

CHAPTER 7

Copper- Silver- and Gold-Hydrogen

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Introduction

At present, hydrides of these Group 11 elements could perhaps be considered as a somewhat intermediate class between transition metal hydrides and either ionic or covalent hydrides. A seemingly non metallic form of copper hydride was initially synthesised by Würtz as early as 1844 and other means of preparation of analogous materials are discussed here below. Nevertheless, however, equivalent corresponding preparations of any related forms of silver or gold hydrides do not seem to have been reported, although a relatively complete bibliography is available concerning earlier studies [1,2].

Pressure dependent hydrogen solubilities of all three elements suggest only very low comparative hydrogen content values[1,2]. At very high hydrogen pressures there are indications of the formation of non metallic forms of hydride by gold.

Table 1* Some properties of copper, silver and gold (*after IUPAC source information)

Property	Cu	Ag	Au
Atomic number	29	47	79
Number of naturally occurring isotopes	2	2	1
Atomic weight	63.546 (± 0.003)	107.8682 (± 3)	196.9665
Electronic configuration	[Ar]3d ¹⁰ 4s ¹	[Kr]4d ¹⁰ 5s ¹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ¹
Electronegativity	1.9	1.9	2.4
Metal radius (12-coordinate)/pm	128	144	144
MP/°C	1083	961	1064
BP/°C	2570	2155	2808
Density (20°C)/g cm ⁻³ (history dependent)	8.95	10.49	19.32
Electrical resistivity (20°C)/μohm cm	1.673	1.59	2.35

Adsorption of hydrogen

Earlier apparent indications that hydrogen is not adsorbed on the Group 11 metals have been convincingly disproved in later studies [3-9] using hydrogen permeability and thermal desorption methods of investigation. Some thermodynamic data of hydrogen adsorption on the metals, taken from data of Christmann [6] are presented in Table 2. Also cited in Table 2 are bond energies E_{hy} of diatomic hydride molecules.

Table 2 Characteristics of hydrogen adsorption parameters on copper, silver and gold

Metal Surface	$E_{ad,0}$ (kJ(mole ⁻¹))	E_{Me-H} (kJ(mole ⁻¹))	E_{hy} (kJ(mole ⁻¹))	Ref.
Cu(311)	39	236	276	7, 8
Ag(111)	~15	241	222	8, 9
Au			310	8

The quoted experimental values for the initial heats of adsorption $E_{ad,0}$ have been obtained from measurements of isosteric heat effect and thermodesorption experiments. The quoted bond strengths of hydrogen chemisorbed on metal surface E_{Me-H} are from single crystal work. It may be noted that these values are considerably lower than those for the adjacent group of transition metals Nickel, Palladium and Platinum which seems to underline an important role of d-electrons in the adsorption process since for these transition metals the d-band value is rather close to the Fermi level while for the triad copper, silver and gold its value is lower by 2-3 eV.

Reported results [3.4] have indicated that hydrogen adsorption on these metals is characterised by activation energy values of 60, 90 and 130 kJ(mole⁻¹) for copper, silver and gold respectively. Adsorption is endothermic and corresponding heat values increase in the same element sequence of +5, +40 and +90 kJ(mole⁻¹). Such bond energies of hydrogen atoms with the Group 11 metal surfaces are much smaller than in the cases of other transition metals.

Lattice hydrogen solubility

Parameters representing temperature dependences of hydrogen solubility derived from different sources are presented in Table 3 from which it is clear that all three metals dissolve negligible quantities of hydrogen at ambient temperature. Some further studies of hydrogen solubility in silver have also been reported in a recent study [15]. In a summary by McLellan [16] the solubility of hydrogen in the triad of metals has been proposed to be represented by the equation:

$$\ln Q_i(C, D) = -(\Delta \overline{H}_i / RT) + \Delta \overline{S}_i / K,$$

where Q_i represents the H/M ratio, and where $\Delta \overline{H}_i$ and $\Delta \overline{S}_i$ represent relative partial enthalpy and entropy of hydrogen solution respectively.

