ELECTROMOTIVE FORCES

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The present theory of the electromotive force of the voltaic cell is due primarily to Nernst¹ and consequently the subject is usually presented in text-books in the form adopted by Nernst, with subsequent modifications to meet special cases. It so happens that the historical development is not a logical or a consistent one; and consequently the different types of cells are not co-ordinated as they should be.

If we have a reversible electrode such as zinc in zinc sulphate, we make use of Nernst's deduction and write for the single potential

$$(1) \quad E = \frac{RT}{nF} \log \frac{P_{Zn}}{p}$$

where P_{Zn} is the hypothetical solution pressure of zinc, p the osmotic pressure of zinc in the solution, n the valence of the zinc ions and F the Faraday constant.

If we make up a cell of two different concentrations of zinc sulphate we write for it the equation

$$(2) \quad E = \frac{RT}{nF} \left\{ \log \frac{P_{Zn}}{p_d} - \log \frac{P_{Zn}}{p_c} \right\} + x = \frac{RT}{nF} \log \frac{p_c}{p_d} + x$$

where x is the potential difference between the two solutions, p_c is the more concentrated solution and p_d the more dilute. If we make up a cell of the Daniell type, the equation becomes

$$(3) \quad E = \frac{RT}{nF} \left\{ \log \frac{P_{Zn}}{p_{Zn}} - \log \frac{P_{Cu}}{p_{Cu}} \right\} + x = \frac{RT}{nF} \log \frac{P_{Zn}}{P_{Cu}} \cdot \frac{p_{Cu}}{p_{Zn}} + x.$$

If the metallic electrode is a phase of varying composition such as a dilute amalgam, it is usual to consider the cell as a whole and to calculate the work done in transferring the dissolved metal from one electrode to the other as pointed out

¹ Zeit. phys. Chem., 4, 129 (1889).

by von Turin¹ and by Meyer.² The equation for the cell is

$$(4) \quad E = \frac{RT}{mnF} \log \frac{p'_1}{p'_2}$$

where p'_1 and p'_2 are the osmotic pressures of the metal in the two mercury solutions and m is the ratio of the molecular weight of the metal in the mercury solutions to the weight of the ion in solution. LeBlanc³ writes for the single potential

$$(5) \quad E = \frac{RT}{nF} \log \frac{P'}{p}$$

where P' is the electrolytic solution pressure of the zinc in the amalgam and m is unity because zinc is monatomic in mercury. This solution pressure is not the one introduced by Nernst because that was a constant. As a matter of fact, LeBlanc gets out of the difficulty only by saying that, since the osmotic pressures of zinc in mercury are proportional to the concentrations, the electrolytic solution pressures of the amalgams may be assumed to be proportional to the osmotic pressures of the dissolved zinc. In a cell with two amalgam electrodes the proportionality factor cancels and everything comes out as it should; but it would be a very clever student who could find out from LeBlanc's book the equation for a cell consisting of zinc and dilute zinc amalgam in zinc sulphate solution. If we assume that the apparent solution pressure is proportional to the osmotic pressure of the monatomic metal in the mercury, the equation for the single potential becomes

$$(6) \quad E = \frac{RT}{nF} \log \frac{P_{Zn}}{p_o} \cdot \frac{p'_1}{p}$$

where P_{Zn} is the solution pressure of zinc against an aqueous solution as in Equation 1, p'_1 is the osmotic pressure of zinc in the amalgam, p_o is the osmotic pressure of a solution of zinc in mercury which is in equilibrium with pure zinc, and p is the osmotic pressure of zinc ions in the solution.

When it comes to gas cells the orthodox thing is to treat

¹ Zeit. phys. Chem., 5, 340 (1890); 7, 221 (1891).

² Wied. Ann., 40, 244 (1890); Zeit. phys. Chem., 7, 477 (1891).

³ "A Text-Book of Electrochemistry," 184 (1907).

them exactly like amalgam cells only considering the solution pressures as proportional to the gas pressures. The equation for the single potential therefore becomes

$$(7) \quad E = \frac{RT}{mnF} \log \frac{p''_1}{p}$$

where p''_1 is the gas pressure. For hydrogen $m = 2$ and $n = 1$. We are not only ignoring the electrode, but also the unknown concentration in the electrode. While this is justifiable thermodynamically, it is of doubtful wisdom pedagogically. We can get back to the strict Nernst formulation if we postulate Henry's law for the relation between the gas pressure and the unknown osmotic pressure in the electrode and substitute this in an equation analogous to Equation 6. If the ratio of the molecular weight of the gas to the molecular weight in the metal electrode is q , we have

