

with iodine takes up one atom of iodine for each atom of nickel. This establishes the formula, as was expected, as  $K_2Ni(CN)_3$ , or  $2KCN.NiCN$ , the complex containing nickel in a univalent condition. Tschugejew and Chlopin<sup>1</sup> have also obtained univalent nickel by the reduction of nickel salts by a concentrated solution of sodium hydrosulfite and nitrite in equimolecular proportion. A violet or blue coloration is produced according to the amount of reagent used. The violet solution contains  $HN(NiSO_3)(HSO_3).nH_2O$ , which could not, however, be obtained in a completely pure condition. Sodium hydroxide gives a blue precipitate of what is apparently  $NiOH$ , but which could not be dried without decomposition. This is converted by sodium sulfide into black  $Ni_2S$ , which can be isolated only in moist condition. The blue hydrate dissolves in  $KCN$  to a red solution, which seems to be identical with that of Bellucci's  $K_2Ni(CN)_3$ .

Barbieri<sup>2</sup> has entered on a systematic study of resemblances between compounds of elements in different groups of the periodic system, when these elements have the same valence. Thus an element of the eighth group, acting with a valence of three, may be, for practical purposes, considered as an element of the third group. As examples he has prepared Ruthenium acetylacetonate,  $Ru(C_5N_7O_2)_3$ , and finds it to closely resemble aluminum acetylacetonate, with which it is isomorphous and gives solid solutions. Ammonium rhodio-molybdate,  $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$ , is in every way similar to the corresponding  $Al$ ,  $Fe'''$ , and  $Cr'''$  salts, as well as to the  $Co'''$  salt of Friedheim and Keller. The isomorphism of palladium acetylacetonate with the corresponding cupric salt was shown by the formation of solid solutions. Delépine<sup>3</sup> has succeeded in preparing the very soluble chloro-iridates and iridites of lithium.  $Li_2IrCl_6$  crystallizes as a hexahydrate, and when crystallized with sodium chloro-iridate does not form any intermediate compound. When reduced by alcohol  $Li_3IrCl_6.12H_2O$  is formed and hydrogen chloro-iridite remains in the mother liquor. No intermediate lithium-hydrogen salt is formed. Better results are obtained by reducing the lithium chloro-iridate with lithium oxalate. By mixing with solutions of sodium chloro-iridite, the intermediate compounds,  $Na_2LiIrCl_6.12H_2O$  and  $Na_{1.1}Li_{1.9}IrCl_6.12H_2O$ , were obtained, but when recrystallized from water the sodium salt resulted, containing very small quantities of lithium. Fraenkel has prepared<sup>4</sup> a number of new salts of rhodium and iridium with organic bases. Chloro-iridic acid gave only the familiar type,  $M_2'IrCl_6$ . With rhodium, however, not only the type  $M_3'RhCl_6$  was obtained, but also  $M_2'RhCl_5$  (with methylamine),  $M_4'RhCl_7$  (with methylamine and tetraethylamine), and  $M_3'Rh_2Cl_9$  (with trimethylamine and tetraethylamine).

#### NOTE.

**A Surficial Burn Produced by an Unknown Radiation.**—Woehler,<sup>5</sup> in 1862, heated carbon and an alloy of calcium and zinc together and

<sup>1</sup> *Compt. rend.*, 159, 62.

<sup>2</sup> *Atti accad. Lincei, Rome* [5] 23, i, 334.

<sup>3</sup> *Compt. rend.*, 158, 1276.

<sup>4</sup> *Monatsh. Chem.*, 35, 119.

<sup>5</sup> F. Woehler, "Bildung des Acetylens durch Kohlenstoffcalcium," *Ann. Chem. Pharm.*, 124, 220 (1862).

obtained a product which evolved acetylene when treated with water. He called the product calcium carbide.

The alloy had been previously described by Caron,<sup>1</sup> who got it by adding metallic sodium to fused calcium chloride in the presence of molten zinc. This alloy is of silvery luster, highly crystalline, and contains from 10% to 15% calcium.

