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Electrolytic Behavior in the Presence of a Tension Impulsion

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 January 30, 1947

WHEN a quick change is brought about in the magnetic field of an electromagnet, in which a conductivity vessel has been placed containing an electrolyte, a tension impulse occurs, which may be expressed as follows:

$$\int_{t_1}^{t_2} E \cdot dt = Q \cdot R,$$

where E is the electromotive force, t is time, Q is the amount of electricity going through the solution, and R is the resistance. Impulse being equal, the product QR for an electrolyte shows a lower value than that estimated for the formula corresponding to a metallic conductor. The difference between both must be traced to an increase in the resistance of the electrolytic vessel, which appears when the flow of the current starts.

This increase has been studied by comparing the values of ordinary electrolytic resistances, measured on Kohlrausch's bridge, against those met with in the presence of a tension impulse, circuits based on Fucks¹ and Weasthorne's being used. Tension impulses were in some cases of a magnetic and origin, and in the rest were brought about by applying a known tension for a small fraction of a second.

A number of sets of measurements have been made, in order to see the influence shown on this resistance increase by the physical and chemical factors which might be related to it. In order to avoid any polarizarion effect, non-polarizable electrodes were used, as well as a device to eliminate the influence of the duration of the former. The following results were obtained:

The resistance increase is independent of the presence of the magnetic field, of the effect of the vessel capacity,² of the amount of electricity going through the solution, and of the voltage applied, provided the latter is not very high. It only appears when the metal in the solution is different from that used as an electrode, and in the zone adjoining these, being greater in the cathodic region than in the anodic one. The smaller the surface of the electrode and concentration, the greater is the resistance increase; but its definite relation to the conductivity of the solution cannot be determined. Surface and concentration being equal and with salts of the same anion, it depends on the activity of the solution, showing the same values in the case of strong electrolytes.

The effect of the resistance increase cannot be traced as caused by any one of the following alone: polarizations of the various sorts, electrostatic capacities,³ or overvoltage,⁴ for in the case of any of these occurrences, it would depend on the charge going through the solution, as well as on the voltage applied to it. Nor is it brought about by relaxation of ionic clouds or by a change of the mobilities,⁵ for it would then be a phenomenon of a general character.

The physical explanations of this effect having been discarded, it may be traced to the layer between the metal and

the solution⁶ brought about by reaction of both, the existence of which has been shown by various investigators. The resistance of this layer as the current begins to flow is greater than after it has flowed for some time, for in this case the stir caused by the alternating current will not allow it to recover its state of balance. This solution agrees with the results of all sets of experimental measurements.

¹ Fucks, *Ann. d. Physik*, **12**, 308 (1932).

² Ebert, *Handbuch der Experimentalphysik*, **12**.

³ Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946).

⁴ Butler and Armstrong, *Proc. Roy. Soc.*, **137**, 604 (1932).

⁵ Debye and Falkenhagen, *Physik. Zeits.*, **24**, 185 (1923).

⁶ Gatty and Spooner, *The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions* (Oxford, 1938).

The Formation of Per-Compounds in Relation to Electronegativities

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 January 31, 1947

A LARGE number of chemical elements form, under the action of H_2O_2 (rarely by electrolytic oxidation), peroxides, per-acids, and per-salts of the $Me-O-O-$ type, in which the valency of the element is not changed relative to that of the normal oxide or acid. When the element possesses several valencies (S, Cr, Mo, etc.), the valency in the per-compound is always the highest valency compatible with the position of the element in the periodic system, with the exception of nitrogen, for which the existence of a pernitrous acid (N^{III}) has been reported. The per-compounds are not well known from the structural point of view and their very existence is sometimes doubtful, but from their chemical behavior it is known that the bridge bond $-O-O-$ is of the same nature as the $-O-O-$ bond in H_2O_2 itself. In many cases an additional compound is probably formed by dipole-dipole action.

The following elements do not appear to form such compounds:

(a)	Cl	Br	I	Se	Te	As ^V	Sb ^V	
	3.0	2.8	2.5	2.3	2.1	(2.2)	(2.1)	
(b)	Ru ^{VII}	Rh ^{IV}	Pd ^{IV}	Os ^{VIII}	Ir ^{VI}	Pt ^{VI}	Ag ^{II}	Au ^{III}
	>2.4	>2.4	>2.5	2.5	>2.4	>2.2	3.2	2.9
(c)	Cu ^{II}	Tl ^{III}	Pb ^{IV}	Bi ^V	Mn ^{VII}	Co ^{III}	Ni ^{III}	Fe ^{VI}
	2.3	2.3	2.4	>2.3	2.4	>2.2	>2.2	>2.1

Group (a) contains metalloids and the corresponding numbers are the electronegatives calculated by Pauling² (except for As and Sb). Group (b) contains the noble metals, and group (c) other metals which show at least 2 degrees of valence.

I have calculated,³ from thermochemical data, the electronegativities of these metals and of some others missing in Pauling's table with the aid of the equation of the latter:

$$Q = 23.06 \Sigma (x_a - x_b)^2 - 24.2 m_o.$$

I have shown in the course of this work that the electronegativities of the metals increase notably with their valency and that they are higher in oxides and fluorides

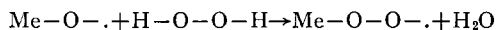
than in the other halogenides. The numbers given above in (b) and (c), as for As and Sb, are the electronegativities calculated from the heats of formation of the oxides.

The electronegativities of all elements which form per-compounds are generally smaller, rarely equal to 2.1, even in the oxide of the highest valency state.

