-Hydrogen

-Isotopes of hydrogen

-Preparation of the hydrogen

-Hydrogen compound

-The hydrogen bonding

Chemical and physical property of hydride compound

1- Factors That Affect Acid Strength of the hydride

2-The acid-base properties of the hydride

3- Reducing properties of the hydride

Hydrogen

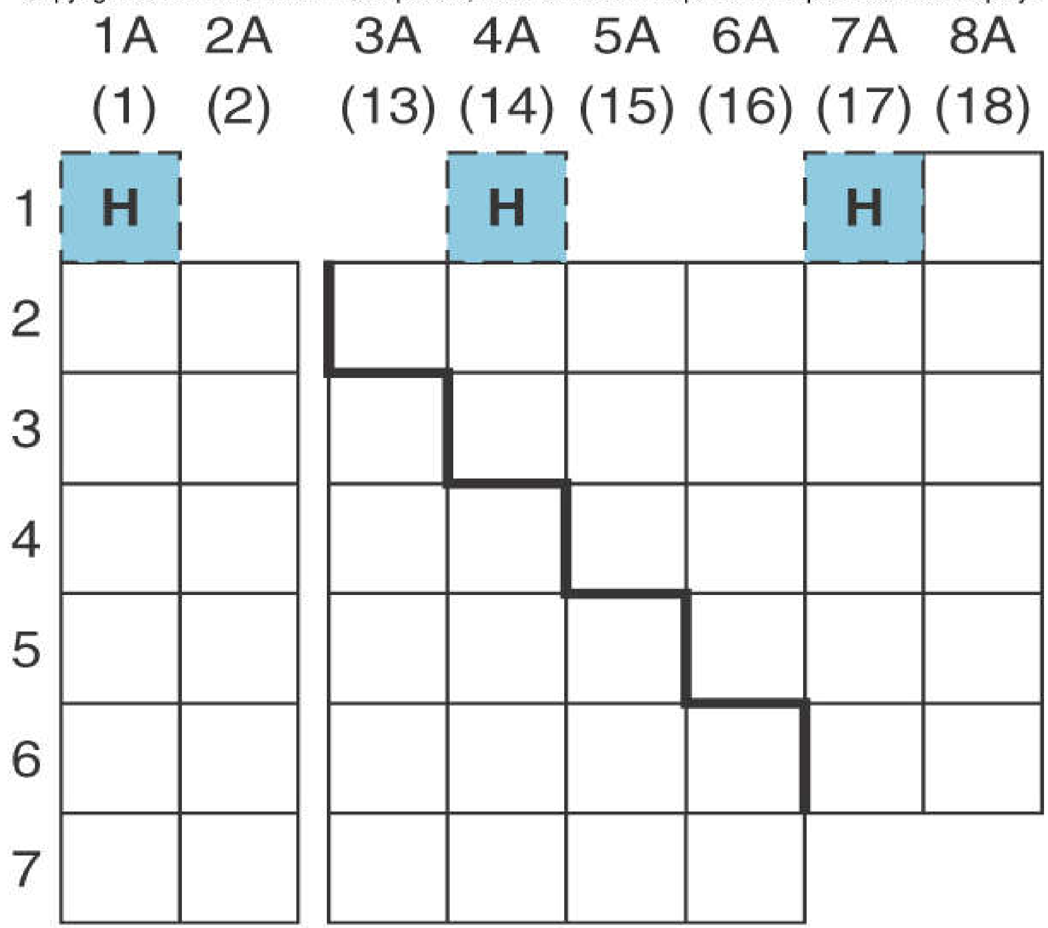
Hydrogen is very simple atomic structure , that of a single electron and a uni positive nucleus, hydrogen is remarkable in forming more compounds than any other elements in the periodic table.

H_2 is color less ,oderless and nonpolar gaseous ,with low melting and boiling point.

The electronic configuration of the hydrogen atom is $1s^1$ thus it has been classed with the alkali metals in group one ,it can lose an electron to form H^+

with the halogens in group seven to form H^- it gain one electron, and with carbon in group four because the outer shell is like that of carbon only half full it can form normal covalent bonds by sharing two electrons with another atom.

Figure 14.1 **Where does hydrogen belong?**



Hydrogen and the Alkali Metals

- ***Like the Group 1A(1) elements, hydrogen***

➢ has an outer electron configuration of ns^1, has a single valence electron, and has a common +1 oxidation state.

