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METAL HYDRIDES FOR ENERGY STORAGE

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ABSTRACT

The use of metal hydrides as hydrogen reservoirs facilitates the storage and subdivision of central-station power for automotive and other purposes. Hydrides with a wide range of properties have been synthesized and studied, and several appear to have promise for specific storage applications. Results are reported on the effect of alloy constituents on hydride stability; on the formation of hydrides by metals reacting with gas mixtures such as those produced by the steam reforming of hydrocarbons; and on the feasibility of integrated systems of hydride reservoir plus engine or fuel cell.

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AT THIS DATE, AND PARTICULARLY AT THIS CONFERENCE, one need no longer justify the use of hydrogen as an energy storage medium. It has become abundantly clear that if it is available in a convenient package, and for the right price, it will be used as a fuel. It is also clear that the usual methods of packaging and transporting hydrogen have serious disadvantages. If it is handled as a compressed gas, the containers are heavy, expensive and bulky. If it is liquefied, complicated vessels are needed, together with a supply of liquid nitrogen. At best, liquefaction is useful only for short-term storage. An even more important drawback to compression or liquefaction is the energy required for these operations; it is necessarily a large fraction of that which is later generated by combustion of the hydrogen.

As we have already pointed out (1,2), a possible solution to the storage problem lies in the use of certain metal hydrides. It is well known that some hydrides contain far more hydrogen per unit volume than does liquid hydrogen. It has been the goal of the Brookhaven research program to develop hydrides - or, rather, hydrogen-metal systems - which will have a high hydrogen content and which will meet certain requirements imposed by their use in conjunction with devices that use hydrogen for the production of energy.

Before describing these requirements, it may be helpful to summarize some of the pertinent properties of metal-hydrogen systems in general. Those of interest for our purpose are exothermic; i.e., heat is evolved when hydrogen is absorbed. They are almost always reversible, and the hydrogen can be recovered by lowering the pressure below, or raising the temperature above, the pressure and temperature required for the absorption process.

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At a given temperature, each hydride is in equilibrium with a definite pressure of hydrogen, its "decomposition pressure". If hydrogen is withdrawn and the pressure drops, decomposition occurs until the evolved hydrogen has built up to the decomposition pressure again.

This pressure is a function not only of the temperature but also of the amount of hydrogen in the solid phase. This quantity is not usually constant, as in stoichiometric compounds such as chlorides, but can often vary within rather wide limits. The way in which the dissociation pressure changes with the composition of the solid is shown in Figure 1 for a typical, if slightly idealized, system, $M-H_2$. As hydrogen is taken up by the metal and the ratio H/M increases, the equilibrium pressure increases rather steeply until the point A is reached. Up to this point the solid consists of a solution of hydrogen in metal rather than a compound. At higher concentrations, however, a second phase appears, having the composition B; and the addition of hydrogen will not result in an increase of pressure until all of the solid phase has attained this composition. Above this "plateau" region, further enrichment of the solid in hydrogen requires a steep increase in pressure. The curves labeled T_2 and T_3 in the same figure show the effect on the pressure-composition relation of raising the temperature. At temperatures above 300°C , hysteresis is usually absent and the equilibrium pressure is the same whether hydrogen has been added to or removed from the system. It is convenient, and customary, to characterize the pressure-temperature relationship of a hydride system by plotting the logarithm of the plateau pressure against the reciprocal of the absolute temperature; such graphs are usually linear. Figure 2 gives data of this sort for a number of hydride systems. It is noteworthy how many orders of magnitude in

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pressure are covered, between the most stable and least stable hydrides.

Hydride heats of formation, ΔH^f , can be determined either by calorimetry or by determining the temperature-dependence of decomposition pressure. Table 1 gives values of ΔH^f for a number of hydrides. Hydrides which have a high decomposition pressure at low temperatures generally have a relatively small value of ΔH^f .

Rates of hydrogen-metal reactions vary widely, and depend on several factors. One is the intrinsic nature of the system. Thus, certain titanium-cobalt alloys react, even when in large chunks, almost as fast as hydrogen can be supplied; while pure magnesium powder reacts very slowly. Another factor is cleanliness of metal surface; an oxide film will often result in a long induction period before a good rate is attained. Still another factor is the state of subdivision of the metal. This can usually be greatly increased by subjecting a sample to a series of hydriding-dehydriding cycles. Absolute surface areas as high as 2 square meters per gram have been obtained in this way, and the product was highly active toward hydrogen. Finally, it is possible to increase the rate of the combination reaction by the addition of small quantities of solid catalysts. Thus, the formation of MgH_2 is accelerated by the presence of nickel.

