294. *Liquid Metals. Part IV.* The Wetting of Zinc by Liquid Sodium: the Significance of the Critical Wetting Temperature.*

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The wetting of metallic zinc by liquid sodium has been studied by measurement of contact angles over ranges of time and temperature. Electropolished zinc surfaces show a critical wetting temperature near 160°, and chemical reaction between sodium and the zinc phosphate film deposited during electropolishing is shown to be responsible for this. No critical wetting temperature is observed for abraded zinc plates. Rates and mechanisms of wetting are discussed from the point of view of diffusion through surface films of zinc phosphate and zinc oxide and the formation of the intermetallic compound $Zn_{13}Na$. The condition of the surface of zinc after wetting by sodium has been studied microscopically.

Factors which influence the wetting of a solid metal by a liquid metal fall into two distinct categories. First, there are those resulting from properties of the pure metals, such as surface tension, atomic volume, and electronic structure; an early attempt was made by Hildebrand and his co-workers [1] to relate wettability with a fundamental property. The limited data available suggest that the two metals must form a layer of intermediate composition at the interface before wetting can occur; this approach permits wetting to be related to some measurable property of the metal system. Secondly, there are those factors which arise from the presence of films at the solid metal surface.

Several workers have suggested that wetting only occurs rapidly above a critical

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* Part III, *J.*, 1955, 3047.

[1] Hildebrand, Hogness, and Taylor, *J. Amer. Chem. Soc.*, 1923, **45**, 2828.

wetting temperature. This has been observed for the systems bismuth–copper, tin–molybdenum, tin–copper,[2] and lead–nickel,[3] when a gas is used as the third phase, and in certain other systems when the third phase is a flux.[4,5] Miller, Ewing, Hartman, and Atkinson [6] studied visually the wetting of nickel and of steel by liquid sodium, and quoted wetting temperatures. Winkler and Vandenburg [7] employed molybdenum, nickel, and steel specimens as ribbons of known electrical resistance. A wetting film of sodium acts as a low-resistance conductor in parallel, and its presence is revealed by change in electrical resistance. In these experiments the specimens were coated with oils and the values have no significance as fundamental properties of the liquid metal–solid metal systems. In spite of these observations of the phenomenon, little attempt has been made to seek a reason for critical wetting.

The work to be described in this and later papers concerns factors governing the wetting of metals by liquid sodium, starting with the transition metals, and first with the zinc group. The readiness with which the metals form intermetallic compounds decreases in the order Hg > Cd > Zn, as shown by the number of compounds revealed in the phase diagrams: Hg_4Na, Hg_2Na, Hg_8Na_7, HgNa, Hg_2Na_3, Hg_2Na_5, $HgNa_3$;[8] Cd_6Na, Cd_2Na;[9] $Zn_{13}Na$.[10,11,12] At 200°, the solubility of mercury in sodium is 44 atoms %, and when clean mercury is placed in liquid sodium it will clearly be wetted immediately. The solubility of cadmium in sodium is 5 atoms % at 200°. A thin plate of cadmium placed in liquid sodium (at 100° and above) was wetted immediately: within a few minutes the plate grew thick because of the formation of the intermetallic compound, some of which also dissolved in the sodium. The case of zinc is of particular interest, since although one intermetallic compound is formed,[10] the solubility of zinc in sodium is not detectable below the melting point of the compound $Zn_{13}Na$ (557°).

RESULTS AND DISCUSSION

Electropolished Plates.—Contact angles were measured by the vertical-plate technique. A thin plate of zinc (partly immersed in liquid sodium) was suspended from an arm attached to a torsion wire; the forces acting on the plate include the surface tension of sodium (γ) acting at some angle θ, and from the balance of forces the term $\gamma \cos \theta$ is evaluated. The apparatus and procedure are described in Part I,[13] and the value of γ used in deriving contact angles is that already determined by this technique.[13] In each measurement the plate was drawn up through the surface in stages, and the contact angle recorded at each stage. The value of θ decreased to a steady minimum value, which represents the true receding angle. The periods of time recorded in this paper as "times of immersion" are the times elapsing since the plate was first immersed in sodium. During each run the plate was normally kept immersed, and was only withdrawn during the actual measurement of contact angle.

