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Electrical Resistivity of Liquid Potassium and of Solutions of Sodium in Liquid Potassium: the Potassium–Sodium Phase Diagram

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The electrical resistivity of liquid potassium and of solutions containing up to 30 atom % sodium in liquid potassium have been determined from the liquidus to 300 °C. Equations for the variation in the resistivity of the liquid metal with temperature and with composition are given. Resistivity–temperature curves at constant composition have been extended into the solid phase to allow determination of part of the phase diagram. The resistivities and phase equilibria are compared with previously reported data.

THE change in electrical resistivity of a liquid metal on addition of solutes provides a method for following chemical reactions in metallic solutions. Accurate data on the resistivity of the pure metals and their mixtures are required [1] and we describe the determination of the resistivity of liquid potassium and solutions of sodium in liquid potassium. These results will be used in the study of the reaction of oxygen with these metallic solutions. It has been reported [2,3] that oxygen reacts preferentially with the solute sodium which is precipitated as the monoxide, Na_2O. Thus the alloy is progressively denuded of sodium and the resistivity of the liquid should change accordingly.

Most resistivity measurements have been carried out at a few isolated compositions [4-8] and it appears that only one study has been carried out over the entire composition range.[9] In this study, resistivity isotherms were constructed at 100, 150, and 200 °C, and were based on measurements on the two metals alone, and on alloys of seven different compositions. The central regions of these isotherms indicate that over a considerable concentration range the resistivity is relatively insensitive to variation in atom fraction, but this is now shown to be incorrect.

In the present work the resistivity of liquid potassium was redetermined from the melting point to 300 °C, and the resistivity of solutions of sodium in potassium has been measured over the range 0 to 30 atom % sodium, also from the liquidus temperature up to 300°. In addition, further information has been provided on this region of the sodium–potassium phase diagram.

EXPERIMENTAL

Two types of steel apparatus were employed in this investigation. The static method, which has been used previously to determine the resistivity of sodium,[10] allowed direct measurement of the resistance of a thread of the liquid potassium contained in a steel capillary of known cross-sectional area and length. The metal (Koch–Light Ltd., 99·9%) was washed free of protective oil with light petroleum and purified before use by filtration at just above the melting point (63·7 °C) through a sintered glass pad (porosity 3). After this procedure, analysis of the metal by carbon-arc emission spectroscopy indicated the presence of calcium and sodium only, at a total concentration of $<0{\cdot}1\%$.

The dynamic method, also described elsewhere,[1] employed a double capillary in the form of a loop through which the sample was circulated by means of an electromagnetic pump. Owing to the more complex geometry of the capillary, accurate measurement of the dimensions of the capillary was not feasible. Hence the cell constant was obtained by measuring the resistance of the capillary when full of potassium, the resistivity of which had been determined by the static method. The resistivity of solutions of sodium in liquid potassium was determined by this technique during both heating and cooling cycles. For temperatures between −15 and 25 °C, use was made of a cryostat (' Kryomat ', Messgeräte-Werk, Lauda) containing industrial methylated spirit as coolant. The sodium was purified as reported previously [10] and the alloys were made up by adding weighed quantities of sodium to the potassium.

RESULTS AND DISCUSSION

The Electrical Resistivity of Liquid Potassium.—The variation in the electrical resistivity of liquid potassium with temperature is shown in Figure 1. The resistivity of the liquid metal was initially determined at 300 °C and measurements were repeated at a series of lower temperatures down to 70 °C. The liquid was then allowed to cool slowly and continuously and the resistivity was followed over the freezing point, where there is a large sharp decrease in the resistivity. In the liquid state the resistivity varies almost linearly with temperature. Over the range 65 to 300 °C, the resistivity may be represented by equation (1) where T is in °C

