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# Reaction of Hydrogen with the Metallic Zirconium Monohalides[1]

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The metallic halides ZrCl and ZrBr reversibly absorb hydrogen, even at room temperature, to form the discrete but slightly nonstoichiometric phases ZrXH$_{0.5}$ and ZrXH (X = Cl, Br). The reactions were characterized via x-ray powder patterns and equilibrium pressure–composition data between 250 and 400 °C. Enthalpies of reaction to form hemi- or monohydrides range from −14.8 to −15.8 kcal/g-atom of hydrogen absorbed while entropy changes (per gram-atom of H) are −15.4 ± 0.2 eu for formation of ZrXH$_{0.5}$ and −20.5 and −19.5 eu for conversion to ZrClH and ZrBrH, respectively. Both enthalpy and entropy values are less than those for formation of the binary metal hydride ($\delta$-ZrH$_{1.5}$), consistent with the expectation that hydride stability is decreased by introduction of a better anion former such as halogen. The stoichiometries and stabilities of the products and the small changes in x-ray powder patterns accompanying the formation of these halide hydrides are consistent with hydride insertion between the double metal layers in the zirconium monohalides.

## Introduction

A considerable number of "metallic" halides have recently been prepared, that is, halide salts which are metallike in their electrical conductivity through delocalization of the differentiating electron. Those so identified and characterized to various degrees have been LaI$_2$, CeI$_2$,[2] GdI$_2$,[3] ThI$_2$,[4] and ScI$_{2.16}$[5] and, more recently, the first noniodide examples, ZrCl, ZrBr, and ScCl.[6-9] Such phases represent a significant penetration of the boundary between normal metals and conventional salts and allow a variation of the chemistry of metals. A combination of an interest in fundamental properties of potential hydrogen storage materials and the lack of a good basis for prediction of the chemical reactivity of these metallic phases with hydrogen led us into this investigation. This paper represents the first report of these studies.

The phases chosen for this study were the recently characterized ZrCl and ZrBr, basically two-dimensional metals consisting of infinite double metal layers (metal–metal separation 3.09 Å) separated by double layers of halogen atoms. The structure thus consists of infinite four-layer sheets close-packed as $(\text{X–Zr–Zr–X})_n$. Both phases have recently been shown to be metallic through measurement of their x-ray photoelectron spectra.[8] The initial prediction of the stability of hydrides of these materials was that the relative stability of a metal hydride is largely determined by the competition between the metal cores and the hydrogen for conduction electrons and that a partial replacement of conduction electrons by a more stable anion such as halide should lead to an increase in hydrogen dissociation pressure. This rather simple prediction has been borne out in all cases studied to date. The only other instance of a metallic halide hydride is the isolated example of the addition of a single hydrogen atom to the center of the Nb$_6$I$_8$ cluster in Nb$_6$I$_{11}$.[10]

To date it appears that *all metallic* halides will form halide hydrides which are stable with respect to the isothermal disproportionation into metal hydride and a more conventional halide, in spite of the considerable stability of many metal hydrides.

## Experimental Section

The ZrCl and ZrBr were prepared by methods developed by Struss[6] and improved by Daake[8] in which zirconium tetrahalides are heated with zirconium turnings in a sealed tantalum tube starting at 500 °C and finishing at 825 °C for 1 week. The reaction temperature is increased about 50°/day to allow time for initial reduction of the tetrahalide pressure by formation of the trihalide. Complete reaction was ensured by using 3–4 mil thick zirconium turnings and a 1% excess of doubly sublimed tetrahalide. The 20–30 g of monohalide obtained per run was passed through a 100-mesh screen to detect unreacted zirconium, and the uniformity of the product was established by comparison of x-ray powder patterns.

Tank hydrogen was passed over a catalyst bed (Matheson Gas Products) to remove O$_2$ and then through a trap cooled to −196 °C before use in the hydrogenation apparatus (Figure 1). A standard volume calibrated with water was used to determine the manifold volume at room temperature and the effective volume of the Vycor reaction vessel when heated at 100–500 °C. The latter volume (and its associated error) was reduced by inclusion of a sealed length of Vycor tubing. Finely ground 0.5–3.0-g samples were held in a Mo boat within the reaction vessel. The vessel used at pressures greater than 0.75 atm incorporated a Hoke metal valve and a ball joint sealed with Apiezon W to prevent hydrogen leakage. A Bourdon gauge (0–1500 Torr, Heiss Bourdon Tube Co. Inc.) and a modified 0.01–1.0-Torr McLeod gauge (Gilmont Instruments, Inc.) were used to measure pressures in one hydrogenation apparatus, while another employed a 0–2000 Torr Bourdon gauge (Heiss) and a 0.001–12.0 Torr McLeod gauge (H. S. Martin Co.). The latter was used when the pressure allowed because of its greater sensitivity. Temperature gradients across the samples were minimized by using either Marshall furnaces or tube furnaces lined with Inconel pipe. Temperatures were measured with a potentiometer using a chromel–alumel thermocouple wired to the reaction vessel. In a few cases oxygen contamination during synthesis, pressure measurements, and drybox transfers was determined by neutron activation analyses of samples after completion of a run. A value of 0.66% by weight oxygen obtained after a 9-day absorption–desorption study of ZrCl at 400 °C probably represents an upper limit because of handling conditions.

