conductivity is relatively small near the λ -point (2.19°), reaches a maximum in the neighbourhood of 2.0° and decreases again at lower temperatures.

We cannot suggest an explanation for these results, for which there is no analogy in the behaviour of other substances. It seems impossible, however, to account for them by any errors in the experimental method; the effect seems actually to be a property of the liquid helium II.

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¹ *Physica*, 2, 557, (1935).

² *Physica*, 3, 359, (1936).

Analysis of Ternary Gas Mixtures by Thermal Conductivity Measurements

It frequently happens in the course of exchange reactions with deuterium and hydrogen that a third gas is present initially, or is produced during such experiments (for example, nitrogen in exchange reactions with ammonia and deuterium). If this gas is non-condensable in liquid air, the deuterium content of the gas cannot be estimated by the convenient thermal conductivity methods, unless a trap cooled with liquid hydrogen is employed to freeze out the third constituent of the mixture. The gases concerned are oxygen, nitrogen, carbon monoxide and methane and the inert gases. The only alternative method is to burn the gases and measure the deuterium content of the water so produced.

The thermal conductivity method described below surmounts this difficulty. Its operation depends on the fact that the thermal conductivity of hydrogen decreases rapidly below 200°K ., owing to the decrease in rotational specific heat of the molecule. The thermal conductivity of deuterium, on the other hand, only decreases slowly, since the rotational specific heat remains practically constant down to

Fig. 1.

about 80°K . For example, at 250°K . the ratio of the thermal conductivities is $1.384:1$; at 75°K . it is $1.095:1$. Consider now a ternary mixture containing hydrogen, deuterium and a third gas (X). At high temperatures (c. 250°K .) a whole series of mixtures will have the same thermal conductivity—as is exemplified by the full lines on the ternary

diagram (Fig. 1). At 75°K ., however, the isothermal conductivity lines will be more nearly parallel to the hydrogen-deuterium side of the triangle, as is indicated by the dotted lines. To perform an analysis of an unknown mixture, then, it is only necessary to measure the thermal conductivity at these *two* temperatures: if, for example, the respective thermal conductivities correspond to the lines *aa* and *bb*, the point of intersection at once gives the composition of the mixture.

Fig. 2.

In practice, the analysis may be carried out by compressing the mixture to a standard pressure, for example, 50 mm., into a micro thermal conductivity cell, of volume 0.05 c.c. (that is, requiring about 0.01 c.c. gas at N.T.P.), dipping into liquid air and attached to the compression capillary of a McLeod gauge¹. The voltages required to maintain the filament at the two chosen temperatures are determined. The isovolt lines obtained for hydrogen-deuterium-nitrogen mixtures are shown in Fig. 2. The filament temperature was 300°K . and 110°K . in the case of the full and dotted lines respectively. The observed voltage value, relative to that required for pure hydrogen, corresponding to each isovolt line is indicated. The observed curvature of the high-temperature lines is attributable to mixture effects. For mixtures of nitrogen-content not exceeding 50 per cent, the accuracy of the method is about 1 per cent deuterium.

It is evident that this method may be applied to any ternary mixture, one component of which is hydrogen and the other two, gases of different thermal conductivity. Mixtures of ortho- and para-hydrogen and a third gas may likewise be analysed.

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¹ Melville and Bolland, *Proc. Roy. Soc.*, in press.