Space Charge in Electrolytes

A. R. Gordon

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Some comments are also appropriate on the results of Langseth and Bernstein[4] on the energy difference in 1,1,2,2-tetrachloroethane in the liquid phase. They found that, in contrast to the small value in the gaseous state, there is an energy difference of *ca.* 1100 cal. mole^{-1} between the isomers in the liquid. A similar change in energy difference between the isomers of 1,2-dichloroethane in the liquid and gas is well known,[5,6] (ΔE is *ca.* 0 and 1200 cal. mole^{-1} respectively) and was explained by Watanabe, Mizushima, and Masiko[7] using an electrostatic model based on the Onsager internal field. Their results show that the more polar forms will always be stabilized in the liquid state due to dipole interactions. In the case of 1,1,2,2-tetrachloroethane, starting with the conclusion from Thomas and Gwinn's dipole moment data that the *trans*- and skew forms have equal stability in the gas phase, the observed change in energy difference on passing to the liquid can thus be explained as due to the extra stabilization of the skew form. This is consistent with the spectroscopic data of Langseth and Bernstein.[4] The alternative possibility, that the compound has a high energy difference between its isomers in the vapor—the stable form would have to be skew because of the observed dipole moment—would lead to an even greater energy difference in the liquid.

The view that in these simple branched paraffins the energy difference between the rotational isomers is approximately zero, would necessitate some change in the model used by Pitzer[8] in calculating their thermodynamic properties.

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[2] G. J. Szasz and N. Sheppard, J. Chem. Phys. 17, 93 (1949).
[3] D. W. E. Axford and D. H. Rank. personal communication, to appear shortly in J. Chem. Phys.
[4] A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1940).
[5] H. Gerding and P. G. Meerman, Rec. Trav. Chim. 61, 523 (1942).
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[8] K. S. Pitzer, J. Chem. Phys. 8, 711 (1940).

Space Charge in Electrolytes

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IN the October issue of this *Journal*, Reed and Schriever[1] report that a space charge exists in a column of electrolytic solution during electrolysis, and consequently state that Ohm's Law is invalid for such conductors. Their method consists in applying a potential of 8 volts to metal electrodes forming the ends of a cell 40 cm in length, the electrolyte being a 0.0024N solution of a salt of the metal (copper, zinc, nickel or aluminum) forming the electrodes. The potential between a probe of the metal in question and the anode or cathode is then determined as electrolysis proceeds. As might be expected, the probe potential was not a linear function of the distance x from the cathode, and Reed and Schriever then compute the space charge from the deviation of the measured potential gradient from 20 mv/mm.

(1) The usual test of Ohm's Law is to determine whether the resistance between two points in a conductor is independent of the current; moreover to obtain the true potential drop between two points in a solution, the conditions must be such that the two liquid-electrode potentials are equal and opposite in sign. Thus Jones and Bollinger,[2] in a classic research employing the a.c. bridge, showed that Ohm's Law was valid within a few thousandths of a percent. Measurements in this laboratory,[3] employing the direct current method in which the potential difference was measured between shielded, reversible probe electrodes remote from the anode and cathode, showed the same to be true. Finally, the results by both methods for a series of salts were in agreement within the precision of either set of data.

(2) "Hard" metals, such as those used by Reed and Schriever, are notoriously erratic in their behavior, and there is no evidence that the "chemical potential" between a probe and a current electrode will be the same when current is passing as when it is not.

(3) Reed and Schriever ignore electrode overvoltage; as is well known, this depends in a complicated way on the nature of the electrode surface, current density and the concentration of the solution in immediate contact with the electrode. See a recent Faraday Society symposium on electrode processes.[4]

(4) No account is taken of concentration changes in solution due to the electrode processes, migration and diffusion. For example, taking the transference number of sulfate ion in zinc sulfate solution[5] as 0.6, a concentration at a point near the anode twice that obtaining in the bulk of the solution, will of itself introduce a concentration e.m.f. of approximately 10 mv. To take the "five minute" curve of Fig. 2 as an example, the deviation is linear within the estimated precision of ± 4 mv for x between 2 and 32 cm, i.e. the results are consistant with an ohmic drop of approx. 7.87 volts and concentration e.m.f. plus overvoltage at the two electrodes of 0.13 volt—an entirely reasonable value.