$$\rho(\mu\Omega\ \mathrm{cm}) = A + BT + CT^2 \qquad (1)$$

[1] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc. (A)*, 1971, 1393.
[2] D. D. Williams, *N.R.L. Report*, 3894, 1951.
[3] J. D. Noden and K. Q. Bagley, *Culcheth Lab. Technical Note*, 1954, No. 80.
[4] F. Roehlich and F. Tepper, *Electrochem. Technology*, 1965, **3**, 234.
[5] R. E. Cleary and S. M. Kapelner, *U.S.A.E.C. Report*, No. BNL 756, 1963.
[6] P. G. Drugas, I. R. Rehn, and W. D. Wilkinson, *U.S.A.E.C. Report*, No. ANL 5115, 1953.
[7] R. H. Rahiser, R. C. Werner, and C. B. Jackson, *M.S.A. Technical Report*, No. 24, 1953.
[8] J. F. Freedman and W. D. Robertson, *J. Chem. Phys.*, 1961, **34**, 769.
[9] P. Müller, *Metallurgie*, 1910, **7**, 730.
[10] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc. (A)*, 1969, 1482.

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and the values of the constants are A 10·065, B 5·120 × 10^{-2}, and C 2·408 × 10^{-5}.

The resistivity is compared with other published results in Figure 2. There is no exact coincidence with any one set of results but the present data, shown by the heavy line (A), correspond approximately with the mean of previous determinations. The resistivity is shown as full lines where equations are reported[4,11] [curves (B) and (C)] and where a line can be presented without destroying clarity[12] [curve (D)]. Other results are shown as isolated experimental points, exactly as reported.

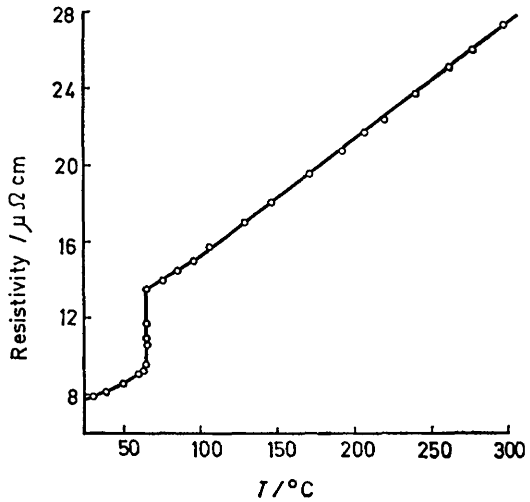

FIGURE 1 The electrical resistivity of potassium

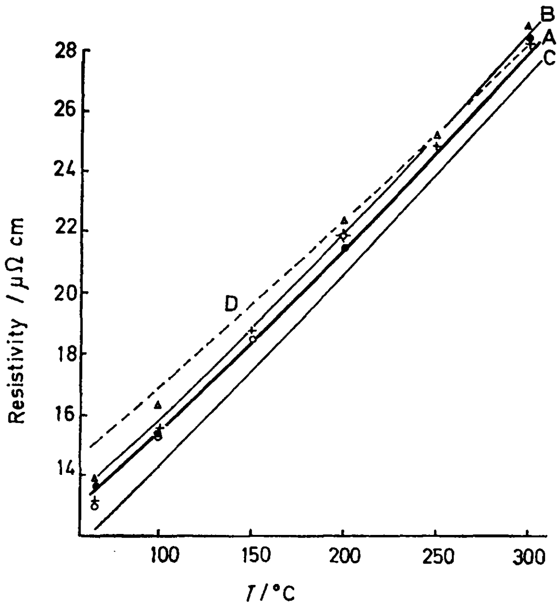

FIGURE 2 The electrical resistivity of liquid potassium. A, this work; B, ref. 11; C, ref. 4; D, ref. 12; open circles, ref. 9; open triangles, A. N. Solov'ev, *Teplofizika Vysokikh Temperatur*, 1963, **1**, 45; closed circles, A. W. Lemmon, *U.S.A.E.C. Report*, No. BATT 4673, 1963; and crosses, K. Bornemann and G. von Rauschenplat, *Metallurgie*, 1912, 510.