No activation of the monohalide samples was found necessary prior to hydrogen absorption. Initial hydrogenation of ZrX occurs at ~1 Torr/s at 100–300 °C using hydrogen pressures of 50–100 Torr, dependent on particle size. At room temperature a comparable rate of absorption is attained at 1 atm hydrogen pressure. Equilibrium was assumed when no pressure change occurred for at least 2 h, a criterion established by consideration of observed rates. Equilibrium pressures for pressure–composition plateaus were checked using 10–12-h equilibration periods. The composition increment per hydrogen addition was adjusted by varying sample weights between 0.4 and 3.0 g. The plateau pressures for the hemihydrides were obtained with a McLeod gauge at a composition of ZrXH$_{0.3}$ (X = Cl, Br). Monohydride equilibrium hydrogen pressures below 9 Torr were measured with a McLeod gauge at composition ZrXH$_{0.75}$, and average values of pressure–composition plateau pressures were used for equilibrium hydrogen pressures above 9 Torr. Compositions are estimated to be uncertain by about 1.0–2.5% for the hemihydride, depending on the preparative route, and 1% for the monohydride.

Powder diffraction data were obtained from samples loaded into 0.2–0.3-mm Lindemann glass capillaries in the drybox. A 114.6-mm diameter camera was used with Ni-filtered Cu K$\alpha$ radiation, and the data were corrected for film shrinkage (Table I).

## Results

The ZrCl and ZrBr react with hydrogen reversibly to form the phases ZrClH$_{0.5}$, ZrClH, ZrBrH$_{0.5}$, and ZrBrH, respectively. Pressure–composition isotherms were used to define the phase compositions at 250–450 °C while the distinct conversions between the monohalide, hemihydride, and monohydride phases were also followed by x-ray powder patterns. Figure 2 shows typical pressure–composition isotherms for the ZrCl–ZrClH$_{0.5}$–ZrClH system. These define the phase in

