

CURRENT NOTES ON CHEMISTRY.—VI.

(Edited by Charles Platt, Ph.D., F.C.S.)

SILICON CARBIDE.

CARBIDE of silicon, or "carborundum,"¹ has already become a familiar term, and the material is now upon the market as a formidable competitor of the highest grade abrasives. It is interesting to note some of the chemical aspects of this substance as given by Dr. O. Mühlhæuser. To obtain the pure compound corresponding to the formula SiC the crystals are heated to dull redness in oxygen, boiled with potash solution, washed, digested with hydrochloric acid, again washed, and finally treated with hydrofluoric and sulphuric acids. It is insoluble in all acids, but is attacked by molten alkalis and by hot ferric oxide and, when very finely divided, can be slowly burned in oxygen. Its specific gravity is given as 3.22 at 15°C, but the fine powder will remain suspended in water for months. The following suggestions are made for analysis: The powder obtained by trituration in an agate mortar is submitted to elutriation and the carbon determination made with that portion which remains in suspension after five minutes. The carbon is best estimated by combustion with twenty parts of lead chromate, the addition of potassium dichromate causing the oxidation to proceed with explosive violence. The silicon is determined by fusion with potassium sodium carbonate for about six hours, during which time the heat should be increased very gradually. A very pure specimen gave by analysis: Carbon, 30.2 per cent; silicon, 69.1 per cent; oxides of iron and alumina, 0.46 per cent; lime, 0.15 per cent; magnesia, 0.09 per cent.

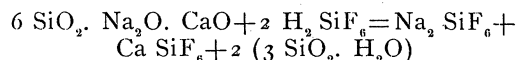
H. Moissan has produced the carbide by dissolving carbon in fused silicon, but states that it can be much more easily prepared by heating in an electric furnace a mixture of twelve parts of carbon with twenty-eight parts of silicon. It is also produced by heating carbon and *silica* in the electric furnace or by allowing the vapors of carbon to come into contact with vapor of silicon, when it is obtained in almost colorless, very hard and brittle, prismatic needles. Moissan gives the specific gravity at 3.12, which is also that determined by Professor J. W. Richards. According to Moissan, the carbide is not affected by oxygen at 1000°C, nor when heated in air by a Schloesing's blowpipe. Sulphur vapor at 1000° is also without action, while chlorine attacks the compound very slowly at 600° and rapidly at 1200°. Fused potassium nitrate, or chlorate, boiling sulphuric acid, nitric acid, and hydrochloric, aqua regia, and mixtures of nitric and hydrofluoric acid are all without action. Fused lead chromate oxidizes the carbide, but repeated treatment is necessary to obtain complete combustion. Fused potassium hydroxide gradually converts it into potassium carbonate and silicate. Mühlhæuser has also described a boron carbide obtained by heating a mixture of boric anhydride with carbon in the electric furnace. A graphite-like mass is obtained, which after further heating in a platinum crucible and boiling with acids yields, on analysis, BC, or B₂C₂. It is described as a black powder having similar properties to graphite, burning with difficulty in oxygen, insoluble in nearly all of the usual solvents and decomposed by fusion with alkali. It is significant that the Carborundum Company are about to increase their capital stock, and that among other recent orders one has come from London calling for \$10,000 worth of material.

FORMATION OF PRECIOUS OPAL BY THE ACTION OF HYDROFLUOSILICIC ACID ON GLASS.

PROFESSOR G. Cesàro, of the University of Liège, describes in the Bulletin of L'Académie Royale de Belgique the formation of precious opal and other substances by the action of hydrofluosilicic acid on a glass-containing vessel.

¹W. R. Blake in *Science*, XXII., 554, p. 141.

The glass was attacked very unequally, the upper portion, that above the level of the liquid, being acted upon most strongly, with the production of cellular cavities containing a white translucent substance. In these cavities and also attached to the bottom of the flask were likewise found beautiful, limpid crystals of hexagonal form with others, unattached, which were apparently tetragonal. The opalescent mass was built up of concentric layers, which were easily separated and which produced fine iridescent effects. This substance proved to have the composition, silica, 90 per cent; water, 10 per cent; corresponding precisely to the precious opal of Hungary and from the chemical point of view to the polysilicic acid, 3 SiO₂. H₂O. The formation of this opal is easily understood from the reaction:



The hexagonal crystals found by their chemical and physical properties were determined as fluosilicate of sodium, Na₂ Si F₆. The crystals give in convergent light a uniaxial interference figure; they are negative in character and show a weak double refraction. The index of refraction for the ordinary ray is 1.300 and for the extraordinary ray 1.296. The remaining crystals, spoken of as apparently tetragonal, were determined to be biaxial and orthorhombic ($\frac{a}{c} = \sqrt{3}$), consisting of a soluble potassium fluosilicate. Finally in the liquid was found a fluosilicate of calcium. It will be seen that both the fluosilicate of calcium and of sodium, as well as the opal itself, are explained in the reaction above given.

