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Abstract

Full Text

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PHYSICS

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SOME FEATURES OF THE ELECTRICAL BREAKDOWN OF ELECTROLYTES

(Presented by Academician M. A. Leontovich, 16 V 1962)

An extensive literature is devoted to the study of the breakdown of liquid dielectrics. In all known cases the liquid (imperfect) "dielectric" had, at least for the most part, electrolytic conductivity and not electronic conductivity (although this is disputed by some authors (^1)). Therefore these studies concern the breakdown of electrolytes, not ideal dielectrics. True, the greatest attention has been attracted by examples of strongly diluted electrolytes, for example, *n*-hexane or transformer oil (^{1}-4), which have very low conductivity. Some works, however, including those of narrowly applied significance (^5), are devoted to the breakdown of water, which has appreciable electrical conductivity (^6). Only two brief notes of limited content (^7, ^8) are devoted to the breakdown of concentrated electrolytes; in (^9) only a few words are allotted to this question. There is a detailed literature, for example (^10), on the "breakdown" of metallic conductors, namely the burning-through of wires by strong pulses of electric current.

Fig. 1. Schematic circuit diagram of the setup

In order to fill this gap, a survey investigation was carried out over a wide range of substances and concentrations, adjoining in content the article (^11). A constant voltage from a transformer-rectifier installation (Fig. 1) is applied through a ballast resistance to the main capacitor C, with a capacitance of $0.25\,\mu$F. By means of short conductors forming an oscillatory circuit of low inductance ($0.6\,\mu$H), the voltage is applied to two series-connected discharge gaps: an air gap, having the construction of a trigatron, and a liquid gap. The upper positive electrode of the latter had the form of the smoothly rounded end of a steel tube of diameter 8/2 mm, tightly surrounded by a countersunk tube of vacuum rubber. The lower electrode was the slightly convex end of a steel bolt of diameter 6 mm; unscrewing it from a fixed nut made it possible to increase metrically the gap of the discharge interval. The surface of the lower negative electrode was not insulated from the liquid, and it was metallically connected with the structural elements of the installation immersed in the liquid. A cylindrical polyethylene vessel with a capacity of about 1 liter served as the reservoir for the liquid.

The voltage on the discharge gap P was recorded through the capacitive divider C_1C_2 by one beam of an OK-17M oscillograph, and the voltage from the shunt r by the other. The trigatron ignition of the air gap was effected through a delay circuit (⌒12) about 1–2 μs after the ignition micrometric

of the adjustable gap K, whose breakdown triggered the oscilloscope sweep through the frame A. The charging voltage on the main capacitor C was chosen to be about 11 or 15 kV, as measured by a kilovoltmeter connected in parallel. The current through the discharge gap was measured oscillographically by means of a shunt r and at times reached 9 kA.

The specific electrical conductivity of the electrolytes under investigation was measured under standard conditions with an MO-47 bridge; it turned out that the results of these measurements did not differ from the published tabular values by more than 10% (13). The same bridge was used to measure the total resistance of the interelectrode gap in the liquid.

From the oscillograms the following were measured: the discharge voltage and current, the random delay time of breakdown, and the time constant in the exponential decay of the charge. From this time constant the "high-voltage" conductivity of the interelectrode gap was determined. In all, about 1400 frames were taken, of which about 1200 were processed. The reproducibility of the oscillograms proved to be exceptionally high. About 400 oscillograms were used for measurements and for formulating conclusions.

Fig. 2. Schematic diagram of the behavior of an electrolyte in a strong electric field on a logarithmic scale. Along the abscissa—the interelectrode distance; along the ordinate—the specific "low-voltage" electrical conductivity of solutions. Three regions: I—breakdown is possible; II—there is no breakdown under aperiodic discharge of the capacitor; III—there is no breakdown under oscillatory discharge.

As electrolytes we used aqueous solutions, not claiming extraordinary purity, of the chemical substances listed in Table 1. Their specific electrical conductivity was varied by dilution from the values indicated in Table 1 down to approximately $5 \cdot 10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. Within the accuracy of the experiments performed, it turned out that the "high-voltage" behavior of all the listed solutions depends only on their specific electrical conductivity, measured with a standard bridge, and does not depend on their chemical composition.

Table 1

Substance	Specific conductivity, $\Omega^{-1} \cdot$ cm^{-1}	Substance	Specific conductivity, $\Omega^{-1} \cdot$ cm^{-1}	Substance	Specific conductivity, $\Omega^{-1} \cdot$ cm^{-1}	Substance	Specific conductivity, $\Omega^{-1} \cdot$ cm^{-1}
HCl	0.74	Na_2SO_4	0.17	$Fe_2(SO_4)_3$	0.05	$MnSO_4$	0.0115
H_2SO_4	0.74	$CaCl_2$	0.15	$ZrO(NO_3)_2$	0.05	$KMnO_4$	0.01
HNO_3	0.73	$BaCl_2$	0.105	$CuSO_4$	0.045	HCOOH	0.01
KOH	0.54	$Na_2S_2O_3$	0.10	$FeSO_4$	0.04	$Co(CH_3COO)_2$	0.0095
NaOH	0.35	$NaHCO_3$	0.07	$ZnSO_4$	0.035	$Pb(CH_3COO)_2$	0.0055
NaCl	0.21	Na_2CO_3	0.065	$Ba(NO_3)_2$	0.017	CH_3COOH	0.0018
KNO_2	0.19	$Al_2(C_4H_4O_6)_3$	0.065	$CdCl_2$	0.016	H_3BO_3	0.0005
$HClO_4$	0.17	$SnCl_2$	0.065	$Na_2B_4O_7$	0.0115	Tap water	0.00005
		$FeCl_3$	0.055				