Table 3: Hydrogen solubility parameters in copper, silver and gold

Metal	A	B	T(K)	Ψ	Q_p	Equation*	Ref.
Cu	-1.62	-3040	682-1356			3	10
Cu	-2.77	-2426	773-1356			1	11
Cu(liq)	-2.35	-2250	1356-1823			1	11
Cu			773-1356	0.396	48.64	2	12
Cu			773-1273	0.04	36.7	2	13
Cu(liq)			1356-1823	0.790	43.58	2	12
Ag	-2.53	-3245				3	14
Ag	-2.99	-3280	823-1234			1	11
Ag(liq)	-2.32	-3560	1234-1923			1	11
Ag-D ₂	-0.92	-1800	803-1003			1	11
Au	-3.4	-1674	973-1373			1	11
Au-D ₂	-3.97	-4905	803-1003			1	11

* - corresponding equations:

1 - $\lg C(Q) = 0.5 \lg P + A + B/T$ where C represents at %H; P is in Pa; T is in K

2 - $C = \Psi P^{1/2} \exp(-Q/RT)$, where C represents $\text{cm}^3/100\text{gM}$; P is in Pa;
 $\Psi - (\text{cm}^3/100\text{g})\text{Pa}^{-1/2}$, Q-IJ/mole

3 - $\lg D(Q) = A + B/T$, where D represents - H/M; T is in K.

Entropy term values derived for copper and silver are consistent with theoretical values for fcc metals but differ greatly in the case of gold which may be accounted for as representing a higher concentration of vacancies in the sample of gold compared to those present in the copper and silver specimens.

Experimental data [13] has confirmed that increases of pressure lead to an increase of hydrogen solubility S_H in copper in the temperature range 773-1325K for the pressure range 0-500 atm which could be represented by an equation:

$$S_H = 52 \sqrt{P_{H_2}} \cdot \exp\left(-\frac{8950}{RT}\right), (\text{cm}^3/100\text{g})$$

where this form of dependence reflects proportionality of hydrogen solubility in copper to the square root of pressure and an enthalpy of solution correspondence to 8.95 kcal(g-at⁻¹).

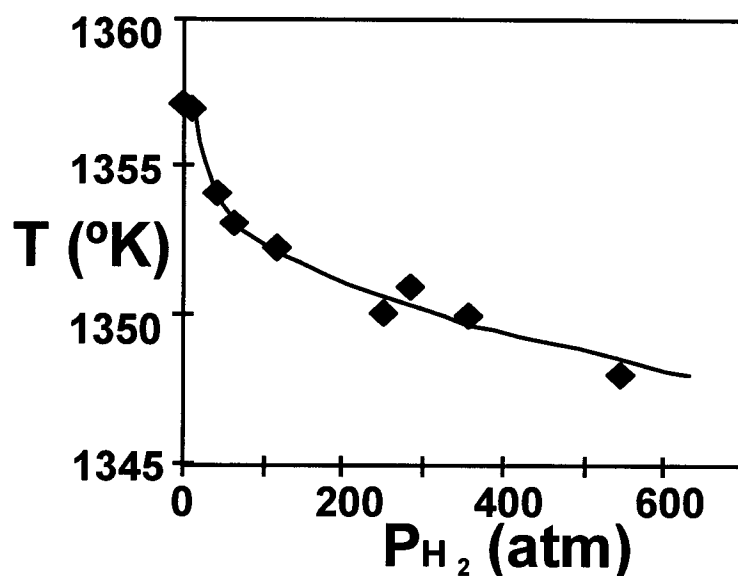


Fig. 1 Copper melting point as a function of hydrogen pressure (after Ref. 13)

With increasing pressure and complementary hydrogen solubility, the melting point of copper gradually decreases, as represented in Fig. 1. The physical sense of this feature is that the metal volume change on hydrogen absorption is smaller than the atomic volume of liquid hydrogen and thus leads to positive values of heats of hydrogen solubility at high pressure. The adjacent part of the copper-hydrogen phase diagram is illustrated in Fig. 2 where the experimental results are compared with phase boundaries calculated from equations of Sieverts and Smithells for hydrogen solubility in solid and liquid copper [17].

During crystallisation of copper containing hydrogen, a gas-eutectic transformation accompanied by evolution of gaseous hydrogen could correspondingly be expected to be observed. Relatedly, at 100 atm and 1353K the solubility of hydrogen in solid and liquid copper has been reported as about 40 cm³/100g, with rather porous ingots formed during the crystallisation, having pore dimensions dependent on the rate of crystallisation [13].