(5) The slow changes in potential with time are much more reminiscent of slow processes such as migration and diffusion than of the electrostatic effect postulated. It would seem probable that Reed and Schriever have been studying the complicated effects of overvoltage and concentration changes in the liquid brought about by diffusion, migration, convection and the solution and deposition of the metal. In the opinion of the writer at any rate, their results do not demonstrate the existence of a space charge.

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[3] H. E. Gunning and A. R. Gordon, J. Chem. Phys. 10, 126 (1942); 11, 18 (1943); G. C. Benson and A. R. Gordon, 13, 470 (1945); 13, 474 (1945).
[4] Faraday Soc., Discussions, 1947 No. 1.
[5] B. B. Owen and R. W. Gurry, J. Am. Chem. Soc. 60, 3074 (1938).

Reply to "Space Charge in the Electrolytes"*

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November 28, 1949

THESE replies to Professor Gordon's criticisms will be in the order given in his letter.

(1) Ohm made three important discoveries, two of which are usually called "Ohm's Law." The first may be written, the potential difference between the ends of a piece of conductor is directly proportional to the current through it. The second may be written, the current in a single-path complete circuit is proportional to the electromotive force in that circuit. The third may be written, the resistance of a piece of uniform conductor is directly proportional to its length and inversely proportional to the area of its cross section. A combination of the first and third leads to the statement that the potential gradient is the same at all points along a uniform conductor. Since the potential gradients were found *not* to be constant by Reed and myself we stated that Ohm's law was not obeyed. This appears to be an entirely proper deduction. Obviously we were not referring to the relatively thin layers next to the two electrodes.

Conductance measurements made by alternating-current methods need not be considered here because such electrical conditions are entirely different from those existing in direct-current methods.

Professor Gordon's cell for determining relative conductances by a direct-current method consisted of a Pyrex glass cylinder approximately 16 cm long by 5 cm in diameter with the current electrodes inserted in 5-cm long axial extensions 13 mm in diameter, at each end of the cylinder. The two probe-electrodes were inserted in lateral extensions 4 cm long and 13 mm in diameter, the centers of the two extensions being 10 cm apart. The axial distance from each current electrode to the nearest potential electrode was some 8 cm (distances were estimated from the drawing in his paper). According to his Table I the currents varied from 0.4 to 2 milliamperes, which lead to current densities in the cylinder to 2 to 10×10^{-5} amp/cm^2. The current through the cell

was reversed after each probe-potential measurement. The time interval during which the current passed through the cell in one direction was not stated. Since the potential probes were 8 cm in front of the current electrodes, and since the current was reversed regularly, it is entirely possible that appreciable space-charge effects never reached into that part of his cell between the potential probes.

(2) Let us grant that the "chemical potential difference" between the probe and the current electrode changed when the current passed. Our deviation-time runs were quite reproducible. Thus whatever change existed at the end of, say, 10 minutes for one run, also existed at the end of 10 minutes for every other run regardless of the position of the probe along the column. The net effect of this change, *if* it existed, would have been to raise, or lower, every point of our deviation-distance curve for 10 minutes, by the same amount. Thus the slope and curvature of the curve at every point would have remained unchanged (except very close to the electrodes where observation could not be made). Therefore the calculated potential gradient and space-charge distributions would have been unaffected.

(3) Overvoltage was not ignored even though it was never mentioned specifically. We did state specifically that in a relatively thin layer next to each current electrode there may have existed electrical double layers and other space-charge effects together with concentration changes which may have caused certain electromotive forces. These were intended to include any and all, known and unknown, complicated effects near these electrodes, including overvoltages. Again, since our deviation-time runs were reproducible, whatever complicated conditions existed near a current electrode at the end of, say, 10 minutes for one position of the probe, that same condition existed for all positions of the probe at the end of 10 minutes. These effects were specifically taken into account in the theory which we presented on page 936. Thus the shape of our potential distribution curves cannot be explained on the basis of "potentials" existing at or near the current electrodes; they must be explained by something taking place throughout the column of electrolyte.

(4) Concentration electromotive forces and all other processes which may have taken place at or near the current electrodes, have been taken into account in (3) above and therefore need not be discussed again. Concentration changes out in the column of electrolyte were considered in our paper on pages 937 and 943 and that material will not be repeated here. Since our current densities were only some 5×10^{-5} amp/cm^2 the resulting concentration changes very near the electrodes after the current had passed 15 minutes, must have been exceedingly small. Appreciable diffusion effects must have taken place only very close to the electrodes since diffusion is a very slow process. All such effects near the electrodes have been taken into account as was stated above. Additional evidence, that these current-electrode effects were properly allowed for, is that our observed deviations for points near the center of the column, were the same when measured with respect to the anode as when measured with respect to the cathode. The shapes of our potential distribution curves cannot be explained by phenomena at and near the current electrodes.