- ***Unlike the alkali metals, hydrogen***

➢ ***shares*** electrons with nonmetals rather than transferring e^- to them,has a much higher ionization energy than any alkali metal, due to its small size.

Hydrogen and Group 4A

- ***Like the Group 4A(1) elements***, H has a half-filled valence level.
- ***H is similar to the other Group 4A elements in terms of***

➢ ionization energy , electron affinity, electronegativity, and bond energies.

Hydrogen and the Halogens

- ***Like the halogens or Group 7A(17), hydrogen***

➢ exists as a diatomic molecule and needs only 1 electron to fill its valence shell.

- ***Unlike the halogens***

➢ H has a much lower electronegativity than any halogen, H lacks the three valence e^- pairs that halogens have, and halide ions (X^-) are common and stable, but the hydride ion (H^-) is rare and reactive.

Isotopes of hydrogen:

There are three isotopes of hydrogen :

- **1-Protium** (simply hydrogen, $_1H^1$, single proton in the nucleus ,
- **2-Deuterium**,called heavy isotope ($_1H^2$ or D one proton one neutron in the nucleus(Deuterium containing water, D_2O Called heavy water or deuterated water
- **3-Tritium** ($_1H^3$ or T one proton two neutrons in the nucleus).Tritium is radio active ($t_{1/2}$ 12.26 year) and decay in to $_2He^3$ with the expulsion of beta particles

TABLE 24.1 Properties of H_2O and D_2O

Property	H_2O	D_2O
Molar mass (g/mol)	18.02	20.03
Melting point (°C)	0	3.8
Boiling point (°C)	100	101.4
Density at 4°C (g/cm^3)	1.000	1.108

Preparation of the hydrogen

In the laboratory, H_2 may be prepared by

1-Reaction of dilute acids with metals such as(Zn , Fe)

$H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$

2-By electrolysis of water : $H_2O \rightarrow 2H^+ + O^{2-}$

$2H^+ + 2e \rightarrow 2H$ on negative pole

$O^{2-} \rightarrow O + 2e$ on positive pole

3-Substitution of the hydrogen in water by some metals

$Na + 2H_2O \rightarrow NaOH + H_2\uparrow$

Industrially H_2 obtained by steam re-forming of CH_4 or light petroleum's over Ni

$$2CH_4 + 2H_2O \xrightarrow{\text{1200 K; Ni catalyst}} 2CO + 6H_2$$

$$C_nH_{2n+2} + {}_nH_2O \xrightarrow{\text{1200 K; Ni catalyst}} n\,CO + (2n+1)\ H_2\ (g)$$

Hydrogen compound

*Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **Hydrides (**Compounds of hydrogen may all be called hydrides , although this term is best reserved for those that are neither organic compounds nor acids). If 'E' is the symbol of an element then hydride can be expressed as EHx (e.g., MgH_2) or EmHn (e.g., B_2H_6).*

Types of hydrides :

- ***The hydrides are classified into three categories :***

  (i) Ionic or saline or saltlike hydrides

  (ii) Covalent or molecular hydrides

  (iii) Metallic or non-stoichiometric hydrides

Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

- Ionic hydrides
- Covalent polymeric hydrides
- Covalent hydrides
- Metallic hydrides

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
LiH 0.97	BeH_2 1.47											BH_3 2.01	CH_4 2.50	NH_3 3.07	H_2O 3.50	HF 4.10	Ne
NaH 1.01	MgH_2 1.23											AlH_3 1.47	SiH_4 1.74	PH_3 2.06	H_2S 2.44	HCl 2.83	Ar
KH 0.91	CaH_2 1.04	ScH_2 1.20	TiH_2 1.32	VH VH_2 1.45	CrH (CrH_2) 1.56	Mn 1.60	Fe 1.64	Co 1.70	$NiH_{<1}$ 1.75	CuH 1.75	ZnH_2 1.66	(GaH_3) 1.82	GeH_4 2.02	AsH_3 2.20	H_2Se 2.48	HBr 2.74	Kr
RbH 0.89	SrH_2 0.99	YH_2 YH_3 1.11	ZrH_2 1.22	(NbH_2) 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	$PdH_{<1}$ 1.35	Ag 1.42	(CdH_2) 1.46	(InH_3) 1.49	SnH_4 1.72	SbH_3 1.82	H_2Te 2.01	HI 2.21	Xe
CsH 0.86	BaH_2 0.97	LaH_2 LaH_3 1.08	HfH_2 1.23	TaH 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	(AuH_3) 1.42	(HgH_2) 1.44	(TlH_3) 1.44	PbH_4 1.55	BiH_3 1.67	H_2Po 1.76	HAt 1.90	Rn
Fr	Ra	AcH_2 1.00															