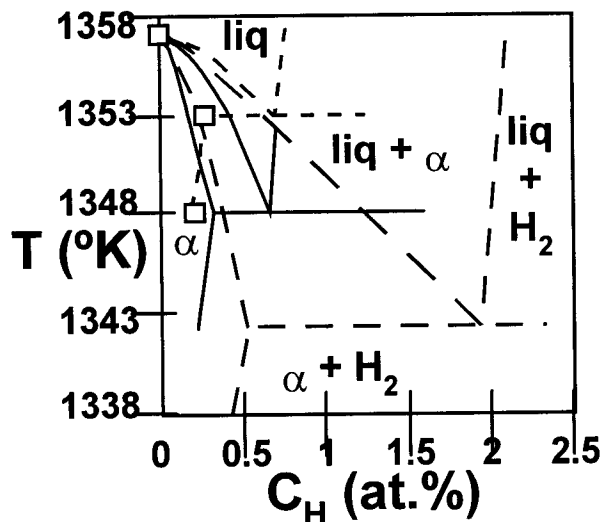


Fig. 2 Copper-hydrogen phase diagram at 500 atm.: (— experimental; — — Sieverts; - - - Smithells) - (after Ref. 17)

On the basis of the equation of state for liquid hydrogen and solubility data under normal pressure, solubilities of hydrogen in the three metals [18] have been calculated at high pressures of up to 10 Gpa (Figs. 3-5). The corresponding temperature dependences at a series of pressures are shown in Figs. 3-5, and illustrate the feature common to these elements of increasing hydrogen solubility with increasing pressure, also found in studies with aluminium, molybdenum, tungsten, iron, nickel and platinum [13].

Hydrides

Only non metallic forms of hydrides of copper and of gold at very high pressures are known up to the present time. In the case of silver, no formation of either metallic or non metallic forms of hydride has been positively reported and hence, only some calculated parameters of a hypothetical hydride can be found in the literature [40].

A simple mean-field lattice gas model has been advanced for the calculation of formation enthalpies and P-C-isotherms and results of these calculations of standard molar formation enthalpy give following corresponding values for copper, silver and gold of 55.91; 56.96; 28.69 kJ(mole H⁻¹) respectively which are in good correlation with data given by McLellan [20].

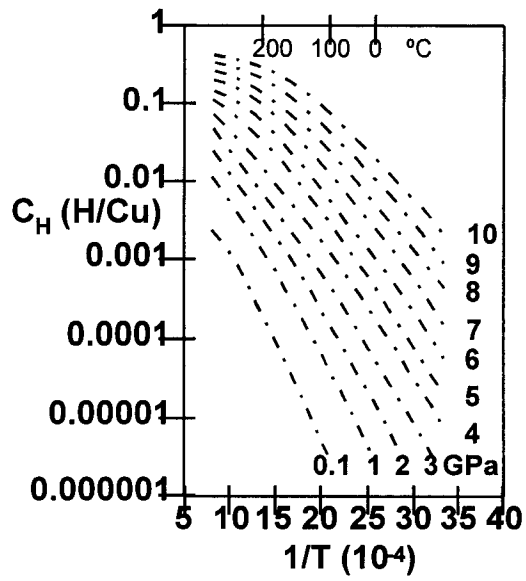


Fig. 3 Solubility of hydrogen in copper as a function of temperature and pressure(after Ref. 18)

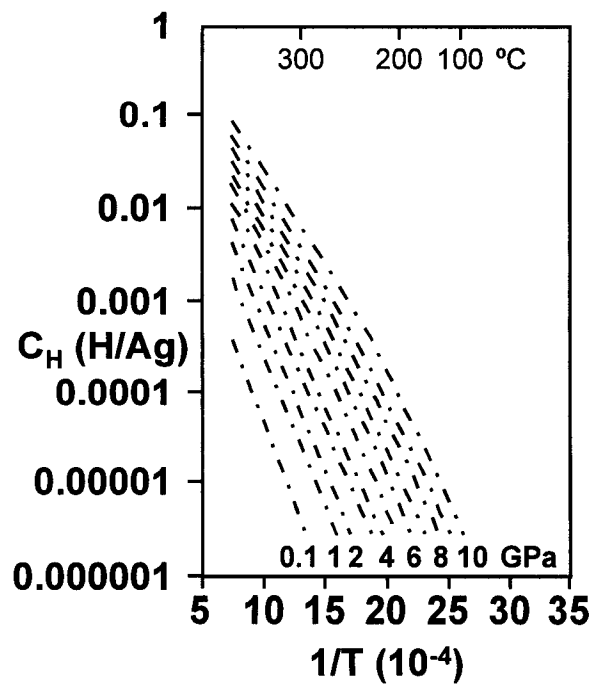


Fig. 4 Solubility of hydrogen in silver as a function of temperature and pressure (after Ref. 18)