When an electropolished (but not degreased) zinc plate is used at a temperature of 180°, θ falls slowly during 30 min. to 20°, and thereafter remains at about this value. When the plate was degreased for 4 hr. in a Soxhlet extractor with acetone and withdrawn from hot acetone, wetting was almost complete after 30 sec., and θ reached 0° within 10 min. However, when a plate was given identical treatment but was withdrawn from acetone after the latter had been allowed to cool, θ was 40° after 10 min., and 0° after 20 min.

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[2] Tammann and Ruhenbach, *Z. anorg. Chem.*, 1935, **223**, 192.

[3] Bailey and Watkins, *J. Inst. Metals*, 1951/2, **80**, 57.

[4] Daniels and Macnaughton, Tech. Pub. Internat. Tin Research Development Council, Series B, 1937, p. 6.

[5] Lakin, *Trans. Faraday Soc.*, 1938, **34**, 1384.

[6] Naval Research Laboratory (U.S.A.), Report C—3105, April 1947.

[7] Knolls Atomic Power Laboratory Report KAPL—P—231, December 1949.

[8] See Hansen, "Aufbau der Zweistofflegierungen," Julius Springer, Berlin, 1936, pp. 790—797.

[9] *Ibid.*, pp. 435—437.

[10] Mathewson, *Z. anorg. Chem.*, 1906, **48**, 196.

[11] Ketelaar, *J. Chem. Phys.*, 1937, **5**, 668; Zintl and Haucke, *Z. Electrochem.*, 1938, **4**, 104.

[12] Shoemaker, Marsh, Ewing, and Pauling, *Acta Cryst.*, 1952, **5**, 637.

[13] Addison, Kerridge, and Lewis, *J.*, 1954, 2861.

Traces of organic contamination thus have a pronounced effect on rates of wetting by sodium (see also Bondi[14]).

Above 160°, the rate of wetting of thoroughly degreased plates increases with temperature (Fig. 1). Below 160°, a different behaviour is observed (Fig. 2). There is a delay (which increases rapidly as temperature decreases) during which the angle passes through a maximum, and the contact angle then falls to 0° at a rate which falls with decreasing temperature. From a graph of the times required for complete wetting against temperature, it is clear that there is a critical wetting temperature near 160°, and on either side of this temperature two quite different processes of wetting are operating.

Nature and Thickness of Film on Electropolished Zinc.—Electropolishing produces a solid film on a metal surface.[15] Raether[16] concluded that the film produced by electropolishing zinc in orthophosphoric acid was more than 50 Å thick; Jacquet and Jean[17] found the phosphorus present on electropolished zinc, after the plate had been washed in alcoholic phosphoric acid and then water, to be 0·6—2·3 × 10^{-7}g./cm.^{2}. The film being assumed to consist of anhydrous zinc phosphate (*d* 4·0 in the massive state[27]), our calculations indicate a film thickness of 20—70 Å. The film may be appreciably thicker before washing; in analogous experiments on electropolished copper, Jacquet and Jean[17] found the washed copper film to contain about the same quantity of phosphorus as does the zinc film, whereas the film on unwashed electropolished copper is about 1000 Å thick.[18]

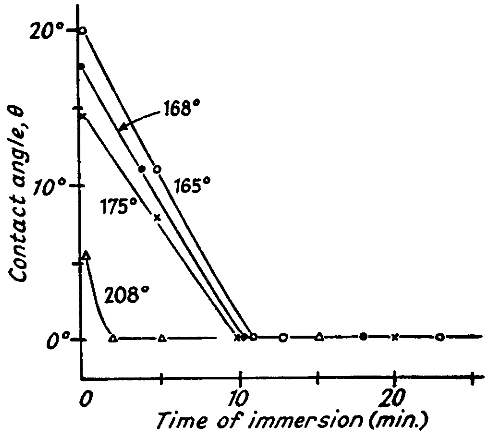

FIG. 1. *Wetting of electropolished zinc by sodium above* 160°.

