

## SEPARATION OF SILVER AND LEAD.

By R. BENEDICT and L. GAUS.

THE authors found their process on the different behavior of silver and lead iodides with dilute nitric acid.

The solution containing silver nitrate and lead nitrate—in all about 0.5 gramme of metal—is diluted with cold water in a capacious glass capsule to from 200–300 c. c., and solution of potassium iodide more than sufficient for the complete precipitation of the silver, but not excessive in quantity, is allowed to flow in. If 0.5 gramme of metal is used, 10 c. c. of a 10 per cent. solution of potassium iodide will be sufficient in any case. We then add 10 c. c. of nitric acid free from chlorine, previously diluted with from 10–20 c. c. of water. The capsule is then covered with a watch glass and heated on the water bath, when the yellow color of the precipitate chiefly passes at first into orange red.

As soon as the liquid has become hot, the lead iodide dissolves, the liquid becomes dark brown, and vapors of iodine are given off. The watch glass is then removed and rinsed into the capsule, boiling water is added, and the capsule is left on the water bath, adding water from time to time to compensate for the loss by evaporation until the liquid has become colorless or pale yellow, when the iodine is expelled. The silver iodide is then weighed. The authors collect it in a small glass tube filled with glass wool, dried at 110°, and weighed. Wash it first with hot water containing nitric acid and then with a few c. c. of hot water, dry at 110° and weigh.

The presence of other metals of the same group, with the exception of mercury, does not interfere. Cuprous iodide, bismuth, and cadmium iodide behave with nitric acid like lead iodide; on the other hand, mercurous iodide is converted into red iodide, which is not further attacked.

The authors publish very favorable results. In the examination of alloys of lead and silver they proceed in the same manner. They dissolve in nitric acid, dilute, precipitate with potassium iodide, and heat on the water bath.

For determining silver in impure leads, from 10–50 grammes of the same, according to the proportion of silver, is dissolved in dilute nitric acid containing tartaric acid. To 10 grammes of the sample they use 10 c. c. nitric acid free from chlorine, and an equal quantity of a saturated solution of tartaric acid. The presence of the latter effects much more rapid and complete solution. The solution is heated until the oxidation is completed, diluted with boiling water, filtered into a glass capsule, diluted to from 300–500 c. c., allowed to cool, 10 c. c. of a 10 per cent. solution of potassium iodide are added and it is heated on the water bath.

The excess of the nitric acid added for solution is generally sufficient for oxidizing the lead iodide; if the development of iodine vapors and the brown color do not appear, a little more dilute nitric acid must be added.

The proportion of silver in galena may be determined in the same manner. It is oxidized with nitric acid with the addition of tartaric acid. It is most convenient to use equal volumes of nitric acid, solution of tartaric acid, and water. After the oxidation is completed, the liquid diluted with hot water, filtered, and well washed with boiling water, the filtrate is allowed to cool. The process is then completed as above.—*Zeit. Anal. Chem. and Chem. Zeitung; Chem. News.*

## A VOLATILE SERIES OF METALLIC COMPOUNDS.

By C. F. TOWNSEND, F.C.S.

THE progress of chemical science is continually bringing to light new wonders and startling paradoxes. Nothing more remarkable and unexpected has occurred in the recent history of chemistry than the discovery of the compounds of nickel and iron with the gas generally known as carbon monoxide or carbonic oxide. The new compounds are called respectively nickel and iron carbonyls, and have evidently a great future before them. Judging from chemical precedent, one would quite as soon have expected oil and vinegar to form a homogeneous mixture as a combination of the bodies referred to. In fact, so anomalous did it appear when Mr. Ludwig Mond first brought the accidentally discovered nickel compound to the notice of the Chemical Society in the middle of 1890, that many almost refused to believe in the possibility of its existence. However, there is no doubt about it. Nickel carbonyl, a considerable quantity of which was exhibited at a *conversazione* of the Royal Society held in June last, and also at the meeting of the British Association, is obtained by merely passing carbon monoxide—a product of the incomplete combustion of coke or charcoal, and which may often be seen burning with a lambent blue flame at the top of a clear fire—over the finely divided metal, and condensing the resulting vapor in a tube surrounded with ice and salt. Its properties have been very fully investigated both by its discoverers, Messrs. Mond, Langer and Quincke, and also by M. Berthelot, who published his results in the *Comptes Rendus*.