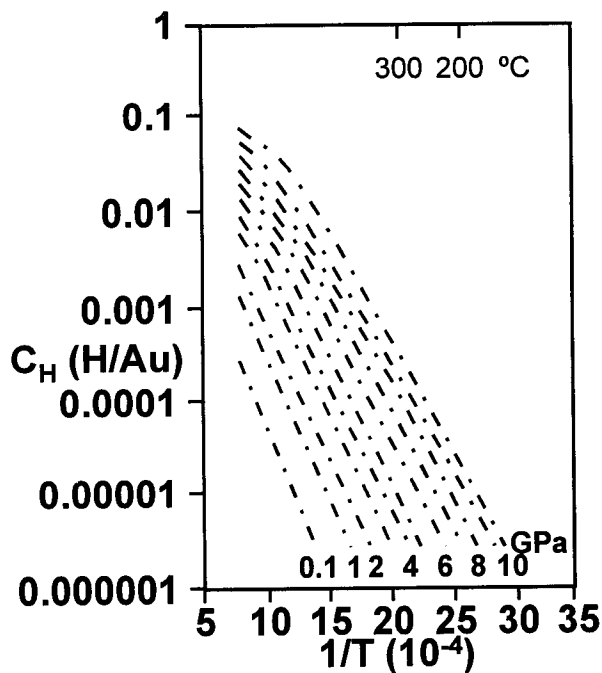


Fig. 5 Solubility of hydrogen in gold as a function of temperature and pressure (after Ref. 18)

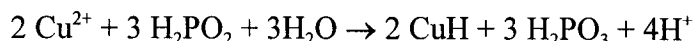
Hydrides of copper

Consideration of extrapolations of trends with increasing Cu contents of p-c(n)-T relationships of a series of Pd-Cu alloys in studies of the Pd-Cu-H system (outlined further below) have indicated a probability that the lattice solubility of hydrogen in pure copper (298K) should be very low (of an order less than $H/Cu \sim 0.001$) in equilibrium with hydrogen gas at very high pressure in similarity to findings for Ag-H, Au-H and also certain Platinum Metal-Hydrogen systems [18].

Non metallic copper hydrides

Non metallic types of hydride of copper are some of only a few hydrides of this generic type which can be synthesised in aqueous solutions. However, the corresponding residues of red-brown or dark-brown colour also usually contain some impurity quantities [1] of copper phosphate, copper, copper(I)oxide and water.

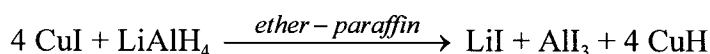
A copper hydride with an ascribed stoichiometric composition CuH was initially obtained by Würtz [20] as a product of a reaction of copper sulphate with hypophosphorous acid:



Subsequent formation reactions of copper hydrides have been rather fully reported in works of Sieverts [22-24], Warf [25-26] and Mikheeva [27,28]. Copper deuteride has been obtained [25] from a reaction of copper sulphate solution with D_3PO_3 in D_2O . Decomposition of copper hydride in an NaOD solution in D_2O leads to formation of hydrogen without deuterium, suggesting that the hydrogen in copper hydride does not bear any negative charge. Samples with very low contents of water or phosphorus are extremely pyrophoric and decompose rapidly and it thus seems likely that the stability of copper hydride are connected with the fact that surfaces may be covered with protecting films of adsorbed water, phosphor-containing oxianions or, if present, halogenide ions.

Formation of copper hydrides also has been reported for reactions of copper salts with barium, calcium and sodium hypophosphites [29, 30], as well as the reaction of copper chloride with sodium borohydride [31], in which case copper borohydride $\text{Cu}(\text{BH}_4)_2$ is formed as an intermediate product.

As a further preparative method for copper hydride mention should also be made [32] of the reaction:



Purified forms of copper hydride have been reported rapidly to decompose with exothermic effects, in such as for example with $\Delta H_f = 5.12 \text{ kcal (mol}^{-1}\text{)}$ in studies of Warf and Feitknecht [24].

