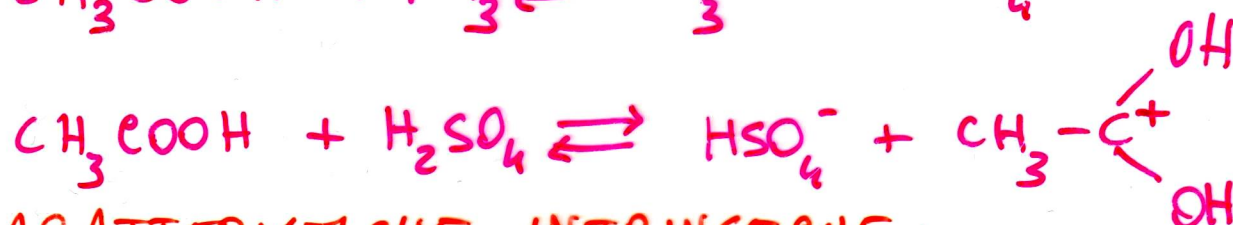


EQUILIBRI ACIDO - BASE

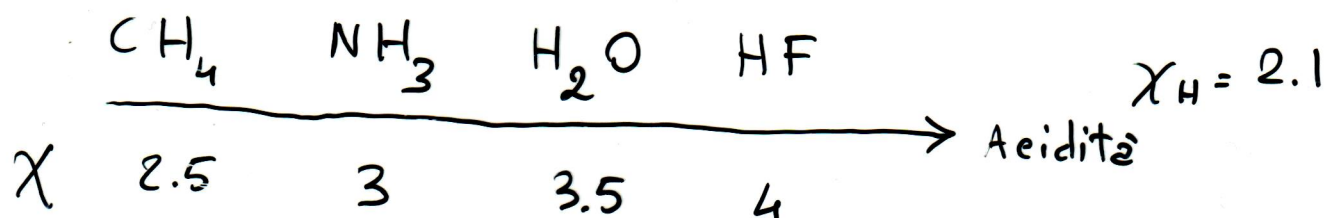
1] CARATTERISTICHE CHE DETERMINANO L'ACIDITÀ DI UN COMPOSTO

Caratteristiche intrinseche
Ambiente in cui si trovano

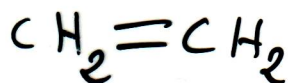
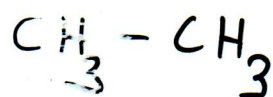


CARATTERISTICHE INTRINSECHE:

(A) L'ELETTRONEGATIVITÀ DELL'ELEMENTO LEGATO ALL'IDROGENO



(B) PERCENTUALE DI ORBITALE S NEGLI IBRIDI



Etano (sp^3)

Etilene (sp^2)

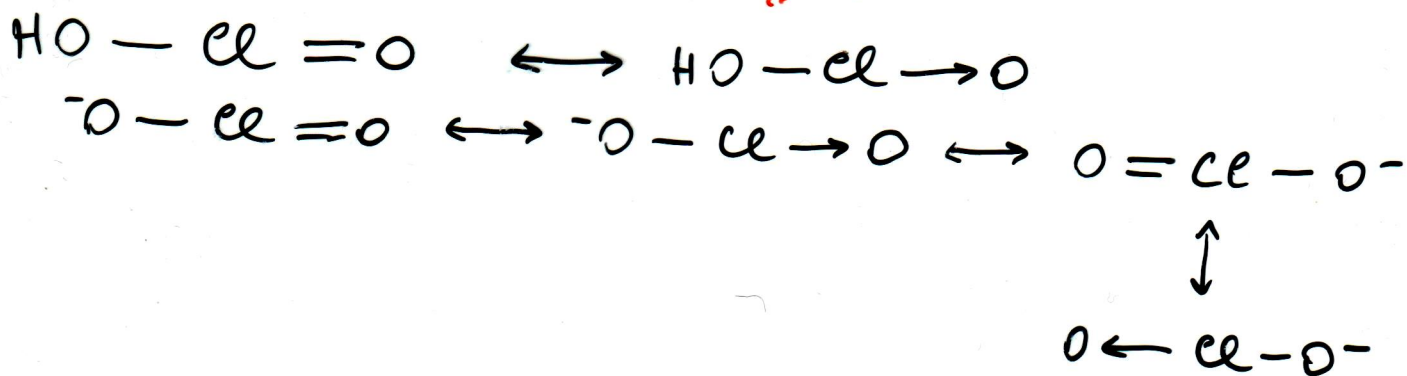
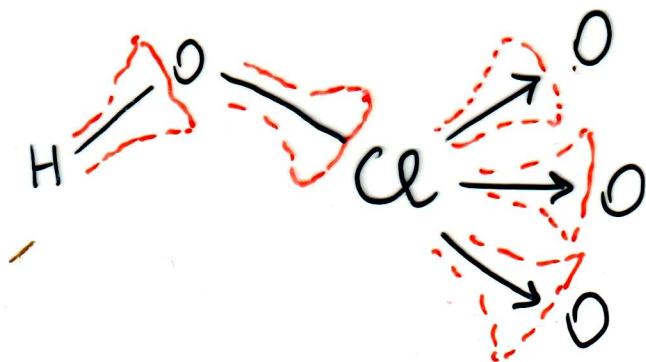
Etino (sp)

