The Reactivity of Liquid Metals

By C. C. ADDISON, B. M. DAVIES, R. M. LINTONBON, and R. J. PULHAM
(*Department of Chemistry, University of Nottingham*)

SOLUTIONS of a metal in another liquid metal (*e.g.*, the alkali metal amalgams) are important reagents in chemistry; their reactivity is expected to be controlled by the distribution of electrons in the conduction band of the mixture, but, as little is known about the conduction bands for metal solutions, reactions and products have to be determined at present by empirical trials.

From our present results it would appear that a direct correlation exists between the liquidus curve for a binary metal solution, and the chemical reactivity of the liquid mixture, even in cases where the electropositive nature of the two metals is not greatly different, and that large and sudden changes in reactivity on varying the composition can be anticipated by reference to the appropriate phase diagram. Much experimental work will be necessary to establish this as a principle, so that we now report some preliminary work which may suggest a general pattern.

Nitrogen is absorbed by a solution of barium in liquid sodium but not by sodium alone. A product Ba_xN (which does not contain free barium metal) is precipitated, and this continues until pure liquid sodium remains. The variation in x with barium concentration is shown in the Figure which also gives the liquidus curve for the sodium–barium mixture. The product changes sharply in composition, from Ba_3N to Ba_2N at about 8 atom % of barium which corresponds with a change in the solid which crystallises. There is another change in composition from Ba_2N to Ba_3N_2 at a higher concentration.

Similar observations have been made in the reactions of nitrogen with solutions of lithium in sodium. In this case the products Li_xN are not stoicheiometric; x varies between 3·0 and 3·9, but its variations with lithium concentration again correlate with the lithium–sodium phase diagram. Over a certain concentration range, lithium dissolved in mercury does not react with nitrogen, and this range can be defined by reference to the phase diagram. The tetraethyl-lead process

$$EtCl + Na\text{–}Pb \rightarrow NaCl + Et_4Pb$$

provides a typical reaction to which the suggested correlation might be applied; apparently conflicting observations have been reported[1,2] which might well have arisen from an assumption that small changes in sodium concentration are irrelevant.

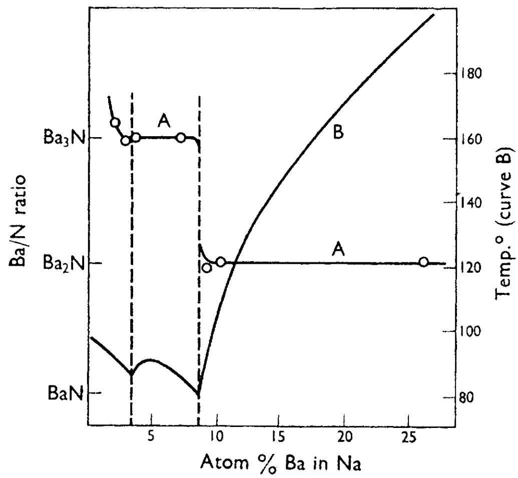

FIGURE. *The reactivity of solutions of barium in liquid sodium with nitrogen at* 300° (A) *and the sodium–barium liquidus curve* (B).

The important step in the reaction of a non-metal such as nitrogen with a liquid metal is its dissociation into ions by transfer of electrons from the conduction band of the metal. The stoicheiometry of the product depends on the proportion of electrons possessing appropriate energy, which in turn depends on the composition of the alloy and the width and profile of the band. The concept of short-range structure in liquid alloys is well supported by density, viscosity, and other properties (*e.g.*, for Na–Ba,[3] Na–Hg,[4] and K–Hg[4]) and a change in liquid structure might well occur at compositions at which the solid structure also changes. A change in the distribution of atoms in space modifies the energy profile of the conduction band, and thus the number of electrons available for chemical reaction. The correlation of reactivity with the liquidus curve is therefore acceptable theoretically in terms of the short-range structure believed to exist in liquid metals.[5]

The change in electrical conductivity of liquid metal mixtures with composition, which is also a function of the electron population of the conduction band, again reflects major changes in the liquidus curve even though the temperature of the liquid may be far above the freezing point.[6] There is therefore a good correlation between chemical reactivity and conductivity also, though for practical purposes the liquidus curves are usually more readily available.

(*Received, January* 16*th*, 1966; *Com.* 052.)

1 G. Colinguert, *Chem. Rev.*, 1926, **2**, 46.
2 B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 1949, 919.
3 C. C. Addison and R. J. Pulham, *J. Chem. Soc.*, 1963, 1232.
4 N. F. Mott, *Phil. Mag.*, 1966, **13**, 989.
5 N. E. Cusack, *Reports Progr. Phys.*, 1963, **26**, 361.
6 Gmelin's "Handbuch der Anorganischen Chemie", 1962, vol. **34**, pp. 916, 929.