 0·5 of phenol) is introduced into a stoppered flask, together with a solution of potassium bromide and some dilute hydrochloric acid, and the liquid then diluted to about 100 c.c. with water. A known volume of the standard solution of sodium bromate is then run in, sufficient being used to ensure a permanent reddish coloration due to excess of bromine. The solution should contain 15·1 grm. of sodium bromate per litre. The flask is then closely stoppered, well shaken, and allowed to stand at rest for half an hour to ensure the completion of the reaction. By the reaction $5KBr + NaBrO_3 + 6HCl = 5KCl + NaCl + 3Br_2 + 3H_2O$, bromine is set free and acts on the phenol. A solution of potassium iodide is then added in excess, and the liquid titrated back with a decinormal solution of sodium thiosulphate (24·8 grm. of the crystallised $Na_2S_2O_3$ per litre), each 1 c.c. of which represents 0·008 grm. of bromine in excess of that which has reacted with the phenol, 0·094 grm. of which causes the disappearance of 0·480 grm. of free bromine, or as much as will be liberated by 10 c.c. of the sodium bromate solution. Instead of preparing a standard solution of sodium bromate, it is preferable to compare the sample to be tested with one of pure phenol.

Titration in carbon disulphide solution is not applicable to the determination of phenol, the proportion of bromine required being much less than corresponds to the formation of tribromophenol, apparently owing to the formation of an additive-compound. Titration by bromine in aqueous solution may be applied to a number of phenoloid bodies with more or less success, but an extensive series of experiments made in the author's laboratory by J. C. Belcher gave very disappointing results in many cases, apparently owing to the occurrence of secondary reactions forming quinones, etc.

h. An iodometric method of estimating phenol has been devised by Messinger and Nortmann.[1] Three grm. of the sample are dissolved in a little more than 4 grm. of sodium hydroxide ($C_6H_5HO + 3NaHO$), the solution made up to 500 c.c. Ten c.c. of this solution are now warmed to 60° C. in a small flask, and decinormal iodine run in until the liquid has attained a deep-yellow color. The mixture is cooled, acidified with dilute sulphuric acid, made up to 500 c.c., and an aliquot part (*e. g.*, 100 c.c.) titrated with decinormal sodium thiosulphate. The amount of iodine used, calculated to the whole amount of the sample taken and multiplied by 0·1235, gives the phenol present.

C. E. Smith[2] has investigated some common methods of assaying commercial phenol and finds them far from accurate. He recommends the following method as an improvement: One grm. of the sample is placed in a 100-c.c. flask, about 90 c.c. of water added, the mixture briskly shaken, and the flask filled to the mark. Two c.c. of sample (0 02 grm.) are withdrawn, avoiding any undissolved matters, placed in a 150-c.c. flask, which can be tightly closed, 10 c.c. of water, 12 c.c. decinormal bromine, and 2 c.c. of hydrochloric acid added, the flask closed and shaken well at intervals during half an hour. Two c.c. of solution of potassium iodide are added in such a manner as to avoid loss of bromine and the liquid is then titrated with decinormal sodium thiosulphate until decolorised. If the sample contains a notable amount of cresol, the solution will again become yellow. This change should be promoted by brisk shaking after each addition of thiosulphate, which must be continued until the solution is colorless after prolonged shaking. The number of c.c. of thiosulphate solution used, deducted from 12, gives the number of c.c. of decinormal bromine required.

A method for determination of phenols, devised by S. B. Schryver,[3] is based on the fact that sodamide, $NaNH_2$, reacts with hydroxides according to the following equation:

$$NaNH_2 + C_6H_5OH = NH_3 + C_6H_5ONa.$$

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[1] *Ber.*, 1890, 2753; Abst. *J. S. C. I.*, 1890, 1070.

[2] *Amer. Journ. Pharm.*, 1898, 369.

[3] *J. S. C. I.*, 1899, 553.

For each molecule of hydroxyl decomposed one molecule of amine is liberated. The process consists in bringing an excess of sodamide into a solution of the phenol, using a solvent upon which the reagent has no action. Benzene free from thiophene has been usually employed. The apparatus used is shown in figure 9.

About 1 grm. of sodamide is finely ground, washed two or three times by decantation with pure benzene, and introduced into a 200 c.c. flask (A) connected with an inverted condenser. About 60 c.c. of benzene are added, and the mixture is then boiled on a water-bath, while a current of air free from moisture and carbon dioxide is drawn continuously through the separating funnel, the lower end of which dips below the liquid. The boiling and aspirating are continued for ten minutes, to draw off the last traces of ammonia which adhere to the amide. Twenty c.c. of normal sulphuric acid are introduced into the absorption bottle (C). The weighed portion of the sample, dissolved in about six times its weight of benzene, is placed in the bulb of the separator funnel and the solution allowed to drop slowly into the mixture of sodamide and

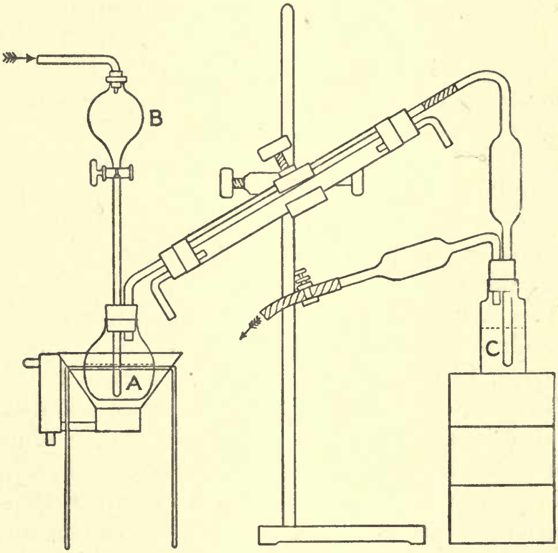

Fig. 9.

benzene, which is kept boiling continuously and connected with an aspirator. As soon as all the solution has been added, the funnel is washed with a little benzene, and air drawn through the apparatus until no ammonia remains unabsorbed. One and a half hours are generally necessary for this, as ammonia is held rather obstinately by benzene. At the end of the operation the excess of acid is determined by titration (methyl-orange was generally used as an indicator).

To obtain accurate results the materials used and the apparatus must be free from moisture. Sufficient benzene must be used to hold the sodium compound in solution, and it must be free from sulphur compounds. A liberal aspiration of air should be employed. No particular advantage results from substitution of toluene or xylene for benzene. The number of c.c. of normal sulphuric acid required to neutralize the ammonia produced by 1 grm. of the phenol is designated by the author of the process as the "hydroxyl value."

Schryver found fused sodium acetate to be the most suitable drying agent for phenol. The process is applicable in the presence of many hydrocarbons which would act on bromine or iodine, but do not act on sodamide. It may also be employed for determining the proportion of water in phenols, and for determination of phenols in certain essential oils.

Riegler[1] has described a method of determining phenol based on its reaction with paradiazonitraniline to form a soluble red diazo-compound of the formula $C_6H_4NO_2N_2C_6H_4ONa$. On strongly acidulating the solution with dilute sulphuric acid the corresponding diazo-acid separates practically quantitatively, and may be weighed after drying at 100° C. The process is also applicable to thymol, guaiacol, etc., but is not available in presence of ammoniacal salts and amines.

A toxicological examination for phenol is not infrequently necessary, owing to the numerous instances in which poisoning has ensued from the accidental administration of the substance internally. In such cases the mouth and esophagus are commonly white, soft, and corroded, but are sometimes found hardened and shrivelled.

The stomach is usually white, contracted, thickened, and shrivelled, but is sometimes intensely congested, with destruction of the

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[1] *Chem. Centr.*, 1899, 322.

mucous membrane. Occasionally, no abnormal appearance is observable. The intestines are usually thickened and congested. The bladder is generally nearly empty; any urine present will have a dark color.

In testing animal matters for phenol the odor is a most valuable indication. For the recognition of the poison the suspected matters are cut up and well shaken with water acidulated with sulphuric acid. The liquid is then distilled as long as bromine water renders the distillate milky, and the tests for phenol applied to the distillate. The characters of most service are: the odor; the reactions with ferric chloride, sodium hypochlorite, and bromine; and the property of coagulating albumin.

The distillate obtained as above is concentrated by shaking with ether, separating the ethereal layer, and examining the residue of its evaporation; when the amount of phenol is very small, the ether should be shaken with a little dilute sodium hydroxide, the alkaline liquid concentrated, and exactly neutralized by dilute sulphuric acid before applying the foregoing tests.

In cases of suspected poisoning it must be remembered that phenols exist normally in minute quantity in urine, and are formed in small quantity during putrefaction.

Commercial Carbolic Acid.

The better varieties of commercial phenol are well represented by the articles manufactured by F. C. Calvert & Company. Their "No. 1 Carbolic Acid," in the form of colorless crystals, may be regarded as chemically pure and absolute, and free from homologous phenols, the proportion of which gradually increases in the lower grades till the dark liquid known as "No. 5 Carbolic Acid" consists chiefly of *cresylic acid*, with smaller proportions of *higher homologues*. A preparation known as "Carbolic Acid No. 4," containing about 95 per cent. of phenols, is much used as a general disinfectant.

In addition to containing water and homologous phenols, the lower grades of commercial phenol are often largely adulterated with *neutral tar oils* ("naphthalene oils") which are of little value as antiseptics.

In the opinion of the author, the various modifications of the bromine process of determining phenols are ill suited for the examination of commercial carbolic acid and its preparations, owing to the fact that ortho- and para-cresol form only dibromo-derivatives. This fact, together with the difference in the molecular weights of phenol and its homologues, renders the results of little quantitative value, unless carbolic acid of the same quality as the sample be used as a standard of comparison. Although, as stated above, the term "carbolic acid" has been extended commercially so as to include products consisting substantially of cresylic acid or still higher homologues of phenol, it is straining its legitimate signification to apply it to products in which real carbolic acid is conspicuous by its absence. The inexact description becomes still more objectionable when the article is purposely mixed with neutral tar-oils, or other hydrocarbons of little direct value as antiseptics. This has been practised to an enormous extent, "carbolic acid" and "carbolic powders" sold to corporations and other sanitary authorities affording a fertile field for the operations of the blender.

For the approximate determination of *tar oils* in crude carbolic acid the following method may be used:—Introduce 10 c.c. of the sample into a graduated tube, and add gradually, noting the effect produced, four times its volume of a 10 per cent. solution of sodium hydroxide free from alumina. Then close the tube and agitate well. The coal-tar acids will be completely dissolved by the alkaline liquid; whilst, on standing, the neutral oils will form a separate stratum above or below the other, according as the admixture consisted of the light or heavy "oil of tar." The volume occupied by the oily stratum at once indicates the extent of the adulteration. After noticing whether the tar oils are light or heavy, a volume of petroleum spirit or benzene equal to that of the sample taken may be advantageously added. Its employment facilitates the separation of the oily stratum and renders the reading of its volume more easy and accurate. Of course, the volume of petroleum spirit or benzene used must be deducted from that of the total oily layer.

If the liquid be subsequently acidulated with dilute sulphuric acid and shaken, the layer that separates will contain the phenol, and its measure deducted from that of the original sample (after allowing for the volume of the hydrocarbon added) will give the amount of water in the sample.

When a more accurate determination of the neutral oils is required, and there is sufficient of the sample at disposal, the modified process described in the section on "Creosote Oils" (page

559) may be used with advantage. The specific gravity of crude phenol at the ordinary temperature should be between 1·050 and 1·065. If less, it is suspicious. In presence of light tar oil the specific gravity is often as low as 1·045 or 1·040.

The determination of the *water* in crude phenol is best effected by distilling a known quantity of the sample, collecting the distillate in a graduated tube, and noting the volume of the aqueous portion. The results are from 0·3 to 0·5 per cent. too low. The inferior grades of crude carbolic acid contain the smallest proportion of water. The following method of assaying crude phenol with a view to ascertaining its quality and the approximate proportion of crystallisable phenol contained in it is due to the late Chas. Lowe, and is largely employed by manufacturers:—1000 grains or 100 c.c. of the sample are placed in a retort (without any special condensing arrangement), and distilled, the liquid which passes over being collected in graduated tubes. Water first distils and may be measured, and is followed by an oily fluid. When 10 per cent. by measure of the latter has been collected, the receiver is changed. The volume of *water* is then read off. If the oily liquid floats on the water, it contains *light oil of tar*. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 per cent. of phenols. The next portion of the distillate consists of anhydrous phenols, and when it measures 62·5 per cent., the receiver is again changed. The residue in the retort consists wholly of cresols and higher homologues. The 62·5 per cent. of anhydrous phenols contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining the solidifying point, which should be between 60° and 75° F. (15·5° and 24° C). Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made in such proportions as to have the same solidifying point. This must be adjusted by trial, or a series of standard specimens may be prepared. The exact point of solidification can be more sharply read if a minute fragment of crystallised carbolic acid be added to induce the commencement of the change of state; or the sample may be solidified, and the liquefying point noted.

Many qualities of crude carbolic acid now contain a comparatively small proportion of light oils (5 to 6 per cent.), and hence a notable quantity of phenol is lost in the 10 per cent. first distilled.

This raises the proportion of cresols in the 62·5 per cent. next collected, and hence a product is obtained having too low a solidifying point. A preferable plan of assaying the second and third qualities would probably be to reject all that passes over below 185°; then distil to 190° or 195°, and take the measure and solidifying point of this fraction. For No. 1 quality, with 62½ per cent. of distillate crystallising above 70° F., only the portion passing over below 180° to 182° should be rejected. About 12 per cent. of water may distil from this kind of acid, though the proportion ranges from 10 to 17 per cent., and also 10 per cent. of neutral oils may be present. By stipulating that a sample should contain a certain proportion of anhydrous phenols (exclusive of neutral oils as estimated by soda) distilling below a given temperature and having a definite solidifying point, a more accurate knowledge of the product would be obtained. The quality of the sample might be also simply expressed in units of anhydrous phenols solidifying at a certain fixed temperature.

The mixtures of phenols from shale-tar and blast-furnace creosote are liable to be sold for crude carbolic acid. They may be distinguished from the coal-tar product, as described on page 290.

CARBOLIC ACID DISINFECTING POWDERS.[1]

A variety of disinfecting powders are now made, which owe their efficacy chiefly to the fact of their containing more or less phenols. In some cases the base of the powder is slaked lime, but the so-called "carbolate of lime" is of little value for antiseptic purposes. "Macdougall's Disinfecting Powder," the oldest preparation of the kind, was made by adding a certain proportion of crude carbolic acid to a crude calcium sulphite, prepared by passing sulphurous acid gas over ignited limestone. Sulphurous acid is introduced into other powders by the direct addition of a solution of calcium acid sulphite. "Calvert's Carbolic Acid Powder" is made by adding carbolic acid to the siliceous residue resulting from the manufacture of aluminum sulphate from shale or kaolin. Calcium sulphate is likewise a suitable absorbent, and kieselguhr has been used for the stronger powders. The use of peat as an absorbent of carbolic acid has been patented by West Knights and Gall, while Allen and Angus have proposed the

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[1] The examination of liquid antiseptic preparations containing phenols and cresols is described on page 261 *et seq.*

use of blast-furnace slag. Limestone is also used. The use of spent gas-lime has been patented by Austin. A mixture of bleaching powder and phenol has also received protection. Macdougall Brothers have employed soluble salts as absorbents, the resultant powder being more readily removed and less liable to choke up drain-pipes than the preparations commonly employed. A step in the same direction is *borophenol*, prepared by absorbing carbolic acid by dried borax.

Good carbolic acid powders contain at least from 12 to 18 per cent. of crude carbolic acid, but higher strengths are obtainable. As much as 50 per cent. is absorbed by kieselguhr. All carbolic powders are liable to lose 1 or 2 per cent. by volatilisation. Some powders in the market contain but 5 or 6 per cent. of total oils, of which less than half is really carbolic and cresylic acids, the remainder being neutral tar oils.

For the determination of the phenols and tar oils in disinfecting powders having a siliceous base, and in others containing the phenol in the free state, 50 grm. should be exhausted with ether in a Soxhlet-tube or similar arrangement. The ethereal solution is then agitated with about 20 c.c. of a 20 per cent. solution of sodium hydroxide, more or less than this quantity being employed according to the percentage of phenols supposed to be present in the powder (and about 1 c.c. of the reagent being used for every 1 per cent. of phenols in the sample). The ethereal layer is separated, and the alkaline liquid again shaken with ether, which is separated as before, and added to the main quantity. The united ethereal solutions are shaken with some caustic soda solution, to dissolve out any phenols which may have escaped the previous treatment. The ether is then driven off by a gentle heat, and the residual oils are weighed. The united alkaline liquid is boiled down in a flask to a small bulk (10 c.c.), and transferred to a burette or other suitably graduated tube, where it is treated with diluted sulphuric acid (1 : 3) in quantity sufficient to render the liquid distinctly acid to litmus after agitation. When the liquid has stood for some time and is *thoroughly cold*, the layer of separated phenols is measured. Each cubic centimetre weighs about 1·050 grm., so that an addition of 5 per cent. to the measure gives the correct weight. The results are fairly accurate, but generally below the truth, owing chiefly to the solubility of phenols. Hence the liberation of the phenol should be effected in a liquid as concentrated as possible.

In cases in which the characters of the separated phenols suggest the presence of fatty acids, resin, or other foreign matter, the contents of the burette should be transferred back to the flask, diluted with water, and distilled. The phenols readily pass into the distillate, whereas any fatty or resin acids will remain in the retort.

In the case of powders made with lime, or others in which the phenols exist in combination, the method of direct extraction with ether or other solvent does not give accurate results. For the determination of the crude carbolic acid in such powders, the disinfectant value of which is very doubtful, the following method may be employed:—50 grm. of the sample should be mixed in a large mortar with 5 c.c. of water. Strong sulphuric acid, previously diluted with an equal bulk of water, is then added very gradually, a few drops only at a time. After each addition the whole is well mixed together with a pestle. The addition of the acid, which should extend over some hours to avoid sensible rise of temperature, is continued until a minute fragment of the well-mixed contents of the mortar shows an acid reaction when placed on a piece of litmus-paper and moistened with water. If the mixture be pasty, sufficient sand is added to cause it to granulate, and the mortar is then covered up and left for some hours. By this method the lime, sulphuric acid, and water form hydrated calcium sulphate and the phenols are liberated. The product is then exhausted with ether in a Soxhlet-tube or similar contrivance.

Whether isolated by the extraction or the distillation process, the crude carbolic acid obtained should be further examined for *neutral tar oils,* which not infrequently constitute the greater part of the so-called "carbolic acid" of disinfecting powders. For their detection, the test with dilute soda described on page 251 will usually be found sufficient. In other cases the crude carbolic acid should be treated with twice its measure of a 20 per cent. sodium hydroxide solution (1·2 sp. gravity), any undissolved oils separated, and the alkaline solution shaken with ether to remove any neutral oils still remaining dissolved. The ethereal layer is separated, added to the neutral oils previously obtained, the ether driven off by a gentle heat, and the residual neutral oils or naphthalene measured or weighed. The alkaline solution of the phenols is boiled in a small flask to drive off the ether, and acidulated in a narrow, graduated tube or a burette with diluted sulphuric acid (1:3), and the layer of separated phenols is measured, as described on page 251.

The *sulphurous acid* contained in certain disinfecting powders may be determined by stirring 1 grm. of the sample in a mortar with a small quantity of distilled water free from air, and decanting the liquid into a flask containing 50 c.c. of the ordinary decinormal solution of iodine and about 250 c.c. of water. The residue in the mortar is repeatedly treated with fresh quantities of water, the resultant liquids being transferred to the flask, and finally the undissolved powder is rinsed in. Very dilute hydrochloric acid is next cautiously added to the contents of the flask, until the reaction is distinctly acid, when the excess of iodine is determined by titration with decinormal thiosulphate in the usual way. Each c.c. of decinormal iodine reduced represents 0·0032 grm. of SO_2.

