

Theory of Electrolytic Ionization

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Abstract

Original Research Article

Semiconductors and aqueous solutions of acids and bases exhibit several common properties and characteristics. First, both are solutions. Semiconductors of the p- and n-types are solid solutions of doping impurities in a pure semiconductor (Silicon, Germanium). Aqueous solutions of acids and bases are liquids but can easily become solids when frozen. Second, the dependences of the main charge carrier's concentrations on the dopants' concentrations for aqueous solutions of electrolytes and doped semiconductors are identical. For aqueous solutions, the dopants are acids (n-type) and bases (p-type), and for crystalline semiconductors, these are Phosphorus, Arsenic, Antimony (n-type), and Boron, Aluminum, Gallium (p-type). Third, the equations for determining the coordinates of singular points in the concentration dependence (equivalence points) for aqueous solutions and doped semiconductors are identical. Fourthly, the semiconductor effect of contact between a frozen acid solution and a frozen base solution is discovered. In this paper, we rethink all the results obtained and put forward a hypothesis about the nature of the electrical conductivity of electrolyte solutions.

Keywords: Electrolytic ionization, Electrolytic dissociation, acid-base diodes, electrolyte diodes.

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INTRODUCTION

We have carried out theoretical and experimental work, the purpose of which was to demonstrate that electrolyte solutions are similar in their electrical properties to doped semiconductors. We have derived the General Equation of State of electrolyte solutions "General equation of state of acid-base balance in solutions..." (Yefimov S, 2023)., we found the solution of this equation - a function and determined the coordinates of the singular points of this function "Finding Singular Points of the Titration Curve..." (Yefimov S, 2023). Then, the same theoretical work was done for crystalline semiconductors doped with donor and acceptor impurities "Derivation of the General Equation of State for a Doped Semiconductor..." (Yefimov S, 2024), and "Finding singular points of the concentration curve of doped semiconductors." (Yefimov S, 2024). It is shown that the equations and their solution coincide with liquid electrolytes and solid semiconductors. Thus, the identity of theoretical models of electrolyte solutions and doped crystalline semiconductors indicates their properties (semiconductors) should be identical. To support the theory with experimental data, we invented a device based on electrolyte solutions with one-way conductivity, the Ice diode. We prepared solutions of acid and base, froze them so that doped ice was formed,

and then tightly connected pieces of doped ice. Thus, a logical connection is established between the electrolyte solution and the doped solid crystal and between the two theoretical models of liquid and solid " Diode Made of Ice " (Yefimov S, 2025).

MATERIALS AND METHODS

The paper compares equations derived for aqueous solutions of electrolytes (Yefimov S, 2023, 2024) with equations derived for doped semiconductors (Yefimov S, 2024). Experiments confirming the semiconductor properties of the contact of acid-doped ice and base- doped ice are described in the paper (Yefimov S, 2025), and in the application for an invention (Yefimov S, 2024). In this work we do not present new experimental data, here we focus on comparing, analyzing, and combining our and known data into one system.

RESULTS AND DISCUSSION

Let us compare the equation of state (Yefimov S, 2023) derived for aqueous solutions of acids (A) and bases (B) with the equation (Yefimov S, 2024) derived for Germanium doped with donor (D) and acceptor (A) impurities (Table 1). As can be seen, the equations are identical up to the designation of variables.

Table 1: Polynomial coefficients of the General Equation of State. The semiconductor (Germanium) is doped with a weak donor and a fully ionizing (strong) acceptor. The water is doped with a weak acid and a strong base (Yefimov S, 2023), (Yefimov S, 2024)

