

sparingly soluble in water, it is not removed by the necessary washing, and gives to the redissolved pellicle a fine yellow color, which altogether prevents the necessity for backing of any kind.

We may add that we experienced some difficulty at first in removing the yellow appearance from the developed plates, but ultimately it yielded readily to a wash with methylated spirit. Our experiments have not been sufficiently extended to warrant any very strong statement as to the superiority of curcumin over other organifiers; but from what we have seen, we believe that it will be found in every way a most important addition to the *matériel* of the emulsion worker.—*British Journal of Photography*.

Correspondence.

Penguins.

To the Editor of the Scientific American:

Notice in your issue of January 29, an illustrated article on penguins, which calls to mind a little incident which occurred three years ago, in the South: A boat's crew and myself went fishing off Goff's Island, in the South Atlantic; on nearing the shore, we saw what appeared to be six or seven persons on a rock, and from their gestures they seemed to be hailing us. Supposing them to be the survivors of some ill-fated vessel, we rowed down to them and found they were penguins, who stood there, nodding their heads and flapping their fins, as if enjoying the trick they had played on us. We soon after went on shore at another part of the island, and there found the birds in large numbers, so thick in fact that they could be kicked over.

We also found great numbers of their eggs, which they lay in the sand, and we secured a large quantity of these and carried them aboard the ship. We also went on shore at Kerguelen's Island (the subject of your illustration) and there one of the sailors had his hands badly bitten, in trying to catch one alive. At the Crozetts, we again met the penguin family; and here several of the seamen brought them aboard, ate the flesh, and made pillows of the feathers. I made a cap of the skin of one, which lasted for a long time, the feathers making it waterproof. The birds are seen in great numbers at sea, and old sailors take warning of a gale by their quack.

But a more beautiful bird is found in the Southern Oceans. It is the albatross, the king of sea fowl. It seldom if ever goes on shore. I have seen hundreds of them, in schools, riding gracefully over the waves, and I succeeded in catching one by baiting a shark hook with a piece of pork. The bird measured 7 feet 8 inches between the tips of his wings. We made tobacco pouches of the skins of his feet, and pipe stems of the small bones of the legs and wings; and the skin was to be made into a muff, as, after pulling out the large feathers, a long heavy down is left, making it very desirable as a substitute for fur. The bill is long and crooked, similar to that of the eagle; and when hungry, the bird will devour food at an alarming rate.

The albatross can be found in immense numbers, and I have often wondered why it would not pay for capitalists to send out vessels to secure these birds for their feathers.

Pittsfield, Mass.

W. E. DAY.

NEW PHOSPHIDES OF SILVER, AND A METHOD OF ESTIMATING SILVER QUANTITATIVELY BY MEANS OF PHOSPHORUS.

BY WILLIAM FALKE, PROFESSOR OF NATURAL AND PHYSICAL SCIENCES IN MANHATTAN COLLEGE.*

In the fall of 1873, the author's attention was attracted to the action of phosphorus upon the salts of silver, in particular the nitrate. If reference be made to most treatises on chemistry, it will be found therein stated that phosphorus is a powerful reducing or deoxidizing agent, and that by introducing a stick or clean piece of phosphorus into many metallic solutions, as, for example, copper sulphate, silver nitrate, or gold chloride, the metals are separated or reduced from their combinations, and are deposited upon the suspended phosphorus in the metallic state: at first such a fine film forming upon the phosphorus as to be transparent. (Gold under these circumstances, appears beautifully green on viewing it by transmitted light, which color is characteristic of this metal, and by it it can be distinguished from spurious foils. Silver and copper are deposited upon the surface of the phosphorus in minute but brilliant crystals; and by very prolonged digestion, the whole, or nearly all, of the metal may be separated from the solution. In these reactions, the phosphorus, or part of it, removes the oxygen (or chlorine) from the metallic salts, precipitates the metal, and enters itself into solution.

In studying and experimenting upon the above detailed reactions, it occurred to me to dissolve the phosphorus in some liquid before adding to the metallic solution, whereby the phosphorus would be almost instantly diffused, and would, of course, offer an immensely increased surface for chemical action. The liquid in which phosphorus is most largely soluble is carbon disulphide, which is the solvent that has been almost exclusively employed in the following experiments:

On adding such a solution of phosphorus, which should not be too concentrated, to a solution of nitrate of silver in water, a dark and sometimes iridescent film is formed, which covers to some extent the sides of the glass vessels and also incases the globules of carbon disulphide at the bottom. A copious separation of the same black substance also precipitates, almost immediately on shaking.

The whole of the silver is thus removed in a short time from the solution, particularly on warming and stirring. Other metallic solutions, with different metals, were thus treated, most of which were completely thrown down in a short time, as copper, gold, platinum, etc.

