Solid-Liquid Equilibrium

Systems of Lithium Hydride with Lithium Oxide, Calcium Hydride, Titanium Hydride, and Zirconium Hydride

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LITHIUM OXIDE and calcium hydride are ionic compounds structurally related to lithium hydride. Lithium oxide is an important impurity in lithium hydride, resulting from contamination by exposure to air. Titanium and zirconium hydrides are of the metallic type, but Libowitz and Gibb (*8*) and Gibb and Schumacher (*5*) have shown, on the basis of ionic radii, that there may be considerable ionic nature in transition metal hydrides. The extent and nature of the freezing point depression of lithium hydride by these solutes would be related to the nature of the bonding in the solutes.

EXPERIMENTAL

Solid-liquid equilibrium was investigated by the method of thermal analysis. The system LiH-Li_2O was studied from 0 to 14 mole % Li_2O, and the system LiH-CaH_2 from 0 to 37 mole % CaH_2. The other two systems were investigated only at 8.0 ± 0.3 mole % titanium hydride in LiH and zirconium hydride in LiH.

The apparatus and technique, and the preparation of lithium hydride, were described in earlier publications (*10, 11*). The average melting point of LiH of 688.6° ± 0.3° C. agreed with earlier values. Warming and cooling runs were made at each composition, between temperatures 25° C. above the liquidus and 25° below the eutectics, the samples having been annealed for at least an hour at the starting temperature before each run. The initial rates of heating or cooling were adjusted to 1–1.5° per minute before the onset of melting or freezing, respectively.

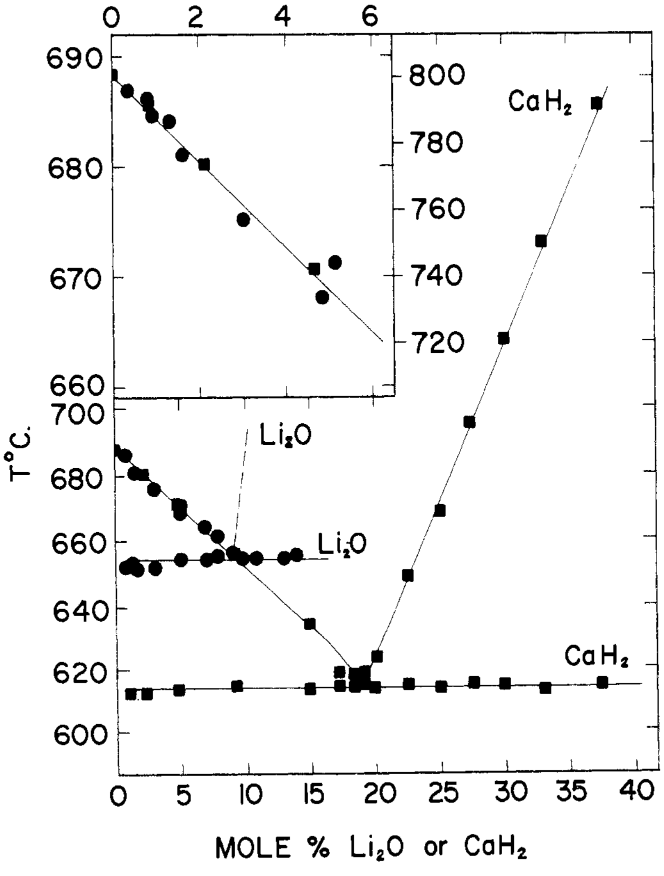

Figure 1. Solid-liquid equilibrium diagrams of systems LiH-Li_2O and LiH-CaH_2

■ Li_2O, ● CaH_2

All runs with Li_2O and CaH_2 were made under a hydrogen pressure of 1 atm., the hydrogen contents approaching stoichiometric. In the systems with titanium and zirconium hydrides, the hydrogen pressures at the start of each run were varied to investigate the effects of the resulting changes in hydrogen content on phase behavior. In the titanium hydride system one set of runs was made at about 10-atm. pressure, to achieve a phase of higher hydrogen content, using a specially constructed high pressure hydrogen system. Although originally designed for vacuum operation, the sample bomb was satisfactorily leaktight at 1 atm.

MATERIALS

The lithium metal used to synthesize LiH and Li_2O was Foote Mineral Co. "low sodium" grade. It was an isotopically enriched sample of chemical atomic weight 6.987.

