

diffraction effects. This view is somewhat strengthened by the observation that the maxima for the liquid state are frequently in positions very similar to those of the strongest maxima for the solid material. It therefore appears that the units in the liquid are probably trying to group themselves according to their customary positions below the melting point.

The testing of any quantitative theory of the liquid state will probably be much simplified if results on simple substances are available. With this end in view, we have recently carried out X-ray diffraction experiments on several liquid metals. So far, liquid sodium, potassium, rubidium, and caesium have been investigated, and work on lithium, lead, zinc, cadmium, bismuth, and other elements is proceeding. Sodium, potassium, rubidium, and caesium are of the body-centred cubic type in the solid state, and the liquids, at temperatures not very far removed from the melting point, each diffract the X-rays in one main direction, so that a single narrow band is observed. Fig. 1, showing the ring for rubidium, gives

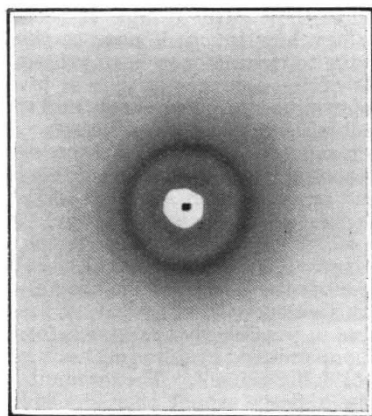


FIG. 1.—X-ray diffraction pattern for liquid rubidium. Copper $K\alpha$ radiation. Spacing of band, 4.09 Å.

some idea of the rather surprising sharpness of definition obtained with all four liquids. The accompanying table gives approximate spacings of the bands. The metals were in each case distilled into exceedingly fine glass capillaries, and the melting carried out by means of an external heating coil.

Element.	Approximate Spacing in Å. of Band due to Liquid.	Approximate Width of Band in Degrees at Half Intensity.	Spacing of (110) Plane for Solid in Å.
Sodium .	3.01	6° 0'	3.04
Potassium	3.87	— *	3.68
Rubidium	4.09	4° 50'	3.97
Caesium .	4.51	9° 30'	4.28

* Microphotometer records of our films for liquid potassium are not yet available.

It may be noted that in each case the spacing of the liquid band is approximately the same as the spacing of the strongest line of the corresponding solid. Work is now proceeding on the correct interpretation of these results, a full discussion of which we hope to publish elsewhere.

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¹ See for example *Phys. Rev.*, **37**, 9; 1931.

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Electrochemical Periodicities

DR. J. A. V. BUTLER and G. ARMSTRONG¹ and DR. E. S. HEDGES² have published some very interesting observations on periodicities in electrolytic cells. I have made similar observations in a cell with 25 per cent sulphuric acid as electrolyte and a copper anode. The e.m.f. and resistance of the circuit being constant, under certain conditions the current through the cell assumes values from a few milliamperes to a fraction of a milliampere alternatively. The time of the alternations is variable, under different conditions, from about one to ten seconds.

This phenomenon lasts from several minutes to one hour or more, changing gradually. It is essential for the production of these oscillations that the ratio between e.m.f. and circuit resistance should have a certain value, corresponding to a critical value of the current density, approximately 43 ma./cm.²

This phenomenon is caused by periodical variations of the cell resistance,³ due to the alternative formation and destruction of a thin insulating layer on the anode. This layer is analogous to that responsible for the passivity of metallic electrodes.

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¹ NATURE, **129**, 613, April 23, 1932.

² NATURE, **129**, 870, June 11, 1932.

³ *L'elettricista*, Feb. 1932.

Thermochemistry and the Periodic Table (ENERGY OF TRANSFER OF ELECTRONS ON OXIDATION)

SINCE the formation of chemical compounds depends on rearrangements among the electrons of the outer shells of the atoms concerned, it may well become the aim of thermochemists to connect changes of energy with the corresponding change in the arrangement of those electrons.

In my endeavours to develop the subject on these lines, I have been handicapped by scarcity of data. The energy of formation of the direct linking of oxygen to a number of elements has, however, now been obtained by C. R. Bailey¹ from the band spectra (in the infra-red) of a number of non-polar compounds examined by him at University College, London.

In the accompanying table these energies are correlated with the covalencies of the elements concerned :

Element.	Energy of Linkage with Oxygen (per gm.-atom of element). Kilo-cal.	Covalency of Element.	Column 2. Column 3. Kilo-cal.
First Periodic Series Hydrogen	110	1	110
Second Periodic Series Carbon	237	4	59.3
Nitrogen	171	3	57.0
Oxygen	118	2	59.0
Fluorine	59	1	59.0
Third Periodic Series Silicon	180 (?)	4	45.0 (?)
Phosphorus	148	3	49.3
Sulphur	101	2	50.5
Chlorine	50	1	50.0

In column 2 of the table, the energy of formation of the linkage H-O, as in water vapour, has been added to the series given graphically by Bailey.¹

These energies of formation are seen to be a periodic function of the atomic number, being large for the early members of a series and decreasing steadily until