Chemistry 3830

Hydrogen

Production of Hydrogen

Laboratory Scale:

Metal + acid:

Some metals + water:

Some metals + base:

Ionic hydrides + water:

Production of Hydrogen

Industrial Scale:

Steam reformation:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 2\,H_2(g)$ 700-830 °C; Ni catalyst
Or 1200-1500 °C; no catalyst

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ Water gas shift reaction

Gasification of coal:

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ Water gas shift reaction

Electrolysis:

$2\,H_2O(l) \rightarrow O_2(g) + 2\,H_2(g)$

Or from chlor alkali process:

$2\,NaCl(aq) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + Cl_2(g) + 2\,H_2(g)$

Hydrogen-Economy

Fuel Cell:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) + \text{energy}$$

Environmentally friendly; zero carbon emissions! (?)

Problems:

Generation of H_2 Where does the energy for the electrolysis come from?

Fossil fuels: Grey Hydrogen

Renewable energy: Green Hydrogen

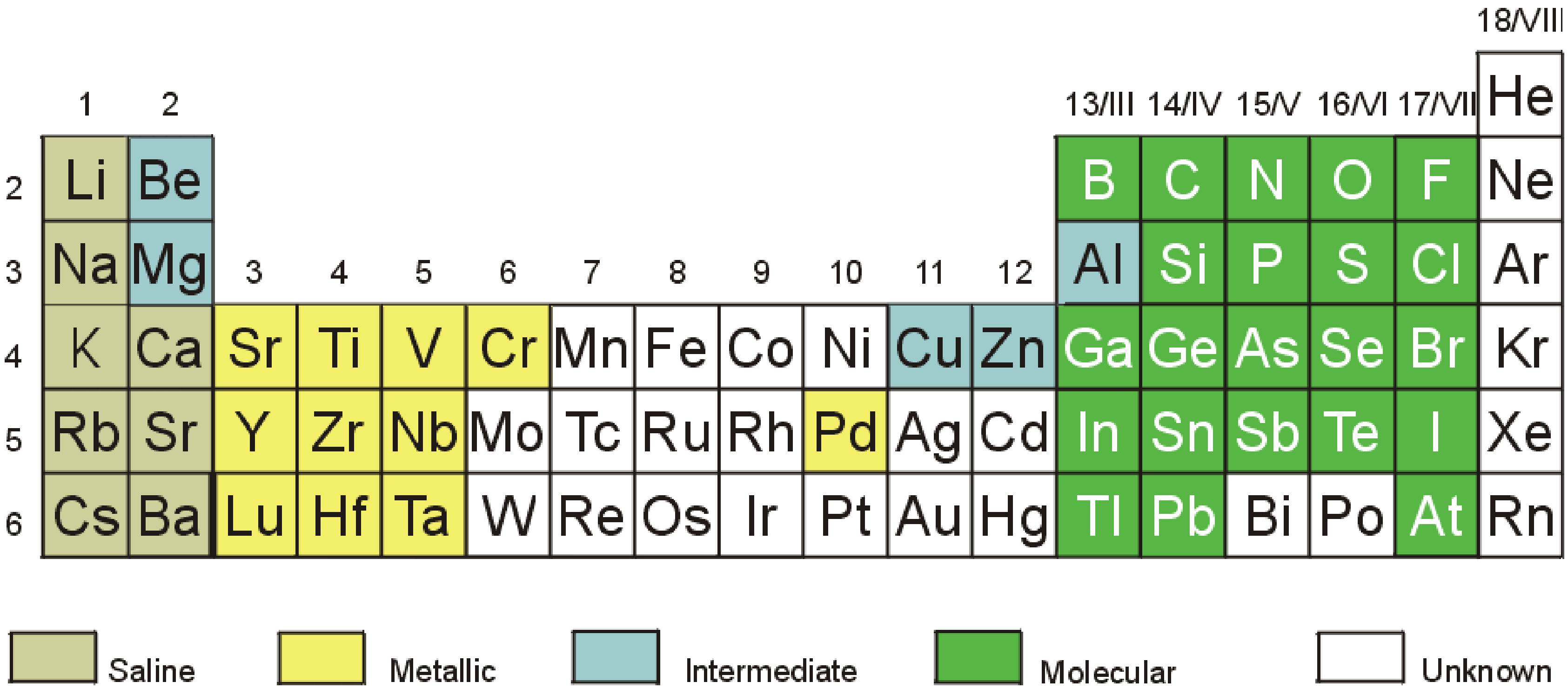
Non-Renewable energy + Carbon Capture: Blue Hydrogen