Let us now return to the criteria by which one may judge the suitability of a metal-hydrogen system for energy storage. It was mentioned above that the hydrides are exothermic and that energy must be supplied for their decomposition. This need not, however, be a source of inefficiency. All energy producing devices, whether fuel cells or combustion engines, produce waste heat as well, and it should be possible to utilize this heat for the decomposition of the hydride. We therefore require a

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balance between the heat produced and that required, both as to quantity and quality (temperature). In other words, the hydride must have an appreciable decomposition pressure (at least one atmosphere) at the temperature of operation of the energy-producing device.

Other obvious criteria are the amount of available hydrogen which can be stored on unit weight, or volume, of metal; and the cost of the metal chosen.

The Brookhaven research program has consisted in screening large numbers of metals and alloys for their behavior towards hydrogen, with the above considerations in mind; and examining in depth those systems which showed promise. Our experimental methods and detailed results have been, or will be, reported elsewhere (3). For present purposes it should suffice to summarize the properties of the most interesting systems. (For completeness, the following account will not be limited to those systems first investigated at Brookhaven).

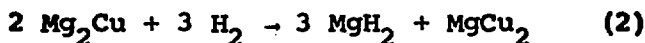
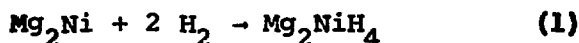
MAGNESIUM AND ITS ALLOYS

Of the binary hydrides known before 1960, MgH_2 was perhaps the most promising for storage applications. It contains 7.65% hydrogen, it decomposes at a lower temperature than most hydrides (1 atmosphere of H_2 at $287^\circ C$) and it is cheap. However, it does not form readily by direct combination of the elements; an overpressure of hydrogen of many times the equilibrium dissociation pressure is required. Its pressure-temperature relation is such that it could conceivably be used in conjunction with a combustion engine or a high-temperature ($>400^\circ C$) fuel cell. The waste heat from such a device would barely be enough to decompose the hydride ($\Delta H^F = -17.8$ kcal). In case of a heat deficit, it might prove economical to burn a portion of the evolved hydrogen in order to decompose the hydride completely; but

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a hydride with a lower dissociation temperature and a smaller heat of combustion is certainly worth seeking.

Some improvement was realized when the systems Mg_2Ni-H_2 and Mg_2Cu-H_2 were explored (3). These alloys undergo the respective reactions:



The equilibrium pressure of H_2 is higher in both these systems than in the $Mg-MgH_2$ system; see Figure 3. Also, the left-to-right hydride formation reactions proceed much more readily than the formation of MgH_2 . Of course, the presence of Cu or Ni lowers the percent of available hydrogen in the solid.

It was observed that the presence of small amounts of Ni, or of Mg_2Ni , catalyzed the reaction $Mg + H_2 \rightarrow MgH_2$. On balance, it is probable that $Mg + 5\% Ni$ is as good a hydrogen storage medium for the higher temperature range as we now have.

DIHYDRIDES OF V, Nb AND THEIR ALLOYS

Vanadium and niobium each forms a relatively stable "monohydride" and an easily decomposed "dihydride"; actually, each phase is far from stoichiometric. Figure 4 shows a set of isotherms for VH_2 ; those of NbH_2 are similar, but slightly lower (3). It is to be noted that the pressure is well over 1 atmosphere at room temperature. If a container of VH_2 is opened to the atmosphere, H_2 is evolved spontaneously, the heat of dissociation being supplied initially by the sensible heat of the system; i.e., the material cools off. Given sufficient heat-transfer surface, heat can be supplied by the ambient air at a rate sufficient to maintain rapid and complete decomposition. As it happens,

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the molar heat of decomposition of VH_2 is relatively low, amounting to only 9.6 kcal per mole of H_2 .