$$(8) \quad E = \frac{RT}{qmnF} \log \frac{P}{Kp_o} \cdot \frac{p''_1}{p}$$

where K is the constant in the equation $p''_1 = K(p'_1)^q$ and p'_1 is the osmotic pressure of hydrogen in the electrode. For hydrogen we know that $qm = 2$. Since there is no concentration at ordinary temperatures for which solid hydrogen is in equilibrium with a platinum electrode, for instance, it is simpler to substitute P_1 for P/Kp_o in which case we may write

$$(9) \quad E = \frac{RT}{2F} \log \frac{P_1 p''_1}{p}$$

remembering however that P_1 is not the solution pressure of solid hydrogen.

When it comes to oxidation and reduction cells, the Nernst formulation is practically ignored. For reversible electrodes such as platinum in a mixture of ferrous and ferric salts we follow the lead of Peters¹ and write one modification of the van't Hoff formulation

$$(10) \quad E = A - \frac{RT}{nF} \log \frac{p_2}{p_1}$$

¹ Zeit. phys. Chem., 26, 193 (1898).

where p_1 is the osmotic pressure of the ferrous ions in the solution, p_2 the osmotic pressure of the ferric ions, n the difference in valence of the ferric and ferrous ions ($n = 1$), and A the value of the electromotive force when p_1 and p_2 are equal.¹ While this same formula could probably have been deduced from the Nernst theory, I am not aware that it has ever been done. Nernst has suggested treating reduction electrodes as hydrogen electrodes; but it is not very satisfactory to call a ferric-ferrous electrode a hydrogen electrode, and the overvoltage complicates the theory of the hydrogen electrode a good deal.

When avowedly measuring chemical affinity, as involved in the reaction $\text{TlSCN} + \text{KCl} \rightleftharpoons \text{TlCl} + \text{KSCN}$, for instance, we make use of another modification of the van't Hoff formulation² and write for the cell

$$(11) \quad E = \frac{RT}{nF} \log \frac{Kp_1}{p_2}$$

where p_1 is the osmotic pressure of the sulphocyanate ion, p_2 the osmotic pressure of the chloride ion, K is the equilibrium constant in the equation $Kp_1 = p_2$, and x is the potential difference between the solutions. The Nernst formulation could have been used in this case. Ostwald³ has shown that the equation for such single potential differences as $\text{Tl} \mid \text{TlSCN} \mid \text{KSCN}$ may be written

$$(12) \quad E = \frac{RT}{nF} \log \frac{Pp_1}{S_1^2}$$

where P is the solution pressure of thallium, p_1 the osmotic pressure of the sulphocyanate ions, and S_1 the solubility of thallos chloride expressed in osmotic pressure units. For the cell $\text{Tl} \mid \text{TlSCN} \mid \text{KSCN} \mid \text{KCl} \mid \text{TlCl} \mid \text{Tl}$ we have the equation

$$(13) \quad E = \frac{RT}{nF} \left\{ \log \frac{Pp_1}{S_1^2} - \log \frac{Pp_2}{S_2^2} \right\} = \frac{RT}{nF} \log \frac{S_2^2}{S_1^2} \cdot \frac{p_1}{p_2}$$

¹ Peters uses the plus sign in his equation; but this is not in keeping with the Nernst formulation that the current flows from the metal to the solution when E is positive. See Haber: *Zeit. Elektrochemie*, 7, 1047 (1901).

² Knüpfner: *Zeit. phys. Chem.*, 26, 235 (1898).

³ Lehrbuch allgem. Chemie, 2, I, 877 (1893).

provided we consider the potential difference between the solutions as zero.

I have distinguished five types of cells: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells. These are usually treated in five more or less different ways, which may be advantageous but which is certainly unsound theoretically. Suppose we take the Daniell cell, $\text{Zn} \mid \text{ZnSO}_4 \mid \text{CuSO}_4 \mid \text{Cu}$. This is usually considered—and very properly—as a cell with reversible metallic electrodes. It may, however, be considered as an oxidation and reduction cell because the zinc is oxidized and the copper salt is reduced.¹ It can also be considered as a case of chemical affinity because we are really studying the reaction

If we start with a zinc amalgam and a copper amalgam instead of with the pure metals, we have the same reaction taking place as before; but it is now an amalgam cell with electrodes of varying composition. If we were to take into account the unknown vapor pressures of zinc and copper, we could consider the cell as a gas cell. Our types are not mutually exclusive and one given combination may be considered from any one of the five differing points of view. Obviously it would be better for the student to have a uniform treatment of the subject and yet I do not know of any text-book on electrochemistry which attempts this. I am not in a position to do much criticizing because I have never attempted it myself in my lectures in the past, though I have pointed out the inter-relation of the different types.