CeH_3 1.06	PrH_2 PrH_3 1.07	NdH_2 NdH_3 1.07	Pm	SmH_2 SmH_3 1.07	EuH_2 1.01	GdH_2 GdH_3 1.11	TbH_2 TbH_3 1.10	DyH_2 DyH_3 1.10	HoH_2 HoH_3 1.10	ErH_2 ErH_3 1.11	TmH_2 TmH_3 1.11	(YbH_2) YbH_3 1.06	LuH_2 LuH_3 1.14
ThH_2 1.11	PaH_3 1.14	UH_3 1.22	NpH_2 NpH_3 1.22	PuH_2 PuH_3 1.22	AmH_2 AmH_3 1.2	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Types of hydrides :

(i) ***Ionic or saline or saltlike hydrides:*** *These are stoichiometric compounds of dihydrogen formed with most of the s-block elements which are* ***highly electropositive and low I.E energy*** *in character. However, significant covalent character is found in the lighter metal hydrides such as* <u>LiH, BeH_2</u> *and* <u>MgH_2</u>*. In fact BeH_2 and MgH_2 are polymeric in structure. All are white, high melting point, solids (e.g. LiH, mp =953 K; NaH, mp =1073 K with decomposition); the group 1 hydrides crystallize with the NaCl lattice.*

- *Saline hydrides are Prepared by direct reaction of the group 1 or 2 metals (except Be) with H_2 at 300—900*

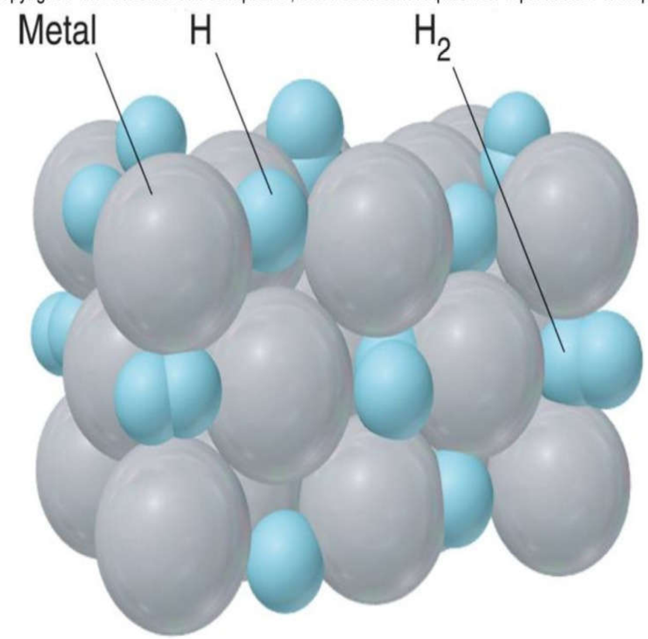
(G1) $M + H_2 \rightarrow MH$ *(M= Li ,Na , Cs)*

