

Preliminary experiments were made several years ago with some of the simpler acid chlorides, but the very imperfect absorption of the phosphine, and the formation of solid hydrogen phosphide seemed to make the attempts unpromising, and the subject was dropped for a time.

A year ago, with Charles E. Vanderkleed, the subject was taken up again, and dichlor-acetyl chloride selected as the acid chloride to experiment with first, since the reaction had been shown to take place with the chlorides of mono- and tri-chlor-acetic acids. The reaction proceeded satisfactorily, though slowly, and the originally liquid chloride gradually thickened to a thick, yellow, transparent mass, from which by solution in alcohol and precipitation by ether a fine crystalline powder was obtained, giving on analysis figures for phosphorus and chlorine corresponding to the phosphide expected, $\text{CHCl}_2\text{COPH}_2$.

This substance is extremely soluble in alcohol, insoluble in ether, chloroform, and petroleum ether, insoluble in but soon decomposed by water, especially on warming, with the formation of hydrogen phosphide (PH_3) and dichlor-acetic acid, judging by the odor. It is quite stable in dry air and chars without melting at about 200° centigrade. Its behavior is what might be expected from a comparison with the amides, especially its greater tendency to decompose with water, on account of the more weakly basic character of phosphine compared with ammonia.

Experiments are being now made by Miss Frances M. DeFrees on the preparation and properties of benzoyl phosphide, $\text{C}_6\text{H}_5\text{COPH}_2$, and a crystalline compound has been obtained, charring without melting, and showing similar solubilities and decompositions to those of the dichlor-acetyl phosphide.

ADSORPTION OF DISSOLVED SUBSTANCES.

P. N. EVANS.

The term "adsorption" is used for the attraction exerted by a solid surface on gases or dissolved substances. With regard to gases, the effects are familiar in the action of porous solids, such as charcoal, which seem to condense gases within the pores as if under considerable pressure; the action is a selective one, however, for in the case of charcoal some gases, ammonia for instance, are very much more affected than others. The numerous chemical reactions taking place in the presence of such porous

solids as platinum sponge may probably be attributed to this surface attraction.

That solids in contact with solutions concentrate the dissolved substances on their surfaces, has been assumed in many cases, and some very superficial quantitative experiments carried out. It is commonly accepted by analysts that the first portion of the solution passing through a filter should be rejected in volumetric work on account of a possible change in concentration due to the action of the filter, but little experimental work has been done to learn how general this effect is among solids and among solutions, and very little to ascertain the magnitude of the change produced. The results obtained by different observers are difficult to harmonize; most of the experimenters simply show that adsorption takes place between certain solids and certain solutions; a few attempt a quantitative examination but omit to report factors essential to the drawing of general conclusions; a very few investigate the influence of concentration—with more or less contradictory results. One claims that the adsorbed quantity, that is, the weight of the solute close to the solid surface in excess of that in the same volume of other parts of the solution, is not dependent on the concentration in the strict sense of Henry's Law, but that dilution always lowers the quantity of the dissolved substance in the solution more markedly than that of the adsorbed substance; another, that Henry's Law applies throughout approximately; still another ascribes the results to chemical union and not physical attraction.

About four years ago the writer, with Donald Davidson, carried out a series of experiments to learn how general the adsorbing action of solids on solutions might be, and the magnitude of the effect. The details of the experiments would be out of place here, and some factors now realized to be essential to their interpretation were not recorded, but briefly, the experiments showed the following facts:

Twentieth-normal tartaric acid showed a loss of nearly 12 per cent. by contact with filter paper; twentieth-normal potassium hydroxide about the same with filter paper; 2.6 per cent. sucrose solution with animal charcoal was reduced to 1.9 per cent.; fiftieth-normal acetic acid with silica gave over 5 per cent. loss; fiftieth-normal hydrochloric acid with silica 2.5 per cent. loss; fiftieth-normal hydrochloric acid with cotton cloth 4 per cent. loss; fiftieth-normal ammonia with cotton cloth about 15 per cent. loss. All of these experiments showed, then, a positive adsorption of from 2.5 to 15 per cent. of the dissolved substance. Several others, however,

showed no effect whatever; 2.5 per cent. sucrose with charcoal made from sugar, with lampblack, with sand; tartaric acid with cloth; tenth-normal sodium thiosulphate with silica.

Some experiments with sodium chloride and filter paper seemed to indicate negative adsorption, that is, the concentration of the solution was increased, possibly by adsorption of the solvent, and the same result has been reported in some cases by another observer, but in this instance it was found to be due to chlorides in the paper, none of the laboratory supply of filter paper being really free.

The weights of adsorbing substances and volumes of the solutions were unfortunately not recorded in these experiments.

The conclusion from this series of experiments is that while adsorption may be very marked in some cases, it is not shown by all solids and all solutions.

Later, experiments were carried out with Miss Frances DeFrees with a view to ascertaining the relation between adsorption and concentration. The adsorber selected was filter paper, and the dissolved substance copper sulphate. The same quantity of the solution was allowed to stand in contact with a fixed weight of paper in every case, and titrations were made with potassium cyanide solutions of suitable concentrations on this copper solution and the same solution not treated with paper. The figures obtained showed the interesting facts that above a certain concentration—about fifth-normal—no adsorption took place; that is, the concentration of the solution underwent no change by contact with the paper. As the concentration was decreased from this point the effect became more and more marked, the amount of copper removed by the paper increasing in absolute quantity up to about twelfth-normal and then decreasing with the concentration to about two-hundred-and-fiftieth-normal, farther than which it could not be followed. The decrease in concentration of 100 c. c. of this solution by contact with 5 grams of paper amounted to over 25 per cent.

To learn whether both parts of the copper sulphate were equally affected a number of determinations were made on the sulphuric acid and showed a very close agreement with the copper results, an evidence that the adsorption is of the non-ionized electrolyte and not of the ions independently.

As to the time required for the action to complete itself, the same results were obtained after a few minutes and after several days, showing that the equilibrium is very quickly established.

A similar series of experiments carried out with potassium chloride and filter paper gave analogous results, the adsorption, however, beginning at twentieth-normal, and only rising to something over 5 per cent. of that present at five-hundredth-normal concentration.

The work is being continued and promises further interesting results.

THE DETERMINATION OF MANGANESE IN IRON AND STEEL.

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The process proposed involves no new principle, but is a combination of several old methods.

REAGENTS.

Ferrous ammonium sulphate.—Dissolve 8.56 g. crystallized ferrous ammonium sulphate in water containing 40 cc. of dilute sulphuric acid (25 per cent.) and make up to one liter.

Potassium permanganate.—A standard solution of such strength that 1 cc. is equivalent to about 0.001 g. Fe. The manganese equivalent for the present method is found by multiplying the iron equivalent by $\frac{5.5}{112}$.

Sodium acetate.—Thirty grams of crystallized sodium acetate, 20 cc. of acetic acid (30 per cent.) and 170 cc. of water.

Bromine water.—A saturated solution.

PROCESS.

Dissolve 1.5 grams of the sample in 20 cc. of nitric acid (1.20) and 5 cc. of hydrochloric acid (1.12). Heat till dissolved, transfer to a 300 cc. flask, add a solution of sodium carbonate till nearly neutral and then zinc oxide slowly till the precipitate of ferric hydroxide forms. After two minutes add an excess of zinc oxide.

Make up the volume to 300 cc., mix by pouring back and forth into a dry beaker and filter through a dry filter. Take 200 cc. of the filtrate, add 20 cc. of the sodium acetate solution and 40 cc. of bromine water..