19. *Liquid Metals. Part X.*[1] *Solutions of Hydrogen in Liquid Sodium.*

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A technique is described whereby known quantities of hydrogen are removed successively from a mixture of sodium hydride in a large excess of liquid sodium. While the hydride is present as a separate phase, the equilibrium hydrogen pressure remains constant at a value corresponding to the dissociation pressure of the hydride. The equilibrium pressure decreases as soon as the hydrogen content of the system falls below that required to saturate the liquid sodium. By this means, the solubility of hydrogen has been determined at 250, 300, 315, and 330°; it increases rapidly with increasing temperature. Equilibrium hydrogen pressures over unsaturated solutions, of known composition, of hydrogen in sodium have also been measured, and the results used to determine relevant free-energy values.

When hydrogen in sufficient quantity is brought into contact with liquid sodium, a solid phase of sodium hydride is formed, together with a liquid phase which is a true solution of hydrogen in liquid sodium. If the liquid sodium is in very large excess, the formation of sodium hydride can be avoided, and only the solution obtained. This composition region below the solubility limit of hydrogen is of particular interest, since equilibrium is established between hydrogen in the gas phase and in solution, and the hydrogen pressure may be used as a measure of the quantity of hydrogen in solution. If sodium is regarded as the reaction medium, such measurements provide a method by which the reactions of hydrogen with other solutes, *e.g.*, oxygen, may be studied. Also, a knowledge of the properties of these solutions is necessary for the interpretation of corrosion processes in metal systems containing liquid sodium.

Williams, Grand, and Miller[2] measured the solubility of hydrogen in sodium over the range 250—450°. In the range 350—450°, techniques involving both desorption and absorption of hydrogen gave results which were in good agreement; these showed that the solubility of hydrogen increases rapidly with increasing temperature above 350°, in contrast to the normal behaviour of gases in molecular liquids. At 250—350°, solubilities are very low; in this region, Williams *et al.* used a technique which involved filtration of undissolved sodium hydride, and the results showed pronounced scatter. We have redetermined the solubility in this range, primarily because the hydrogen pressures involved are convenient for the subsequent studies of reactions in solution and the solutions can be handled in glass apparatus at these temperatures. Solubilities have been measured for four temperatures in the range 250—350°, and values for the equilibrium pressures of hydrogen over solutions of known concentration are reported for the first time.

EXPERIMENTAL

Mixtures of sodium hydride and liquid sodium were prepared, in which the proportion of hydride was greater than that required to give a saturated solution, and then known quantities of hydrogen were removed from the system. While sodium hydride was present as a separate phase, the equilibrium pressure of hydrogen, measured after each removal, remained constant at a value corresponding to the dissociation pressure of sodium hydride at the temperature of the experiment. Eventually the equilibrium pressures began to decrease, at a composition corresponding to the solubility of sodium hydride in sodium.

Preparation of Mixtures.—Since solubilities are very small at 250—350°, the main difficulty lies in the preparation of mixtures containing minute but known quantities of sodium hydride, which are completely free from contamination. Sodium[3] and argon[4] were purified, and pure

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[1] Part IX, Addison and Pulham, *J.*, 1963, 1232.

[2] Williams, Grand, and Miller, *J. Phys. Chem.*, 1957, **61**, 379.

[3] Addison, Pulham, and Roy, *J.*, 1964, 4895.

[4] Addison, Iberson, and Raynor, *Chem. and Ind.*, 1958, 96.

sodium hydride[3] was prepared, as already described. The cylindrical 200-ml. Pyrex glass vessel A was connected to a capillary tube through tap B (Fig. 1). For filling purposes, a second side-arm fitted with a B24 joint was also initially attached at the top of A; *ca.* 20 g. of liquid sodium were added by means of this arm, which was then stoppered. The sodium hydride (0·01—0·1 g.) was contained in a thin stoppered B14 tube. These pieces of apparatus were exposed to a high vacuum at room temperature in a steel dry-box for several hours, after which the box was filled with dry argon. The hydride was added to solid sodium by tipping the vessel A on its side and then inserting the B14 tube containing the hydride into the B24 side-arm on A until the mouth of the tube almost touched the sodium. By this means, the hydride was placed directly onto the sodium surface and was incorporated with the sodium on subsequent melting and stirring; under these extremely dry conditions, the hydride crystals developed an electrostatic charge, and if they were dropped through a few cm. of the gas in A, they tended to scatter to the glass walls of A and were not subsequently incorporated. The B14 hydride-tube was withdrawn and reweighed, and the B24 side arm of A was drawn off, using a counter-flow of argon to avoid contamination. The vessel A was then joined to a vacuum line, as shown in Fig. 1.