In view of the extreme chemical reactivity of the liquid metal the spread in the results may be due to small quantities of impurities introduced during the measurements. However, the observed spread in the results could be caused by the presence of as little as 0·5 atom % sodium (see later). It may be significant that in the one instance where an analysis is quoted[11] the sodium content was 0·56 atom %.

The Electrical Resistivity of Solutions of Sodium in Liquid Potassium.—The resistivities of eleven alloys of compositions between 0·72 and 30·06 atom % sodium were determined. For each solution the resistivity obeys equation (1). The values of the constants for sodium solutions are given in Table 1 together with the temperature range over which they are valid.

TABLE 1

The resistivity of potassium–sodium alloys

Composition (atom % sodium)	A	$B \times 10^2$	$C \times 10^5$	T/°C
0·72	10·970	5·205	2·842	62—300
7·55	18·490	4·934	3·445	42—300
10·32	21·598	4·533	4·167	33—310
11·05	21·894	5·126	2·920	32—300
12·82	24·705	4·078	5·264	30—300
15·43	25·707	5·094	2·720	21—300
17·81	28·965	3·764	5·764	60—300
19·24	28·123	5·463	2·286	150—300
25·61	32·373	5·239	2·515	0—300
27·51	34·903	4·008	5·460	20—300
30·06	34·879	5·239	2·653	−9—300

The effect of composition on the resistivity is shown in Figure 3 for five temperatures. The isotherms are smooth parabolic curves. This parabolic dependence of the resistivity on composition has been derived theoretically[13] and is characteristic of liquid binary metallic solutions in which there are no strong interactions between components. Thus our results can be represented by the general equation (2) where ρ is

$$\rho - \rho_M = A(C - C^2) \qquad (2)$$

the resistivity of the alloy containing an atom fraction C of sodium ρ_M is the resistivity which an alloy of composition C would have if the resistivities of sodium and potassium were purely additive. Thus

$$\rho_M = \rho_K C_K + \rho_{Na} C_{Na} \qquad (3)$$

and ρ_M is therefore the resistivity obtained from the broken straight line joining ρ_K and ρ_{Na} in Figure 4 for any given concentration. Values of A are given in

[11] S. M. Kapelner and W. D. Bratton, *U.S.A.E.C. Report No.* PWAC 376, 1962.

[12] B. Y. Semyachkin and A. N. Solov'ev, *Zhur. priklad. Mekhan. Tekhn. Fiz.*, 1964, **2**, 176.

[13] T. E. Faber and J. M. Ziman, *Phil. Mag.*, 1965, **11**, 153.

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Table 2, together with related quantities. By use of these values, the resistivity of any solution in the 0—30 atom % sodium range, and at any temperature,

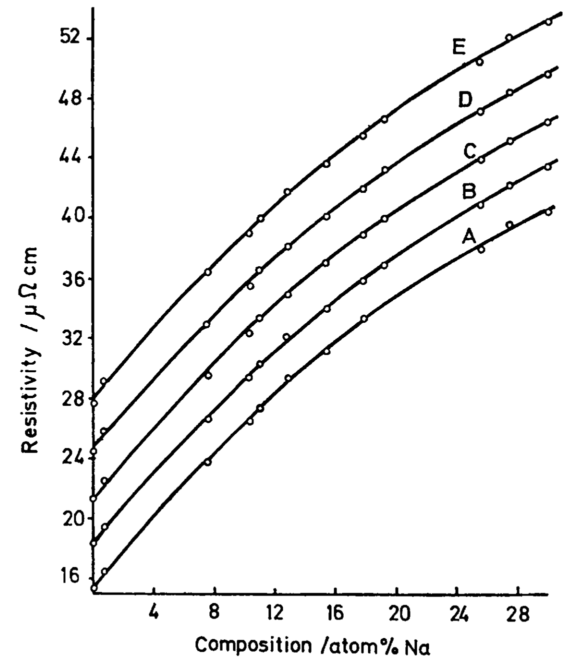

FIGURE 3 The electrical resistivity of solutions of sodium (up to 30 atom per cent) in liquid potassium at A 100, B 150, C 200, D 250, and E 300 °C

may be calculated readily from equations (2) and (3), with greater precision than it is possible to show in Figure 3. The value of A increases only slightly in

