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Water as a Semiconductor

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1. ANALOGY BETWEEN SEMICONDUCTORS AND AQUEOUS SOLUTIONS OF ELECTROLYTES

Over 10 years ago, Reiss and Fuller[1,2] drew attention to the qualitative similarity between electronic semiconductors (such as germanium) and solutions of electrolytes, and suggested a chemical approach to a better understanding of physicochemical phenomena in semiconducting crystals. Later, this concept was successfully applied to the discussion of chemical equilibrium and of impurity and defect interactions in crystalline semiconductors[3,4].

The principle of this analogy is that both water and germanium provide a dielectric medium for the motion and the interaction of charged particles. Water has an electrical conductivity due to its dissociation into H^+ and OH^- ions, the product of the concentrations of these ions remaining constant at a given temperature:

$$[H^+] \cdot [OH^-] = K_w . \quad (1)$$

This relationship is the exact analogue of the expression for the product of the concentrations of holes and electrons in an intrinsic semiconductor:

$$n \cdot p = n_i^2 = K_i . \quad (2)$$

Since both K_w and K_i are equilibrium constants, depending only on the temperature, the dissociation enérgy at constant pressure can be calculated from the van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} . \quad (3)$$

This energy amounts to 13.5 kcal mole^{-1} or 0.59 eV per molecule for water, and to ~ 15.7 kcal mole^{-1} or 0.68 eV per bond for germanium. The ionisation energy of germanium or silicon atoms defines the width of the forbidden band in these semiconductors.

The phase transformations which water undergoes, and also other, more complex phenomena, set a limit to the validity of this analogy. In any case, ΔH^0 is slightly dependent on T, leading to departures from linearity. In the case of semiconductors the effect manifests itself as a temperature dependence of the width of the forbidden band.

Expressions (1) and (2) apply not only to the dissociation of the pure materials, but also in the presence of ionised impurities, when the concentrations of charge carriers of opposite signs are no longer equal. Addition of an acid to water raises the concentration of H^+ above the equilibrium value and at the same time lowers the concentration of OH^-, so that the value of K_w remains constant. The corresponding process in semiconductors is a decrease in the concentration of electrons following addition of an acceptor impurity (which raises the concentration of holes). Thus, the terms "n-type" and "p-type" conductivity become the analogues of the terms "basic" and "acidic". We note, in this connection, that the concept of the "Fermi level", of fundamental importance in semiconductor physics, is identical to the electrochemical potential or partial molar free energy of the electron gas per electron[5]. Hence, the height of the Fermi level in the forbidden gap becomes analogous to the pH of an aqueous solution. When the Fermi level is located in the upper half of the forbidden band the system corresponds to a "basic" solution, and when the Fermi level is in the lower half of the borbidden band it corresponds to an "acidic" solution. In this sense, neutralisation of an acid by a base or dissolution in water of the salt of a strong base (e.g. KCl) is analogous to the compensation of an acceptor by a donor impurity.

The ionisation energies of donors and acceptors in semiconductors are comparable to the ionisation energies of weak bases and weak acids.

It has been pointed out[4] that the entropy factor ΔS_i^0 can be negative for weak electrolytes, whereas no entropy change has been reported for current carriers in semiconductors. Nevertheless, the ionisation energies of many weak acids lie in the same range as the ionisation energies of many acceptors in germanium (0.01–0.1 eV).

For example, the ionisation energy (or heat of dissociation for the following equilibria can be determined by means of Eqn. (3):

$$B \rightleftarrows B^- + e^+ \text{ (in the silicon lattice)}$$
$$CH_3COOH \rightleftarrows CH_3COO^- + H^+ \text{ (in aqueous solution)} ,$$

The values obtained are, respectively,

$$\Delta H^0_{CH_3COOH} = 4000 \text{ cal} = 0.17 \text{ eV}$$
$$\Delta H^0_B = 100 \text{ cal} = 0.043 \text{ eV}$$
(at room temperature) .

The fraction of donors or acceptors which are ionised depends on the position of the Fermi level, just as the degree of ionisation of a weak base or a weak acid depends on the pH of the solution.

Multiply ionised solutes, and also amphoteric solutes, are found both in aqueous and in semiconductor solutions. The dissociation of zinc hydroxide can be taken as an example of an amphoteric electrolyte in aqueous solutions.