Transport of of H_2

One Proposal: Synthesis of NH_3 from N_2 and H_2
Shipping of NH_3
Decomposition of NH_3 to give H_2

Storage of H_2

Hydrogen Compounds



	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
																		⬜ He
2	🟫 Li	🟦 Be											🟩 B	🟩 C	🟩 N	🟩 O	🟩 F	⬜ Ne
3	🟫 Na	🟦 Mg											🟦 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	⬜ Ar
4	🟫 K	🟫 Ca	🟨 Sr	🟨 Ti	🟨 V	🟨 Cr	⬜ Mn	⬜ Fe	⬜ Co	⬜ Ni	🟦 Cu	🟦 Zn	🟩 Ga	🟩 Ge	🟩 As	🟩 Se	🟩 Br	⬜ Kr
5	🟫 Rb	🟫 Sr	🟨 Y	🟨 Zr	🟨 Nb	⬜ Mo	⬜ Tc	⬜ Ru	⬜ Rh	🟨 Pd	⬜ Ag	⬜ Cd	🟩 In	🟩 Sn	🟩 Sb	🟩 Te	🟩 I	⬜ Xe
6	🟫 Cs	🟫 Ba	🟨 Lu	🟨 Hf	🟨 Ta	⬜ W	⬜ Re	⬜ Os	⬜ Ir	⬜ Pt	⬜ Au	⬜ Hg	🟩 Tl	🟩 Pb	⬜ Bi	⬜ Po	🟩 At	⬜ Rn

🟫 Saline

🟨 Metallic

🟦 Intermediate

🟩 Molecular

⬜ Unknown

(Saline or) Ionic Hydrides

Structure:

Compound	**Crystal Structure**
LiH, NaH, KH, RbH, CsH	Rock salt (NaCl)
MgH_2	Rutile
CaH_2, SrH_2, BaH_2	Distorted $PbCl_2$ (coord. number about Pb = 9)

Source: A.F. Wells, Structural Inorganic Chemistry, Oxford University Press (1984)

Reactivity:

Desiccant:

$$CaH_2(s) + 2\ H_2O(l) \rightarrow Ca(OH)_2(s) + 2\ H_2(g)$$

Reducing agents: NaH, $LiAlH_4$

Or “superhydride”:

