

Intramolecular Forces between NonBonded Atoms

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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^{-8} amp/cm² 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. Simanouti¹ has applied the Urey-Bradley field² to a number of halogen derivatives of CH₄, C₂H₆ and SiH₄. 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 studies⁴ (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 CF₄ or abnormally like SiF₄.

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.

¹ T. Simanouti, J. Chem. Phys. 17, 245, 734, 848 (1949).

² H. C. Urey and C. A. Bradley, Phys. Rev. 38, 1969 (1931).

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).