Cresols. Cresylic Acids. METHYLHYDROXYBENZENES.

$$C_7H_8O = C_6H_4(CH_3)(HO).$$

Cresol being formed by the substitution of two of the hydrogen atoms in benzene, by methyl and hydroxyl respectively, three isomeric forms are possible (see page 235), all of which occur in the crude cresylic acid from coal-tar. Any modification of cresol can be obtained pure by dissolving the corresponding form of toluidine and an equal weight of sulphuric acid in about thirty parts of hot water. An aqueous solution of potassium nitrite is next added in quantity sufficient for the reaction :

$$C_7H_7.NH_2 + KNO_2 + H_2SO_4 = C_7H_7.OH + KHSO_4 + H_2O + N_2.$$

The liquid is then saturated with common salt or sodium sulphate, allowed to cool, and the layer of cresol separated and purified by distillation. The following table shows some distinctions between the cresols, according to various observers :

	ORTHOCRESOL.	METACRESOL.	PARACRESOL.
Melting point ° C, . .	30; 31–31·8	4; 3–4	36; 36–37
Boiling point ° C, . .	188; 190·8	201; 202·8	201·8; 198–199
Specific gravity at 0° C, ...	1·0578	1·0498	1·0522
Coefficient of expansion, ...	0·00072	0·00078	0·00086
Solubility in water, .	1 in 40	1 in 200	1 in 55
Highest bromo-derivative, ...	Br_2; m. p. 52°	Br_3; m. p. 82°	Br_2; m. p. 49°
Highest nitro-derivative, ...	$(NO_2)_2$; m. p. 85·8°	$(NO_2)_3$	$(NO_2)_2$; m. p. 82·5

The melting and boiling points recorded by different observers are not in very perfect concordance. The specific gravities and coefficients of expansion are figures by Pinette (Annalen, 243, 43), and apparently refer to the liquid cresols, which exhibit, in a marked manner, the phenomenon of superfusion. The "highest bromo-derivative" means the most highly brominated substitution-compound which does not react with potassium iodide. Thus, in the case of phenol it would be $C_6H_2Br_3.OH$, not $C_6H_2Br_3.OBr$.

Metacresol forms a tribromo- and trinitro-derivative, whereas the ortho- and para- forms give only di-substitution products.[1]

When fused with potassium hydroxide, the cresols are converted into the corresponding forms of hydroxybenzoic acid (see under Salicylic Acid).

Orthocresol forms a hydrate of the composition $C_7H_8O + H_2O$, which is liquid at ordinary temperatures, has a specific gravity of 1·06, and is soluble in ether and alcohol in all proportions. According to H. Nördlinger, 100 parts of cold water dissolve 3 parts of orthocresol; but Gruber gives the solubility as 2·5 per cent. by measure: the figure for metacresol being 0·53; for paracresol, 1·8; for mixed coal-tar cresols, 2·55; for mixed cresols from toluidine, 2·2; and for phenol, 6·0 per cent. The last figure is certainly too low.

Nördlinger states that orthocresol is less poisonous and corrosive than its isomers, and can be produced with ease in large quantities and at a lower price than the other forms. A 1 per cent. aqueous solution of orthocresol is not decomposed or rendered turbid by acids or neutral salts, does not affect the skin or render the hands slippery or numb, and has no action on metals. Solutions containing 0·25 to 1 per cent. are stated to have an antiseptic power equal to solutions of phenol containing from 2 to 5 per cent. of phenol.

According to Nördlinger, the three modifications of cresol may be distinguished by their behavior with ammonia. When a few drops of orthocresol are shaken with a few c.c. of ammonia solution the mixture becomes bluish on standing,—like a dilute solution of cupric sulphate,—but after a few days it acquires a deep indigo-blue color and becomes opaque. Paracresol, when treated similarly,

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[1] According to Ditz and Cedivoda (*Zeit. Angew. Chem.*, 1899, 873, 897), ortho- and paracresol form tribromo-derivatives, but these are converted into the corresponding dibromocresols by potassium iodide. Metacresol forms $C_7H_4Br_3OBr$, which is converted into $C_7H_4Br_3OH$ by potassium iodide.

gives a transparent pale yellow liquid. Metacresol also gives a transparent liquid, which at first has a faint steel-blue color, afterward becoming bluish, but the tint is distinguishable from the deep indigo-blue yielded by orthocresol.

CRESYLIC ACID FROM COAL-TAR.—The three isomeric cresols are stated by Schulze to exist in gas-tar approximately in the proportions of 35 per cent. of orthocresol, 40 of metacresol, and 25 per cent. of paracresol. 1 : 3 : 5 and 1 : 2 : 4 xylenols have been found in the fraction of gas-tar phenols boiling between 170° and 210°. Cresylic acid from gas-tar has a density of 1·039 to 1·044. It closely resembles phenol, but is liquid at common temperatures, far less soluble in water, and boils at a higher temperature. The boiling point of commercial cresol is variable, as it contains more or less phenol and higher homologues. Samples of commercial phenol (even when anhydrous) containing much cresylic acid remain fluid at ordinary temperatures, and are less soluble in water and dilute alkaline liquids than is pure phenol. Cresylic acid resembles phenol in its reaction with ferric chloride. With some samples the blue coloration first produced rapidly changes to brown (compare page 288).

Cresylic acid dissolves in dilute sodium hydroxide solution containing far less alkali than corresponds to the proportion C_7H_8O : NaHO, but on adding water two layers are formed, the lower one of which closely resembles cresylic acid, but sometimes occupies a considerably greater volume than that of the sample used. When acted on by strong nitric or sulphuric acid cresol gives similar, but not identical, products with those yielded by phenol. With excess of bromine it produces a similar body, but brominated cresol from coal-tar cresylic acid is liquid at ordinary temperatures, whereas the phenol derivative is solid.[1]

The following table shows the chief differences of analytical value existing between phenol and cresylic acid. The statements have been personally verified by the author upon a sample of Calvert's "No. 1 carbolic acid" and a cresylic acid prepared purposely by careful fractional distillation of a sample of Calvert's "No. 5 carbolic acid." The cresylic acid was further purified by dissolving it in sodium hydroxide and agitating the solution with ether to remove naphthalene and other hydrocarbons, the cresol being subsequently recovered by addition of acid. If

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[1] See the author's paper on Commercial Cresylic Acid, *J. S. C. I.*, 1890, 141.

this treatment be omitted, scales of naphthalene, &c., are liable to separate on treating the sample with ammonium hydroxide.

	PHENOL.	CRESYLIC ACID.
Melting point.	Solid at ordinary temperatures; liquefied by addition of water; in both absolute and hydrated condition solidified by freezing mixture.	Liquid at ordinary temperatures; neither absolute nor hydrated acid is solidified by freezing mixture.
Boiling point.	182° C.	198° to 203° C.
Solubility of hydrated acid in cold water.	1 volume in 11.	1 volume in 29.
Solubility in ammonium hydroxide (sp. grav. 0·880) at 15° C.	Completely and readily soluble in equal volume; solution not precipitated by addition of less than 2½ volumes of water.	Soluble in equal volume; the solution is precipitated by slight cooling or dilution.
Reaction with petroleum spirit.	Absolute acid is miscible with *hot* petroleum spirit in all proportions. Miscible with only ½ volume of *cold* petroleum spirit; precipitated by greater proportion. With 3 volumes petroleum spirit, bulk unchanged; upper layer contains carbolic acid, which crystallises out on sudden cooling by freezing mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum spirit.
Behavior with glycerol of 1·258 sp. grav. at 15° C.	Miscible in all proportions. One measure of phenol with an equal volume of glycerol is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 volumes of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerol, is completely precipitated by 1 measure of water.

All the cresols possess antiseptic and disinfectant properties to a greater degree than phenol, metacresol being the most active, but the sparing solubility of all the cresols in water is a serious disadvantage (see page 257).

From these reactions it will be seen that cresylic acid is less soluble than phenol in water, ammonia, and glycerol, but it is more soluble in petroleum spirit.[1] Although the above tests suffice for the detection of considerable proportions of cresylic acid in admixture with phenol, they afford no basis for its quantitative determination, except of the roughest kind. Encouraging results have been obtained by Ewell and Prescott by the use of a 9 per cent. solution of sodium hydroxide.[2] The best means of even approximately determining the proportion of cresylic acid present in samples of crude phenol is by fractional distillation, as described on page 252.

The following table shows the behavior of three typical samples of *commercial cresylic acid* when distilled in a flask furnished with a dephlegmator:

	COMMERCIAL.	COMMERCIAL.	ONCE-RUN.
Specific gravity,	1·041	1·049	1·038
Water,	trace	8·5	0·5
First drop distilled at	120°	90°	95°
Percentage distilling below 180°,	0·2	2·5	0·5
,, ,, from 180° to 190°,	4·6	4·0	1·0
,, ,, ,, 190° to 195°,	56·6	16·5	15·5
,, ,, ,, 195° to 200°,	23·0	20·0	36·0
,, ,, ,, 200° to 205°,	10·0	16·0	19·5
,, ,, ,, 205° to 210°,	. .	9·5	11·0
,, ,, ,, 210° to 215°,	. .	6·0	6·0
,, ,, ,, 215° to 225°,	. .	6·6	6·5
Total,	96·4	89·5	96.5

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[1] According to W. W. Staveley, absolute phenol is soluble in petroleum spirit, but is separated by water. The separation is prevented by the presence of from 20 to 25 per cent. of benzene in the petroleum spirit. Anhydrous cresol is also soluble in petroleum spirit, and is separated by water. On adding a saturated solution of calcium chloride, the water is taken up and the cresol redissolves in the petroleum spirit. The first fraction of neosote behaves like cresol. As a whole, neosote dissolves in petroleum spirit and is not separated by water.

[2] *Analyst*, 1888, 237.

A sample of Calvert's "No. 5 carbolic acid," when fractionated in the same manner, gave 6·8 per cent. over below 180° (including 5·5 per cent. of water), 5·6 between 180° and 186°, 46·8 between 186° and 190°, 28·8 between 190° and 195°, and 7·0 between 195° and 200°; the total over at this temperature being 95·0 per cent. by measure. The last three fractions distilled had a specific gravity of 1·0541, 1·0430, and 1·0370, respectively. The gradual decrease of gravity with increase in the boiling point is a constant feature in the fractionation of phenols.

The phenoloids of blast-furnace tar, contained in the "neosote" of commerce are chiefly cresols.

Phenolic Disinfecting Liquids.

According to Engler and Dieckhoff (*Arch. Pharm.*, 1892, CCXXX, 562) cresol is only very slightly soluble in a solution of sodium acetate, but is miscible in all proportions with a 50 per cent. solution of sodium valerate. It also dissolves readily in a 15 per cent. solution of sodium oleate, one part of this compound rendering five parts of cresol soluble in water. Solution of rosin soap also dissolves cresols in large proportions. These facts explain the possibility of preparing phenolic disinfectant liquids (*e. g.*, "Jeye's fluid," "lysol"), some of which contain as much as 50 per cent. of cresylic acid. The aqueous solutions of the salicylates, benzoates, phenylacetates, &c., of the alkali metals, ammonia, and of aniline, also dissolve cresylic acid, and their use for the preparation of soluble disinfectants containing the higher phenols has been patented by F. von Heyden (*Eng. Patent*, 1890, No. 9103).

While the higher phenols are rendered soluble in water by the presence of a suitable proportion of soap, the use of soap also furnishes a means of preparing aqueous solutions of hydrocarbons, the solubility of which is greatly increased by the simultaneous presence of phenols.

The popularity of phenol and the cresols as antiseptics and disinfectants has led to the production of many proprietary and patented preparations containing, or purporting to contain, these bodies.[1] The following may be mentioned, but the sanitary applications of this class of bodies are of much less importance than formerly, since the more exact investigations of modern bacte-

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[1] For a list and brief statement of the character of many of these preparations see *The Newer Remedies*, by V. Coblentz.

riology have discredited in part the value of the phenols as germicides:

Creolin (Cresoline, Sanatol).—Two forms of this preparation are sold, known respectively as Artmann's and Pearson's. The former is obtained by the action of sulphuric acid on crude cresol. The latter contains cresol and some of the hydrocarbons of coal-tar held in emulsion by a resin-soap.

Lysol.—This is the fraction of coal-tar which boils between 190° and 200° C., dissolved in fat and saponified. It is a clear, brown syrup, containing about 50 per cent. of cresols and is miscible with water. A little naphthalene is also present.

Saprol (which must not be confounded with *Asaprol*, see page 206) is a mixture of crude cresols with some petroleum products.

Sapocarbol is a solution of crude cresols in a potassium soap.

Solutol and *Salveol* contain sodium cresylate with excess of cresol.

The following method for the analysis of sheep dips and the foregoing phenolic disinfecting liquids is that employed in the author's laboratory:

<table>
<tr><td colspan="4">Treat 50 grm. of the sample with dilute sulphuric acid (1 : 3) until the liquid is distinctly acid to litmus, shake with ether, and separate.</td></tr>
<tr><td rowspan="3">ACID LIQUID.—Render alkaline with caustic soda and distil. Titrate distillate with seminormal acid, using methyl-orange as an indicator. (1 c.c. normal acid neutralises 0·079 grm. *pyridine.*)</td><td colspan="3">ETHEREAL LAYER.—Shake with 20 c.c. (more or less, according to the amount of phenols, &c., supposed to be present) of a 25 per cent. solution of caustic soda, and separate.</td></tr>
<tr><td rowspan="2">ETHEREAL LAYER.—Distil off ether and weigh residue of *hydrocarbons* (*e.g.*, rosin-oil, tar-oil, naphthalene, &c.).</td><td colspan="2">ALKALINE LIQUID.—Acidify with sulphuric acid (1 : 3) and distil until no more oily drops pass over.</td></tr>
<tr><td>DISTILLATE.—Evaporate to low bulk with 20 c.c. of a 25 per cent. solution of caustic soda (or sufficient to fix all the phenols), transfer to a burette, acidify slightly with sulphuric acid (1 : 3), keeping thoroughly cool all the time, and measure layer of *phenols.* The volume in c.c. multiplied by 1·05 equals the weight of phenols in sample taken.</td><td>RESIDUE IN RETORT.—Shake with ether, separate, distil off ether, and weigh residue of *fatty and resin acids.*</td></tr>
</table>

Ditz and Clauser[1] have devised a process for the analysis of lysol, creolin, and similar preparations, depending on the fact that barium oleate is insoluble in water and but slightly soluble in 50

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[1] *Chem. Zeit.*, 1898, 732; Abst. *Analyst*, 1898, 298.

per cent. alcohol, whereas barium phenate dissolves in 40 per cent. of its weight of water at 100° C., the orthocresylate in 150 per cent., the paracresylate in 320 per cent., while the rare metacresylate is very soluble. Barium oleate, however, being somewhat uncertain in composition, cannot be weighed as such; it is necessary again to liberate the oleic acid. Moreover, the fatty acids in lysol, &c., are not pure oleic, but contain stearic and palmitic as well, the barium salts of which are partially decomposed by water. Preliminary experiments have shown that with lysol, which usually contains about 40 per cent. of fatty acids and 40 per cent. of phenols, the amount of the former recovered is only 0·5 per cent. too low, and this is a deficiency of no importance in the present investigation. The operation is as follows: 5 grm. of the sample are dissolved in 100 c.c. of warm water, 20 to 30 c.c. of 10 per cent. solution of sodium hydroxide added, and the mixture extracted two or three times with ether to remove the hydrocarbons. The ethereal solution is washed with very weak sodium hydroxide, and the latter combined with the bulk of the aqueous liquid; the ether is dried over solid potassium hydroxide, cautiously evaporated, and the residue dried over sulphuric acid to constant weight. The aqueous solution is carefully freed from ether on the water-bath, neutralised with hydrochloric acid, cooled completely (this is most important), and treated with excess of barium chloride and a quantity of barium hydroxide solution roughly equivalent to the phenols present. The mixture is filtered quickly, avoiding unnecessary exposure to the air, the precipitate washed with barium hydroxide solution, then cold and finally hot water, rinsed back into the original beaker, decomposed with 1 : 1 hydrochloric acid, and thrown on to the first filter again. The oleic acid is washed with hot, weak acid till free from barium, with water till free from acid, dissolved in absolute alcohol and ether, and evaporated to constant weight at 100° C.

The filtrate from the barium oleate, &c., may be acidified, extracted with ether, and the phenols recovered by evaporation; but it is better to operate as follows: In a convenient fraction of the acidified liquid the mixed phenols are determined by the Koppeschaar method (calling the bromine-absorption calculated on the whole bulk x grams). Another portion is extracted with ether, the solvent evaporated, and the residue dried for two or three hours at 100° to 110° C. (loss by volatilisation is of no consequence in this test). It is then dissolved in sodium hydroxide or barium hydroxide and titrated as before. The weight of the whole residue being a grams, its bromine-absorption b grams, and the weight of the sample originally taken c grams, the percentage of phenols is given by the formula:

$$\frac{100\,a\,x}{b\,c}$$

For the estimation of phenols in soap, Fresenius and Makin[1] recommend the decomposition of the soap by diluted sulphuric acid in slight excess, and distillation of the mixture in current of steam. The results are about 1 per cent. too high, owing probably to the presence of small amount of fatty acids in the distillate. The phenol in the distillate is determined by any suitable method.

W. Spalteholz[2] points out that in the examination of neutral substances, where the phenols are not in a state of combination, it is not necessary to add acid before distillation. The sample is placed in an iron retort and distilled in a current of steam between 200° and 220° C. until the distillate no longer yields any oily matter. Bodies which contain soaps of oleic acid must not be heated above 210° C. lest the latter are decomposed; this will be indicated by an oily layer on the top of the water in the receiver. Alkali-rosin soaps easily resist a temperature of 220°. The distillate consists of phenols alone in the case of lysol; of phenols and tar hydrocarbons in the case of creolin, mixed with the water; and the simplest way of separating them is to extract the whole with benzene, remove the aqueous portion, and estimate the phenols themselves with sodium hydroxide. With products of known composition the method has given results usually 0·5 per cent., but occasionally 1·0 per cent., below the theoretical, and it is therefore accurate enough for ordinary work.

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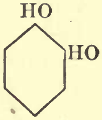
[1] *Zeit. Anal. Chem.*, 1896, 325; Abst. *Analyst*, 1896, 301.

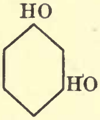
[2] *Chem. Zeit.*, 1898, 58; Abst. *Analyst*, 1898, 98.

DIHYDROXYBENZENES. DIHYDRIC PHENOLS.

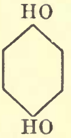
The substitution of two hydrogen atoms in benzene by hydroxyl will give rise to three isomeric forms, exactly analogous in structure to the xylenols and cresols described in the preceding pages.



Catechol, Pyrocatechin
(ortho-; 1–2)



Resorcinol, Resorcin
(meta-; 1–3)



Hydroquinone, Quinol
(para-; 1–4).

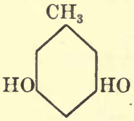
All three forms are known. They were originally obtained from natural products by destructive distillation, but are now mostly prepared by synthetic methods from benzene. When the monohalogenphenols (*e. g.*, C_6H_4ClOH), phenolsulphonates, or benzenedisulphonates are fused with potassium hydroxide the corresponding dihydroxybenzene is usually obtained, but the reaction is sometimes irregular, the meta-form being often produced when one of the isomerides is expected. The nature of the reactions is shown by the following equations:

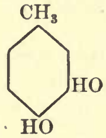
$$
\begin{aligned}
&C_6H_4I(OH) &&+ K(OH) = C_6H_4(OH)_2 + KI,\\
&C_6H_4(OH)SO_3K &&+ K(OH) = C_6H_4(OH)_2 + K_2SO_3,\\
&C_6H_4(SO_3K)_2 &&+ 2K(OH) = C_6H_4(OH)_2 + 2K_2SO_3.
\end{aligned}
$$

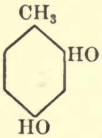
If the temperature be high, resorcinol is always obtained, as it is more stable than its isomers. The three dihydroxybenzenes are volatile crystallisable bodies, readily soluble in water, alcohol, and ether, and extracted from their aqueous solutions by agitation with ether. They form ethers when their hydrogen is displaced by alkyl-radicals, and resemble glycols in many respects. The following table shows the chief distinctions between them. In addition to the reactions given, resorcinol is characterised by its behavior with nitric acid, bromine, bleaching powder, and phthalic anhydride (see page 267). Catechol and quinol exert marked reducing action at ordinary temperatures; resorcinol only at the boiling point of water.

