

Note on Kohlrausch's Theory of Ionic Velocity

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but a slight diminution, quite beyond the limits of accuracy of the apparatus. For instance, a 5-per-cent. solution of naphthalene has a diminution of under 1 per cent.

A strict interpretation of the theory of osmotic pressure in solutions has been made by Prof. J. J. Thomson, in his "Applications of Dynamics to Physics and Chemistry," § 97, where he finds that 1 gram-equivalent per litre would decrease the compressibility by 1 part in a thousand. Non-electrolytes in dilute solution appear to follow this law; this is in agreement with their other properties, such as alteration in boiling- or freezing-points.

The diagram will serve to explain the general arrangement of the apparatus.

XX. *Note on Kohlrausch's Theory of Ionic Velocity.* By
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of Trinity College, Cambridge *.

KOHLRAUSCH calculates his numbers for the specific velocities of different ions from measurements of the conductivities of salt-solutions, and of their migration constants, on the supposition that all the molecules of the salt present in solution are actively concerned in conveying the current. The values thus obtained were found to agree with experiment in certain cases by Prof. Oliver Lodge, and an investigation I am now engaged in carrying out seems also to confirm them. It seems to be generally supposed that this is inconsistent with any theory (such as that of dissociation) which supposes only a certain part of the salt to be active (see Lodge, B. A. Report, 1886, p. 391), though some such form of theory seems to be required by the relations shown to exist by Arrhenius, Van't Hoff, Ostwald, and others. If we examine the matter a little more closely, however, I think the two suppositions can be reconciled. Suppose that the ratio of the numbers of the active and the inactive molecules (which is generally supposed to measure the "dissociation") represents in reality the average ratio of the time during which each molecule is active to the time during which it is inactive. Every mole-

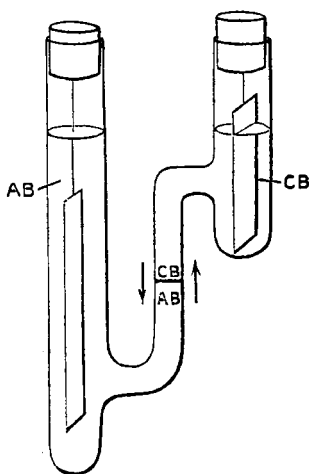
* Read May 9, 1891.

cule is in turn active, but *at any instant* only a certain fraction of the molecules are active. [In terms of the dissociation hypothesis, the dissociation ratio measures the ratio of the mean free time to the mean paired time of the ions.] This is, of course, equivalent to supposing a certain fixed fraction of the whole number of molecules to be active, as far as statical effects, such as osmotic pressure, are concerned, but when we consider the velocities of the ions the case is different.

Kohlrausch calculates the relative velocity of the two ions $U = u + v$ from the molecular conductivity k/m , where k = specific conductivity of the solution, and m its contents in gramme equivalents of salt, $U_1 = u + v = k/m$. If now we suppose that at any instant only $1/n$ th of the number of molecules are active, we should apparently have to put $U_2 = \frac{kn}{m}$ in order that the same current may be carried, which would give $U_2 = nU_1$.

But this U_2 represents the actual velocity of the ions while they are "free," and if we take a "dynamical" view of the dissociation equilibrium, they are only free for $1/n$ th of their time; while combined they have no relative velocity, and so their *average* velocity for any *long* time is $\frac{1}{n}U_2 = U_1$, the same as on Kohlrausch's hypothesis.

The investigation alluded to above, at which I am now working, seems to yield excellent results for certain cases, though it is of somewhat limited application. It consists in observing the phenomena at the junction of two salt-solutions, one of which is differently coloured to the other, when a current of electricity is passed across it. Salts are chosen which have one ion in common and the other different. Let us represent them by AB and CB, and consider the junction phenomena. The effect of the molecular interchanges will be a motion of B ions in one direction, and a motion of C ions and of A ions in the other.



When a C ion crosses

the boundary, it again forms CB, but the colour of CB is different to that of AB, hence the boundary between the colours will move.

The method will be discussed when more experimental results are obtained; it appears that by measuring the rate of this motion the velocity of the ions can be arrived at. The present is merely a preliminary communication in explanation of the experiments shown to the Physical Society of London on the occasion of their recent visit to Cambridge.

XXI. *A Steam-Engine Indicator for High Speeds.*

By Prof. JOHN PERRY, *F.R.S.**

MEMBERS who are not practically acquainted with the errors of the ordinary steam- or gas-engine indicator are referred to a paper in the 'Proceedings of the Institution of Civil Engineers' (vol. lxxxiii. 1885) by Professor Osborne Reynolds, and an exhaustive discussion of the subject.

Whether we do or do not share Prof. Reynolds's view that even at low speeds of engines the errors in calculating horsepower are very considerable, because of the friction of the paper barrel and the stretching of the cord or wire which gives to the paper barrel a miniature motion of the engine piston, it is obvious that there will be more confidence in an indicator in which the motion-copying mechanism gives a very short stroke, is opposed by very small forces, and requires no string or wire. I do not pretend to get rid of the error in a spring which is due to change of temperature, but where great accuracy is required it is always worth while, when using this or any other indicator, to have a "boiler-pressure" line drawn upon the diagram, as well as an "atmospheric line;" and these two lines, with a pressure-gauge on the boiler, will give the scale to which the indicator at the time represents pressure and prevent error due to change of temperature of the spring.

In these days of high-speed machinery the most important defect of an indicator is its slow natural period of vibration.

* Read May 22, 1891.