An interesting feature of the VH_2 and NbH_2 systems is that the hydrogen pressure is very sensitive to the presence of impurities in the reactant metal. Thus, a factor of over two is found between VH_2 made from zone-refined vanadium and that made from commercial metal containing no more than 1% of metallic impurities; see Figure 5. Of the impurities, silicon is particularly efficacious; Figure 6 gives a series of isotherms for VH_2 containing varying amounts of Si. Chromium is also active in this way. A wide spectrum of hydride pressure-temperature relationships is thus made available, providing some flexibility in system design. The disadvantages of vanadium-based absorbers are the rather high cost of the metal, and its relatively low (compared with magnesium) content of easily available hydrogen - around 2%.

THE AB_5 ALLOYS

An interesting class of hydrides was discovered by van Vucht and others in the Philips Laboratory at Eindhoven (4). Certain alloys of the formula AB_5 , where A is a rare earth metal and B is Fe, Co, Ni or Cu can absorb up to seven hydrogen atoms per AB_5 unit. Many of them have high dissociation pressures at room temperature. We have confirmed, and added to, the Philips results. So far, the highest-pressure system we have found is that of the alloy $MmNi_5$, where Mm stands for "Mischmetal", a commercial mixture of rare earth metals. Its approximate composition is Ce, 50; La, 27; Nd, 16; Pr, 5; other rare earths, 2. The hydride has the following dissociation pressures: 50 atm at 60° ; 10 atm at 7° ; 2 atm at -31° . It could thus be used as a source of hydrogen down to $-30^\circ C$; that is, even at that

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temperature the heat of dissociation could be supplied by the surroundings, in a properly designed system. The Army has shown interest in such an application, and tests are in progress on a reservoir employing this system which can yield 1-lb of hydrogen.

An unusual property of some of the Al_3 alloys is their ability to absorb hydrogen from gas mixtures containing O_2 , H_2O , CO_2 and CO . Usually any of these will deactivate a potentially hydride-forming metal. Table 2 gives the results of several experiments on mixtures. The components were those which would be encountered in gas produced by the steam-reforming of a hydrocarbon fuel. Such fuels are potentially a convenient source of hydrogen for fuel cells or other purposes, but at present it is necessary to use palladium-silver membranes to isolate the hydrogen from the reformer gas. The use of a hydride-forming metal instead of a diffusion membrane would not only save the cost of palladium but would have the added advantage of providing a ballast hydrogen capacity. This in turn would permit a much shorter start-up time.

OTHER SYSTEMS

In looking for systems of high hydrogen content, one naturally focuses attention on the lighter elements and their alloys. One alloy of possible interest is the iron-titanium intermetallic compound, $FeTi$. Figure 7 shows several pressure-composition isotherms. The complex hydrides of aluminum are also worth considering. Clasen (5) and Abby (6) have shown that some of these can be made directly from the elements, although the presence of a solvent is required.

Much research clearly remains to be done in the exploration of new ternary hydrides, and the optimum system

is yet to be found. Those found so far, however, show enough promise to justify further work. Table 3 compares hydrides with various other energy sources with respect to energy density by weight and by volume. It may be concluded that, if considerations other than economic ones, such as pollution, are included in one's appraisal, hydride systems are worth further development. We are in the process of designing and building an integrated system of hydride reservoir plus power source in which the heat decomposes the hydride. The power source will probably be a Wankel engine. We have established that a Wankel will run very smoothly on hydrogen-air mixtures, over a wide range of composition. No mechanical changes were required. In the particular model we used, in which lubrication is ordinarily provided by premixing oil with the gasoline fuel, it was necessary to inject an oil spray into the hydrogen feed. Even this minor complication would not be needed in a Wankel which had a separate lubrication system, as many models do. Hydrogen and liquid fuels are thus in principle interchangeable and this feature makes the Wankel a good choice for a hybrid system. A vehicle using it could burn gasoline, with its high energy density, in rural areas and then switch to hydrogen when approaching a city. Another factor favoring the use of a Wankel in our experiments is of course its apparent promise as a replacement for piston engines, as evidenced by the auto companies' investment of large sums in Wankel patent rights and technology.

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Table 1 - Hydride Heats of Formation

<u>Initial and Final Compositions*</u>	<u>ΔH^f, kcal. per mole H_2</u>
FeTiH _{0.1} -FeTiH _{1.0}	- 5.5
VH _{0.95} -VH _{2.0}	- 9.6
Mg ₂ NiH _{0.3} -Mg ₂ NiH _{4.2}	-15.4
Mg-MgH ₂	-17.8
K-KH	-27.2
U-UH ₃	-30.4
Zr-ZrH ₂	-39.7
Ca-CaH ₂	-41.7
Li-LiH	-43.3
Ce-CeH ₂	-49.2

*When a metal or alloy is indicated as the initial phase, it is actually a hydrogen-saturated metal phase.