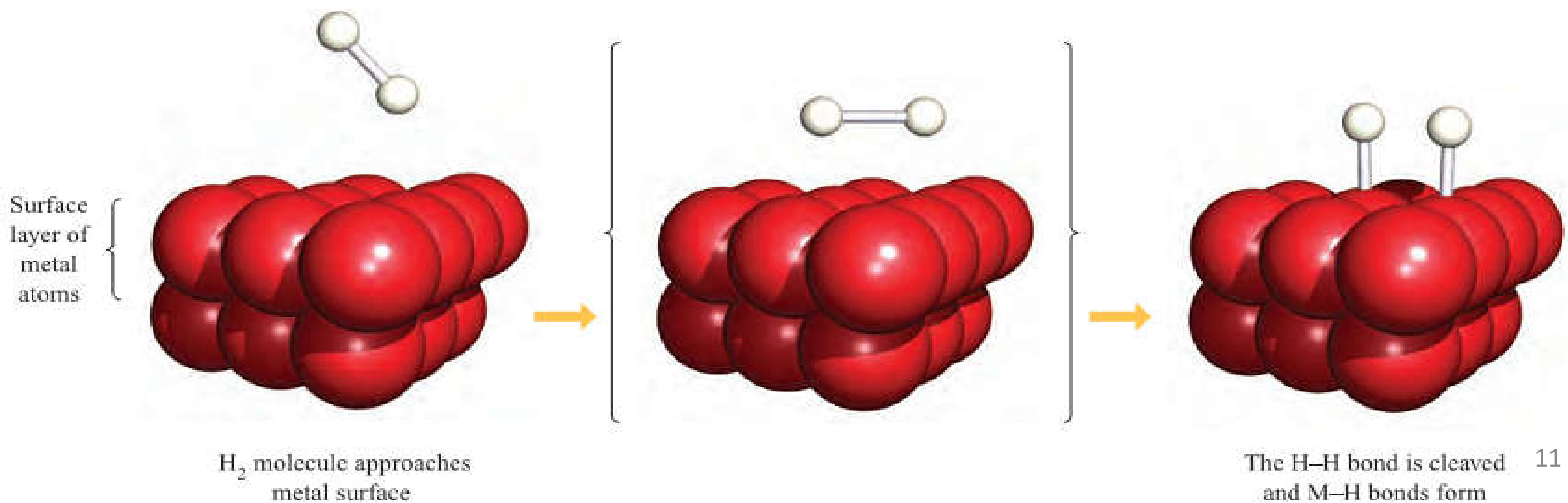
(G2) $M + H_2 \rightarrow MH_2$ *(M = Ca, Sr Ba)*

The reactivity of the group 1 hydrides increases with an increase in atomic number and ionic size of the metal.

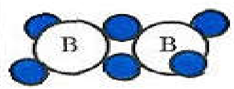
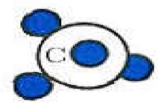
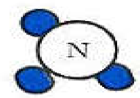
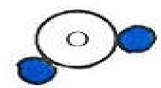
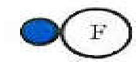
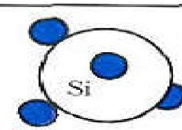
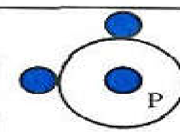
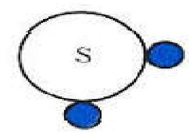
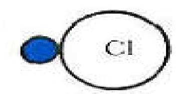
- ***(ii) Covalent or molecular hydrides***
- *Those are formed between hydrogen and the p-block elements(which have the electronegativity about 2 or more) in groups 13 to 17.*
- *Hydrides of the halogens, sulfur and nitrogen are prepared by reacting these elements with H_2 under appropriate conditions*
- $F_2(g) + H_2(g) \rightarrow 2HF(g) \qquad \Delta H^\circ_{rxn} = -546$ kJ

- ***(iii) Metallic or non-stoichiometric (interstitial) hydrides***
- Several of the d and f transition elements form ***metallic (interstitial) hydrides***, in which H_2 molecules and H atoms occupy the holes in the crystal structure of the metal , forming hydrides with exhibit many of the physical characteristic of metals high thermal high electrical conductivity.





Hydrogen compounds of the elements in the first three rows of periodic table ,combing ratios of the elements with hydrogen

 Hydrogen Z = 1 H/H = 1/1 mp = −259°C bp = −252°C						
$(LiH)_x$ Lithium Z = 3 Li/H = 1/1 mp = 680°C bp = (decom.)	$(BeH_2)_x$ Beryllium Z = 4 Be/H = 1/2 mp = (decom.)	 Boron Z = 5 B/H = 1/3 mp = −165°C bp = −92°C	 Carbon Z = 6 C/H = 1/4 mp = −182°C bp = −161°C	 Nitrogen Z = 7 N/H = 1/3 mp = −78°C bp = −33°C	 Oxygen Z = 8 O/H = 1/2 mp = 0°C bp = 100°C	 Fluorine Z = 9 F/H = 1/1 mp = −83°C bp = 20°C
$(NaH)_x$ Sodium Z = 11 Na/H = 1/1 mp = 700–800°C (decom.)	$(MgH_2)_x$ Magnesium Z = 12 Mg/H = 1/2 mp = (decom.)	$(AlH_3)_x$ Aluminum Z = 13 Al/H = 1/3 mp = (decom.)	 Silicon Z = 14 Si/H = 1/4 mp = −185°C bp = −111°C	 Phosphorus Z = 15 P/H = 1/3 mp = −134°C bp = −88°C	 Sulfur Z = 16 S/H = 1/2 mp = −86°C bp = −60°C	 Chlorine Z = 17 Cl/H = 1/1 mp = −114°C bp = −85°C