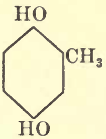
	CATECHOL, PYROCATECHIN. ORTHO- (1 : 2).	RESORCINOL, RESORCIN. META- (1 : 3).	QUINOL, HYDROQUINONE. PARA- (1 : 4).
Chief modes of formation, ...	Fusion of phenol ortho-derivatives, kino, benzoin, or guaiacum, with caustic alkalies. Dry distillation of protocatechuic acid. Action of hydrogen iodide at 200° on guaiacol.	Fusion of phenol meta-derivatives, galbanum, asafœtida, &c., with caustic alkalies. Dry distillation of extract of brazil-wood. On the large scale from benzenedisulphonic acid.	Fusion of phenol para-derivatives with caustic alkalies. Dry distillation of quinic acid. Hydrolysis of the glucoside arbutin, by dilute sulphuric acid. Reduction of quinone by aqueous sulphurous acid.
Appearance and crystalline form, .	Rhombic prisms or thin pearly plates.	Rhombic prisms or plates.	Hexagonal prisms or monoclinic plates.
Specific gravity, ...	1·344	1·272	1·330
Action of heat (°C.), ...	Melts at 104°; boils at 245°; may be sublimed, forming pungent fumes which excite coughing. Does not distil with steam.	Melts at 118°; boils at 276°; distils almost unchanged; volatilises with steam. Sublimes in silky needles.	Melts at 169°; sublimes when carefully heated, but decomposes if heated suddenly.
Solubility, ...	Very soluble in water, alcohol, and ether; extracted by ether from aqueous solutions.	Soluble in less than equal weight of cold water, very soluble in hot water; very soluble in alcohol, ether, and glycerol; extracted by ether from aqueous solutions. Nearly insoluble in chloroform, carbon disulphide, and cold benzene.	Soluble in 17 parts of cold water, very soluble in hot water. Very soluble in alcohol and ether; extracted by ether from aqueous solutions. Difficultly soluble in benzene.
Behavior of aqueous solution with reagents—			
(*a*) Exposed to air in presence of alkali,	Becomes green, brown, and black.	Turns brown.	Turns brown.
(*b*) Coloration with ferric chloride (avoiding excess).	Dark green, changed to violet-red by ammonium hydroxide or acid sodium carbonate.	Dark violet, destroyed by ammonium hydroxide.	Forms green crystals of quinhydrone, changed to yellow, sparingly soluble quinone by excess of the reagent.
(*c*) Reaction with lead acetate, .	White precipitate.	No precipitate.	No precipitate unless ammonium hydroxide be added.
(*d*) Reaction with silver nitrate,	Reduction of metallic silver in the cold.	No reaction in the cold; metallic silver reduced on boiling or on addition of ammonium hydroxide.	Metallic silver reduced on warming.
Taste of aqueous solution, ...	Bitter.	Sweetish.	Sweetish.

The *homologues* of the dihydroxybenzenes have as yet little importance. Six dihydroxytoluenes are possible, of which the following four have been obtained:


Orcinol, Orcin
(1-3-5)


Homocatechol
(1-3-4)


Isorcinol
(1-2-4)


Toluhydroquinone
(1-4).

In toluhydroquinone the methyl-group may be assumed to be at either 2, 3, 5, or 6, without changing the stereochemic relations. The methyl ether of homocatechol, $C_6H_3(OCH_3)(CH_3)(HO)$, is known as *creosol* (not to be confounded with cresol) and is found in beechwood tar (see page 278).

Resorcinol. Resorcin. Metadihydroxybenzene.

Resorcinol was originally obtained by the action of fused alkalies on certain resins, and subsequently by their action on meta-iodo-phenol. It is now manufactured on a large scale by heating sodium hydroxide to about 250° C. with sodium metabenzenedisulphonate. The fused mass is allowed to cool, dissolved in water, and the solution acidified. From the solution, the resorcinol is extracted by agitation with amyl alcohol and purified by distillation under reduced pressure.

Resorcinol crystallises in rhombic prisms from water, alcohol, and ether, but in needles from benzene. The crystals gradually become pink, and appear phosphorescent when struck or rubbed in the dark. The odor is peculiar and the taste sweetish bitter. Fuming sulphuric acid dissolves resorcinol to an orange-red solution, which gradually darkens, becomes greenish blue and then pure blue, and changes to purple-red on gently warming.

On adding bromine water to an aqueous solution of resorcinol, *tribromoresorcinol,* $C_6HBr_3(OH)_2$, is thrown down as a white flocculent precipitate consisting of crystalline needles, closely resembling tribromophenol (page 245). Resorcinol does not react with the usual indicators of neutrality, but with Poirrier's blue, C4B, it behaves like a dibasic acid.

With hypochlorites resorcinol gives a violet catechol an evanescent green, and quinol slowly develops a yellowish-red coloration.

When treated with excess of nitric acid, resorcinol is converted into a trinitroresorcinol, $C_6H(NO_2)_3(HO)_2$. This body, formerly called styphnic or oxypicric acid, forms sulphur-yellow hexagonal crystals, melting at 175° C. It closely resembles picric acid, except that it is astringent instead of bitter.

A solution of resorcinol, mixed with cupric sulphate and sufficient ammonium hydroxide to redissolve the precipitate first produced, yields a deep black liquid with which wool and silk may be dyed black.

Edlefson has observed that if a few drops of a 1 per cent. solution of resorcinol be added to a dilute, freshly-prepared, aqueous solution of β-naphthoquinone, and followed by a few drops of ammonium hydroxide, a dark bluish-green liquid is formed, from which ether does not extract the color; but if sufficient nitric acid be added to produce an acid reaction, a red liquid is produced, from which the color is extracted by either ether or chloroform. Watson Smith[1] has confirmed these statements, and noted also that phenol-α-naphthol and β naphthol do not give similar reactions.

When resorcinol is heated with excess of phthalic anhydride to about 200° C. for half an hour, the mixture acquires a yellowish red color, and contains the resorcinolphthaleïn or fluoresceïn, $C_{20}H_{12}O_5$. If the melt be dissolved in dilute sodium or ammonium hydroxide, the presence of resorcinol becomes apparent by the production of a dark red solution changing on dilution to reddish yellow and yellow, and exhibiting after dilution a fine yellowish-green fluorescence, which is visible in solutions so weak as to appear colorless by transmitted light. On acidulating the solution and agitating with ether the fluoresceïn is taken up, and will be again dissolved on agitating the ethereal solution with soda. When similarly treated, *phloroglucol* yields a yellow and *pyrogallol* a blue liquid, neither of which is fluorescent. The blue color due to pyrogallol may be destroyed by cautious addition of potassium permanganate, which acts only slowly on the fluoresceïn.[2]

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[1] *J. S. C. I.*, 1886, 580.

[2] Catecholphthaleïn, formed by gently heating catechol with phthalic anhydride and a little sulphuric acid, dissolves in caustic alkali solution with fine blue color. Quinolphthaleïn, or quinizarin, formed in a similar manner, dissolves in alkalies with violet-blue color, and if the solution be acidulated with sulphuric acid it becomes red, and the quinizarin may be extracted by agitation with ether and recovered from the ethereal solution by shaking with sodium hydroxide solution, which acquires a violet-blue color.

Other properties and reactions of resorcinol are described on page 266.

When resorcinol is fused with excess of sodium hydroxide, phloroglucol and some diresorcinol are produced.

Commercial Resorcin usually contains from 92 to 94 per cent. of resorcinol, the remainder being chiefly phenol and tarry matters. A purer product is furnished for medicinal purposes. The solution in ten parts of water should be colorless (empyreumatic impurities impart a yellow tint), neutral to litmus, and should evolve no odor of phenol on warming. The solid should leave no residue on ignition.

According to the German Pharmacopeia, if 0·05 grm. of resorcinol be warmed with 0·1 grm. of tartaric acid in ten drops of sulphuric acid, a dark carmine-red coloration is produced.

Resorcinol has marked antiseptic properties, and has been employed in medicine, but its chief value is derived from the numerous coloring matters obtainable from it.

Picrol is a trade-name for *potassium diïodoresorcinolmonosulphonate*, $C_6HI_2(SO_3H)(OH)_2$. It contains 52 per cent. of iodine, and is said to be powerfully antiseptic and not very poisonous.

Quinol. Hydroquinone. Paradihydroxybenzene. (See also page 265.)

Quinol may be prepared by the methods indicated on page 266, but is more conveniently obtained by oxidising aniline with chromic acid mixture and reducing the resultant quinone, $C_6H_4O_2$,[1] with sulphurous acid.

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[1] QUINONE, $C_6H_4O_2$, is a product of the oxidation of a great number of bodies of the aromatic para-series. It is best prepared by dissolving 1 part of aniline in 8 parts of sulphuric acid and 30 parts of water, and adding 31½ parts of powdered potassium bichromate. The liquid is allowed to stand for some time at the ordinary temperature, and is then warmed to about 35° C. The quinone is extracted by ether or petroleum spirit.

Quinone crystallises with great facility from petroleum spirit in fine yellow needles or prisms which melt at 115·7°, but sublime readily at the ordinary temperature. Quinone has a peculiar, characteristic odor, and the vapor is very irritating both to eyes and nose, but the substance does not appear to be poisonous when taken internally. It dissolves moderately in cold water, very readily in boiling water and alcohol, and volatilises easily with steam.

Quinone liberates iodine from potassium iodide, and acts otherwise as an oxidising agent of moderate power. By sulphites, stannous chloride, and similar reducing agents it is converted into quinol.

Quinone can be determined with accuracy, in the absence of other oxidising agents, Quinol has received a limited application in medicine. Its chief use is a developer in photography.

Catechol. Pyrocatechin. Orthodihydroxybenzene. (See also page 266.)

Catechol is produced by the action of heat on protocatechuic acid, and on tannins and other bodies allied to it. It also results from the action of an excess of fusing caustic potash on orthophenolsulphonic acid, $C_6H_4(SO_3H)OH$.[1]

Catechol is conveniently prepared from the fraction of beech-wood-tar creosote boiling between 200° and 205°, which consists essentially of guaiacol or catechol methyl-ester. On heating this to the boiling point, and passing in hydriodic acid gas as long as methyl iodide distils over, catechol is produced and may be purified by fractional distillation and crystallisation from benzene. The reverse action is employed for producing guaiacol from catechol, which is now made on a considerable scale.

Catechol forms short, square prisms or thin, pearly plates, resembling benzoic acid. It sublimes readily and condenses in brilliant

by treating the solution with dilute hydrochloric acid and excess of potassium iodide, and titrating the liberated iodine by standard solution of sodium thiosulphate.

An extremely delicate reaction of quinone consists in adding to the dilute solution a few drops of a saturated solution of hydrocerulignone, $C_{12}H_4(OCH_3)_2(OH)_2$. The liquid immediately acquires a yellowish-red color, which rapidly becomes deeper, and steel-blue, iridescent needles of *cerulignone* separate out.

By the action of a mixture of hydrochloric acid and potassium chlorate, or of other powerful oxidising agents, quinone is converted into *tetrachlorquinone*, or *chloranil*, $C_6Cl_4O_2$. The same substance, mixed with *trichlorquinone*, $C_6HCl_3O_2$, is obtained by the action of hydrochloric acid and potassium chlorate on phenol, aniline, &c. Chloranil crystallises in golden-yellow plates or prisms, soluble in boiling benzene and moderately soluble in ether; but only slightly soluble in alcohol, and insoluble in water. Chloranil sublimes readily at about 200° and melts at a higher temperature. It is not attacked by strong sulphuric acid, nitric acid, or aqua regia. It is converted by reducing agents into colorless tetrachlorquinol. Chloranil is used in the color-industry as an oxidising agent, as for converting dimethylaniline into chloranil violet.

[1] According to a process patented by J. H. Baum (*Eng. Patent*, 1893, No. 21853) catechol is prepared by heating sodium α-phenoldisulphonate with an equal weight of sodium hydroxide at a temperature of 280° to 300° under pressure. The resultant catecholsulphonic acid is hydrolysed by heating it to 180° to 220° C. with sulphuric acid of 50 per cent. Unaltered phenol is volatilised by blowing steam through the liquid, which is then decolorised by animal charcoal and the catechol extracted by agitation with ether. The yield is stated to be about 50 per cent. of the theoretical.

For other synthetic methods of preparing catechol see *Pharm. Jour.*, **24** (1893-4), 730.

laminæ. The taste is bitter, and the fumes are pungent and excite coughing. Catechol differs from resorcinol in not volatilising appreciably in a current of steam.

The aqueous solution of catechol rapidly turns brown.

Catechol forms unstable compounds with bases. With lime-water an aqueous solution of catechol gives a reddish or brown color, but the solution remains clear for some time. Caustic alkalies behave similarly to lime-water, the solution becoming, in succession, green, brown, and black. Catechol is not precipitated by gelatin or alkaloids. With lead acetate it yields a white precipitate, which is easily soluble in acetic acid. Catechol reduces silver nitrate at ordinary temperatures and Fehling's solution on warming.

An aqueous solution of catechol gives no reaction with ferrous salts. With ferric chloride, avoiding excess, it gives a grass-green coloration, which on addition of acid sodium carbonate is changed to a fine violet-red, not much altered by boiling, but restored to green on the cautious addition of sodium hydroxide. (These reactions distinguish catechol from pyrogallol.) Pine-wood moistened with hydrochloric acid mixed with a solution of catechol acquires a violet-blue color. Phloroglucol gives a similar reaction.

The aqueous solution of catechol is neutral to litmus, but on addition of borax the liquid shows a marked acid reaction and acquires the power of decomposing carbonates. Pyrogallol and tannates and gallates of the alkali-metals behave similarly. All these bodies belong to the ortho-series. Resorcinol, quinol, and orcinol, which contain hydroxyl-groups in the meta- or para-positions, do not form acid solutions on addition of borax.[1]

By treatment with sulphuric acid, catechol is converted into mono- or disulphonic acids, according to the temperature and the strength of acid employed.[2]

HOMOCATECHOL OR METHYLCATECHOL occurs as a methyl-ether in wood-tar creosote, and may be obtained therefrom by boiling with hydrobromic or hydriodic acid. Homocatechol is a syrupy liquid, which dissolves readily in water, alcohol and ether, but not

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[1] The thermo-chemical experiments of Berthelot and Werner have shown that, in case of polyphenols containing two hydroxyl groups in the ortho-position, one of these has an alcoholic and not a phenolic function, and this fact is related to the power of forming a conjugated acid with borax. (See *Comp. rend.*, **108** (1889), 1016, and *J. C. S.*, 1889, 845, 864.)

[2] H. Cousin, *Comp. rend.*, **117** (1893), 113.

in benzene (distinction from catechol). It reduces silver nitrate and Fehling's solution in the cold. With ferric chloride, homocatechol gives a green coloration, which is changed to reddish-violet on cautious addition of ammonia or sodium hydrogen carbonate.

By treatment with strong sulphuric acid, homocatechol yields a sulphonic acid. No disulphonic acid is obtainable.

Ethers of Catechol and Homocatechol.—By suitable means one or both the hydrogen-atoms of the hydroxyl-groups of catechol and homocatechol can be replaced by alkyl-radicals. Thus, the following methyl-ethers can be obtained:

Catechol.

$$C_6H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right..$$

Methyl catecholate. Catechol methyl-ether. Guaiacol.

$$C_6H_4\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right..$$

Dimethyl catecholate. Catechol dimethyl-ether. Veratrol.

$$C_6H_4\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right..$$

Homocatechol. Methylcatechol.

$$C_6H_3(CH_3)\left\{\begin{matrix}OH\\OH\end{matrix}\right..$$

Methyl homocatecholate. Homocatechol methyl-ether. Creosol.

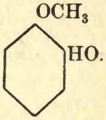
$$C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right..$$

Dimethyl homocatecholate. Homocatechol dimethyl-ether.

$$C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OCH_3\end{matrix}\right..$$

Guaiacol, creosol, and homocatechol dimethyl-ethers form the greater part of the fraction of beechwood-creosote boiling between 200° and 220° (see page 278). Veratrol is also very probably present. The dimethyl-ethers shown above can be prepared from guaiacol and creosol respectively by dissolving these bodies in a strong solution of potassium hydroxide in methyl alcohol and boiling with methyl iodide. They are distinguished from the monomethyl ethers by their insolubility in aqueous solutions of caustic alkalies, and by giving no green or blue coloration with ferric chloride. Both the mono- and dimethyl-ethers can be demethylated by heating them with excess of a halogen-acid, catechol and homocatechol being thereby formed.

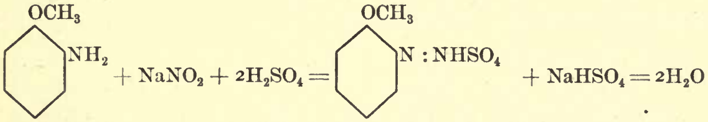
Guaiacol. Methyl catecholate. Catechol methyl ether,



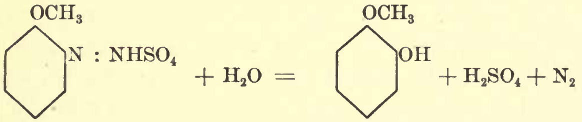
This substance has attracted much attention on account of its vogue as a remedy in tuberculosis. It is prepared from beechwood creosote by treating the fraction which distils between 200° and 205° C. with an alcoholic solution of potassium hydroxide by which potassium guaiacol is formed, and this is converted into guaiacol by the action of dilute acids. Guaiacol may also be prepared by several synthetic methods, as when catechol (1–4 dihydroxybenzene) is heated with equivalent quantities of potassium methyl sulphate and potassium hydroxide or sodium hydroxide. The action is:

$$C_6H_4(OH)_2 + K(CH_3)SO_4 + KOH = C_6H_4(CH_3)(OH) + K_2SO_4 + H_2O.$$

W. Kelle[1] has devised a process for the production of guaiacol depending on the diazotising of 1–2 anisidine [methoxyamidobenzene, $C_6H_4(OCH_3)(NH_2)$] in the presence of excess of diluted sulphuric acid, after which the solution is run into a quantity of stronger sulphuric acid containing sodium sulphate, heated to 140° C. The guaiacol is distilled as fast as formed by blowing steam through the liquid. The product is distilled at about 200° C. and the distillate crystallised on cooling. The reactions are:



1-2-Anisidine. 1-2-Methoxydiazobenzene sulphuric acid.



Pure guaiacol was formerly described as a liquid, but was obtained by Béhal and Choay[2] as a white solid, which, when crystallised from petroleum spirit, is obtained in hard, uniaxial, dihexagonal prisms. Guaiacol melts at temperatures variously stated at 28·5° to 33°, and boils at 204° to 205°. When melted, guaiacol remains indefinitely in a state of super-fusion, and may even be cooled to —2° C. without solidifying; but on addition of a crystal of the solid substance the whole immediately crystallises, the temperature rising to 27°. The specific gravity of liquid guaiacol at 0° C. is 1·1543, and at 15° from 1·143 to 1·149. Guaiacol is only slightly soluble in water, but dissolves readily in most organic solvents, including absolute, but not aqueous, glycerol. It

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[1] Watson Smith, *J. S. C. I.*, 1898, 314.

[2] *Comp. rend.*, **116** (1893), 197.

is also soluble in solutions of caustic alkalies, and with an alcoholic solution of potassium (not sodium) hydroxide forms a crystalline mass of the potassium derivative. The same compound speedily separates on mixing equal measures of guaiacol and aqueous potassium hydroxide solution of 1·3 specific gravity. Impure guaiacol, even if containing 70 per cent. of the real compound, remains liquid under the same conditions. According to A. Trillat,[1] if 4 c.c. of guaiacol be shaken with 10 c.c. of milk of lime containing 0·1 grm. of lime, colorless crystals of a calcium-derivative are formed.

Guaiacol has a sweet taste, and when placed on the tongue melts and produces a feeling of intense astringency, but it is without action on the mucous membrane.

According to P. Marfori, the physiological action of guaiacol is analogous to that of phenol or catechol, and it is eliminated from the system in a similar condition, but it is less poisonous than these bodies. Guaiacol has received an extensive application in medicine as a substitute for creosote in the treatment of phthisis, especially in the earlier states.

When treated in aqueous solution with ferric chloride, guaiacol gives a brownish turbidity; but if ferric chloride (avoiding excess) be added to a 1 per cent. solution of guaiacol in alcohol, a fine blue coloration is obtained, rapidly changing to green and yellow.

The determination of guaiacol is described under "wood-creosote."

Commercial Guaiacol is of very variable quality, some specimens being stated to contain not more than 30 per cent. of the pure substance, but good samples contain fully 90 per cent. Inferior samples have a low specific gravity,—*e. g.*, 1·046,—but those rich in guaiacol have a gravity approaching that of the pure substance. Pure guaiacol requires eight times its measure of cold petroleum spirit for solution, but many commercial specimens are soluble in four measures or even less.

According to Marfori,[2] the solubility of guaiacol in water is notably reduced by the presence of impurities. Heated with chloroform and solid potassium hydroxide pure guaiacol gives a purple-red coloration, while the impure product gives a less marked reaction. Marfori states that the pure substance gives with concentrated sulphuric acid a stable purple-red coloration, while the least impurity detracts from the purity of the color formed. On the

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[1] *J. S. C. I.*, 1892, 1028.

[2] *Gazz. Chim.*, **20** (1890), 537.

other hand, some observers state that pure guaiacol gives no color, or only a slight yellow, with cold strong sulphuric acid.