Max. degree.	Water. Diprotic acid. (AH ₂) $h^4 + a \cdot h^3 + b \cdot h^2 + c \cdot h + d = 0$	Germanium. Two-stage ionizing donor. $n^4 + a \cdot n^3 + b \cdot n^2 + c \cdot n + d = 0$
4	1	1
3	B + K ₁ + K ₂	A + K ₁ + K ₂
2	B*(K ₁ + K ₂) + K ₁ *K ₂ - W - A*K ₁	A*(K ₁ + K ₂) + K ₁ *K ₂ - Ge - D*K ₁
1	B*K ₁ *K ₂ - W*(K ₁ + K ₂) - 2*A*K ₁ *K ₂	A*K ₁ *K ₂ - S*(K ₁ + K ₂) - 2*D*K ₁ *K ₂
0 (const.)	-W*K ₁ *K ₂	-Ge*K ₁ *K ₂

Solving the equation of state, i.e. finding the root of the polynomial, gives us a functional dependence of the charge carrier concentration on the amount of added dopant. Fig.1 a, b shows these dependencies for an

aqueous solution (Yefimov S, 2023) and for doped Germanium (Yefimov S, 2024). The nature of the dependencies is the same, in both cases these are 2-step, monotonically increasing, continuous functions.

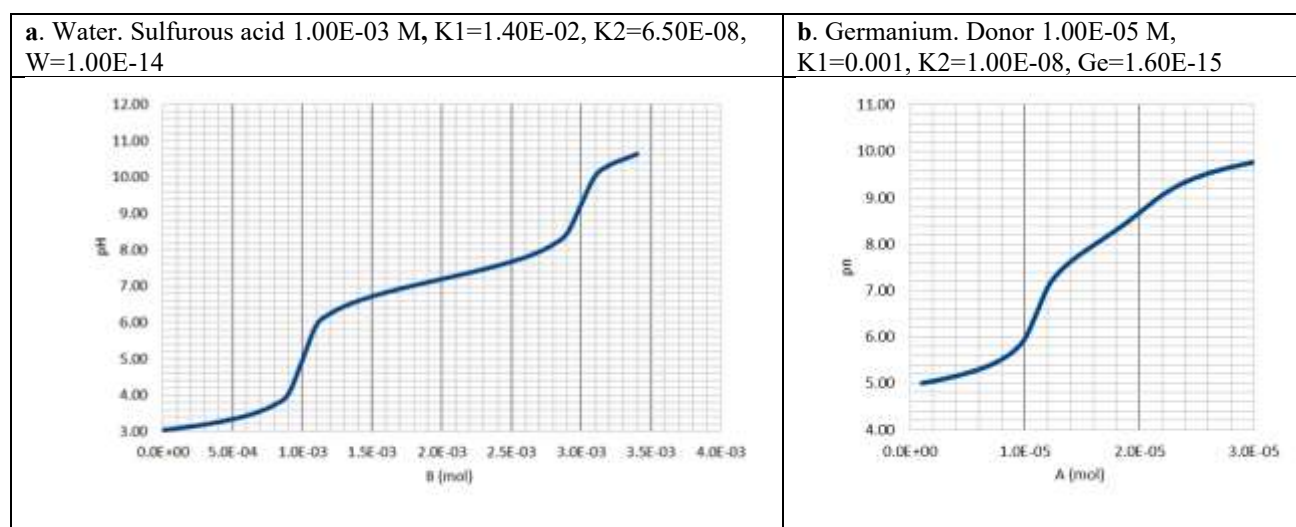


Figure 1: a, b. Roots of polynomials (Table 1) as functions of variables and parameters. 1 a. - titration curve of acid by base. 1 b. - electron concentration as a function of added acceptor

The equation of state can be represented as an inverse function - the dependence of the dopant concentration on the charge carrier concentration (Table 2). This representation allows one to determine the coordinates of the special points (inflection points) of the curves by the double differentiation method (Yefimov S, 2024). The coordinates of the inflection points of the titration curve, shown in Figure 1a, are the coordinates

of the equivalence points and the local maximum buffer capacity of the solution. They have a similar meaning for doped semiconductors. We draw attention to the fact that both the inverse functions (Table 2, middle row) and their second derivatives (Table 2, bottom row) are identical for electrolyte solutions and doped semiconductors up to the designation of variables.

