

On Diffusion Equilibria of Electrolytes

Otto Halpern

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Rule II

Draw the shortest set of n paths of the kind described in rule I. If there is a point common to p paths (only points for which p is 3 or greater are to be considered) the number of times B will occur in uncrossing A is $(p-2)$. In determining p we note that frequently for an eigenfunction A parts of the lines in A are not traversed by the set of n paths. All points connected by untraversed lines are for this purpose to be counted as one point. Having done this one further procedure may be necessary in applying rule II. Any path which passes through a point and which with the perimeter circle separates other paths common to the point into two groups is omitted in determining p for the point. This discarding is continued until there are no more such paths.

The coefficients for all uncrossed bonds are positive if the convention is adopted in every B and A of arranging the orbitals in order around a circle and always directing the arrow representing a bond toward the orbitals with the higher ordinal number.

These rules have been checked for all possible patterns of 5 bonds or less. A more complicated rule is required for direct application to more than 5 bonds. However, eigenfunctions involving 6 or more bonds are readily reduced by comparatively few uncrossings to cases to which our simple rules apply.

HENRY EYRING
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Frick Chemical Laboratory,
Princeton University,
April 13, 1934.

On Diffusion Equilibria of Electrolytes

A study of the fundamental elements contained in the theory of electrolytic conductivity which will be reported later, has led among others, to some results about the limiting case, i.e., diffusion equilibrium under the influence of external forces.

Consider for the purpose of illustration the distribution of charged colloidal particles and ions in a gravitational field. If there are only very few ions present which carry charges of the same sign as those present on the colloidal particles, the problem can be solved with sufficient accuracy for dilute solutions. It is found that there occur large deviations from the Boltzmann distribution which tend to make the latter more uniform. At the same time the rate of establishment of equilibrium is greatly reduced. An increase in concentration tends to diminish the deviation

from the Boltzmann distribution. The presence of ions carrying charges of the same sign as the colloidal particles acts in the same direction.

Similarly it can be shown that the diffusion potential in electrolytes does not assume its classical value.

These effects can perhaps be described by the statement that the activity coefficients of the charged particles lead to an apparent reduction in the value of their diffusion coefficient.

The writer hopes to be able to present shortly a more detailed account of these investigations.

OTTO HALPERN

New York University,
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April 14, 1934.

Observations on the Synthesis of Tetra-Deutero Methane

In the course of the synthesis of tetra-deutero methane with the object of studying its physical properties, we have made some observations on the relative velocities of reactions between the proto water and aluminum carbide and the deutero water and aluminum carbide.

Carefully prepared aluminum carbide in fairly finely divided form was placed in a sealed container fitted with a small reflux condenser, and the proto water added at low temperatures. The whole system was evacuated and the mixture allowed to come to room temperature. Gas bubbles formed at ordinary temperatures and in the course of 10 or 15 minutes raised the pressure in the apparatus to atmospheric. The mixture was then raised to about 80°C and the methane generated collected over mercury. It required on the average 2 minutes to collect 100 cc of methane.

With the same apparatus and aluminum carbide from the same batch and of the same fineness of division, the same method was attempted using the deutero water. At room temperatures, no reaction took place in the course of two hours. We then filled the apparatus with CO₂ at atmospheric pressure and raised the temperature

to 80°. It now required 46.5 minutes to collect the first 100 cc of methane gas. This gives a ratio of the velocities for the two reactions of approximately 23. This seems to be the highest ratio so far observed for reactions involving compounds of the two hydrogens. Not until the reaction vessel was heated to about 65° were we able to see any bubbles of methane form in the reaction vessel. The next 100 cc were collected at 90°. At this temperature, the rate of evolution of the gas was about three times that at 80°.

The temperatures were controlled by maintaining the temperature of a water bath within a degree or two of the temperatures given. There is a possibility, of course, of slight error in this way, but that there is an enormous difference in the velocities of the reactions cannot be doubted.

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DONALD PRICE

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April 16, 1934.