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The Solubility of Hydrogen Isotopes in Lithium*

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Summary

The individual solubilities of hydrogen, deuterium and tritium in lithium have been measured as a function of temperature (700 to 1000°C) and pressure (0.1 to 760 torr). The individual solubilities decrease with increasing temperature, and, for the same hydrogen isotope concentration in the molten lithium, the equilibrium gas pressures for the isotopes are of the order $P_{T_2} > P_{D_2} > P_{H_2}$. When the mole fraction of LiH, LiD, or LiT is less than about 0.1, the temperature dependence of the individual solubilities can be expressed as $\ell n(N_{LiH}^{-1} P_{H_2}^{1/2}) = 9.842 - 6242/T(°K)$, $\ell n(N_{LiD}^{-1} P_{D_2}^{1/2}) = 9.515 - 5644/T(°K)$, and $\ell n(N_{LiT}^{-1} P_{T_2}^{1/2}) = 9.226 - 5085/T(°K)$. In these equations, N is the mole fraction in the liquid phase, P is the equilibrium pressure of the gaseous hydrogen isotope (torr), and T is temperature (°K).

The mutual solubilities of hydrogen and deuterium in lithium have been measured for the plateau region at 800°C. Both the total pressure and the individual partial pressures of H_2, HD, and D_2 have been determined as a function of the mole fraction of LiH and LiD in the lithium solution with varying hydrogen-to-deuterium ratios. The total pressure and the partial pressures of hydrogen and deuterium in the plateau region at 800°C may be expressed as $P_{total}^{1/2}$ (torr) $= -3\, N_{LiH}/(N_{LiH} + N_{LiD}) + 15.9$, $P_{H_2}^{1/2}$ (torr) $= 12.9\, N_{LiH}/(N_{LiH} + N_{LiD})$, and $P_{D_2}^{1/2}$ (torr) $= 15.9\, N_{LiD}/(N_{LiH} + N_{LiD})$.

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Adequate tritium management schemes for controlled thermonuclear reactors (CTR) with lithium blankets will require detailed information on the vapor-liquid equilibria for the hydrogen isotope-lithium systems. These equilibrium studies are needed to define the tritium pressures that will exist in a CTR system. This information also aids in the prediction of permeation of hydrogen isotopes through the system. All of this information will be needed in the design of a process to maximize recovery of the bred tritium and minimize the loss of tritium to the environment.

The individual equilibrium pressures of the hydrogen isotopes in Li-LiH-H_2, Li-LiD-D_2, and Li-LiT-T_2 systems were measured between 700°C and 1000°C using a modified Sieverts apparatus. Samples of lithium were encapsulated in iron, which is highly permeable to the hydrogen isotopes, and the equilibrium pressure was established inside and outside the capsule which was held at constant temperature. Utilizing the measured equilibrium pressures and a mass balance on the system, the experimental data were considered in terms of the equilibrium

$$\mathrm{Li(d)} + 1/2\ \mathrm{H_2(g)} = \mathrm{LiH(d)} \qquad (1)$$

in which (g) and (d) indicate the gas and the liquid Li-LiH phases, respectively, and H represents the hydrogen isotopes. The experimental results for solubility of pure hydrogen, deuterium, and tritium in lithium as a function of pressures at 800°C are shown in Fig. 1. The tritium measurements were limited to 150 Ci total which, in our system, was about 50 torr equilibrium pressure. The first rising portion of the plot ($N_{LiH} \leq \sim 0.4$) represents a homogeneous liquid phase of lithium hydride dissolved in lithium and the second rising portion ($N_{LiH} \geq \sim 0.9$) represents lithium dissolved in liquid lithium hydride. The constant-pressure plateau between the two portions defines the two-phase coexistence region. When the mole fraction, N, of LiH, LiD, or LiT was less than 0.1, the Sieverts relationship [1]

$$\sqrt{P_{H_2}(g)} = K_s\ N_{LiH(d)}, \qquad (2)$$

was obeyed by each system. The temperature dependence of the solubility is given by the equations:

hydrogen

$$\ell n\ K_s\ (\mathrm{torr}^{1/2}/\mathrm{mole\ fraction}) = 9.842 - 6242/T(°K), \qquad (3)$$

deuterium

$$\ell n\ K_s\ (\mathrm{torr}^{1/2}/\mathrm{mole\ fraction}) = 9.515 - 5644/T(°K), \qquad (4)$$

tritium

$$\ell n\ K_s\ (\mathrm{torr}^{1/2}/\mathrm{mole\ fraction}) = 9.226 - 5085/T(°K), \qquad (5)$$

The solubilities decrease with increasing temperature and, for the same hydrogen isotope concentration in the molten lithium, the equilibrium gas pressures for the isotopes are in the order $P_{T_2} > P_{D_2} > P_{H_2}$.

The mutual solubilities and isotopic exchange of hydrogen and deuterium in lithium have been measured for the plateau region at 800°C. A Sieverts apparatus was modified for these measurements by the addition of a gas pump to circulate and mix the gases (H_2, HD, and D_2) and a sampling station to permit sampling and mass spectrometric analysis of the equilibrium gas phase. In these experiments sufficient hydrogen (or deuterium) was added to the lithium to produce a Li-LiH-H_2 (or Li-LiD-D_2) system in the plateau region, then deuterium (or hydrogen) was added in small increments. The results are shown in Fig. 2. The results were independent of whether the initial addition was hydrogen or deuterium and did not depend on the relative amounts of the two coexisting liquid phases. The equilibrium pressures depended only on the relative amounts of the isotopes present. The total equilibrium pressure in the mixed hydrogen-deuterium-lithium system follows the relationship

$$P_{total}^{1/2}\ (torr^{1/2}) = -3\ \left(\frac{N_{LiH}}{N_{LiH} + N_{LiD}}\right) + 15.9 \qquad (6)$$

Partial pressures of hydrogen and deuterium are represented by

$$P_{H_2}^{1/2}\ (torr^{1/2}) = 12.9\ \left(\frac{N_{LiH}}{N_{LiH} + N_{LiD}}\right), \qquad (7)$$

$$P_{D_2}^{1/2}\ (torr^{1/2}) = 15.9\ \left(\frac{N_{LiD}}{N_{LiH} + N_{LiD}}\right) \qquad (8)$$

respectively. The equilibrium partial pressure of HD is defined by the pressures of H_2, D_2 and the gas phase equilibrium constant which at 800°C is [2]

$$K(g) = 3.8 = \frac{P_{HD}^2}{P_{H_2}\ P_{D_2}}\ . \qquad (9)$$

The boundaries of the two phase region (single isotope present) were found to be identical for hydrogen and deuterium (Fig. 1). Our data (Fig. 1) are in excellent agreement with those of Veleckis [3]. The boundaries at 800°C for the mixed hydrogen-deuterium-lithium system are identical to those for the single isotopes and are independent of the ratio of hydrogen to deuterium. They are given by the relationships $N_{LiH} + N_{LiD} = 0.33$ and $N_{LiH} + N_{LiD} = 0.96$

The equilibrium isotope effect measured in the mutual solubility work at 800°C may be obtained by dividing Eq. (8) by Eq. (7),

$$\frac{P_{D_2}^{1/2}}{P_{H_2}^{1/2}} = 1.23\ \frac{N_{LiD}}{N_{LiH}} \qquad (10)$$

Studies of the mutual solubilities and the equilibrium isotope effects are being extended to other temperatures, to the Sieverts region, and to the hydrogen-tritium-lithium system.