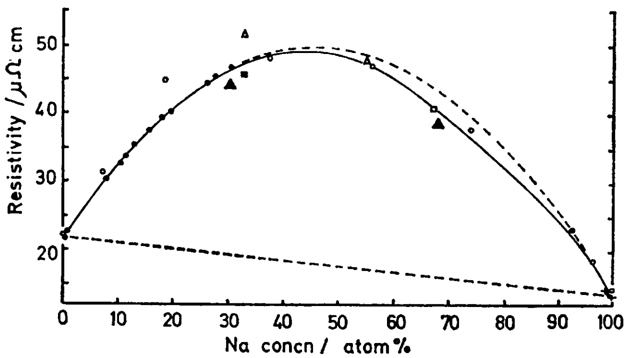

FIGURE 4 The electrical resistivity of liquid alloys of sodium and potassium at 200 °C; closed circles, this work; closed squares, ref. 4; open squares, ref. 5; closed triangles, ref. 6; open triangles, ref. 7; crosses, ref. 8; and open circles, ref. 9

the temperature range 100—300 °C, so that the enhanced resistivity caused by the introduction of an atom of sodium is virtually independent of temperature.

[14] 'Liquid Metals Handbook,' Sodium–Potassium Suppl. TID 5277, U.S.A.E.C., U.S. Government Printing Office, Washington, 1955.

The resistivities at 200° are compared with previously reported values in Figure 4. Most reported values are for one or two specific concentrations and only those of Müller extend over the full composition range. In the 0—30 atom % sodium range, our resistivity values are lower than his, and also indicate a more symmetrical relationship: his curve has a relatively flat region

TABLE 2

Calculated values of A [equation (2)]

T/°C	$\rho_K/\mu\Omega$ cm	$\rho_{Na}/\mu\Omega$ cm	A
100	15·41	9·70	127
150	18·30	11·37	129
200	21·28	13·26	131
250	24·37	15·28	133
300	27·59	17·33	135

between 20 and 60 atom % sodium. The full line in Figure 4 takes account of all but two of the available measurements (those at 18·5 and 33 atom % sodium by Müller [9] and Rahiser [7] respectively). Superimposed

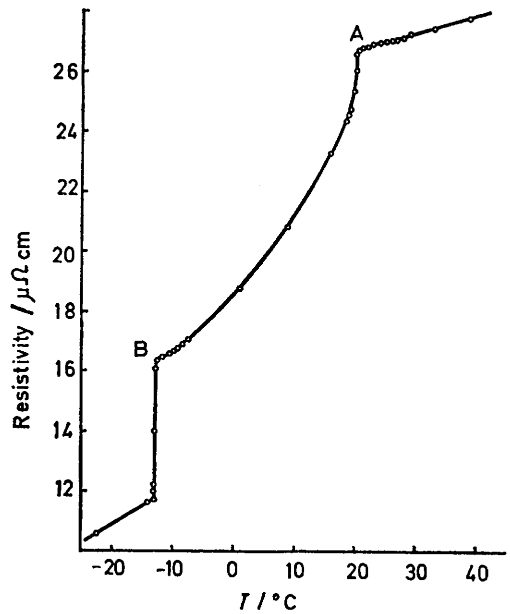

FIGURE 5 Resistivity–temperature curve for the solidification of a solution of sodium (15·43 atom %) in potassium

on the full line is a broken line calculated from equations (2) and (3), using an A of 131 at 200 °C. The experimental begins to diffeı from the theoretical curve at sodium concentrations above the eutectic value, and the difference is greatest in the 60—80 atom % sodium range. It is significant that in this region the two metals form an incongruently melting compound Na_2K.[14] Although the liquid is at 200 °C and solid is not present at this composition above 14 °C, some slight ordering may persist in the liquid to lower the resistivity below the theoretical value.