It is a liquid of very high refractive power and brilliant appearance, and considerably heavier than water, under which it may be kept without change, provided the vessel is completely filled and the water contains no air. It solidifies at 13° F., and boils at 109° F., and the vapor, if lighted, burns with a strongly luminous flame, which appears smoky in consequence of the separation of metallic nickel. The liquid is very volatile, and if the vapor is suddenly heated, a sharp detonation is caused. A mixture of nickel carbonyl with air takes fire, if brought into contact with a very hot body, and occasionally explodes. A mixture of the dry vapor and oxygen may be detonated by simple agitation over mercury, and strong oil of vitriol produces the same effect in a few minutes. The vapor, when heated to 358° F., splits up again into its original constituents, the metal and the gas, and the nickel deposits itself as a brilliant coating on the sides of the vessel. Advantage is taken of this circumstance to apply the carbonyl to nickel plating, and a patent has been taken out by its discoverers for working it on a commercial scale. At the last meeting of the British

Association, Mr. Ludwig Mond described the various uses to which the discovery might be put, and the possibilities which it opened up. The nickel plating can be accomplished by simply exposing the goods, after being heated to the temperature just mentioned, to nickel carbonyl vapor, and solid articles can be similarly formed by passing the vapor through heated moulds. For this purpose, it is found advantageous to dilute the vapor considerably with air. Nickel can also be deposited on any substance by treating it with the liquid itself, or better, by nickel carbonyl dissolved in suitable solvents. These processes possess a great advantage over electro-plating, as not only metal but any substance, however intricate in design or fragile in structure, can be coated with a brilliant film of nickel by its means without the tedium and risk of first covering it with a surface of blacklead. Some very beautiful specimens of real flowers, plated with different metals, principally gold and silver, so as to bring out the various parts of their structure, were exposed for sale at the Frankfurt Electrical Exhibition. A syringa blossom, for instance, would have its stamens and anthers plated with gold, its corolla with silver, and the stalk and calyx with copper. Needless to say, they found a ready market. The field before this new process is practically unlimited, for not only could it be applied to ornaments and articles of household use, but, if required, to delicate muslins, and dress or other fabrics.

The liquid nickel carbonyl is highly poisonous, and, if injected subcutaneously, acts very powerfully on the animal system, producing an immediate and remarkably prolonged fall of temperature. It might, perhaps, be introduced into medical practice as an antipyretic in the treatment of fevers, were it not for the difficulty of administering it in sufficiently small doses, and its intensely poisonous action. The carbon monoxide alone is the active agent in causing this effect, the symptoms being those of respiratory poisoning; and the blood of animals killed by it exhibits the same appearances as that of persons suffocated by inhaling the fumes of burning charcoal. This kind of poisoning is particularly dangerous, and in cases of recovery the effects do not wear off for several hours after. The red corpuscles of the blood owe their color to a complex chemical substance known as hæmoglobin, which acts as the carrier of oxygen. In passing through the lungs oxygen is taken up, and it is converted into oxy-hæmoglobin, which, when placed so as to intercept the rays of light in the spectroscope, gives quite different absorption bands to the hæmoglobin itself; from the lungs the oxygen is carried to different parts of the body to be exchanged for carbonic acid, which is brought back to be eliminated and again replaced by oxygen, thus completing the cycle. Carbonic oxide combines with the hæmoglobin to form carboxy-hæmoglobin, an exceedingly stable substance, which can only be displaced by oxygen with the greatest difficulty. The consequence is that the blood is unable to perform its functions, and the animal rapidly dies from suffocation. The absorption spectrum of this last body is remarkably characteristic and quite unmistakable, forming an infallible test in case of suspected poisoning by charcoal fumes. The vapor of nickel carbonyl is as deadly as the liquid, and is dangerous in air even to the extent of only 0.5 per cent.

