Fraction V.—Oxide red-brown. Absorption spectrum indicated very small quantities of neodymium and dysprosium.

It will be observed from the above fractionations that the rate of separation of the rare earths is vastly greater than practically all the methods given up to the present time. Lanthanum, cerium, praseodymium, neodymium are left at once in the mother liquor. Samarium, europium, and gadolinium are much less soluble than those previously mentioned, while they are more soluble than terbium, dysprosium and holmium. Erbium, thulium, yttrium, ytterbium, etc., collect in the least soluble portions.

Since the solubilities of these compounds are the reverse of the usual type, they may be used for the rapid purification of many of the rare earths. For instance, we can easily remove traces of neodymium from samarium by this means, as the samarium dimethyl phosphate separates before the neodymium compound.

It is necessary to state that there is some inconvenience when working with the salts of dimethyl phosphoric acid, since they undergo a very gradual decomposition. A gelatinous precipitate is formed, very slowly, in the case of the rare earths, which filters with difficulty.

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THE UTILIZATION OF DIFFUSION PROCESSES IN THE PREPARATION OF PURE SUBSTANCES.

BY JOHN JOHNSTON.

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The possibilities of utilizing diffusion processes in preparing certain substances in the form of relatively large crystals appear to be much less widely known than they deserve to be, in view of the simplicity of the procedure and the purity of the resultant product. This type of method is quite generally applicable; its use is especially advantageous in the formation, by precipitation, of sparingly soluble substances. Such substances, as ordinarily prepared, tend to separate out in very fine powder which, by reason of its large extent of surface, often contains much absorbed material, in which case they are extremely difficult to purify satisfactorily. By allowing the solutions to mix by the operation of diffusion we may ensure very slow precipitation, and in this way obtain large, well-developed crystals, which can easily be washed free from any adherent foreign material.

The size of grain of a precipitate *AD* (*e. g.*, $Ca(OH_2)$), formed by the interaction of solutions *AB* and *CD* (*e. g.*, $CaCl_2$ and NaOH), depends upon the virtual concentration in the mixed solution of the ions A^+ and D', relative to their concentrations in the solution which, under the conditions of experiment, is saturated with respect to *AD*. This was demonstrated directly by von Veimarn for precipitates of barium sulfate;[1]

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[1] P. P. von Veimarn, *Z. Chem. Ind. Kolloide*, **2**, 3.

and all available lines of evidence substantiate its general applicability. In other words, the fineness of grain is determined by the virtual and momentary degree of supersaturation of the substance *AD* in the mixed solution. Indeed, the truth of this is apparent from general principles, for a high degree of supersaturation is obviously most readily dispersed by the precipitation of a large number of particles, consequently by the formation of very fine particles. Moreover, growth of larger particles will occur only if the degree of virtual supersaturation is so low that the rate of deposition from the solution does not exceed a certain maximum characteristic of the particular crystal.

The formation of large particles of slightly soluble substances, therefore, is favored: (1) by causing the separation of the substance to proceed very slowly; (2) by so choosing the temperature and composition of the medium as to have the substance as soluble as possible. Moreover, the average size of grain of a precipitate is increased when it remains in contact with a medium in which it is soluble at all, because a solution saturated with respect to the larger grains is unsaturated with respect to the smaller.[1] Advantage can be taken of all of these favorable factors by making use of a process in which mixing of the reacting solutions is effected by diffusion.

Such diffusion methods were used many years ago by Daubrée and others of the French school, in their work on the artificial production of minerals. They generally placed the reacting solutions in two vessels connected by some sort of siphon—a glass tube or a wick; but this procedure has the disadvantage that precipitation takes place within the siphon and closes it up. It is much better to allow each of the solutions to diffuse separately into a large volume of liquid within which they come together slowly and react. The choice of liquid depends upon the solubility of the substance, being either a saturated solution of the substance (*AD*), or water alone, or a solution containing some foreign substance which increases the solubility of *AD* but at the same time does not separate out along with it as a solid double salt.

To carry out such a process the easiest way is to fill up with appropriate liquid a large vessel at opposite sides of which two small evaporating dishes[2]—one containing the solid *AB*, the other *CD*—are carefully placed; the whole is left in some place not exposed to violent temperature fluctuations, in order to eliminate the disturbing effects of convection. In this way, beautiful crystals of calcium hydroxide formed by interaction of calcium chloride with sodium hydroxide in a large desiccator (24 cm. di-

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[1] Just as small liquid drops are unstable in presence of larger drops, by reason of the greater vapor pressure of the former.