From this statement and an examination of the numbers given above we can announce the following rule:

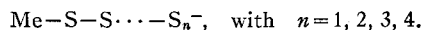
The elements whose electronegativities are smaller or at most equal to 2.1 form per-compounds; those whose whole electronegativities are greater than 2.1 do not form per-compounds. C (2.5), S (2.5), Hg (2.5), and N (3.0) are exceptions to this rule. Nitrogen presents another anomaly already mentioned (formation of a per-oxide of lower valency state).

The general rule can be easily accounted for if it is remembered that the electronegativity of hydrogen is 2.1. From the way in which the electronegativities have been calculated, it is to be expected that, for energetical reasons, the reaction



will not be carried out if $x_{\text{Me}} > x_{\text{H}}$.

The exceptions require a more detailed study. Note that sulfur has already a very marked tendency to form bridge bonds in the polysulfides and polythionates;



¹ We will, consequently, not consider here compounds which are called peroxides or per-acids, but which form with valency change, e.g., PbO_2 , MnO_2 , HMnO_4 , HIO_4 , etc.

² L. Pauling, *Nature of the Chemical Bond* (New York, 1944).

³ M. Haïssinsky, *J. Physique* 7, 7 (1946).

Selection Rules for Ionic Crystals

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February 2, 1947

IN the appendix of his article¹ Halford gives the standard symbol for the space group, followed by the symbols describing the various sites; each of those symbols is preceded by the number of distinct sets of this kind and followed by the number of equivalent sites per set. (The numbers are appended only when they differ from unity.)

But when the site group is one of the following: C_p , C_{pv} , C_s , with $p=1, 2, 3, \dots$, the number of distinct sets is infinite, for an axis or a plane of symmetry may contain several atoms belonging to different sets. Instead of $V_k^{16}:2C_i(4)$; $C_s(4)$, one should write: $V_k^{16}:2C_i(4)$; $\infty C_s(4)$.

In aragonite, the symmetry C_s for CO_3 ions does not exclude the symmetry C_s for Ca ions, which is the actual symmetry² instead of C_i . This will alter the theoretical conclusions: the lattice modes attributable to Ca ions are not forbidden in the Raman spectrum, and this, according to Halford's method, brings the number of lattice modes of aragonite up to nine.

I shall now discuss the validity of this method as applied to ionic crystals. In these crystals (in contrast to molecular crystals, e.g., organic crystals, rhombic sulfur) the number of Raman lines observed is often greater than the number deduced from Halford's method. For aragonite and cerussite this method permits 9 lattice modes in the Raman

spectrum; experimental data give more lines, 12 for aragonite, 17 for cerussite (the general theory permits 18 lines). For barites, Halford's method gives 9 Raman lines caused by internal vibrations; the Raman spectrum actually contains 13 lines, a close approximation to the number of lines given by general theory which predicts 18 lines, 4 of them being very weak.

Moreover, the coupling of like vibrations between different ions of one set gives rise to distinct Raman lines; their polarization shows that the symmetry of the corresponding vibration is related to the whole symmetry of the unit cell. For instance: $1363\text{--}1377\text{ cm}^{-1}$, Raman lines of internal vibrations for cerussite; $630\text{--}647\text{ cm}^{-1}$, etc. . . ., for barites³ $122.5\text{--}130\text{ cm}^{-1}$, Raman lines of rotational vibrations of ClO_3 ions in ClO_3Na ;⁴ even in some molecular crystals there appear separations caused by the coupling: $46\text{--}54$, $74\text{--}76$, $109\text{--}127\text{ cm}^{-1}$, in Raman spectrum of rotational vibrations for naphthalene.⁵

In the case of calcite, however, the selection rules obtained by Halford's method are in agreement with experimental data. This is due to the particular fact that the unit cell contains only two CO_3 ions which are symmetrical in relation to a center of symmetry. The theoretical conclusions are the same whether one takes the coupling into account or not. We have seen that this is not the general case.

Therefore, I conclude that, in ionic crystals, coupling of vibrations between the ions of a set cannot be neglected and that Halford's method, which is applicable to molecular crystals, cannot be applied to ionic crystals, even as a first approximation.

¹ R. S. Halford, *J. Chem. Phys.* 14, 8 (1946).

² W. L. Bragg, *Proc. Roy. Soc. London* A105, 16 (1924).

³ L. Couture, *Comptes rendus* 218, 669 (1944); 220, 87 (1945); 222, 495 (1945); and also a paper which will shortly appear in *Ann. de physique*.

⁴ A. Rousset, *Comptes rendus* 216, 886 (1943).

⁵ A. Kastler and A. Roussett, *J. Phys.* 2, 49 (1941).

Theoretical Interpretation of Vibration Frequencies of Paraffinic Hydrocarbons

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February 17, 1947

IN a recent paper Ahonen¹ has calculated the normal frequencies of vibration for a number of octanes on the assumption of a valency force field. The values obtained are compared with the experimental data and although some degree of correlation is obtained, it would be difficult to apply these results to the discussion of the spectra of other paraffins. The purpose of the present note is to report briefly some calculations made during the war as part of a program of research² on the vibration spectra of hydrocarbons (primarily for analytical purposes), since these deal with certain skeletal frequencies common to many branched hydrocarbons and have therefore a wider application than the results of Ahonen.

Instead of attempting to calculate the frequencies of an isomeric series of hydrocarbons, we have concentrated on calculating the skeletal frequencies of certain structural units which are common to many paraffins. The particular