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## The Theory of Galvanic Potentials. I

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In this paper a thermodynamic study of the theory of galvanic electrode potentials is presented. It is shown that, starting from strictly equilibrium conditions, the series of normal electrode potentials can be expressed through other partly known thermodynamic quantities, one group of which refers to the solid phase only, independent of the solvent used, while the other is characterized by the type of solvent.

### I. INTRODUCTION

THERE exists a large literature on the theory of galvanic potential series and in particular on their suspected connection with the voltaic series. Among the papers most important in this connection we only want to point out the investigation by K. F. Herzfeld,<sup>1</sup> who succeeded in deriving thermodynamic relations between normal electrode potentials and other thermal quantities like heat of solution, etc. Though, from this, as well as from other investigations, it was apparent that the problem possesses an intrinsic complexity, still century old attempts are being revived again and again for the purpose of showing that the galvanic and the voltaic series are essentially equivalent. Though all these attempts are theoretically unsound, as will become even more apparent from the following, it could be said for their justification that the order of the metals in both series shows a certain amount of parallelism, a fact that encouraged the construction of theories which aim to derive this parallelism from general principles.

In the present paper we shall give a thermodynamic derivation for the differences in normal electrode potentials. (It is, of course, the difference only which can be brought in connection with observable thermodynamic quantities). From formula (6) of paragraph II it will become apparent that the differences in the normal electrode potentials can be expressed essentially by the differences in two groups of quantities; the first group of these quantities refers only to the properties of the substances forming the electrode, containing quantities like the heat of vaporization of the neutral electrode atom, and

the ionization energy of the metallic atom in the gaseous phase, or on the Richardson constants for the electrons or positive ions which can be emitted from the electrode. The second group refers to the free energy which becomes liberated when a *gaseous* ion of the substance forming the electrode becomes dissolved in the solvent. While the first group of quantities is completely independent of the nature of the solvent used, the second group does not depend on the structure of the metal electrode itself.

### II. THERMODYNAMIC EXPRESSIONS FOR GALVANIC ELECTRODE POTENTIALS

We consider an electrolytic solution containing two different univalent cations and a common anion. Two electrodes are dipping into this electrolytic solution; they consist respectively of the metals 1 and 2, which form the cations present in the solution.

The solution and the metals shall be considered to be in thermodynamic equilibrium with the gas phase present above the solution, this gas phase containing all neutral and charged particles as given by the equilibrium relations of thermodynamics.

The restrictions as to the valency of the cations present, the common anion, etc., are only made to give the following formulae the simplest form and do not diminish the generality of the considerations.

In general the solution and the gas phase will not be in equilibrium. It is *this fact* which produces the electromotive force of the element just described. To obtain equilibrium it is necessary that the two cations in the solution be present in a ratio which can be determined from the following simple consideration: In equi-

<sup>1</sup> Herzfeld, Ann. d. Physik 51, 257 (1917).

librium the work done by carrying a unit charge from one electrode to the other must be independent of the path chosen. The work done in carrying a charge from the electrode 1 to the electrode 2 through the solution is given by the expression:

$$G_{12} = \Delta_{10} - \Delta_{20} + (RT/F) \log (c_1^*/c_2^*),$$

in which  $\Delta_{10}$  stands for the potential difference between the metal and the solution at the concentration (1) of its ion and  $c_1, c_2$  denote, respectively, the concentration of the cations 1 and 2. We should more correctly take the activity of the ions but this difference can be neglected for our purposes. Carrying the same charge through the gas phase, the work done would be equal to  $V_{12}$ , the Volta potential difference between the metals 1 and 2. The equation

$$\Delta_{10} - \Delta_{20} - V_{12} = (RT/F) \log (c_2^*/c_1^*) \quad (1)$$

gives us the conditions of equilibrium. The right-hand side of (1) equals the difference of the normal electrode potentials of the metals 1 and 2.

We now express  $c_1^*$  and  $c_2^*$  through the concentrations of the ions and atoms in the gas phase, which in turn are determined by the ionization equilibria of the gas atoms and the vapor pressures of the metals. We thus have the following relations:

$$\frac{c_2^*}{c_1^*} = \frac{c_2^{+g}}{c_1^{+g}} e^{-(W_2 - W_1)/RT} = \frac{c_2^{+g}}{c_1^{+g}} e^{-[(W_2' - W_1')F]/RT}. \quad (2)$$

Here  $W_1$  and  $W_2$  stand for the difference in free energy of the ions 1 and 2 in the liquid and in the gas phase. This difference in free energy consists of two parts: (possibly) of a surface potential difference  $F\phi$  between the liquid and the gaseous phase and of the work  $FW'$  gained or lost by transferring the ion from the vacuum into the liquid. This work is due to the interaction between the ion and molecules of the solvent. In conformity with general thermodynamic principles, the first part drops out of the formula.