L'orbitale S è più vicino al nucleo (leg. o è sulle congiungenti dei nuclei), quindi il C con maggiore percentuale di orbitale S è più elettronegativo.

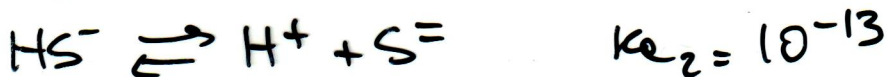
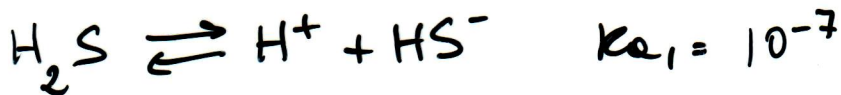
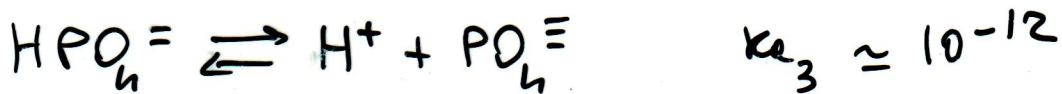
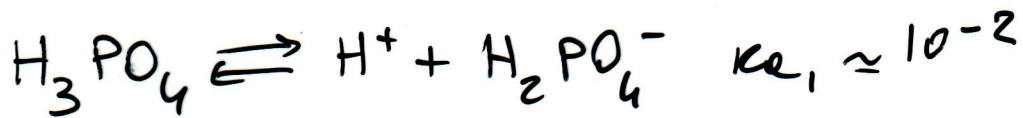
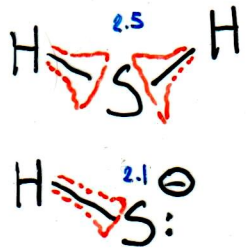
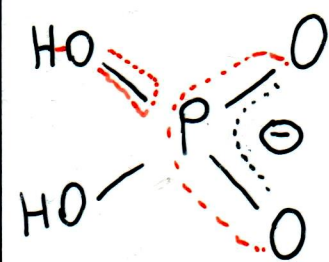
(C) NUMERO DI ATOMI DI OSSIGENO NEGLI ACIDI OSSIGENATI

HClO	ae. ipocloroso	pKa 7,5
HClO_2	ae. cloroso	pKa 2,0
HClO_3	ae. clorico	pKa -2,7
HClO_4	ae. perclorico	pKa -7,3

