

## **Nobel Prize in Chemistry 1925**



**Richard Adolf Zsigmondy**

The Nobel Prize in Chemistry 1925 was awarded to Richard Zsigmondy *"for his demonstration of the heterogenous nature of colloid solutions and for the methods he used, which have since become fundamental in modern colloid chemistry"*.

### **RESEARCH INFORMATION:**

Around the middle of the 19th century the English scientist Graham put forward a new principle of subdividing matter by classifying all substances into one of the two great classes: crystalloids and colloids. A crystalloid, e.g. common salt, is characterized in that it passes in the dissolved state readily through membranes such as parchment paper or collodion films and also that it exhibits a rapid free diffusion. A colloid, on the other hand, e.g. glue, is unable to pass through such membranes and diffuses extremely slowly, in contrast to the crystalloid. In passing it may be mentioned that the name colloid originates precisely from *κolla*, the Greek word for glue. Other examples of colloids well known to everyone are proteins, starch, rubber, water glass, etc.

It was very soon found that sometimes one and the same substance can occur in one case as a crystalloid and in another case as a colloid. For instance, gold with mercury produce a crystalloidal solution, whilst gold in an aqueous solution exists only in the

colloidal state. It is consequently more correct to differentiate between crystalloidal and colloidal *states* rather than between crystalloidal and colloidal *substances*. When it then became a question of forming an opinion of the reason for these different states, several people, e.g. the American scientist Lea, had recourse to the concept of allotropy which existed previously in chemistry, and was illustrated by the typical example of phosphorus with its two so-called allotropic modifications, the yellow and the red. Others again imagined the difference to be that the colloidal solutions were not uniform throughout, not homogeneous as the crystalloidal ones, but that they contained particles, molecule aggregates, of a size which exceeded by many times the size of the molecules in a crystalloidal solution. But which of the two interpretations was the correct one?

This difficult problem was brought a decisive step nearer to its solution by the invention of the *ultramicroscope* at the beginning of the 20th century. The idea originated from Zsigmondy and was developed in detail by him in cooperation with Siedentopf, an able optician with the firm of Zeiss. The principle of this instrument is briefly that the intensely illuminated object, the solution to be examined, is observed by means of a microscope from the side, i.e. vertically to the axis of the incident light beam. In this way it is possible to differentiate between particles of such small size that they could not be observed under an ordinary microscope, just as the dust particles suspended in the air in our rooms, which are invisible under ordinary conditions, sometimes become visible when the sun's rays shine through the window in a definite direction in relation to the observer. With the ultramicroscope, and especially the improved type which is called the immersion ultramicroscope, progress has been such that particles with a diameter of down to 8  $\mu$  are recognized with arc-light illumination, and down to 4  $\mu$  when using the sun as the light source.

Zsigmondy now found that various gold colloids prepared by him contained delimited particles under the ultramicroscope although they had appeared completely homogeneous under an ordinary microscope. He further showed by a systematic study of the gold colloids that they can be produced in a varying distribution of fineness, onwards

from colloids the particles of which are invisible even in the ultramicroscope, up to ones whose particles lie at the limit of visibility in the microscope. He showed that Lea's solutions of so-called allotropic silver are really built up from small, ultramicroscopic silver particles. He finally showed that the examination of other colloids also gave similar results. This proved the correctness of the particle hypothesis, and the heterogeneous nature of colloidal solutions was established. It has also been possible to determine quantitatively the size of the particles. The procedure is to delimit optically a small volume of the colloid to be examined, after which the number of particles in it is counted. If the mass concentration of the colloid is known, it is easy to obtain the mass of the particles, and from this - assuming, for example, a spherical shape and normal specific gravity - the size can be calculated.

As mentioned, there are colloids which are so fine-grained that their particles cannot be distinguished even in the ultramicroscope. However, Zsigmondy has made also these accessible to scientific observation by the invention of the so-called *nucleus method*. This was also first applied to gold, the classical metal of colloid research, and it is carried out by introducing the fine-grained gold colloid into a reducing solution from which metallic gold is slowly precipitated. This now settles on the invisible, colloidal gold particles so that they - the so-called gold nuclei - gradually increase in size, and finally become visible in the ultramicroscope. In this way gold particles with a diameter of down to  $1\frac{1}{2}$  have been measured, and it has become possible to determine the particle size - thus, the degree of heterogeneity - in the case of all gold colloids. It was possible to apply the method later to a large number of other metals, and it has proved to be of the greatest importance for a whole number of investigations which had the object of establishing general principles for colloids, indeed it may seem doubtful whether these investigations could have been at all possible without Zsigmondy's nucleus method.

It is a generally known fact that when a colloidal solution, for example one of protein, is treated with certain substances such as salts or acids - in short, electrolytes - it coagulates or "solidifies to a jelly", i.e. it passes into a semi-solid form or a so-called gel.

Corresponding, although not completely similar, conditions also arise in regard to colloidal metals, the reason being that the primary particles join together to form large aggregates, i.e. they increase in size whilst diminishing in number.

Zsigmondy's work has quite simply been pioneering as regards the explanation of the mechanism of the coagulation phenomenon and also as regards the study of the structure of gels. It has been found that coagulation progresses extremely slowly at a low concentration of the electrolyte, whilst with increasing concentration the rate of coagulation gradually increases up to a certain stage - at the so-called threshold value - when it rapidly reaches a limiting value which then no longer increases further or changes when the concentration is further increased. Within the rapid coagulation, as Zsigmondy found, the coagulation time is independent not only of the concentration of the electrolyte but also of its nature, whilst on the other hand, the threshold value and the rate within the range of slow coagulation are characteristic for each individual electrolyte.

Based on these facts, Zsigmondy expressed several important fundamental ideas for explaining the coagulation mechanism which were later formulated more accurately and developed to a mathematical theory of coagulation by Smoluchowski. In turn, Zsigmondy and his pupils have been able to verify experimentally this theory in its various details whereby its great general validity has been proved in a brilliant manner.

The brief review given here of some of the most important work of Zsigmondy is necessarily highly incomplete, if not to say fragmentary, but should surely suffice to show how it pioneered the way and opened up new regions in a field of research which had so far been difficult of access, a field which must be recognized as having the very greatest importance for human knowledge. Let us only remember in this connection that all manifestations of organic life are finally bound to the colloidal media of the protoplasm.

This by way of motivation for the decision of the Academy of Sciences to award the Chemistry Nobel Prize for 1925 to Dr. Richard Zsigmondy, Professor of Chemistry at the University of Göttingen, for proving the heterogeneous nature of colloidal solutions and for the methods used which have laid the foundation of modern colloid chemistry.

Professor Zsigmondy. When the Royal Swedish Academy of Sciences after mature consideration decided to award you the Nobel Prize in Chemistry for the year 1925, it did this in the firm conviction that it would only be making itself the executor of the unanimous verdict of the entire scientific world.

Convinced that the significance of your pioneering work which is generally recognized today, will in future times stand possibly in an even clearer light, the Academy allows itself to offer you its sincere congratulations on the well-deserved reward the external insignia of which you are now about to receive.

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