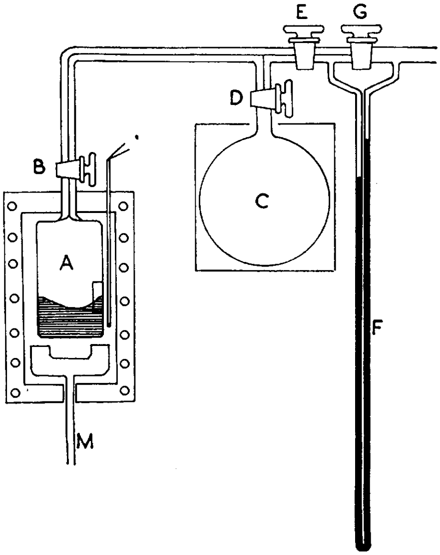

FIG. 1. Apparatus for determination of solubility of hydrogen in liquid sodium.

Stirring.—Liquid sodium can be conveniently stirred by use of a rotating permanent magnet outside the vessel, and an internal bar magnet is not necessary. Because of its low density, vigorous movement of the sodium is possible by this means; the rotatory flow of the liquid was broken by a vertical glass baffle sealed into the side of the vessel A which was enclosed in a furnace (controlled to ±1°) incorporating a rotating magnet M.

Procedure.—The vessel A was first evacuated to 10^{-6} mm. The furnace temperature was then raised to 110°, and the liquid sodium was stirred vigorously under a vacuum for *ca.* 1 hr. This removed any final traces of gas associated with the sodium and mixed the sodium hydride into the liquid metal. At 110°, dissociation of sodium hydride is negligible.[3] The furnace was then raised to the required temperature. The flask C (volume 525 ml., including free-space between B and manometer) was held in a Dewar vessel and maintained at 20°. In early experiments, taps B, D, and E were opened and G was closed, and the variations of pressure during 1—2 hr. were noted while the temperature of A was held constant. Under these conditions, however, sodium vapour slowly diffused from A into C; the hydrogen pressures obtained were low and decreased with time, indicating recombination of sodium and hydrogen in C and in the capillary tube. This was overcome by opening B for short periods of time, and using C only for removal of hydrogen from the system. Thus, with D and B closed and E open, A was heated to the required temperature. Tap B was then moved through 180° (B was open for less than 1 sec.). The gas expanded into the capillary tube and the manometer F, and the hydrogen pressure was measured on F (this was normally a mercury manometer, although silicon oil is a suitable manometer fluid at the lower pressures). This process was repeated at 5-min. intervals. Within 1 hr., pressure balance was established and no further change in pressure occurred on turning tap B.

In order to change the composition in A, the system was evacuated beyond B. Taps E and D were opened, and B was then opened briefly to allow hydrogen to expand into the manometer and vessel C. With B closed, the system was again evacuated, and the process described above was then repeated in order to determine the equilibrium pressure corresponding to the new composition. Equilibrium pressures were not affected by change in composition as long as the vessel A contained sodium hydride as a separate phase, but the stage at which equilibrium pressures began to decrease was clearly defined. Thereafter, the equilibrium pressures are characteristic of the solutions of hydrogen in liquid sodium.

RESULTS AND DISCUSSION

There is no existing evidence on which we can base conclusions regarding the species present in solutions of hydrogen in liquid sodium, and most of the established techniques for the study of species in solutions in molecular liquids are not applicable to liquid-metal solutions. The same solution is obtained when hydrogen is added in the form of molecular hydrogen or of sodium hydride. The hydrogen species must be regarded as existing in a " sea " of free electrons, so that the molecular species H_2 is highly unlikely, and, of the possible atomic species, H or H^- would appear to be more probable than H^+. However, whether or not a dissolved species must necessarily be associated with an integral number of electrons depends upon the medium itself; the concept is largely valid for solutions in molecular liquids and molten salts, but need not be valid for solutions in liquid metals.

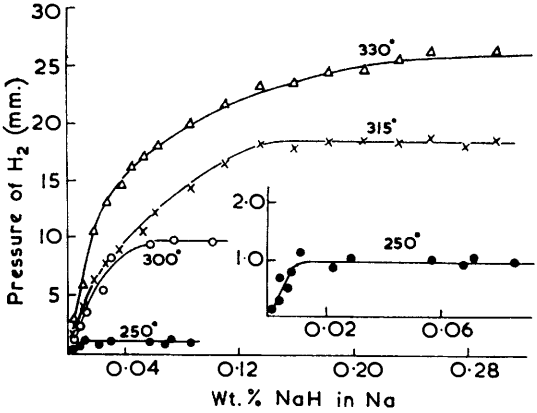

FIG. 2. Pressure–composition isotherms for solutions of hydrogen in liquid sodium.