Here it is important to observe that the precipitates and films thus obtained consisted not only of a part of the metals, but compounds had formed—combinations of phosphorus and metal.

After the above preliminary indications of an hitherto unobserved character, minute investigations were instituted in order to determine the nature of the compounds thus formed, and to see to what use, if any, they could be put. At present this report will confine itself entirely to the investigations on silver: the other results will appear in future communications. The following proportions were employed: Silver nitrate (fused), 5 grammes (77.16 grains); phosphorus, 1 gramme (15.41 grains); carbon disulphide, 10 cubic centimeters (0.61 cubic inch); water, 100 cubic centimeters (6.1 cubic inches). The fused nitrate of silver is dissolved in the water (more or less) and the phosphorus is then dissolved in the disulphide of carbon, which is then poured into the silver solution; the small vessel containing the phosphorus should be rinsed with a little carbon disulphide which should be added to the rest, as, if any phosphorus remains in the vessel, the volatile carbon disulphide would evaporate and leave some phosphorus in a finely divided state behind which may ignite or burn spontaneously when dry in the air. The mixture is then stirred in the cold, and allowed to stand for some hours until all the silver has been removed or separated, which can be determined by taking a drop out with a glass rod and touching it with a drop of hydrochloric acid or a chloride, until no longer a white curdy precipitate or opalescence of chloride of silver appears.

Immediately on mixing the above solutions, the silver begins to separate in films and in powder, which appears highly crystalline in part, and which is combined with phosphorus. When the reaction is complete, the liquid is poured off from the precipitate, and the latter washed two or three times with water by decantation, then with some strong alcohol to remove the water, and lastly with carbon disulphide to remove excess or free phosphorus, which is not in combination and must be removed.

The above is a brief description of the method employed whereby the black phosphide of silver was prepared and carefully purified from any free phosphorus. I was greatly surprised when the above compound suddenly took fire spontaneously while drying on the filter in the cold upon the funnel. A second portion was prepared with the utmost care, and washed at last with carbon disulphide until some drops of the filtrate could be evaporated from paper without becoming luminous in the dark, proving that all free phosphorus had been removed from the compound. The second time, I again had the opportunity to behold my fugitive black substance undergoing combustion, leaving metallic silver behind. The case was evident: the new phosphide was a pyrophorus, and burned spontaneously when dry in the air or in contact with oxygen.

In order to preserve some of the new phosphide in the dry state for examination, it was introduced into a tube or small flask while yet moist, and closely stopped with a rubber stopper through which two small glass tubes passed, one for the purpose of passing into the flask a dry current of carbonic acid gas and the other as the exit tube.

The flask with the moist phosphide is then placed over a water bath heated to boiling, and a steady current of the dry gas passed over it, which soon dries by the moisture being carried off by the warm gas through the exit tube. If a much higher heat than that of a water bath be employed, say a direct application of the flame from a Bunsen's burner (melting point of tin), the whole of the compound will be decomposed, and silver remain behind, presenting a beautiful spongy appearance, while the phosphorus is carried off with the current of hot gas, which is decidedly luminous as it escapes into the air and oxidizes. If the compound is dried without too great an application of heat, and is afterwards poured out into the air upon a plate, it takes fire, and leaves metallic silver with a little phosphoric acid behind, which latter can be removed by washing with some warm water. It was with the greatest difficulty that the molecular formula of this phosphide of silver was determined; it seems to be Ag₂P. Its molecular weight is 139. The affinity of silver for the nitrogen-phosphorus group is very feeble, as this compound, among others, plainly shows.

The action of nitric acid on the black phosphide led to a series of highly interesting observations, whereby several new and definite phosphides were obtained. On adding nitric acid (concentrated) in the cold to some of the moist black phosphide, which is generally mixed with some metallic silver, chemical action is set up and red fumes are evolved, during which some of the compound is dissolved, with whatever metallic silver may be mixed with it. A precipitate remains behind, having a brick red color, which at first was supposed to be amorphous phosphorus, but proved upon examination to be another phosphide, having the composition: Ag₂P₂. Calculated: Silver, 69.90; phosphorus, 30.09; total, 99.99. Found: Silver, 69.44; phosphorus, 30.55; total, 99.99. This red compound is permanent in the air, and is much more stable than the first. It will be observed that, as the amount of silver increases, the stability of the silver phosphides becomes greater.

The red phosphide is soluble in concentrated boiling nitric acid, with perhaps the exception of a trace of a yellow compound which is undergoing investigation.

Other methods of operating were now employed. Instead of dissolving the nitrate of silver in water, it was acted upon

in the dry way by a solution of phosphorus in carbon disulphide. Plenty of the solvent should be employed for the phosphorus; in this case, at least twenty times the weight of the phosphorus was employed.