Table 2 - Absorption of Hydrogen by Alloys
From Flowing Gas Mixtures, at 25°C

<u>Alloy</u>	<u>Gas Composition</u>			<u>H₂O, dew pt. °C*</u>	<u>Air %</u>	<u>Press. psia</u>	<u>Composition of Product</u>
	<u>H₂,%</u>	<u>CO₂,%</u>	<u>CO,%</u>				
LaNi ₅	74	26	-	-	-	400	LaNi ₅ H _{6.1}
LaNi ₅	97	-	-	-	-	475-375	LaNi ₅ H _{5.1}
LaNi ₅	72	28	-	25°	3	286-195	LaNi ₅ H _{4.1}
LaCu ₄ Ni	95	-	5	-	-	700	LaCu ₄ NiH _{5.3}
LaNi ₅	79.3	20.3	.002	20°	-	175	LaNi ₅ H _{6.4}

*Where no dew point is given, no water was added; the dew point was probably below -50°C.

Table 3 - Energy Density in Storage Media

<u>System</u>	<u>Mg 93.1 wt % Ni 6.2 wt %</u>	<u>V (commercial)</u>	<u>Nb</u>	<u>H₂ gas, at 3000 psi* n</u>
Plateau limits, in H/M(atomic)	0.1 to 1.85	0.83 to 1.87	1.15 to 1.95	-
Plateau pressure	3 atm at 323°	4 atm to 9 atm at 36°C	3 to 9 atm at 58°	-
Available H, in gm atoms H per gm of H- containing material	0.070	0.021	0.0084	0.99
Gm atoms H per cc	0.125	0.103**	0.071	0.017
Calories per gm of solid for combustion to H ₂ O(l)	2400	704	285	33900
Calories per cc	4270	3520**	2430	568

* Numbers in this column refer to gas alone, without corrections for weight volume of pressure vessel.

**These figures assume a density of 5 for the H containing solid.

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- Fig. 1. - Pressure vs. composition isotherms in a typical hydrogen-metal system.
- Fig. 2. - Dissociation pressures of metal hydrides, I. The approximate compositions of the solid phases to which these curves refer are as follows: LaH_2 , CaH_2 , NaH , UH_3 , MgH_2 , $\text{PdH}_{0.6}$, VNBH_3 , FeTiH .
- Fig. 3. - Dissociation pressures of metal hydrides, II.
- Fig. 4. - Dissociation behavior of vanadium "dihydride".
- Fig. 5. - Relative dissociation pressures of hydride made from pure and commercial vanadium.
- Fig. 6. - Effect of silicon on stability of VH_2 . Silicon contents are, in weight per cent, A, 0.04; B, 0.06; C, 0.22; D, 0.28; E, 0.92.
- Fig. 7. - Pressure vs. composition isotherms in the system, FeTi-H_2 .

