

Citation:

Lobry de Bruyn, C.A., The condition of substances insoluble in water formed in gelatine, in:
KNAW, Proceedings, 1, 1898-1899, Amsterdam, 1899, pp. 39-42

Chemistry. — *„The condition of substances insoluble in water formed in gelatine.”* — By prof. C. A. LOBRY DE BRUYN.

The condition of matter called the colloid, is in many respects a subject of interest. The physiologist, the physicist, the chemist take, each in his department, an interest in the peculiar qualities of the colloids. For to a great extent the processes of life take place in a colloidal medium or between colloids; the part taken by colloid bodies in osmose is generally known; every chemist knows a certain number of examples in which some substances appear in a colloid form, between liquid and solid-amorphous or as so-called colloidal solutions.

An important study on the qualities of colloidal mixtures or solutions, especially in a physico-chemical direction, we already owe for many years to Mr. VAN BEMMELEN. In these important experiments Mr. VAN BEMMELEN has studied, besides other qualities, quantitatively the changes taking place in a colloidal mixture prepared with water (a hydrogel) in varying the temperature or the relative humidity of the surrounding atmosphere.

The observations of which I beg leave to give a concise survey, do not refer in the first place to changes of a colloid mixture itself, but to the influence exercised by a hydrogel on the physical condition of amorphous, insoluble substances, created in a hydrogel as a medium. These observations are partly the result of former experience gained in the daily practice of the laboratory, as the non-appearance of precipitates if in a qualitative analysis, say on metals, there is an admixture of substances like gum; the non-precipitating of chromate of silver in a gelatine solution a. s. o. Such observations are in my opinion not indicated with sufficient accuracy by stating that the substances formed remain in suspension.

Experiences like those just mentioned were recalled to my memory by a communication of Dr. ERNST COHEN in a meeting of the „Amsterdamsch Genootschap.” Mr. GAEDICKE had asserted in a photographic journal that if equivalent quantities of AgNO_3 and KBr (somewhat more of the latter) are mixed in a gelatine solution of 5%, these two salts are only partially transformed, while this reaction is complete in aqueous solution in consequence of the excessively small solubility of AgBr . This assertion of GAEDICKE will appear strange to no one who performs this reaction; he will namely not see a precipitate of AgBr forming itself, but only a mild opalescence; while in aqueous solutions he will notice a strong troubling arising. GAEDICKE rested his assertion on the observation (proved to

be incorrect by Dr. COHEN) that when placing the mixed, solidified Ag Br-gelatine in water, there appeared in the latter Ag Br-flakes; he ascribed their formation to the diffusion of non-transformed K Br and Ag NO₃ from the gelatine into the water, where the reaction then takes place and the ordinary flaky Ag Br appears.

This opinion of GAEDICKE's seemed improbable to Dr. COHEN; and he has proved it to be incorrect by determining the conductivity of the gelatine solutions before and after mixing. The reasoning was simple; if the transformation is complete, the conductivity of the gelatine solution (tested in a liquid state at 30°) must be equal to that of K NO₃; if no reaction has taken place, the conductivity should be greater and reach the total of the conductivities of Ag NO₃ and K Br in ratio to the imperfectness of the transformation effected. The experiment decided in the former sense; the conductivity was equal to that of K NO₃ alone and the hardly visible transformation had yet completely taken place; the Ag Br is not dissociated into ions, does therefore not conduct.

So we have here before us some examples of phenomena that must strike the chemist; the apparent non-appearance of transformations and of precipitation when gelatine is present in cases in which a strong precipitation is observed in water alone. I have further extended these observations over a long series of reactions in which precipitation takes place. It has appeared then that what has been observed in different cases under peculiar circumstances for purely aqueous solutions viz. the interesting phenomenon that some bodies (silicic acid, titanitic acid, chrome- and ferrichydrate, arsenious-, antimony- and coppersulphide, silver, gold, selenium) can remain in colloidal solution, is a rule for solutions in aqueous gelatine. The colloidal medium keeps amorphous bodies which are created in it, colloiddally dissolved. This holds good for instance for the halogenous combinations of silver, the sulphides, and many hydrates of the heavy metals, for metallic silver, gold and mercury, for chromate of silver, Prussian blue, copper-ferrocyanide, iodide of lead, peroxyde of manganese a. s. o. They all give transparent gelatines which solidify on cooling, preserve their transparency, but often show an internal reflection or fluorescence. Especially for the coloured bodies, which I have cited here in the first place, the phenomenon is still remarkable in so far as, by the very appearance of the color one need not be in doubt about the question of the chemical change (as in the case of Ag Cl or Ag Br) and need therefore not convince oneself of its having taken place by determining the conductivity.