The pressures of hydrogen in equilibrium with solutions of known concentration are given for four temperatures in Fig. 2. From the compositions at which the curves level off, the solubility of hydrogen can be determined (see the Table).

The solubility of hydrogen in liquid sodium.

Temperature	250°	300°	315°	330°
Solubility (wt. % hydrogen)	0·00042	0·0022	0·0052	0·0104

The striking feature is the rapid increase in solubility with increasing temperature; the solubility rises to 0·2 wt. % at 450°.[2] This is in contrast to the solution of gases in molecular liquids, which is usually a weakly exothermic process, so that the solubility decreases at higher temperatures. Considering the Born–Haber cycle for the formation of sodium hydride, standard energy values indicate that the process

$$Na(l) + \tfrac{1}{2}H_2(g) \longrightarrow Na^+ + H^-$$

is endothermic to the extent of 180·2 kcal. mole^{-1}, but the overall reaction is weakly exothermic because of the high value of the lattice energy (193·8 kcal. mole^{-1}).[5] In the formation of a solution of the ionic hydride in a large excess of sodium, the processes

$$\mathrm{Na} \longrightarrow \mathrm{Na}^{+} \quad \text{and} \quad \tfrac{1}{2}\mathrm{H}_2 \longrightarrow \mathrm{H} \longrightarrow \mathrm{H}^{-}$$

together require 154 kcal. mole^{-1}, and the only other major factor involved is the heat of solution of H^- in sodium. Neither this nor any solvation energy involved is likely to be comparable with the lattice energy, so that the formation of these solutions will be strongly endothermic. It follows that the solubility of hydrogen in liquid sodium should increase pronouncedly with increasing temperature.

The present solubility values are compared, in Fig. 3, with those of Williams *et al.*,[2] and are seen to be much higher than the values which these authors obtained over the lower-temperature range by use of a filtration technique. However, our results support the consistent results which they obtained at the higher temperatures by the absorption method. We therefore regard the solubility–temperature relation as being represented more accurately by the full line A of Fig. 3, the equation for which is

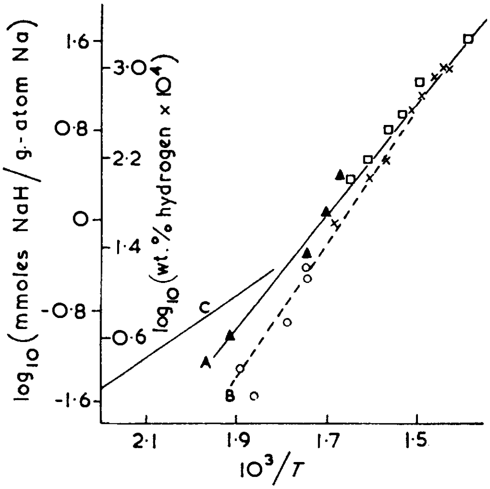

FIG. 3. The solubility of hydrogen in liquid sodium.
□ Absorption method.[2,6]
× Desorption method.[2,6]
○ Filtration method.[2,6]
▲ Present results.
For the significance of lines A, B, and C, see text.

$$\log_{10}\,(\text{wt. \% hydrogen}) = 6{\cdot}211 - 5021/T$$

than by the broken line B suggested by Williams *et al.*[6] Solubility values have also been determined by Thorley,[7] by means of the analysis of samples taken from a large-scale dynamic sodium circuit in which sodium was equilibrated with sodium hydride at different temperatures. The temperature-coefficient of solubility obtained by Thorley (line C, Fig. 3) differs considerably from the present results.

Free-energy Changes for Solutions of Hydrogen in Sodium.—When a second metal, M, is in contact with liquid sodium containing hydrogen, the position of the equilibrium

$$n\mathrm{NaH} + \mathrm{M} \rightleftharpoons \mathrm{MH}_n + n\mathrm{Na}$$

will be determined by (*inter alia*) the hydrogen potential of the liquid phase. Whether or not this is equal to the free-energy change (ΔG) for sodium hydride formation depends upon the hydrogen concentration. For unsaturated solutions of hydrogen in sodium, the relevant equilibrium is

$$\mathrm{NaH}\ (\text{in solution}) \rightleftharpoons \mathrm{Na}\ (\text{liquid}) + \tfrac{1}{2}\mathrm{H}_2$$

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[5] Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 191.
[6] Williams, Grand, and Miller, N. R. L. Memo Rept. 424 (1955).
[7] Thorley, unpublished results.

