

Calculation of the Absolute Potential of the Normal Calomel Electrode from the Free Energy of Hydration of Gaseous Ions

In a recent article Latimer, Pitzer and Slansky¹ make an attempt to calculate the absolute potential of the calomel electrode using values for the energies of hydration of gaseous ions which they consider the most probable. It is not the aim of this letter to discuss the reliability of the data used, but I should like to summarize the reasons which make *a priori* their calculation of the absolute potential (as well as any calculation of this kind) erroneous.

Among the reactions they sum up to calculate the free energy of the reaction



on which the calculation of the absolute potential is based is the reaction $\text{Na}(g) = \text{Na}^+ + E^-(g)$. The gaseous sodium ion is introduced in another step in the solution and the electron in mercury. To do this they must be brought first in the neighborhood of the corresponding interfaces, and as there exists a potential drop (Volta potential) between two points situated in the neighborhood of the two interfaces this involves an additional free energy term which the authors do not consider. Let us denote the potential differences at the interfaces gas/mercury, mercury/solution and gas/solution by φ_1 , φ_2 and φ_3 , respectively. The Volta potential between mercury and solution, and therefore the energy term which must be subtracted from the value of ΔF (0.495 v) calculated for reaction (a), is equal to $(\varphi_1 + \varphi_2 - \varphi_3)$. It follows from this consideration that ΔF determines the equilibrium value of $\varphi_1 + \varphi_2 - \varphi_3$, and not the equilibrium value of φ_2 as it is supposed by Latimer, Pitzer and Slansky. The Volta potential between a metal and a solution of its salt in electrical equilibrium with the metal, is a quantity which can be determined with a certain approximation by experiment, as it was shown recently by Klein and Lange.² They found a Volta potential between mercury and Hg^+ solution of unit activity equal to 0.69 v, which corresponds to a value of 0.17 v for the Volta potential between mercury and norm. KCl, sat. with HgCl . This determination would provide a possibility of checking the calculation of hydration energies but for another difficulty which has escaped the attention of Latimer, Pitzer and Slansky. The hydration energies involved in their calculations correspond to the passage of ions through the gas/solution interface with its potential drop φ_3 ("real" hydration energies according to the terminology of Lange); they differ from the energies calculated from the interaction of ions and water molecules by the quantity $n\varphi_3$ (n -valence of the ion).

It is still interesting to compare the values of hydration energies obtained by both methods. To fit the experimental value of the Volta potential cited above (0.17 v) using the same reactions as Latimer, Pitzer and Slansky, the hydration energy of the sodium ion should be increased by $0.495 - 0.17 = 0.325$ v or 7.5 kcal. We obtain thus (instead of 89.7 and 94.6, respectively, as given by Latimer and collabora-

tors) 97 kcal. for the free energy change and 102 kcal. for the heat of hydration, the latter value, as it should be expected, coincides with the value given for the same quantity by Klein and Lange (101 kcal.).

The absolute value of φ_3 is not known, but from different considerations concerning the structure of the surface layer of water, it follows that the oxygen atoms of the water molecule on the surface are probably turned outwards; φ_3 must have therefore a negative value amounting to a few decivolts. The energy of hydration of a cation calculated from the interaction of the ion and the water molecules is therefore probably larger than the "real" hydration energy which is diminished by the electric work spent during the passage of the ion through the surface layer. In this sense the values of the heats of hydration given by Bernal and Fowler³ (114-116 kcal. for Na^+) appear more probable than the new values calculated by Latimer, Pitzer and Slansky.

From the point of view of the modern theory of electrocapillarity, the assumption that the value 0.56 really expresses the absolute potential of the calomel electrode is devoid of any foundation.

Let us consider the relation which exists between this quantity and the Volta potential mercury/solution which can be calculated from "real" hydration energies. If the mercury/solution interface is brought to the potential of the electrocapillary zero the Volta potential between mercury and solution will be equal to $0.17 - 0.56 = -0.39$ in the case of normal NaCl and to $0.17 - 0.50 = -0.33$ in the case of a more dilute solution, where the disturbing effect of the anion adsorption might be neglected. This value -0.33 v is equal to $\varphi_1 + \varphi_2' - \varphi_3$, where φ_2' represents the potential difference at the mercury/solution interface in the absence of ionic exchange between the two phases; accordingly

$$\varphi_2' = \varphi_3 - \varphi_1 - 0.33.$$

When a mercury/solution interface is formed from a mercury/gas and a gas/solution interface, the resulting potential drop in the absence of any ionic exchange is thus shifted to more negative values as compared with the sum of the original potential differences. This could be caused by a more pronounced orientation of the negative ends of the water molecules towards mercury as compared with their orientation towards the gas phase—an assumption which appears very probable, as a similar effect is really observed in the case of various organic molecules dissolved in water.⁴

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¹ W. Latimer, K. Pitzer and C. Slansky, J. Chem. Phys. **7**, 108 (1939).

² O. Klein and E. Lange, Zeits. f. Elektrochem. **43**, 570 (1937); **44**, 562 (1938). An earlier rough measurement of the Volta potential mercury/solution was carried out by A. Frumkin and A. Donde, Zeits. f. physik. Chemie **123**, 339 (1926).

³ J. Bernal and R. Fowler, J. Chem. Phys. **1**, 538 (1933).

⁴ A. Frumkin, Coll. Symp. Ann. **7**, 96 (1930).