

## LETTERS TO THE EDITOR.

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## The Second Law of Thermodynamics.

THE point which Mr. Browne (p. 102) raises is covered by Voigt ("Thermodynamik," vol. ii., § 69, pp. 209 *et seq.*). Ordinary diffusion of two gases at equal pressure and temperature is an irreversible process involving loss of available energy, but when the diffusion takes place through porous membranes this available energy can be utilised in a greater or less degree in the form of work, and this is the case in Mr. Browne's experiment. By introducing the conception of "semi-permeable partitions," Voigt obtains a reversible method of mixing or separating gases. In this case the partial pressure of the mixture is equal to the sum of the partial pressures of the components. In ordinary diffusion the volume of the mixture is equal to the sum of the volumes of the components. The work of expansion from the former to the latter final state can be utilised if a reversible transformation is employed. It is lost in the case of ordinary diffusion. An equal amount of work must, however, be supplied from without to separate the gases. The results are fully in accordance with the second law.

G. H. BRYAN.

MR. M. A. BROWNE'S letter (p. 102) raises an interesting and difficult question which at some period of his career must be faced by every student attempting to grasp for himself the significance of the second law of thermodynamics. As I, with difficulty and without much help from the text-books, extricated myself from a similar dilemma, perhaps the steps in the train of reasoning which helped me may interest others.

There is no need to take the complicated case chosen by Mr. Browne of the diffusion of hydrogen and nitrogen through a palladium septum. A precisely analogous difficulty exists in the simpler case of an ordinary cylinder of compressed gas doing external work on expansion either at the expense of its own heat or of the heat of uniform temperature of its environment. The gas expands and does an amount of external work  $W$ , while the equivalent  $H$  units of heat flow into the gas from the surroundings, so that the result of the process is that  $H$  units of heat at the uniform temperature of the surroundings have been quantitatively converted into external work. This is, no doubt, contrary to many of the earlier statements of the second law.

The test, of course, is to compress back the gas into the cylinder, when at least  $W$  units of work have to be converted back into heat during the process. Moreover, this must be done whether or not the gas did work on expansion. Although a gas expands freely into a vacuum, doing no work, and, as Joule has shown, experiencing no appreciable change of total energy in the process, to get it back again into the cylinder, at least  $W$  units of work must be converted into heat. I know of no better way of introducing thermodynamical considerations to the chemical student than by commencing with the concrete case of a gas cylinder. The extension of the same considerations to all processes naturally occurring, the flow of heat from a hot to a cold body, the diffusion of gases through septa, the change of one allotropic form of element into another, all follow as illustrations of the "majestic" and "universal" law that that mysterious something which is not energy, but an abstraction of energy—its availability for work—tends always to a minimum, or, as others have it, the entropy increases. The student passes his examination, no doubt, but if he is a philosopher he may prefer to meet his difficulties singly, and not have them "concentrated in a phrase." It is possible that he may like to think sometimes of a gas as expanding, because it is its nature to. The reason is easily understood on mechanical or kinetic considerations. But the attempt to replace these

considerations by the two *ex cathedra* statements—(1) the entropy of a gas increases during increase of volume, (2) the entropy of the universe tends to increase—and to deduce from them the direction of natural tendency in the case of a gas changing in volume, seems to the writer to involve the thermodynamical equivalent of the fallacy of "putting the cart before the horse." We cannot escape mechanical and molecular considerations.

The University, Glasgow.

F. SODDY.

## Atomic Disintegration and the Distribution of the Elements.

WITH reference to the association of uranium and radium, would you permit me to put on record a point that must have occurred to many, though possibly not to some, of those who are speculating so brilliantly about uranium and its disintegration products. I refer to the extraordinary conjunction in nature between silver and lead. This conjunction is so frequent that it can hardly be casual. A lead mine is a silver mine and a silver mine a lead mine all the world over, and yet the chemical attraction between silver and lead is slight, and the two metals are not sufficiently common to concur by chance. It is to be noted also that the concurrence, if the word may be used in this sense, is usually of the order of ounces for silver and tons for lead, and that the atomic weight of lead is 207 and of silver 108. Hence there appears to be some ground for the suspicion that silver is a disintegration product of lead. Lead also happens to present special facilities for experiment to test this surmise. It is cheap, and it is a comparatively inexpensive matter to free ten tons of lead from all traces of silver by the usual crystallising process, and then put it aside for ten years and test again for silver by the same process.

There are several other curious groupings of elements in nature that seem to be worthy of consideration from the transmutation point of view. One of these is the frequent concurrence of copper and gold. In the Great Cobar copper mine in New South Wales the gold occurs in the ratio of about four ounces to the ton of copper. Such conjunctions as gold and quartz are, of course, easily explained by chemistry and coincidence, and chemical forces also sufficiently explain the concurrence of sulphur with silver and lead, but the giant deposits of silver, lead, and zinc, with smaller quantities of copper and still smaller quantities of gold at Broken Hill, in Australia, to say nothing of similar vast deposits in many other countries, can hardly be due entirely to chemical and casual forces. Anyone interested in the subject will find much statistical and other information in the annual report of the Broken Hill Proprietary Company. This document affords considerable food for reflection, and a visit to the mine itself is absolutely awe-inspiring. Walking through galleries of glittering grey crystals of silver, lead, and zinc sulphide—solid ore—for 300 feet across the lode, which is a mile or more in length and of unknown depth, is one of the experiences of a lifetime.

DONALD MURRAY.

3 Lombard Court, London, E.C., November 30.

## Zoology at the British Association.

IN your account, under the above heading, of the proceedings of Section D of the British Association at Johannesburg, you state (p. 40) that in my paper on Cephalodiscus I "gave a preliminary account of the new species discovered in African seas by Dr. Gilchrist."

I shall be obliged if you will allow me to say that my communication to Section D consisted of an abstract of the results which were published, last July, in my report on "The Pterobranchia of the *Siboga* Expedition," and that it did not include any account of Dr. Gilchrist's specimens of Cephalodiscus.

S. F. HARMER.

King's College, Cambridge, November 4.

[Our contributor was unfortunately engaged in the committee room during Dr. Harmer's introductory remarks, and this led to the misunderstanding to which Dr. Harmer directs attention.—EDITOR.]