Generic forms of copper hydride crystallise in the ZnS (wurtzite) structure type [33] with hydrogen atoms situated in positions (0; 0; 3/8), (1/3; 1/3; 7/8), copper atoms in positions (0; 0; 0), (1/3; 2/3; 1/2) and cell parameters of: $a = 2.93 \text{ \AA}$, $c = 4.63 \text{ \AA}$; and density $d = 6.28 \text{ g/cm}^3$. No phase transitions in copper hydrides have been found at ambient temperature and in studies at hydrogen pressures of up to 23 Gpa [34,35]. The molar volume of hydrogen, calculated by using the Murnagan equation ($B_0 = 72.5 \pm 2$; $B_0 = -2.7 \pm 0.3$) as a difference between corresponding values of the volumes of copper hydride and pure copper, has been estimated as $1.7 \text{ cm}^3(\text{moleH}_2^{-1})$ at 60 Gpa which is characteristic of most metal hydrides of similar type. *In vacuo* or at

pressures near atmospheric, copper hydrides noticeably decompose at 323K and maximum exothermic decomposition is observed in the range of 373-398K [36,37]. A study of decomposition under high pressure has not led to identification of a stability range for copper hydride [38].

Silver hydride

Neither formation of a hydride phase, nor even a hydrogen solubility amounting to a value of $H/M > 0.001$ could be observed [39] in a study of direct interaction of silver with hydrogen gas at 723K under hydrogen pressures of up to 67 kbar.

Electroconductivities have been studied [40] of silver hydrides and deuterides of different compositions prepared by means of low temperature ion implantation, employed to create thermodynamically nonequilibrium states. It has been proposed that the hydrogen (deuterium) atoms occupy octahedral sites in the fcc metal matrix, which is consistent with the experimental data from related hydrogen systems [18]. Main electronic states of silver hydride have been calculated [40] on the basis of a complete active space multi configuration of self-consistent field (MCPF) followed by full second-order configuration interaction (SOC) calculations including Davidson corrections in conjunction with large valence (6s6p5d) Gaussian basis sets: results are summarised in Table 4.

Table 4 Spectroscopic constants of AgH

State	$R_e(\text{Å})$			$\omega_e(\text{cm}^{-1})$			$\mu_e(\text{D})$		$D_e(\text{eV})$		
	SOC	MCPF	Expt	SOC	MCPF	Expt	SOC	MCPF	SOC	MCPF	Expt
$^1\Sigma^+$	1.626	1.656	1.62	1745	1703	1759.9	3.06	2.93	2.20	2.22	2.39
	(1.625)	(1.628)		(1770)	(1731)				(2.26)		

Gold hydride

The first report of the existence of gold hydride dates back to 1931 [41] in terms of formation of a bright film while passing a flow of atomised hydrogen over gold foil.

Subsequently a gold hydride has been obtained [42] from the reaction of hydrogen with polycrystal gold under a pressure of 65 kbar in a "toroid cell". Gold wire ($d = 0.2$ mm) has been held at 673K under a pressure of 60 kbar for 1 h. Temperature has then been lowered to the ambient value with a simultaneous release of pressure. After such treatment the wire has become bright grey in colour, the wire diameter has increased by a factor of 1.5, and fracture has clearly shown that the hydride consists of small (up to 40 $m\mu$) white crystals. During a subsequent silicon isothermal anneal for 1 h, decomposition of the hydride was found to take place at 443K. Maximum content of hydrogen corresponds to a composition of $AuH_{0.43}$ and X-ray analysis have shown that the hydride has a rhombic crystal structure with cell parameters of $a = 6.8 \text{ \AA}$, $b = 9.61 \text{ \AA}$, $c = 7.85 \text{ \AA}$. It is noteworthy that rhombic structures with closely similar c/a ratios are also characteristic of dihydrides of calcium, strontium, barium, europium and ytterbium. Studies using the induction method [42] also have reported an absence of superconductivity of gold hydride at $T \geq 2K$.

Hydrogen diffusion coefficients

Despite problems associated with the very low values of hydrogen solubilities, rather accurate measurements of hydrogen diffusion coefficients in copper, silver and gold at higher ranges of temperature are available by derivations from the skilful measurements of Eichenauer and his colleagues [43-45]. An example is provided by studies of the rates of hydrogen absorption into gold spheres [46] of different diameters (1.6 and 3.0 diameter). Results over the temperature range 500°C to 940°C are illustrated in Fig. 6 where they are compared with extrapolations of previous studies with copper [43] and silver [44]. Results in Fig. 6 could be represented [45] by the relation

$$D = 5.6 \times 10^{-4} \exp(-5640/RT) \text{ cm}^2\text{s}^{-1}$$

where the activation energy of 5640 cal/g.atom gold is sequentially lower (in keeping with slopes in Fig. 6) to those of 9200 cal/g.atom for copper and 7500 cal/g.atom for silver [45].

