including that for x-ray crystallography, were effectively sabotaged as many times as they were passed. The experimental basis for the rapidly growing theoretical branch was becoming systematically narrower. Leading laboratories were forced to resort to the import of necessary equipment, while the rest had to work with either homemade instrument or with local low-serial industrial "monsters," in which, as one of the stoics put it, everything had to "burn down" before one could make any use of them.

In spite of the difficulties, the science of chemical crystallography in the country was making progress. About 10% of the world amount of solved structures, including a wide variety of different chemical compounds, was supplied by the research groups based in Moscow (where there were at least five or six major centers), Kishinev, Gorkii, Baku, Lvov, Novosibirsk, and other locations. The national conferences were held regularly. They were well attended and invariably brought out new names, along with recognized authorities.

In the eighties, the surge in the number of national publications related to the fields of crystal chemistry and x-ray crystallography produced a significant effect, among others, on the publishing portfolio of the Journal of Structural Chemistry [Zhurnal Strukturnoi Khimii]. In 1989, the relative number of contributions in these fields grew so much that several issues of the journal were completely dedicated to chemical crystallography.

As all living organisms that possess considerable reserve of life force and are prepared for sudden transformations and fasting diets of moderate duration, the unified science of crystallography in all the republics of the union remained on a decent level approximately until 1989. The European Crystallographic Meeting in Moscow gathered many local participants: about 350 from Moscow and vicinities; 30 to 40 from Kiev, Leningrad, Sverdlovsk, Kharkov, and Novosibirsk; 15 to 25 from Kishinev, Lvov, Donetsk, Minsk, Rostov-on-Don, Kazan, Krasnoyarsk, and Baku; 4 to 10 from Erevan, Gorkii, Irkutsk, Dnepropetrovsk, Tomsk, Ufa, Riga, Syktyvkar, Dushanbe, Tashkent, Petrozavodsk, Izhevsk, etc. Such a detailed account is needed as a historical evidence of functional capability of a small yet important part of the Great Power, before its sudden collapse.

Hopefully, the national science, including chemical crystallography, will not have to repeat the bitter path of the post-revolutionary years. One can also hope that the experience of veterans, who worked with x-ray diffraction for almost half of the celebrated anniversary period, will be taken up by new generations and used for future growth.

CENTENNIAL OF THE RÖNTGEN'S PAPER ON THE STRUCTURE OF WATER

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The Röntgen's paper is discussed in which he suggested, for the first time, the structural model of water with two different types of molecules. The evolution of this model throughout the past century is traced.

Wilhelm Konrad von Röntgen is widely known for his great discovery of radiation that was named after him (Röntgen rays or x rays). The discovery (made in 1895) was but culmination of his brilliant career in experimental physics. Among experimentalists, who even today are often too strongly attached to facts, he was an exception being open to bold hypotheses and generalizations. An excellent example of his scientific thinking was his paper in which he tried to explain anomalous properties of water. Today we celerate the centennial of his paper.

The paper entitled "The Structure of Liquid Water" was published in 1892 [1]. It is often referred to as one of the first papers in which a hypothesis on the structure of water was proposed (see, for example, [2], p. 154). The ideas set forth in this paper appear to be quite modern and are used even today, with corresponding modifications. The science of the water structure hence celebrates its centennial, and it seems timely to trace the logic of its first steps.

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Röntgen's paper has no introduction. It begins with the statement that the well-known property of water to have its smallest volume at 4°C is not the only water anomaly. Other lately discovered anomalous featues of its behavior that make water different from other liquids (ether, benzene, alcohol, etc.) include the following: 1) in the 0-50°C temperature interval, compressibility of water decreases when temperature is increased; 2) thermal-expansion coefficient increases when pressure is increased up to 3000 atm; 3) viscosity of water decreases when pressure is increased.

All those anomalous properties, as Röntgen believes, can be explained if one assumes that "liquid water consists of two types of molecules with different structures. Molecules of the first type, which we would like to call ice molecules since we are going to ascribe to them some properties of ice, undergo transformation into molecules of the second type when temperature is increased. Thus, we consider water at any temperature as a saturated solution of ice molecules whose concentration is higher when the temperature is lower."

Röntgen neither describes properties of the second-type molecules nor gives them any name. It is assumed though that the liquid composed of such molecules has the same properties as other liquids, with no anomalies. Assuming that transformation of the first-type molecules into molecules of the second type (I → II transformation) is accompanied by decrease in volume (as it happens when ice is melting), Röntgen provides explanation for the density minimum: at $T < 4°C$, mostly the I → II transformation takes place; at $T > 4°C$, normal thermal expansion is predominant. The remark made by Röntgen at this point is interesting: he says that this explanation is not new and that he is not aware of its origin. In the earlier models, though, the formation of ice molecules was considered to begin at 4°C, which was unnecessary and hardly probable.