Zinc hydroxide dissociates as a base when the pH of the medium is low, and as an acid when present in solutions of high pH:[6]

$$Zn(OH)_2 \overset{\text{acidic medium}}{\rightleftharpoons} ZnOH^+ + OH^-$$
$$H_2ZnO_2 \overset{\text{alkaline medium}}{\rightleftharpoons} H^+ + HZnO_2^- .$$

In a similar way, atoms of gold, say, in germanium and in silicon ionise as acceptors or as donors depending on the position of the Fermi level[7,8].

Many other examples of the similarity between aqueous and semiconductor solutions can be given. The basic concepts of mobility, drift, and diffusion of charge carriers are applicable to electrolytes as well as to semiconductors, although large differences in the numerical values are often found. Thus, the mobility of the H^+ ion in water is approximately 10^6 times lower than the mobility of the electron in germanium. Some properties of germanium and of water are compared in the Table.

As Fuller points out, the analogy between electronic semiconductors and aqueous solutions of electrolytes breaks down when we consider that the ionised atoms of donor and acceptor impurities in semiconductor crystals are immobile, whereas the ions formed by the dissociation of acids and bases are freely mobile throughout the bulk of

the solution. Another difference is the fact that interstitial ions are absent in aqueous solutions[4] whereas they play a major role in the physics of semiconductor crystals.

However, the mobility difference of ionised impurities does not set an absolute limit to the analogy, bearing in mind the appreciable mobility of lithium ions in germanium and silicon at elevated temperatures. In many cases this

Comparison of related parameters in germanium and water*.

Germanium parameters	Germanium properties	Water parameters	Water properties
1. Charge carriers	Electrons, holes, mobile impurity ions (lithium)	1. Charge carriers	Proton, hydroxyl ion, mobile impurity ions
2. Concentration product of intrinsic charge carriers, at 25°C (atoms cm^{-3})^2	5.61×10^{26}	2. Ionic product of water at 25°C (ions cm^{-3})^2	3.6×10^{27}
3. Effective mass of the electron	Density-of-states mass $m_\alpha = 0.22$	3. Effective mass of the proton	1836
4. Mobility of charge carriers at 290°K, $cm^2\ V^{-1}\ s^{-1}$		4. Mobility of charge carriers at 293°K, $cm^2\ V^{-1}\ s^{-1}$	
electrons	3900 ± 100	protons	3.0×10^{-3}
holes	1900 ± 50	hydroxyl ions	1.7×10^{-3}
5. Ionisation energy of donors and acceptors (Groups III and V)	0.01–0.1 eV	5. Heat of dissociation of weak acids and bases	0.01–0.1 eV
6. Resistivity in the intrinsic region, ohm-cm, at 25°C	47	6. Resistivity of pure water, ohm-cm, at 25°C	20×10^6
7. Lifetime of non-equilibrium charge carriers, ms	2000	7. Lifetime of non-equilibrium ions, ms	6.6×10^{-6} 1.3×10^{-5}
8. Diffusion length of extrinsic charge carriers, cm	0.3	8. Diffusion length of extrinsic charge carriers, cm	2×10^{-8}

* This Table was assembled from published data [2,3,4,20,23].

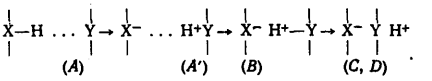
leads to the formation of donor–acceptor ion pairs, corresponding to the Debye–Hückel effect in electrolyte solutions. Furthermore, the acidic and basic residues in aqueous solutions can be spatially fixed in a high-polymer network, as is the case with the functional groups of ion-exchange resins and membranes[9].

2. THEORY OF PROTONIC SEMICONDUCTORS

The analogy between semiconductors and electrolyte solutions presented above is not a purely formal one. Studies of the physicochemical properties of water and of some other hydrogen-bonded substances have revealed that there are good reasons for classifying these materials as amorphous ionic semiconductors with a conductivity of the protonic type[10,11]. Shakhparonov[10,12,13] has introduced the concept of a protonic metallic bond, i.e. of a collective interaction between a proton gas and a system of negatively charged proton defects in whose field the proton gas is forced to move.

Shakhparonov bases his theory on a general proof that localised energy levels are converted into energy bands when charged particles interact in condensed systems[14].