The lithium oxide was generated as needed in the sample bomb by the reaction of lithium hydroxide with a part of the lithium hydride already present, by the reaction: $LiH + LiOH = Li_2O + H_2$, which occurs above 300° C. The hydroxide was prepared by the reaction of lithium metal with dioxane-water in the absence of air, followed by evaporation to dryness at 150°.

The hydroxide was analyzed by titration with standard HCl, to the bromothymol blue and modified methyl orange end points. The difference between the two indicated 0.23% Li_2CO_3, which was considered of negligible effect at the low lithium oxide compositions investigated here. The percentages of LiOH found by analyses were:

Sample A initial: 101.13, 101.03, 101.09, 101.17.
Sample A after 6 months in dry box: 100.93, 100.07.
Sample B initial: 100.27, 99.72, 100.00, 100.27 (used up in one month).

Calcium metal was obtained from Dominion Magnesium, Ltd., of Toronto, Canada. It was in the form of granules about 6 mm. in diameter, and assayed 99.9% Ca.

The calcium hydride was synthesized as needed from this calcium and hydrogen in the bomb, with the lithium hydride already present. The reaction was begun at 400° C., the temperature then being allowed to drop to 250° to 300° after hydrogen uptake was well started. Exposure to hydrogen was continued until no further gas was taken up at a pressure close to 1 atm. Final exposure and measurement of the volume of gas combined was made at 725° C. and 1 atm. In addition, those samples with liquidus temperatures above 725° were heated above the liquidus before cooling to 725° for the final measurement.

The titanium and zirconium hydrides were synthesized from iodide process crystal bar metals, the former separately from the LiH, the latter in the thermal analysis bomb in the presence of the prepared lithium hydride. The compositions of these samples as originally synthesized were: $TiH_{1.97}$, $TiH_{1.98}$, and $ZrH_{1.99}$.

COMPOSITION OF THERMAL ANALYSIS SAMPLES

For the LiH-Li_2O mixtures, this was calculated in two ways: first, from the weight of LiH initially present and the weight of LiOH added, and second, from the initial weight of LiH and the measured volume of H_2 evolved in the reaction of the LiOH with the LiH. The mole percentages of Li_2O calculated by the two methods agreed in all cases to within 0.1%, the gas evolution value in most cases being lower by 0.05 to 0.07%.

The composition of the LiH-CaH_2 samples was based upon the Li-Ca ratio. The lithium absorbed 99.8% of theoretical hydrogen on original conversion to LiH, but the added calcium absorbed this much only up to 15 mole % CaH_2, the percentage absorbed then decreasing until at 37.2% CaH_2 only 95% of theoretical hydrogen was absorbed by the Ca.

In the systems with titanium and zirconium hydrides at and below 1 atm., the hydrogen content could be calculated at any point from the original composition of the sample, plus *P-V-T* data on hydrogen gained and lost. This could not be done in the 10-atm. runs because the high pressure system was not calibrated.

RESULTS

The solid-liquid equilibrium curves in the systems LiH-Li_2O and LiH-CaH_2 are shown in Figure 1. Eutectics were found at 654.3° ± 0.3° C. and 9.3 mole % Li_2O, and at 614.0° ± 0.3° and 18.3 mole % CaH_2.

To the left of the eutectics, the precision of the temperature measurements was 0.2° to 0.5°. To the right, the precision in the CaH_2 system was 1° to 2°. In the Li_2O system, no liquidus points could be detected in this region, presumably because of the very steep slope of the liquidus curve resulting from the high melting point of lithium oxide.

In both of these systems the cooling run liquidus temperatures were lower than the warming run values. The eutectic temperatures from warming and cooling agreed in the CaH_2 system; in the Li_2O system, the warming run value was 3° ± 1° higher. These differences are presumably due to relatively slow achievement of equilibrium during the melting and freezing processes. Hence, the warming run values were chosen for the eutectics, and the cooling run values for the liquidus points.

The liquidus curves for the two systems coincide to well within experimental error (insert, Figure 1). Cryogenic values for the latent heat of fusion of LiH were calculated from these by the method of least squares, assuming linear variation of log mole fraction LiH with reciprocal of absolute temperature. The results in calories per mole were

$$\text{From system LiH-Li}_2\text{O: } \Delta H_f = 5010 \pm 400$$

$$\text{From system LiH-CaH}_2\text{: } \Delta H_f = 5160 \pm 230$$

$$\text{Over-all result: } \Delta H_f = 5095 \pm 460$$

The over-all value gives an entropy of fusion of 5.3 ± 0.5 cal. per mole-deg., as compared with values for the lithium halides (*2*) ranging from 5.77 for LiF to 4.7 for LiI.

