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Equilibrium Dissociation Pressure of Hydrogen in Molten LiCl-LiH Mixtures

Kazuhiko Ichikawa* and Kazutaka Kawamura†

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

†*Research Laboratory of Nuclear Reactors, Tokyo Institute of Technology, Tokyo 152*

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Synopsis. Pressure-composition-temperature data were collected for the LiCl–LiH system in the respective ranges 0.1—10 mmHg††, 4.5—22.3 mol% LiH, and 550—700 °C by measuring equilibrium hydrogen pressure in a Sieverts' apparatus. The square root of hydrogen pressure *vs.* composition isotherm follows Sieverts' relation for compositions below 10 mol% LiH.

The recent increased interest in physicochemical and thermodynamic properties of solutions containing lithium hydride as one component, such as those of hydrogen isotopes in liquid lithium,[1–4] has been motivated by their use for direct energy conversion devices. The simplest ionic crystal of LiH consisting of Li^+ and H^- has a NaCl-type structure, in which the ionic radius of H^- is as large as 0.2 nm. The molten LiH may be of simple ionic melt like molten lithium halide and may have a high decomposition-pressure of hydrogen at a temperature just above its melting point 686 °C under 1 atm of $H_2(g)$. According to the study[5] on solid-liquid phase equilibrium the LiCl–LiH system has eutectic temperature 496 °C at 34.0 mol% LiH and no formation of solid solutions was observed. In this work we report variation of equilibrium dissociation pressure of hydrogen with concentration and temperature for molten LiCl–LiH binary mixtures.

Experimental

Experiments were carried out in a so-called Sieverts' apparatus[6] which consisted of four main sections designed, respectively, for (a) gas metering, (b) gas equilibration with LiCl-LiH melt, (c) gas pumping, and (d) gas supply. The gas metering section consisted of a mercury manometer (1—760 mmHg) and a McLeod gauge (10^{-4}—1 mmHg). The equilibration section was a fused-silica tube containing a molybdenum crucible filled with sample; the crucible was kept in a long sintered-Al_2O_3 tube because hydrogen is permeable through fused silica at higher temperatures. Before measuring the equilibrium hydrogen pressure, P_{H_2}, the apparatus, with no sample contained, was evacuated up to 10^{-5} mmHg at the high temperature of interest. P_{H_2} was measured as a function of temperature from 550 °C to 700 °C at each of the LiH concentrations, 4.5, 5.3, 7.5, 9.8, 12.3, 20.2, and 22.3 mol%.

Results and Discussion

Figure 1 shows variation of hydrogen pressure with temperature and Fig. 2 shows isothermal plots of the square root of hydrogen pressure *vs.* composition.

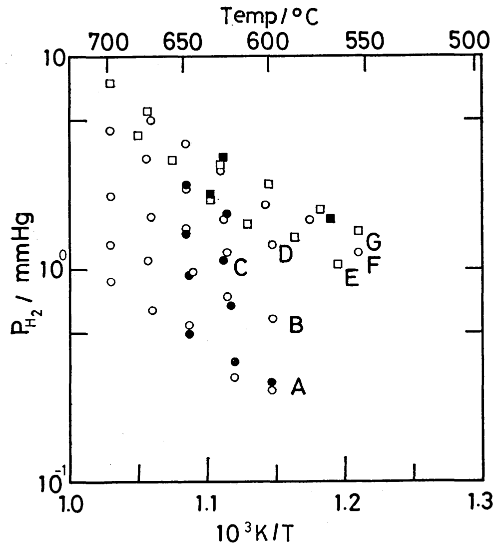

Fig. 1. Temperature dependence of hydrogen pressure for the LiCl–LiH system with each concentration of A: 4.5, B: 5.3, C: 7.5, D: 9.8, E: 12.3, F: 20.2, and G: 22.3 mol% LiH.
The measurements of P_{H_2} with increasing and decreasing temperatures correspond to the open circles or squares and the solid circles or squares, respectively.