The proper starting point, as Haber² has pointed out, is van't Hoff's formula for the reaction isotherm. In the case of a reversible reaction, A, the chemical affinity per unit chemical weight is given by the equation

$$(14) \quad A = RT \log K \frac{\Sigma p_1}{\Sigma p_2}$$

¹ Haber: *Zeit. Elektrochemie*, **7**, 1046 (1901).

² *Ibid.*, **7**, 1045 (1901).

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed. If it is possible to arrange the reaction so that electricity is generated, we have the relation

$$(15) \quad A = nFE$$

By combining Equations 14 and 15, we get the working equation

$$(16) \quad E = \frac{RT}{nF} \log K \Sigma p_1 / \Sigma p_2.$$

If we apply Equation 16 to the Daniell cell,

which involves the reaction

we have

$$(17) \quad E = \frac{RT}{nF} \log K \cdot \text{Zn} \cdot p_{\text{Cu}} / \text{Cu} \cdot p_{\text{Zn}} + x$$

where x represents the potential difference between the solutions and Zn and Cu are written to denote the unknown constant terms for zinc and copper respectively. By combining these latter with K we get

$$(18) \quad E = \frac{RT}{nF} \log K_1 p_{\text{Cu}} / p_{\text{Zn}} + x$$

which is identical with Equation 3, provided we put $K_1 = P_{\text{Zn}} \mid P_{\text{Cu}}$. The single potential difference at the zinc electrode can be written

$$(19) \quad E = \frac{RT}{nF} \log K \cdot \text{Zn} / p_{\text{Zn}} = \frac{RT}{nF} \log K_2 / p$$

which is the same as Equation 1 with K_2 written for P_{Zn} . The equation for a concentration cell with zinc electrodes and two zinc sulphate solutions becomes

$$(20) \quad E = \frac{RT}{nF} \log \frac{K_2 \cdot p_1}{K_2 \cdot p_2}$$

which is the same as Equation 2, p_1 being the more concentrated solution. The direction of the current is to be predicted from the Theorem of Le Chatelier.

If the molecular weight of zinc in a zinc amalgam is m times the atomic weight of zinc the potential difference between it and the solution will be given by the equation

$$(21) \quad E = \frac{RT}{mnF} \log K p'_1 / p$$

which is the same as Equation 6 with K written for P_{Zn} / p_o . The equation for an amalgam cell with electrodes of different concentrations becomes

$$(22) \quad E = \frac{RT}{mnF} \log \frac{K p'_1}{K p'_2} \cdot \frac{p}{p} = \frac{RT}{mnF} \log \frac{p'_1}{p'_2}$$

which is the same as Equation 4.

In the case of a gas electrode we can write at once

$$(23) \quad E = \frac{RT}{qmnF} \log K p''_1 / p$$

where qmn is the ratio of the molecular weight of the gas to the ionic weight, p''_1 is the gas pressure and p is the osmotic pressure of the ion for which the electrode is reversible. In the case of hydrogen or chlorine $qmn = 2$. Equation 23 is the same as Equation 9 if $K = P_1$.

The equation for a reversible reduction electrode consisting of platinum in a mixture of ferrous and ferric salts becomes

$$(24) \quad E = \frac{RT}{nF} \log K p_1 / p_2$$

where p_1 refers to the ferrous salt and p_2 to the ferric salt. This is the same as Equation 10 when one writes $A = (RT/nF) \log K$.

I have already shown that the equation for the Daniell cell simplifies to

$$(25) \quad E = \frac{RT}{nF} \log K_1 p_{Cu} / p_{Zn} + x$$

whether we consider the cell as a case of chemical affinity or as made up of two reversible electrodes. For the cell $Tl \mid TlSCN \mid KSCN \mid KCl \mid TlCl \mid Tl$ the reaction is

Considering this as a case of chemical affinity and combining the constant terms for thallous chloride and thallous sulphocyanate with the equilibrium constant we get

$$(25) \quad E = \frac{RT}{nF} \log K_1 p_{\text{SCN}} / p_{\text{Cl}} + x$$

which is identical with Equation 11.

It is possible to apply the general equation of van't Hoff to the contact electromotive force between two solutions, in case the process is a reversible one.¹ For the same electrolyte in different concentrations, Nernst has derived the expression

$$(26) \quad E = \frac{u - v}{u + v} \cdot \frac{RT}{nF} \log \frac{p_1}{p_2}$$

where the valence n of the ions is the same, p_1 and p_2 are the osmotic pressures of the ions in the concentrated and dilute solutions, respectively, and u and v refer to the ionic mobilities.

