

# THE INFLUENCE OF THE DIMENSIONS OF IONS ON THE ELECTROMOTIVE FORCE OF A GALVANIC ELEMENT

G. S. KOSHURNIKOV

It is known that the electrode potentials of metals (in solutions of electrolytes) depend on the chemical nature of the electrolyte. In particular, the electrode potentials of metals in solutions of KCl, KOH, and HCl of normal concentration have different values [1].

It is also known that the chloride ion has a stronger corrosive action on metals than the other halogen ions. Akimov [1] explains this by the fact that the chloride ion, because of its small dimensions, more easily penetrates the surface of the metal across the protective layer of oxides which cover it than do the other ions (the nitrate ion, sulfate ion, etc.).

Our experiments, conducted under conditions in which the possibility of formation of oxide layers on the metal was kept at a minimum, showed that a change in the electromotive force of a galvanic element and therefore of the electrode potential of the metal, which resulted when the chemical nature of the electrolyte was changed, depended on the magnitude of the ions which acted on the metal in solution.

## EXPERIMENTAL

The galvanic element with which the experiments were carried out consisted of a zinc anode and a platinum cathode, dipping into a solution of electrolyte of the proper concentration. Both electrodes were prepared from platinum wire, which was sealed in a glass holder (sleeve); one of the electrodes was covered electrolytically with zinc (composition of bath: 150 g of  $ZnSO_4$  and 100 g of water; current strength 50 ma.; time of plating 2 minutes) and then used as an anode. To reduce the oxide layer to a minimum, the electrodes were subjected to a simultaneous cathode treatment. They were placed in a bath with a 1 N solution of chemically pure sulfuric acid, joined to the negative pole of an accumulator battery (a third platinum electrode served as the positive pole) and an electric current passed through. The electrodes, thus treated with electrolytic hydrogen, were then washed with boiling water (twice distilled), dried with filter paper, and quickly transferred to the solution of electrolyte.

By means of a sensitive galvanometer, joined in series with a high resistance whose value could be varied from 1 to 100,000 ohms, and with the electrodes of the galvanic element, it was possible to measure the strength of the current flowing on the boundary of the element, and to calculate the electromotive force. The measurements were carried out under uniform conditions (temperature, total resistance of the hookup, etc.).

This method of measurement was worked out as the result of a large number of

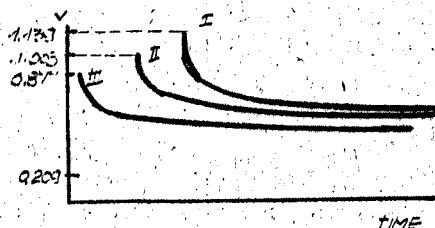
preliminary experiments carried out under other conditions. In particular preliminary experiments were carried out with the galvanic pairs: carbon-zinc, carbon-aluminum, carbon-iron, carbon-copper. "Coarser" measuring apparatus was employed, and the measurements were made with low resistances of the boundaries of the hookup.

Later on, in the tables, we shall employ several abbreviated symbols:  $T$  is the temperature of the electrolyte;  $C$  is the concentration of electrolyte;  $C_n$  is that of the normal,  $C_{sat}$  that of the saturated solution;  $V_g$  is the e.m.f. of the galvanic element (in volts);  $R_0$  is the total resistance of the boundary of the circuit;  $r_a$  is the radius of the anion of the electrolyte;  $r_c$  is the radius of the cation of the electrolyte;  $A$  is the current strength on the boundary (in amperes).

## RESULTS OF MEASUREMENTS

### 1. Data from Preliminary Experiments.

In Curves I, II, and III of the figure are shown the oscillograms from which it can be seen that the e.m.f. of the galvanic element changed depending on the chemical nature of the electrolyte (KCl, KBr, KI), and also on the duration. Despite the "coarse" method of measurement (galvanic pair of carbon and zinc, small total resistance of boundaries of the hookup, as a result of which polarization took place with great speed) it can be seen that the e.m.f. of the galvanic element changed as the chemical nature of the electrolyte changed. It was greatest (1.139 V) in a solution of KCl, less in a solution of KBr (1.003 V), and least of all (0.877 V) in a solution of KI.



Velocity of band 2 cm/sec. Temperature of solution 23°. Oscillograms: I - 2N KCl; II - 2N KBr; III - 2N KI.

As is known, the radii of the Cl, Br, and I ions vary [2,3,4]; according to Pauling, they have the values 1.81 Å, 1.95 Å, and 2.16 Å, respectively. From this we may roughly draw the conclusion that with an increase in the radius of the anion (in the solution of electrolyte) the e.m.f. of the galvanic element has a tendency to decrease.