[2] It is advisable that the upper edge of these vessels be sensibly horizontal; otherwise, flow may take place over the lowest point of the rim.

ameter, capacity about 6 liters) in about 3 weeks at room temperature; the crystals thus formed being hexagonal prisms, with the base about 1 mm. thick and 2–3 mm. long.[1] Similar experiments carried out at 100° yielded fine crystals of barium sulfate,[2] 1–2 mm. long, which were, within the unavoidable error of the determination, free from the occluded material carried down by barium sulfate when it is precipitated in the ordinary way. In carrying out experiments of this kind at temperatures other than room temperature, it is a matter of considerable difficulty to prevent premature mixing by convection at the moment when the components are introduced. To surmount this difficulty, recourse may be had to the following modified procedure, illustrated in the figure, the principle of which is that the component solutions siphon very slowly into the medium:

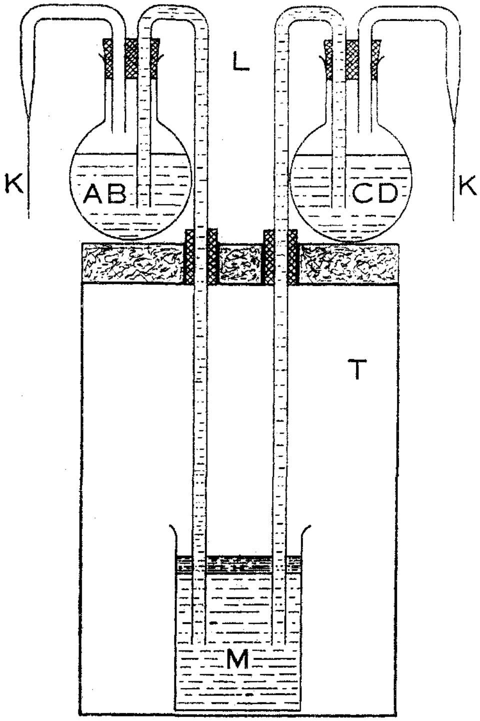

Diagram of arrangement for securing slow mixing at 100° of the component solutions (*AB* and *CD*). *T* is the steam bath; *M* the vessel containing the main mass of liquid, evaporation of which is prevented by a layer of paraffin wax. The rate of transfer of the solutions down through the siphons *L* is regulated by the entrance of air through the extremely fine capillary tubes *K*.

Into the main mass of liquid[3] dip two tubes, each of which serves as a siphon for the transfer of one of the component solutions; the latter are contained in stoppered flasks placed, if desirable, outside of the temperature bath. These siphon tubes are not constricted, because they choke up very soon if they are narrow enough to be effective for the purpose in hand; but a very slow transfer of each solution is secured by allowing air to enter each of the flasks only through a second tube which is drawn out to an exceedingly fine capillary. It is somewhat difficult to draw down two such capillaries so as to obtain equal rates of flow; this may be helped by adjusting the concentrations of the two solutions.

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[1] A crystallographic description of these crystals will be published elsewhere.

[2] J. Johnston and L. H. Adams, This Journal, 33, 834 (1911).

[3] Evaporation of this liquid is readily prevented by a floating layer of paraffin.

It may be remarked that, in spite of a long and varied series of diffusion experiments, we have been unable to prepare magnesium hydroxide in good crystals, presumably because the actual rate of diffusion was still not small enough in view of the limiting saturation of this substance. Similar attempts with silicates resulted in the separation of colloidal material only; this may be due to hydrolysis, or to the insolubility of the silicate, or to both of these factors. The only possibility of increasing the saturation limit in this case would seem to be increase of temperature; and it is very doubtful if this would avail much, since the indications are that silicates are still very sparingly soluble in water even at temperatures of 360° or higher. A few trials made at 200° in a small autoclave were unsuccessful; indeed the experimental difficulties in the way of securing sufficiently slow mixing at temperatures above 100° are very great, so that we abandoned attempts to prepare crystalline silicates in this way.

Nevertheless, it is probable that, by means of diffusion experiments as described above, one may prepare good crystals of many sparingly soluble substances, which otherwise cannot readily be obtained except as very fine powder, usually more or less contaminated with occluded material. The slowly formed crystals obtained in this way are practically free from impurity and hence constitute first-rate material with which to undertake physico-chemical determinations, such as measurements of solubility. The use of this type of material for such purposes would doubtless yield quite definite and reproducible results which would, with advantage, replace some of the present uncertain data.

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A NEW METHOD FOR THE PREPARATION OF COLLOIDAL FERRIC HYDROXIDE.

BY THEODORE COHEN.

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Many of the methods already in use for the preparation of soluble ferric hydroxide are based upon the hydrolysis of a ferric salt. The soluble ferric hydroxide thus formed is held intact without any appreciable evidence of the settling of the solid phase, after standing for some time. A typical reaction of this kind takes place when a molar ferric chloride solution is neutralized with a molar ammonium carbonate solution. If the liquid thus obtained is filtered and then dialyzed, ferric hydroxide will be obtained in the colloidal state, brought about through the hydrolysis of the ferric salt, according to the main reaction:[1]

$$FeCl_3 + 3HOH = Fe(OH)_3 + 3HCl.$$

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[1] A. A. Noyes, THIS JOURNAL, **27**, 94 (1905).