$c_1^{+g}$  and  $c_2^{+g}$  are, respectively, determined by their ionization equilibria

$$c_1^{+g}c_e/c_1^g = e^{-I_1 F/RT} f(T), \quad (3a)$$

$$c_2^{+g}c_e/c_2^g = e^{-I_2 F/RT} f(T). \quad (3b)$$

$f(T)$  denotes the phase-volume of the electron. In (3a) (3b),  $I_1 F$  and  $I_2 F$  stand for the ionization energy of the atoms. We here neglect excited electronic levels of the atoms which lie far too high to be of any importance for the problem under consideration. Finally, since the electron concentration  $c_e$  is common to both ionization equilibria, we can determine the ion concentrations in the gas phase by making use of the vapor-pressure equation and thus describe everything by properties of the solid phase. We obtain the relation

$$c_1^g/c_2^g = (A_1/A_2) e^{-(Q_1 - Q_2)F/RT}. \quad (4)$$

$A_1, A_2$  are known constants,  $QF$  denotes the heat of vaporization at absolute zero. Connecting now Eqs. (2), (3) and (4) we can express  $c_2^*/c_1^*$  in the form

$$c_2^*/c_1^* = (A_2/A_1) e^{-F(W_2' - W_1' + I_2 - I_1 + Q_2 - Q_1)/RT}. \quad (5)^2$$

We insert (5) into the equilibrium condition (1) which contains the difference of normal electrode potentials and so finally obtain for them the following relations:

$$E_{01} - E_{02} = (RT/F) \log (A_2/A_1) + (I_1 - I_2) + (a_1 - a_2) + (W_1' - W_2'). \quad (6)$$

The first term in (6) is in all practical cases very small and can be neglected.

(6) contains the formal justification for the statements made in the introduction. We first of all notice that the surface potential of the liquid has dropped out since it is the same for both cations. The first three terms (on the right side of (6)) refer to properties of the *electrode material only*. We can express the sum of the ionization potential and the heat of vaporization with the help of two other quantities, namely, the Richardson constants  $b$  for the electrons and positive ions which determine the work necessary to remove either of these two particles from the metal to the gas phase at absolute zero. From the first law of thermodynamics it is obvious that the relation

$$Q + I = b_+ + b_- \quad (7)$$

must hold. This relation mainly expresses the fact that we can produce an ionized atom in the gas phase at absolute zero with the same amount

<sup>2</sup> Similar considerations have been used in a paper by T. J. Webb, J. Am. Chem. Soc. **48**, 2589 (1926).

of energy either by evaporating a neutral atom and then ionizing it or by evaporating the charged components. If  $W_1' - W_2'$  would be zero, then the galvanic potential difference would still not be given by the voltaic potential difference between the two metals, which is equal to the difference between the *Richardson constants for the electrons alone*, since the difference between the values of the Richardson constants for the positive ions has to be added, which in general is of the same order of magnitude. Still a certain parallelism between the voltaic and galvanic potentials could then be expected because the Richardson constants for the positively and negatively charged particles go somewhat parallel to each other.

Now the difference between the Richardson constants, being of the order of magnitude of 1

volt, cannot in general be considered to be large compared to the difference in the work done by immersing a charged ion into a liquid. The simple electrostatic considerations: work done by a sphere of radius  $a$  when transferred from a medium with the dielectric constant 1 to another with the dielectric constant  $D$  leads to values for  $W_1' - W_2'$  which are of the same order of magnitude as the other terms in (6). There does not therefore exist any general theoretical principle which would justify the much discussed hypothesis of equivalence of voltaic and galvanic potentials. In a subsequent communication the authors intend to present what evidence can be derived from a study of ionic diameters and correlated quantities as to the magnitude of the work done by transferring ions from the gaseous into the liquid phase.

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## Rotating Polar Groups in "Organic" Molecules

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The temperature dependence of the electric moment, observed in the case of molecules with rotating polar groups, permits a quantitative explanation in terms of intra-molecular forces opposing free rotation of the groups. Specifically, the following questions have been raised and treated: I. The statistical weight to be associated with a configuration. II. Approximation of the periodic potential function by its first and second Fourier component. III. An application to 1,2-dichloroethane is given and a

plausible potential of interaction between the two  $\text{CH}_2\text{Cl}$  groups is obtained. The result suggests the presence of repulsive forces between two bound chlorine atoms at distances as large as 4.0 Angstrom. IV. The related question of the thermal equilibrium ratio of the *cis* and *trans* isomers of dichloroethylene is discussed. A new explanation of the observed value is proposed, which attributes about equal heat of formation to both isomeric forms.

### INTRODUCTION: STATEMENT OF THE PROBLEM

IT is now generally recognized that the deviations of the molar polarization *vs.*  $T^{-1}$  curves from a straight Debye line, as are observed with 1,2-dichloroethane, diacetyl, and similar molecules,<sup>1</sup> must be attributed to the presence of forces restricting free rotation of the polar groups around the single C—C bond,<sup>2, 3</sup> and that from the temperature variation of the dipole moment we can gather information with regard to these

forces.<sup>4, 5, 6</sup> This information is important and, indeed, unique because in this particular phenomenon—unlike others where interatomic forces manifest themselves (second virial coefficient, friction in gases)—the groups approach each other under rigidly defined geometrical conditions which can be derived with great accuracy from x-ray and electron diffraction data.

<sup>1</sup> Lennard-Jones and Pike, *Trans. Faraday Soc.* **30**, 830 (1934).

<sup>2</sup> Mizushima and Higasi, *Proc. Imp. Acad. Japan* **8**, 482 (1932).

<sup>3</sup> Mizushima, Morino and Higasi, *Physik. Zeits.* **35**, 905 (1934).

<sup>4</sup> C. T. Zahn, *Trans. Faraday Soc.* **30**, 804 (1934).

<sup>1</sup> C. T. Zahn, *Phys. Rev.* **38**, 521 (1931); **40**, 291 (1932).  
<sup>2</sup> L. Meyer, *Zeits f. physik. Chemie* **B8**, 27 (1930).  
<sup>3</sup> Smyth, Dornte and Wilson, *J. Am. Chem. Soc.* **53**, 4242 (1931).