Guaiacol Carbonate, $C_6H_4(OCH_3).(CO_3).C_6H_4(OCH_3)$.—This compound, also called "*Duotal*," is obtained by the action of carbonyl chloride on sodium-guaiacol. It is a white, crystalline, insoluble powder, melting between 86° and 90° C. Guaiacol carbonate is tasteless, odorless, neutral, and non-toxic, and is free from the irritating and caustic action of guaiacol itself, over which it presents marked advantages as an internal antiseptic. It passes through the stomach unchanged, but is decomposed into its constituents in the intestines. Guaiacol is found in the urine in from thirty to sixty minutes after the ingestion of the carbonate.

A similar product prepared direct from beechwood creosote has been introduced under the name of "*Creosotal*." It is a yellow, transparent liquid, viscid at low temperatures, but rapidly thinning on warming. Creosotal has a specific gravity of 1·165, and a slight taste and odor of creosote. It is insoluble in water, glycerin, and dilute spirit, but is soluble in all proportions in strong alcohol, ether, chloroform, &c. Creosotal contains 92 per cent. of creosote, and has been recommended as a remedy in phthisis. In doses of 10 to 20 grains daily it is stated not to disturb the digestive functions.

Guaiacol-carboxylic acid, $C_6H_3(OCH_3)(OH)COOH$, is obtained by saturating sodium-guaiacol with carbon dioxide under pressure, and decomposing the product with hydrochloric acid. It crystallises with $2H_2O$. The anhydrous substance melts at 148° to 150°, and decomposes into guaiacol and carbon dioxide at a higher temperature. It gives a blue coloration with ferric chloride.

Benzoyl guaiacol, or *Guaiacyl Benzoate*, $C_6H_4(OCH_3)OCOC_6H_5$.—This compound, also called "*Benzosol*," is obtained by the reaction of potassium-guaiacol and benzoyl chloride at 100°, or by the direct action of benzoic anhydride on guaiacol. It forms small colorless crystals melting at 50°, almost insoluble in water, sparingly soluble in glacial acetic acid, and readily soluble in hot alcohol, ether, or chloroform.

CREOSOL. Methyl Homocatecholate. Homocatechol Methylether.

This substance is homologous with guaiacol, and occurs in the fraction of beechwood creosote boiling at about 220°. When freshly distilled, it is a colorless liquid, having a pleasant odor of vanilla, especially when dilute. It dissolves in aqueous alkalies, and with a strong solution of potassium hydroxide in alcohol sets to a mass of needles of the potassium compound, $C_8H_8O.OK + 2H_2O$. A solution of creosol yields a metallic mirror when warmed with silver nitrate, and gives a green coloration with ferric chloride. Creosol differs from guaiacol in its higher boiling point (219°), in not crystallising, and in its greater solubility in petroleum spirit. In its therapeutic effects creosol appears to present a close resemblance to guaiacol.

Creosol methyl ether, or *dimethyl homocatecholate*, $C_6H_3(CH_3):(OCH_3)_2$, also occurs in beechwood creosote. It boils at 218°, gives no coloration with ferric chloride, and is insoluble in aqueous solutions of caustic alkalies.

CREOSOTE AND CREOSOTE OILS.

The name "kreosot" was first applied by Reichenbach, in 1832, to the characteristic antiseptic principle contained in wood tar.[1] Carbolic acid was discovered soon after by Runge in coal-tar, and was long confused with the wood-tar principle; and the crude carbolic acid from coal-tar is still known as "coal-tar creosote." Somewhat similar products are now obtained from other sources, so that much confusion has arisen. The term "creosote," when used without qualification, ought to be understood as signifying the product from wood-tar, but it is better to describe Reichenbach's body as "wood-tar creosote," and employ the unqualified word "creosote" in a generic sense as meaning the mixed phenols and phenoloid bodies obtained from wood-tar, coal-tar, blast-furnace tar, shale-oil, bone-oil, or other sources. The term "creosote" should be restricted to the phenoloid bodies from the above or similar sources, the crude products from which they are derived being the corresponding "creosote oils." Some of these products differ materially in their chemical and physical characters, from the creosote from either wood- or coal-tar. These may be separated approximately from the accompanying neutral and basic oils by treating the fraction boiling between 170° and about 300° C. with caustic potash or soda, and then mixing the alkaline solution

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[1] C. Rice, *Amer. Jour. Pharm.*, 1894, 167.

with a slight excess of dilute sulphuric acid, when the phenols are separated and form an oily layer of "creosote."

The creosote oil from coal-tar is described on page 294 *et seq.;* the following sections treat of the creosotes from the other sources.

Wood-tar Creosote.

Wood-tar creosote is usually obtained by distilling beechwood tar, and treating the fraction heavier than water with diluted sodium hydroxide solution. The alkaline solution is separated from the insoluble oily layer, boiled with contact of air to oxidise some of the impurities, and decomposed by diluted sulphuric acid. The crude creosote which separates is purified by re-solution in alkali and reprecipitation with acid, and is then redistilled, the fraction passing over between 200° and 220° C. constituting purified creosote.

Wood-tar creosote is a strongly refracting liquid which is colorless when freshly distilled, but acquires a yellow or brown color on keeping. It has a peculiar, persistent, smoky, aromatic odor, distinct from that of phenol. The specific gravity ranges between 1·040 and 1·087. Wood creosote is not solidified by moderate cold. It is a powerful antiseptic, but does not coagulate albumin. It preserves animal matters without causing disintegration as phenol is liable to do, and is less powerfully caustic than that substance.

Wood-tar creosote is only slightly soluble in water, but is with difficulty rendered anhydrous. Like absolute phenol and cresol, it is miscible in all proportions with alcohol, ether, glacial acetic acid, chloroform, benzene, and carbon disulphide. It dissolves in concentrated sulphuric acid to a red liquid, which slowly changes to purple-violet. Shaken with concentrated hydrochloric acid in the absence of air, wood-creosote becomes red, the color changing in contact with air to dark brown or black. Wood-creosote is violently attacked by nitric acid. With bromine-water it forms a derivative of a reddish color.

Wood-creosote is soluble in solutions of caustic alkalies, and forms a crystalline compound with potassium hydroxide, but not with sodium hydroxide.

Wood-tar creosote is a complex mixture of phenoloid bodies, the proportions of which differ according to the modes of distillation and purification. It may be regarded as composed of a mixture of bodies belonging to several homologous series, but chiefly of methylic ethers of catechol (pyrocatechol) and its homologues.[1] Thus, the presence of the following bodies has been established:

NAME.	FORMULA.	BOILING POINT; °C.
MONOHYDRIC PHENOLS—		
Phenol, ...	$C_6H_5 . OH$	182
Cresols (1–2, 1–3, 1–4), ...	$C_6H_4(CH_3)OH$	203
Xylenols, phlorols (1–3–4, 1–3–5),	$C_6H_3(CH_3)_2OH$	220
Ethyl-phenol (1–2), ...	$C_6H_4(C_2H_5)OH$	203
ETHERS OF DIHYDRIC PHENOLS—		
Guaiacol, Methyl catecholate, .	$C_6H_4\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$	200
Creosol, Methyl homocatecholate,	$C_6H_3(CH_3)\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$	219
Dimethyl homocatecholate, . . .	$C_6H_3(CH_3)(OCH_3)_2$	214 to 218
Methyl creosol, Dimethyl-guaiacol, ...	$C_6H_2(CH_3)_2\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$	above 230
Ethyl-guaiacol (1–3–4), ...	$C_6H_3C_2H_5\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$	. . .
Propyl-guaiacol, Cerulignol, . .	$C_6H_3(C_3H_7)\left\{\begin{matrix}OCH_3\\OH\end{matrix}\right.$	241
ETHERS OF TRIHYDRIC PHENOLS—		
Dimethyl pyrogallate, ...	$C_6H_3\left\{\begin{matrix}OCH_3\\OCH_3\\OH\end{matrix}\right.$	253
Dimethyl methylpyrogallate, . .	$C_6H_2(CH_3)\left\{\begin{matrix}OCH_3\\OCH_3\\OH\end{matrix}\right.$	265
Dimethyl propylpyrogallate, . .	$C_6H_2(C_3H_7)\left\{\begin{matrix}OCH_3\\OCH_3\\OH\end{matrix}\right.$	285
Methyl propylpyrogallate, . . .	$C_6H_2(C_3H_7)\left\{\begin{matrix}OCH_3\\OH\\OH\end{matrix}\right.$	290

Béhal and Choay[2] have reported the presence of a sulphur derivative, probably a thiophenol, in beech- and oak-tars; also a body, distinct from pittacal, which, under the joint influence of

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[1] *Asbolin,* a syrupy liquid, obtained by Braconnet from the soot formed by burning wood, has been shown by Béhal and Desoignes to be a complex mixture, containing catechol and homocatechol as leading constituents.

[2] Abst. *J. C. S.,* 1894, 508.

ammonium hydroxide and air, yields a substance that produces with alkali an intense blue solution, changed to red on acidifying. Phenol is present in genuine wood-tar creosote in very small quantity, the cresols in somewhat larger, and the xylenols in sensible proportions; but the two chief constituents are guaiacol and creosol. In Rhenish creosote, guaiacol predominates, but a sample of Morson's creosote from "Stockholm tar," examined by the author, boiled at about 217° C. and consisted chiefly of creosol. Dimethyl-guaiacol and propyl-guaiacol are present in but insignificant proportions,[1] but the latter body is highly objectionable, since a single drop causes bleeding when placed on the tongue. Hence purified creosote should be absolutely free from this constituent, the presence of which may be recognised by the blue coloration produced with baryta-water.

The solubility of the constituents of creosote in alkalies decreases as the molecular weight increases, and with the number of hydroxyl groups substituted. Thus, methyl pyrogallate dissolves in a weak solution of sodium hydroxide, dimethyl pyrogallate, in a strong solution thereof, while trimethyl pyrogallate is insoluble in the cold alkali. Similarly, dimethyl homocatecholate, which constitutes the greater portion of the fraction of beechwood creosote distilling between 210° and 220° C., is insoluble in aqueous solution of sodium hydroxide.

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[1] The following method may be employed for the separation of the phenoloid constituents of wood-creosote boiling between 195° and 240°, and might be used for the detection and determination of coal-tar acids purposely added: The sample is dissolved in twice its measure of ether, and the solution shaken with a 5 per cent. solution of potassium hydroxide, which dissolves the phenoloid bodies. The alkaline liquid is separated, acidulated with hydrochloric acid, and shaken up with ether. The phenoloid oils obtained on evaporating the ethereal solution are distilled, mixed with half their volume of ether, and twice their volume of a saturated alcoholic solution of potassium hydroxide. Creosol and guaiacol are converted into crystalline potassium compounds, while the similar compounds of phenol and cresol remain in solution. The crystalline pulp is pressed through a cloth, the filtrate evaporated, the residue treated with water, and the solution acidulated with hydrochloric acid. The liberated phenols are re-treated with ether and alcoholic potassium hydroxide, the process being repeated, if necessary, so long as crystals are deposited in the cold, when the phenols are once more liberated, and may be weighed, measured, or titrated with bromine. The crystals may be dissolved in water and the solution decomposed by hydrochloric acid, when the guaiacol, creosol, and higher homologues are liberated, and may be purified and separated by fractional distillation. (Tiemann and Koppe, *Ber.*, 1881, 2005.)

The less volatile fractions of crude wood-tar creosote have been found by A. W. Hofmann to contain the methylic ethers of pyrogallol and its homologues. These bodies derive their chief interest from the remarkable coloring matters (originally discovered by Runge) which can be derived from them by oxidation. Thus, if the sodium dimethyl pyrogallate (prepared by adding sodium hydroxide to an alcoholic solution of dimethyl pyrogallate) be mixed with the sodium dimethyl methylpyrogallate and excess of sodium hydroxide, and heated in the air, a body called eupittonic acid[1] is formed according to the following equation:

$$2C_8H_{10}O_3 + C_9H_{12}O_3 + O_3 = C_{25}H_{26}O_9 + 3H_2O.$$

On oxidising the pyrogallic ethers from wood-tar creosote with more powerful reagents than atmospheric air, such as dilute chromic acid mixture, they are converted into quinones. Thus, dimethyl pyrogallate yields cerulignone, $C_{16}H_{16}O_6$, a body which is identical with Reichenbach's "cedriret."

Beechwood oil is of very variable composition. The following results were obtained by the author, in 1891, in the examination of two representative samples:

	No. 1.		No. 2.	
Specific gravity,	1·0210		1·0130	
Initial boiling point, . . .	110° C.		120° C.	
Distillation commenced at	120° C.		140° C.	
Distillate below 315° C., . .	66 per cent.		12 per cent.	
Containing—				
Water, . . .	2 ,, ,,		1 ,, ,,	
Phenoloids, .	40 ,, ,,	40 per cent.	4 ,, ,,	16 per cent.
Phenoloids in distillate above 315° C.,	traces		12 ,, ,,	

The phenoloids extracted from the oils by caustic alkali had the

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[1] Eupittonic acid has the constitution of a hexamethoxyl-aurin, $C_{19}H_8(OCH_3)_6O$. Reichenbach's "pittical," called by Wichelhaus "eupittone," was a salt of eupittonic acid (see *J. S. C. I.*, 1885, 152).

following characters, the whole 16 per cent. from No. 2 sample being mixed and examined together:

	No. 1.	No. 2.
Specific gravity,	1·0686	1·0760
Water,	7 per cent.	12 per cent.
Initial boiling point,	103° C.	101° C.
Distillate below 220° C.,	10 per cent. (including 7 per cent. of water)	15 per cent. (including 12 per cent. of water)
Distillate below 230°,	32 per cent.	25 per cent.
,, ,, 240°,	52 ,, ,,	45 ,, ,,
,, ,, 250°,	67 ,, ,,	50 ,, ,,
,, ,, 260°,	76 ,, ,,	62 ,, ,,
,, ,, 270°,	82 ,, ,,	...
,, ,, 280°,	86 ,, ,,	75 per cent.
,, ,, 290°,	90 ,, ,,	76 ,, ,,

These results present a striking contrast. Even including the 12 per cent. in the portion of the oil distilling above 315° C., No. 2 yielded only 16 per cent. of phenoloids. The large proportion of water taken up by the phenoloids of No. 2 is remarkable.

Béhal and Choay[1] give the following as the comparative composition of beechwood and oak creosotes, freed from hydrocarbons:

	BEECH.	BEECH.	OAK.
Distillation-temperature, ° C.,	200 to 220	200 to 210	200 to 210
Specific gravity,	1·085	1·085	1·068
Monophenols,	39·0	39·0	55
Guaiacol,	19·7	26·5	14
Creosols and homologues,	40·0	32·1	31
Loss,	1·3	2·4	

In making the foregoing analyses, the heavy oil was acidulated with hydrochloric acid and agitated with water to remove certain basic substances. The oily layer was then treated with sodium hydroxide, a very considerable quantity of water added (since concentrated alkali-solutions of phenoloids dissolve a certain quantity of indifferent oils), the undissolved oil separated, the alkaline liquid shaken with benzene to remove traces of hydrocarbons, &c., and then treated with a current of steam until the distillate no longer smelled strongly. The phenols were then set free by hydrochloric

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[1] *Compt. rend.*, **119** (1894), 166; Abst. *J. S. C. I.*, 1894, 1087 and 1187.

acid, separated, the acid liquid agitated with benzene, and the phenols thus extracted recovered by evaporating off the benzene and added to the main quantity.

From these results it would appear that the fraction of beechwood creosote distilling between 210° and 220° contains no guaiacol. Oak creosote contains less guaiacol and more monophenols than the beechwood product, and it is to the presence of these latter constituents that oak creosote owes its greater causticity.

The following figures show the results obtained by the author, in 1891, by the examination of four typical samples of beechwood creosote as supplied by leading manufacturers:

	A.	B.	C.	D.
Initial boiling point, .	. .	. .	201° C.	198° C.
First drop distilled at	197° C.	218° C.	210° C.	204° C.
Distillate below 207° C.	.	. .	. .	10 per cent.
,, ,, 209°	. .	. .	. .	25 ,,
,, ,, 210°	5 per cent.	. .	. .	48 ,,
,, ,, 213°	.	. .	. .	65 ,,
,, ,, 215°	20 per cent.	. .	10 per cent.	78 ,,
,, ,, 216°	. .	. .	25 ,,	. .
,, ,, 217°	35 per cent.	. .	28 ,,	82 per cent.
,, ,, 218°	42 ,,	. .	45 ,,	. .
,, ,, 219°	50 ,,	. .	50 ,,	92 per cent.
,, ,, 220°	53 ,,	5 per cent.	60 ,,	. .
,, ,, 221°	. .	. .	64 ,,	95 per cent.
,, ,, 222°	. .	. .	70 ,,	. .
,, ,, 223°	63 per cent.	28 per cent.	. .	. .
,, ,, 224°	. .	.	82 per cent.	. .
,, ,, 225°	70 per cent.	50 per cent.	. .	. .
,, ,, 226°	. .	. .	90 per cent.	. .
,, ,, 227°	77 per cent.	64 per cent.	. .	. .
,, ,, 228°	. .	. .	95 per cent.	. .
,, ,, 230°	84 per cent.	78 per cent.	. .	. .
,, ,, 235°	90 ,,	90 ,,	. .	. .
Specific gravity, . . .	. .	. .	1·0656	1·0778
Behavior with baryta-water, ...	Distinct reaction.	No reaction.	No reaction.	Slight pink coloration.
Behavior with alcoholic potash, ...	Solidified.	. .	Solidified at once.	Solidified on standing.

These results indicate almost entire absence of guaiacol from A, B, and C, and almost entire absence of creosol also in the case of B.

A detailed analysis of beechwood creosote distilling between 200° and 210° is given by Béhal and Choay as follows:

Phenol,	5·2
1–2-cresol,	10·4
1–3 and 1–4-cresols,	11·6
1–2-ethylphenol,	3·6
1–3–4-xylenol,	2·0
1–3–5-xylenol,	1·0
Phenols, various,	6·2
Guaiacol,	25·0
Creosol and its homologues,	35·0
	100·0

According to this analysis the proportion of guaiacol in beechwood creosote is much smaller than is usually stated. The author's results (already given) obtained by distilling commercial creosote go generally to confirm the above figures, but show that the composition of the product is very variable. Fréyss states that commercial beechwood creosote contains from 3 to 30 per cent. of guaiacol, from 10 to 40 per cent. of creosol, and a very variable proportion of monophenols.

In consequence of the large demand of recent years for guaiacol and its preparations, much of the wood-creosote now sold has been deprived of its guaiacol, so that it is now rare to find specimens containing even 20 per cent. of that constituent.

Béhal and Choay[1] have devised a method for the determination of guaiacol in wood-creosote, based on the following principles: 1. Treatment of the sample with hydrobromic acid, whereby the methyl-ethers of the polyphenols are completely demethylated. Thus, guaiacol by such treatment yields catechol, and creosol gives homo- or methyl-catechol. 2. Distillation of the demethylated oil in a current of steam, whereby the monophenols (phenol, cresols, xylenols) are carried over and are thus separated from the polyphenols. 3. Extraction of catechol, homocatechol, and any traces of unvolatilised monophenols by ether. 4. Separation of catechol from homocatechol by treatment with benzene, which dissolves the former substance only. The following are the working details of the process as modified by M. Adrian:[2]

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[1] *Comp. rend.*, **116** (1893), 197.

[2] *Nouv. Rem.*, 13, 97; Abst. *J. S. C. I.*, 1897, 367.

100 grm. weight of guaiacol or creosote is placed in a flask of 250 c.c. capacity, connected on the one hand with another flask which serves as a generator of gaseous hydrogen bromide (generated by the action of water on phosphorus tribromide) and on the other with an inclined reflux condenser. The exit-tube from the condenser leads the gas through two wash-bottles containing water. The delivery tube between the generator and the guaiacol is furnished with a large bulb to prevent aspiration of the liquid when cooling. The gas is allowed to pass slowly through the guaiacol, which is gently warmed after the process has been in operation for half an hour, and continued for ninety minutes. It is then cooled, transferred to a large flask, diluted with 5 or 6 volumes of water, and all volatile bodies removed by steam-distillation. When no more oily liquid comes over, the distillation is stopped, the catechol in the residual liquor extracted, together with homocatechol, by washing out with ether, the ether cautiously distilled off, and the residue dried. This is then treated with dry benzene, which extracts the whole of the catechol produced by demethylation of the guaiacol originally present, leaving the homocatechol undissolved. From the solution of benzene the catechol is crystallised out and weighed. Care must be taken at the end of the process to avoid the least trace of moisture in the residue and in the solvent, or crystallisation will not take place; and even with perfectly dry benzene the mother-liquor must be concentrated and the catechol which crystallises out added to the main quantity.