The validity of the cryogenic latent heat of fusion in this type of ionic system was tested by means of the data of Roake (*13*) on the system LiF-CaF_2. The value found for LiF was 6650 ± 600 cal. per mole; the calorimetric value (*1*) is 6470 cal. per mole.

Table I shows the differences between the liquidus temperatures of the mixtures with titanium and zirconium hydrides and those of the corresponding samples of LiH alone. With one possible exception, the differences are zero within the experimental errors of temperature measurement. The uncertainties are those of the 95% confidence intervals. The pressure ranges are those observed in the runs of each set at the 688° C. melting point of LiH during each run; the composition ranges are those calculated from *P-V-T* data observed at 688° C. during the runs. The phases shown are those which are predicted from published phase diagrams (*3, 4, 9*) to present the equilibrium conditions in the Ti-H and Zr-H systems at 688°.

Table I. Effect of Titanium and Zirconium Hydrides on Liquidus Temperature of Lithium Hydride

		8.0 ± 0.3 Mole % MH_n At 688° C.				
					Phase(s) Predicted M-H System,	
Added Substance	Liquidus Difference °C.	Pressure range, atm.	Compn. range, atoms H/atom M	Ref.	From compn.	From press.
$TiH_{1.97}$	+0.5 ± 0.5	0.77–0.81	0.89–0.94	9	β	β
$TiH_{1.97}$	+2.4 ± 0.5	0.75–1.04	1.0 –1.6	9	$\beta+\gamma,\gamma$	β
$TiH_{1.97}$	+1.5 ± 1.5[a]	0.30–0.35	1.5 –1.7	9	γ	β
$TiH_{1.98}$	+0.1 ± 0.3	10.0 ± 0.2	1.75[b]	4	γ	γ
$ZrH_{1.99}$	+1.0 ± 1.1	0.84–0.90	1.80–1.90	3	δ	δ

[a] Difference was increased above experimental value by 1° ± 1° C., because at hydrogen pressures as low as 0.3 atm., the melting point of LiH could be lowered by this amount due to loss of hydrogen (*10*).

[b] Predicted from reference (*4*) at 688° and 10 atm.

In the titanium-hydrogen system at 688° and at and below 1 atm., only β-phase should exist at equilibrium. The observed compositions show that metastable γ-phase must have been present, presumably because of the slowness of the γ-β transition. In general, the samples with titanium hydride contained more than the equilibrium hydrogen content throughout, with the smallest discrepancies at the highest temperatures (approaching 725° C.).

DISCUSSION

The addition of the ionic solutes Li_2O and CaH_2 to molten LiH resulted in considerable solubility, with eutectics well below the melting point of LiH. The addition of TiH_2 or ZrH_2 produced virtually no effect; the marginal increases shown in Table I conceivably could have been caused by a combination of Ti or Zr with residual oxygen impurity in the LiH. This lack of effect constitutes one piece of evidence that the metal-metal interaction in titanium and zirconium hydrides may be sufficient to offset any tendency of these substances to dissolve in molten LiH due to their ionic character. In the zirconium hydride runs, and in most of the titanium hydride runs, the hydrogen contents were high enough to favor the existence of the metal-hydrogen systems in the relatively more ionic δ and γ phases, respectively.

POSSIBILITY OF SOLID SOLUTIONS

The absence of eutectic halts on warming of the mixtures containing 0.38 and 0.93 mole % Li_2O led to the investigation of the possibility of limited solubility of Li_2O in solid LiH. The time durations of the eutectic halts were observed from the warming curves, and certain corrections were applied for variations in sample size and warming rate, and for the fact that eutectic melting took place over a temperature range. The corrected halt times, graphed against mole fraction Li_2O, gave a straight line which extrapolated to zero time at 0.7 ± 0.4 mole % Li_2O, indicating this extent of solid solubility of Li_2O in LiH at 654° C.

A similar calculation, based on the data of this research, for CaH_2 in LiH gave 0.4 ± 0.4 mole % CaH_2 in LiH at 614° C.

Such solid solubility would also give a value of the cryogenic latent heat of fusion lower than the previously given value by 5 to 10%.

Haven (*7*) has shown the solubility of Li_2O in LiF to be less than 0.1% at the eutectic, by electrical conductivity measurements. The close interionic distances—$d_{\text{Li-H}}$ = 2.04 A. (*14*), $d_{\text{Li-F}}$ = 2.01 A. (*12*), and $d_{\text{Li-O}}$ = 200 A. (*12*)—in the individual crystals favor the solubility of Li_2O in both

LiF and LiH. Haven showed that lattice energy considerations accounted for the lack of solubility in the case of LiF, but the data on LiH for the same type of calculation are lacking.