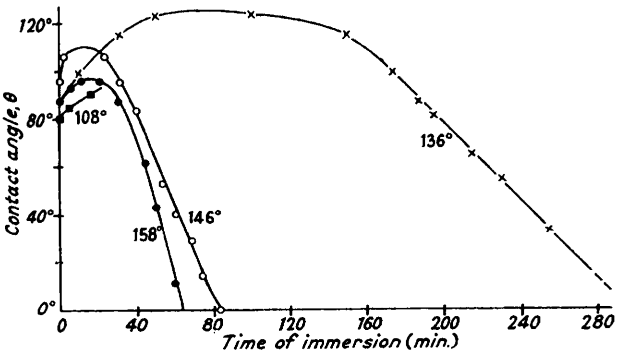

FIG. 2. *Wetting of electropolished zinc by sodium below* 160°.

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[14] Bondi, *Chem. Rev.*, 1953, **52**, 418.

[15] Hoar and Farthing, *Nature*, 1952, **169**, 324.

[16] Raether, *Métaux et Corrosion*, 1949, **24**, 148.

[17] Jacquet and Jean, *Rev. Métallurgie*, 1951, **48**, 537.

[18] Raether, *Métaux et Corrosion*, 1947, **22**, 2.

In the present experiments a tracer technique was used to study the film: 1 ml. of a dilute aqueous solution of phosphoric acid containing 1 mc activity of ^{32}P was added to an orthophosphoric acid bath in which a plate was electropolished under normal conditions. From the ratio of active to inactive phosphorus, it was found that $(7{\cdot}0 \pm 2) \times 10^{-6}$ g. of phosphorus per cm.^{2} were deposited. The plate was then wetted with sodium at 175°, washed quickly with water to remove the sodium film, rinsed in pure acetone, and dried in hot air; all the activity was retained on the plate. The latter was then dissolved in dilute hydrochloric acid, and sodium phosphate added to the solution. The total phosphate was precipitated as magnesium ammonium phosphate, and all the activity was found in the precipitate. Since these conditions are not such as to convert phosphide, phosphite, etc, into phosphate, there is little doubt that the phosphorus was deposited on the metal surface during electropolishing as an orthophosphate, and the radioactivity measurements indicate a film thickness of 1000 ± 300 Å.

Reaction of Sodium with Anhydrous Zinc Phosphate.—Pure anhydrous zinc phosphate, shaped into thin blocks, was immersed in liquid sodium at various temperatures. The observations are collected in the annexed Table. The critical reaction temperature coincides with the critical wetting temperature for zinc metal in sodium. Analysis of reaction products showed the reaction to be

Fused $Zn_3(PO_4)_2$	
Temp.	Observation
<160°	No wetting by sodium; $Zn_3(PO_4)_2$ block gradually became black
160°	Vigorous reaction: block disintegrated
>160°	Vigorous reaction

Sintered $Zn_3(PO_4)_2$	
Temp.	Observation
<162°	No wetting by sodium No reaction, but block gradually blackened
162°	Some visible reaction, but slower than with fused $Zn_3(PO_4)_2$
>162°	Reaction becomes more vigorous with increasing temperature

$$6Na + Zn_3(PO_4)_2 \xrightarrow{160°} 3Zn + 2Na_3PO_4$$

The darkening in colour of the zinc phosphate block below 160° probably results from penetration of sodium into the block. The anhydrous sodium phosphate produced above 160° is not rapidly soluble in water, since it was not removed on washing the plate in water after the tracer experiment.

Mechanism of Wetting.—Below 160° the zinc phosphate film does not react; since wetting eventually takes place in spite of this, we must assume that diffusion of zinc atoms or ions through the film takes place, and that complete wetting only occurs when sufficient zinc has migrated through the film to give a continuous layer of the compound $Zn_{13}Na$. Tammann[20] observed that diffusional mobility in salts became appreciable when the absolute temperature reached half of the m. p. of the salt. Since the m. p. of zinc phosphate is about 900°, the temperatures used in these experiments appear to be low for normal diffusion, but this may be offset by the short distances involved. An Arrhenius plot of log $(1/T_w)$ (where T_w is time for complete wetting) against the reciprocal of absolute temperature over the range below 160° indicates an "activation energy" (E) of the order of 35 kcal. A similar value of E is obtained from the slopes of the linear parts of the wetting curves (Fig. 2). This might be the activation energy for diffusion of Zn^{2+} through a $Zn_3(PO_4)_2$ film, and it is of interest to compare it with $E = 37{\cdot}8$ kcal. for diffusion of Cu^+ through Cu_2O[21] at 800—1000°, and $E = 73{\cdot}7$ kcal. for diffusion of Zn^{2+} through ZnO at 800—1370°.[22]