The monophenols which distil with steam are separated by Béhal and Choay by fractionation and subsequent conversion into benzoates (see page 240). The methyl-derivatives of the diphenols are separated by precipitation with strontium hydroxide, the precipitate being decomposed by hydrochloric acid. They are then fractionated, and, if necessary, converted into carbonates by carbon oxychloride, and further separated by fractional crystallisation.

L. F. Kebler[1] has described the following process of determining guaiacol in creosote: 5 c.c. of the sample are mixed with 50 c.c. of a 20 per cent. solution of potassium hydroxide in alcohol. The crystalline mass of the potassium-derivatives of guaiacol and creosol, which forms in the course of half an hour, is pressed between filter-paper until dry and treated in a test-tube with 5 c.c. of 20 per cent. sulphuric acid. On heating the mixture,

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[1] *Amer. Jour. Pharm.*, 1899, 409.

the guaiacol and creosol rise to the surface. The liquid is then diluted with sufficient water to cause the oily layer to sink, when the aqueous portion is decanted and the oil treated with 4 c.c. of concentrated ammonium hydroxide. A hard crystalline compound is immediately formed by the guaiacol, and a semi-crystalline mass is given after some time by the creosol. On treating the crystalline mixture with petroleum spirit, all but the ammonium compound of guaiacol is dissolved, and this can be purified by filtration and washing with petroleum spirit. The compound is then decomposed by dilute sulphuric acid, the liberated guaiacol extracted by agitation with petroleum spirit, and the solution evaporated in a tarred flask.

Kebler[1] finds the proportion of guaiacol in commercial wood-creosote to range from 16 per cent. down to *nil*, and doubts the statement that creosote ever contained 60 per cent. of guaiacol.[2] He suggests that a range of boiling point from 200° to 220° should be permitted. This extension would admit creosol to an equality with guaiacol as a legitimate and valuable constituent of creosote, which would appear to be justifiable both from analogy and from what is positively known of the therapeutic action of creosol.

A useful indication of the proportion of guaiacol present in wood-creosote is afforded by the specific gravity of the sample, or preferably of the fraction distilling between 200° and 205° C. The specimens having the highest specific gravity are richest in guaiacol. The U. S. Pharmacopeia (1890) requires wood-creosote to have a specific gravity not below 1·070 at 15° C., a character that does not exclude an article destitute of guaiacol. The British Pharmacopeia (1898) is slightly more rigid, requiring a specific gravity of not less than 1·079.

Creosote is commonly stated to be optically active. The British Pharmacopeia of 1885 alleged that it was dextro-rotatory, while the edition of 1898 asserts that it is levo-rotatory, both statements being misleading. As a rule, wood-creosote exhibits no sensible optical activity, and the same is true of pure guaiacol and creosol. Occasionally, specimens of creosote are met with which exhibit an insignificant activity, but the character is valueless as a practical test.

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[1] *Amer. Jour. Pharm.*, 1899, 409.

[2] Kebler gives the following data obtained by the examination of six samples of commercial wood-creosote, purchased in the United States, though the results show

Wood-tar creosote of good quality has an agreeable, vanilla-like odor, and darkens in a marked manner on prolonged exposure to light.

An alcoholic solution of wood-tar creosote should not give any coloration whatever (neither blue nor reddish) with barium hydroxide. The test may be made by dissolving the creosote in twice its measure (or a sufficiency) of petroleum spirit, which should form a perfectly clear solution; and on shaking this liquid with an equal measure of saturated baryta-water no blue, violet, or red color should appear in either stratum. Such colors indicate the presence of *cerulignol* or other objectionable impurities.

Wood-tar creosote is practically insoluble in strong solution of

that none of the samples complies with the requirements of the United States Pharmacopeia.

	1	2	3	4	5	6
Specific gravity, ...	1·0748	1·0748	1·0650	1·0642	1·049	1·069
Percentage distilling below 200° C., ...	5	20	None.	None.	18	32
Percentage distilling from 200° to 205°, ...	34	20	None.	None.	12	18
Percentage distilling from 205° to 210°, ...	26	30	None.	2	12	8
Percentage distilling from 210° to 215°, ...	23	19	30	37	39	24
Percentage distilling from 215° to 220°, ...	6	7	25	21	14	9
Percentage distilling from 220° to 238°, ...	3	1	40	36	..	4
Behavior with diluted glycerol, ...	Normal.	Normal.	Emulsion.	Emulsion.	Emulsion.	Normal.
Number of c.c. of 7½ per cent. NaHO required to dissolve 2 c.c. of sample, ...	9	8	9	7	8	8
Behavior of 1 c.c. of sample when mixed with 20 c.c. of a 20 per cent. solution of KHO in absolute alcohol, ...	Crystals in 15 minutes; solid in 40	No crystals in 5 hours; solid in 18 hours.	Crystals in 4 minutes; solid in 15	Solidified almost immediately.	Solidified on cooling.	Solidified on cooling.
Percentage of guaiacol, .	None.	None.	8	16	..	..
Percentage of mixed potassium compounds of guaiacol and creosol (page 284), ...	60	48	60	106	..	..

ammonium hydroxide, and when shaken with one or two measures thereof (sp. gr. 0·880) the mixture separates on standing into two layers, of which the lower or creosotic layer considerably exceeds the volume of the sample used.[1] Genuine and pure wood-creosote, when agitated with ammonium hydroxide, will not acquire a color deeper than lemon-yellow in half an hour, and the upper aqueous stratum should be pale or yellowish. In twenty-four hours the creosote should have acquired a brown or olive-green tint,—not blue.

According to the U. S. Pharmacopeia (1890), "on mixing 2 c.c. of creosote with 8 c.c. of a 7·5 per cent. solution of sodium hydroxide, a clear, pale-yellowish liquid results, which becomes turbid when diluted with water, but clears up after 50 c.c. have been added (absence of neutral oils)."

ADULTERATIONS OF WOOD-CREOSOTE.

Wood-tar creosote has been sometimes adulterated with, or wholly substituted by, the crude phenols of coal-tar. The reactions of the cresols and xylenols resemble those of wood-creosote still more closely than do those of phenol, and many of the proposed tests for differentiation are valueless.

The reactions described below have been carefully studied by the author on specimens of pure phenol, Calvert's No. 5 carbolic acid (representing cresols), and Morson's creosote. The descriptions should be compared with the reactions of phenol and cresol given on page 259.

a. Wood-tar creosote is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose. Shaken with half its measure of collodion, Calvert's No. 5 carbolic acid coagulates the gun-cotton to a transparent jelly, best observed by inclining the tube and causing the liquid to flow gently from one end to the other. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution. Addition of much wood-creosote to a mixture of collodion and a coal-tar acid causes a re-solution of the precipitated nitrocellulose. When a mixture of equal volumes of Morson's creosote and Calvert's No. 5 carbolic acid is shaken with half its measure of collodion, decided signs of precipitation are observed. With two-

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[1] According to the British Pharmacopeia (1898), if wood-creosote be agitated with five times its measure of solution of ammonium hydroxide (sp. gr. 0·959) its volume will not be diminished materially unless coal-tar phenols be present.

thirds of the coal-tar acids to one-third of creosote, the precipitation of nitrocellulose is very marked.

b. When carefully used, a solution of ferric chloride affords a very satisfactory means of distinguishing wood-creosote from coal-tar acids, but not for distinguishing either in mixtures of the two. The reaction produced varies, however, in a somewhat curious manner, according to the way in which the test is performed, the following being, in the author's experience, the most satisfactory methods of operating. 1. On placing a drop of Morson's wood-tar creosote in a hemispherical porcelain dish and adding a few drops of neutral solution of ferric chloride, a yellowish-brown coloration is produced, and on stirring the undissolved creosote acquires a reddish-brown and the ferric solution an olive-brown tint. Calvert's No. 5 carbolic acid, when similarly treated, acquires a light straw-color, while the ferric solution assumes a fine violet coloration, which is permanent. On slightly diluting the mixtures with alcohol they both yield olive-brown solutions, but on further addition of alcohol the creosotic mixture becomes a light olive-brown tint with a shade of green, while the carbolic solution turns light brown or amber without any green tinge. 2. On the other hand, if a drop of wood-creosote be dissolved in 10 drops of alcohol, and a drop or two of dilute ferric chloride added, a bluish-green coloration is produced, changing to a fine green, while Calvert's No. 5 carbolic acid yields a greenish-blue color under similar conditions. On adding sufficient ferric chloride to precipitate the wood-creosote from its solution, an olive-brown coloration changing to deep brown is obtained; while the carbolic mixture retains its greenish-blue tint, though more or less disguised by the yellow color of the ferric solution. 3. The addition of one drop of a 10 per cent. aqueous solution of ferric chloride to 15 c.c. of an aqueous solution of wood-creosote produces a green coloration, changing very rapidly to brownish yellow. The solution of a coal-tar acid when similarly treated gives a permanent violet-blue coloration.

c. Morson's wood-tar creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerol (sp. gr. 1·258), whether one, two, or three times its volume of that liquid be employed. Other varieties of wood-creosote are somewhat more soluble in glycerol, but the solutions are readily precipitated on adding water. Guaiacol dissolves in absolute glycerol, but is precipitated by dilution.

d. Hager modifies this test by using somewhat diluted glycerol. Three measures of absolute glycerol mixed with one measure of water is an appropriate strength. For the detection of coal-tar acids in wood-creosote, 1 measure of the sample should be thoroughly agitated in a Mohr's burette with 3 measures of the diluted glycerol, and the liquid allowed to stand till separation has occurred. If the creosote be pure, the volume will remain unchanged. If reduced, the glycerol layer is tapped off, and the remaining creosote again shaken with three times its measure of diluted glycerol and the measure again observed. This second treatment will always suffice for the removal of the coal-tar acids, unless their proportion is very large, and hence the volume of the residual layer will indicate the proportion of real wood-creosote in the quantity of the sample taken. The nature of the residual creosote can be verified by the collodion test (*a*), while the coal-tar acids can be recovered from the glycerol solution by filtering it to remove suspended traces of wood-creosote, diluting with water, and agitating with chloroform. On spontaneous evaporation of the separated chloroform, the coal-tar acids are obtained in a condition of sufficient purity to allow of their positive recognition.[1]

From the foregoing reactions it will be seen that phenol, cresols, and wood-tar creosote can be readily distinguished from each other. The case is different when a mixture of the substances has to be

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[1] Hager's modification of the glycerol test for creosote has been examined in the author's laboratory by W. Chattaway with fairly favorable results. The following figures, obtained with mixtures of wood-creosote and Calvert's No. 5 carbolic acid, show the approximation to the truth of which the method is capable:

TAKEN.		FOUND.	
Wood-creosote.	Coal-tar Phenols.	Residual Layer.	Recovered by Chloroform.
9 c.c.	1 c.c.	9·0 c.c.	·96 grammes.
8 ,,	2 ,,	8·0 ,,	1·82 ,,
6 ,,	4 ,,	6·3 ,,	3·46 ,,
4 ,,	6 ,,	4·0 ,,	5·22 ,,

The portion left undissolved after the second treatment with dilute glycerol had all the characters of wood-creosote. It did not coagulate collodion. The portion dissolved by the glycerol and subsequently recovered by chloroform behaved like coal-tar acids with collodion and ferric chloride. Hence the separation by glycerol is fairly perfect.

dealt with, as in the case of a sample of wood-creosote adulterated with crude carbolic acid. As the problem is to detect the coal-tar acids in presence of wood-tar creosote, rather than the reverse, only affirmative tests for the former bodies are of service, and in many cases these are seriously modified by the simultaneous presence of creosote. In fact, the reactions with glycerol and collodion are the only two simple tests of real service, and these are much affected by the presence of a considerable proportion of wood-creosote. If, however, the sample be treated with diluted glycerol, as described under *d*, and the ferric chloride and collodion tests be applied to the residue recovered by chloroform from the glycerol solution, the recognition of the coal-tar acids can be satisfactorily effected. These tests are best applied to the portion dissolved by the first treatment with glycerol, a second treatment being necessary to complete the extraction of the coal-tar acids, but the additional quantity dissolved is liable to contain sufficient creosote to obscure the blue coloration with ferric chloride. In employing these tests it must be remembered that genuine wood-tar creosote contains distinct traces of phenol and cresols and still more of xylenols, and hence adulteration should not be assumed unless the treatment with diluted glycerol effects the removal of a very notable quantity of coal-tar acids.

A possible addition to wood-tar creosote, but one which does not appear to have been noted, is that of *blast-furnace creosote*. This, being of very similar composition to wood-creosote, is very difficult to detect. The phenoloid bodies from blast-furnace creosote oils were distilled, and the fraction passing over between 210° and 220° examined in the author's laboratory by the foregoing tests for wood-creosote. The fraction itself readily gelatinised collodion, and gave with ferric chloride (test *b* 1) a slate-blue coloration changing to dirty brown. On treatment with diluted glycerol the greater part remained undissolved, but the dissolved portion when recovered by chloroform had the odor of common phenol, coagulated collodion, and reacted with ferric chloride almost exactly like Calvert's No. 5 carbolic acid, except that by test *b* 1 the violet-blue changed to brown instead of being permanent (page 288). These reactions would allow of the detection of blast-furnace creosote in wood-creosote, but the insolubility of the greater part of the former product in diluted glycerol would render a separation of the two impossible by that means. If the adulteration of wood-creosote by the portion of the blast-furnace product insoluble in glycerol were to be attempted, the reaction with ferric chloride and the gelatinisation of collodion would suffice to detect the substitution. The same is true of the fraction boiling below 240° of the *phenoloid bodies* from a crude *shale oil,* in addition to which their peculiar odor would attract attention.

Blast-furnace Tar Creosote.

The tar obtained by cooling the waste gases from blast-furnaces (see page 44) yields very little naphtha on distillation, and hence the "creosote oil" consists of the whole distillate up to the point at which the oils solidify on cooling. Blast-furnace creosote oil is a thin, brown liquid, lighter than water. It contains no naphthalene, but is rich in basic constituents and phenols.

On treating 14 gallons of creosote oil (sp. gr. 0·988) condensed from blast-furnace gases with sodium hydroxide solution of 1·07 specific gravity (6 per cent. NaHO), and decomposing the solution with dilute sulphuric acid, Watson Smith[1] obtained 2 gallons of crude creosote as a dark-brown liquid of 1·07 specific gravity. On fractionally distilling this product Smith obtained only 1·33 per cent. of phenol boiling at 182° C., whereas the tar-acids from Lancashire coal-tars yield about 65 per cent. of crystallisable phenol. The fraction which would contain the cresols amounted to 4·5 per cent. of the total tar-acids. The larger fraction (19·4 per cent.), distilling between 210° and 230°, probably consisted mainly of xylenols with guaiacol and creosol (see page 278). These results show that a close similarity exists between the phenoloid bodies of blast-furnace creosote and those contained in wood-tar. A large proportion of the creosote distilled at a temperature above 230°, but the exact nature of this fraction is not at present known. The fraction distilling above 360° gave, on treatment with soda and exposure to air, unstable coloring-matters, which are probably allied to the eupittonic acid obtained from wood-tar (see page 280).

It is probable that the extraction of the phenoloid bodies from the sample examined by Smith was not complete, as he used a dilute alkali. By repeatedly treating a sample of blast-furnace creosote oil of 0·956 specific gravity with 19 per cent. solution of sodium hydroxide (sp. gr. 1·21), the author extracted 34 per cent. by measure of tar-acids, having a specific gravity of 1·0355. One hundred c.c. of these acids gave very little distillate below 200° and

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[1] *J. S. C. I.,* 1883, 497.

59·5 per cent. below 250° C., the largest fraction (24 per cent.) distilling between 220° and 230°. The fraction distilling between 210° and 220° is described on page 290. On treating a portion of the mixed tar-acids extracted by strong alkali with dilute sodium hydroxide solution (3·5 per cent. of NaHO), separating the insoluble portion, and acidulating the aqueous liquid, the phenols obtained were completely soluble in dilute glycerol, and gave a fine violet-blue coloration with ferric chloride.

In a later contribution[1] Smith reports the detection of the following constituents of blast-furnace creosote: Ordinary phenols, cresols (chiefly 1–3), xylenols (chiefly 1–3–4), trimethylphenols, and naphthols.

Two samples of blast-furnace creosote oil examined by L. Archbutt had a specific gravity of 0·969 and 0·956 respectively, and yielded 35 and 29 per cent. of phenols to sodium hydroxide solution of 1·21 sp. gr. (19 per cent. NaHO).

The phenoloids of blast-furnace tar contained in the "neosote" of commerce are chiefly cresols.

NEOSOTE.—The phenoloids of blast-furnace tar (page 44) have been patented by Allen and Angus under the name of *neosote* ("new preservative"). This is obtained by treating blast-furnace creosote oil with caustic soda, separating the insoluble hydrocarbon oils, and decomposing the solution of the sodium compound by the waste-gases from the blast-furnaces. The carbon dioxide in the gases converts the sodium into carbonate and the phenoloids are set free. The solution of sodium carbonate is causticised with lime, and thus furnishes caustic soda for treating a fresh quantity of the creosote oil. The crude phenoloids are redistilled, the distillate constituting the "neosote" of commerce. The figures in the table on opposite page, obtained by the author, show the behavior of a typical sample of neosote when distilled with a Glynsky's fractionator.

It will be observed that 27·8 per cent. passed over between 195° and 200°, and an additional 19·8 per cent. between 200° and 205°. The temperature remained absolutely constant at 197° for a considerable time, and again at 204°. The regular decrease in the specific gravity of the fractions is interesting. The original sample contained 3·15 per cent. of hydrocarbons.

Neosote contains only one or two units per cent. of crystallisable phenol, a large proportion of cresols, and gradually decreasing

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[1] *J. C. S.*, 49 (1886), 17.

proportions of the higher homologues. Oxyphenols, similar to or identical with those of wood-creosote, are also present, but the method of purification adopted eliminates a large proportion of these constituents. When freshly distilled, neosote is almost as colorless as water, but it acquires a dark yellow or brown color by keeping. Experiments made to test the antiseptic value of neosote have shown that it is fully able to compare with crude carbolic acid, while its caustic properties (when applied in a concentrated condition to the skin) appear to be much less marked than those of the gas-tar product.

	Per Cent. by Measure.	Specific Gravity of Fraction.
Below 174° (Water), ...	1·0	. .
From 174° to 190°, ...	4·4	. .
,, 190° to 195°, ...	10·8	1·0495
,, 195° to 197½°, ...	21·2	1·0450
,, 197½° to 200°, ...	6·6	1·0390
,, 200° to 202½°, ...	11·2	1·0340
,, 202½° to 205°, ...	8·6	1·0290
,, 205° to 210°, ...	10·9	1·0255
,, 210° to 215°, ...	7·8	1·0185
,, 215° to 220°, ...	8·2	1·012
,, 220° to 225°, ...	1·0	. .
Total below 225° C., . .	91·7	. .

Residue (by difference) 9·3, containing 1·05 per cent. of hydrocarbons.

Shale-oil Creosote.

In the manufacture of hydrocarbon products from the crude oil or tar obtained by the distillation of bituminous shale, the different fractions are washed with a strong solution of sodium hydroxide (page 39, *et seq.*). On decomposing the resultant viscous liquid or "soda-tar" by dilute acid, a mixture of crude phenoloid bodies is obtained, usually amounting to 1½ to 2 per cent. of the crude shale oil. The proportion and nature of the product vary with the character of the shale and the manner in which the distillation was conducted.

The "creosote" from shale oil presents a close general resemblance to the parallel products from beechwood tar (page 280) and blast-furnace tar, with, however, the notable difference that creosol seems to be wholly absent. On the other hand, xylenols are present, also a cymenol, $C_{10}H_{14}O$, boiling at 237° C. Three isomeric phenols of the formula $C_{10}H_{13}OH$ appear to be present. The behavior with reagents of the fraction distilling below 240° is described on page 291. The pyrogallic ethers boiling respectively at 253°, 265°, and 285° (page 278), found by Hofmann in wood-tar creosote, have also been isolated from shale creosote. Other bodies of very high boiling point are present, but these have not been fully examined.

Coal-tar Creosote and Creosote Oils.

The term "creosote oil" was formerly used to denote that portion of the distillate from coal-tar intermediate between "crude naphtha" and pitch. It is practically synonymous with the "heavy oil" or "dead oil," so called from its being heavier than water.

The name "creosote oil" is now sometimes applied to certain oils obtained by the distillation of bituminous shale and by the cooling of the waste gases from blast-furnaces, and also to the bone-oil produced in the manufacture of animal charcoal. All these products are decidedly different in their chemical and physical characters from the wood-tar and coal-tar products to which the name of creosote oil was first applied (see page 276).

