tion of a decay particle with the expected characteristics, it is necessary in principle to take at least 2×10^5 photographs without the accelerator beam, since the *a priori* estimate of the background from cosmic rays depends strongly on the details of location of the apparatus, which makes such an estimate practically impossible.

An advantage of experiments in the proton synchrotron at the High Energy Laboratory is the possibility of bombarding the chamber by heavy nuclei with an easily controlled energy. It is possible that an increase of density is easier to achieve if the target is bombarded by heavy nuclei.

An advance to shorter lifetimes is possible by construction of bubble chambers with a steeper rise of the expansion curve.

In principle it is possible to use streamer chambers and single crystals of AgCl, which may permit searches for decays of superdense nuclei to be accomplished over a wide range of lifetime.

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Temperature breaking of hydrogen bonds in water on negative-pion capture by hydrogen

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The probability W for capture of π^- mesons by hydrogen in water has been measured in the temperature range from -120 to $+440$°C. It is shown experimentally that in the transition from 0°C to the critical state the probability W rises by 100%, while at temperatures below zero and above the critical temperature up to 440°C, $W = \text{const}$. The data show that on formation of hydrogen bonds in water the electron density in the hydrogen atom decreases. These results are in good agreement with the model of breaking of hydrogen bonds in water on heating proposed by Haggis, Hasted, and Buchanan [J. Chem. Phys. **20**, 1452 (1952)].

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One of the most important properties of water is its capacity for formation of hydrogen bonds. The great interest in this type of chemical interaction is explained by its major role in physical, chemical, and particularly biological processes. Modern ideas regarding the nature of the hydrogen bond permit it to be discussed as a bond of the donor-acceptor type.[1]

The best studied system with hydrogen bonds is water.[2] It occupies one of the first places in the series of compounds in which the hydrogen bond is manifested most strongly.[2] For example, it is the existence of hydrogen bonds which explains the strange dependence of the density of water on temperature: at $p = 1$ atm the density of ice is less than the density of water, the density of water having a maximum at 4 °C. It is considered that hydrogen bonds O–H...O in water are broken on heating. According to the model of Bernal and Fowler,[3] and according to the data of x-ray structure analysis (see Ref. 2, page 311) and the work of Tödheide (Ref. 2, p. 463) water, when heated above 200 °C, loses the properties of an associated liquid. However, according to newer ideas, hydrogen bonds in water exist, although in a decreasing fraction of cases, up to the critical temperature 374.15 °C. In 1952 Haggis, Hasted, and Buchanan[4] (see also Ref. 2, p. 255) proposed a model of the temperature breaking of hydrogen bonds in water, by means of which it has been possible to explain the dependence of the static dielectric constant ε_s and the heat of evaporation L on temperature. According to this model, in ice there exist all possible hydrogen

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bonds of water, i.e., all hydrogen atoms achieve a hydrogen bond; in liquid water at 0 °C 9% of the hydrogen bonds are broken and the fraction of broken hydrogen bonds f_T increases with increasing temperature up to 100% at the critical temperature.

It is known that formation of a hydrogen bond brings about a change in the physical and chemical characteristics of the material (boiling point, heat of evaporation, infrared vibrational spectrum of the bonds, and so forth). However, it is not possible to deduce uniquely from these changes the nature of the change in electron density in the hydrogen atom, i.e., the change in the ionic nature of the O–H bond. Thus, Emsley *et al.*[5] conclude on the basis of NMR spectra that there is an increase in the electron density in the hydrogen atom on formation of an O–H...O hydrogen bond, while Glasel (Ref. 2, p. 216) established on the basis of NMR spectra a decrease of the electron density on formation of a hydrogen bond. Evidently the NMR chemical shifts may not be directly related to the electron environment of the proton. This can be seen from the fact that the chemical chifts in the series of isoelectronic molecules CH_4, NH_3, H_2O, and HF are approximately the same,[6] while the degree of ionic bonding in these molecules is different. In addition, in CH_4 there are not hydrogen bonds, but in NH_3, H_2O, and HF there are such bonds and their role increases with advance in this series.

Previously we established a correlation between the probability of capture of π^- mesons by chemically bound hydrogen and the physical and chemical quantities associated with the state of the electron shell of the hydrogen atom (dissociation constants,[7] induction constants[8]). It follows from the indicated experiments that we can deduce from the probability of capture of negatively charged pions by hydrogen in chemical compounds the change in the electron density in the hydrogen atom (see for example Ref. 9).

The present work was intended to determine the temperature dependence of the role of hydrogen bonds in water in the change of the probability for capture of π^- mesons by hydrogen in water. The measurements were made in an 80-MeV beam of π^- meson at the JINR synchrocyclotron. Capture of pions by hydrogen was identified on the basis of the nuclear charge-exchange reaction

$$\pi^- + p \rightarrow n + \underset{\substack{\downarrow \\ 2\gamma}}{\pi^0}. \qquad (1)$$

In the experiment we measured the counting rate of γ-ray pairs from reaction (1) as a function of the target temperature T. The measure of the change in capture probability W was

$$P_T = (W_T - W_{25})/W_{25}. \qquad (2)$$

The subscripts on the quantity W indicate the target temperature in °C.

In our first experiments[10] in measurements at 220 °C the water was placed in the pion beam in flat cuvettes of stainless steel. In the present experiments in study of water at temperatures above room temperature we used a high-pressure target consisting of three tubes of stainless steel ($h = 250$ mm, $R_{\text{int}} = 18$ mm, wall thickness 2 mm) placed closely against each other in a plane perpendicular to the beam. Heating of the target was accomplished by a flow of hot air. The temperature was monitored by copper-Constanton ($T \leqslant 385$ °C) or Chromel-Alumel ($T > 385$ °C) thermocouples and maintained constant with an accuracy ±(2–5)°C by means of a temperature regulator employing a contact millivoltmeter.