Acidity



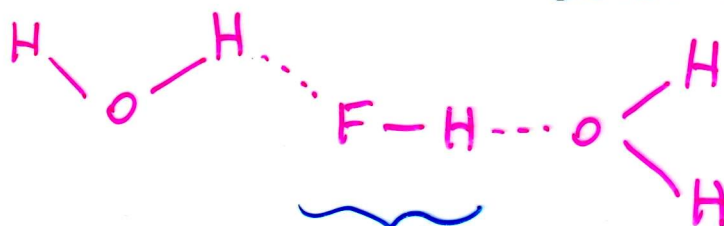
① ACIDI POLIPROTICI



⑤ RAGGI IONICI (O COVALENTI) E SOLVA- TAZIONE

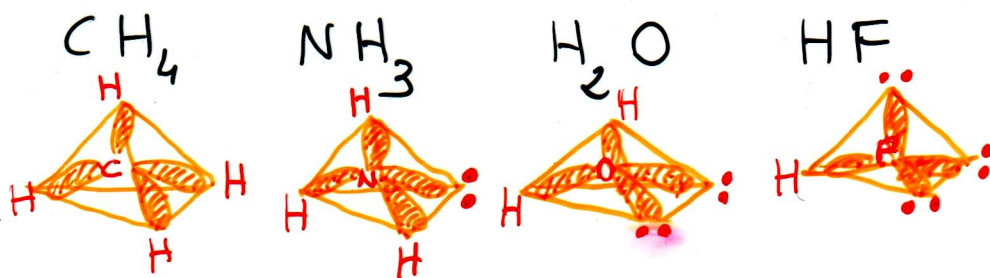
	χ_A	r_{ionico}	pK_a
HF	4	1.36	3.3
HCl	3.0	1.81	-7.4
HBr	2.8	1.95	-9.0
HI	2.5	2.16	-9.5

acidità



più stabile in acqua per le solvata-
non tende a dissociarsi.

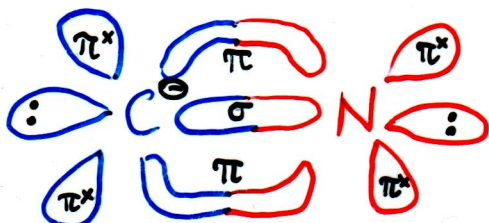
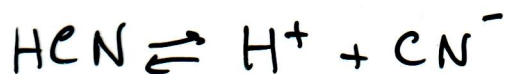
⑥ DOPPIETTI ELETTRONICI NON CONDIVISI: CARATTERE BASICO



basicità ← χ 2.5 3 3.5 4.0

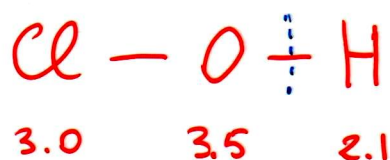
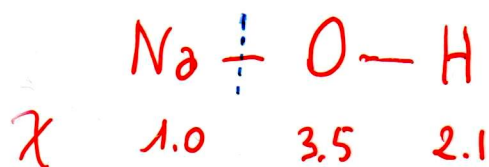
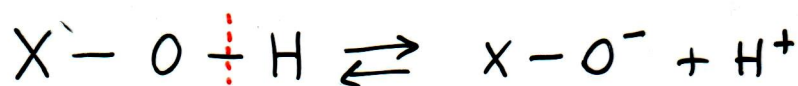


$K_a = 10^{-9}$

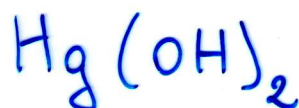


G CARATTERE ANFOTERO

1. Teoria di Arrhenius



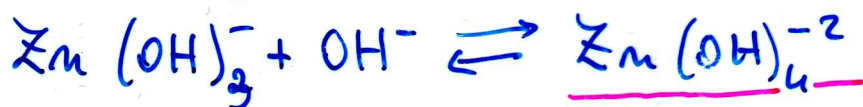
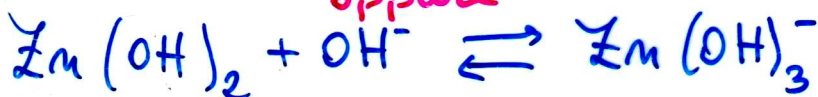
idrossido anfotero