Coal-tar Creosote Oil commonly consists of that portion of coal-tar which distils between 200° and 300° C., together with the residual oils from the manufacture of crude carbolic acid, naphthalene, and anthracene (see page 200). This description, however, applies especially to the creosote oil produced in the best-managed works. In some works, every residue which cannot be used for any other purpose finds its way into the creosote-oil well.

Fresh coal-tar creosote oil is greenish yellow and highly fluorescent, the latter character being still more evident after exposure of the oil to air and light. After a time the oil becomes bottle-green by reflected and dark red by transmitted light. The smell is unpleasant and highly characteristic. When rubbed between the fingers, the feel is at first oily, but the tar-acids soon act on the skin, producing a sensation of friction. Creosote oil is always somewhat heavier than water, the specific gravity of the portions last distilling being as high as 1·10. It usually contains more or less naphthalene, phenanthrene, anthracene, diphenyl, and other solid hydrocarbons; phenol, cresols, and higher phenoloid bodies; about 2 per cent. of pyridine, cryptidine, quinoline, acridine, and other bodies of basic character; and the so-called indifferent oils, fluid at ordinary temperatures, and about which comparatively little is known, notwithstanding the enormous quantity of creosote oil produced (see "Naphthalene Oils," page 200).

Noetling believes that the volatile phenoloids of creosote oil contain, in addition to α- and β-naphthol and higher homologues of phenol, the phenols of anthracene and phenanthracene.[1] The dihydric phenols characteristic of wood-tar are conspicuous by their absence.

	Specific Gravity 32° C.	Percentage of Distillate 315° C.	Percentage of Tar-acids from Distillate.
A. *Whole runnings of heavy London oils*—			
Highest, ...	1075	79	8·0
Lowest, ...	1048	60	3·0
Average of 20 samples, .	1058·8	71·5	5·6
B. *Partial runnings of London oils*—			
Highest, ...	. .	91	10·2
Lowest, ...	. .	78	8·2
Average of 20 samples, .	. .	82·8	9·15
C. *English country oils*—			
Highest, ...	1056	90	24·0
Lowest, ...	1024	72	13·5
Average of 18 samples, .	1033·5	81·8	18·6

The preceding table shows the general character of coal-tar creosote oils of different kinds. The samples under A were the *whole runnings* of heavy oils distilled from samples of tar obtained from twenty different London gas-works. The samples of oil under B were produced at the works of the Gaslight and Coke Company at Beckton, and represent creosote oils from which portions of the green oils and naphthalene were excluded. Hence these samples are comparatively rich in tar-acids, and give a larger distillate below (315° C.) than the whole runnings described under A. The liquefying point of the B samples ranged from 37° to 32° C., and the point of turbidity on cooling from 31° to 29° C. The samples in series C were

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[1] *Ber.*, 1885, 385.

analysed by L. Archbutt. All were completely fluid at 33° C., and many at 15·5° C. The sample yielding 72 per cent. of distillate and 13·5 of tar-acids was the product of a special treatment. The samples in series C are probably somewhat richer in tar-acids than the generality of country oils.

Writing in February, 1885, the late C. M. Tidy, who analysed the B samples, stated that the best London creosote oils contain a proportion of tar-acids closely approximating to 8 per cent., and he stipulated for this amount, believing it to secure the genuine character of the oil.

The dead oils made in London, and from the tar from Newcastle coal generally, are the richest in naphthalene and constituents of high boiling point, but contain only a moderate percentage of tar-acids. The "country oils," or oils from the Midland districts, are lighter, thinner, and more volatile than "London oils," and usually contain less naphthalene and a larger proportion of tar-acids than the latter. The Scotch oils are largely derived from cannel coal, are still thinner and more volatile, and are sometimes lighter than water.

Creosote oils from coal-tar receive their main application in the creosoting or preserving of timber, and their technical assay is practically limited to an examination of their suitability for this purpose. The impregnation of wood with creosote oil chokes up the pores and materially hinders the subsequent absorption of water. The odor of creosote oil is one much disliked by the lower animals, while certain of the constituents have a powerful antiseptic action.[1]

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[1] The preservation of timber has been a subject of active investigation for many years and many patents have been issued. Probably the most thorough synopsis of the value and practicability of these processes is contained in the report made to the American Society of Civil Engineers in 1885. The conclusion reached is that creosoting is the best method and that the applicability is merely a question of expense. Where decay is rapid or timber costly, creosoting will be economical, but the reverse where decay is slow or timber cheap. The decay of wood is due partly to direct oxidation, but mostly to the action of microbes and the mycelium of fungi. Direct destruction and removal of woody tissue is also brought about by the action of insects and worms. All these influences are much more potent when the timber is exposed to the joint or rapidly alternating action of water and air; hence the rapid decay of railroad cross-ties, telegraph poles, and wharf-piling. In the last case the most serious damage is done by several boring animals, especially the *teredo*. Creosoting, when well done, protects timber work against all the destructive influences, and in tropic waters is absolutely necessary, since a few months will suffice for the teredo to destroy a thick pile.

Many failures in creosoting have occurred in consequence of the use of materials of inferior value. It is probable that the utilisation of coke-oven tar, which is now

The preservative properties of creosote oil have been ascribed to the "tar-acids," or phenoloid constituents, as they are powerful antiseptics, coagulating albumin and rendering animal life impossible, but it is probable that their value has been greatly overrated, since the solubility and volatility of the lower members prevent a permanent antiseptic influence. Hence the phenoloid bodies of high boiling point and slight solubility may be of more value for creosoting timber than phenol and the cresols, but the lower members are doubtless valuable as coagulators of albumin, and should be present in sufficient quantity to effect this. If dissolved or volatilised from the timber, they will probably create an antiseptic atmosphere, and thus prevent the approach of living organisms. The basic constituents are also possibly of antiseptic value, and certain of them are not readily washed out or volatilised. The naphthalene of coal-tar creosote volatilises only from the superficial strata of the timber, and, by solidifying and filling up the pores of the wood, probably acts mechanically as a valuable preservative agent.

Creosote oils have also been employed as fuel, for production of illuminating gas, carburetting coal-gas, softening hard pitch, manufacturing lubricating compounds, burning for lamp-black, and production of antiseptic preparations. The so-called "Lucigen light" is obtained by projecting a spray of creosote oil by compressed air, whereby a circular brush of flame of high illuminating power is produced.

attracting much attention from industrial engineers, will so reduce the cost of creosote that the financial phase of the problem will be in a more satisfactory state.

Much valuable information on the nature and mode of action of creosote oils will be found in a paper by S. B. Boulton in the *Proceedings of the* (*British*) *Institute of Civil Engineers* for May, 1884; for a copious abstract of which see *J. S. C. I.*, 1884, 622.

R. Rittmayer (*Ding. Polyt. Jour.*, **271**, 228), has published a historical description of the methods for preserving timber, with comparisons of the results obtained.

The process of creosoting may be effected by placing the timber in a vessel so constructed that the air can be exhausted. The creosote oil, previously heated to a temperature of 35° to 50° C., is allowed to enter the exhausted receiver, and pressure is then applied by pumps in order to effect the better penetration of the antiseptic fluid. According to an improved method invented by S. B. Boulton, the exhaustion is continued after the entrance of the creosote, which is heated to a temperature somewhat above 100° C. By this means the moisture contained in the pores of the wood is volatilised and removed, and the creosote oil subsequently penetrates the wood very thoroughly. Timber can be treated by this method without being previously seasoned. The amount of creosote oil taken up varies considerably, but is usually about one gallon per cubic foot of wood.

ASSAY OF CREOSOTE OILS.

As previously stated (page 296), the value of creosote oils for preserving timber depends on several constituents, all of which should therefore be taken into account in the examination. Unfortunately, the assay of creosote oils is often conducted according to the arbitrary conditions of a contract-note drawn up without much reference to the chemical nature of the article to be assayed, or to the possibility of obtaining a fairly accurate determination of the leading constituents by the mode of operation prescribed. The early specifications often stipulated for a certain specific gravity; the absence of a deposit when cold; the presence of a certain proportion of tar-acids; the volatility of a certain percentage below 315° C.; and, occasionally, still more arbitrary stipulations were made. Later specifications include no reference to the specific gravity, allow the presence of a considerable proportion of naphthalene, and stipulate that a certain percentage of the oil shall not distil below a given temperature, instead of the opposite—this modification being a recognition of the value of the fractions of high boiling point.[1] No practical recognition has yet been made of the

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[1] The specification of the "Crown Agents for the Colonies" (July, 1882) stipulated that "the creosote shall not contain more than 30 per cent. of naphthalene, paranaphthalene, or any other (solid) substance when subjected to a temperature of 40° F." It also stipulates for a specific gravity of 1·035 to 1·055 at a temperature of 60° F.; for a distillate of at least 75 per cent. below 610° F., containing at least 10 per cent. of tar-acids (extracted by soda of 1·125 specific gravity), of which one-half should distil below 450° F.

The following are details of recent specifications for creosote oil supplied to the Midland Railway Company:

The creosote supplied is to be obtained exclusively by the distillation of coal-tar, and must not contain more than 3 per cent. of mechanically mixed water.

It must become perfectly fluid when raised to a temperature of 100° F., and must remain perfectly fluid at a temperature of 90° F.

It must have a specific gravity of from 1·040 to 1·065 at 90° F., as compared with water (= 1·000) at 60° F.

It must contain not less than 25 per cent. (by volume) of constituents that do not distil over at a temperature of 600° F., and, when tested in accordance with the instructions annexed, it must yield not less than 6 per cent. (by volume) of crude tar-acids.

The following details of the method of testing creosote oils supplied to the Midland Railway Company (England) under the foregoing specifications have been communicated by L. Archbutt.

1. The sample is to be warmed, if necessary, until it is perfectly fluid. One hundred c.c. of the well-mixed creosote are then to be poured into a 4-oz. tubulated retort, and heated gradually to a temperature of 600° F. by the aid of a naked flame, sur-

antiseptic value of the basic constituents of creosote oil, nor of the fact that the portion of the oil distilling below 315° C. does not contain the whole of the tar-acids.

The specific gravity of creosote oil is not a criterion of its suitability for treating timber, but is an indication of genuine character of the samples: that is, their derivation from coal-tar only.

The presence of solid naphthalene in the cold creosote oil is no detriment, but the deposit should wholly dissolve on warming. A sample should become quite clear below 38° C., and should not become turbid again till cooled to 32° C.

The liquefying point is usually ascertained by transferring an average sample of the oil to a test-tube, immersing a thermometer, and warming it gently till it becomes liquid. The point of turbidity is similarly observed by allowing the tube to cool spontaneously. (See Vol. II, part 1, p. 37.)

These simple tests are much more satisfactory than the assay for solid naphthalene, as required by the Crown Agents for the Colonies. If necessary, the approximate determination of the naphthalene may

rounded by a screen, the distillate being collected in a 100 c.c. graduated cylinder. The thermometer is to be immersed, so that at the end of the distillation the bulb is just out of the oil. The distillation should be carried on as quickly as possible, due precaution being taken to prevent any loss by volatilization; and the time occupied should not exceed thirty minutes. The distillate is to be measured at the same temperature as the original creosote.

2. The distillate obtained above is to be poured into a stoppered flask of about 250 c.c. capacity, and vigorously shaken with 30 c.c. of a solution of caustic soda having a specific gravity of 1·21. The flask is then to be placed in a water-oven, heated for two or three minutes, and again shaken vigorously for at least one minute. The contents of the flask are next to be poured into a separating-funnel, allowed to stand until the liquids have completely separated, and the soda solution then drawn off into a 10-oz. stoppered globular separator. The oil left in the separating-funnel is to be returned to the flask and treated exactly as before, but using only 15 c.c. of the caustic soda solution. After the soda solution has again been drawn off, the treatment is to be repeated a third time if necessary.

3. The mixed alkaline solution in the separator is next to be well shaken with about 70 c.c. of ether, to remove any creosote which has escaped separation, and after the ether has completely separated, the soda solution is to be drawn off into an 8-oz. wide-necked flask, the ether being washed with 2 to 3 c.c. of fresh soda solution which are added to that in the flask. The flask is next to be placed over a steam-bath, and allowed to remain until the ether has completely evaporated; after which the alkaline liquid is to be cooled and treated with diluted sulphuric acid (1 vol. of acid to 3 vols. of water) until the solution is slightly acid and the crude tar-acids have completely separated. The whole is then to be poured into a graduated 100 c.c. or 150 c.c. cylinder and the volume of tar-acids read off when cold.

be effected in the manner carried out in the works-laboratory of Messrs. Burt, Boulton & Haywood, as follows:—"100 grm. of the sample are placed in a small beaker and cooled to a freezing mixture to 4·5° C. The oil is kept at that temperature for about fifteen minutes, after which it is thrown on a cloth filter, placed in a small funnel inserted in a larger one containing a freezing mixture, so that a temperature of 40° F. may be maintained during the filtration. The filter-cloth and contents are then removed from the small funnel as quickly as possible, and pressed strongly between coarse filter-paper in a copying press or vise. The pressed product is then detached from the cloth and weighed."

The following method, also employed in the works-laboratory of Messrs. Burt, Boulton & Haywood, is that usually adopted for ascertaining the behavior of creosote oil on distillation[1]:—100 c.c. measure of the oil are gradually heated in a 4 oz. tubulated retort, by a small, naked flame surrounded by a tin-plate cylinder. A thermometer should be arranged in the retort in such a position that on the termination of the distillation the bulb shall only just touch the residual liquid. The flame is arranged so that the distillation shall occupy about thirty minutes. The distillate should be collected in a graduated glass cylinder, and the proportion of water observed at an early stage of the operation, as later on it is again more or less completely taken up by the phenoloid constituents of the oil. The proportion of water in creosote oils is very variable, ranging from 1 or 2 to nearly 10 per cent. The distillation is arrested at 315° C., 321° C., or other temperature, as specified in the contract-note, the measure of the distillate being then observed.

For the determination of the *tar acids*, it is usual to employ the distillate obtained in the last operation. This is transferred to a stoppered flask, holding about 250 c.c., and treated with 30 c.c. of a solution of sodium hydroxide, made by dissolving 23 grm. of pure sodium hydroxide in water, and diluting to 100 c.c.). The liquid is thoroughly agitated, heated for a few minutes in a water-bath, and again thoroughly agitated for about a minute. The whole is then poured into a separating funnel, the alkaline liquid drawn off, and the oil agitated with a further quantity of 15 c.c. of the solution, which is then separated as before. To ascertain if the extraction of the phenols is complete, it is neces-

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[1] For the details of this and the following test, as also for much other information on creosote oils and other tar-products, the author is indebted to Mr. D. Bendix.

sary to agitate the undissolved portion with alkali a third time, and slightly acidify the liquid separately. Complete extraction is generally indicated by the solution ceasing to acquire a reddish tint. The alkaline liquids are mixed, well cooled, separated from any further stratum of oil, and treated with a slight excess of diluted sulphuric acid (1 : 3), of which about 30 c.c. will be required. The mixture is then transferred to a graduated cylinder and allowed to *cool completely*, after which the volume of tar-acids is observed, the number of c.c. obtained being the percentage by measure of tar-acids in the sample under examination. This method is substantially that prescribed by Abel and Tidy. In the specification of the Crown Agents for the Colonies a ten per cent. solution of sodium hydroxide (sp. gr. 1·125) is employed, but otherwise the process is the same.

Tidy employs 20 c.c. of alkaline solution for the second and third extractions. The tar-acids are separated and redissolved in 20 c.c. of sodium hydroxide solution (20 per cent.), and 10 c.c. of water. The solution is then boiled and filtered through a funnel containing a plug of asbestos. The plug is washed with not more than 5 c.c. of boiling water, and the filtrate allowed to cool *perfectly* in a 100 c.c. measure. It is then rendered slightly acid with diluted sulphuric acid, of which about 10 c.c. will be required, allowed to stand for two hours till perfectly cold, when the percentage of tar-acids is read off. The results are lower than those given by processes in which the re-solution of the tar-acids is omitted, owing to their imperfect recovery from the aqueous liquid.

The foregoing modes of operation ignore such tar-acids as occur in the fraction of the oil distilling above 315° to 320° C., and do not ensure the complete extraction of the acids existing in the less volatile portion of the oil. The proportion of these higher phenoloïd bodies extractable by strong solution of sodium hydroxide from London coal-tar creosote varies from 2 to 4 per cent. A more accurate and practical assay of creosote oil for the content of tar-acids would be effected by the following process:—The oil should be distilled to the point of pitching, and the whole of the distillate subjected to the treatment with solution of soda. The alkali should at first be of moderate strength (*e. g.*, 10 per cent.), but the operation should be repeated with fresh quantities of 30 per cent. solution (sp. gr. 1·34) until the extraction is complete, as shown by the separation of mere traces of tar-acids on acidifying the alkaline liquid.

To cause the alkaline liquid to separate completely and promptly from the stratum of indifferent oils, an addition of petroleum spirit should be made, and the whole again agitated. The petroleum spirit acts as a solvent for the oils, and also prevents the naphthalene from solidifying or being partly dissolved by the alkaline liquid. Instead of liberating and measuring the tar-acids in a graduated cylinder, a more accurate plan is to employ a flask with a narrow, graduated neck. The layer of tar-acids is brought to the zero-mark by running in mercury from a burette. The tar-acids thus separated are not anhydrous. They can be further examined as described in the section treating of the assay of crude phenol.

The foregoing modified method of estimating the tar-acids in creosote oils by isolation and measurement is far more satisfactory than any process based on their conversion into the bromo-derivatives, as the latter plan involves the knowledge or assumption of their mean molecular weight and of their exact reaction with bromine.

Although not usually practised, a valuable addition to the ordinary method of examining creosote oils consists in a determination of the basic constituents. This may be effected by distilling the sample to the point of coking and agitating the distillate with diluted sulphuric acid (1 to 3). The acid liquid is separated, rendered distinctly alkaline with sodium hydroxide, any oily layer separated, and the aqueous liquid distilled nearly to dryness. This second distillate is mixed with the oily layer, the whole acidulated with hydrochloric acid, and evaporated to dryness on the water-bath. The residue consists of the hydrochlorides of the tar-bases, from which the bases themselves may be liberated by solution in a small quantity of water and addition of solid sodium hydroxide to the liquid until saturated. If desired, the bases may be further examined by converting them into platinochlorides.

APPENDIX.

EXTRACTION APPARATUS.

The disadvantage of the Soxhlet apparatus is the use of cork connections, which require frequent renewal and are very apt to leak. Ground-glass joints do not altogether prevent leakage. An improved apparatus, designed by Knorr, has been much used in the laboratory of the Department of Agriculture at Washington, and is described by Wiley about as follows: "The principle of the construction of the apparatus lies in the complete suppression of stoppers and the sealing of the only joint with mercury.

"*A* (Fig. 10) is the flask containing the solvent; *W* a steam bath made by cutting off the top of a bottle, inverting it, and conducting the steam by one of the tubes shown, while the condensed water runs out of the other. Concentric copper rings enable the opening to be made of any desired size. *C*, the condenser, is a long glass tube on which a number of bulbs have been blown, and which is fused to the hood for holding the material to be extracted, making a solid glass union. Before joining the tube at *B* the rubber stopper which is to hold it into the outside condenser of *B* is slipped on, or the rubber stopper may be cut into its center and slipped over the tube after the union is made. In case alcohol is to be used for extraction, the flask holding the solvent is placed entirely within the steam bath.

"More detailed representations of the apparatus are shown in figures 12 and 13. In *A* (Fig. 10) is represented a section of the flask which holds the solvent, showing how the sides of the hood containing the matter to be extracted pass over the neck of the flask, and showing at *S* a small siphon inserted in the space between the neck of the flask and the walls of the hood for the purpose of removing any solvent that may accumulate in this space. The flask is made by softening an ordinary flask at the neck, and pressing this in so as to form a cup to hold the mercury which

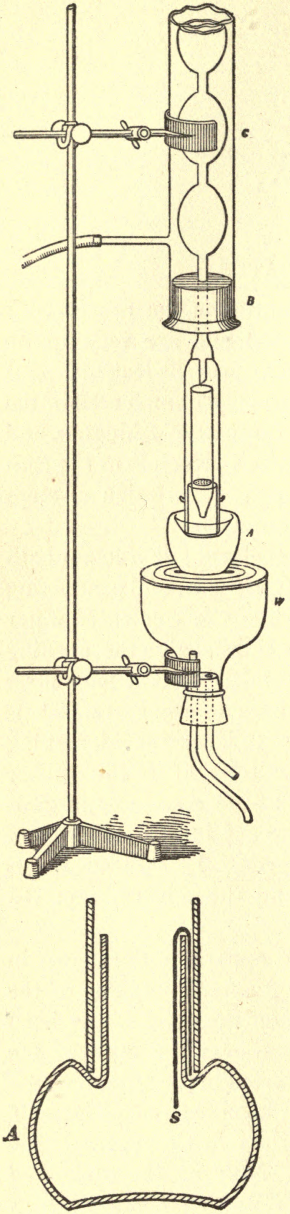

FIG. 10.