$$LiH + B(C_2H_5)_3 \rightarrow Li[HB(C_2H_5)_3]$$

Metallic or Interstitial Hydrides

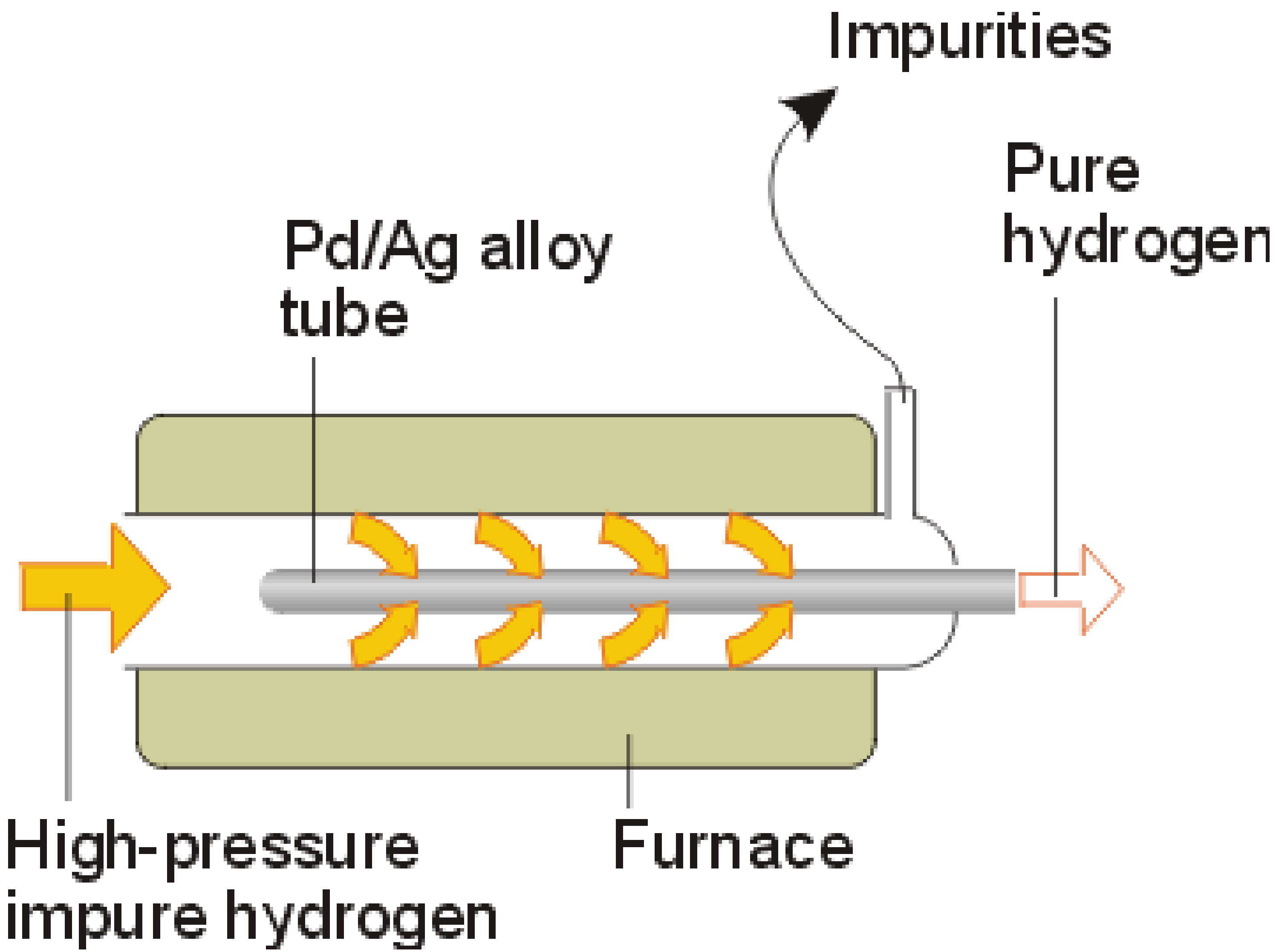
- Hydrogen atoms will occupy (tetrahedral or octahedral) holes in the metallic lattice