(5) The factors mentioned by Professor Gordon in his paragraph (5) have all been considered in (2), (3), and (4) above, except for "convection." Any stirring of the solution either by convection or otherwise made reproduction of data impossible. A thorough stirring removed all space-charge effects and other effects. Our data were reproducible. Therefore, I believe it is safe to say that "convection" cannot help to account for our observed potential distribution curves.

In Professor Gordon's first paragraph, in referring to our work, he stated, "As might be expected, the probe potential was not a linear function of the distance x from the cathode." All relative conductivity measurements by a d.c. method require an electrolyte standardized by an absolute determination of its conductivity by a d.c. method. The absolute determination requires the measurement of the length, the cross-sectional area and the resistance of a uniform column of the electrolyte, together with the assumption that the potential gradient in that column is constant. If the potential gradient in our work was "expected" to be variable, would not one also "expect" the potential gradient in the absolute determination apparatus to be variable? If so then the absolute determination would cease to be a measure of the actual conductivity.

* A. R. Gordon, J. Chem. Phys. **18**, 145 (1950).

Intramolecular Forces between Non-Bonded Atoms

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IN a recent series of papers T. Simanouti[1] has applied the Urey-Bradley field[2] to a number of halogen derivatives of CH_4, C_2H_6 and SiH_4. The important conclusion reached by T. Simanouti is that, in molecules of the above type, repulsion forces between non-bonded atoms are not negligible compared with the valency forces. Terms to take account of such forces should, therefore, be included in functions giving the variation of molecular potential energy with changes of internal configuration. We had reached the same conclusion by considering the tetrahalides of the Group IV elements, the trihalides of boron and some analogous oxy-anions, and the hexafluorides of the Group VI elements.[3] We had found moreover, as T. Simanouti has done, that the force constants necessary to take account of these van der Waals' type repulsion effects are of the order of magnitude to be expected from a consideration of the known potential energy functions for the interaction between analogous inert gas atoms which have been deduced from equation of state studies[4] (see Table IV in Part III of Simanouti's series, and Table II in Part IV and Table II in Part V of our series). It seems to us that this is a most important conclusion concerning intramolecular forces. Moreover, it is confirmed by the calculations of F. H. Westheimer and J. E. Meyer,[5] those of T. L. Hill,[6] and by other observations.[7]

It is noteworthy that this general conclusion regarding the magnitude of the forces between non-bonded atoms has been reached independently by T. Simanouti and by us even though the two sets of calculations are made using rather different force fields. T. Simanouti has used a simple valency force field plus these repulsion terms, whereas we have used, as our basic field, one which is based more closely on modern ideas of directed valency. We have called it the orbital valency force field.

In silicon tetrafluoride T. Simanouti found that the ratio of F to F' for F$\cdots$F repulsion is very different from what would be expected from a consideration of Ne$\cdots$Ne repulsion (see Table IV of his Part III). We had come to the same conclusion and commented on this fact in Part II of our series (see also Table II in Part II). On the other hand the behavior of carbon tetrafluoride seems to be quite normal. It would be interesting if the vibration frequencies of the tetrafluorides of the other Group IV elements could be determined to see whether they behave normally like CF_4 or abnormally like SiF_4.

Our calculations and those of Simanouti show clearly that, in a variety of molecules, it is important to take account of the repulsion between non-bonded atoms in constructing force fields to account for their vibration frequencies.

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[3] D. F. Heath and J. W. Linnett, Trans. Faraday Soc. **44**, 561, 873, 878, 884 (1948); ibid. **45**, 264 (1949).
[4] See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 285.
[5] F. H. Westheimer and J. E. Meyer, J. Chem. Phys. **14**, 733 (1946); ibid. **15**, 252 (1947).
[6] T. L. Hill, J. Chem. Phys. **16**, 399, 938 (1948).
[7] See references in E. H. Hughes, Quart. Rev. Chem. Soc. **2**, 132 (1948); see also, J. R. Lacher, J. Am. Chem. Soc. **69**, 2067 (1947).