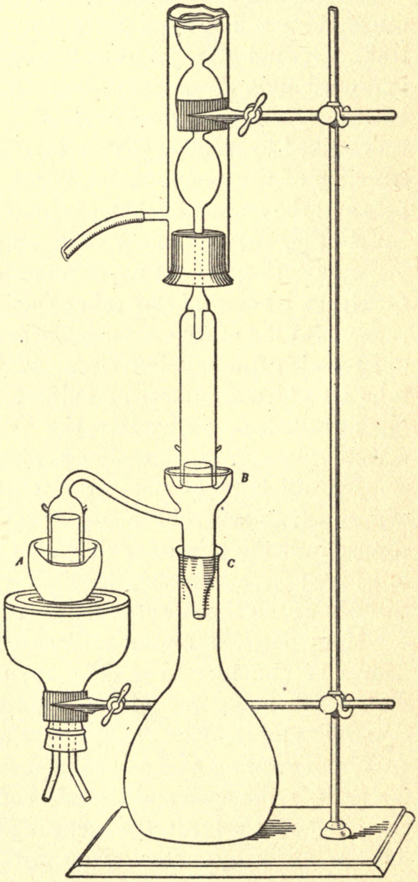

FIG. 11.

seals the union of the flask with the condenser. The flask is held in position by passing below it a rubber band, which is attached to two glass nipples blown on to the hood, as shown in the figure. The material to be extracted may be contained in an ordinary tube (Fig. 12), which may be made from a test-tube drawn out and a perforated platinum disk sealed in at *D*. The containing tube rests upon the edges of the flask containing the solvent by means of nipples, shown at *t*. If a siphon tube is to be used, one of the most convenient forms is shown in figure 13, in which the siphon, lying entirely within the extraction tube, is protected from breakage. By means of Knorr's apparatus, extractions can be carried on with small quantities of solvent, scarcely any leakage occurring even with the most volatile liquids. The apparatus is always ready for use, no corks are to be extracted, and no ground-glass joints to be fitted."

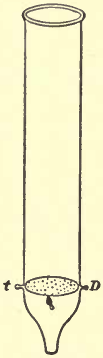

FIG. 12.

FIG. 13.

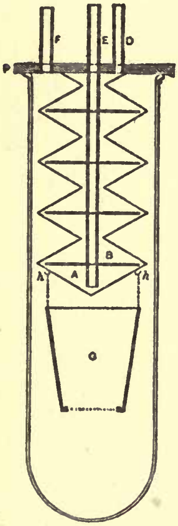

FIG. 14.

It must not be overlooked that mercury seals exposed constantly to the air of badly ventilated rooms may emit sufficient vapor to cause chronic mercurial poisoning in some persons.

For the recovery of the solvent the apparatus shown in figure 11 is used, in which *A* is the flask containing the liquid. *C* may be a ground joint; the joints of *A* and *B* are sealed with mercury.

Wiley[1] has devised a form of continuous extraction apparatus, which is shown in figure 14.

The outer vessel is a stout glass tube shaped like a test-tube. The inner vessel is made of nickel-plated metal in the form of a series of double cones; the flat plate at the top fits tightly on the ground surface of the glass vessel. Cold water passes continually through the interior of the metal vessel, by which the solvent is constantly condensed and drops

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[1] *J. A. C. S.*, 1893, 123.

upon the material to be treated, which is contained in a porcelain or platinum bucket, o, with a detachable perforated bottom. The extract drops through this bottom into a vase-like receiver resting on the bottom of the outer glass vessel. This is not shown in the cut, and will not be required if the estimation be made by the indirect method. Wiley operates the apparatus in a battery of four or more, immersed in water or other liquid heated to the proper temperature.

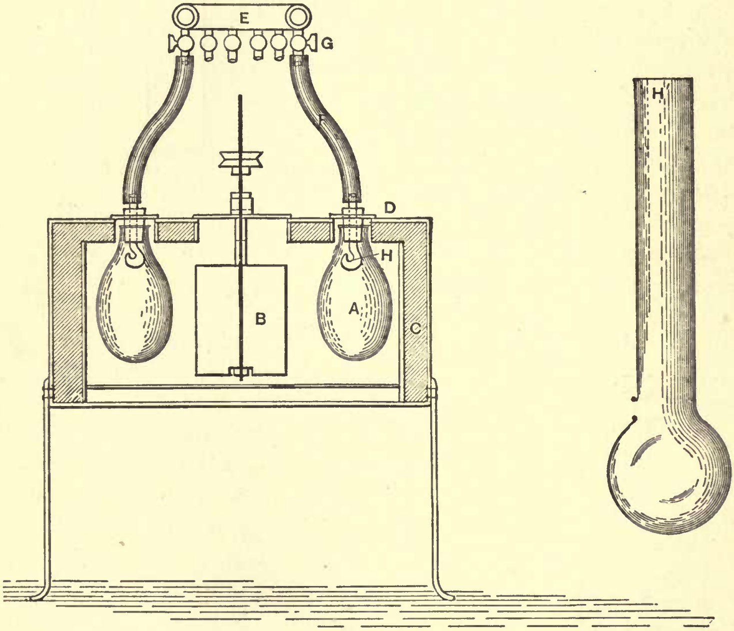

FIG. 15.

DRYING APPARATUS.

Temperatures of 100° and above are best maintained by an air bath, a satisfactory form being that of Spencer (Fig. 15), in which an even temperature is maintained by means of a fan, run by electricity or other means. The oven is made of Russia iron, with double walls, and is cylindrical in shape. The walls are about one inch apart and the space between them is filled with plaster-of-Paris or other non-conducting material. The bottom of the oven is also double, the outer metal being Russia iron and the inner copper, with an air space between. The apparatus is arranged to permit of drying in a partial vacuum or in hydrogen, for which purpose the drying flasks A are employed. The top of the oven is made double, with perforations sufficiently large to admit the flasks. The space between the tops is also filled with non-conducting material. After the flasks are placed in position the open space is closed with a cover, in the center of which is a hole through which the neck of the flask passes. The oven is heated with a cylindrical, flat, copper lamp, which is regulated by an ordinary mercury regulator. The temperature at which the drying is to be made can be fixed at any desired point, from low temperature up to as high as can safely be used without charring the material to be desiccated. For ordinary work the regulator is set for 100° C.

The drying flask A is made with a rounded bottom, and its content ranges from 150 to 200 c.c. It is closed with a rubber stopper carrying a water trap bulb, H H′, arranged that the vapor of water which condenses within the exhaust tube, instead of falling back into the flask, remains trapped in the water bulb. All the flasks in the oven are connected by means of a common connection, E, with a vacuum pump capable of producing a vacuum of from 26 to 27 inches. A layer of sand or pumice may be placed in the bottom of the flask, on which is placed the sample to be dried, and the water is determined by weighing the flask and contents before and after the drying. If desired, a current of hydrogen or other gas may be introduced into the flask during the operation by passing a very small glass tube through the cork joined to another tube by a rubber connection immediately below the cork. The inner tube should pass nearly to the bottom of the flask and be weighed with

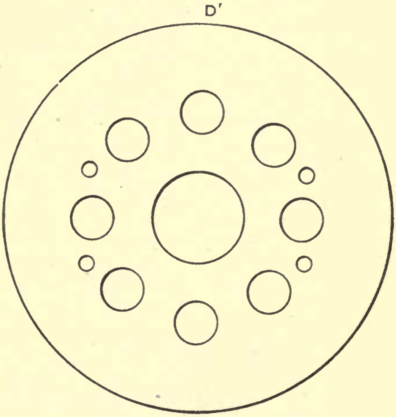

FIG. 16.

it. The hydrogen is drawn into the flask, passing through a wash-bottle containing caustic soda, another containing sulphuric acid, and lastly over solid potash. The speed of the current, which need not be very great, is controlled by a stop or pinch-cock. Any of the sample which may touch the inner tube during the intumescence caused by desiccation remains thereon, and is weighed, at the end of the operation, with the tube, which is detached and left in the drying bulb.

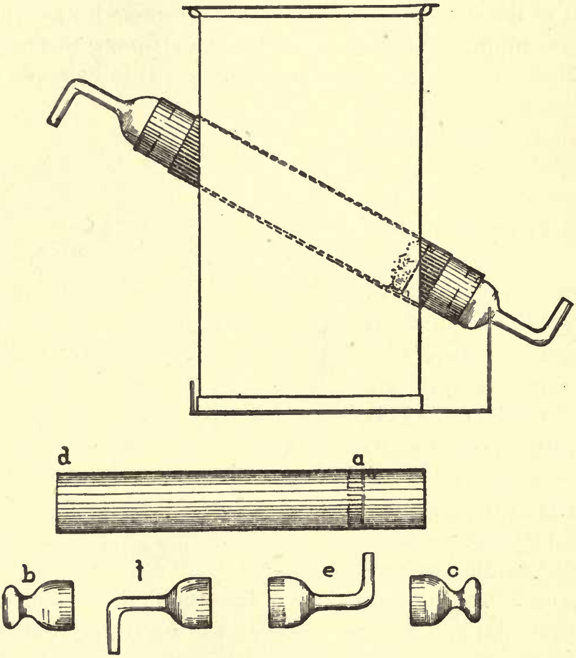

FIG. 17.

Figure 17 shows a very convenient form of drying oven for use with a current of hydrogen. The apparatus was designed by Caldwell especially to carry out the methods of determining moisture, ether-extract, and crude fiber prescribed by the A. O. A. C., all three data being determined on the same sample.

The bath is made of copper and is 24 cm. long, 15 high, and 8½ broad. This bath stands in a piece of sheet copper bent up at right angles along the sides, as shown in the end view; on one side this vertical part need not be over 1 cm. high, just enough to project a little up the side of the bath, which rests snugly against it; along the other side it projects upward, at a little distance from the side of the bath, about 15 mm., and to about the height of 4 cm.; opposite each of the tubes of the bath a slot is cut in this vertical part, which serves then as a shoulder against which the glass tube rests when in place, to keep it from slipping down and out of position.

The tube for containing the substance has at the zone *a* three small projections on the inner surface, which support a perforated platinum disk of rather heavy platinum foil carrying the asbestos filter. This tube is 13 cm. long and 23 mm. inner diameter, and weighs, with its closed stoppers, about 30 grms.

The filter is readily made in the same manner as the Gooch filter, the tube being first fitted to a suction flask by an enlargement of one of the holes of the rubber cork, or, better still, by slipping a short piece of rubber tube over it, of such thickness that it will fit tightly in the mouth of a suction flask provided with lateral tube for connection with the suction. A thin welt of asbestos is sufficient; if it is too thick, the gas and ether will not flow through readily.

About 2 grms. of the substance are put in this tube, previously weighed with the stoppers *b* and *c*, and the weight of the substance accurately determined by weighing tube and contents. The stoppers are removed, a band of thin asbestos paper is wound around the end *d* of the tube, a little behind the slight shoulder at the rim, as many times as may be necessary to make a snug fit when this tube is slid down into the copper tube in the bath, thus preventing circulation of air between the glass and the copper tubes that would retard the heating of the former; the stopper *e* is put in the lower end of the tube for connection with the hydrogen supply, and the stopper *f* in the upper end; this latter stopper is connected by rubber tube with a glass tube slipping easily through one of the holes of a rubber cork closing a small flask containing a little sulphuric acid, into which this tube just dips; when as many tubes as are to be charged are thus arranged in place and the hydrogen is turned on, the even flow of the current through the whole number is secured by raising or lowering a very little the several tubes through which the outflow passes, so as to get a little more back pressure for one, or a little less for another, as may be found necessary. When the drying is supposed to be completed, the tubes are weighed again with their closed stoppers, and so on.

For ether-extraction the unstoppered tube with contents is put directly into the extractor.

TABLE A.

COMPARISON OF SPECIFIC GRAVITY AND BEAUMÉ DEGREES.

The figures of the third column (15.5° C.) are according to the American Standard.

B°.	12·5° C. $\frac{146}{136 + \text{B}^\circ}$.	15·5° C. $\frac{140}{130 + \text{B}^\circ}$.	B°.	12·5° C. $\frac{146}{136 + \text{B}^\circ}$.	15·5° C. $\frac{140}{130 + \text{B}^\circ}$.	B°.	12·5° C. $\frac{146}{136 + \text{B}^\circ}$.	15·5° C. $\frac{140}{130 + \text{B}^\circ}$.
10	1·0000	1·0000	41	0·8242	0·8187	72	0·7018	0·6931
11	0·9931	0·9929	42	0·8190	0·8139	73	0·6985	0·6897
12	0·9865	0·9859	43	0·8155	0·8092	74	0·6951	0·6863
13	0·9800	0·9790	44	0·8111	0·8045	75	0·6919	0·6829
14	0·9733	0·9722	45	0·8066	0·8000	76	0·6887	0·6796
15	0·9688	0·9655	46	0·8022	0·7954	77	0·6854	0·6763
16	0·9605	0·9589	47	0·7978	0·7909	78	0·6822	0·6731
17	0·9542	0·9523	48	0·7935	0·7865	79	0·6790	0·6699
18	0·9480	0·9459	49	0·7892	0·7821	**80**	0·6759	0·6667
19	0·9419	0·9395	**50**	0·7849	0·7777	81	0·6728	0·6635
20	0·9359	0·9333	51	0·7807	0·7734	82	0·6697	0·6604
21	0·9299	0·9271	52	0·7765	0·7692	83	0·6667	0·6572
22	0·9240	0·9210	53	0·7724	0·7650	84	0·6636	0·6542
23	0·9179	0·9150	54	0·7684	0·7608	85	0·6606	0·6511
24	0·9125	0·9090	55	0·7644	0·7567	86	0·6576	0·6482
25	0·9068	0·9032	56	0·7604	0·7526	87	0·6547	0·6452
26	0·9012	0·8974	57	0·7564	0·7486	88	0·6518	0·6422
27	0·8957	0·8917	58	0·7525	0·7446	89	0·6489	0·6492
28	0·8902	0·8860	59	0·7486	0·7407	**90**	0·6460	0·6363
29	0·8848	0·8805	**60**	0·7449	0·7368	91	0·6432	0·6334
30	0·8795	0·8750	61	0·7411	0·7329	92	0·6404	0·6306
31	0·8742	0·8695	62	0·7373	0·7290	93	0·6376	0·6278
32	0·8690	0·8641	63	0·7336	0·7253	94	0·6348	0·6250
33	0·8639	0·8588	64	0·7299	0·7216	95	0·6320	0·6222
34	0·8589	0·8536	65	0·7263	0·7179	96	0·6293	0·6195
35	0·8538	0·8484	66	0·7227	0·7142	97	0·6266	0·6167
36	0·8492	0·8433	67	0·7191	0·7106	98	0·6239	0·6141
37	0·8459	0·8383	68	0·7155	0·7070	99	0·6212	0·6115
38	0·8390	0·8333	69	0·7120	0·7035	**100**	0·6186	0·6087
39	0·8342	0·8284	**70**	0·7087	0·7000	101	0·6160	0·6060
40	0·8295	0·8235	71	0·7053	0·6965	102	0·6134	0·6034

TABLE B.

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES.

All degrees are + unless otherwise marked.

1° F. = 0.55° C.
1° C. = 1.8° F.

C.	F.	C.	F.	C.	F.
2000·0	3632·0	1371·1	2500·0	800·0	1472·0
1900·0	3452·0	1300·0	2372·0	760·0	1400·0
1800·0	3272·0	1200·0	2192·0	704·4	1300·0
1700·0	3092·0	1100·0	2012·0	700·0	1292·0
1648·7	3000·0	1093·3	2000·0	648·8	1200·0
1600·0	2912·0	1000·0	1832·0	600·0	1112·0
1500·0	2732·0	900·0	1652·0	593·3	1100·0
1400·0	2552·0	815·5	1500·0	537·7	1000·0

C.	F.	C.	F.	C.	F.
537·7	1000·0	421·1	790·0	304·4	580·0
532·1	990·0	420·0	788·0	300·0	572·0
530·0	986·0	415·6	780·0	298·6	570·0
526·6	980·0	410·0	770·0	293·1	560·0
521·1	970·0	404·4	760·0	290·0	554·0
520·0	968·0	400·0	752·0	287·6	550·0
515·6	960·0	398·6	750·0	282·1	540·0
510·0	950·0	393·1	740·0	280·0	536·0
504·4	940·0	390·0	734·0	276·6	530·0
500·0	932·0	387·6	730·0	271·1	520·0
498·0	930·0	382·1	720·0	270·0	518·0
493·2	920·0	380·0	716·0	265·6	510·0
490·0	914·0	376·6	710·0	260·0	500·0
487·7	910·0	371·1	700·0	259·4	499·0
482·1	900·0	370·0	698·0	259·0	498·2
480·0	896·0	365·6	690·0	258·9	498·0
476·6	890·0	360·0	680·0	258·3	497·0
471·1	880·0	354·4	670·0	258·0	496·4
470·0	878·0	350·0	662·0	257·8	496·0
465·6	870·0	348·6	660·0	257·2	495·0
460·0	860·0	343·1	650·0	257·0	494·6
454·4	850·0	340·0	644·0	256·6	494·0
450·0	842·0	337·6	640·0	256·1	493·0
448·6	840·0	332·1	630·0	256·0	492·8
443·1	830·0	330·0	626·0	255·5	492·0
440·0	824·0	326·6	620·0	255·0	491·0
437·6	820·0	321·1	610·0	254·4	490·0
432·1	810·0	320·0	609·0	254·0	489·2
430·0	806·0	315·6	600·0	253·9	489·0
426·6	800·0	310·0	590·0	253·3	488·0

C.	F.	C.	F.	C.	F.
253·0	487·4	236·6	458·0	220·0	428·0
252·8	487·0	236·1	457·0	219·4	427·0
252·2	486·0	236·0	456·8	219·0	426·2
252·0	485·6	235·5	456·0	218·9	426·0
251·6	485·0	235·0	455·0	218·3	425·0
251·1	484·0	234·4	454·0	218·0	424·4
251·0	483·8	234·0	453·2	217·8	424·0
250·5	483·0	233·9	453·0	217·2	423·0
250·0	482·0	233·3	452·0	217·0	422·6
249·4	481·0	233·0	451·4	216·6	422·0
249·0	480·2	232·8	451·0	216·1	421·0
248·9	480·0	232·2	450·0	216·0	420·8
248·3	479·0	232·0	449·6	215·5	420·0
248·0	478·4	231·6	449·0	215·0	419·0
247·8	478·0	231·1	448·0	214·4	418·0
247·2	477·0	231·0	447·8	214·0	417·2
247·0	476·6	230·5	447·0	213·9	417·0
246·6	476·0	230·0	446·0	213·3	416·0
246·1	475·0	229·4	445·0	213·0	415·4
246·0	474.8	229·0	444·2	212·8	415·0
245·5	474·0	228·9	444·0	212·2	414·0
245·0	473·0	228·3	443·0	212·0	413·6
244·4	472·0	228·0	442·4	211·6	413·0
244·0	471·2	227·8	442·0	211·1	412·0
243·9	471·0	227·2	441·0	211·0	411·8
243·3	470·0	227·0	440·6	210·5	411·0
243·0	469·4	226·6	440·0	210·0	410·0
242·8	469·0	226·1	439·0	209·4	409·0
242·2	468·0	226·0	438·8	209·0	408·2
242·0	467·6	225·5	438·0	208·9	408·0
241·6	467·0	225·0	437·0	208·3	407·0
241·1	466·0	224·4	436·0	208·0	406·4
241·0	465·8	224·0	435·2	207·8	406·0
240·5	465·0	223·9	435·0	207·2	405·0
240·0	464·0	223·3	434·0	207·0	404·6
239·4	463·0	223·0	433·4	206·6	404·0
239·0	462·2	222·8	433·0	206·1	403·0
238·9	462·0	222·2	432·0	206.0	402·8
238·3	461·0	222·0	431·6	205·5	402·0
238·0	460·4	221·6	431·0	205·0	401·0
237·8	460·0	221·1	430·0	204·4	400·0
237·2	459·0	221·0	429·8	204·0	399·2
237·0	458·6	220·5	429·0	203·9	399·0