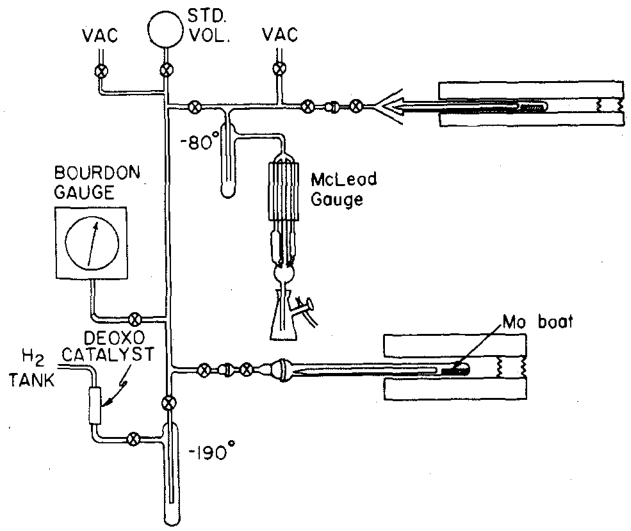

**Figure 1.** Hydrogenation apparatus.

**Table I.** Powder Patterns of Zirconium Halide Hydrides[a]

| $ZrClH_{0.5}$ | | $ZrClH$ | | $ZrBrH_{0.5}$ | | $ZrBrH$ | |
|---|---|---|---|---|---|---|---|
| *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* |
| 8.97 | 10 | 9.26 | 10 | 9.62 | 7 | 9.78 | 6 |
| 4.57 | 8 | 4.64 | 4 | 4.78 | 9 | 4.88 | 9 |
| 3.037 | 8 | 3.090 | 8 | 3.014 | 4 | 3.019 | 7 |
| 2.933 | 1 | 2.946 | 8 | 2.921 | 4 | 2.568 | 10 |
| 2.808 | 4 (d) | 2.80 | 3 (d) | 2.751 | 4 | 2.434 | 8 |
| 2.497 | 3 (d) | 2.52 | 5 (d) | 2.701 | 2 | 2.211 | 3 |
| 2.304 | 2 | 2.334 | 7 | 2.625 | 6 | 1.947 | 4 |
| 2.276 | 9 | 1.701 | 9 | 2.485 | 5 | 1.895 | 5 |
| 1.825 | 3 | 1.675 | 2 | 2.381 | 10 | 1.744 | 7 |
| 1.725 | 4 | 1.599 | 3 | 2.124 | 4 | 1.642 | 4 |
| 1.697 | 1 | 1.539 | 3 | 1.963 | 2 | 1.626 | 5 |
| 1.659 | 4 | 1.489 | 3 | 1.907 | 6 | 1.510 | 3 |
| 1.608 | 4 | 1.472 | 3 | 1.817 | 3 | 1.443 | 4 |
| 1.519 | 5 | 1.41 | 3 (d) | 1.765 | 5 | 1.418 | 5 |
| 1.473 | 2 | 1.357 | 5 | 1.711 | 5 | 1.400 | 1 |
| 1.423 | 1 | 1.146 | 4 | 1.657 | 5 | 1.302 | 2 |
| 1.377 | 3 | 1.117 | 2 | 1.590 | 6 | 1.285 | 2 |
| 1.305 | 3 | 1.09 | 3 (d) | 1.510 | 2 | 1.266 | 1 |
| 1.290 | 2 | 1.046 | 2 | 1.479 | 2 | 1.190 | 6 |
| 1.176 | 4 | 0.987 | 4 | 1.445 | 2 | 1.143 | 2 |
| 1.142 | 3 | 0.938 | 1 | 1.419 | 2 | 1.131 | 2 |
| 1.100 | 2 | 0.927 | 1 | 1.366 | 1 | 1.112 | 7 |
| 1.056 | 1 | 0.909 | 2 | 1.334 | 1 | 1.035 | 3 |
| 1.014 | 1 | 0.856 | 3 | 1.316 | 2 | 1.021 | 1 |
| 0.984 | 2 | 0.832 | 3 | 1.298 | 2 | 1.008 | 3 |
| 0.974 | 2 | 0.816 | 2 | 1.220 | 4 | 0.986 | 1 |
| 0.952 | 1 | 0.809 | 1 | 1.183 | 3 | 0.976 | 1 |
| 0.915 | 2 | 0.802 | 2 | 1.154 | 1 | 0.948 | 1 |
| 0.850 | 2 | | | 1.133 | 2 | 0.932 | 2 |
| 0.836 | 2 | | | 1.091 | 1 | 0.921 | 1 |
| 0.832 | 2 | | | 1.080 | 1 | 0.888 | 1 |
| 0.809 | 2 | | | 1.070 | 2 | 0.874 | 2 |
| 0.807 | 2 | | | 1.011 | 2 | 0.857 | 2 |
| 0.785 | 2 | | | 1.296 | 1 | 0.853 | 2 |
| | | | | 0.985 | 3 | 0.827 | 3 |
| | | | | 0.909 | 1 | 0.822 | 1 |
| | | | | 0.870 | 3 | 0.792 | 1 |
| | | | | 0.868 | 2 | | |
| | | | | 0.860 | 1 | | |
| | | | | 0.781 | 2 | | |

[a] Intensities based on 10 as the strongest; d = diffuse.

equilibrium with ZrCl as $ZrClH_{0.5}$, with additional hydrogen absorption to $ZrClH_{0.65-0.70}$. Further hydrogen absorption affords the new phase $ZrClH_{0.95}$ with the upper limit composition being $ZrClH_{1.0}$ within experimental error. Both phases may be formed at room temperature as well, while no further reaction was observed at pressures up to 33 atm.