- Non-stoichiometric compounds are possible

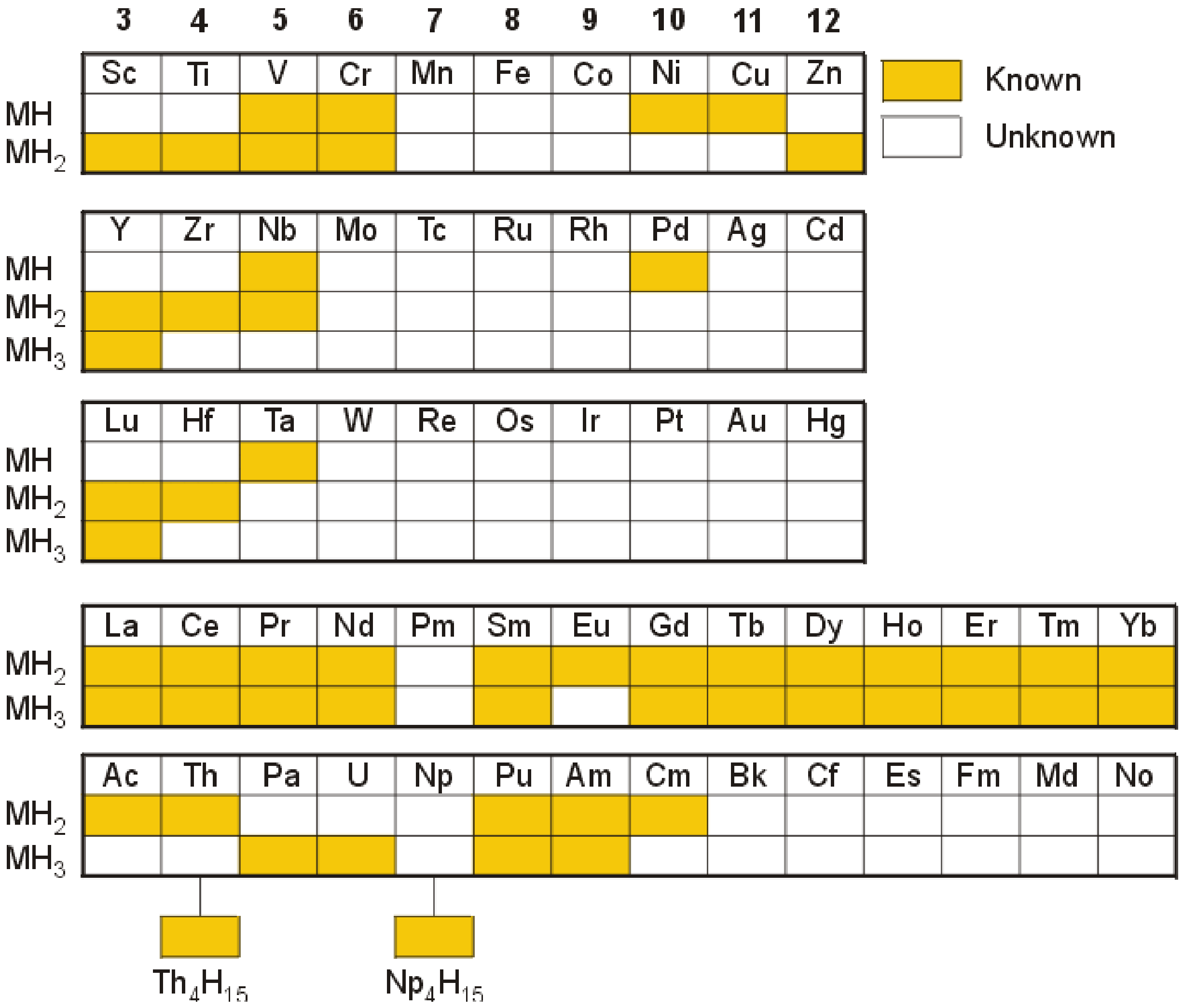
- First: the reasonably strong H–H bond needs to be broken on metal surface

- This explains the function of transition metals as hydrogenation catalysts

Purification of Hydrogen



Metallic or Interstitial Hydrides



🟨 Known

⬜ Unknown

	3	4	5	6	7	8	9	10	11	12
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
MH	⬜	⬜	🟨	🟨	⬜	⬜	⬜	🟨	🟨	⬜
MH_2	🟨	🟨	🟨	🟨	⬜	⬜	⬜	⬜	⬜	🟨

