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AN APPLICATION OF THE
CONDUCTIVITY and FREEZING POINT METHODS
for the determination of the
MOLECULAR WEIGHTS OF ELECTROLYTES

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OBJECT.

To determine whether in such compounds as potassium permanganate, ferric chloride, etc., the formula should be written in its simplest form or should be doubled.

It is a well known fact that in writing reactions in which the oxidation by permanganate is taken into account either the simple molecular weight is doubled, or else the formula $K_2MnO_4$ is used. According to Remsen, and others, we should always use the simplest molecular formula unless we have good evidence that a more complex formula should be used. If we use the formula $K_2MnO_4$, we must consider that in the oxidizing phenomena each molecule of permanganate gives up two and one-half atoms of oxygen. For a number of years the idea of half atoms has grated upon the nerves of the writer and has led to the investigation of which this paper is an important part. The writer is aware of the fact that there is no argument in the above any more than there would be to state that the formula for nitric acid should be $H_2N_2O$, because in the formation of nitric anhydride two molecules of nitric acid give off one of water. Or, in other words, a molecule of nitric acid gives off one-half molecule of water.

However this may be, the incentive to this work has been the desire to know whether the simple formula, $K_2MnO_4$, or the doubled formula, $K_2Mn_2O_8$, is the correct one.

This has led to a combination of methods which would seem to be applicable in the solution of our problem.
In the course of this investigation two other compounds have presented themselves as being of the same order and as having problems to be solved by the same methods. These are Ferric chloride and Aluminum chloride. For each of these both formulas are used, namely, FeCl₃ and Fe₂Cl₆, and also AlCl₃ and Al₂Cl₆. A study of vapor density shows the simpler formula to be correct in either case at something above 400°, and below that temperature the doubled formula should be used. As these molecular weight determinations have been made for the gaseous state and as very few, if any, of our ordinary chemical reactions take place in this state, it is evident that the determinations of molecular weights of substances in solution and primarily in solution in water are by far the most important.

The work of de Coppet (1) and of Raoult (2) in 1871 and 1882-84 respectively, have given us the method for determining the molecular weights of certain compounds in solution. As yet there is no general way to determine the molecular weights of solids as such, although probably in a few instances such determinations have been made.

It is evident, then, that the applications of methods to the determination of molecular weights of substances in solution is a contribution to general knowledge and will serve not alone to answer the questions above proposed, but to serve as a new method which can be applied to substances which have heretofore been considered exceptions.
METHOD

Determine the molecular weight by the freezing point method regardless of dissociation as though the substance were a non-electrolyte, then measure the conductivity and calculate the amount of dissociation. As dissociation can be measured by the freezing-point method as well as by conductivity one has simply to apply the correction to obtain the correct molecular weight.

THEORY.

The molecular lowering for non-electrolytes— that is, the lowering by a gram-molecule dissolved in 1000cc of water— is 1.88. That for electrolytes may be called $x$ as it varies for different electrolytes depending upon the amount of dissociation. As the greater dissociation means more particles which shall exert osmotic pressure and lower the freezing-point, the following formula must obtain where $i$ is the van't Hoff ($\beta$) coefficient of dissociation.

$$\frac{x}{1.88} = 1$$

Now $\Lambda$, the activity coefficient or amount of dissociation, can can be gotten readily from the formula $\Lambda = \frac{\lambda}{\lambda_0}$ where $\lambda$, and $\lambda_0$ are the conductivities at the given dilution and infinite dilution respectively, and $\Lambda$ can be easily obtained by the conductivity method. In terms of $\Lambda$, $i = 1 + (K - 1)\Lambda$ where $K$ is the number of ions into which the substance dissociates.