The larger distance $d_{\mathrm{Ca\text{-}H}}$ = 2.35 A. (mean) (*5*, *15*) would be expected to be much less favorable to solid solubility of CaH_2 in LiH. However, Grube and Rüdel (*6*) report limited solid solutions in the system LiCl-$CaCl_2$.

Direct calorimetric eutectic latent heats of fusion would be preferable to the corrected eutectic halt times used here, since the heat transfer characteristics of the apparatus might simulate solid solubility of a fraction of 1%.

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Thermodynamic Functions for Nitryl Chloride

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RYASON and Wilson (*6*) have investigated the infrared spectrum of gaseous NO_2Cl and the Raman spectrum of liquid NO_2Cl and assigned the fundamental frequencies; however, they were unable to establish definitely whether the molecule was planar or pyramidal. Millen and Sinnott (*3*) established the planar structure of the molecule. More recently (*4*), they assigned rotational transitions in the microwave spectra of $NO_2^{35}Cl$ and $NO_2^{37}Cl$, and evaluated the molecular rotational constants. Clayton, Williams, and Weatherly (*1*) reported microwave data and rotational constants in agreement with the values of Millen and Sinnott.

These data permit calculation of thermodynamic functions for the isotopic NO_2Cl mixture. Using the rigid rotator–harmonic oscillator approximation, we have calculated Cp°, $(H^\circ - E_0^\circ/T)$, $-(F^\circ - E_0^\circ/T)$, and S° for nitryl chloride (Table I). The constants used are: h = 6.62377×10^{-27} erg-sec., k = 1.380257×10^{16} ergs per degree, N_0 = 6.02380×10^{23} and R = 1.98719 cal. per mole-degree, selected by Rossini and others (*5*).

A summary of data used in the calculation follows. The fundamental frequencies in reciprocal centimeters are 1293, 794, 651, 1685, 367, and 411. None are degenerate. The molecular weight of the isotopic mixture is 81.465. The molecule has type C_{2v} symmetry. The moments of inertia in a.m.u. sq. A. are I_A = 38.1822, I_B = 97.710, and I_C = 135.845. Vibrational contributions were calculated using the Einstein tables of Johnston, Savedoff, and Belzer (*2*).

Thermodynamic Functions for Nitryl Chloride

		$H_0 - E_0^\circ$	$-(F_0 - E_0^\circ)$	
T, ° K.	C_p°	T	T	S°
		Cal./Mole ° K.		
150	9.56	8.35	49.07	57.42
175	10.16	8.57	50.39	58.95
200	10.74	8.80	51.54	60.34
225	11.30	9.05	52.59	61.64
250	11.82	9.30	53.55	62.85
273.15	12.26	9.53	54.39	63.92
275	12.30	9.55	54.45	64.00
298.15	12.71	9.78	55.23	65.01
300	12.74	9.80	55.29	65.09
325	13.16	10.04	56.09	66.13
350	13.55	10.28	56.84	67.12
375	13.92	10.51	57.56	68.07
400	14.26	10.73	58.24	68.97
425	14.57	10.95	58.90	69.85
450	14.87	11.16	59.53	70.69
475	15.15	11.36	60.14	71.50
500	15.41	11.56	60.73	72.28
525	15.65	11.75	61.30	73.04
550	15.88	11.93	61.85	73.77
575	16.09	12.10	62.38	74.49
600	16.29	12.28	62.90	75.17
625	16.48	12.44	63.40	75.84
650	16.65	12.60	63.89	76.49
675	16.81	12.75	64.37	77.12
700	16.97	12.90	64.84	77.74
750	17.24	13.18	65.74	78.92
800	17.49	13.44	66.60	80.04
850	17.70	13.69	67.42	81.11
900	17.89	13.91	68.21	82.12
950	18.05	14.13	68.97	83.09
1000	18.20	14.33	69.70	84.02
1050	18.33	14.52	70.40	84.92
1100	18.45	14.69	71.08	85.77
1150	18.55	14.86	71.74	86.59
1200	18.65	15.01	72.37	87.39
1250	18.73	15.16	72.99	88.15
1300	18.81	15.30	73.59	88.88
1350	18.88	15.43	74.17	89.60
1400	18.94	15.56	74.73	90.28
1450	19.00	15.67	75.28	90.95
1500	19.05	15.78	75.81	91.59

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