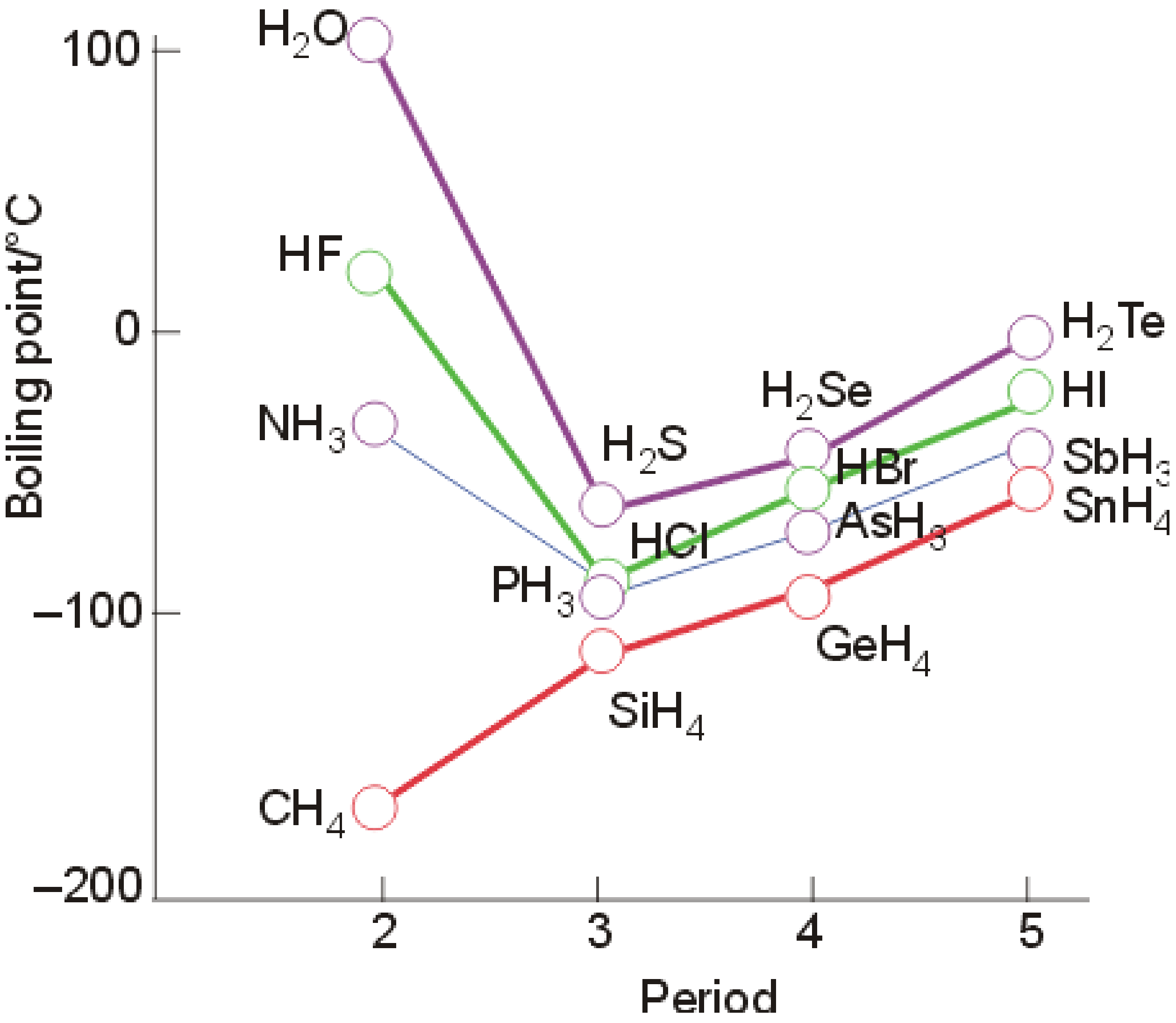
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
MH	⬜	⬜	🟨	⬜	⬜	⬜	⬜	🟨	⬜	⬜
MH_2	🟨	🟨	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜
MH_3	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜