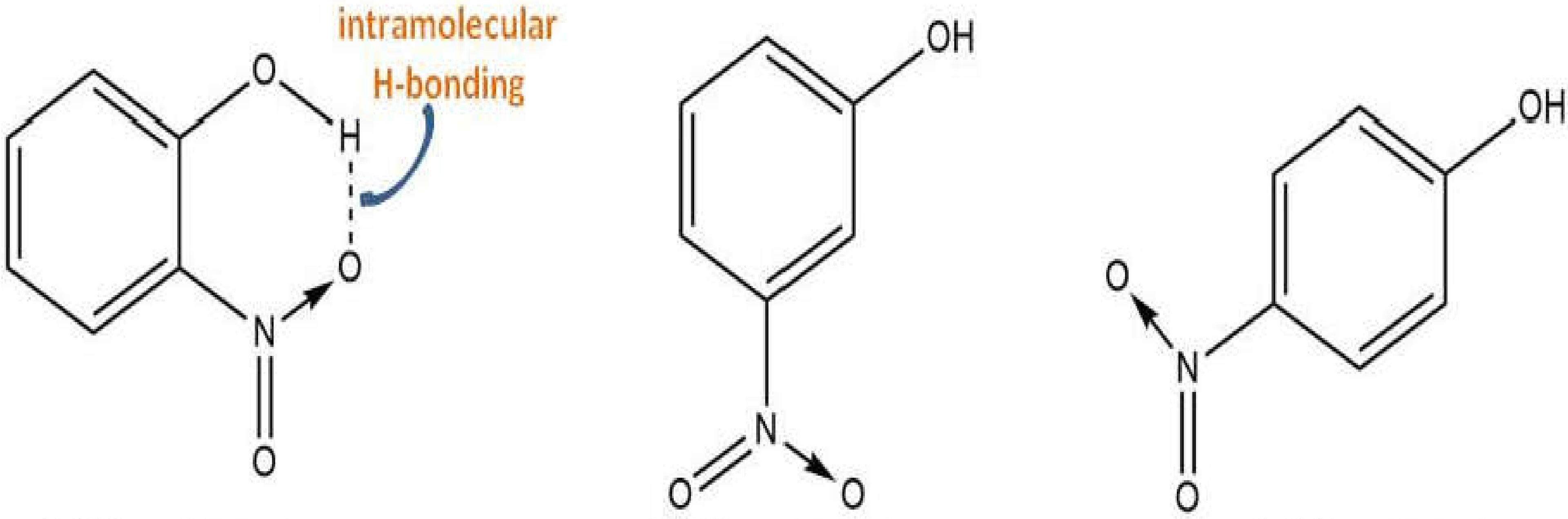
The hydrogen bonding

- ***The hydrogen*** *bonding : The H-bond is the term given to the relatively weak secondary interaction between a hydrogen atom bound to an electronegative atom and another atom which is also generally electronegative and which has one or more lone pairs and thus act as a base. We can thus refer to proton doners, XH and proton acceptors Y .*

$$X^{-} — H^{+} \text{------} Y$$

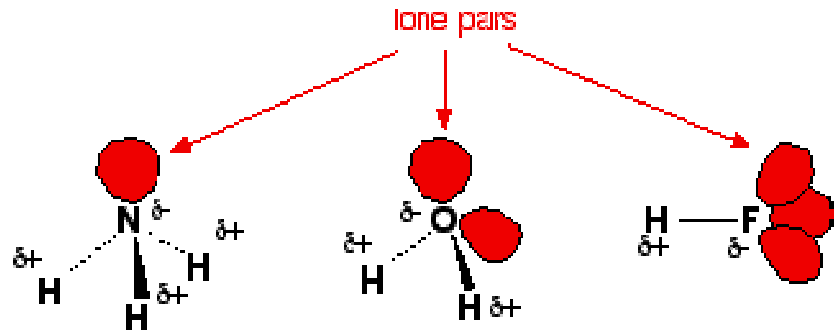
- *For hydrogen bonding formed Only when hydrogen bonded to one of these three elements (F ,O , N). Molecules with hydrogen bonds have higher boiling points than molecules that don't.*
- *Thus high boiling points of NH_3, H_2O ,and HF due to ability of these compound to forming H-bond.*