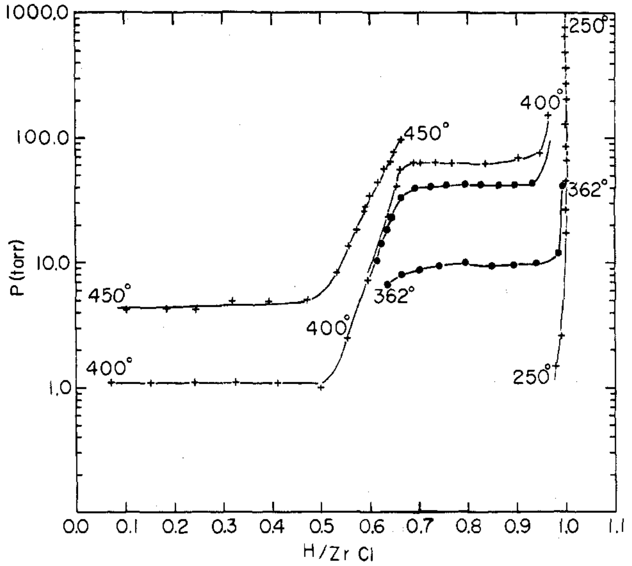

**Figure 2.** Typical pressure–composition isotherms for the $ZrCl-H_2$ system: +, absorption data; •, desorption data.

Color changes accompanying the conversion from monohalide to hemihydride only involve a darkening of the graphite gray. Reaction to the monohydride is more striking as it involves development of brass (ZrClH) and bronze (ZrBrH) colors.

The phases formed are thermodynamically stable with respect to disproportionation to $ZrH_2$ and $ZrX_4$ (or other phases) although such reactions can be forced with high $H_2$ pressures. The experimental conditions used in this study also allow some *nonequilibrium* disproportionation to take place since $ZrX_4(g)$ can diffuse out of the heated zone and condense. The process is appreciable only at or above 400 °C. For example the 450 °C isotherm in Figure 2 is only accurate to a composition of $ZrClH_{0.65}$ since further heating for 5 days led to 39% (nonequilibrium) disproportionation of the original sample. In contrast disproportionation was limited to 6.5% after 9.1 days at 400 °C in the biphasic system $ZrClH_{0.5}$–$ZrClH_{1.0}$.

Some hysteresis in the absorption–desorption isotherm was observed in the $ZrClH_{0.5}$–ZrClH system at 400 °C. However, absorption–desorption cycling lowered the absorption pressures while the desorption values remained unchanged, implying more facile equilibration after a decrease in particle size. In general more rapid equilibrium was obtained on desorption, so all two-phase data used for thermodynamic parameters were taken in this manner.

The compositions and properties of the hemi- and monohydrides obtained from ZrBr are similar to those from ZrCl (Figure 2), but nonequilibrium disproportionation through $ZrBr_4$ diffusion from the heated zone is slightly greater. For example, 16% disproportionation after 5 days at 400 °C occurs with $ZrBrH_{0.6}$. However, the upper limit composition and pressure obtained for the phase on desorption agreed with that on absorption when this decomposition was taken into account, indicating that the two reactions are independent.

The temperature dependence of the four biphasic equilibria studied are illustrated in Figure 3, and the enthalpy and entropy changes calculated therefrom are summarized in Table II. These values are also compared with those for $\delta$-$ZrH_{1.5}$, the phase observed on decomposition.

## Discussion

The metallic phases ZrCl and ZrBr both react with hydrogen to form discrete but somewhat nonstoichiometric phases $ZrXH_{0.5}$ and $ZrXH_{1.0}$ which are thermodynamically stable

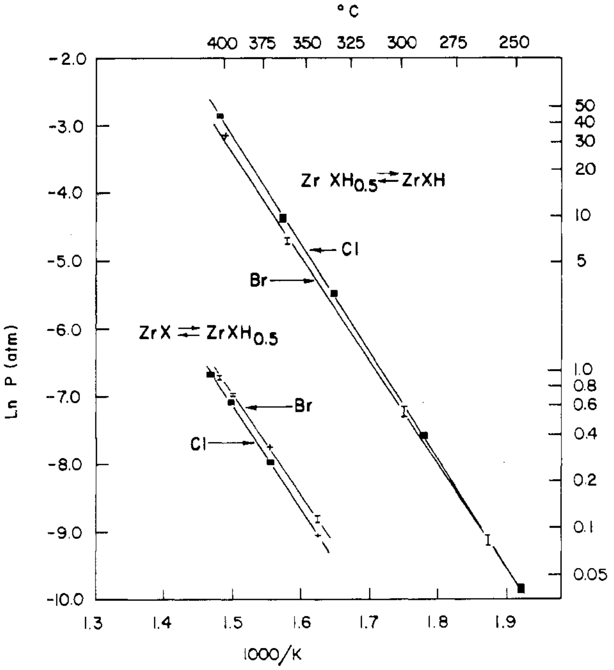

**Figure 3.** Pressure–temperature data for zirconium halide hydrides. Point heights represent observed standard deviations.