	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
MH	⬜	⬜	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜
MH_2	🟨	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜
MH_3	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
MH_2	🟨	🟨	🟨	🟨	⬜	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
MH_3	🟨	🟨	🟨	🟨	⬜	🟨	⬜	🟨	🟨	🟨	🟨	🟨	🟨	🟨

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
MH_2	🟨	🟨	⬜	⬜	⬜	🟨	🟨	🟨	⬜	⬜	⬜	⬜	⬜	⬜
MH_3	⬜	⬜	🟨	🟨	⬜	🟨	🟨	⬜	⬜	⬜	⬜	⬜	⬜	⬜
		🟨 Th_4H_{15}			🟨 Np_4H_{15}									

Covalent/Molecular Hydrogen Compounds



Covalent/Molecular Hydrogen Compounds

Class	Group	Formula	Trivial name	IUPAC name
Electron-Deficient	13	B_2H_6	Diborane	Diborane(6)
	13	AlH_3 (polymeric)	Alane	Alane
	13	Ga_2H_6 (< –30°C)	Gallane	Gallane
Electron-Precise	14	CH_4 and hydrocarbons	Methane	Methane
	14	SiH_4 and silanes	Silane	Silane
	14	GeH_4 and germanes	Germane	Germane
	14	SnH_4 and stananes	Stanane	Stanane
Electron-Rich	15	NH_3	Ammonia	Azane
	15	PH_3	Phosphine	Phosphane
	15	AsH_3	Arsine	Arsane
	15	SbH_3	Stibine	Stibane
	16	H_2O	Water	Oxidane
	16	H_2S	Hydrogen sulfide	Sulfane
	16	H_2Se	Hydrogen selenide	Sellane
	16	H_2Te	Hydrogen telluride	Tellane
	17	HF	Hydrogen fluoride	Hydrogen fluoride
	17	HCl	Hydrogen chloride	Hydrogen chloride
	17	HBr	Hydrogen bromide	Hydrogen bromide
	17	HI	Hydrogen iodide	Hydrogen iodide

Covalent/Molecular Hydrogen Compounds

Group 15 hydrogen compounds	**Bond angle**	**Group 15 hydrogen compounds**	**Bond angle**
NH_3	106.6°	H_2O	104.5°
PH_3	93.8°	H_2S	92.1°
AsH_3	91.8°	H_2Se	91°
SbH_3	91.3°	H_2Te	89°

Source: A.F. Wells, Structural Inorganic Chemistry, Oxford University Press (1984)

- Why does the H–E–H decrease for heavier elements?
  - The angle for heavier elements is close 90°:
    Reluctance of heavier elements to hybridize.
  - Possibly the s-p separation?
    BUT: the s-p separation decreases for heavier elements!!!
  - Kutzelnigg (Theoretical Chemist) has proposed one explanation:
    the overlap between s and p decreases for heavier elements:
    Therefore: mixing/hybridization is not preferred.

Second-Order Jahn-Teller Distortion

Another explanation: Second order Jahn-Teller Distortion

(First-order) Jahn-Teller Distortion/Effect:

- Any non-linear molecule with an incompletely and unevenly filled degenerate MO level will undergo a structural distortion that will remove the degeneracy.

- Important for octahedral transition-metal complexes.

Second-order Jahn-Teller Distortion/Effect:

- Interaction/mixing between a filled MO and an empty MO, resulting in a structural distortion, lowering the filled MO and raising the empty MO.