In the schematic Fig. 2 is shown the behavior of electrolytes with specific electrical conductivity σ from $0.52 \cdot 10^{-4}$ to 0.74 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ (a range of variation greater than 14,000 times) at liquid discharge-gap lengths from 0.25 to 20 mm (a range of 80 times). By the character of the oscillograms, the entire diagram is div—

is divided into three regions. In region *I* there is a distinct jump (discharge, breakdown) of the voltage (“breakdown”); in region *II* there is an exponential decrease of the voltage (charge leakage) without a sharp jump; in region *III* there is an oscillatory discharge of the capacitor with a period of about 2.5 μsec, without jumps.

In region *I* one can note: a) a gradual decrease in the height of the jump U as the conductivity of the solution increases (owing to leakage of the capacitor charge through the electrolyte before the jump is formed); b) a gradual lengthening of the delay time τ for the voltage drop in the liquid gap after breakdown of the air gap as the gap is lengthened. The average duration of the delay of the practically instantaneous jump is satisfactorily described by the relation

$$\frac{\tau + \tau_0}{\tau_0} = \frac{\sigma_0}{\sigma} \frac{U_0 - U}{U_0}.$$

Here $\tau_0 = 1.6 \pm 30\%$ μsec, $\sigma_0 = 0.05 \pm 20\%$ $\Omega^{-1} \cdot \mathrm{cm}^{-1}$ are experimental constants; U_0 is the voltage on the main capacitor, measured with a static voltmeter; U is the voltage at the moment of the jump according to the oscillograms.

In region *II* a gradual acceleration of charge leakage is observed as the conductivity of the solution increases. The conductivity of the liquid gap, measured from the rate of the exponential voltage drop on the oscillograms, g_{out}, revealed a systematic overstatement of the "high-voltage" conductivity in comparison with the results of bridge measurements g_{bridge} (similar to "Wien' s law"). The following dependence is fulfilled strikingly well:

$$R_0 g_{\text{bridge}} = (R_0 g_{\text{out}})^n,$$

where $R_0 = 13500\ \Omega, \quad n = 0.879.$

In region *III* a gradual decrease in the damping of the oscillatory discharge is observed as the electrical conductivity of the solution increases and the liquid gap shortens.

In the region of low conductivities, the boundary A between the region of delayed jumps I and the region of exponential decay II passes with a slope of $-3 : 1$. This means that the distance broken down is inversely proportional to the cube root of the electrical conductivity of the solution, i.e., of the ion concentration. Such a regularity may be interpreted as though, for breakdown to develop, the average potential difference between neighboring unlike ions in the electrolyte must exceed a certain minimum. For a capacitor charge energy of 15 J, this minimum turned out to be approximately equal to the average thermal energy of molecular motion at room temperature, calculated per monovalent ion.

In the region of high conductivities, the boundary , with slope $1 : 1$, between the periodic and aperiodic discharge of the capacitor without breakdown is characterized by the critical resistance of the circuit, equal to twice its wave resistance. It represents a line of equal resistance of the liquid gap according to the oscillograms.

In the middle part of the figure there passes, parallel to , the boundary B, characterized by a certain density of the discharge current. Above and to the left of it lies the region of thermal breakdowns of the liquid: thermal breakdown occurs if the current density before breakdown reaches a certain minimum, namely about 10 A/cm^2. The oscillograms show that each jump here begins not instantaneously, but with a smooth (approximately exponential) fall of the voltage: the oscillograms begin with characteristic knee-shaped bends with a time constant on the order of 0.1 μsec. If one takes the temperature coefficient of the electrical conductivity of the solution as 2.5% per 1°, then the onset of thermal breakdown in the right tongue of region I can be interpreted as the result of local heating accompanied by an approximately 40-fold concentration of the flowing current at individual points of the electrode.

The diffuse boundary , with slope $-1 : 1$, separates the region with very small voltage jumps from the region without jumps. In the neighborhood of line pro- breakdown is observed if, per 1 $\mathring{A}^2$ of the anode surface in the discharge gap, the calculated number is no more than 500 oppositely charged ions (and conversely).

The investigation carried out has revealed the decisive influence of the "low-voltage" specific conductivity of solutions, measured by the usual bridge method, on their "high-voltage" behavior. At different specific conductivities of the solutions and at different lengths of the interelectrode gap, several separate groups of phenomena are observed, separated from one another by characteristic critical values of certain, sometimes unexpected, parameters. The experimental data presented may serve as a basis for filling an important gap: the construction of a rational theory of the electrical breakdown of electrolytes.

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Note: Figure translations are in progress. See original paper for figures.

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