**Table II.** Thermodynamic Values for Formation of Zirconium Monohalide Hydrides

| Reaction | $P_{400°C}$, Torr | $\Delta H_f°$,[a] kcal | $\Delta S_f°$,[a] eu |
|---|---|---|---|
| $2ZrCl(s) + {}^1/_2H_2(g) = 2ZrClH_{0.5}(s)$ | 0.95 ± 0.01 | −15.16 ± 0.16 | −15.6 ± 0.2 |
| $2ZrBr(s) + {}^1/_2H_2(g) = 2ZrBrH_{0.5}(s)$ | 0.91 ± 0.02 | −14.74 ± 0.16 | −15.2 ± 0.2 |
| ${}^{10}/_3ZrClH_{0.7}(s)^b + {}^1/_2H_2(g) = {}^{10}/_3ZrClH(s)$ | 43.5 ± 0.9 | −15.80 ± 0.06 | −20.54 ± 0.1 |
| ${}^{10}/_3ZrBrH_{0.7}(s)^b + {}^1/_2H_2(g) = {}^{10}/_3ZrBrH(s)$ | 39.9 ± 0.5 | −15.26 ± 0.24 | −19.50 ± 0.4 |
| ${}^2/_3Zr(\alpha) + {}^1/_2H_2 = {}^2/_3ZrH_{1.0}(\delta)$ | 0.06 | −22.2[c] | −24.2[c] |

[a] Per 0.50 mol of $H_2$ reacted. [b] Approximate upper composition limit of hemihydride. [c] Reference 11.

with respect to isothermal disproportionation into binary halides and hydrides. The nature of the reactions thus resembles those in metal–hydrogen systems in which a separate phase forms rather than a broadly nonstoichiometric "interstitial" product. The reactions may still involve stepwise occupation of the interstitial positions between the double metal layers in the ZrX structure.

Although there was no prior basis for the prediction of formation or relative stability of these halide hydrides, the results obtained seem reasonable. Not only the zirconium monohalides but all other metallic halides studied to date ($Gd_2Cl_3$, $Sc_2Cl_3$, $LaI_2$, $ThI_2$, ...) react with hydrogen reversibly; however, on the other hand the nonconducting reduced halides $ZrCl_3$, $TiI_2$, and $TiCl_2$ do not hydrogenate under the fairly mild conditions used.[12] The abilities of other metallic and nonmetallic reduced halides to react with hydrogen are being compared to further test the hypothesis that conduction electrons are a necessary condition for reversible hydrogen absorption. The metallic halide–hydrogen reactions will also provide a basis for a comparison of structural type and metal electronic environment.

The stabilities of the halide hydrides formed relative to the binary metal hydrides are as postulated (cf. Introduction); viz., the substitution of halide anions for conduction electrons destabilizes the hydride and hence increases the hydrogen dissociation pressure. The lower enthalpy changes for hydride formation, −15 to −16 kcal/g-atom of H, in all four zirconium halide hydrides vs. −22 kcal in $ZrH_{1.5}$ (Table II) reflect this well, although a smaller entropy change associated with the formation of $ZrXH_{0.5}$ suggests some positional disorder and serves to partly counteract the reduced enthalpy change.

The ZrCl structure consists of cubic, close-packed, homoatomic layers sequenced Cl–Zr–Zr–Cl, with these four-layer sheets being approximately cubic close-packed.[7] The ZrBr structure differs in that the Br–Zr–Zr–Br sheets pack in the alternate arrangement so that second nearest neighbors to bromine are hexagonal close-packed.[8] The Zr–H interactions observed are sufficiently strong to conclude that we are dealing with hydridic compounds or phases at least as hydridic as the binary zirconium hydrides. Furthermore, the x-ray powder patterns of the hydrides show considerable similarity to those of the respective monohalides (although they are not easily indexible on any obvious basis) which suggests that hydrogen is positioned between the double zirconium layers. Other locations between Zr–Cl or Cl–Cl layers would seem considerably less likely because of increased anion–anion repulsion. There are precisely 1.0 tetrahedral and 0.5 octahedral holes per ZrX formula unit in the structures, to accommodate the hemi- and monohydride stoichiometries. Proton NMR line widths on the two monochloride hydride phases are consistent with a two-site model.[13] Occupation of the large octahedral hole first might seem more likely, although tetrahedral interstices only are occupied in both γ- and δ-$CaF_2$ zirconium hydrides.[11] Combined neutron and x-ray diffraction studies of this problem are presently under way.[14]

Finally, the fact that these materials react with hydrogen at room temperature and subatmospheric pressures without noticeable induction seems noteworthy, and this aspect is also under further study.

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**Registry No.** $ZrClH_{0.5}$, 60967-31-9; ZrClH, 60921-39-3; $ZrBrH_{0.5}$, 60967-29-5; ZrBrH, 60921-40-6; ZrCl, 14989-34-5; ZrBr, 31483-18-8.

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