The extraction of the metal from its ores is another valuable use to which the discovery of this compound will almost certainly be put. The principal sources of nickel are the copper colored arsenical mineral which the German miners—after working it unsuccessfully for years in the hope of obtaining copper—called *Kupfer-nickel* (i. e., false copper), and in which the metal was first discovered by Cronstadt in 1751, and *spieß*, an impure residue formed at the bottom of the melting pots in the manufacture of the bright blue pigment known as *smalt*, which is largely used by paper stainers. Metallic nickel is obtained from these by heating them with charcoal in a furnace, but the product only contains about 60 per cent. of the pure metal. It appears now that it will be sufficient to pass carbon monoxide over the crushed mineral, and by simply heating the resulting nickel carbonyl to 358° F. chemically pure nickel will be deposited.

All attempts to obtain a similar compound with other metals for a long time proved unsuccessful. As it seemed improbable that nickel should be the only metal forming such a compound, the investigators persevered with the work, and finally succeeded in volatilizing distinct quantities of iron in a current of carbon monoxide. The issuing gas burned with a yellowish flame, and if passed through a heated tube deposited a metallic mirror in the glass, which answered to all the tests for iron with unusual brilliancy. The quantity produced was, however, very small, and the process exceedingly laborious, for it took no less than six weeks to volatilize about thirty grains of iron. Even under the most favorable conditions the gas never contained more than 0.2 per cent. of the compound, but by varying the details of the process a much larger yield was obtained.

The iron carbonyl thus produced is a pale yellow viscous liquid, nearly half as heavy again as water. It distills without decomposition at 220° F., and solidifies below 6° F. into yellowish needle-shaped crystals. It decomposes slowly on exposure to air and, like the nickel compound, is completely broken up by heating its vapor to 356° F. On the other hand, it is much less active than its analogue and is not attacked by dilute oil of vitriol. Its composition was at first thought to be similar to that of nickel carbonyl, but on accurate analysis it was found to contain five proportions of carbon monoxide [Fe(CO)<sub>5</sub>] instead of the four which constitute the latter [Ni(CO)<sub>4</sub>].

While engaged in some experiments on the utilization of water gas (which is manufactured by passing steam over red hot coke, and contains about 40 per cent. of carbonic oxide) for illuminating purposes by means of the Farneshelm system, in which a comb of magnesia is raised to incandescence by a number of fine gas jets, Sir H. E. Roscoe and Mr. Scudler noticed that a red deposit of oxide of iron was formed on the rods after the water gas had impinged on them for a few hours.

This was a serious drawback, as the illuminating power became much reduced. As the experiments were being conducted in a steel works, the first supposition naturally was that the stain was caused by fine particles of iron present in the atmosphere, but closer

inspection showed that the deposit was of a "coraloid" structure and must, therefore, have been produced by the gas itself. In order to ascertain whether the iron existed in the gaseous state or was carried forward chemically, the gas was filtered through several tight plugs of cotton wool. No difference whatever was observed, and it was concluded that the gas contained a very minute quantity of a volatile compound of iron. Shortly after it was subjected to various chemical tests, which left very little doubt as to its identity with iron carbonyl.

Coal gas has also been found to contain iron, derived, no doubt, from the slow action of the 7 or 8 per cent. of carbon monoxide it contains on the iron of the mains and gas pipes. This accounts for the hitherto unexplained black stain so frequently observed on steatite and other burners. Compressed coal gas has begun to take the place of hydrogen in the production of lime light, and the stain formed on the lime cylinders is very noticeable, being, it is almost needless to say, somewhat of a drawback to its use.

