Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Solubilities of $LiBH_4$ and LiH in Diethyl Ether

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IN A STUDY of compounds containing lithium and boron, the solubilities of lithium borohydride and lithium hydride in anhydrous diethyl ether were determined. While this work was not entirely completed before the study was terminated, the data are believed to be very accurate and to justify publication, particularly since few published data are available. The solubility of $LiBH_4$ was determined from 1° to 38.8° C., but with some uncertainties in the 24° to 27° C. region. The melting point of the monoetherate was not quite reached, but it is evidently very slightly above 38.8° C.

The solubility of lithium hydride at room temperature was found to be less than 0.05 p.p.m. by weight.

No satisfactory method of purification of purchased $LiBH_4$ was found, so it was made by reacting LiH with B_2H_6 in diethyl ether. The LiH was a 10- to 40-micron powder containing 95% LiH, the balance being chiefly metallic lithium. The B_2H_6 was not analyzed but was reported as being of high purity and was used soon after it was manufactured. The anhydrous reagent-grade ether was agitated with $CaCl_2$ for several days, filtered, agitated with LiH for several days, and carefully distilled, retaining only the middle portion. The reaction mixture was filtered through a fritted glass disk to remove metallic lithium, unreacted LiH, and any insoluble impurities.

For the solubility measurements a sample of the $LiBH_4$ solution was transferred from the synthesis vessel to a 35-ml. glass bottle containing a Teflon-covered magnetic stirring bar and closed with a precision-ground Teflon stopper. As an added precaution the top of the bottle and the Teflon stopper were covered by a tight-fitting rubber cap. All of the operations described above in which traces of moisture had to be excluded were carried out in a dry nitrogen atmosphere in a dry box. The sample was weighed and then stored at a low temperature so that much of the $LiBH_4$ separated as the solid monoetherate. It was then immersed in a water bath and the temperature of the bath was carefully raised 2° to 4° C. per hour, the sample being continuously agitated by the magnetic stirrer. The temperature at which the last trace of solid disappeared was measured by a calibrated thermometer in a water bath. The temperature was rechecked several times by cooling and reheating the sample. These repeat determinations always agreed to within 0.1° C.

After making the first determination with a sample of $LiBH_4$ it was placed in a desiccator and the stopper removed so as to permit a small amount of ether to be evaporated under vacuum. It was then weighed and the above operations of heating, cooling, and measurement of the disappearance temperature of the solid were repeated. Solubilities could thus be measured at several temperatures with a single sample.

The quantity of $LiBH_4$ in the sample was determined from initial weight of the sample and by final gravimetric analysis for lithium. The method (2) involved treating with dilute H_2SO_4, evaporating to dryness, heating the residue three times with hydrochloric acid–methanol to remove the boron as the volatile methyl borate and igniting the lithium sulfate at 850° C. to constant weight.

The solubility values are thus based on the assumption that the only lithium present in the solution is that from the $LiBH_4$. Validity of this assumption is upheld by these facts: that the only significant impurity in the reactants was lithium, which is insoluble in ether and which did not pass through the fine fritted glass-disk filter; that a check of the lithium to boron ratio gave the value 0.986 to 1.000, which was considered close enough to the theoretical 1 to 1.

The data obtained are given in the Table I in the order of increasing temperature. Published data of others are also given in Table I along with the smoothed values at even temperature intervals, the 0° C. value being found by extrapolation. Figure 1 is a plot of the data presented here and of the previously published values.

When the data were plotted it was found that a smooth curve could be drawn. However, in the interval 24°–27° C.

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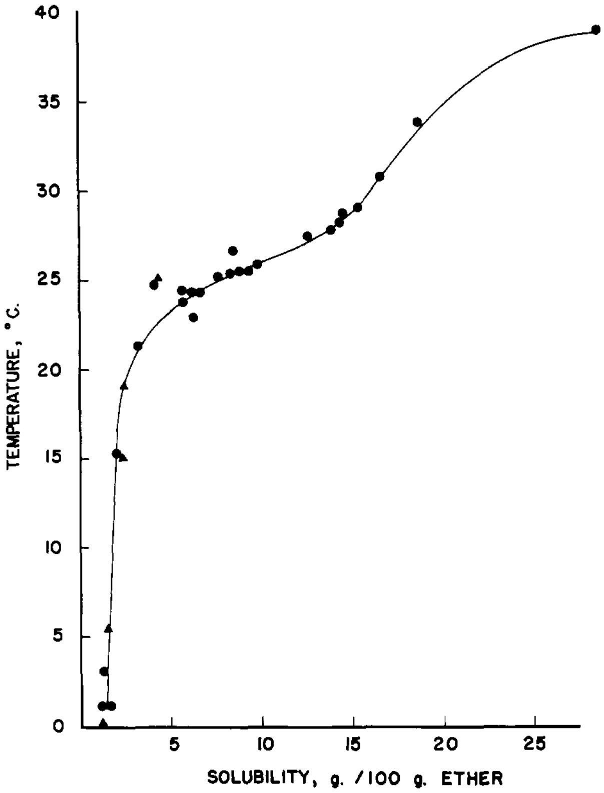