His theory of protonic semiconductors offers a unified approach to the qualitative (and in many cases the quantitative) description of the basic features of dielectric polarisation and conductivity processes in water, alcohols, and many other substances with intermolecular hydrogen bonds. At the same time, the existing fund of experimental data on the temperature and frequency dependence of the dielectric constant can be used to refine the band structure model of protonic semiconductors. The energy spectrum of the states of a proton taking part in hydrogen bonding includes, in order of increasing energy, (a) a valence band, (b) an intermediate band in which states of the H_3O^+ type are formed, (c) levels associated with protonic excitons (exciprotons), (d) a conduction band. The energy band structure is shown schematically in Fig. 1. The change in energy state of a proton on being transferred from atom X to atom Y along the direction of the hydrogen bond (with simultaneous transfer from the valence to the conduction band) can be characterised by the following scheme



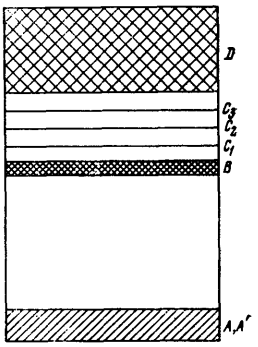


Figure 1. Energy level diagram for protonic semiconductors with intermolecular hydrogen bonds[13]:
A, A' valence band; B intermediate level; C_1, C_2 levels of proton excitons (exciprotons); D conduction band.

According to this scheme, both complex ions (such as H_3O^+) and free ions may be present in substances containing intermolecular hydrogen bonds. Transition from state A to state A' along the line of the hydrogen bond occurs by the tunnel effect with a frequency of the order of 10^{12}–10^{13} s^{-1}. The probabilities of finding a proton in states A and A' are approximately the same. Transition from A to B is accompanied by hydrogen bond breaking. There is evidence that this transition also can occur by the tunnel effect[15] provided the orientation of the molecules is favourable (i.e. when the donor atom is in direct contact with the acceptor atom). The contact may be broken (by thermal motion) at the instant when the proton is located on the acceptor atom, giving rise to the ions H_3O^+ and OH^- in water or ROH_2^+ and RO^- in alcohols, where R is a hydrocarbon radical. Unless the proton is immediately transferred from state B to state C after rupture of the intermolecular hydrogen bond, the ions HY^+ and X^- can readily recombine. Recombination can occur also by the tunnelling of a proton along the line of the intermolecular hydrogen bond. Hence, the lifetime of an H_3O^+ ion is only 10^{-13}–10^{-14} s. Transition from B to C, i.e. to any of the exciproton levels, leads to further expenditure of energy. The mutual repulsion of the protons in the H^+Y ion raises the energy of the proton. Therefore, the difference in potential energy of a proton in positions B and C may not be very large. This transition involves surmounting a potential

barrier whose free enthalpy of activation in the liquid phase usually amounts to 2–5 kcal mole^{-1} (i.e. 0.09–0.2 eV). Transition of a proton from C to D (i.e. to the conduction band) requires a small expenditure of energy of the order of $2kT$ and involves a change in the entropy of the system.

Upon entering the conduction band, protons acquire various properties not unlike the properties of electrons in electronic semiconductors. Protons and proton defects (the ions OH^-, RO^-, etc.) show an anomalously high mobility. The concentration of protons is an exponential function of $1/T$. Protons in the conduction band can be treated as a proton gas [16]. Hence there are grounds for assuming that some of the relationships derived in the band theory may apply also to protonic semiconductors. Since the mass of the proton is 1836 times that of the electron, the degeneracy condition [17] is not fulfilled in aqueous solutions:

$$kT_{deg} \simeq \frac{h^2}{8m^{(N)}} n_{deg}^{2/3} , \qquad (4)$$

where $m^{(N)}$ is the effective density-of-states mass of the charge carriers and n is their concentration. Hence, the proton gas in the conduction band is non-degenerate.