The experiments carried out by us with the same electrolytes (KCl, KBr, and KI) but with other galvanic pairs (C-Al, C-Cu, C-Fe) showed that a change in the e.m.f. of the galvanic element took place also when the other galvanic pairs were used. In all cases there was a tendency for the e.m.f. of the galvanic pair to decrease as the value of the anion radius increased. We were therefore forced to draw the conclusion that this influence was not specific, but was in accordance with some general law.

### 2. The Measurement of the E.M.F. in Unsaturated Solutions

Later we investigated and eliminated the defects present in the preliminary experiments. To measure the e.m.f. we used more complete electrodes (platinum-platinum, zinc-plated), we increased the resistance of the boundaries of the galvanic element, introduced a treatment to reduce the electrodes with electrolytic hydrogen, etc. (as described in the section on method of measurement). As a result, we achieved reproducibility of results, and a decrease in the velocity of polarization of the electrodes.

Table 1 gives the data on measurements of the e.m.f. in solutions of the

T A B L E 1

Temperature of solutions 23°. Total resistance of hookup = 70,300 ohms. Galvanic pair: platinum-zinc.

| NaCl           |       |       |       |       |       |
|----------------|-------|-------|-------|-------|-------|
| C <sub>n</sub> | 3.17  | 2.11  | 1.58  | 1.05  | 0.78  |
| V              | 1.052 | 1.074 | 1.063 | 1.071 | 1.074 |
| KCl            |       |       |       |       |       |
| C <sub>n</sub> | 2.02  | 1.35  | 1.01  | 0.67  | -     |
| V              | 1.117 | 1.104 | 1.104 | 1.098 | -     |
| KBr            |       |       |       |       |       |
| C <sub>n</sub> | 2.03  | 1.35  | 1.01  | 0.67  | -     |
| V              | 1.027 | 1.027 | 1.014 | 1.014 | -     |
| KI             |       |       |       |       |       |
| C <sub>n</sub> | 1.95  | 1.30  | 0.97  | 0.65  | -     |
| V              | 0.842 | 0.862 | 0.851 | 0.842 | -     |

alkali metals halides (the average values of 4 or 5 measurements are given).

As is shown by the numerical data of Table 1, the e.m.f. of the galvanic element fell as the anion radius increased and the cation radius of the electrolyte decreased ( $r_{Na} = 0.95$  A,  $V_g = 1.07$ ;  $r_c = 1.33$  A,  $V_g = 1.117$ ).

### 3. The Measurement of the E.M.F. in Saturated Solutions

Table 2 lists the data on the measurements of the e.m.f. in saturated solutions of the alkali metal halides (average values of 5 to 7 measurements).

T A B L E 2

Temperature of solutions 24°. Total resistance of hookup 70,300 ohms. Galvanic pair: platinum (saturated solution)-zinc.

| Electrolyte ..... | KCl   | NaCl  | KBr   | KI    | NaF   |
|-------------------|-------|-------|-------|-------|-------|
| E.M.F.....        | 1.008 | 0.746 | 0.944 | 0.842 | 0.952 |

As can be seen from Table 2, the same rule holds true for saturated solutions: the e.m.f. of the galvanic element decreases as the radius of the anion increases and the radius of the cation in the electrolyte decreases:

$$V_g = \frac{\kappa \cdot E_c}{r_a} \quad (\kappa \text{ is a coefficient of proportionality})$$

### E V A L U A T I O N   O F   R E S U L T S

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We calculated the value of the coefficient of proportionality in the above equation for various electrolytes.

The radii of the ions, according to Pauling [2,3,4] equal:

|                 |        |                 |        |                 |        |
|-----------------|--------|-----------------|--------|-----------------|--------|
| K <sup>+</sup>  | 1.33 A | F <sup>-</sup>  | 1.36 A | Br <sup>-</sup> | 1.95 A |
| Na <sup>+</sup> | 0.95 A | Cl <sup>-</sup> | 1.81 A | I <sup>-</sup>  | 2.16 A |

Substituting the values of the ionic radii and the data of Table 2 in the equation, we obtain:

$$k_{KCl} = \frac{1.81 \cdot 1.008}{1.33} = 1.371 \text{ V}$$

$$k_{NaCl} = \frac{1.81 \cdot 0.746}{0.95} = 1.421 \text{ V}$$

$$k_{KBr} = \frac{1.95 \cdot 0.944}{1.33} = 1.383 \text{ V}$$

$$k_{NaF} = \frac{1.36 \cdot 0.952}{0.95} = 1.362 \text{ V}$$

$$k_{KI} = \frac{2.16 \cdot 0.842}{1.33} = 1.367 \text{ V}$$

As can be seen from these calculations, the value of  $k$  for the five electrolytes given is almost constant. If we consider the fact that the concentrations of electrolytes in the saturated solutions differ considerably from each other [5]:

| Electrolyte | Solubility at 25°                  |
|-------------|------------------------------------|
|             | (In moles/1000 g H <sub>2</sub> O) |
| KCl .....   | 4.81                               |
| KBr .....   | 5.85                               |
| KI .....    | 8.86                               |
| NaCl .....  | 6.145                              |
| NaF .....   | 1.00                               |

and the deviation from the average value does not exceed 3%, then we must conclude that the value of  $k$  for saturated solutions of electrolytes containing singly charged ions and the given galvanic pair is almost constant.

