

total scattering probability with allowance for pair production in arbitrarily possible states is equal to unity (as predicted by Feynman), i.e., the Klein paradox actually disappears when the field-theoretical approach is used.

¹N. P. Klepikov, *Zh. Eksp. Teor. Fiz.* 16, 19 (1954).

²T. Erber, *Rev. Mod. Phys.* 38, 626 (1966).

³A. I. Nikishov and V. I. Ritus, *Zh. Eksp. Teor. Fiz.* 46, 176 and 1768 (1964); 47, 1130 (1964); 52, 1707 (1967) [*Sov. Phys.-JETP* 19, 126 and 1191 (1964), 20, 757 (1965); 25, 1135 (1967)].

⁴N. B. Narozhnyi, A. I. Nikishov, and V. I. Ritus, *ibid* 47, 930 (1964) [20, 622 (1965)].

⁵V. I. Ritus, *ibid* 56, 986 (1969) [29, 532 (1969)].

⁶V. I. Ritus, *ibid* 57, 2176 (1969) [30, 1181 (1970)].

⁷A. I. Nikishov, *ibid* 57, 1210 (1969) [30, 660 (1970)].

⁸N. B. Narozhnyi and A. I. Nikishov, *Yad. Fiz.* (1970).

V. B. Deryagin. New Data on Superdense Water.

In the June 1968 session of the Division of General Physics and Astronomy I already reported on a modification of water, which we shall call for brevity water II, with composition H_2O but physical properties that differ significantly from those of ordinary water, namely, it is much more viscous, has a density 1.4, a refractive index 1.48, it is not volatile at room temperature, has a linear expansion in the interval -40 – $60^\circ C$, and goes over into vitreous form at $-40^\circ C$ because of the increased viscosity.

At the same time, the idea was advanced that the "anomalous" or "modified" water consists of polymer molecules $(H_2O)_n$. Since that time, research continued in our laboratory by the late M. V. Talanev, V. V. Krasev, Ya. I. Rabinovich, Z. M. Zorin, N. N. Zakhavaeva, G. V. Zheleznyi, and D. S. Lychnikov under the general direction of N. V. Churaev and myself.

The question was first raised of the possibility of explaining the properties of water II as being due to the presence of organic or inorganic impurities.

Measurements have shown that the surface tension of solutions of water II increases in water I by 2–3%, indicating that the anomalous component, water II, cannot be identified with any known organic compound. A spectrochemical analysis with laser excitation, carried out by Lippincott in the USA, revealed only traces of certain elements, incapable of explaining the sharp difference between water II and water I, in view of the extremely small concentration. For further identification and clarification the structure of the polymer complexes of water II, a number of microscopic methods of physico-chemical analysis were employed. The decrease of the vapor pressure of water I as a function of the concentration of the water II dissolved in it has made it possible to determine the (average) molecular weight: $M = 150 \pm 30$. This value coincides with the value of M obtained from the curve of the composition vs. temperature of the phase lamination of the binary mixture water I–water II at temperatures below zero. It should be noted that the value $M = 150$ is possibly somewhat too high, and furthermore represents an

average value if not all the polymer complexes of water II are the same.

This value of M is compatible with the assumption that water II exists when dissolved in water I mainly in the form of hexamers. Important conclusions were obtained by studying the thermal properties of water II. It was shown that below $700^\circ C$ water II is redistilled via a vapor-like state without noticeable decomposition and without loss of the "anomalous" properties. At higher temperatures, water II becomes depolymerized and is transformed into water I. An analogous transformation was observed by Lippincott on the basis of the IR spectrum. We have measured the saturated vapor density of "pure" water II as a function of the temperature (its boiling point lies near 450°), making it possible to determine the heat of evaporation, $L = 7$ kcal/mole. The low value of L is obviously due to the rather weak interaction of the polymer (hexamer?) complexes of water II with one another. It should be noted that there exists apparently a higher-molecular fraction of water II, which is not redistilled at $350^\circ C$, with a refractive index close to the initial value 1.48 and with other attributes of water II.

Recently, water II has been diligently investigated in England and especially in the USA, and all the basic experiments on the production of water II in water I by condensation of vapor of the latter in capillaries of quartz or pyrex have been reproduced. However, Pethica and co-workers obtained, as seen from the depression of the melting point, small amounts of a low-concentration solution, and it was impossible to observe the difference between its IR and NMR spectra and those of water I.

To the contrary, Bellami and Lippincott, using more concentrated solutions, observed differences in the Raman-scattering spectra.

Lippincott, Stromberg, Cessac, and Grant obtained (by evaporation), just as in our case, pure water II, the IR spectrum of which revealed two strong absorption lines at wave numbers 1595 and 1400 cm^{-1} . This IR spectrum differs strongly from the spectrum of any of the 100,000 compounds listed in the corresponding catalogue. These absorption bands have allowed the authors to assume that the polymer molecules of water II are connected by a symmetrical O–H–O bond with a binding energy of approximately 40 kcal.

This estimate agrees with our observations of the thermal stability of water II. However, Allen and Kollman, on the basis of quantum-mechanical calculations, obtained for the O–H–O bond the same distance $\sim 2.3\text{ \AA}$ between the O atoms as Lippincott, but a much lower binding energy.

The thermal stability of water II is attributed by them to the larger activation barrier required to break a six-element ring with O–H–O bonds.

As noted by the same authors, the discovery of water II becomes less surprising if it is recalled that, for example, acetaldehyde and carbon disulfide can exist also in a stable polymer modification ("black carbon disulfide").