The Potassium–Sodium Phase Diagram.—The electrical resistivity of metals is particularly sensitive to

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phase changes (Figure 1); after determining the resistivity of the liquid, further use was made of the alloy

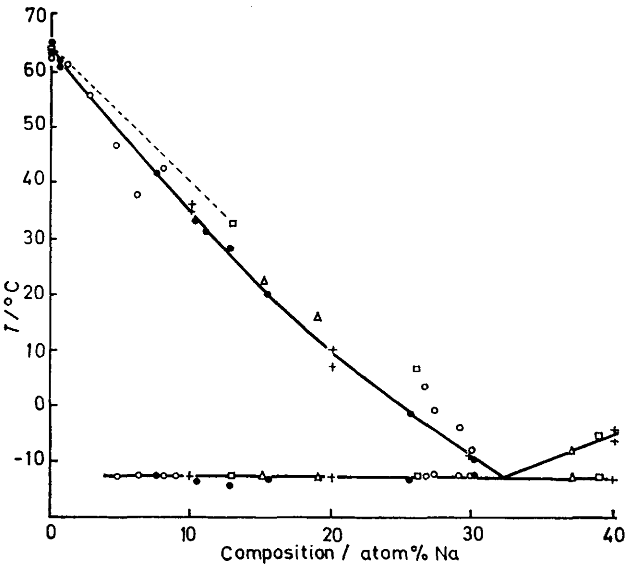

FIGURE 6 The potassium-rich region of the potassium–sodium phase diagram; closed circles, this work; crosses, ref. 15; open squares, ref. 16; open triangles, ref. 17; open circles, ref. 18; and broken line, S. L. Walters and R. R. Miller, *Ind. and Eng. Chem.* (*Analytical edn.*), 1946, **18**, 468

by measuring the resistance as it solidified. A slow cooling rate of 0·15 °C min^{-1} was employed. By this means part of the potassium–sodium phase diagram has been determined.

A typical resistivity–temperature cooling curve is shown in Figure 5. The first sharp inflection (A) corresponds to the liquidus temperature where potassium begins to precipitate from the solution. The resistivity then decreases with temperature as solid metal, which has a lower resistivity, replaces liquid. At the eutectic temperature (B) the whole alloy freezes isothermally. The phase diagram obtained from such curves is shown by the full line in Figure 6. For the purpose of comparing liquidus boundaries, previous determinations are also included in the figure. The present results indicate that the eutectic temperature is −12·5 °C in agreement with van Bleiswijk,[15] Rinck,[16] and Miller[17] *et al.* (−12·3 °C) who used thermal analytical methods. Macdonald *et al.*[18] have investigated the full composition range by use of the resistance cooling curve technique and report the eutectic at −12 °C. Their apparatus was suitable for the study of phase equilibria, but did not permit a determination of the resistivities of the solutions. Extrapolation of the liquidus curve derived from the present results to the eutectic temperature, gives a eutectic concentration of 67·8 atom % (78·2 wt. %) potassium.

[1/487 *Received, April 5th*, 1971]

[15] G. L. C. M. van Bleiswijk, *Z. Anorg. Chem.*, 1912, **74**, 152.
[16] M. E. Rinck, *Compt. rend.*, 1933, **197**, 49.
[17] R. R. Miller, C. T. Ewing, R. S. Hartmann, and H. B. Atkinson, jun., *N.R.L. Report*, No. C 3105, 1947.
[18] D. K. C. Macdonald, W. B. Pearson, and L. T. Towle, *Canad. J. Phys.*, 1956, **34**, 389.