The discovery of this series of compounds is quite a revelation to the metallurgical chemist, and already explains many mysteries. In the cementation process for the manufacture of steel, bars of iron are embedded in powdered charcoal, and kept at about the melting point of copper (2,192° F.) for eight or ten days. Steel, as is well known, is an alloy of iron, with a combination of carbon and iron, called carbide of iron, and the principle of all steel making is the same: carbon must be added to soft iron in definite proportions. If the iron contains no carbon, it is comparatively soft and malleable. Wrought iron contains less than 0.3 per cent. of carbon; steel from 0.3 to 1.5 per cent. Above this the metal takes the character of cast iron. The charcoal which surrounds the bars of iron in the process just referred to occludes a large quantity of air in its pores, which, when heated, forms carbonic oxide. This gas permeates the iron and gives up its carbon to the metal, returning again to take up a fresh supply from the charcoal, and thus acts as a carrier of carbon to and fro in the interstices of the iron, which it gradually converts into almost homogeneous steel, known technically as *blister steel*, owing to its peculiar vesicular appearance caused by the penetration of the gas. These compounds must play a very important part too in the blast furnace and in both the Siemens and the Bessemer process, especially the latter. Bessemer steel is made from cast iron; the carbon and impurities are burnt out of it by driving a current of air through the molten metal. When this has been accomplished, a highly carburated cast iron, called *spiegel-eisen*, is thrown into the converter in properly regulated quantity, and the carburating of the iron is rapidly effected.

Renewed attention has recently been directed to some volatile compounds of platinum with chlorine and carbon monoxide, which are broken up by water with deposition of pure platinum, thus forming a possible way of extracting the metal from its ores. If any discovery of this kind were to facilitate the extraction of gold, which at its present rate can barely keep up with the demands of the increasing consumption, an immense boon would be conferred on the civilized world.—*Knowledge.*

## THE MANUFACTURE OF LIQUORS AND PRESERVES.\*

By J. DE BREVANS, Chief Chemist of the Municipal Laboratory of Paris.

## PART II.—CHAPTER V. (Continued.)

## SECTION III.—SUPERFINE LIQUORS.

*Liqueur surfin.*

THE quantities of alcohol (85°), sugar, and water usually employed in the preparation of superfine liquors are:

Alcohol (85°).....	3 l.
Sugar.....	5 k. 500 grm.
Water.....	2 l. 600 c. c.

For 10 l.

## Cream of Absinthe.

*Crème d'absinthe.*

Essence of absinthe.....	0.6 grm.
Essence of English mint.....	0.6 grm.
Essence of anise.....	3 grm.
Essence of sweet fennel.....	0.8 grm.
Essence of lemon distilled.....	3 grm.

## Anisette.

Essence of star anise.....	7 grm.
Essence of anise.....	2 grm.
Essence of sweet fennel.....	0.8 grm.
Essence of coriander.....	0.1 grm.
Essence of sassafras.....	0.6 grm.
Extract of orris.....	6 grm.
Extract of ambrette.....	0.8 grm.

*Crème de Barbades.*

Essence of lemon, distilled.....	6 grm.
Essence of Portugal, distilled.....	3 grm.
Essence of cinnamon of Ceylon.....	0.4 grm.
Essence of cloves.....	0.4 grm.
Essence of nutmeg.....	0.2 grm.

## Chartreuse.

*Liqueur de la grande Chartreuse.*

Essence of lemon balm.....	0.2 grm.
Essence of hyssop.....	0.2 grm.
Essence of angelica.....	1 grm.
Essence of English mint.....	2 grm.
Essence of Chinese cinnamon.....	0.2 grm.
Essence of nutmeg.....	0.2 grm.
Essence of cloves.....	0.2 grm.

Color, yellow or green.

## Curaçao.

Essence of curaçao, distilled.....	10 grm.
Essence of Portugal, distilled.....	4 grm.
Bitter infusion of curaçao a sufficient quantity; color with Pernambuco wood.	

\* Continued from page 14269, SUPPLEMENT No. 893.