The contact angle–time curves in Fig. 2 are also consistent with a diffusion mechanism.

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[19] Cabrera and Mott, *Rep. Prog. Phys.*, 1948–9, **12**, 163.

[20] Tammann, *Z. anorg. Chem.*, 1926, **157**, 321.

[21] Castellan and Moore, *J. Chem. Phys.*, 1949, **17**, 41.

[22] Lindner, Campbell, and Akerström, *Acta Chem. Scand.*, 1952, **6**, 457; Secco and Moore, *J. Chem. Phys.*, 1955, **23**, 1170.

The compound $Zn_{13}Na$ is the only one formed; we may suppose that intermetallic compound formation does not occur until sufficient zinc atoms have diffused to the surface. Since each sodium atom in the compound $Zn_{13}Na$ is surrounded by 24 zinc atoms at the vertices of a "snub cube,"[12] this may require several atomic layers of zinc. Until this stage is reached, no wetting can occur. The time at which wetting commences will depend on diffusion rates, and should therefore be highly dependent on temperature. When wetting commences, the contact angle changes linearly with time. The zinc metal surface is composed of crystal faces of different orientation, which react to differing degrees. The thickness of the electropolishing film, and the ease with which zinc atoms diffuse from the crystal surface, will vary with crystal face. Wetting will not therefore commence at all parts of the plate at the same time, and the recorded angle is the mean of several angles which operate round the sodium meniscus. There was visible evidence for this heterogeneous wetting, especially at the stage when wetting had just commenced.

Above 160°, the zinc phosphate film reacts on contact with sodium, and since the contact angle falls to below 20° within a few seconds of immersion (Fig. 1), this reaction is regarded as being completed almost immediately. A film of sodium phosphate will remain; since it is formed as a result of chemical reaction at the surface it may be less cohesive than the zinc phosphate film. The time (up to 10 min.) during which θ falls to 0° will represent the time required for the migration of zinc through this new film. The plot of log $(1/T_w)$ against $1/T$ for this temperature range indicates an activation energy of about 8 kcal.

Wetting of Untreated and Abraded Zinc Plates.—Zinc plates which were untreated (*i.e.*, not abraded or degreased, and exposed to the atmosphere for months) gave an initial contact angle near 180° in sodium at a temperature of 180°. This angle decreased to about 30° in 30 min., remained at that value for about 2 hr., and then increased slightly; the more incomplete is the wetting, the greater is the tendency for dewetting to occur on prolonged immersion. When similar plates were abraded with emery paper the final angle was 20°, and there was no evidence of dewetting. The capillary grooves on the surface caused by abrasion may contribute towards this rather lower contact angle.[3] When an abraded plate degreased for 6 hr. in hot acetone was used, θ was less than 30° within 30 sec., and decreased to 0° within 10 min. This behaviour is very similar to that observed with an electropolished degreased plate (Fig. 1), and there was again visual evidence of non-uniformity of wetting. Plates cleaned by reaction in aqueous hydrochloric acid or sodium hydroxide showed similar behaviour in sodium : wetting was not quite so rapid, θ reaching 0° in 15 min.

Some measurements upon abraded and degreased plates over a temperature range are given below :

Temperature	108°	108°	124°	175°
θ after 30 secs.	24°	39°	38°	18°
Time to reach $\theta = 0°$ (min.)	9·0	10·0	10·0	8·0

In this case the wetting time changes very little with temperature (in sharp contrast to the behaviour of the electropolished plates) and there is no evidence for a critical wetting temperature.