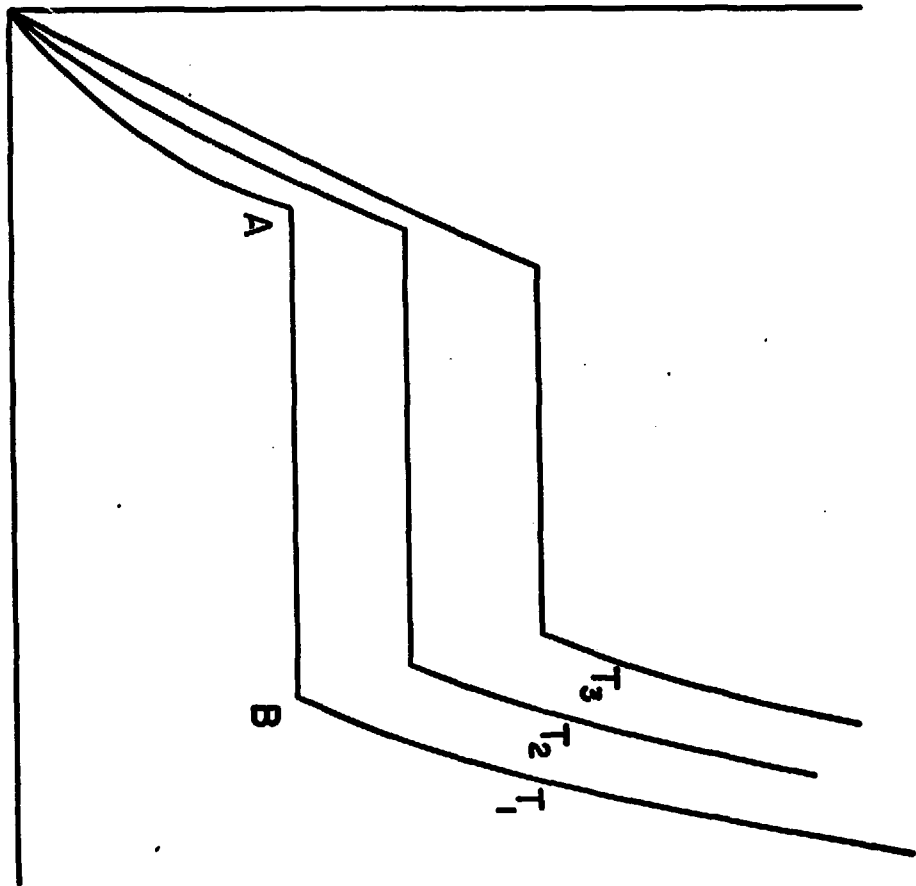
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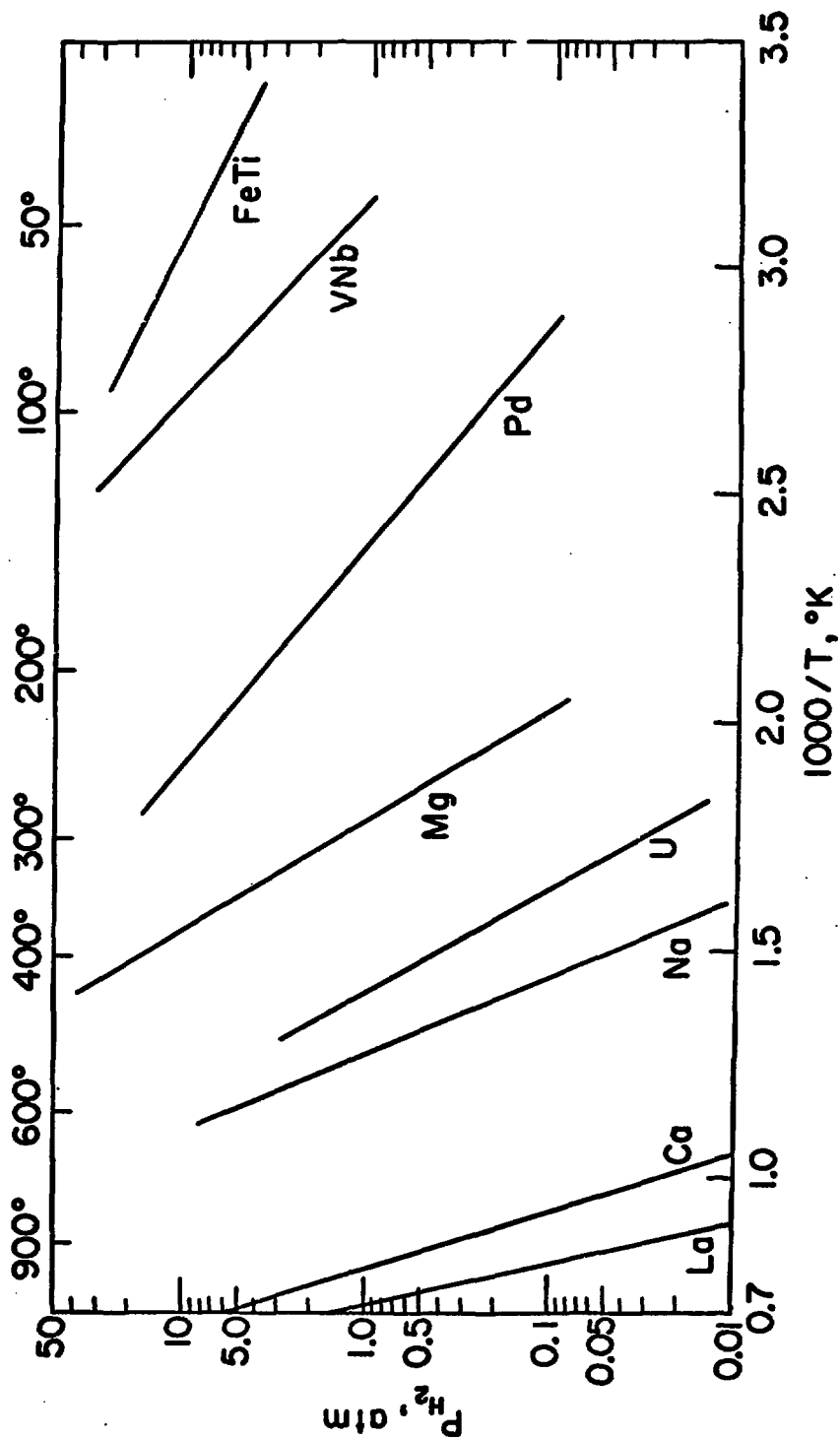
