LETTERS TO THE EDITORS

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Avogadro's Number and Loschmidt's Number

IN his Rutherford Memorial Lecture[1] Sir Charles Darwin writes: "The first estimate of Avogadro's number is due to Maxwell himself", and expresses his astonishment that Maxwell "should have published a fact of such tremendous importance in a manner that cannot have drawn much attention to it".

The reason for Maxwell's choice seems to have been that he did not claim to communicate anything fundamentally new, but only to discuss a line of reasoning which Loschmidt had published eight years earlier in the *Proceedings* of the Vienna Academy[2]. Using Maxwell's own words[3], he "followed the track of Prof. Loschmidt", who had been the discoverer of the "fact of tremendous importance"; in his paper, Loschmidt stated explicitly only the radius of the molecules, but as his argument included the assumption that in the liquid state the molecules practically touch each other, the number of atoms in 1 c.c. of a gas can instantly be inferred from his result. To quote from Maxwell's lecture delivered before the British Association at Bradford[4]: "Loschmidt, in 1865, made the first estimate of the diameter of a molecule. . . . According to the Table, which I have calculated from Loschmidt's data the size of the molecules of hydrogen is such that about two millions of them in a row would occupy a millimetre. . . . In a cubic centimetre of any gas at standard pressure and temperature there are about nineteen million million million molecules".

It is somewhat surprising that Loschmidt's brilliant achievement has been overlooked so frequently, in spite of Maxwell's full acknowledgment. Whoever wants the opinion of another most competent judge on the importance of Loschmidt's contribution may read Boltzmann's memorial lecture on Loschmidt[5], which will dispel any possible doubt as to the real discoverer of this fundamental constant. To call it Avogadro's number is justified only in a restricted sense, as Avogadro did not even know the order of magnitude of this figure approximately; he died nine years before Loschmidt's paper appeared. In Germany, Austria and Switzerland, some physicists speak of 'Loschmidt's number', if the number of molecules per c.c. is quoted, and of 'Avogadro's number', if it is related to a mole; this practice rather obscures the fact that in both cases one and the same constant is expressed in but slightly different ways, but it may be a useful distinction and does justice to Avogadro's basic idea. Maxwell, however, would never have claimed any share in the discovery of Loschmidt's (or Avogadro's) number.

F. A. PANETH

Max-Planck-Institut für Chemie,
Mainz.
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[1] Darwin, Sir Charles, *Proc. Roy. Soc.*, A, **236**, 285 (1956).
[2] Loschmidt, J., *Sitzber. Wien Akad.*, **52**, II, 395 (1865).
[3] Maxwell, J. Clerk, *Nature*, **8**, 298 (1873); "Scientific Papers", **2**, 343.
[4] Maxwell, J. Clerk, *Nature*, **8**, 437 (1873); *Phil. Mag.*, **46**, 453 (1873); "Scientific Papers", **2**, 361.
[5] Boltzmann, L., "Populäre Schriften", 228 (Leipzig, 1905).

I MUST plead guilty to the charge of not having made a very deep search of the older literature in connexion with the evaluation of 'Avogadro's Number'. This name has only come into general use in rather recent years; for example, in the first edition of Kaye and Laby's Tables (1911) the constant N_m is given no name at all. However, I am afraid that the use of Avogadro's name in this connexion led me to overlook Loschmidt's work, so that I was content to find and verify a short reference to Maxwell. I am grateful to Prof. Paneth for putting this matter right.

C. G. DARWIN

Newnham Grange,
Cambridge.

Type of Ion Migration in a Metal/Metal Oxide System

ONE of the essential factors in the study of the formation of oxide films is to determine experimentally which of the ions, the metal cation or the oxygen anion, moves the faster during thermal or anodic oxidation of the metal.

Ion migration in several metal/metal oxide systems has been studied by the marker technique introduced by Pfeil[1]. This method, in which an inert marker is covered by the oxide if the metal ion moves outwards, or alternatively which remains free on the oxide surface if the oxygen ion moves inwards through the oxide, is most suitable when the degree of oxidation is considerable, as, for example, at high temperatures.

In this communication a technique to determine the nature of the ion migration under a relatively small electric field at room temperature is outlined. The first metal chosen for study was zirconium, and it is this experiment, together with its interpretation, which will now be described.

Two electrodes of zirconium metal with, of course, a thin oxide layer on their surfaces, were separated by a sintered compact of zirconia. Between the upper and lower surfaces of the zirconia compact and the corresponding electrode surfaces were placed pieces of Whatman No. 31 (electrophoresis grade) filter paper. These filter papers were previously prepared as a colour detector for zirconium ions by soaking in a solution of alizarin-*S* dissolved in alcohol followed by drying at 125° C.

The following chemical experiments were performed on the reagents.

(*a*) It was established that in the presence of nascent oxygen from hydrogen peroxide the alizarin-*S* reagent turned yellow.

(*b*) In the presence of zirconium ions the typical red colour given by the alizarin-*S* is retained in the presence of nascent oxygen from hydrogen peroxide.

The assembly described above was placed in a tube at room temperature through which dry nitrogen gas was flowing. After the tube had been well flushed of air and contained dry nitrogen gas only (free from oxygen) a d.c. voltage of the order of 1,000 V./cm. was applied for several hours.

Examination of the filter papers after dismantling revealed the following:

(1) The filter paper in contact with the positive electrode had changed from the orange-pink colour of the original condition to a yellow colour in that region where contact was established. In the

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