previously brought up to a bright red heat and kept at such temperature, or if the vapours produced at a relatively low tempera­ture are passed through intensely heated pipes before reaching the condenser (Pettenkofer’s method for producing illuminating gas from wood),—the gas produced contains a considerable admixture of luminiferous hydrocarbons, the proportions of methyl-alcohol, acetone, and acetic acid get less, and the tar proper assumes more of the character of coal-gas tar (see below). Similar observations we make in the case of coal. About 1862 Wigan cannel coal used to be distilled industrially at low temperatures to produce “light oils.” Schorlemmer examined these and found them to consist chiefly of “paraffins” (see Paraffin) from C5H12 upwards. A similar result is obtained with ordinary coal, although in its case the “ benzols ” are more largely represented. If we distil any kind of coal at high temperatures—*i.e.*, in the way customary for illumin­ating-gas making—the distillable part of the tar proper consists chiefly of benzene, C6H6, and benzene-derivatives, *i.e.,* benzols, C6H6 + *n*CH2; phenols, C6H6O, and homologues, (C6H5.*n*CH2)OH ; amido-bodies, C6H5NH2 (aniline), and homologues ; condensed benzols, such as naphthalene, C10H8 = 2C6H6-C2H4; anthracene, C14H10 = 3C6H6-C4H8 ; chrysene, C18H12 = 4C6H6 - C6H12, &c. The paraffins then become an altogether subordinate feature.

A great and meritorious research of Berthelot’s has thrown con­siderable light on the chemical mechanism of dry distillation. As found by him, even the most complex of the substances named are producible by the interaction upon one another of a few bodies of very simple constitution, or even one or other of these by the mere action of a high temperature. To give a few examples. Marsh­gas, CH4, when passed through red-hot tubes, yields olefines, C2H4, C3H6, C4H8, &c., with elimination of hydrogen, H2. The same CH4, if subjected to a spark-current *(i.e.,* local application of intense heat), yields acetylene and hydrogen, 2CH4=C2H2 + 3H2, and the acetylene produced passes partly into benzene, C6H6=3C2H2. Ethylene, C2H4, when passed through a porcelain tube kept at a moderate red heat, yields benzene, C6H6, styrolene = phenyl - ethylene, C2H3.C6H5, naphthalene, C10H8, and perhaps also its hydride, C10H10. Acetylene, *qua* potential benzene, and ethylene yield styrolene and hydrogen, C6H6 + C2H4 = C6H5.C2H3 + H2; and styrolene plus ethylene yields hydrogen and naphthalene, C10H8.

Benzol at a high temperature loses hydrogen, and, so to say, doubles up into di-phenyl, C12H10 ; and this latter, when heated with ethylene, yields anthracene, C14H10, and hydrogen, C12H10 + C2H4 — C14H10 + 2H2. Conversely, hydrogen may, so to say, turn out its equivalent of a hydrocarbon ; thus, for instance, chrysene, C18H12 + 2H2, yields di-phenyl, C12H10, + benzene, C6H6.

Pyrogenic reactions generally are reversible ; thus, any of the following three equations is correct, whether we read it from the left to the right or from the right to the left :—

1. C2H6 (ethane), at a red heat becomes C2H4+H2.
2. C12H10+C6H6=C18H12+2H2 .
3. C14H10+2H2=2C6H6+C2H2.

Hence no single pyrogenic reaction goes to the end ; if it does not, so to say, check its own progress, other secondary reactions set in and do so, the general result being that ultimately, but in general slowly, a state of dynamic equilibrium is attained in which a set of synthetic reactions on the one hand and a set of analytic reactions on the other compensate one another.

*Industrial Working of Coal Tar*.@@1*—*Coal tar, as it comes from the gas-works, is used for a variety of purposes, such as—(1) for fuel, the tar being made into a spray by means of a steam-injector and the spray kindled ; (2) for the preservation of building materials, porous stones, and bricks, &c. ; (3) for making roofing­felt (in 1868, five-sixths of the 9000 tons of tar produced at the Berlin gas-works was thus utilized ; the case, however, is different now) ; (4) for making a low quality of lamp-black. At present, however, most of the tar produced, in centres of industry at least, is worked up by distillation. The tar as it comes from the gas­works is allowed to rest in a “pond” until the tar-water (solution chiefly of ammonia and certain ammonia salts) has gone to the top. The tar proper is then pumped into a large wrought-iron still (of upright-cylinder form preferably) and therein subjected to distilla­tion over a naked fire. A necessary preliminary, however, is the removal of the unavoidable remnant of water, which is best effected by cautiously heating the tar in the still so as to render it more fluid and enable the water to rise to the top and then letting the upper stratum run out by an overflow tap at the side. The dis­tillation is then started. It involves the formation of two sets of volatile products, namely—(1) combustible gases (including sulphur­etted hydrogen and bisulphide of carbon vapour), which must be led away to avoid nuisance and danger of fire, and (2) a very complex liquid or semi-liquid distillate. This latter is collected in successive fractions, generally in this manner:—(1) as “first runnings,” what comes over at temperatures below 105° to 110o C. ; (2) as “light oils,” at temperatures between 110° and 210° C.; (3) as “carbolic oil,” at temperatures between 210° to 240° C. ; (4) as

“creosote oil,” at temperatures between 240° to 270° C.; (5) as anthracene oil, at temperatures above 270°.