Figure 1. Plot of data presented compared with previously published work

● This work

▲ Previous work

three points deviated significantly from the curve for an unknown reason. Time limitations prevented a careful recheck of this region.

The most probable explanation for the deviation of these three points is that errors occurred in the lithium analysis. While most of the compositions having nearly identical disappearance temperatures checked very well, errors might have been introduced by the succession of treatments to eliminate boron. The temperature measurements were very reliable, since various rates of heating, up to 15° C. per hour, showed no effect on the temperature at which the solid disappeared. Only one crystalline form of $LiBH_4$ appeared to be present, since determinations in which the crystals were formed 40° C. below the disappearance temperature checked exactly with those in which the crystals were formed only a few degrees below the disappearance temperature. There was no visual evidence that transition from one etherate to another ever occurred in temperature range covered.

The work of Schlesinger, Brown, Hoekstra, and Rapp (*5*) and of Kolski, Moore, Roth, Martin, and Schaeffer (*4*) has established the existence above 0° C. of the monoetherate of lithium borohydride for mole fractions less than 0.5 $LiBH_4$, and of the hemi-etherate for mole fractions greater than 0.5 $LiBH_4$. The solubility curve plotted from the values obtained in this work shows at the highest concentration reached—i.e., 28.5 grams of $LiBH_4$ per 100 grams of ether, or a mole fraction of 0.493 $LiBH_4$, an equilibrium temperature which is evidently only very slightly less than the maximum temperature to be expected at the 0.50 mole fraction $LiBH_4$—i.e., the melting point of the monoetherate. Since the composition of the pure monoetherate was almost reached, its melting point must be only very slightly above 38.8° C.

Table I. Solubilities of $LiBH_4$ per 100 Grams of Diethyl Ether

Temp., ° C.	Wt. % Determinations	Temp., ° C.	Wt. %
1.0	1.37	25.2	8.35
1.0	1.53	25.3	8.96
3.0	1.40	25.3	9.21
15.2	2.18	25.7	9.79
21.1	3.22	26.6	8.46
22.8	6.34	27.4	12.6
23.6	5.65	27.8	13.8
23.7	5.76	28.2	14.3
24.1	6.16	28.6	14.5
24.3	6.40	28.9	15.4
24.3	5.65	30.6	16.6
24.6	4.14	33.7	18.6
25.1	7.53	38.8	28.5
Previous Data			
0.0	1.28(*4*)	19.0	2.5(*5*)
5.3	1.52(*4*)	25.0	4.28(*4*)
15.0	2.32(*4*)	25.0	3
Smoothed Values			
0.0	1.4	20.0	2.9
5.0	1.65	25.0	7.8
10.0	1.7	30.0	16.2
15.0	1.8	35.0	20.2

When solubility of lithium hydride was measured in an effort to obtain a saturated solution, several grams of LiH were put into a nitrogen-blanketed, 2000-ml. graduate filled with pure, dry ether. Because it was known that the solubility was extremely low the temperature was not closely controlled and ranged from 20° to 35° C.—i.e., the room temperature. Vigorous agitation was provided by a magnetic stirrer. After several days samples of the solution were taken through a fritted glass disk in the dry box. A wetted glass capillary dipped into the filtrate caused no hydrogen evolution, indicating that the solubility of LiH in ether is less than 0.05 p.p.m. by weight, our estimated sensitivity of this test. To eliminate the possibility that dissolved LiH was absorbed by the filter disk, an unfiltered sample was centrifuged to remove any solid. The upper portion of this ether was tested, with the same results as above. Additionally, gravimetric lithium determinations confirmed the absence of any solute LiH down to 1 p.p.m.

The literature presents no quantitative data for the solubility of LiH in diethyl ether; Hurd (3) mentions that LiH appears to be very slightly soluble in polar organic solvents, such as ether, whereas the other alkali metal hydrides, such as NaH, appear to be insoluble.

LITERATURE CITED

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