The equilibrium constant, K, is given by $K = p^{1/2}(\text{Na})/(\text{NaH})$, where p is the hydrogen pressure over an unsaturated solution and (Na) and (NaH) represent activities. With (Na) assumed to be unity,

$$\Delta G = -\boldsymbol{R}T \ln K = -\boldsymbol{R}T \ln [p^{1/2}/(\text{NaH})]$$

so that for unsaturated solutions, ΔG can only be evaluated if the activity of sodium hydride is also known. This is not proportional to concentration (see below), so that it is more convenient to discuss unsaturated solutions in terms of the hydrogen potential ($-\boldsymbol{R}T \ln p^{1/2}$); the ordinate of Fig. 4 is expressed in this form. For the limiting case represented by saturated solutions, p becomes the dissociation pressure, p_D, the relevant equilibrium now becomes

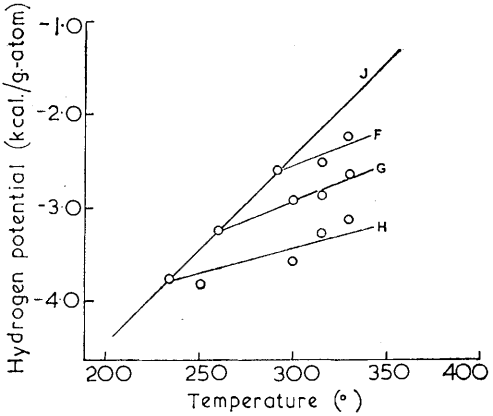

FIG. 4. Variation of hydrogen potential with temperature for solutions of constant composition.

Hydrogen concentrations (wt.% hydrogen): F, 0·00208; G, 0·000617; H, 0·000208. For the significance of line J, see text.

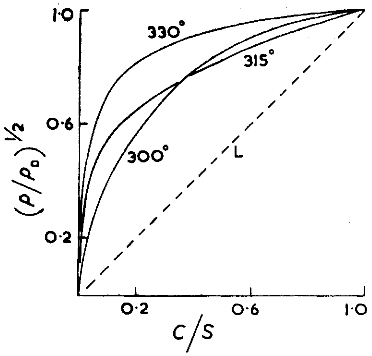

FIG. 5. Deviations from ideal behaviour for solutions of hydrogen in liquid sodium.

$$\text{NaH (solid, sat. with Na)} \rightleftharpoons \text{Na (liquid, sat. with NaH)} + \tfrac{1}{2}H_2$$

and ΔG is given directly by the expression $\Delta G - \boldsymbol{R}T \ln p_D^{1/2}$. The hydrogen potential and ΔG therefore become synonymous for saturated solutions. The hydrogen potentials are significant in the formation of the hydride of those metals in contact with solutions of hydrogen in liquid sodium, but, since hydrogen pressures over unsaturated solutions have not previously been measured, only estimated values have been available.[7-9] Line J (Fig. 4) is derived from dissociation pressures, and thus also represents the variation of ΔG with temperature for saturated solutions. The variation of p (for unsaturated solutions) with temperature has been derived from Fig. 2 for three concentrations, and the composition isopleths F, G, and H (Fig. 4) represent the variation of hydrogen potential with temperature at constant hydrogen concentration.

Deviations from Ideality.—In Fig. 5, the ratio $(p/p_D)^{1/2}$ is plotted against C/S, where p is the pressure of hydrogen in equilibrium with concentration C of hydrogen in liquid sodium, and S is the saturation solubility of hydrogen at the same temperature. If the activity of sodium hydride is proportional to concentration, the results should lie on the straight line L; however, there are pronounced positive deviations. Since all solutions are extremely

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[8] Sinclair, Pool, and Ross, 2nd Conf. on Nuclear Reactor Chemistry, Gatlinburg, 1961, Report T.I.D. 7622.

[9] Thorley and Tyzack, "Thermodynamics of Nuclear Materials," International Atomic Energy Agency, Vienna, 1962, p. 365.

dilute, these deviations are most readily explained in terms of a difference between the nature of hydrogen in the solid hydride and in solution in sodium. For example, the presence of an equilibrium

$$Na^+ + H^- \rightleftharpoons Na + H$$

in solution should result in hydrogen pressures higher than those over a solution in which all hydrogen is present as H^-, since one of the energy terms in the process $H^- \longrightarrow H \longrightarrow H_2$ is eliminated if hydrogen is present in atomic form.

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