- Requirement: correct symmetry and small energy difference

Second-Order Jahn-Teller Distortion

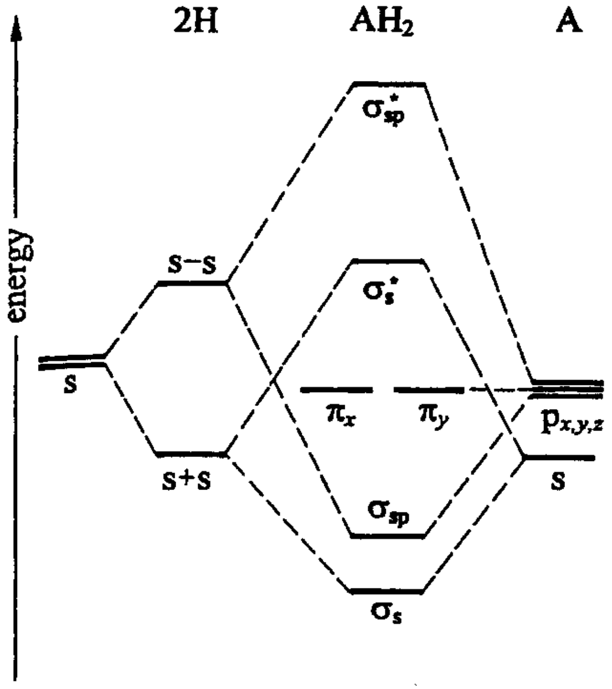


Fig. 114a Energy level diagram for the formation of σ and π MOs of linear AH_2 molecules (energy positions of the molecular orbitals essentially depend on A).

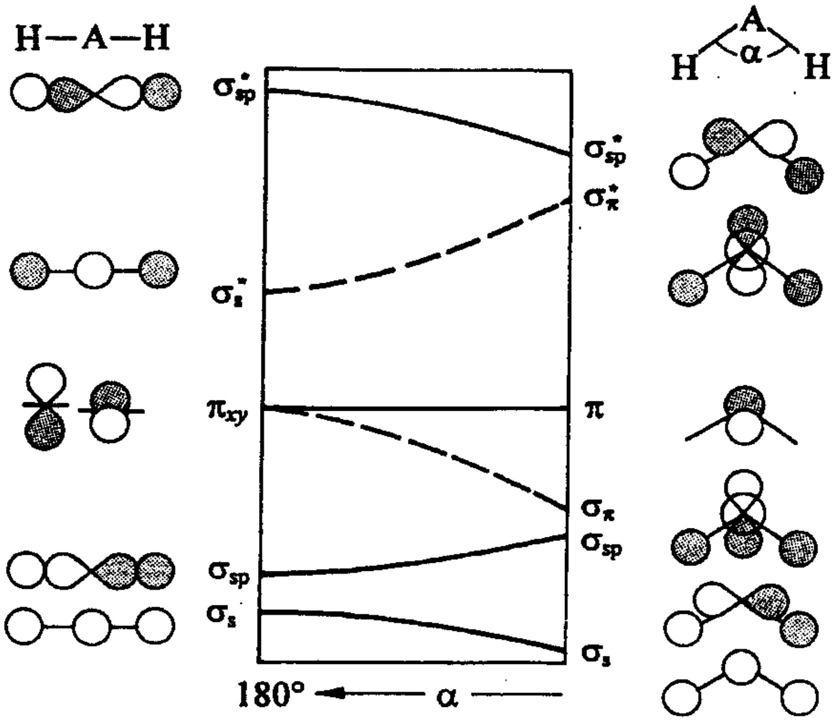


Fig. 114b Walsh diagram for AH_2 molecules with linear to bent structures (empty and full orbital areas indicate positive and negative signs of the wavefunctions).

Hydrogen Bonding

Hydrogen bond	**E––E distance, pm**	**∑v.d.Waals radii, pm**	**Energy (kJ/mol)**	**Covalent Bond**	**Energy (kJ/mol)**
$\mathrm{HS{-}H\cdots SH_2}$		370	7	S–H	363
$\mathrm{H_2N{-}H\cdots NH_3}$	294 – 315	300	17	N–H	386
$\mathrm{HO{-}H\cdots OH_2}$	248 – 290	280	22	O–H	464
$\mathrm{F{-}H\cdots F{-}H}$	245 – 249	270	29	F–H	565
$\mathrm{HO{-}H\cdots Cl^-}$	295 – 310	320	55	Cl–H	428
$\mathrm{[F\cdots H\cdots F]^-}$	227	270	165	H–F	565