These experiments recall the historic ones of Daubrée in Paris, who, by superheated water alone, altered a glass-containing tube with the production of hydrated silicates resembling zeolites (Pectolite?) and of an alkaline silicate in solution, together with innumerable colorless, bipyramidal crystals of quartz, minute spherulites, microlites and even a green pyroxene (Diopside?).

INERTNESS OF QUICKLIME.

It is now a well-known fact that in the absence of moisture many elements and compounds which ordinarily react upon each other readily and even with explosive rapidity are rendered inert. Thus mixtures of oxygen and hydrogen if perfectly dry can not be exploded by the electric spark. Many chemists are now working on these lines, and all contributions are of interest in extending the experimental data. Mr. V. H. Veley has already shown in the Journal of the Chemical Society of London that quicklime does not combine to an appreciable degree with carbonic or sulphurous acids at temperatures below 300°C., and now in a more recent paper he has investigated the reaction between the same substance and chlorine. The result of Mr. Veley's experiments is to confirm the observation of others, his conclusions being, first, that dry chlorine does not combine with dry lime at ordinary temperatures to form the so-called bleaching powder; second, that no appreciable chemical change is observable between these two substances below a temperature of 300°, when a partial replacement of oxygen by chlorine takes place, the conditions being analogous to that of baryta and chlorine not specially dried and at ordinary temperatures. It seems probable to the writer that Veley's method of "drying" is the real explanation of the slight reactions obtained below 300°, in other words that *no* action would take place below that temperature were the chlorine and lime *absolutely* dry.

BARIUM AND STRONTIUM IN SILICATE ROCKS.

At a recent meeting of the Geological Society of Washington, and later at the Baltimore Meeting of the American Chemical Society, Mr. W. F. Hillebrand presented a

valuable series of papers on the widespread occurrence of barium and strontium in the silicate rocks, with methods for the determination of these elements in small amounts. Mr. Hillebrand also deplored the laxity existing in rock analysis and brought forward a strong appeal for greater completeness in the future. The papers are of extreme interest and hardly permit of abstract but can be found in full in the February Journal of the Chemical Society.

THE EXAMINATION OF BEESWAX.

MR. LYMAN F. KEBLER has recently published the results of an investigation of commercial beeswax, his general conclusions being as follows: He finds the beeswax upon the market to be adulterated to the extent of 50 per cent, while in the English markets this adulteration may even reach 66 per cent. The melting point varies from 62°–74°C. It is raised by adding carnaüba wax, stearic acid, certain mineral waxes and paraffin, and is lowered by China wax, Japan wax, cacao butter, resin, tallow, spermaceti, vegetable wax, etc. On the other hand the melting point is apparently unaltered when suint wax and certain of the mineral waxes are used. The specific gravity of the pure wax varies from 0.960 to 0.973, and this appears to be greatly influenced only by resin, carnaüba wax and certain mineral waxes, which raise it, and by paraffin, which lowers it. The "acid number" ranges from 19–21 mg. of potash per gramme of beeswax. Stearic acid resin and suint wax increase, while carnaüba wax, mineral wax, cacao butter, paraffin and spermaceti decrease the acid number. The "ether number" varies from 73–76 mg. of potash per gramme of beeswax and is increased by China wax, Japan wax, cacao butter, tallow and vegetable wax. It is unaffected by addition of carnaüba wax but is lowered by mineral wax, paraffin, resin, stearic acid, etc. It must be noted in this connection that wax bleached by certain chemical agents may have on either number as high as 84 and yet be pure. The percentage of iodine varies from 8–11, but here also certain bleaching agents, such as chlorine, destroy the value of this test. Paraffin, mineral wax and stearic acid lower the percentage, while cacao butter, resin, suint wax and tallow increase it. The volume of hydrogen (53–57.5cc) evolved from one gramme of beeswax and the percentage (12.5–14.5 per cent) of hydrocarbons evidently are the most reliable data securable, the former being vitiated by all adulterants excepting tallow, and the latter by all except suint wax. The author gives a resumé of the best methods employed with many references to the literature.