- *From the B.P and M.P of isomers of nitrophenols there are evidence for different hydrogen bonding depending on the position of functional group.*

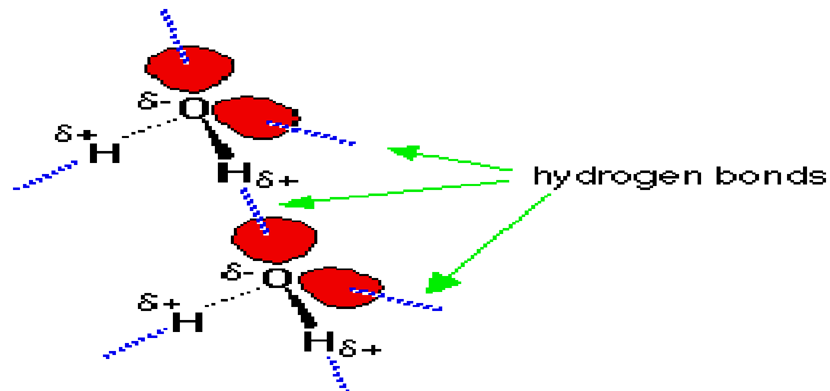


2-Nitrophenol 3-Nitrophenol 4-Nitrophenol

- Hydrogen attached directly to most electronegative atoms
  - ➢ Partial positive charge of hydrogen
  - ➢ Partial negative charge on the electronegative atoms as well as at least one lone pair

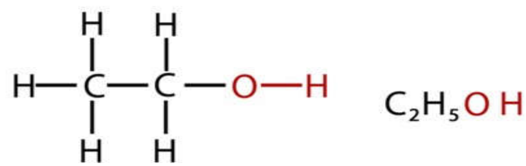


➢ The partially positive hydrogen strongly attracted to the lone pair, Interaction much stronger than dipole-dipole interaction

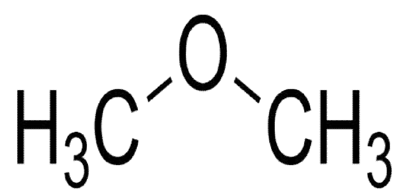


Ethanol (BP = 78.5 C)

Ethanol

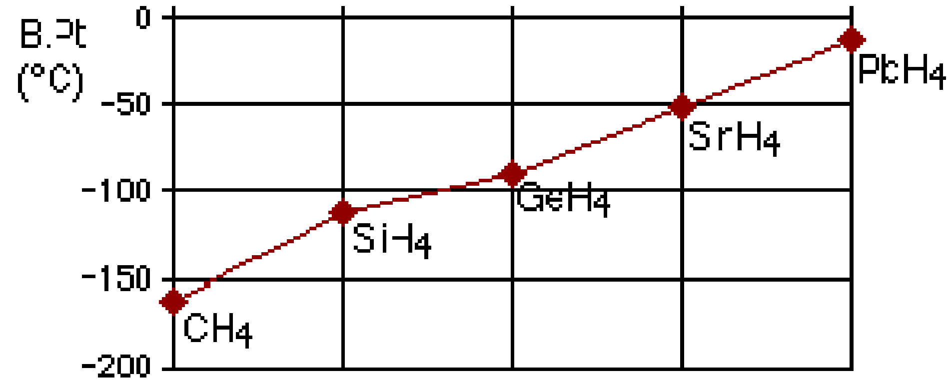


- Methoxymethane (BP = -24.8 C)