According to Shakhparonov [13], the methods of the band theory, developed for electronic semiconductors, can be used to a first approximation to treat the motion of protons and proton defects in the conduction band. The mobility of protons is found to be

$$\mu = \frac{e}{(m^*)^{1/2}} \left(\frac{m_0}{m_0 + m^*}\right)^{1/2} \frac{1}{2N_0 r_0^2 (2\pi kT)^{1/2} Y(\rho,T)} , \qquad (5)$$

where N_0 is the number of neutral molecules in 1 cm^3, m_0 and r_0 are the mass and the radius of the molecules, m^* is the effective mass of the protons, and $Y(\rho,T)$ is a semi-empirical Enskog function depending on the structure of the material as well as on the density ρ and the temperature T. Since the values of m^* and $Y(\rho,T)$ are not known, a quantitative test of the validity of Eqn. (5) cannot readily be made. However, it is possible to calculate the theoretical ratio of the mobility of hydrogen ions in water to that of deuterium ions in heavy water. The structure of D_2O is practically indistinguishable from the structure of H_2O. At the same temperature, the quantities N_0 and r_0 for H_2O and D_2O are identical. Assuming $m_D^*/m^* = 2$ and $Y_{D_2O} = Y_{H_2O}$ we obtain, from Eqn. (5), $\mu_H/\mu_D = 1.43$, which agrees exactly with the value found experimentally at 18°C.

3. SEMICONDUCTOR DEVICES BASED ON WATER

Various types of electrochemical transducers (or chemotrons) have been used successfully in technology for a number of years as rectifiers, stabilisers, logic cells, relays, d.c. and a.c. amplifiers, etc. [18]. The vast majority of these devices are not true analogues of semiconductor devices. However, many attempts have been made to realise devices of the diode or even the triode type using water as a semiconductor.

Fuller was the first to point out the analogy, in 1956, [2] between a p–n junction in a semiconductor and an electrochemical concentration cell. Fig. 2 shows a schematic comparison of the acid–base cell $H_2|HCl_{aq}|NaOH_{aq}|H_2$ with a semiconductor p–n junction. The ions H^+ and OH^- correspond to electrons and positive holes.

We had previously pointed out [9] that the junction between two ion-exchange membranes of opposite sign offers an even closer analogy to the junction between two semiconductors of opposite conductivity type, because the immobile, ionised, functional groups of the resin give rise to an electric field of the appropriate sign whilst the mobile ions of the electrolyte play the part of charge carriers (see Fig. 2). Independently, Bockris and coworkers [19] showed that the mobility of the counterions can be suppressed not only by using ion-exchange membranes with oppositely charged functional groups but also by separating aqueous solutions of high-molecular polyacids and polybases by a thin semipermeable membrane.

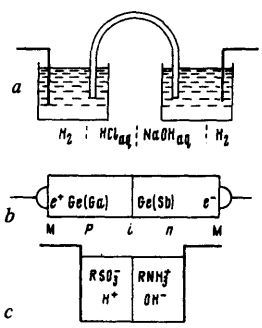


Figure 2. Analogy between (*a*) the acid–base concentration cell, (*b*) the p–n junction, and (*c*) the ion-exchange cell with membranes containing functional groups of opposite signs.

In either case, the application of an external electric field results in asymmetrical electrical conduction in the resin cell, i.e. in the rectification of electric current. Thus, when the cell is connected in the forward direction the mobile H^+ and OH^- ions move towards each other and recombine at the interface between the two membranes. In the blocking direction, the mobile charge carriers are drawn away from the interface, forming a region which is depleted of charge carriers and in which H^+ and OH^- ion pairs can arise only as a result of the termal dissociation of water—a relatively slow process.

A typical, static current–voltage characteristic for an ion-exchange resin rectifying cell, as published by many workers [19–21], is reproduced in Fig. 3. Its shape is reminiscent of a semiconductor diode characteristic, but it shows an additional hysteresis loop. This is ascribed to polarisation of the electrodes, the loop area being significantly decreased by the addition of depolarisers. The nature of the metal electrodes also plays a part [9]. Rectification coefficients do not usually exceed a value of 40. [9,21,22] The change in shape of a 50 Hz sine wave caused by the rectifying action of ion-exchange cells is illustrated in Fig. 4. A strong dependence of the rectification coefficient on frequency was noted in attempts to use cells of this type to rectify alternating current. Most authors [9,19] observed rectification up to frequencies not above 50–60 Hz, but Friedländer [22] reports an appreciable effect even at 6000 Hz. Seno and Yamabe [20] made a special study of this effect, and found that the rectification coefficient falls off rapidly above 1 Hz (Fig. 5), tending to zero above 1000 Hz.