It should be added that it was demonstrated in our laboratory that it is possible to obtain modified methyl alcohol, acetone, and acetic acid by vapor condensation, as was recently confirmed also by Lippincott.

Summarizing, one can state that there exists a new type of polymer and a new type of catalysis—condensation. Apparently, there exists also a hitherto unknown O-H-O bond.

Note added in proof. At the International Symposium on the Structure and Physical-Chemical Properties of Water, organized by the Italian Physical-Chemical Association (18-20 December), papers were delivered by B. V. Deryagin and by Lippincott (USA) on the investigation of water II (polymer or superdense). Lippincott has shown diapositives demonstrating on the basis of the electronic-sampling method, the distribution of the atoms of the possible impurities over a substrate on which water II was redistilled from a quartz capillary (the electronic-sampling method is based on recording the characteristic x-rays excited by an electron beam).

The distribution of the oxygen atoms showed distinctly the shape of a spot covered by polymerized water. To the contrary, the atoms of silicon, nitrogen, sulfur, calcium, etc. produced a weak and completely uniform background, from which it was impossible to guess the presence and the form of the layer of water II. Thus, it was clearly demonstrated that water II (with density 1.49) contains no impurities. It was also reported, that Soviet work on modification of other liquids (methyl and propyl alcohol, acetic acid, and also formic acid) has been confirmed, citing by way of an example the strongly altered IR spectrum of methyl alcohol. It was also reported that in the USA three theoretical groups, independently of one another, have performed a quantum-mechanical calculation of the symmetrical hydrogen bond between oxygen atoms, explaining, according to Lippincott, the polymerization of the water. The data on the energy and length of this bond were in agreement, indicating that this phenomenon has a quantum-chemical foundation. It was also reported that water II is being produced and investigated in a number of laboratories in the USA and in England.

The subsequent discussion at the symposium offered evidence of the full recognition of the reality of water II as a polymer formation.

¹B. V. Deryagin, N. N. Fedyakin, Dokl. Akad. Nauk SSSR 147, 403 (1962).

²B. V. Deryagin, M. V. Talaev, N. N. Fedyakin, *ibid* 165, 597 (1965). N. N. Fedyakin, Kolloid. zhur. 24, 497 (1962).

³N. N. Fedyakin, B. V. Deryagin, A. V. Novikov, and M. V. Talaev, Dokl. Akad. Nauk SSSR 165, 878 (1965).

⁴B. V. Deryagin, I. G. Ershova, B. V. Zheleznyĭ, and N. V. Churaev, *ibid* 170, 876 (1966).

⁵B. V. Deryagin, N. N. Fedyakin, and M. V. Talaev, J. Coll. Interfac. Sci. 24, 132 (1967).

⁶V. I. Anisimova, B. V. Deryagin, I. G. Ershova, D. S. Lychnikov, Ya. I. Rabinovich, V. Kh. Simonova, and N. V. Churaev, Zh. Fiz. Khimii 41, 2377 (1967).

⁷B. V. Deryagin, I. G. Ershova, B. V. Zheleznyĭ, N. V. Churaev, Dokl. Akad. Nauk SSSR 172, 1121 (1967).

⁸B. V. Deryagin, N. V. Churaev, N. N. Fedyakin, M. V. Talaev, and I. G. Ershova, Izv. AN SSSR, ser. khim. 10, 2178 (1967).

⁹B. V. Deryagin, Z. M. Zorin, and N. V. Churaev, Kolloid, zh. 30, 308 (1968).

¹⁰B. V. Deryagin, I. G. Ershova, V. Kh. Simonova, and N. V. Churaev, Zh. Teor. eksper. khim. 4, 527 (1968).

¹¹B. V. Deryagin, D. S. Luchnikov, K. M. Merzhanov, Ya. I. Rabinovich, and N. V. Churaev, Dokl. Akad. Nauk SSSR 181, 823 (1968) [Sov. Phys. Dokl. 13, 763 (1969)].

¹²B. V. Deryagin, N. V. Churaev, and I. G. Ershova, *ibid*. 182, 368 (1968).

¹³B. V. Deryagin, Z. M. Zorin and N. V. Churaev, *ibid*. 182, 811 (1968) [Sov. Phys.-Dokl. 13, 1030 (1969)].

¹⁴B. V. Deryagin and N. N. Fedyakin, *ibid*. 182, 1300 (1968) [13, 1053 (1969)].

¹⁵B. V. Deryagin, Z. M. Zorin, V. V. Karasev, V. D. Sobolev, E. N. Khromova, and N. V. Churaev, *ibid*. 187, 605 (1969).

¹⁶L. I. Bellami, A. R. Usborn, E. R. Lippincott, and A. R. Bandy, Chemistry and Industry, May 24, 1969.

¹⁷E. R. Lippincott, R. R. Stromberg, N. H. Grant, and G. L. Cessac, Science 164, 1482, 1969.

¹⁸L. C. Allen and P. A. Kollman, Science (in press).

¹⁹E. Willis, G. K. Renuil, C. Smart, and B. A. Pethica, Nature 222, 159 (1969).

²⁰G. Petsko, Nature (in press).

²¹M. L. Hair and W. Hertl, Nature (in press).

²²E. G. Butcher, M. Alsof, I. A. Weston, and H. A. Gebbie, Nature 199, 756 (1963) (black carbon disulfide).

²³B. V. Derjaguin, Pure and Appl. Chemistry (J. of the Intern. Union of Pure and Appl. Chem., London), 10, 975 (1965).

²⁴B. V. Derjaguin, Disc. Farad. Soc., No. 42 109 (1966).

Translated by J. G. Adashko