It is evident that having obtained $i$ by conductivity methods its value can be substituted in the first equation and the abnormality of freezing-point can thus be measured and so the true molecular weight of our compound can be obtained.
The conductivity need not be measured at the same concentration as the freezing point lowering, as for strongly dissociating substances which we can assume we have in the present investigation, Rudolphi's law (4) will help us determine, the conductivity at any dilution. His formula is \( \frac{x}{(1-\alpha)v} = \text{const.} \)

Ostwald's law, it will be remembered, holds only for the weakly dissociated substances although why this is so is not yet known. Ostwald's formula (5) is based on the application of gas laws for dissociated gases to dissociated solutions. His law is expressed by the equation \( \frac{x^2}{(1-\alpha)v} = \text{const.} \) Rudolphi's is purely empirical.

In comparing "i" by conductivity methods with "i" from freezing point lowering results, the number of ions is taken into account and \( \alpha = \frac{1}{K - 1} \) where \( K = \) the number of ions. This is another form of the equation above \( i = 1 - (K - 1)\alpha \).

In brief, then, we have all of the data to work with when we have obtained \( \Delta \) by the freezing point method and \( \mu_v \) and \( \mu_a \) by the conductivity method.

**HISTORY.**

Having indicated the methods to be carried out and having outlined the theory of the procedure a short history of the work done in the lines above alluded to will be given for the sake of completeness and as a basis for the work reported in this paper.

Cavendish's assistant Blagden in 1788 (6) showed that the depression of freezing points caused by solutions was proportion-
al to the amounts of the solute. Rudorff (7) and de Coppet (1) (1861 and 1871) brought out the same principle and the latter showed that the depressions would be the same for equimolecular quantities of the solutes provided the solutes were of the same nature.

Raoult (8), in 1882, by a study of organic substances arrived at the conclusion that "equimolecular solutions have the same point of solidification". It is evident that from this it is but a step to the principle of molecular weight determinations calculated from the depressions of the freezing points. Raoult's work, then, has resulted in a method for the determination of molecular weights of solids and liquids in solution. The apparatus for making these determinations was devised by Beckmann (9) in 1888 and will be described later. It is satisfactory for molecular weight determinations but hardly accurate enough for the measurement of dissociation and so has been improved by Loomis, (10) Nernst and Abegg, (11), Ponsot, (12), Jones, (13), Lewis, (14), and others. Raoult, (15), has used the best points of each and perfected the apparatus so that dissociation measurements may be made very accurately.

The improvements have been made in the details while all forms have been based on the same principle. Jones uses a large amount of solvent, has a special stirrer which he considers very efficient, and uses a Beckmann thermometer graduated to thousandths which can be read to ten-thousandths. Loomis reads his thermometer by a specially constructed telescope with parallel cross hairs so arranged that he can read accurately to ten-thousandths. Certain modifications for hygroscopic solvents have been made by Beckmann, (16), and he
also devised the differential thermometer known by his name and to be described later.

The pioneer of work along the lines of electrolytic conductivity was Faraday, (17), although Davy and Berzelius had advanced theories to explain it as also had Grotthus in 1805. The positive and negative parts of the molecules Faraday named ions.

Hittorf's work, (18), on the migration of ions during electrolysis has become a classic. This he studied under different conditions and not only obtained the relative velocities but determined just what ions were present. Kohlrausch, (19), has devised the best apparatus for measuring the conductivity of electrolytes. This will be described later. Pfeffer's classical researches, (20), on osmotic pressure led him to the generalization that strong acids and bases and their salts give an excessive osmotic pressure and van't Hoff, (21), showed the mathematical relations between the gas laws and the laws for solutions.

Arrhenius, whose theory of electrolytic dissociation is becoming more and more accepted among chemists and physicists, in the first volume of the Zeit.f. Phys. Chem.said, "If a gas shows (such) a deviation from the law of Avogadro, it is explained by assuming that the gas is in a state of dissociation.............The same expedient may, of course, be made use of to explain the exceptions to van't Hoff's law." This is practically his text and very few theories have been advanced which have explained, at least one step further, so many previously unexplained phenomena. (e.g. The colors of
solutions; the action of indicators; etc.) It will thus be seen that, though heretofore the molecular weights of electrolytes have not been obtained cryoscopically as they were considered exceptions, nevertheless, if the dissociation is measured and made allowance for, we can, from the freezing point lowering, calculate the molecular weights.