On repeating Woehler's experiment, in connection with other experiments on making calcium carbide by different methods, use was made of a gas crucible of present day type. The objection was raised that a temperature was thus secured higher than that Woehler probably worked with. Accordingly, an old-fashioned assay furnace of French clay, which had come to me as an heirloom, was set up. This furnace was in three sections, the lower one having a grate and ash pit, the second section being merely a ring, and the third, or top section being dome shaped, and having a central round opening on top which was connected to a wide chimney by means of a sheet iron smoke stack.

Caron alloy was made by melting lumps of fused C. P. calcium chloride and granulated zinc, 20 mesh, in a Dixon graphite crucible and adding slices of metallic sodium. The reaction is at times violent. There results on cooling a fine regulus of the calcium zinc alloy. Charcoal was used as fuel.

Separate portions of this alloy were made at different times and heated with different varieties of carbon, such as charcoal, coke, lampblack and gas carbon, a sample of the latter dating from 1850 to 1860 being found among apparatus left me.

On Nov. 30, 1907, two charges were run in the furnace. In the first, use was made of alloy and gas carbon, in the second alloy and lampblack. The operation was conducted with 1100 g. of a 14% alloy and 110 g. of lampblack, using a No. 6 Dixon crucible. It took three hours to distill off the zinc, during which time I sat with the furnace between my knees feeding in the charcoal used as fuel through a side opening in the stack. Though the work was somewhat dirty no inconvenience was felt at the time. Later on, undressing for a bath, the inner surface of each knee was found red, and there was a water blister, about 1 cc. in diameter, in the center of the red surface on the left knee. The red patch was about the size of my hand, that on the right knee half that size.

Since this effect had been produced not only through a pair of thick trousers but thick woolen drawers under them, without my noticing any sensation, and as the burn appeared like one made by X-rays, with which I was familiar, it was later shown to Drs. Robert Abbe and Henry G. Piffard, both of whom were familiar with X-ray and radium burns and they agreed with my diagnosis, and considered the burn was similar in character to burns produced by those agencies.

<sup>1</sup> H. Caron, *Compt. rend.*, 50, 547 (1860).

The nature of the burn was further confirmed by the fact that it took long to heal, traces of it were visible Mar. 31, 1908, or four months later.

To further test the theory, at Dr. Abbe's suggestion, the experiment was repeated on Dec. 21, and to eliminate the personal equation a sheet of lead, perforated with five holes, was interposed between the Cramer X-ray "X" plate, enclosed in the usual black and yellow papers, and the portion of the furnace corresponding to the height of my knee from the floor, while the zinc was distilled. There is a crack around the furnace at this point, and it was about there that the fumes of burning zinc could be seen within the furnace. Alloy and lampblack were again used in the charge. The plate was exposed for 1 hr. and 17 min. at a distance of 2 ft. from the furnace, and a thermometer placed beside the plate showed a temperature ranging from 25° to 35°, with one time a temperature of 42°.

The plate was given to a photographer to be developed along usual lines, but he was not told what might appear on the plate. The developed plate and a positive printed from it show the five holes in the lead covering plate and thus confirm the diagnosis of the nature of the burn.

Later, other plates were exposed during runs but no distinct effects produced. Nor was there any similar result to the first obtained when Messrs. Stone and Riggs kindly exposed similar plates behind the perforated lead plate to the light of burning zinc at the furnaces of the New Jersey Zinc Company.

Both the burn and the effect on the X-ray plate were produced when alloy and lampblack were used. When coke, charcoal, and gas carbon were used with the alloy no photographic evidence was obtained. The lampblack was purchased in open market, as also the zinc, calcium chloride, and sodium, the other chemicals used. The fuel was either ordinary charcoal or in the later experiments coke or coal or both together. The Dixon crucibles and covers were new.

As an opportunity has not presented itself for me to repeat these experiments methodically and determine the cause of the phenomena the facts are placed on record in the hope that sometime an explanation will be forthcoming.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## THE INFLUENCE OF TEMPERATURE IN ACID CATALYSIS.

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Since the suggestion was put forward by Goldschmidt,<sup>1</sup> Snethlage<sup>2</sup>

<sup>1</sup> *Z. physik. Chem.*, **70**, 627 (1910); **81**, 30 (1912).

<sup>2</sup> *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 211 (1913).