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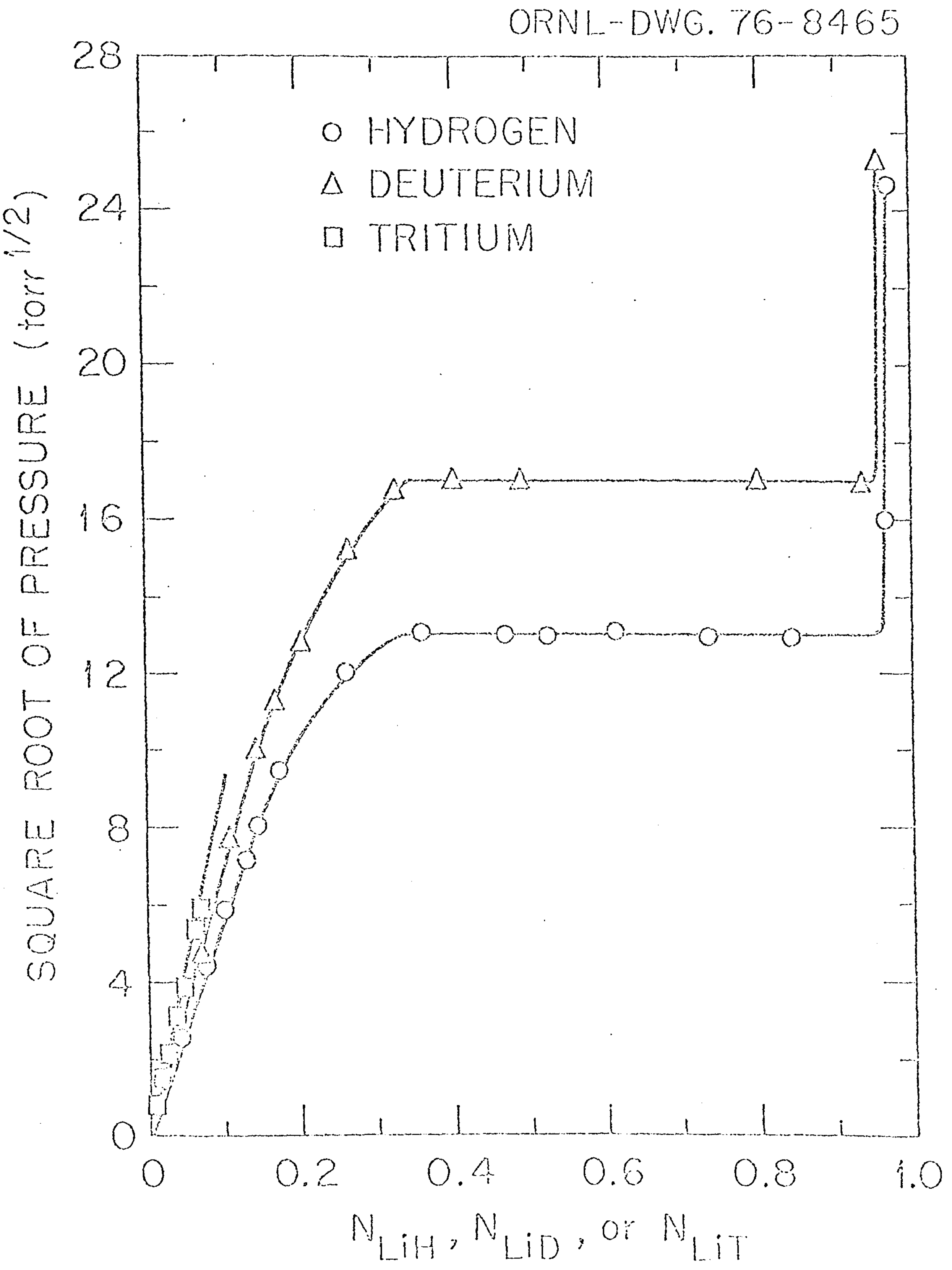

Fig. 1 Solubility of Individual Hydrogen Isotopes In Lithium at 800°C.