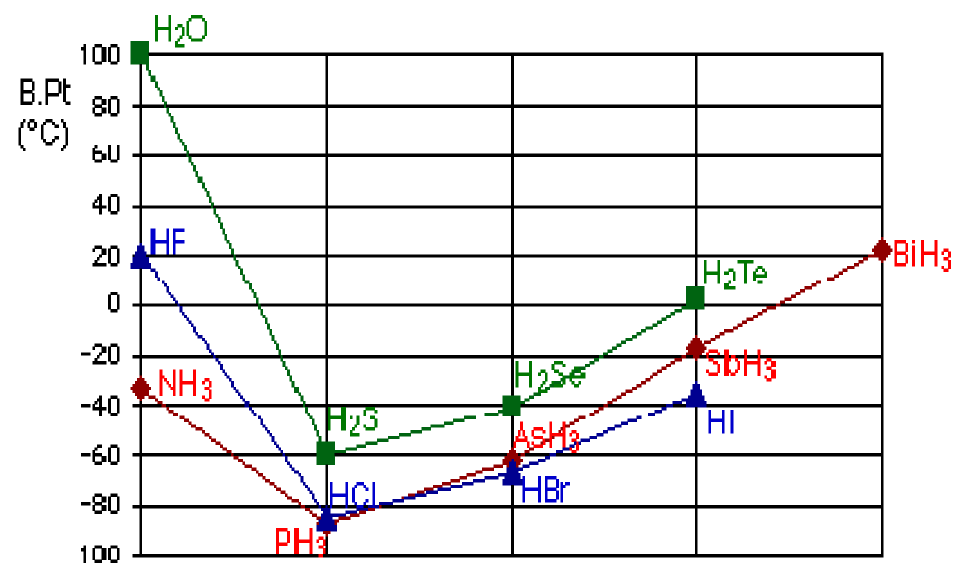


Early evidence of hydrogen bonding

- Many elements form hydrides
- Plot BP of hydrides of Group 4 elements
- BP increases as we go down a group
    - Van der Waals forces



- Plot BP of hydrides of gp 5,6, and 7 Similar results
- EXCEPT the hydride of the first element in each of groups 5,6, and 7
- NH_3, H_2O, and HF must be having some additional intermolecular forces of attraction



Chemical and physical property of hydride compound

1-Factors That Affect Acid Strength of the hydride

*A molecule containing **H** will transfer a proton only if the H --X bond is polarized in the following way:*

In ionic hydrides such as NaH, the reverse is true; the H atom possesses a negative charge and behaves as a proton acceptor .

Nonpolar H--X bonds, such as the H--C bond in CH_4, produce neither acidic nor basic solutions.

A second factor that helps determine whether a molecule containing an H X bond will donate a proton is the strength of the bond. Very strong bonds are less easily dissociated than are weaker ones. This factor is of importance, for example, in the case of the hydrogen halides. The H--F bond is the most polar H--X bond. You therefore might expect that HF would be a very strong acid if the first rule were all that mattered. However, the energy required to dissociate HF into H and F atoms is much higher than it is for the other hydrogen halides, HF is a weak acid, whereas all the other hydrogen halides are strong acids in water.

- ***2-The acid-base properties of the hydride***
- *The acid-base properties of the hydride of an element can be related to its position in the periodic table. the most basic hydrides are on the left. Most the **Alkali and alkali earth Metals hydride(saline hydride) are basic hydride.**represented reaction of [H^-] ion, the are very strong base .*

- *For example, in the second row of the table, NaH is a basic hydride.*

$$NaH + H_2O \xrightarrow{-\Delta} NaOH + H_2$$

$$CaH_2 + H_2O \xrightarrow{-\Delta} Ca(OH)_2 + H_2$$

- ***in the group the basic property increase with increase (Z) for element***

The most acidic hydrides are on the right of periodic table

In the period the acidity increases in the order

- $PH_3 < H_2S < HCl$.

This general trend is related to the increasing electronegativity of the element as we move from left to right in any horizontal row.

In any **vertical column of nonmetallic elements**, there is a tendency toward increasing acidity with increasing atomic number. For example, among the group 6A elements the acid dissociation constants vary in the order