base

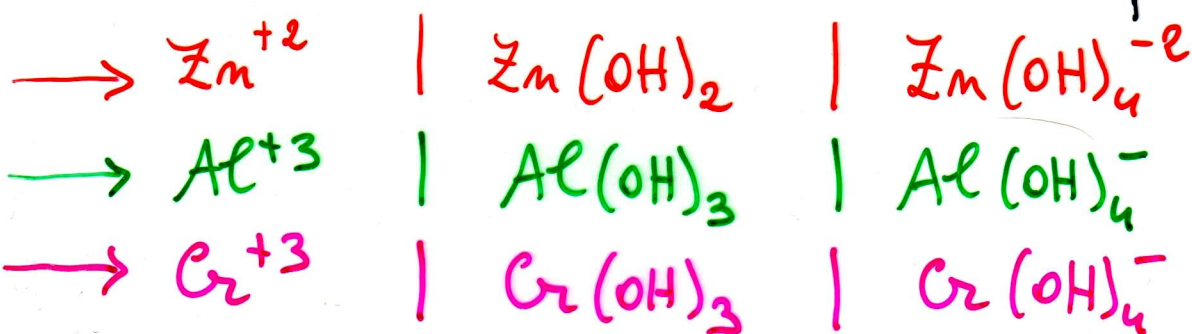
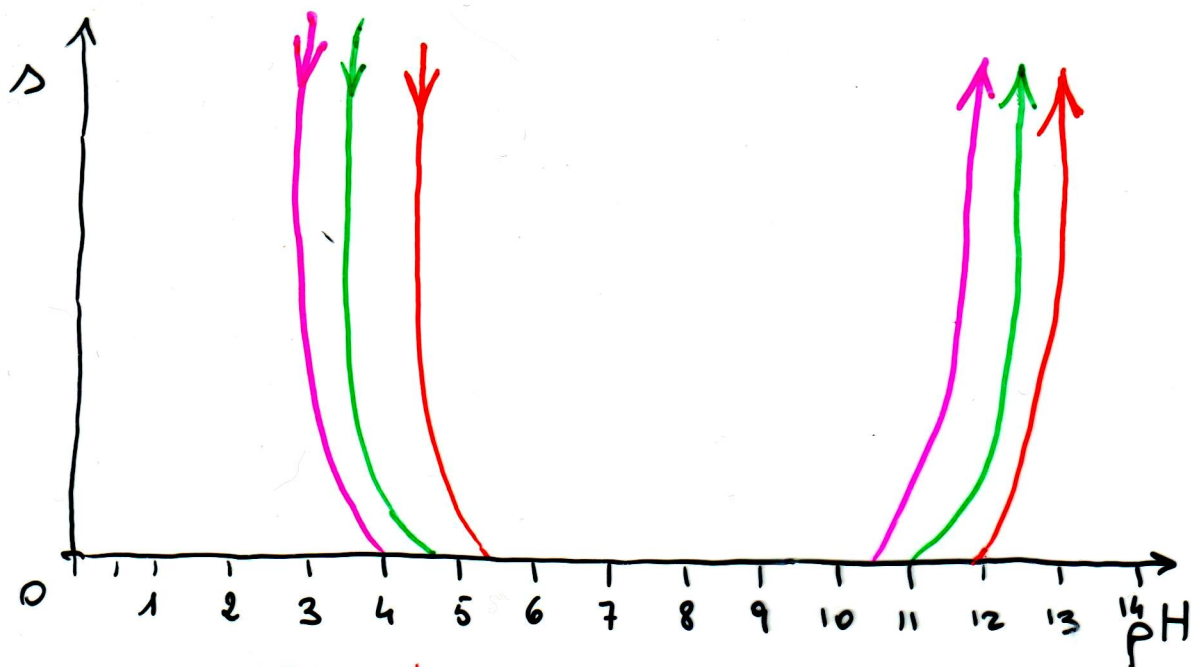