According to the theory developed by Seno and Yamabe, the net current through the membrane cell is satisfactorily described by the expression

$$i = e\left(\frac{D_A n_A}{L_n} - \frac{D_m m_A}{L_m}\right)[\exp(eV/kT) - 1] , \qquad (6)$$

where the subscript n refers to protons and m to hydroxyl ions. L_n and D_n are the diffusion length and the diffusion

coefficient of protons in the region of the anionic resin, L_m and D_m are the corresponding quantities for hydroxyl ions; n_A and m_A are the concentrations of protons and hydroxyl ions in the anionic resin region.

Eqn. (6) is the analogue of Shockley's equation for a p–n junction in a semiconductor [23]. This suggests that the same rectification mechanism is operative in both systems,

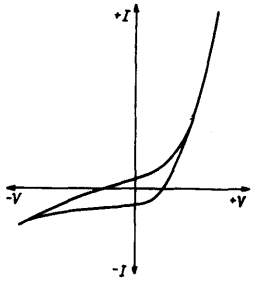


Figure 3. Typical current–voltage curve of an ion-exchange cell [21].

the cationic membrane corresponding to the n-type semiconductor and the anionic to the p-type. Thus, we conclude that a system in which the positive electrode is connected to the cationic exchange resin and the negative electrode is connected to the anion exchange resin will offer a higher resistance to direct current than a system of the opposite polarity.

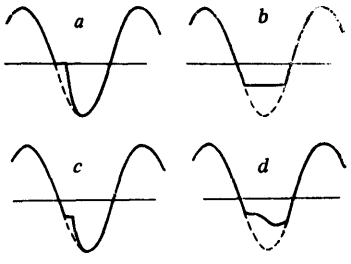


Figure 4. Change in shape of a current sine-wave at 50 Hz frequency resulting from rectification by ion-exchange cells [9]. *a*, *b*, *c*, and *d* are the characteristics of different ion-exchange cells.

Studies of the electrical characteristics of systems based on ion-exchange membranes of different polarities have not been confined to realising the simplest analogue of a semiconductor diode. Bockris and coworkers [19] obtained a rectification efficiency of 85% by connecting several membrane diodes in series.

Later workers [24] showed that the rectification efficiency for homogeneous membranes depends on the ratio of the concentration of fixed charges in the membrane to the concentration of ions in solution. The rectification effect shows a marked increase when this ratio is increased. In addition, the pore size has an important effect in the case of inhomogeneous membranes.

Lovreček and Kunst [25], in some later work on the membrane non-linear element, described an amplifier consisting of two cationic and two anionic membranes, shown diagrammatically in Fig. 6. A current I_i in the input circuit produces an excess current I_e in the main circuit:

$$I_e = I_m - (I_m^0 + I_i), \qquad (7)$$

where I_m is the effective current in the main circuit during the measurement period, I_m^0 is the effective current in the main circuit when this circuit alone is connected, and I_i is the effective current in the input circuit†.

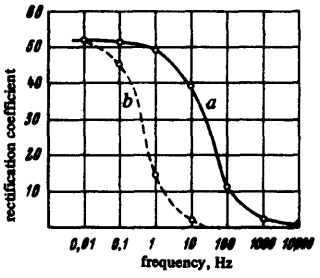


Figure 5. Frequency characteristic of an ion-exchange cell [20]: *a*) characteristic explored from reverse to forward current; *b*) from forward to reverse current.

The current amplification coefficient $P = I_e/I_i$, calculated as the ratio of the excess current to the current in the input circuit, can reach a value of 4. Current amplification is obtained because the current flowing in the input circuit produces injection of mobile ionic charge carriers in whichever diode is biassed in the blocking direction.

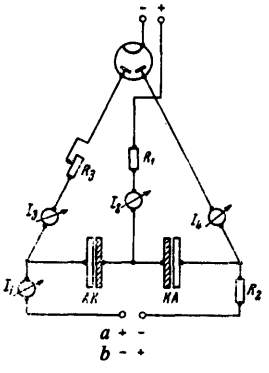


Figure 6. Circuit diagram of a current amplifier based on ion-exchange membranes [25,26].

As a result, the resistance of the diode drops and the current in the main circuit increases.