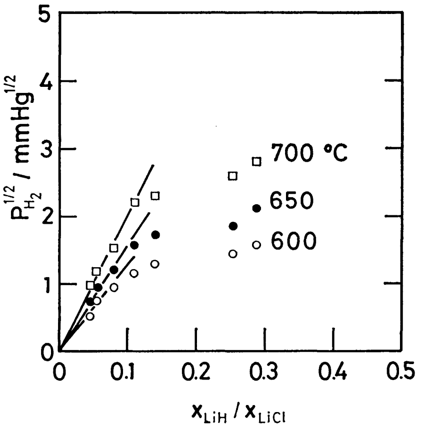

Fig. 2. Isothermal data on the square root of hydrogen pressure *vs.* mole fraction ratio, x_{LiH}/x_{LiCl}, for the LiCl–LiH system.

Since component LiH in a molten LiCl dissociates into a host of ions Li^+ and H^-, the binary solution has a common cation of Li^+ and the equilibrium reaction between the gaseous and liquid phases may be written as

$$\frac{1}{2}H_2(g,\ T,\ P_{H_2}) + Cl^-(soln,\ T,\ P_{Cl_2}) \rightleftharpoons H^-(soln,\ T,\ P_{H_2}) + \frac{1}{2}Cl_2(g,\ T,\ P_{Cl_2}). \qquad (1)$$

The equilibrium constant, $K(T)$, for this reaction is given by

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[††] 1 mmHg=133.322 Pa.

$$K(T) = a_{\mathrm{LiH}}P_{\mathrm{Cl_2}}^{1/2}/a_{\mathrm{LiCl}}P_{\mathrm{H_2}}^{1/2}, \tag{2}$$

where a is activity for each component and P is equilibrium pressure of H_2 or Cl_2. Activity coefficient of LiCl, γ_{LiCl}, has been calculated by use of the temperature-composition solid-liquid equilibrium diagram, with no formation of solid solutions, for the LiCl–LiH system.[5] It is equal to *ca.* unity up to 10 mol% LiH around 600 °C, whereas for component LiH at low concentrations γ_{LiH} may be interpreted as being equal to the constant $k(T)$ in Henry's law. The magnitude of $K(T)$, as evaluated with the aid of chemical potentials[7] of pure liquids LiH and LiCl and pure gases H_2 and Cl_2, indicates that the partial pressure of Cl_2 is very low as compared with that of H_2. If we assume that the square root of $P_{\mathrm{Cl_2}}$ is proportional to the concentration of chlorine anion or x_{LiCl}, the square root of $P_{\mathrm{H_2}}$ in Eq. 2 is given by

$$P_{\mathrm{H_2}}^{1/2} = K_{\mathrm{app}}(T)\frac{x_{\mathrm{LiH}}}{x_{\mathrm{LiCl}}}, \tag{3}$$

where $K_{\mathrm{app}}(T)$ is apparent Sieverts' constant. The three straight lines shown in Fig. 2 correspond, respectively, to the values of $K_{\mathrm{app}}(T)$, $K_{\mathrm{app}}(700\ ^{\circ}\mathrm{C}) = 20$, $K_{\mathrm{app}}(650) = 16$, and $K_{\mathrm{app}}(600) = 13$ mmHg$^{1/2}$/(mole fraction ratio, $x_{\mathrm{LiH}}/x_{\mathrm{LiCl}}$), though experimental values for the square root of $P_{\mathrm{H_2}}$ deviate from Sieverts' law toward the lower values for compositions above 10 mol% LiH. The experimentally determined $K_{\mathrm{app}}(T)$ values are equal to *ca.* one third of those for the hydrogen isotope–lithium system.[4] The knowledge of the Sieverts' law constant is of importance to evaluate $P_{\mathrm{H_2}}$ for dilute solutions.

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