auxiliary calibration fixing this point, and the solution allowed to stand with occasional shaking in order to come to equilibrium. The ether meniscus is then raised to the graduation on the constriction at "F" and the amount of residual oxygen computed from the total pressure and the vapor pressure of the solvent. A correction is applied for the amount of oxygen dissolved in the solvent at the partial pressure of the oxygen existing at the time equilibrium is being established. The compression of the oxygen, as the solution is raised, increases its solubility. However, the surface of contact is so small at the constriction that the new equilibrium is approached very slowly. Since this is a correction to a correction it is not of importance. When ether is used as a solvent the largest error is due to the changing vapor pressure of ether with slight change in temperature. The table illustrates the accuracy which may be obtained without thermostating the water jacket. Doubtless a more accurate control of the temperature by circulating water at constant temperature through the jacket would still further improve the results. The apparatus was checked by determining the solubility of oxygen in ether using a sample of ether about three times as large as that required in the determination of the purity of a free radical. An error of 10% in determining the solubility of oxygen in ether amounts to about 0.5% in the correction to be applied to a run on a free radical. The data on diphenyl α-naphthylmethyl in the table give an idea of the accuracy of the method.

ABSORPTION OF OXYGEN BY DIPHENYL α-NAPHTHYLMETHYL

Concn. of cpd. from soly., wt. %	1.427	1.427
Ether soln., g.	3.074	3.279
O_2 (N. T. P.) added, cc.	2.535	3.065
Inert gas in capsule, cc.	0.165	0.119
Gas after run, cc.	.982	1.275
O_2 abs. by cpd. $\times 10^3$, g.	2.34	2.55
Concn. cpd. in wt. %	1.395	1.426
Purity, %	98.7	100.0

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The Catalytic Oxidation of Carbon

BY HANS M. CASSEL

The activating effect of sodium chloride on the combustion of soot in contact with it, described by R. K. Taylor,[1] has recently been the object of further interesting experiments by Day, Robey and Dauben,[2] using other salts as activating substances. In explaining their observations these authors refer to a theory proposed by H. S. Taylor and H. A. Neville[3] for the heterogeneous reaction of steam with carbon.

It should be taken into consideration, however, that the topochemical relations in the two cases are distinctly different: in the steam experiments the salt particles are imbedded in the carbon surface; in the combustion experiments, on the other hand, the oxygen molecules have to penetrate the soot layer before they can possibly reach the salt surface.[4] It is difficult to see how the contact of the soot with the salt is maintained and continues to be effective once the reaction has started in the interface.

On the basis of the earlier work of Eucken[5] two observations made by me may offer a more satisfactory explanation. Eucken, studying the combustion of graphite under low pressures, observed a rather low rate on smooth surfaces. But after a longer attack by oxygen the carbon surface takes on a velvet-like appearance, accompanied by an acceleration of the reaction. The condition of the surface may, however, be "ironed out" again by a process which Eucken calls "healing." Probably this is due to the reaction $2CO = C + CO_2$ which takes place in the range of not too high temperatures, the formation of CO being the first step of oxidation. According to R. K. Taylor, this process of regeneration seems to occur also in the case of burning soot, for he observed a slowing down of the reaction "presumably because of the more rapid oxidation at first of smaller particles or more active patches on the carbon surface."

I deposited a layer of soot on Pyrex glass by cracking CH_2Cl_2 at about 450°. In burning this by exposing it to a current of oxygen at about 600° the reaction once started generally spreads parallel to the surface, the soot being removed as if swept out by a piston. The fact that the reaction does not visibly proceed perpendicularly to the surface indicates that the carbon deposit is more easily attacked from the sides than from the

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(1) R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).

(2) J. E. Day, R. F. Robey and H. J. Dauben, *ibid.*, **57**, 2725 (1935).

(3) H. S. Taylor and H. A. Neville, *ibid.*, **43**, 2055 (1921).

(4) The impermeability of thin layers of soot is evident in the case where it acts as an emulsifier.

(5) A. Eucken, *Z. angew. Chem.*, **43**, 986 (1930).

surface. This should be expected if the soot particles, as hexagonal crystals,[6] have grown orientated with their cleavage planes lying parallel to the glass surface.[7]

This view is in agreement with the theory of Eucken, which assumes that the adsorption of gas molecules or atoms by graphite takes place preferentially in the planes perpendicular to the cleavage planes of the crystal lattice.[8] The reaction, therefore, should be facilitated wherever two adjacent crystals touch each other or project into the gas phase.