The modus operandi is nearly the same in all cases; deviations

in the concentration of some of the salt-solutions, required by the precipitation of the gelatine itself, betray themselves. I started with a 10 pCt. gelatine solution, which was filtered through a sievefunnel¹⁾ when warm. By adding to this the same quantity of the salt-solutions to be mixed (which were generally $\frac{1}{10}$ à $\frac{1}{20}$ normal) I got solutions containing 5 pCt. gelatine with the salt as $\frac{1}{20}$ or $\frac{1}{40}$ normal. These still liquid solutions (temp. $\pm 30^\circ$) were mixed under strong stirring and cooled quickly to the point of solidification. I then get a perfectly transparent gelatine, more or less opalescent according to the concentration and the thickness of the layer, which reflect a light internally and as it seems to me also show fluorescence. The formation of colloidal silver, which as we know, was first made by CAREY LEA in an aqueous solution, already takes place in gelatine with AgNO_3 alone, especially under the influence of light; it appears in a very concentrated form after the addition of some formaldehyde; it is then black-brown, still perfectly transparent in thin layers and homogenous with the strongest magnifying; only on the glass wall it deposits very slowly as a metallic layer.

Without investigating the different cases more particularly, I only wish to observe that I have not succeeded in keeping substances, that precipitate crystalline or at all events crystallize very quickly, colloiddally soluted in a medium of gelatine. Calcium oxalate, barium sulphate, ammonium- magnesium-phosphate and some other substances form in gelatine microscopically correct crystals or crystalline particles. In general it seems to me that from the many cases I have investigated, this conclusion may be drawn that the visible precipitation of amorphous bodies is prevented by gelatine, that of crystalline bodies not or not so easily.

Now the question is which is the degree of division of the substance, the size of the particles which are prevented by their origin in a colloidal surrounding to join to visible matter? It is here, in my opinion, not a phenomenon of suspension or emulsion; these terms are applied to microscopically visible particles; and therefore I have spoken of colloidal solutions in a colloid. The size of the particles is undoubtedly far beyond the limit of the microscopically visible and therefore embraces the vast field extending between the molecules themselves and the particles that are visible under the strongest magnifier. According to the nature of the substances and

¹⁾ The gelatine contains a little chlorine ($\pm 0.1\%$ H Cl) and some sulphuric acid. This must be taken into account in some reactions f. i. when forming Ag_2CrO_4 .

the *modus operandi* (concentration of the gelatine and of the salts) greatly different dimensions may be expected. PICTON and LINDNER who among others have proved the extremely small conductivity of the aqueous colloidal solution of arsenious sulphide, admit four different „grades” of division of this substance¹⁾. It will be found impossible however to make clearly defined distinctions in this respect, a gradual change in the size of the particles being much more probable.

The study of the phenomenon of the internal light-reflexion and fluorescence, that shows itself more or less distinctly in several substances formed in gelatine, may perhaps lead to further insight; these optical phenomena are also found in bodies as milky colored glass, that also contains invisible, extremely small particles. Others however of the colloid solutions in gelatine are not only perfectly transparent, but do not show any reflection of the light or fluorescence; it may therefore be admitted that the division of matter in gelatine approaches that of bodies soluted in water. In view of phenomena as those stated here, the idea of being soluted seems to lose its sharpness of outline.

Equally interesting are the chemical reactions, which are the effect of diffusion, on the substances formed in gelatine and in which one may be passed into the other. If a Na Cl-gelatine is surrounded by a Ag_2CrO_4 gelatine the Na Cl diffuses from the former gelatine into the latter, the colloidal Ag_2CrO_4 being not (or very little) diffusible, while it is known (f. i. by experiments of GRAHAM and HUGO DE VRIES) that the salts dissociated into ions diffuse as quickly in gelatine as in water. Now when the Na Cl ions penetrate in the bright red Ag_2CrO_4 the latter is converted into Ag Cl which, equally colloidal in solution, remains transparent and spreads in the form of a ring.

Astronomy. — *On the motion of the Pole of the Earth according to the observations of the years 1890—1896.* By Dr. E. F. VAN DE SANDE BAKHUYZEN. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN.)

1. In treating the meridian-observations made at Leiden in the last 20 years, it was necessary to arrive at a knowledge as exact as possible of the change in latitude during that period and, before investigating the Leiden observations in this respect, it seemed de-

¹⁾ Journ. Chem. Soc. **61**, 137, **67**, 63, **71**, 568.