Lovreček and Kunst investigated also the variation of amplification with frequency and time [26], and they showed

† The currents I_m, I_m^0, and I_i are complex functions of the currents I_1, I_2, I_3, and I_4 shown in the circuit diagram of Fig.6.

that the amplification coefficient is decreased four or five-fold by changing the frequency from 50 to 2000 Hz.

In an attempt to carry the analogy between the membrane cell and the p-n junction a stage further, the Japanese workers Oshida and Yoshida [27,28] constructed a model of a photogalvanic cell. The cation exchange membrance in the H^+ form was saturated with the basic dye thionine in 5×10^{-5} M aqueous solution. The anion exchange membrane was immersed in a 5×10^{-3} M solution of ascorbic acid. (A mixture of thionine and ascorbic acid solutions is known to be bleached by the action of light.) Platinum gauze electrodes were pressed against the assembled membranes with Perspex plates. The cell was illuminated with a 150 W xenon lamp through a filter which absorbed infrared radiation. By measuring the electrical potential of the cell with and without illumination from the lamp, the growth and decay of a photo-e.m.f. was observed against the background of the gradually decreasing membrane potential of the cell. Photocurrents were very small (of the order of a few microamperes): this was ascribed, in particular, to the high internal resistance of the cell (3500 ohm). The power generated by the photogalvanic cell was 10^{-7} W.

4. PROSPECTS OF FURTHER WORK ON SEMICONDUCTOR DEVICES BASED ON WATER

The theory of protonic semiconductors is still in its initial stages of development. We still do not know how far the parallelism between the energy states of charge carriers in electronic semiconductors and in their protonic analogues may be taken. Theoretical studies, in depth, of the band model of protonic semiconductors are needed, because there must be substantial differences between the final expressions of the energy band theory for protonic and for electronic semiconductors respectively, despite the generality of the main starting premises.

The energy band model for protonic semiconductors considered here is only a first approximation. Thus, several intermediate levels or bands can be expected to arise in solutions containing several substances capable of forming hydrogen bonds [10].

Nothing appears to have been published on the band structure of aqueous solutions of electrolytes, which can obviously be considered as impurity protonic semiconductors in contrast to water—a protonic semiconductor with intrinsic conduction. The band theory of protonic semiconductors has not yet been developed to the stage where the parameters of devices based on these materials can be calculated and predicted theoretically.

Nevertheless, the results of the work reviewed here show unambiguously that the semiconductor properties of water can be exploited to realise analogues of a number of familiar devices—in particular, those relaying on the operation of p-n junctions. However, the low mobility of the charge carriers and the occurrence of electrochemical side-reactions at the electrodes introduce serious limitations on the frequency behaviour and other characteristics of devices based on ion-exchange membranes. As a result, these devices are hardly ever in a position to compete with their prototypes, based on electronic semiconductor materials. It should be noted that ion-exchange cells have also a number of favourable properties. For example, these cells can be used to construct models of processes occurring at p-n junctions [9], thanks to the simplicity of assembly and to the lack of critical requirements on size and geometrical shape. Radiation, also, is known to have very little effect on the dissociation and structure of water, and therefore ion-exchange devices can be expected to have a high radiation stability [2]. In principle, ion-exchange devices, like chemotrons, are capable of operation at elevated temperatures, of the order of 500°C and higher, if the electrolyte solutions are replaced by fused salts [18]. In contrast to electronic semiconductors, the difference in chemical nature of the charge carriers and the ability (in principle) to choose systems in which chemical interaction of the components produces both carrier recombination and carrier generation can lead to the realisation of new types of device quite unlike any of the devices based on electronic semiconductors.

We note also that the interest which has been shown in semiconductor devices based on water stems largely from the realisation of the outstanding role played by semiconducting membranes in the operation of the functions of nerve cells (neurons) [17]. Neurophysiological investigations have shown that the propagation of the nerve impulse and the transmission of the impulse from one axon to the next can probably be explained in terms of the rectification which occurs at junctions between cation and anion exchange membranes [21,29,30] present in the cell walls. It follows that the development and study of characteristic active elements based on water may prove to be a path to the realisation of logic cells of the neuristor type and of complex biological models of the "artificial brain" type.

Undoubtedly, the most interesting problem posed by the study and the practical application of the semiconductor properties of water, a problem straddling the boundary of physics, chemistry, semiconductor technology, and biology, will prove to be the object of intensive theoretical and experimental research in the next few years.

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