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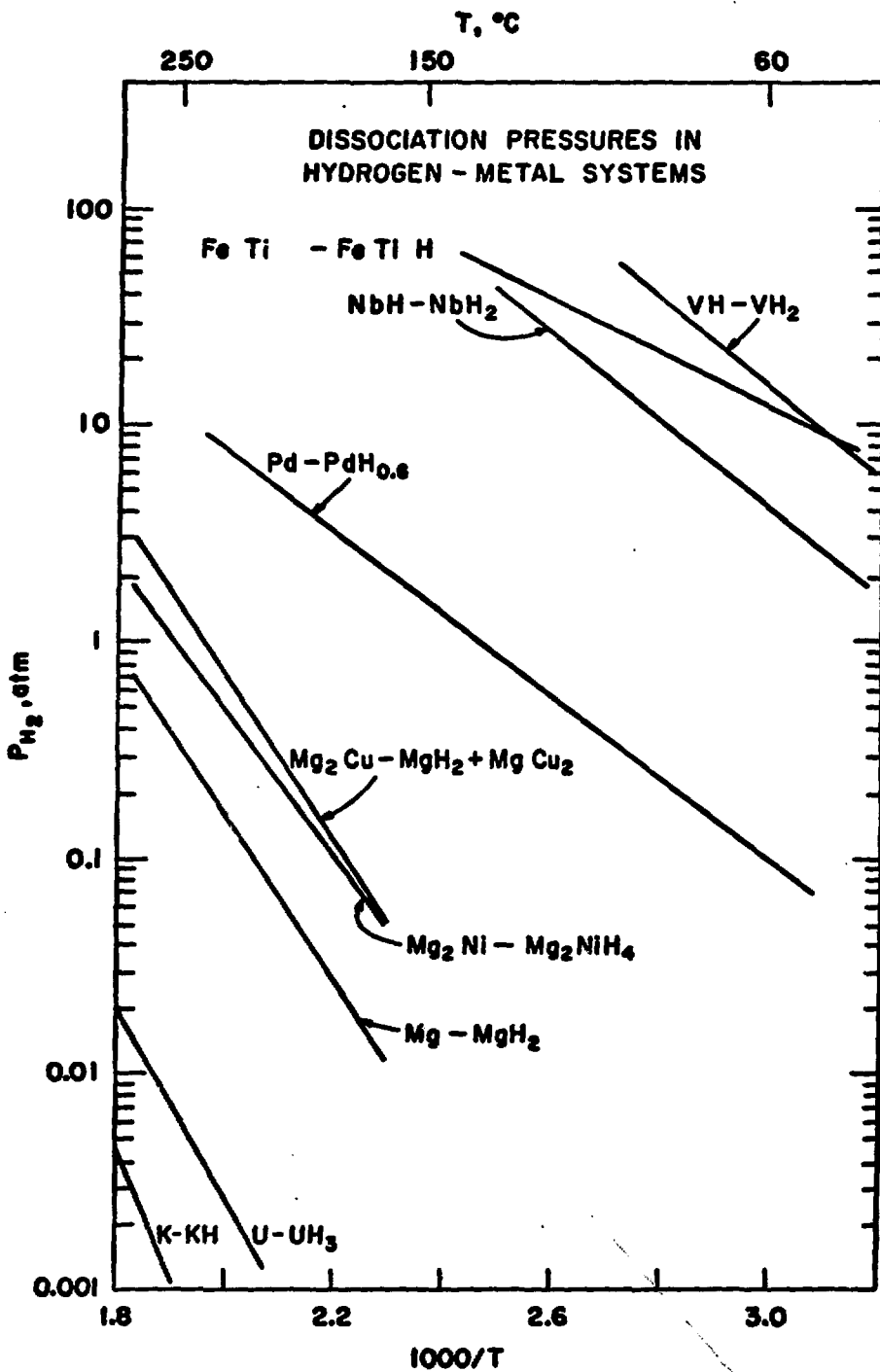