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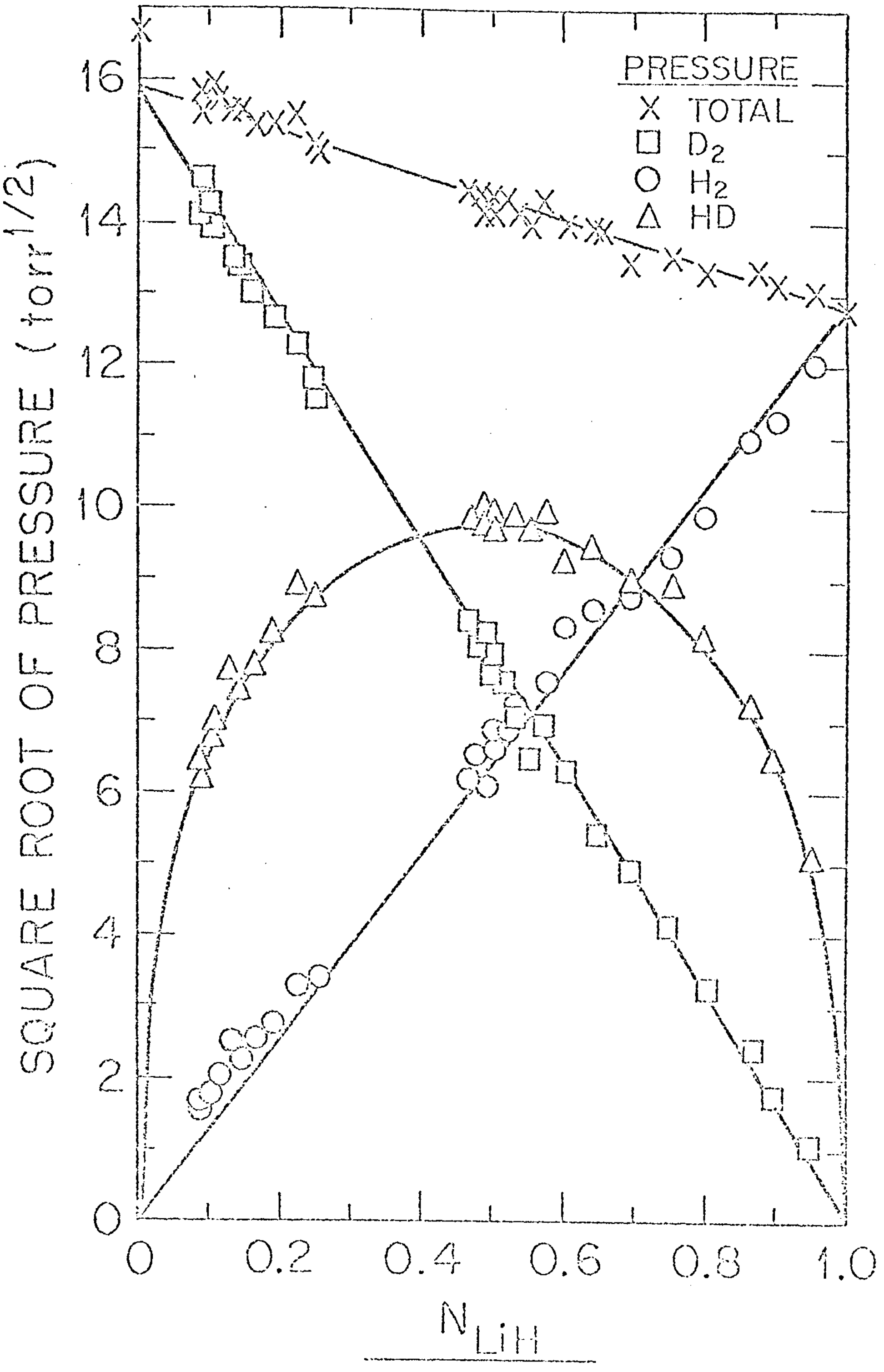

Fig. 2. Mutual Solubility of Hydrogen and Deuterium in Lithium for the Plateau Region at 800°C.