Table 2: Representation of the General Equation of State as an inverse function and the second derivative of this inverse function (bottom row), (Yefimov S, 2023), (Yefimov S, 2024)

a. Water. Sulfurous acid 1.00E-03 M, K₁=1.40E-02, K₂=6.50E-08, W=1.00E-14	b. Germanium. Donor 1.00E-05 M, K₁=0.001, K₂=1.00E-07, Ge=1.60E-15
$B = (-h^4 - h^3 \cdot K_1 - h^2 \cdot K_2 - h \cdot (K_1 \cdot K_2 - W - A \cdot K_1) + h^2 \cdot ((K_1 + K_2) \cdot W + 2 \cdot A \cdot K_1 \cdot K_2) + W \cdot K_1 \cdot K_2) / (h^3 + h^2 \cdot (K_1 + K_2) + h \cdot K_1 \cdot K_2)$	$A = (-n^4 - n^3 \cdot K_1 - n^2 \cdot K_2 - n \cdot (K_1 \cdot K_2 - S - K_1 \cdot D) + n^2 \cdot ((K_1 + K_2) \cdot Ge + 2 \cdot D \cdot K_1 \cdot K_2) + Ge \cdot K_1 \cdot K_2) / (n^3 + n^2 \cdot (K_1 + K_2) + n \cdot K_1 \cdot K_2)$
$B'' / \&^2 = (-16 \cdot h^4 - 9 \cdot h^3 \cdot (K_1 + K_2) - 4 \cdot h^2 \cdot (K_1 \cdot K_2 - W - A \cdot K_1) + h \cdot (W \cdot K_1 \cdot K_2 + 2 \cdot A \cdot K_1 \cdot K_2) + B' / \& \cdot (6 \cdot h^3 + 4 \cdot h^2 \cdot (K_1 + K_2) + 2 \cdot h \cdot K_1 \cdot K_2) - B \cdot (9 \cdot h^3 + 4 \cdot h^2 \cdot (K_1 + K_2) + h \cdot K_1 \cdot K_2)) / (h^3 + h^2 \cdot (K_1 + K_2) + h \cdot K_1 \cdot K_2)$	$A'' / \&^2 = (-16 \cdot n^4 - 9 \cdot n^3 \cdot (K_1 + K_2) - 4 \cdot n^2 \cdot (K_1 \cdot K_2 - Ge - D \cdot K_1) + n \cdot (Ge \cdot K_1 \cdot K_2 + 2 \cdot D \cdot K_1 \cdot K_2) + A' / \& \cdot (6 \cdot n^3 + 4 \cdot n^2 \cdot (K_1 + K_2) + 2 \cdot n \cdot K_1 \cdot K_2) - A \cdot (9 \cdot n^3 + 4 \cdot n^2 \cdot (K_1 + K_2) + n \cdot K_1 \cdot K_2)) / (n^3 + n^2 \cdot (K_1 + K_2) + n \cdot K_1 \cdot K_2)$

Figure 2 a, b shows the graphs of the dependence of the second derivatives on the concentration of charge carriers on a logarithmic scale. The coordinates of the intersection of the curve with the

abscissa axis are the coordinates of the inflection points. It is obvious that the nature of curves 2a and 2b is generally the same.