If this is true, and if the soot deposits are always orientated, the combustion of soot deposits should be accelerated when the underlying glass surface is etched or ground. In order to check this the externally ground part of a Jena glass ground joint and the adjacent smooth surface were coated with soot from a natural gas flame and exposed to oxygen at about 600° for a few seconds. This treatment cleaned the ground part perfectly of carbon, while no visible attack took place on the smooth glass surface, a sharp line dividing the two.

Considering that the deposits in the salt experiments naturally have a very coarse structure, it may be concluded that the function of the salts in the case of soot combustion is quite the same as that of the ground glass, in the above described experiment, namely, interrupting the primary growth of large crystals and preventing a secondary regeneration.

From the same point of view the theory of the mechanism of the steam–carbon reaction should be revised. It is known from the experiments of Frankenburger[9] that sodium chloride inserted into iron deposits causes a highly dispersed structure by inhibiting the growth of coherent crystals. Such iron appears remarkably activated. Accordingly the increased activity of the impregnated graphite seems to be due to the opening of the prismatic planes[6] of the crystal lattice combined with the hygroscopic action of the salt ions.

CONTRIBUTION FROM THE
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[6] U. Hofmann, *Z. angew. Chem.*, **44**, 841 (1931).

[7] The orientation of soot particles is also very probable in its operation as emulsifying agent.

[8] The findings of L. Meyer [*Z. physik. Chem.*, **B17**, 385 (1932)] and U. Hofmann [*Ber.*, **65**, 1821 (1932)] who describe the basal planes of graphite as being attacked preferentially are related to temperatures above 750°.

[9] W. Frankenburger, *Z. Elektrochem.*, **37**, 473 (1931).

Resin Studies. IV. Sublimed *l*-Abietic Acid

BY DAVID LIPKIN AND W. A. LA LANDE, JR.

l-Abietic acid (and rosin) have been observed to give a "sublimate" when heated under a variety of conditions at a temperature below the distillation point of the acid.[1] We have studied this sublimate carefully and find that it shows certain marked differences from the products obtained by Shaw and Sebrell and by Labatut and Duffour. Dupont[2] considered the sublimate obtained by the latter investigators to be identical with *l*-abietic acid.

To obtain a sufficient quantity of the sublimate the previously described procedure of La Lande[1] was used, except that stirring was eliminated and a large glass tube substituted for the reaction vessel. The yield of dry and colorless product was highest in the range 175–275°; at 330–385° the yield was negligible and the product quite impure due to the rapid decomposition. About 0.5 g. of sublimate was collected during an eight-hour period from a 14-g. charge; none was obtained from various rosins, and air or oxygen could not be substituted for the pure nitrogen.

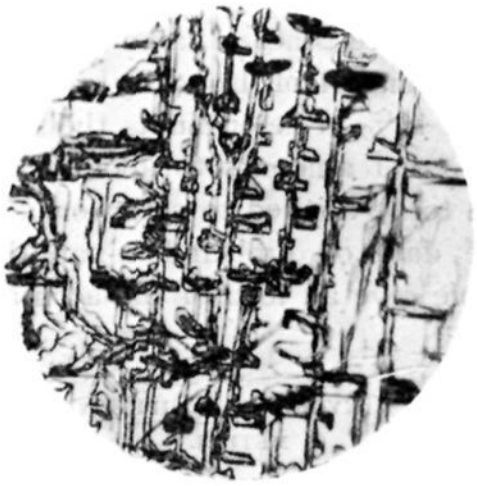

Fig. 1.—"Sublimed" *l*-abietic acid (× 100).

The product, which is illustrated in the accompanying figure, showed the following properties as compared with a sample of *l*-abietic acid prepared according to Steele.[3]

The rotary power of the sublimate was practically constant regardless of the temperature and its rate of formation. It underwent no change on exposure to the light (including occasional sunlight) and air of the laboratory for a few months,

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[1] Labatut and Duffour, *Soc. des Sc. de Bordeaux*, 31 (1919); Shaw and Sebrell, *Ind. Eng. Chem.*, **18**, 612 (1926); La Lande, *ibid.*, **26**, 678 (1934).

[2] Dupont, *Bull. soc. chim.*, [4] **35**, 1209 (1924).

[3] Steele, THIS JOURNAL, **44**, 1333 (1922).