Mechanism of Wetting.—The difference in wetting behaviour between abraded and electropolished zinc results from the differing physical and chemical properties of zinc oxide and zinc phosphate films. By direct weighing, the thickness of the zinc oxide film on abraded, degreased zinc at room temperature has been shown to be 65 Å after 24 hr. and 90 Å after 100 hr.[23] Electron diffraction indicates that a single crystal of zinc in dry air at room temperature develops a film of zinc oxide 20—40 Å thick, which does not change appreciably during 16 days.[24] In the present experiments the zinc plates were abraded about 20 hr. before use, so that the zinc oxide film is probably less than 100 Å thick.

The reaction between sodium and zinc oxide shows no evidence for a critical reaction

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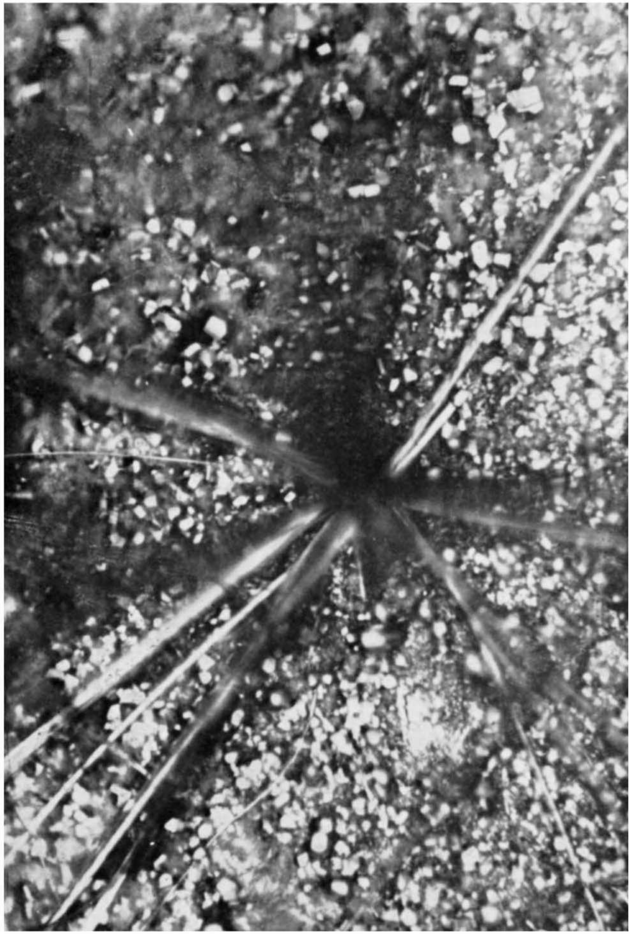
[23] Vernon, Strand, and Akeroyd, *J. Inst. Metals*, 1939, **65**, 301.

[24] Raether, *J. Phys. Radium*, 1950, **11**, 11.

Fig. 3 (*a*).