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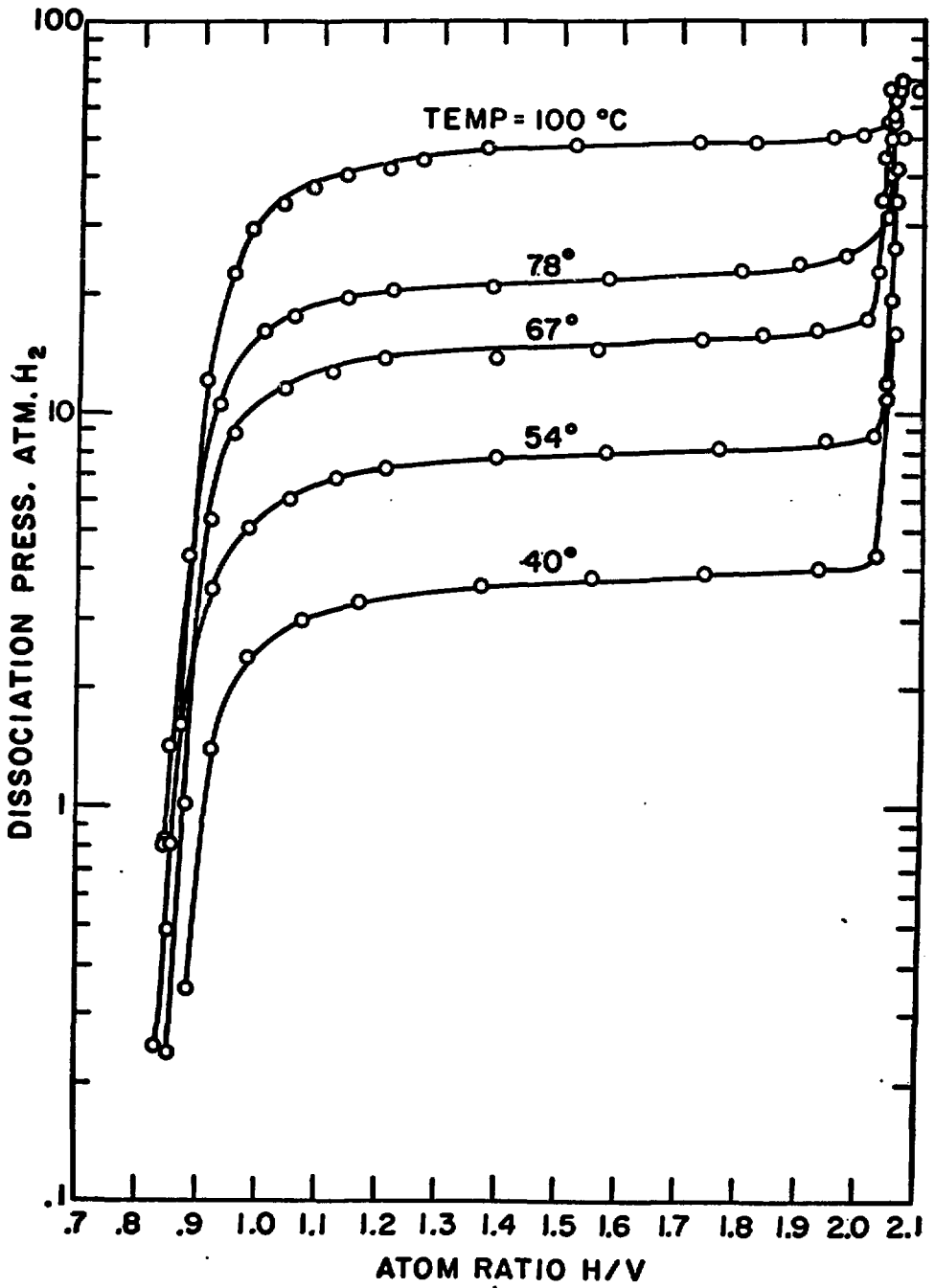
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