APPARATUS.

The well known apparatus of Beckmann, (9), was used for the freezing point measurements consisting of a battery jar about 22 x 15 cm which contained the freezing mixture, the air jacket about 3 x 15 cm and the freezing vessel 2 1/2 x 18 cm.

The difference in temperature was read by a Beckmann differential thermometer reading to hundredths which by a lens was read to thousandths of a degree with considerable accuracy. The readings and the calculations are appended to this paper.

The apparatus to be used for measuring the conductivity from which to calculate the dissociation values was proposed by Kohlrausch, (19), and consists of a standard resistance box, a slide wire Wheatstone's bridge, Kohlrausch conductivity cell, an induction coil and storage battery, and a telephone receiver.

PRECAUTIONS and CORRECTIONS.

Only the purest crystals were used and these weighed to tenths of a milligram. The solvent, water, was redistilled from a permanganate solution and as the freezing point of
this did not vary from that of the distilled water of the laboratory it was probable that there was no reaction between the permanganate and the water.

The water was weighed to centigrams and about 20 grams taken. That is, the water was weighed to one part in 2000. Not far from a quarter of a gram of permanganate was taken in each experiment.

The ferric chloride solution was titrated with standard silver nitrate after the iron was removed by ammonia, filtered, and neutralized exactly with nitric acid.

Change in concentration due to undercooling was calculated by the formula of Jones, (23), \( T = \frac{su}{w} \) where \( T \) = amount solidifying, \( s \) = specific heat \( = 1 \), \( w \) = latent heat of fusion \( = 80 \) and \( u \) = amount of undercooling in degrees. The usual precautions were taken in reading the thermometer and readings were estimated to thousandths of a degree by the use of a lens.

**FORMULA.**

\[
M = \frac{C'w}{\Delta W}
\]

- \( M \) = Molecular weight of substance.
- \( C' \) = constant \( \times 100 = 1880 \)
- \( w \) = weight of dissolved substance.
- \( W \) = weight of solvent.
RESULTS

Experiment I Permanganate.
Freezing point of water 3.793°
W = 20.165 gr.  w = .3145 gr.
Freezing point of solution 3.450°
\[ \Delta = 0.343° \quad M = 85.58 \]

Experiment III Permanganate
F. Pt of water 3.788°
W = 19.92 gr.  w = .2741 gr.
F. Pt of solution 3.510°
Undercooling 1.28°  \[ \Delta = 0.278° \]
M = 94.57

Experiment V Ferric Chloride
W = 20.00 g  w = 2.605 g
F. Pt of water 3.788°
F. Pt of solution 2.270°
\[ \Delta = 1.518° \quad M = 161.33 \]
Undercooling very slight

Experiment VII Ferric Chloride
W = 15.00 gr.  w = 1.3025 gr.
F. Pt of water 3.812°
F. Pt of solution 2.807°
\[ \Delta = 1.005° \quad M = 162.43 \]
Undercooling prevented.

Experiment II Permanganate.
Freezing point of water 3.788°
W = 19.92 gr.  w = .2741 gr.
F. Pt. of solution 3.510°
\[ \Delta = 0.288° \quad M = 92.06 \]
Corrected for undercooling 1.95°

Experiment IV Ferric Chloride
F. Pt of water 3.788°
W = 19.923 gr  w = .4534 g
F. Pt of solution 3.359°
\[ \Delta = 0.429° \]
Undercooling 0.90°  M = 96.42

Experiment VI Ferric Chloride
W = 20.00 g  w = 2.605 g
F. Pt of water 3.812°
F. Pt of solution 2.27°
\[ \Delta = 1.542° \quad M = 159.4 \]
Undercooling 0.3°
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