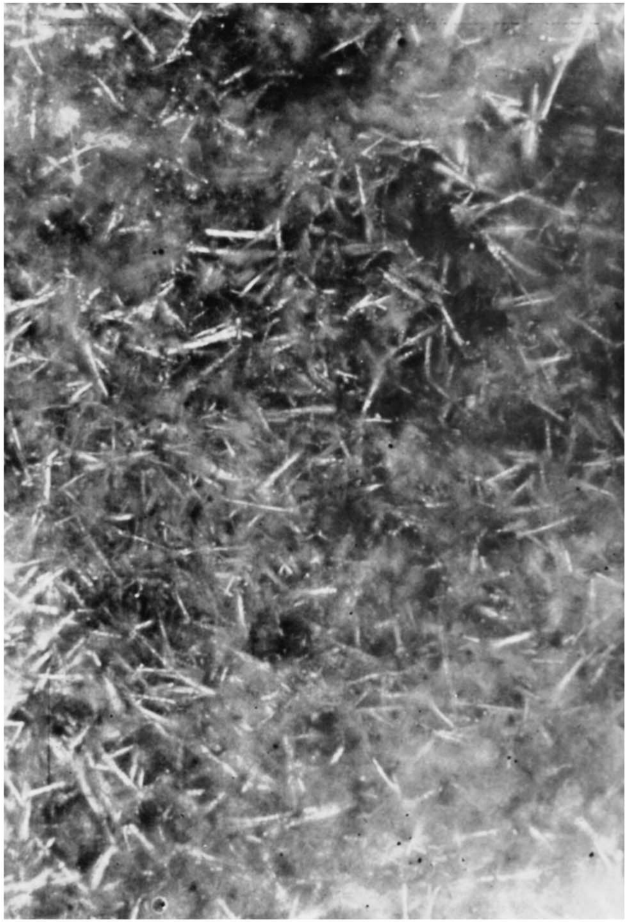


Electropolished zinc : immersed at 168° for 130 min. (× 644.)

Fig. 3 (*b*).

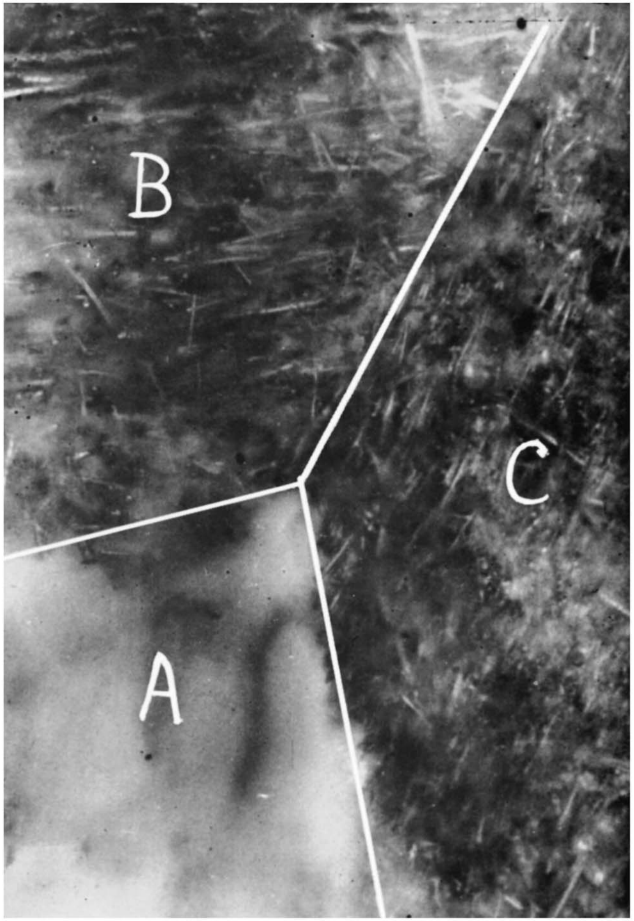
Abraded zinc : immersed at 180° for 80 min. (× 644.)

FIG. 3 (*c*).



Abraded zinc : immersed at 168° for 30 min. (× 800.)

FIG. 3 (*d*).



Electropolished zinc : immersed at 130° for 150 min. (× 800.)

temperature. At 120° there was a slow reaction when a thin sintered zinc oxide block was immersed in sodium. The block became brown-black and changed to yellow on exposure to the atmosphere; this is attributed to sodium penetrated into the block. The reaction $ZnO + 2Na \longrightarrow Na_2O + Zn$ occurs with a decrease in free energy of 12 kcal.[25] The reaction proceeded a little more quickly with increase in temperature in the range 120—200°.

If the times required for complete wetting of electropolished plates above 160° (Fig. 1) are extrapolated towards 100°, they indicate times for wetting which are much longer than the 8—10 min. actually observed for abraded plates. The diffusion of zinc through the zinc oxide film can be the rate-determining step, and partial reaction of the film to give sodium oxide will not eliminate this factor, since sodium oxide has an extremely small solubility in sodium at these low temperatures.[26] The zinc oxide film is sufficiently thin for the Cabrera–Mott mechanism, which is inapplicable to the zinc phosphate films, to be important here; in this mechanism the directional movement of cations across the film is enhanced by the electrical field set up by electrons which have penetrated the film by the " tunnel " effect, and migration of zinc through the film would then be much more rapid than in the case of normal diffusion. The very small change in rate of wetting with temperature indicates an activation energy of much less than 1 kcal. This is in agreement with the activation energy (300 cal.) for the oxidation of zinc at room temperature,[23] which is again a process involving diffusion of zinc through very thin zinc oxide films.