To explain the pressure effects, Röntgen assumes that ice molecules become transformed into molecules of the second type when pressure increases. There are then two possible mechanisms for decrease in volume: natural contraction and the I → II transformation. The first is typical for normal liquids, and the effect is smaller at low temperatures than at high temperatures; the second has the opposite sign because the concentration of ice molecules is greater at low temperatures. These two mechanisms provide explanation for the compressibility minimum.

The anomaly in the thermal expansion coefficient is explained in a similar manner. To explain the anomalous viscosity, Röntgen assumes that internal friction in water is greater when concentration of ice molecules is greater. Here he predicts that at high pressures the viscosity of water will increase as pressure increases, resulting in the gradual disappearance of this anomaly, as well as others, with the increase in pressure. This prediction was later reliably confirmed (see [2]).

The Röntgen's paper hence describes for the first time and in quite a detail what is now known as the two-structure model of water. How then the Röntgen's ideas were modified in the following century? There are many different opinions about the meaning of the I and II type molecules. The latter are usually considered to be monomeric, whereas the former are believed to represent some kind of molecular association (or, in multi-structure models, a combination of such molecular associations). As to the properties of such molecules, there is, of course, no limit to imagination and concrete models. For example, in a rather recent work [3], a simple main idea about the equilibrium between several types of molecules in the same liquid was studied, but it became covered with so many elaborate details that the model lost its clarity and reliability.

A really new idea that was brought into the Röntgen's picture by the subsequent hundred years is that now we speak about equilibrium between two types of structures (or positional configurations of individual water molecules), rather than about equilibrium between two types of molecules. The structures may be given different names: dense and loose, ordered and disordered, tridymite-like and quartz-like, etc. With such interpretation, The Röntgen's idea remains valuable even today. Understanding that properties of liquids depend not only on properties of comprising molecules but also on their mutual positions is an important result brought by the developments of the past century.

In this paper, Röntgen uses no equations and stays within the limits of qualitative considerations. It would be a mistake to regard that as a shortcoming of the paper. On the contrary, the very fact that the paper is still not outdated shows that qualitative ideas and images, and not mathematical expressions, constitute the foundation of physical thinking.

This work of Röntgen is an example of the classical German style of thinking in physics, to which we owe so much.

It is not difficult though to convert Röntgen's ideas into formulas. For a derivative of any extensive variable A with respect to temperature (or pressure), we have

$$\frac{\partial A}{\partial T} = x_1 \frac{\partial A_1}{\partial T} + (1 - x_1) \frac{\partial A_2}{\partial T} + \Delta A \frac{\partial x_1}{\partial T}.$$

Here A_1 and A_2 are the partial molar magnitudes of variable A; x_1 is the molar fraction of molecules (or structures) of the first type; and $\Delta A = A_1 - A_2$. The first two terms represent the so-called static change of property A, and the last term is a relaxation contribution. The latter is caused by mutual transitions between two types of molecules resulting from changing temperature (or pressure), that is, from the changes in the structure of water. In [4, 5], one can find simple estimates of the relaxation term, as well as mathematical expressions of the above kind that practically repeat on a quantitative level Röntgen's qualitative considerations.

The incorporation of a relaxation term into the description of properties of water will always remain the most valuable fundamental contribution provided by Röntgen in his paper. In fact, this term remains valid for any model with two types of molecules (or structures), as well as for multi-structure models with greater number of types. Moreover, the relaxation term is present also in continual models of water where a continuous array of distorted hydrogen-bond configurations is postulated (as compared to optimal tetrahedral configurations). Distortion of the network of hydrogen bonds caused by the temperature, pressure, embedded impurity molecules, etc., is a significant part of the continual concept.

Although Röntgen's contribution to physics of water is highly appreciated, we don't want to say that his main idea about the two-structure model of water plays the leading role today. On the contrary, the continual concept proves to be more realistic. In this respect (and since we were talking here about the German tradition of thinking), it seems appropriate to mention the recent work of Franck [6]. Although for several decades he interpreted his remarkable results for vibrational spectra of water at high temperatures and high pressures from the point of view of the two-structure model, he finally came to the conclusion that for the structure of water the continual concept must be preferable.

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