The average value of the coefficient  $k$  is 1.381 V. Starting with the constancy of the coefficient  $k$ , we made attempts to determine the "radii" of several univalent ions, in particular of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, by measuring the e.m.f. of the galvanic pair dipping into a saturated solution of NH<sub>4</sub>Cl or KNO<sub>3</sub>.

E.M.F. Pt (sat. solution NH<sub>4</sub>Cl) Zn 1.0173 V,

E.M.F. Pt (sat. solution KNO<sub>3</sub>) Zn 0.8217 V.

Therefore:

$$r_{NH_4^+} = \frac{1.81 \cdot 1.0173}{1.381} = 1.333 \text{ A},$$

$$r_{NO_3^-} = \frac{1.381 \cdot 1.33}{0.8217} = 2.23 \text{ A}.$$

Comparing the values of the radii of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> obtained in this manner with those calculated from the "covalent radius" we obtain fairly good agreement. See Table 3.

T A B L E 3

Covalent radii [4]: H - 0.30 A; O - 0.74 A; N - 0.74 A

| Effective radius of the ion, calculated from ... | NH <sub>4</sub> <sup>+</sup> |                         | NO <sub>3</sub> <sup>-</sup> |                   |
|--------------------------------------------------|------------------------------|-------------------------|------------------------------|-------------------|
|                                                  | Covalent                     | 0.74 + 0.3 · 2 = 1.34 A | Covalent                     | 0.74 · 3 = 2.22 A |
|                                                  | E.M.F.                       | 1.333 A                 | E.M.F.                       | 2.23 A            |

We may therefore draw the conclusion that by means of the measurement of the e.m.f. under definite conditions, by using the above equation, we can determine the "effective radius" of ions acting in solution on a metal.

Why does a change in the dimensions of the ions in a solution of an electrolyte produce an increase or decrease of the e.m.f.? No final answer to this

question can yet be given. We can only suppose that the cause of the phenomenon of an electric current in a galvanic element is the action of the ions of the electrolyte on the surface of the metal in the solution. Apparently the anions of the electrolyte "bombard" the surface of the metal, as a result of which the "electron gas" of the metal undergoes constriction, and a kind of electron "pressure" penetrates the metal. The greater the number of anions acting on a unit surface of the metal at any time, the greater will be the "pressure on the electron gas". The increase in the e.m.f., related to the decrease in the radius of the anion of the electrolyte, indirectly confirms the latter supposition. In fact, the smaller the anion of the electrolyte, the greater the number of anions which can act simultaneously per unit of metallic surface submerged in the electrolyte, and the greater will be the constriction of the "electron gas" in the metal, and the greater the "pressure of the electron gas". On the other hand, apparently, "the constriction of the electron gas" is far from being uniform with different metals, and therefore the electrons will be transferred from a zone of high "electron gas pressure" to a zone of low pressure, i.e., they will pass along the conductor from one metal to the other (from the anode of the galvanic element to the cathode). The cations of the electrolyte must oppose the action of the anions on the metal as a result of their special action not only on the anions of the solution, but also on the "the electron gas" of the metal (in the case of exchange reactions), and hence the "retarding" action will appear all the stronger the smaller the value of the cation radius. The transfer of electrons from the metal (anode) leads to the positive ions of the metal breaking their mutual bonds, and being transferred, as a result, into the solution.

#### S U M M A R Y

1. The electromotive force of a galvanic element depends on the size (radius) of the ions present in a solution of electrolyte. It decreases as the radius of the anions increases and as the radius of the cations decreases.

2. The influence of the radius of the ions in a saturated solution of electrolyte on the e.m.f. can be expressed by the following empirical formula:

$$V_g \approx \frac{k \cdot r_c}{r_a},$$

where  $V_g$  is the e.m.f. of the galvanic element,  $k$  is the coefficient of proportionality, with almost constant value for univalent ions and a given galvanic pair;  $r_a$  is the radius of the anion,  $r_c$  is the radius of the cation.

3. The above empirical formula makes it possible to determine approximately the radius (effective) of singly charged ions in a solution.

4. In the light of these facts, we have expressed a hypothesis concerning the mechanism of the interaction of the ions of the electrolyte solution with the metal placed in solution.

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