Microscopical Examination of Zinc Surface after Wetting with Sodium.—Sodium was removed by washing in water, and the plates were dried with acetone and hot air. To the naked eye the plates had a mat grey surface, but under the microscope crystals were observed; photomicrographs (taken by using a Vickers Projection microscope) are shown in Fig. 3 (*a*)—(*d*). A completely wetted zinc surface, completely drained on withdrawal of the plate from liquid sodium, was covered with a mat of small granular crystals about 0·005 mm. across, but in places clumps of larger needle-shaped crystals up to 0·1 mm. long and 0·005 mm. wide occurred (Fig. 3*a*). Both crystals appear to consist of zinc metal. They have a bright, metallic appearance, which was unchanged when the plate was kept in a stoppered tube containing atmospheric air for six months, whereas the compound $Zn_{13}Na$ is grey and brittle, and reacts slowly with water and the atmosphere to give a coating of sodium hydroxide.[10] However, the phase diagram [10] indicates that the intermetallic compound, rather than zinc metal, crystallises from solution in sodium. We assume therefore that when the plates are washed in water, the compound $Zn_{13}Na$ reacts to leave zinc metal without major change in crystal form; zinc atoms in the compound are 4- or 5-valent, whereas the valency of sodium is 1—1·25.[12] Although the solubility of the compound in sodium is small,[10] the crystals are considered to be formed by a process of solution of the compound as first formed, and its redisposition in one or other of the crystalline forms, as the plate cools on each withdrawal from sodium. In areas where drainage is efficient, few clumps of needles are observed, but near the meniscus, or round an area of the plate not properly wetted, a ridge of liquid sodium is retained on the plate. More needles are then deposited, and the surface has the appearance shown in Fig. 3 (*b*).

Fig. 3 (*c*) shows the mat of small crystals (about 0·01 mm. long) which is obtained when the plate is wetted in either of two ways : by using either (*a*) high temperature and short immersion times (insufficient time has been allowed for the secondary process involving growth of large crystals at the expense of the small ones), or (*b*) long immersion times at low temperatures. In the latter case the velocity of both primary and secondary processes will be reduced. By using electropolished plates which were only partially wetted [Figs. 2 and 3 (*d*)], the non-uniformity of wetting can be related directly with the differing behaviour of the film covering the crystal faces. Fig. 3 (*d*) shows three separate crystals. Crystal A (not clear in the figure because of the necessarily shallow depth of focus) had resisted wetting; it was slightly etched, but retained the smooth surface formed by electropolishing. Crystals B and C had been wetted; the needles were mostly oriented in one direction, which varied with the crystal face involved.

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[25] Osborne, *J. Metals* (Trans. A.I.M.E.) 1950, **188**, 600.

[26] " Liquid Metals Handbook," 2nd Edn., NAVEXOS P—733, p. 114; U.S. Govt. Printing Office, Washington 1952.

EXPERIMENTAL

Sodium.—The purification of sodium was described in Part I.[13]

Preparation of Zinc Plates.—" AnalaR " granulated zinc was melted in a silica crucible and cast in a steel mould to form a slab which was then machined to 0·5 mm. in thickness. Plates 2 cm. × 4 cm. were then cut from the sheet. Abrasion was carried out by rubbing with emery paper of decreasing coarseness (1—3/0), each grade being used in a direction at right angles to the previous one until all previous scratch marks were removed. Alkali-cleaned plates were boiled for 1 hr. in N-sodium hydroxide solution, then washed with water, alcohol, and ether. Acid-cleaned plates were immersed in 2N-hydrochloric acid for 30 sec., and washed as above. Plates were electropolished in a bath of 62·5% absolute alcohol and 37·5% syrupy phosphoric acid at room temperature,[28] a current density of 1·67 amp./sq. dm. at 2·6 volts being used. They were washed with water and acetone, and dried in hot air.