In preparing the phosphides by adding a solution of phosphorus upon powdered dry silver nitrate, if not sufficient carbon disulphide is employed, a violent decomposition may take place. Operating thus upon a large quantity with an insufficient amount of the solvent, the writer was painfully injured by a powerful explosion, which produced a report like a blast.

A red compound is the result, that is, the particles of the dry powdered nitrate are covered by a red coating.

On treating the red precipitate with water, after pouring off the carbon disulphide, the nitrate of silver, which still remained undecomposed, is dissolved, and the reddish substance disappears, leaving a flocculent black precipitate, which was found to have the formula Ag₂P. Calculated: Silver, 91.26; phosphorus, 8.73; total, 99.99. Found: Silver, 91.1; phosphorus, 8.8; total, 99.9. It is permanent in the air, unless highly heated.

It is curious to note the different results obtained by acting upon silver nitrate dissolved in water by means of the phosphorus solution, by changing the conditions: thus, by acting upon a concentrated silver solution in the cold without stirring, nearly pure silver separates in films which become quite thick, as, for example, in the following proportion: Silver nitrate, 4 grammes (61.7 grains); phosphorus, 0.9 gramme (13.8 grains); carbon disulphide, 10 cubic centimeters (0.61 cubic inch); water, 30 cubic centimeters (1.83 cubic inches).

By treating a very dilute solution of the nitrate, the silver completely separates into beautiful crystals, after the lapse of twenty-four hours. Silver nitrate, 1 gramme (15.43 grains); phosphorus, 0.2 gramme (3.08 grains); carbon disulphide, 5 cubic centimeters (0.305 cubic inch); water, 500 cubic centimeters (30.5 cubic inches). By this means very pretty crystals may be separated.

A New Cause of the Breakage of Railroad Rails.

Some interesting observations have recently been made on an Austrian railway line, which possibly may shed considerable light on the hitherto unexplained causes of the breakage of steel rails during cold weather. Cases have frequently occurred when such rails have been fractured, and yet the adjacent metal has presented no flaw to which the rupture could be traced.

The section of the Austrian road referred to is about eight miles in length, and is often blocked with snow. This obstacle is generally surmounted by strewing sand in front of the driving wheels of the locomotives and in putting on extra steam while running over the slippery section. The rails are of Bessemer and Martin steel, weighing about 62.8 lbs. to the yard. It was suggested that the sanding of the tracks caused them to heat, to be suddenly cooled again, however, by the low temperature of the air and by the falling snow. Besides the molecular construction of the metal being thus injured, there would be an extra amount of abrasion on the surface at the spots where stoppages occurred.

Examinations proved, says the *Ironmonger*, that these abraded portions varied in length from 2 to 9 English inches, $\frac{1}{2}$ to $\frac{3}{4}$ inch in depth, and extended over the whole breadth of the rail. A train, in passing over the depressions so caused, necessarily experiences a certain shock; and it is reasonable to suppose that the concussion thereby communicated to the rail will be most felt when the ground beneath is frozen hard, so that the natural elasticity of the rail has no room to play. In three instances, rails so worn snapped asunder suddenly at the abraded portion, although no flaw or defect in the metal could be detected. This led to the removal of all abraded rails from this section of the line, amounting to twenty-eight lengths of Martin steel rails, and ten lengths of Bessemer rails. No similar case of fracture is known to have occurred in the iron or puddled steel rails previously in use, although the amount of abrasion they underwent must have been at least as great. The inference is that the improved rails of Bessemer and other steels, their superior strength notwithstanding, are less capable of withstanding concussion than the older rails, and consequently whenever they are used increased vigilance is requisite to prevent accidents in the winter time.

Proposed Optical Barometer.

When a refracting prism is successively immersed in media of different refractive indices, the ultimate angular deviation of the ray will, as is well known, depend in each case on the relative indices of the glass and the medium surrounding it at the time of the experiment. And as the refractive index of atmospheric air varies with its density, the amount of deviation of the refracted ray will be a measure of the density of the air, that is, will give the means of ascertaining the reading of the barometer at the time.

If the ray of light were made to pass through a number of refracting and totally reflecting prisms, the deviation would be increased. If with these prisms a microscope were combined, the prisms might be used as a barometer. Or if the ray be received obliquely on a number of pieces of glass, having parallel faces and slightly separated from each other, although there would be no angular deviation, there would be horizontal displacement which would admit of being measured by a micrometer. How far such an application would be of practical value is certainly doubtful, as the effect of changes of temperature on the prism itself might interfere with the very limited range of the instrument. Or again, it is possible that easterly, westerly, or other currents—or perhaps differences in the hygrometric state of the atmosphere

* A part of this article formed the subject of a paper read before the New York Academy of Sciences (late Lyceum of Natural History), December 13, 1875.