BUTTER NOSTRUMS.

VARIOUS nostrums for increasing the yield of butter have long been more or less secretly upon the market, and notwithstanding their frequent exposure, they no doubt meet with considerable sale. Professor H. W. Wiley has again called attention to these frauds in Farmers' Bulletin No. 12, United States Department of Agriculture. It is claimed that from one pound of butter, one quart of milk and a little of the magic butter compound, two pounds of butter can be made! Analysis shows this compound to consist of common salt, coloring matter and a little pepsin or rennet. Such a mixture churned with the butter and milk merely coagulates the latter and allows of its incorporation, together with considerable water, into the resulting "butter" mass. Such outrageous adulteration can be easily detected by melting a sample in a test tube and comparing with a similar sample of genuine butter, the latter showing the fat in a clear limpid mass with only a small amount of water and a little curd, while with the former almost half of the whole volume will be a mixture of water, curd, and foreign substance. These compounds are retailed at from \$2.00 to \$2.50 a box of about two ounces.

LETTERS TO THE EDITOR.

* * * Correspondents are requested to be as brief as possible. The writer's name is in all cases required as a proof of good faith.

On request in advance, one hundred copies of the number containing his communication will be furnished free to any correspondent.

The Editor will be glad to publish any queries consonant with the character of the journal.

Comment on "A New Thermo-Electric Phenomenon."

AN article has recently appeared in *Science*,¹ entitled "A New Thermo-electric Phenomenon." It is from the pen of W. Huey Steele, and has been copied and abstracted in several journals. Previous to seeing Mr. Steele's article, but not previous to its writing, I had made a few rough experiments along the same lines and had looked up the subject, historically, to see what had been already done.

From what I have been able to find out, in the course of my reading, it seems to me that Mr. Steele's phenomenon is not "new" at all, but is, perhaps, a slightly different phase of an old phenomenon first discovered by Becquerel in 1829.² Becquerel found that in a platinum wire, strained by a spiral and heated at one side of the strained portion, there is an electric current set up, and he thought that this was due to a difference in the propagation or movement of the heat to right and left of the heated portion. However, Magnus and Matteucci have shown that in a homogeneous metal the differences of temperature and of section are not sufficient to produce a current, and Becquerel's phenomenon should be attributed to a difference in the molecular state.

In addition, Sir William Thomson³ has shown that thermo-electric currents were set up between the strained and unstrained portions of a single metal constituting a circuit; the effects in copper and iron being opposite, and the residual effect in each case being the reverse of the effect when the metals are temporarily strained. He also found the relations between hammered and unhammered iron and between brittle and soft iron.

To my mind these experiments are almost identical with those of Mr. Steele; practically no wire can be obtained that has not been through its own history of various strains. (The process of wire-drawing leaves the metal in a permanent state of elongation, and the residual thermo-electric effect, in that case, is the reverse of the effect which is induced by the force applied during the wire drawing.) As for the metals which he completely melted, I think there can be no doubt (from the very fact that "the effects are not always steady; in fact, they very seldom keep steady" and the *direction* of the currents keep shifting) that the melted metal was continually undergoing strains brought about by currents and strata of the metal shearing past one another, or, in other words, by a difference in the molecular state at different times. In addition there is probably, in the case of the melted metals, a large effect due to the thermo-electric action between the melted and solid metal that leads to the galvanometer, those at the opposite ends of the "clay tubes" being in different and continually changing molecular relations.

Becquerel must have obtained a considerable E. M. F. when he heated his platinum wire to a *white heat* and strongly affected a galvanometer of 1829. From these considerations I do not think that Mr. Steele's is a "new" phenomenon, and I think that everybody that reads his article and compares it with those of Becquerel and Thomson (which are far too extensive to even outline in this note) will agree with me.

In the opening lines of his paper Mr. Steele says that it has been "generally known that electric currents may be produced by heating a single metal, if there be any

¹Nov. 10, 1893.

²Becquerel's "Traité d'Elec. et Mag.," Vol. I., p. 155.

³Phil. Trans., 1856, p. 711 et seq.