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are now occurring which, at pressures of hydrogen of the order of 3 mm., may be identified as (1) the ordinary homogeneous gas reaction with the characteristics already described, and (2) a reaction on the glass surface. This newly observed heterogeneous reaction is characterised by having an initial velocity (a) independent of sulphur concentration over a wide range, (b) proportional to the hydrogen pressure, and (c) proportional to the area of glass surface. Its real interest, however, lies in the fact that it ceases completely when it has produced an amount of hydrogen sulphide sufficient to cover the surface of glass with a unimolecular layer, and, furthermore, that its velocity, high at first, falls off rapidly with time, becoming zero when the surface concentration specified has been reached. From this it appears that a unimolecular layer of hydrogen sulphide effectively prevents the glass surface from promoting further combination of the two elements, either under these conditions or at pressures of hydrogen up to 760 mm. By comparison with that from the homogeneous reaction, the actual contribution of hydrogen sulphide from this surface reaction is exceedingly small and thus its presence is disclosed only at low pressures.

The experiments furnish results from which further deductions may be made :

1. Since the surface reaction is independent of the sulphur concentration and the gaseous reaction is related thereto, the two processes must proceed independently, otherwise the hydrogen sulphide formed in the gaseous phase, if adsorbed on the surface, would decrease the velocity of the surface reaction.

2. Independence of sulphur concentration also implies that the heterogeneous reaction is between sulphur already present on the surface and bombarding rather than adsorbed hydrogen molecules. When, however, reaction takes place on the surface of liquid sulphur, there is no inhibition by the product, hydrogen sulphide continuing to be produced so long as there is liquid sulphur available. The two processes are evidently manifestations of the same reaction, because they have the same temperature coefficient and the ratio between the effective collisions of the hydrogen molecules in the two cases is approximately unity. Since, however, the film of sulphur produces only a single layer of hydrogen sulphide molecules and these adhere to the surface, it appears extremely probable that the sulphur film is itself unimolecular. That such a sulphur film should cover the glass completely is readily understood from other evidence which shows that hydrogen is not adsorbed by glass and therefore would not seriously compete for the surface.

3. The molecules in the film are likely to be specifically oriented, and since those in an ordinary liquid surface behave similarly, support is lent to the view that such surfaces are formed of definitely disposed molecules.

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J. Amer. Chem. Soc., 40, 1361; 1918.
ibid., 45, 63; 1923.
Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, 1933, p. 306.
Narure, 131, 471, April 1, 1933.
ibid., 132, 101, July 15, 1933.

X-Ray K- and L-Spectra of Aluminium

IN our recent letter¹ on the L-series of the lighter elements, we pointed out that the characteristic feature of the lines of silicon, aluminium and magnesium, showing very broad lines with a sharp limit at the side of the short wave-lengths, may be interpreted as due to the transition of electrons from the free electronic levels (the conduction electrons) to an empty L-level. Independently, analogous results and this explanation have been put forward by T. H. Osgood and by O'Bryan and Skinner².



It was of interest in further verification of this interpretation to study the structure of the L-line with a non-conducting compound. As shown by the photometer curves (Fig. 1), the L-line of aluminium from the oxide, Al₂O₃, is not only displaced towards longer wave-lengths but has also quite a different structure without the sharp edge. (The small maximum at $212 \cdot 4$ A. is the oxygen K-line in the 9th order.)

The photometer curve of metallic aluminium also shows a fainter edge (169.90 A.) just in front of the main one (170.49 A.). From the difference in wavelengths it is obvious that these correspond to the L_{III} - and L_{IIII} -levels respectively.

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Nov. 2.

¹ NATURE, 132, 750, Nov. 11, 1933. ² Phys. Rev., Oct. 1933.

In connexion with the results given in the above letter by Siegbahn and Magnusson on the L-spectrum of aluminium, we have made a study of the K-series of the same element to see if analogous effects are to be found here, and also of course at the β -line. The two spectrograms reproduced in Fig. 2 of metallic aluminium and aluminium oxide, Al₂O₃, were obtained with a bent crystal of gypsum as grating, radius of curvature 0.5 metre. As seen from these spectrograms, the same characteristic differences appear in the K-series (at about 8 A.) as had been found in the L-series (at about 200 A.). The aluminium metal gives a β -line, corresponding to a transition from the free electron levels to the K-level, with a sharp edge at the side of the short wave-lengths, which is not formed by the oxide, where the corresponding line is more symmetrical.

The agreement is not only qualitative. The width of the *L*-line as shown in Fig. 1 is about 13 ± 2 volts; in the K-series; from Fig. 2 it is about 12 ± 2 volts. The displacement of the centre of the line for the