The remaining measurements were carried out at atomospheric pressure ($p = 1$ atm). The measurements with ice at temperature below zero (–10 and –120 °C) were carried out in a flat steel cuvette placed in a glass Dewar; at –120 ° this was over liquid nitrogen. Ice at 0 °C and water at 0 and 4 °C were measured in a glass Dewar; here the error in determination of the temperature was <0.1 °C.

The results of the measurements carried out with ice at temperatures –120, –10, and 0 °C and with water at temperatures 4, 25, 220, 300, 385, 410, and 440 °C are given in the table and in the figure. In the table we have also given the effective stopping thickness of the targets Δ in units of g/cm² of carbon, obtained by interpolation of the experimental data of Ref. 11, and the values of f_T from Ref. 4. The correctness of the procedure of determining the number of pion stoppings in targets of different stopping thickness was checked with targets of LiH whose thicknesses varied from 0.9 to 5.4 g/cm².

It can be seen from the table and the figure that the capture probability W does not depend on temperature for ice, increases with increasing temperature of water up to the critical temperature, and remains constant with further increase of temperature. No appreciable changes were observed at the ice-water phase transition and at 4 °C—the temperature corresponding to the maximum density. The only explanation of the obsreved effect can be the breaking of O–H...O hydrogen bonds on increase of the temperature. The effect cannot be explained either by ice-liquid and liquid-gas phase transitions or by variation of the density of the target material. In similar experiments with ethane (in which it is known that there are no hydrogen bonds) the gas-liquid transition and changes in density by 110 times did not affect the capture probability.[12]

According to the Haggis model[4] at a temperature T a hydrogen atom in a water molecule has a probability

TABLE I.

T, °C	Phase*	Δ, g/cm² carbon	P_T	$\langle P_T \rangle$	$W_T \cdot 10^3$	f_T[4]
–120	*I*	3.7	–0.09±0.05	–0.10±0.04	3.5±0.2	0
–10	»	4.0	–0.12±0.06			
0	»	5.4	–0.10±0.06			
0	*L*	6.2	–0.05±0.07	–0.04±0.05	3.7±0.3	0.09
4	»	6.2	–0.03±0.06			
25	»	1.7...6,2	0±0.03	0.00±0.03	3.9±0.1	0.11
220 [10]	»	1.4 and 3.8	0.16±0.03	0.15±0.03	4.5±0.2	0.38
220	»	3.0	0.13±0.04			
300	»	2.6	0.27±0.14	0.27±0.14	5.0±0.7	0.62
385	SC	0.9 and 1,1	0.83±0.07	0.81±0.05	7.1±0.3	1.00
410	»	0.9	0.78±0.10			
440	»	0.9	0.79±0.10			

*I—ice, L—liquid, SC—supercritical state.

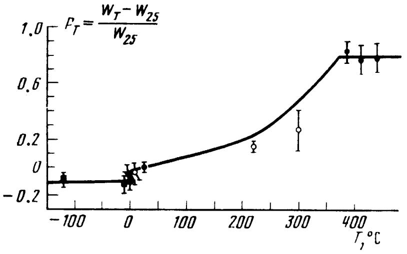

FIG. 1. Experimental values of P_T—the relative change of the probability W—with change of the temperature from 25 °C up to T: ■—ice, ○—liquid water, ●—supercritical state. The curve was obtained from Eq. (4) with $q = 2.0 \pm 0.1$.

f_T of being free of a hydrogen bond and a probability $1 - f_T$ of forming a hydrogen bond. On this assumption the probability of capture of pions at a temperature T can be written in the form

$$W_T = W_0 f_T + W_1 (1 - f_T), \tag{3}$$

where W_0 and W_1 are the probabilities of capture of pions by hydrogen atoms respectively free of and in a hydrogen bond. Combining Eqs. (2) and (3), we obtain

$$P_T = \frac{f_T - f_{25}}{f_{25} + (q-1)^{-1}}, \tag{4}$$

where $q = W_0/W_1$. According to the hypotheses of Haggis *et al.*, for ice $f_{T<0} = 0$, i.e., $W_1 = W_{T<0}$, and for supercritical water $f_{T>T_c} = 1$, i.e., $W_{T>T_c}$, so that we obtain for the parameter q

$$q = W_0/W_1 = 2.0 \pm 0.1. \tag{5}$$

As can be seen from the figure, the curve drawn on the basis of Eq. (4) with $q = 2.0 \pm 0.1$ is in good agreement with our data. Thus, hydrogen of "free" water molecules captures pions twice as effectively as the hydrogen of molecules associated as the result of hydrogen bonds. Our result is in qualitative agreement with quantum-mechanical calculations carried out in recent years.[13] According to these calculations, in a hydrogen atoms of water molecules entering into a hydrogen bond with a formation of the dimer $(H_2O)_2$, the decrease of the electron density amounts to $(0.03-0.04)e$.

As we have mentioned above, the conclusions regarding the direction of the redistribution of the electron density of the O–H bond, which occurs on formation of the hydrogen bond, are rather contradictory. The apparent explanation of this is that there are no adequate experimental methods for tracing the change of electron density in a hydrogen atom which is part of a complex molecule. The traditional methods have a low sensitivity to the electron density in the hydrogen atom, which comprises a small part of the electrons of a complex molecule. At the same time a pion is selectively sensitive only to that part of the electron density of a molecule which is associated with hydrogen atoms, which greatly increases the sensitivity of our method.

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