One may imagine the potential difference between two solutions of hydrochloric acid to be produced by two opposing tendencies, one of these being the diffusion of hydrogen ions into the dilute solution and the other being the diffusion of chlorine ions in the same direction. If the rates of ionic diffusion are equal no boundary electromotive force is produced.

Consider separately the part played by the hydrogen ions. Since the ion concentrations in the two solutions are equal when equilibrium is reached, K in the van't Hoff formula becomes unity and disappears. The substance consumed is the ionic hydrogen in the concentrated solution and Σp_1 refers to its osmotic pressure; similarly Σp_2 refers to the dilute solution where hydrogen ions are increasing in number. If the total electromotive force were produced by the migration of hydrogen ions only, the following expression would hold for this hypothetical single potential:

$$(27) \quad E_1 = k_1 \frac{RT}{nF} \log \frac{p_1}{p_2}$$

¹ This was pointed out to me by Professor Briggs, who has written this section for me.

where k_1 is a constant proportional to the relative rate of ionic diffusion.

On the other hand, negatively charged chlorine ions are passing from the concentrated into the dilute solution. Considering the chlorine ions separately, the hypothetical single potential would be:

$$(28) \quad E_2 = -k_2 \frac{RT}{nF} \log \frac{p_3}{p_4}$$

where p_3 is the osmotic pressure of the chlorine ions in the concentrated solution, p_4 refers to the dilute solution and k_2 is a constant proportional to the relative ionic mobility of the chlorine ions.

Actually, therefore, the contact potential is equal to the sum of the effects due to the cation and anion and, since $p_1 = p_3$ and $p_2 = p_4$, we may combine Equations 27 and 28 into the following:

$$(29) \quad E = E_1 + E_2 = (k_1 - k_2) \frac{RT}{nF} \log \frac{p_1}{p_2}$$

If we substitute $\frac{u}{u+v}$ for k_1 and $\frac{v}{u+v}$ for k_2 , Equation 26, the Nernst equation, is obtained.

I have tried to make clear that all the different types of reversible cells which have been discussed can be treated from one point of view if one makes use of the van't Hoff formula given in Equation 16. This is, in my opinion, a much better way of treating the subject than the ordinary, haphazard and illogical method. On the other hand this treatment ignores the historical development and fails absolutely to bring out the important part played by Nernst. It seems to me that the following compromise ought to be fairly satisfactory both to the historical and the logical enthusiasts. First give Nernst's deduction of the potential difference between solutions. This would also include Planck's modification of Nernst's formula,¹ and later work along this line.

Then take up Nernst's formula for the potential difference between a metal and a solution, applying it to con-

¹ Planck: Wied. Ann., 39, 161; 40, 561 (1890).

centration cells, to the Clark cell, and to the Daniell cell, much as Nernst has done; but introducing at once Ostwald's explanation of electrodes of the second class. Next, deduce the van't Hoff formula, Equation 16, and apply it to the case already studied, after which one should take up in order the so-called chemical affinity cells, the oxidation and reduction cells, the amalgam cells, and the gas cells. It is usual, I know, to discuss gas cells before oxidation and reduction cells, but I think that this is another case of a too slavish following of the historical development. It is certainly more logical to study first the effect of varying concentration in the solution, then the effect of varying concentration in the electrode, and lastly the effect of varying concentration in the vapor phase. Certainly nobody can question the advantage of having studied the relation between chemical affinity and electromotive force before taking up the case of the hydrogen-oxygen gas cell.

The general results of this paper are:

1. Five types of reversible cells have been recognized, which are usually treated in five more or less different ways, even though a particular cell could be classed under any one of the five types.

2. The five so-called types of cells are: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells.

3. All these cells can be treated from the same point of view provided one starts with the van't Hoff formula

$$E = \frac{RT}{nF} \log K \Sigma p_1 / \Sigma p_2,$$

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed.

4. It has been shown how the van't Hoff formula is to be applied in the special cases.

5. Since a consistent logical development of the theory of the electromotive force of voltaic cells does not do justice to the pioneer work of Nernst, a compromise treatment is suggested.

6. It is suggested that Nernst's work be presented as an historical introduction, after which the van't Hoff equation should be deduced and applied to all cases.

7. It is desirable to study, in order, the effect of varying concentration in the solution, in the electrode, and in the vapor. Consequently the amalgam cells should be considered after the oxidation and reduction cells, and before the gas cells.

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