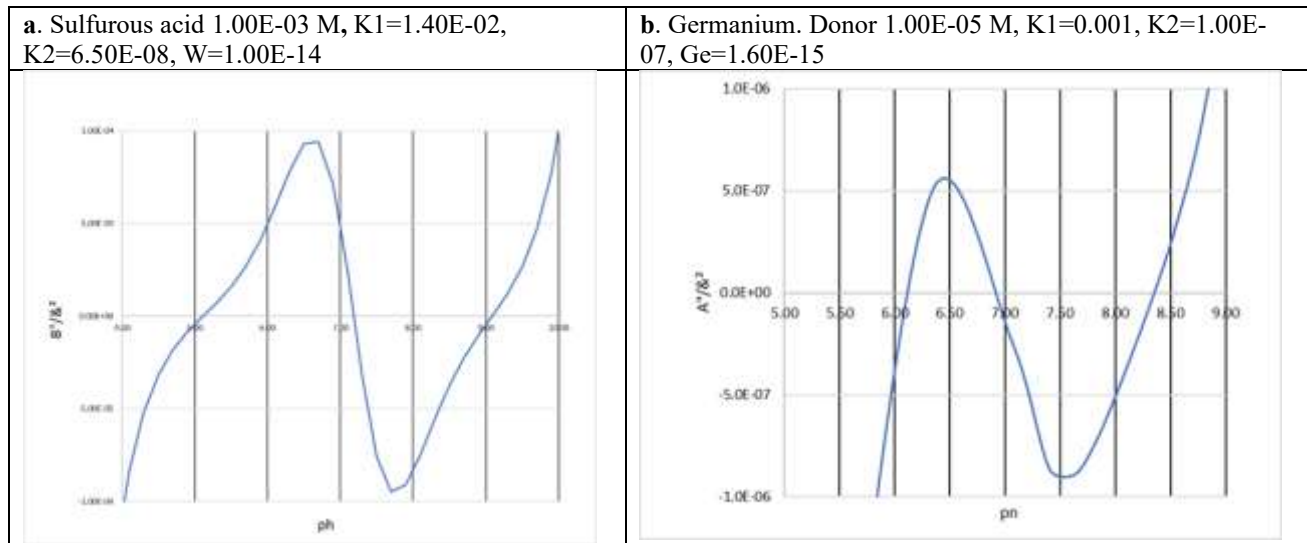


Figure 2: a, b. Graph of the dependence of the second derivative on the charge carrier concentration (logarithmic scale)

The experiment with freezing of aqueous solutions confirms the commonality of solid doped semiconductors and aqueous solutions of acids and bases. In both cases we are dealing with doped crystals, and in both cases, we observe the semiconductor effect (Yefimov S, 2025). Table 3 presents the results of measuring the voltage drop across the contact of two pieces of ice, one of which is doped with acid and the other with a base. The measurements were carried out on a multimeter in the diode testing mode. The data indicate

that the conductivity in the base $\rightarrow$ acid direction is significantly higher than in the opposite direction. Figure 3 helps to interpret the measurement data. When the voltage is applied to the contacts as in Figure 3a, the diode is closed, and when the polarity is opposite (3b), the diode is open. Based on this, we conclude that the acid is an n-type dopant, and the base is a p-type dopant of the ice semiconductor. The n-p junction is created in the contact.

Table 3: In the diode test mode, the doping concentration in the ice is 0.1 M, temperature 0°C. The voltage drop on the diode was measured (Yefimov S, 2025)

Diode Test (mV) 0.1 M, 0°C			
#	Acid (+)	Acid (-)	ΔmV
1	1198.00	625.00	573.00
2	1211.00	612.00	599.00
3	1200.30	601.10	599.20
average	1203.10	612.70	590.40
Standard error	16.02	27.63	34.80