- $H_2O < H_2S < H_2Se < H_2Te$.
-

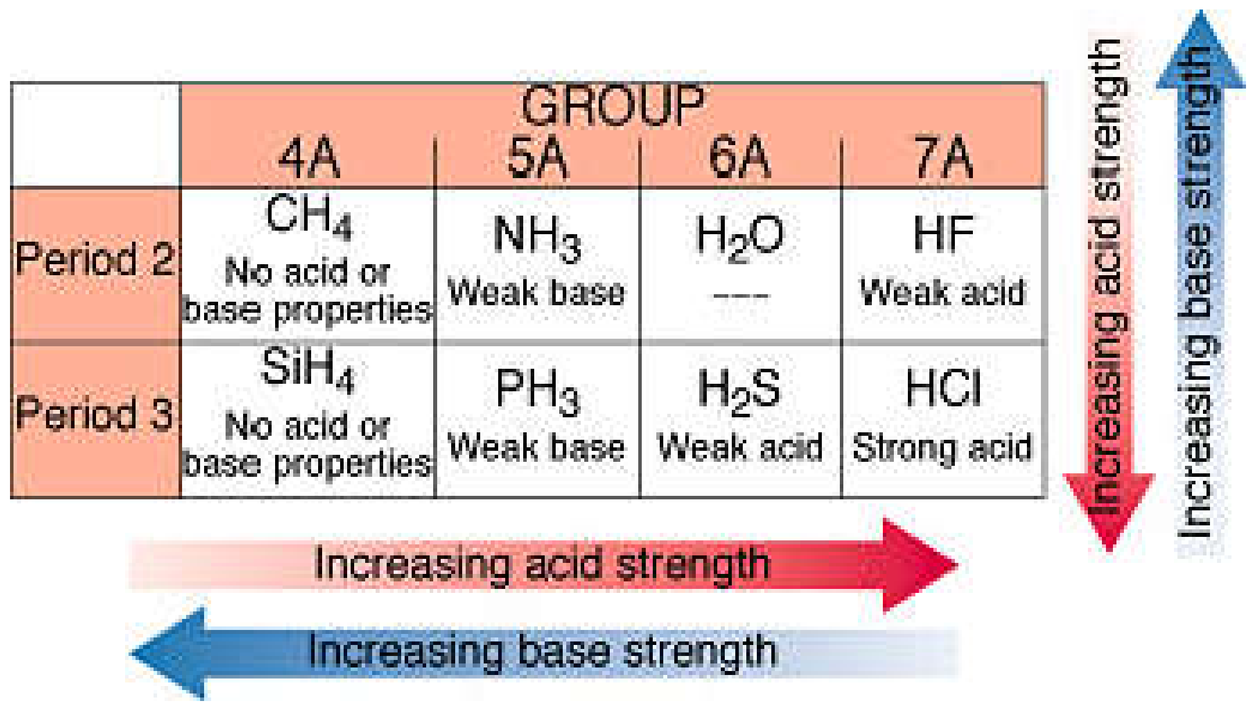
This order arises primarily because the bond strengths steadily decrease in this series as the central atom grows larger and the overlaps of atomic orbitals grow smaller.

In general, *metal hydrides are either basic or show no hydrides range from showing no pronounced acid-base properties to being acidic.* Note that the base ammonia, NH_3, is an exception to this rule.

Acid/base character of hydrides

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

- strongly alkaline
- alkaline
- weakly alkaline
- neutral
- weakly acidic
- strongly acidic



	GROUP 4A	5A	6A	7A
Period 2	CH_4 No acid or base properties	NH_3 Weak base	H_2O ---	HF Weak acid
Period 3	SiH_4 No acid or base properties	PH_3 Weak base	H_2S Weak acid	HCl Strong acid

3-Reducing properties:-

- ***Ionic hydrides*** *show reducing properties at high temperatures which is probably due to the formation of atomic hydrogen* ***and reducing properties increases with increase ionic property****.*

  $2CO + NaH \rightarrow HCOONa + C$

  $PbSO_4 + 2CaH_2 \rightarrow PbS + 2Ca(OH)_2$

  $NaH + 1\backslash 8\ S_8 \longrightarrow Na_2S + H_2$

- ***LiH*** *and* ***NaH*** *are used as strong reducing agents in synthetic chemistry. LiH and NaH are used to produce other important hydrides, particularly lithium aluminum hydride* $Li[AlH_4]$ *and sodium borohydride* $Na[BH_4]$*,which have important uses as reducing agents in both organic and inorganic synthesis.* $\mathbf{CaH_2}$ *is used for military purposes as a source of* H_2 *for balloons and hence the name of hydrolith.*
- $4LiH + AlCl_3 \rightarrow Li[AlH_4] + 3LiCl$
- $4NaH + B(OCH_3)_3 \rightarrow Na[BH_4] + 3NaOCH_3$

- ***In the group*** *the reducing agent propriety in covalent hydride increases from top to down for exm. the hydride for group V A(N,P,As....) the* AsH_3 *oxidize mere easily than* NH_3*, and also* SiH_4 *is more sensitive to react with halogen and* H_2O *than* CH_4 *.*

$$Ag^{+} + NH_3 \longrightarrow [Ag(NH_3)_2]^{+}$$

$$Ag+ + AsH_3 + H_2O \longrightarrow AsO_3^{-} + Ag + H^{+}$$

- ***In the period*** *the reducing agent propriety decreases from left to right(with increases Z in the period)exm.*

$$Fe^{+3} + H_2S \longrightarrow Fe^{2+} + 2H^{+} + S$$

- *But HCl can not reduce ferric ion*