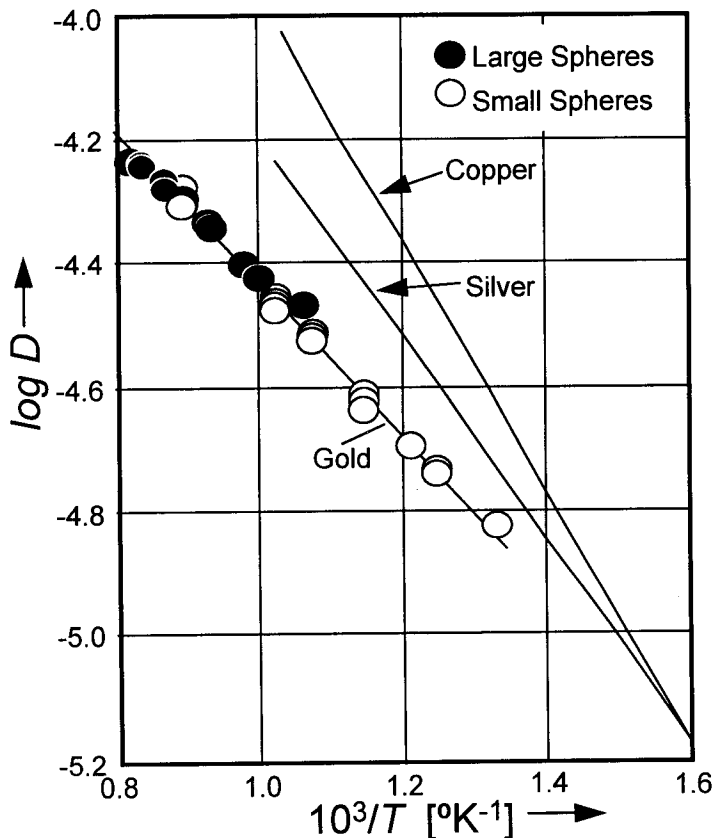


Fig. 6 Diffusion coefficients of hydrogen in gold, silver and copper (after Ref. 46)

Pd-Cu-H, Pd-Ag-H and Pd-Au-H Systems

Each of the series of Pd-(Cu, Ag or Au)-H with the three similarly fcc alloying elements Cu, Ag and Au have each been substantially investigated, particularly so in the case of the Pd-Ag-H system [46]. These three systems will be more fully reviewed in Chapter 6 together with other Pd alloy-hydrogen systems. However with relevance to other information above in this chapter it seems important to note here that trends of the derived p-c(n)-T relationships (18,46,48) are consistent with likelihoods of only very low lattice solubilities ($H/M < 0.01$) of hydrogen in either copper, silver or gold in equilibria with hydrogen gas at pressures up to $\sim 30,000$ atm and with utilisation of thin plated layers of copper or gold as means of the retention of hydrogen specimens in other studies such as Gorsky Effect [49]. Studies of superconductivity in the Pd-Cu-H system have attracted some particular attention [50].

Complex hydrides

Ternary hydrides of copper, silver and gold have been rather infrequently studied. It is known that the alloys and intermetallic compounds of these metals with magnesium, titanium, zirconium, hafnium, rare-earth metals absorb hydrogen readily, such as the report [51] of formation of $ZrAgH$ and $Zr_3AgH_{4.5}$ hydrides and reported structure data for $TiAuH_{2.8}$ and $LaCuH_{3.4}$ [52]. Such complex hydrides have characteristics of the triad metals in that they are mainly rather unstable and highly reactive.

Copper boron hydride: $CuBH_4$ is stable in mixtures of ether, tetrahydrofuran, pyridine and decomposes easily with the formation of CuH and diborane [53,54].

Copper aluminium hydride: the bright-yellow substance $CuAlH_4$ decomposes rapidly at temperatures higher than 203K [55,56].

Silver boron hydride: $AgBH_4$ is a colourless substance soluble in pyridine, but is insoluble in ether, tetrahydrofuran and triethylamine. It decomposes at temperatures higher than 243K with the formation of metal silver [57].

Silver aluminium hydride: $AgAlH_4$ has a golden-yellow colour and decomposes with formation of metal silver at temperatures higher than 203K [32,58, 59].

Silver gallium hydride: $AgGaH_4$ is an orange coloured substance which decomposes to component metals at temperatures higher than 198K [52].

Analogous compounds of gold seem so far unknown, but synthesis of further ternary hydrides of these elements may be expected [60].

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Hydrogen Metal Systems II

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Copper- Silver- and Gold-Hydrogen

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