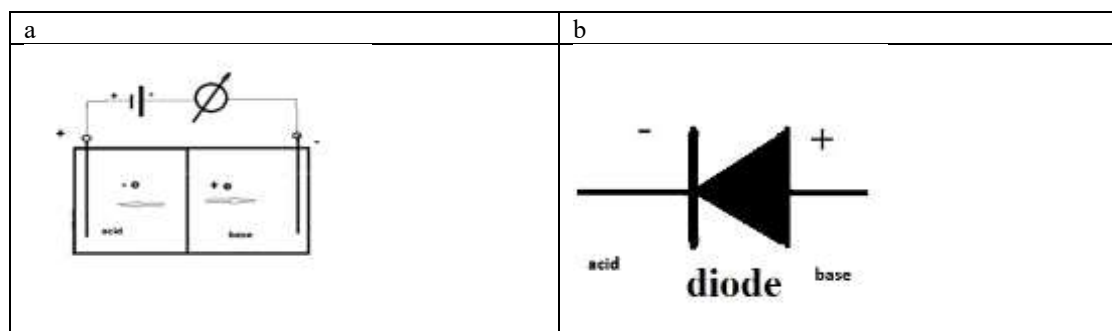
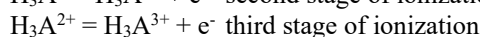
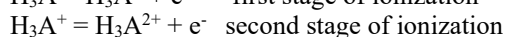
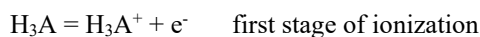
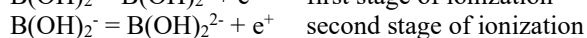
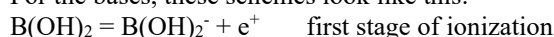


Figure 3: a, b. In Figure 3a, “-e” are the main carriers of electric charge in acid-doped ice, “+e” are the main carriers of electric charge in base-doped ice. At a given polarity of the applied electric potential, the diode is “closed”. The diode is “open” when the polarity is reversed, Figure 3b (Yefimov S, 2025)

The identity of theoretical models and the semiconductor properties of crystalline semiconductors and aqueous solutions indicate the possibility of combining the two models. Such a combination would be convenient. As a general model, one should choose a model suitable for crystalline semiconductors, and it is the only possible option. The model for aqueous solutions of electrolytes is modified as follows: The expression "electrolytic dissociation" is replaced by "electrolytic ionization". Corresponding ionization schemes replace dissociation schemes. So, for tri-protonic acids, these schemes look like this:



For the bases, these schemes look like this:



The acid and base ionization constants (K_a , K_b) look like this:

$$K_a^1 = \frac{[H_3A^+] \times [e^-]}{[H_3A - H_3A^+]}$$

where e^- (electron); H_3A (donor, acid); H_3A^+ (ionized donor)

$$K_b^1 = \frac{[B(OH)_2^-] \times [e^+]}{[B(OH)_2 - B(OH)_2^-]}$$

where e^+ (hole); $B(OH)_2$ (acceptor, base); $B(OH)_2^-$ (ionized acceptor).

The numerical values of the ionization constant are equal to the known dissociation constants of acids and bases, which follows from the method of their determination (Determination of dissociation constants. 2025). Considering the definitions and notations made, we can reduce two parallel systems of equations for acids and bases in water and doped semiconductors to one system of equations, namely, to the system of equations derived for doped semiconductors (Yefimov S, 2024). The Electrolytic Ionization Hypothesis and the Arrhenius' Electrolytic Dissociation Hypothesis are two formal descriptions of the same natural phenomenon - an increase in the number of particles during the dissolution of an electrolyte, where particles are molecules, atoms, ions, electrons, and holes. Both hypotheses are equally indirectly confirmed by the electrical conductivity of solutions, an increase in osmotic pressure, a decrease in the freezing point, and an increase in the boiling point. The advantage of the Electrolytic Ionization model over the Electrolytic Dissociation model is that the former is suitable for both solid and liquid solutions, while the latter is only suitable for liquid solutions. Regardless of which model we prefer, Faraday's law for electrolysis is valid for both models.

CONCLUSION

The theory of electrolytic ionization of electrolyte solutions presented here allows us to look at the behavior of electrolytes in solutions from a different angle. This model facilitates the description of the ice diode phenomenon and unites doped semiconductors and electrolyte solutions with one mathematical model.

Abbreviations

- A- Acid in solution
- A- Acceptor in solid semiconductor
- B- Base in solution
- D- Donor in solid semiconductor
- h- hydroxide ion in solution
- n- negative charged carrier (electron) in solid semiconductor
- K1, K2- dissociation/ionization constants
- W- ionization constant of water
- Ge- ionization constant of Germanium
- e^- - electron
- e^+ - hole

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