

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

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Citation: *The Journal of Chemical Physics* **7**, 552 (1939); doi: 10.1063/1.1750486

View online: <http://dx.doi.org/10.1063/1.1750486>

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## LETTERS TO THE EDITOR

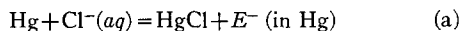
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### Calculation of the Absolute Potential of the Normal Calomel Electrode from the Free Energy of Hydration of Gaseous Ions

In a recent article Latimer, Pitzer and Slansky<sup>1</sup> 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  $\varphi_1$ ,  $\varphi_2$  and  $\varphi_3$ , respectively. The Volta potential between mercury and solution, and therefore the energy term which must be subtracted from the value of  $\Delta F$  (0.495 v) calculated for reaction (a), is equal to  $(\varphi_1 + \varphi_2 - \varphi_3)$ . It follows from this consideration that  $\Delta F$  determines the equilibrium value of  $\varphi_1 + \varphi_2 - \varphi_3$ , and not the equilibrium value of  $\varphi_2$  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.<sup>2</sup> They found a Volta potential between mercury and  $\text{Hg}^+$  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  $\text{HgCl}$ . 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  $\varphi_3$  ("real" hydra-

tion 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 collaborators) 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  $\varphi_3$  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;  $\varphi_3$  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 Fowler<sup>3</sup> (114–116 kcal. for  $\text{Na}^+$ ) 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  $\varphi_2'$  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.<sup>4</sup>

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May 20, 1939.

<sup>1</sup> W. Latimer, K. Pitzer and C. Slansky, *J. Chem. Phys.* **7**, 108 (1939).  
<sup>2</sup> 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).

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

<sup>4</sup> A. Frumkin, *Coll. Symp. Ann.* **7**, 96 (1930).

### The Raman Effect of Dibromo-Difluoromethane and Dibromo-Chloromethane

Nine Raman lines have been observed for both dibromo-difluoromethane and dibromo-chloromethane using our usual equipment.<sup>1</sup> A sodium nitrite filter was used with the former substance and it was kept cold during exposures by means of a jacket through which cold water circulated. There was no perceptible photochemical action under these conditions.

The dibromo-chloromethane, which was run without a filter or cooling, showed slight photochemical decomposition under the mercury lamps and was redistilled in a current of nitrogen between successive exposures.

The results obtained are shown in the Tables I and II.

Three faint sharp lines were also observed on the dibromo-chloromethane plates at 155, 222 and 541  $\text{cm}^{-1}$  as Stokes lines from 4358. They can be attributed to bromoform present as an impurity. The line reported at 658.7, even though it nearly coincides with the bromoform line at 655, is too intense relative to the other bromoform lines to be due to bromoform alone.

The dibromo-chloromethane was synthesized from chloro-acetal according to the method of Jacobsen and Neumeister.<sup>2</sup> (Boiling range 119–120° at 748 mm. Density 2.462 at 15°.)

TABLE I. *Raman lines of dibromo-difluoromethane.*  
 $a=4046$ ;  $b=4077$ ;  $c=4358\text{A}$ .

$\Delta\gamma \text{ cm}^{-1}$	% MEAN DEVIATION	EXCITING LINES		NO. OF READINGS	RELATIVE INTENSITIES
165.3	0.48	<i>a</i>	<i>c</i>	9	7
282.2	.32		<i>c</i>	4	3
330.1	.30		<i>c</i>	4	3
340.0	.26	<i>a</i>	<i>b</i>	10	10
367.4	.49		<i>c</i>	2	2
622.9	.24	<i>a</i>	<i>c</i>	9	6
815.8	.06		<i>c</i>	3	4 (broad)
1076.7	.06		<i>c</i>	3	4 (broad)
1142.0	.03		<i>c</i>	2	1 (diff.)

TABLE II. *Raman lines of dibromo-chloromethane.*  
 $a=4046$ ;  $b=4077$ ;  $c=4358\text{A}$ .

$\Delta\gamma \text{ cm}^{-1}$	% MEAN DEVIATION	EXCITING LINES		NO OF READINGS	RELATIVE INTENSITIES
168.3	0.53	<i>a</i>	<i>c</i>	8	8
201.1	.50	<i>a</i>	<i>c</i>	8	7
279.4	.43	<i>a</i>	<i>b</i>	10	10
568.9	.28	<i>a</i>	<i>c</i>	7	8
658.7	.27	<i>a</i>	<i>c</i>	6	5 (broad)
749.5	.32	<i>a</i>	<i>c</i>	3	3 (diff.)
1145.5	.14		<i>c</i>	2	1
1193.8	.24		<i>c</i>	2	1
3022.6	.03	<i>a</i>	<i>c</i>	6	7

The dibromo-difluoromethane was furnished by the E. I. duPont de Nemours Company and was laboratory fractionated with a boiling range of about 0.5°. We wish to thank Dr. A. F. Benning of the Jackson Laboratory for the loan of this substance. Further consideration of these results will appear in a later publication.

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<sup>1</sup> G. Glockler and C. E. Morrell, *J. Chem. Phys.* **4**, 15 (1936).

<sup>2</sup> O. Jacobsen and R. Neumeister, *Berichte* **15**, 600 (1882).

### A Thermal Method for the Separation of Isotopes

Various experiments have been carried out in this laboratory to determine the final efficiency that can be obtained with the thermal method for the separation of isotopes and gases.<sup>1</sup> The separation chambers used in these tests were of the concentric glass tube design, the diameter of the inner tube being one cm and the wall separation seven mm. Chambers one and three meters in length were studied. A 50–50 ammonia-methane mixture at 25 cm pressure was chosen for convenience of analysis.

The results obtained so far can be summarized as follows.

(1) The change in the separation factor (ratio of initial to final concentrations) for a definite time interval is independent of the height of the tube, provided the separation has not reached a value greater than 90 percent of the final equilibrium concentration.

(2) The final equilibrium value for the separation factor varies directly as the height of the tubes within wide limits.

(3) Measurements for the variation of the separation in samples of gas drawn from different heights within the tubes show that, for the three-meter tube, the relative concentration of the two components is very nearly constant for a distance of several centimeters from the bottom of the tube; for greater distances the separation factor changes appreciably.

(4) The mass speed appears independent of the length of the tube. At least 8 cc of gas (NTP) can be withdrawn per hour without changing the separation factor. For the one-meter tube the separation factor was 1.3 and for the three-meter tube 2.0.

(5) The efficiency of separation of a component of low concentration can be improved by the addition of sufficient