

be great, when it comes to jostling their way for an appreciable distance in a definite direction through the surrounding crowd of solvent molecules, they will only be able to move very slowly. The migration of the ions is really a process of diffusion under the influence of electric forces, and will, of necessity, be very slow. I can assure Prof. Armstrong that no dissociation apologist will argue "that the charges act as brakes." It is by reason of their charges that the ions are urged forward by the electric forces. Without them, the velocities would not reach even those present figures which appear so despicable, but would merely take the much smaller values given by ordinary liquid diffusion. By placing in contact a coloured and a colourless solution, containing one ion in common, and passing an electric current across the junction, Prof. Armstrong can actually watch the ions migrating, and check the accuracy of the "conventional time-table."

W. C. D. WHETHAM.

Trinity College, Cambridge, November 27.

I FEEL sure that many readers, like myself, must have welcomed the sentiments expressed by Prof. Armstrong, in his article on this subject which appeared in your issue of November 26. It seems to me a duty of teachers to protest against the growing tendency there seems to be of putting forward the crude hypotheses of the ionist school, as though they had the same claim to acceptance as well established scientific laws, about which no reasonable doubt exists. So far from this being the case, the arguments commonly advanced in support of this theory seem to consist mainly of the misapplication of physical laws to a few carefully selected cases, aided by plausible but misleading assertions.

The objections that have from time to time been urged against both the views and the methods of argument have never received proper attention at the hands of the advocates of ionic dissociation. (Prof. G. F. Fitzgerald's Helmholtz Lecture; a paper by Prof. S. U. Pickering, *Journ. Phys. Soc.*, vol. xi., &c., remain unanswered.) It is, therefore, with the object of drawing attention to certain further difficulties and, as I conceive, errors in the above theory, rather than of evoking a discussion, that I now write.

In answer to the question—how is it that substances that are supposed to dissociate have "abnormally" large values for osmotic pressure, lowering of freezing-point, and reduction of vapour pressure?—we are told that the dissolved substance exerts the same pressure as if it were a gas and occupied the volume of the solvent, and that when dissociated it exerts a greater pressure on the solvent. Now, surely the term "osmotic pressure" in such a sense is misleading; not only is there no evidence of the substance exerting *pressure* on the solvent, but rather that by an attractive force it can allow water to pass into it, and hold it, up to a certain particular pressure, which, if exceeded, will cause water to pass out again through the semi-permeable wall. There is in this nothing at all comparable to gaseous *pressure*, which certainly never is the cause of another fluid entering it in a closed vessel; for I suppose it will hardly be imagined that in a gas diffusion-cell it is the pressure of the gas inside that causes another gas to pass by endosmosis into it. Similarly with regard to vapour pressure, an attraction between solvent and dissolved substance can account for a reduction of the vapour tension, but a pressure exerted on the solvent by the so-called gasified dissolved body cannot.

In regard to the lowering of freezing-point, we are actually sometimes told that this is a direct effect of the pressure of the salt on the solvent, with a beautiful reference to the lowering of the freezing-point of water by pressure, but with a calm oblivion of the fact that an increase of pressure would raise the freezing-point of other solvents in common use, such as benzene, acetic acid, &c. The alleged fact that the vapour pressures of a solution and of the solid solvent are the same at the temperature of the lowered freezing-point, may be true, but it affords no explanation of the way in which such depression of the freezing-point is brought about.

Ostwald, in his "Outlines of General Chemistry," p. 139, suggests a cyclic change of frozen solvent cooled to  $T - \Delta$ , melted by addition of the active substance, and raised to  $T$  again, but his data are fallacious in not taking into account the considerable difference in specific heat of the solid and liquid solvent, and the consequent variation of latent heat with temperature; so that

the heat evolved on freezing and absorbed on melting are not the same as he assumes them to be.

In that same Bible of the ionists a very curious representation of the action of a current on an electrolyte is given (p. 273), where Ostwald states that there is no place for any energy of the current being expended in doing the work of dissociation, and "that it has to perform no work in the matter at all." So much for the researches of Favre, Joule, &c., let alone the most elementary fact that the adverse E.M.F. of polarisation is roughly proportionate to the heat of combination of the electrolyte, and that E.Q. units of work must be expended in the transference of Q. units of electricity through the electrolytic cell, quite apart from work done against ohmic resistance. Apparently this idea owes its origin to the observation of Helmholtz, that feeble E.M.F.s can send exceedingly small currents through an electrolyte; but he points out in one of his papers, that if only one cubic centimetre of detonating gas were dissolved in the liquid, "its constituents need only migrate once in thirty-six days from the anode to the kathode in order to produce the observed current." He also showed that under so small a pressure as 10 m.m. an E.M.F. of 1.64 volt is necessary to separate visible gas, while the value calculated from the heat of combination of  $H_2$  and O is 1.49 volt.

In the same chapter (p. 275), Ostwald asks us to "imagine" two insulated vessels A and B, connected by a syphon and filled with solution of potassium chloride. Let a negatively charged body be brought near A, remove the syphon and charged body, then A is left with a positive charge. Now, he says, in A there must be an excess of free potassium ions, and if the electricity be conducted away, the potassium assumes its ordinary form, and, acting on the water, develops hydrogen "*which can be collected in a suitable apparatus and tested.*" Now I have calculated the electric capacity of such an arrangement, and supposing a very large beaker and an inductor placed close to it, to be used, the capacity of the condenser so formed could hardly be so large as .0001 microfarad. We can be generous and suppose that the vessel A is charged to a potential of 50,000 volts above the earth; with this potential the quantity would be  $5 \times 10^{-6}$  coulomb, which would yield approximately .0000005 milligramme of hydrogen! Did Ostwald repeat the charging by induction, removal of the syphon, and discharging 20 million times, and so obtain a milligramme of hydrogen which he "collected" and "tested." Even if this be "imagined," it would evidently do just as well to leave out the potassium chloride altogether, as water, as pure as Kohlrausch ever obtained it, would, with 50,000 volts, answer the purpose equally well.

When from this experiment (?) he draws the conclusion that—"The assumption that electrolytes contain free ions is not only possible but necessary," one may form some opinion of the kind of evidence that ionists consider conclusive.

In conclusion, I would like to ask ionists the following questions:—

Why do not ions, if free to move under the influence of small external electric forces, attract each other with immense force if they be charged with such enormous quantities of + and - electricity?

Where did they get these charges from?

Does dissociation absorb or evolve heat?

Why does not an E.M.F., however small, liberate gas from dilute sulphuric acid?

Why does solid  $Ag_2S$  conduct electrolytically? Is it "dissociated into ions"?

There are many other questions, but I should really like to know the answers to these first. I believe many of the points I have here raised have been brought forward by others before, so I lay claim to no originality in their suggestion, but hope that their consideration may give pause to those who are at present only partly "dissociated," until, at least, some reasonably satisfactory explanations are forthcoming.

E. F. HERROUN.

Queen's College, Harley-street, W., December 2.

### Responsibility in Science.

MY first letter (NATURE, October 15, p. 572) on this subject maintained that Prof. Poulton had no right to hold physicists as a body *responsible* for views presented by two or three of their number, however eminent. Prof. Poulton (NATURE,