C.	F.	C.	F.	C.	F.
203·3	398·0	187·0	368·6	170·5	339·0
203·0	397·4	186·6	368·0	170·0	338·0
202·8	397·0	186·1	367·0	169·4	337·0
202·2	396·0	186·0	366·8	169·0	336·2
202·0	395·6	185·5	366·0	168·9	336·0
201·6	395·0	185·0	365·0	168·3	335·0
201·1	394·0	184·4	364·0	168·0	334·4
201·0	393·8	184·0	363·2	167·8	334·0
200.5	393·0	183·9	363·0	167·2	333·0
200·0	392·0	183·3	362·0	167·0	332·6
199·4	391·0	183·0	361·4	166·6	332·0
199·0	390·2	182·8	361·0	166·1	331·0
198·9	390·0	182·2	360·0	166·0	330·8
198·3	389·0	182·0	359·6	165·5	330·0
198·0	388·4	181·6	359·0	165·0	329·0
197·8	388·0	181·1	358·0	164·4	328·0
197·2	387·0	181·0	357·8	164·0	327·2
197·0	386·6	180·5	357·0	163·9	327·0
196·6	386·0	180·0	356·0	163·3	326·0
196·1	385·0	179·4	355·0	163·0	325·4
196·0	384·8	179·0	354·2	162·8	325·0
195·5	384·0	178·9	354·0	162·2	324·0
195·0	383·0	178·3	353·0	162·0	323·6
194·4	382·0	178·0	352·4	161·6	323·0
194·0	381·2	177·8	352·0	161·1	322·0
193·9	381·0	177·2	351·0	161·0	321·8
193·3	380·0	177·0	350·6	160·5	321·0
193·0	379·4	176·6	350·0	160·0	320·0
192·8	379·0	176·1	349·0	159·4	319·0
192·2	378·0	176·0	348·8	159·0	318·2
192·0	377·6	175·5	348·0	158·9	318·0
191·6	377·0	175·0	347·0	158·3	317·0
191·1	376·0	174·4	346·0	158·0	316·4
191·0	375·8	174·0	345·2	157·8	316·0
190·5	375·0	173·9	345·0	157·2	315·0
190·0	374·0	173·3	344·0	157·0	314·6
189·4	373·0	173·0	343·4	156·6	314·0
189·0	372·2	172·8	343·0	156·1	313·0
188·9	372·0	172·2	342·0	156·0	312·8
188·3	371·0	172·0	341·6	155·5	312·0
188·0	370·4	171·6	341·0	155·0	311·0
187·8	370·0	171·1	340·0	154·4	310·0
187·2	369·0	171·0	339·8	154·0	309·2

C.	F.	C.	F.	C.	F.
153·9	309·0	137·2	279·0	121·0	249·8
153·3	308·0	137·0	278·6	120·5	249·0
153·0	307.4	136·6	278·0	120·0	248·0
152·8	307·0	136·1	277·0	119·4	247·0
152·2	306·0	136·0	276·8	119·0	246·2
152·0	305·6	135·5	276·0	118·9	246·0
151·6	305·0	135·0	275·0	118·3	245·0
151·1	304·0	134·4	274·0	118·0	244·4
151·0	303·8	134·0	273·2	117·8	244·0
150·5	303·0	133·9	273·0	117·2	243·0
150·0	302·0	133·3	272·0	117·0	242·6
149·4	301·0	133·0	271·4	116·6	242·0
149·0	300·2	132·8	271·0	116·1	241·0
148·9	300·0	132·2	270·0	116·0	240·8
148·3	299·0	132·0	269·6	115·5	240·0
148·0	298·4	131·6	269·0	115·0	239·0
147·8	298·0	131·1	268·0	114·4	238·0
147·2	297·0	131·0	267·8	114·0	237·2
147·0	296·6	130·5	267·0	113·9	237·0
146·6	296·0	130·0	266·0	113·3	236·0
146·1	295·0	129·4	265·0	113·0	235·4
146·0	294·8	129·0	264·2	112·8	235·0
145·5	294·0	128·9	264·0	112·2	234·0
145·0	293·0	128·3	263·0	112·0	233·6
144·4	292·0	128·0	262·4	111·6	233·0
144·0	291·2	127·8	262·0	111·1	232·0
143·9	291·0	127·2	261·0	111·0	231·8
143·3	290·0	127·0	260·6	110·5	231·0
143·0	289·4	126·6	260·0	110·0	230·0
142·8	289·0	126·1	259·0	109·4	229·0
142·2	288·0	126·0	258·8	109·0	228·2
142·0	287·6	125·5	258·0	108·9	228·0
141·6	287·0	125·0	257·0	108·3	227·0
141·1	286·0	124·4	256·0	108·0	226·4
141·0	285·8	124·0	255·2	107·8	226·0
140·5	285·0	123·9	255·0	107·2	225·0
140·0	284·0	123·3	254·0	107·0	224·6
139·4	283·0	123·0	253·4	106·6	224·0
139·0	282·2	122·8	253·0	106·1	223·0
138·9	282·0	122·2	252·0	106·0	222·8
138·3	281·0	122·0	251·6	105·5	222·0
138·0	280·4	121·6	251·0	105·0	221·0
137.8	280.0	121·1	250·0	104·4	220·0

C.	F.	C.	F.	C.	F.
104·0	219·2	87·8	190·0	71·1	160·0
103·9	219·0	87·2	189·0	71·0	159·8
103·3	218·0	87·0	188·6	70·5	159·0
103·0	217·4	86·6	188·0	70·0	158·0
102·8	217·0	86·1	187·0	69·4	157·0
102·2	216·0	86·0	186·8	69·0	156·2
102·0	215·6	85·5	186·0	68·9	156·0
101·6	215·0	85·0	185·0	68·3	155·0
101·1	214·0	84·4	184·0	68·0	154·4
101·0	213·8	84·0	183·2	67·8	154·0
100·5	213·0	83·9	183·0	67·2	153·0
100·0	**212·0**	83·3	182·0	67·0	152·6
99·4	211·0	83·0	181·4	66·6	152·0
99·0	210·2	82·8	181·0	66·1	151·0
98·9	210·0	82·2	180·0	66·0	150·8
98·3	209·0	82·0	179·6	65·5	150·0
98·0	208·4	81·6	179·0	65·0	149·0
97·8	208·0	81·1	178·0	64·4	148·0
97·2	207·0	81·0	177·8	64·0	147·2
97·0	206·6	80·5	177·0	63·9	147·0
96·6	206·0	80·0	176·0	63·3	146·0
96·1	205·0	79·4	175·0	63·0	145·4
96·0	204·8	79·0	174·2	62·8	145·0
95·5	204·0	78·9	174·0	62·2	144·0
95·0	203·0	78·3	173·0	62·0	143·6
94·4	202·0	78·0	172·4	61·6	143·0
94·0	201·2	77·8	172·0	61·1	142·0
93·9	201·0	77·2	171·0	61·0	141·8
93·3	200·0	77·0	170·6	60·5	141·0
93·0	199·4	76·6	170·0	60·0	140·0
92·8	199·0	76·1	169·0	59·4	139·0
92·2	198·0	76·0	168·8	59·0	138·2
92·0	197·6	75·5	168·0	58·9	138·0
91·6	197·0	75·0	167·0	58·3	137·0
91·1	196·0	74·4	166·0	58·0	136·4
91·0	195·8	74·0	165·2	57·8	136·0
90·5	195·0	73·9	165·0	57·2	135·0
90·0	194·0	73·3	164·0	57·0	134·6
89·4	193·0	73·0	163·4	56·6	134·0
89·0	192·2	72·8	163·0	56·1	133·0
88·9	192·0	72·2	162·0	56·0	132·8
88·3	191·0	72·0	161·6	55·5	132·0
88·0	190·4	71·6	161·0	55·0	131·0

C.	F.	C.	F.	C.	F.
54·4	130·0	38·0	100·4	21·6	71·0
54·0	129·2	37·8	100·0	21·1	70·0
53·9	129·0	37·2	99·0	21·0	69·8
53·3	128·0	**37·0**	**98·6**	20·6	69·0
53·0	127·4	36·6	98·0	20·0	68·0
52·8	127·0	36·1	97·0	19·4	67·0
52·2	126·0	36·0	96·8	19·0	66·2
52·0	125·6	35·5	96·0	18·9	66·0
51·6	125·0	35·0	95·0	18·4	65·0
51·1	124·0	34·4	94·0	18·0	64·4
51·0	123·8	34·0	93·2	17·7	64·0
50·5	123·0	33·9	93·0	17·2	63·0
50·0	122·0	33·3	92·0	17·0	62·6
49·4	121·0	33·0	91·4	16·6	62·0
49·0	120·2	32·8	91·0	16·1	61·0
48·9	120·0	32·2	90·0	16·0	60·8
48·3	119·0	32·0	89·6	**15·55**	**60·0**
48·0	118·4	31·6	89·0	15·0	59·0
47·8	118·0	31·1	88·0	14·4	58·0
47·2	117·0	31·0	87·8	14·0	57·2
47·0	116·6	30·5	87·0	13·9	57·0
46·6	116·0	30·0	86·0	13·3	56·0
46·1	115·0	29·6	85·0	13·0	55·4
46·0	114.8	29·0	84·2	12·7	55·0
45·5	114·0	28·9	84·0	12·2	54·0
45·0	113·0	28·3	83·0	12·0	53·6
44·4	112·0	28·0	82·4	11·6	53·0
44·0	111·2	27·9	82·0	11·1	52·0
43·9	111·0	27·3	81·0	11·0	51·8
43·3	110·0	27·0	80·6	10·6	51·0
43·0	109·4	26·7	80·0	10·0	50·0
42·8	109·0	26·2	79·0	9·4	49·0
42·2	108·0	26·0	78·8	9·0	48·2
42·0	107·6	25·6	78·0	8·9	48·0
41·6	107·0	25·0	77·0	8·3	47·0
41·1	106·0	24·4	76·0	8·0	46·4
41·0	105·8	24·0	75·2	7·7	46·0
40·5	105·0	23·9	75·0	7·2	45·0
40·0	104·0	23·3	74·0	7·0	44·6
39·4	103·0	23·0	73·4	6·6	44·0
39·0	102·2	22·7	73·0	6·1	43·0
38·9	102·0	22·2	72·0	6.0	42·8
38·3	101·0	22·0	71·6	5·6	42·0

C.	F.	C.	F.	C.	F.
5·0	41·0	—11·6	11·0	—28·0	—18·4
4·4	40·0	—12·0	10·4	—28·3	—19·0
4·0	**39·2**	—12·2	10·0	—28·9	—20·0
3·9	39·0	—12·7	9·0	—29·0	—20·2
3·3	38·0	—13·0	8·6	—29·4	—21·0
3·0	37·4	—13·3	8·0	—30·0	—22·0
2·7	37·0	—13·9	7·0	—30·5	—23·0
2·2	36·0	—14·0	6·8	—31·0	—23·8
2·0	35·6	—14·4	6·0	—31·1	—24·0
1·6	35·0	—15·0	5·0	—31·6	—25·0
1·1	34·0	—15·5	4·0	—32·0	—25·6
1·0	33·8	—16·0	3·2	—32·2	—26·0
0·6	33·0	—16·1	3·0	—32·7	—27·0
0·0	**32·0**	—16·6	2·0	—33·0	—27·4
—0·5	31·0	—17·0	1·4	—33·3	—28·0
—1·0	30·2	—17·2	1·0	—33·9	—29·0
—1·1	30·0	**—17·7**	**0·0**	—34·0	—29·2
—1·6	29·0	—18·0	—0·4	—34·4	—30·0
—2·0	28·4	—18·3	—1·0	—35·0	—31·0
—2·2	28·0	—18·8	—2·0	—35·5	—32·0
—2·7	27·0	—19·0	—2·2	—36·0	—32·8
—3·0	26·6	—19·4	—3·0	—36·1	—33·0
—3·3	26·0	—20·0	—4·0	—36·6	—34·0
—3·9	25·0	—20·5	—5·0	—37·0	—34·6
—4·0	24·8	—21·0	—5·8	—37·2	—35·0
—4·4	24·0	—21·1	—6·0	—37·7	—36·0
—5·0	23·0	—21·6	—7·0	—38·0	—36·4
—5·5	22·0	—22·0	—7·6	—38·3	—37·0
—6·0	21·2	—22·2	—8·0	—38·9	—38·0
—6·1	21·0	—22·7	—9·0	—39·0	—38·2
—6·6	20·0	—23·0	—9·4	—39·4	—39·0
—7·0	19·4	—23·3	—10·0	**—40·0**	**—40·0**
—7·2	19·0	—23·9	—11·0	—40·5	—41·0
—7·7	18·0	—24·0	—11·2	—41·0	—41·8
—8·0	17·6	—24·4	—12·0	—41·1	—42·0
—8·3	17·0	—25·0	—13·0	—41·6	—43·0
—8·9	16·0	—25·5	—14·0	—42·0	—43·6
—9·0	15·8	—26·0	—14·8	—42·2	—44·0
—9·4	15·0	—26·1	—15·0	—42·7	—45·0
—10·0	14·0	—26·6	—16·0	—43·0	—45·4
—10·5	13·0	—27·0	—16·6	—43·3	—46·0
—11·0	12·2	—27·2	—17·0	—43·8	—47·0
—11·1	12·0	—27·7	—18·0	—44·0	—47·2

C.	F.	C.	F.	C.	F.
—44·4	—48·0	—61·1	—78·0	—77·7	—108·0
—45·0	—49·0	—61·6	—79·0	—78·0	—108·4
—45·5	—50·0	—62·0	—79·6	—78·3	—109·0
—46·0	—50·8	—62·2	—80·0	—78·8	—110·0
—46·1	—51·0	—62·7	—81·0	—79·0	—110·2
—46·6	—52·0	—63·0	—81·4	—79·4	—111·0
—47·0	—52·6	—63·3	—82·0	—80·0	—112·0
—47·2	—53·0	—63·8	—83·0	—80·5	—113·0
—47·7	—54·0	—64·0	—83·2	—81·0	—113·8
—48·0	—54·4	—64·4	—84·0	—81·1	—114·0
—48·3	—55·0	—65·0	—85·0	—81·6	—115·0
—48·8	—56·0	—65·5	—86·0	—82·0	—115·6
—49·0	—56·2	—66·0	—86·8	—82·2	—116·0
—49·4	—57·0	—66·1	—87·0	—82·7	—117·0
—50·0	—58·0	—66·6	—88·0	—83·0	—117·4
—50·5	—59·0	—67·0	—88·6	—83·3	—118·0
—51·0	—59·8	—67·2	—89·0	—83·8	—119·0
—51·1	—60·0	—67·7	—90·0	—84·0	—119·2
—51·6	—61·0	—68·0	—90·4	—84·4	—120·0
—52·0	—61·6	—68·3	—91·0	—85·0	—121·0
—52·2	—62·0	—68·8	—92·0	—85·5	—122·0
—52·7	—63·0	—69·0	—92·2	—86·0	—122·8
—53·0	—63·4	—69·4	—93·0	—86·1	—123·0
—53·3	—64·0	—70·0	—94·0	—86·6	—124·0
—53·8	—65·0	—70·5	—95·0	—87·0	—124·6
—54·0	—65·2	—71·0	—95·8	—87·2	—125·0
—54·4	—66·0	—71·1	—96·0	—87·7	—126·0
—55·0	—67·0	—71·6	—97·0	—88·0	—126·4
—55·5	—68·0	—72·0	—97·6	—88·3	—127·0
—56·0	—68·8	—72·2	—98·0	—88·8	—128·0
—56·1	—69·0	—72·7	—99·0	—89·0	—128·2
—56·6	—70·0	—73·0	—99·4	—89·4	—129·0
—57·0	—70·6	—73·3	—100·0	—90·0	—130·0
—57·2	—71·0	—73·8	—101·0	—90·5	—131·0
—57·7	—72·0	—74·0	—101·2	—91·0	—131·8
—58·0	—72·4	—74·4	—102·0	—91·1	—132·0
—58·3	—73·0	—75·0	—103·0	—91·6	—133·0
—58·8	—74·0	—75·5	—104·0	—92·0	—133·6
—59·0	—74·2	—76·0	—104·8	—92·2	—134·0
—59·4	—75·0	—76·1	—105·0	—92·7	—135·0
—60·0	—76·0	—76·6	—106·0	—93·0	—135·4
—60·5	—77·0	—77·0	—106·6	—93·3	—136·0
—61·0	—77·8	—77·2	—107·0	—93·8	—137·0

C.	F.	C.	F.	C.	F.
—94·0	—137·2	—111·0	—167·8	—127·2	—197·0
—94·4	—138·0	—111·1	—168·0	—127·7	—198·0
—95·0	—139·0	—111·6	—169·0	—128·0	—198·4
—95·5	—140·0	—112·0	—169·6	—128·3	—199·0
—96·0	—140·8	—112·2	—170·0	—128·8	—200·0
—96·1	—141·0	—112·7	—171·0	—129·0	—200·2
—96·6	—142·0	—113·0	—171·4	—129·4	—201·0
—97·0	—142·6	—113·3	—172·0	—130·0	—202·0
—97·2	—143·0	—113·8	—173·0	—130·5	—203·0
—97·7	—144·0	—114·0	—173·2	—131·0	—203·8
—98·0	—144·4	—114·4	—174·0	—131·1	—204·0
—98·3	—145·0	—115·0	—175·0	—131·6	—205·0
—98·8	—146·0	—115·5	—176·0	—132·0	—205·6
—99·0	—146·2	—116·0	—176·8	—132·2	—206·0
—99·4	—147·0	—116·1	—177·0	—132·7	—207·0
—100·0	—148·0	—116·6	—178·0	—133·0	—207·4
—100·5	—149·0	—117·0	—178·6	—133·3	—208·0
—101·0	—149·8	—117·2	—179·0	—133·8	—209·0
—101·1	—150·0	—117·7	—180·0	—134·0	—209·2
—101·6	—151·0	—118·0	—180·4	—134·4	—210·0
—102·0	—151·6	—118·3	—181·0	—135·0	—211·0
—102·2	—152·0	—118·8	—182·0	—135·5	—212·0
—102·7	—153·0	—119·0	—182·2	—136·0	—212·8
—103·0	—153·4	—119·4	—183·0	—136·1	—213·0
—103·3	—154·0	—120·0	—184·0	—136·6	—214·0
—103·8	—155·0	—120·5	—185·0	—137·0	—214·6
—104·0	—155·2	—121·0	—185·8	—137·2	—215·0
—104·4	—156·0	—121·1	—186·0	—137·7	—216·0
—105·0	—157·0	—121·6	—187·0	—138·0	—216·4
—105·5	—158·0	—122·0	—187·6	—138·3	—217·0
—106·0	—158·8	—122·2	—188·0	—138·8	—218·0
—106·1	—159·0	—122·7	—189·0	—139·0	—218·2
—106·6	—160·0	—123·0	—189·4	—139·4	—219·0
—107·0	—160·6	—123·3	—190·0	—140·0	—220·0
—107·2	—161·0	—123·8	—191·0	—140·5	—221·0
—107·7	—162·0	—124·0	—191·2	—141·0	—221·8
—108·0	—162·4	—124·4	—192·0	—141·1	—222·0
—108·3	—163·0	—125·0	—193·0	—141·6	—223·0
—108·8	—164·0	—125·5	—194·0	—142·0	—223·6
—109·0	—164·2	—126·0	—194·8	—142·2	—224·0
—109·4	—165·0	—126·1	—195·0	—142·7	—225·0
—110·0	—166·0	—126·6	—196·0	—143·0	—225·4
—110·5	—167·0	—127·0	—196·6	—143·3	—226·0

C.	F.	C.	F.	C.	F.
—143·8	—227·0	—149·0	—236·2	—154·4	—246·0
—144·0	—227·2	—149·4	—237·0	—155·0	—247·0
—144·4	—228·0	—150·0	—238·0	—155·5	—248·0
—145·0	—229·0	—150·5	—239·0	—156·0	—248·8
—145·5	—230·0	—151·0	—239·8	—156·1	—249·0
—146·0	—230·8	—151·1	—240·0	—156·6	—250·0
—146·1	—231·0	—151·6	—241·0	—157·0	—250·6
—146·6	—232·0	—152·0	—241·6	—157·2	—251·0
—147·0	—232·6	—152·2	—242·0	—157·7	—252·0
—147·2	—233·0	—152·7	—243·0	—158·0	—252·4
—147·7	—234·0	—153·0	—243·4	—158·3	—253·0
—148·0	—234·4	—153·3	—244·0	—158·8	—254·0
—148·3	—235·0	—153·8	—245·0	—159·0	—254·2
—148·8	—236·0	—154·0	—245·2	—159·4	—255·0

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