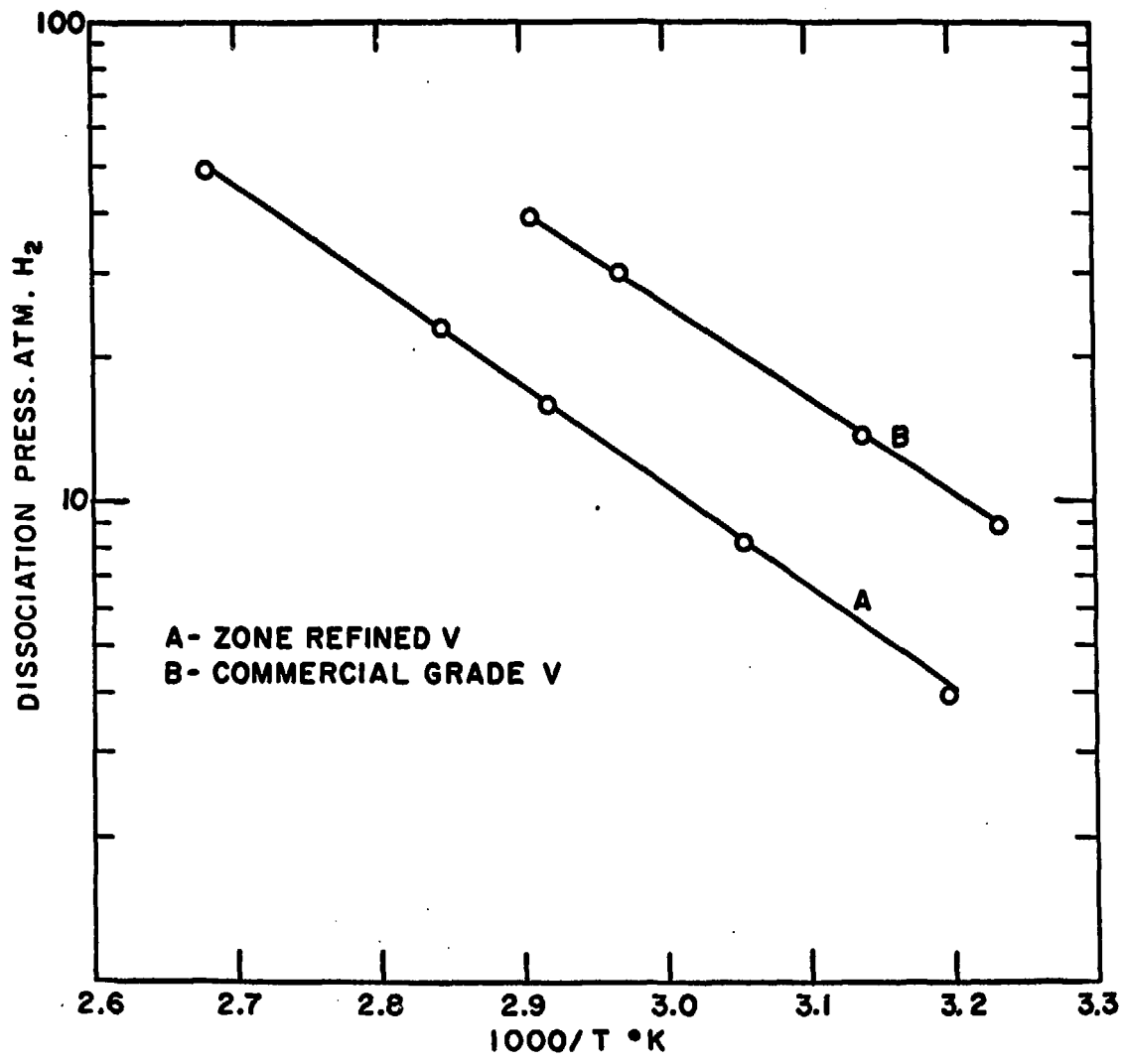
HYDROGEN-TO-METAL RATIO











DISSOCIATION PRESSURE atm H₂