In the earlier part of the “first runnings” and light-oil period the condenser must be kept cold ; towards the end it must be kept warm to prevent choking by solidified naphthalene. In practice, the operator does not go entirely by the boiling point, but to a great extent by the specific gravity of the distillate, which, in general, increases as the boiling point rises. As soon as a drop of the last runnings floats in water (exhibits the specific gravity 1), the “light oil” is supposed to be over. That the fractionation is not always and everywhere effected in the same way needs hardly be said. If the manufacture of carbolic acid is aimed at, it is best (according to Lunge) to select the fraction 170° to 230° C. for this purpose. Naphthalene boils as high as 217°, yet a deal goes into this carbolic-acid fraction. As soon as naphthalene begins to crystallize out largely (on cooling down a sample of distillate), the carbolic acid may be presumed to be over. What follows next is put aside as creosote oil, until, after the disappearance of the naphthalene, a new solid product, namely, anthracene, begins to show itself. With any tar that contains a remunerative proportion of anthracene, the anthracene oil is the most valuable of the pro­ducts, as the raw material for the making of artificial alizarins.

Supposing the anthracene to have been extracted as completely as practicable, the residue in the still consists of “hard pitch,” a viscid black fluid which on cooling freezes into a fragile solid. In former times more commonly than now “soft pitch" used to be produced by leaving more or less of the anthracene oil and even creosote oil in the still. At the end of the anthracene stage of the distillation it is as well, if not necessary, to help the very high boiling vapour out of the still by means of superheated steam, and to keep the worm at 100° C. to prevent choking. At a German establishment a vacuum is used with great advantage.

We come now to explain briefly how the several fractions are worked up.

The pitch (which we assume to be “hard pitch”) must be run off hot through a tap at the bottom of the still and led into a low- roofed and well closed-in “house,” because it would take fire in the open air. After it has cooled down sufficiently in the “ house,” the pitch is run into pitch-holes in front of the house and allowed to freeze there. The depth of pitch in a hole is about 12 inches. The solid pitch is hacked out with pickaxes and sent into com­merce. A superior apparatus for the recovery of the pitch, which precludes all danger of conflagration and many inconveniences of the ordinary system, has been devised for the Paris gas-works by Regnault.@@2 Lunge found, from many distillations, that tar from the midland counties yields about 55 per cent. of hard pitch.

Hard pitch is used chiefly for making the following. (1) *Asphalt.—*The pitch is fused up—perhaps in the still which pro­duced it—with the requisite proportion of creosote and anthracene oil, previously freed from their valuable components. Such asphalt is used for street-paving, *i.e.,* filling up the spaces between the paving-stones, and, in admixture with sand and generally more or less of natural asphalt, for the making of footpaths and floorings generally. In Germany it serves for the making of pipes for con­veying acid liquids in works and chemical laboratories, &c. End­less hemp-paper is soaked in liquefied asphalt and wound spirally around an iron core, previously smeared over with soft soap, in about 100 layers. The whole is then exposed to strong pressure while still hot, and is separated from the core after being allowed to cool. Such pipes stand almost any kind of acid, but they must not be used for hot liquids. (2) *Varnishes.—*The pitch is dissolved in suitable tar oils,—creosote oil for a lower and light oil for a higher quality. (3) *Coke.—*In former times more frequently than now pitch was made into coke by transferring it to a special flat still and distilling as long as any volatile products came off. The coke which remains is a very pure and consequently valuable fuel. (4) *Lamp Black* (as a last resource, if no other mode of utilization is practicable).—The pitch is subjected to partial com­bustion on hot iron plates and the smoke conveyed into chambers to deposit its carbon. The yield is about 40 per cent.

*Anthracene Oil.—*The oil is allowed to stand cold for a week or so until the anthracene has crystallized out as completely as possible. The mother-liquor is then eliminated, the bulk by means of a filter-press, the rest, at a higher than the ordinary temperature, by hydraulic pressure. The crude product includes far more than half its weight of impurities—phenanthrene, paraffin, naphthalene, &c. To remove these as far as possible, the crude anthracene is ground up and treated with petroleum spirit (boiling at 70° to 100° C. ) or coal tar naphtha (120° to 190°), in which real anthracene is relatively insoluble. The insoluble part is separated by filtering arrangements and presses (so constructed as to avoid danger of fire), and at last sublimed, more with the view of bring­ing it into a customary convenient form than with the object of effecting further purification. Such final anthracene may contain 50 to 65 per cent. of pure substance. The only reliable method for

@@@1 For wood tar, see Wood Spirit and Vinegar.

@@@2 It is described in Lunge’s *Treatise on the Distillation of Coal Tar,* London, 1882. to which this article is largely indebted.