Preparation of Anhydrous Zinc Phosphate.—de Schulten's [29] method, which involves heating zinc phosphate tetrahydrate in boiling zinc chloride, followed by extraction of the latter with water and dilute acetic acid, could not be repeated; in each case the tetrahydrate was recovered, unchanged in analysis but in a different crystalline form. The anhydrous salt was prepared by heating the tetrahydrate in a silica boat for 3 hr. at about 900°. This gave a white sintered mass of the anhydrous salt, which fused on further heating. Weight loss on heating was 16·0% [Calc. for $Zn_3(PO_4)_2,4H_2O$: 15·75%]. Zinc was determined as zinc ammonium phosphate, and phosphate as ammonium phosphomolybdate [Found : Zn, 50·5; PO_4, 51·5. Calc. for $Zn_2(PO_4)_3$: Zn, 50·9; PO_4, 49·1%]. No trace of silicate was found in the product. The deviations in the analyses indicate some slight decomposition, probably with the formation of pyrophosphate. This occurs by sublimation of zinc oxide from the anhydrous salt, since loss of phosphoric acid from the hydrated salt during heating would give discrepancies in the reverse directions. The zinc phosphate blocks were degreased before use, in the same manner as the zinc plates, by extraction with acetone, the latter being then removed by heating the blocks in a stream of argon.

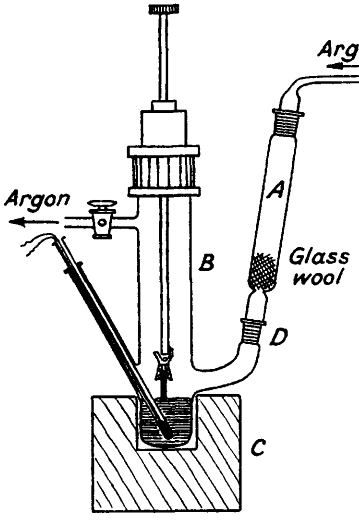

FIG. 4.

Zinc Oxide Blocks.—" AnalaR " zinc oxide was strongly compressed in a pellet screw press. The soft cylinders so obtained were cut to the desired shape, and heated for several hours at 1000°. The resulting ivory-coloured product was not friable.

Reaction of Sodium with Zinc Phosphate and Zinc Oxide.—A stream of argon (purified as described in Part I) was passed through the apparatus (Fig. 4) continuously during an experiment. Solid sodium in the filter tube *A* was melted by means of Electrothermal heating tapes. The liquid metal (about 10 ml.) was forced through the glass-wool filter plug in *A*, by pressure of argon, into the main tube *B*, which fitted closely into an electrically heated furnace *C*. The temperature was measured by immersing the thermocouple in the liquid metal. The block of reactant was attached, by crocodile clip, to the end of a brass rod which passed out of the tube, through a 1" vacuum coupling and a Wilson seal. During each experiment, the temperature was increased at the rate of about 0·5° per min. The block was withdrawn, observed, and reimmersed at two-minute intervals. At the end of each experiment the sodium was poured from *B* through the B14 joint *D* into a cold steel mould. It was then examined for reaction products.

Reaction Products with Zinc Phosphate and Zinc Oxide.—After reaction with zinc phosphate, the products contained in a large excess of sodium were treated with absolute alcohol. A grey-black alcohol-insoluble sludge remained, which gave a black powder on being shaken with water. This was metallic zinc, and all dissolved with effervescence in dilute hydrochloric acid. The aqueous extract contained sodium phosphate, and the quantities of sodium phosphate and zinc

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[27] de Schulten, *Bull. Soc. chim.*, 1889, **1**, 472.

[28] Jacquet, *Métaux Corrosion Usure*, 1944, **19**, 71.

[29] de Schulten, *Bull. Soc. chim. France*, 1889, **2**, 300.

were respectively 96·5 and 82·5% of the theoretical yields. After reaction with zinc oxide, the excess of sodium was removed by absolute alcohol. A very small quantity of black powder remained which gave positive tests for zinc.

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