comportamento da base:
l'ambiente acido
perche l'eq. a destra



comportamento da
acido: l'ambiente
basico perche l'eq.
a destra

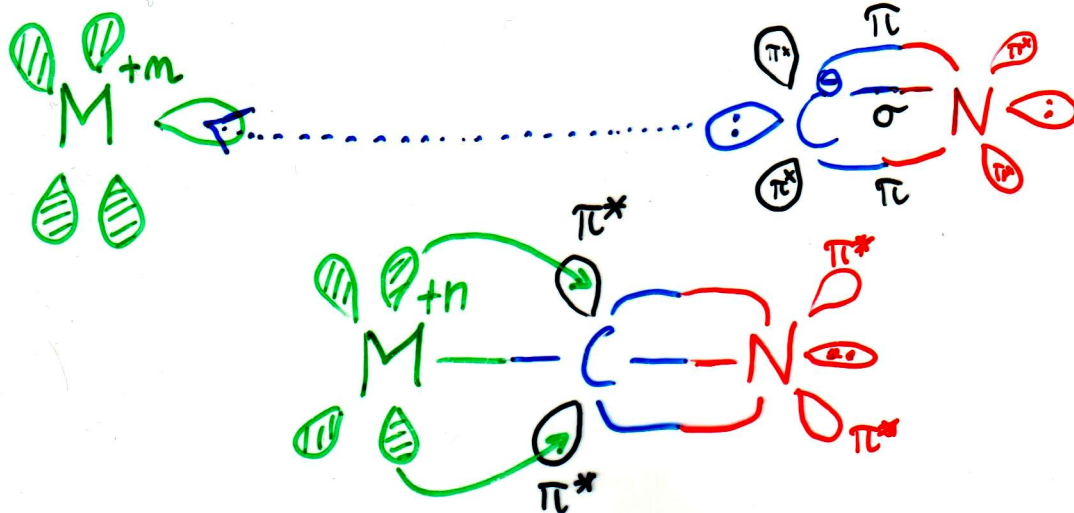




2. Teoria di Brønsted



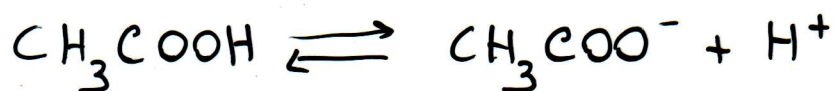
3. Teoria di Lewis



$$\chi_{\text{C}^-} = 2.2 \quad (2.5)$$

$$\chi_{\text{H}^+} = 1.4 \quad (1.3)$$

(H) IL K_a .



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1,8 \cdot 10^{-5}$$

$K_a \gg 1$ = acidi fortissimi

$K_a > 1$ = acidi forti

$10^{-4} < K_a < 10^{-1}$ = acidi di media forza

$10^{-9} < K_a < 10^{-4}$ = acidi deboli

$K_a < 10^{-9}$ = acidi debolissimi

CALCOLO DEL pH CHE SI OTTIENE DA:

ACIDI FORTI: $[\text{H}^+] = C_a$

ACIDI DEBOLI: $[\text{H}^+]^2 + K_a[\text{H}^+] - K_a C_a = 0$

se $K_a \cdot C_a \gg K_w$ e $C_a \gg K_a$:

$$[\text{H}^+] = \sqrt{K_a \cdot C_a}$$

BASI FORTI: $[\text{OH}^-] = C_b$

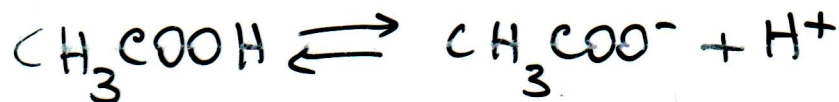
BASI DEBOLI: $[\text{OH}^-]^2 + K_b[\text{OH}^-] - K_b C_b = 0$

se $K_b C_b \gg K_w$ e $C_b \gg K_b$:

$$[\text{OH}^-] = \sqrt{K_b \cdot C_b}$$

2] COME VARIANO LE FORME DISSOCIATE ED INDISSOCIATE DEGLI ACIDI IN FUNZIONE DEL pH

Es.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1,8 \cdot 10^{-5}$$

2.1) COME VARIA LA FORMA DISSOCIATA IN FUNZIONE DEL pH

Conservazione della massa dell'acido:

$$C_a = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

Dal K_a abbiamo: $[\text{CH}_3\text{COOH}] = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{K_a}$

per cui:

$$C_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{K_a} + [\text{CH}_3\text{COO}^-]$$

$$C_a = [\text{CH}_3\text{COO}^-] \left(\frac{[\text{H}^+]}{K_a} + 1 \right) \quad \text{da cui}$$

$$[\text{CH}_3\text{COO}^-] = \frac{C_a \cdot K_a}{[\text{H}^+] + K_a}$$

2.2) COME VARIA LA FORMA INDISSOCIATA IN FUNZIONE DEL pH

$$C_a = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-] \quad [\text{CH}_3\text{COO}^-] = \frac{[\text{CH}_3\text{COOH}] K_a}{[\text{H}^+]}$$

$$C_a = [\text{CH}_3\text{COOH}] + \frac{[\text{CH}_3\text{COOH}] K_a}{[\text{H}^+]} = [\text{CH}_3\text{COOH}] \left(1 + \frac{K_a}{[\text{H}^+]} \right)$$

$$[\text{CH}_3\text{COOH}] = \frac{c_a [\text{H}^+]}{K_a + [\text{H}^+]}$$

2.3) COMPORTAMENTO SUL GRAFICO

E.s. CH_3COOH $K_a = 1,8 \cdot 10^{-5}$ $c_a = 0,1 \text{ M}$

$\text{pH} = 0$ $[\text{H}^+] = 1 \text{ M}$

$$[\text{CH}_3\text{COO}^-] = \frac{c_a K_a}{[\text{H}^+] + K_a} = \frac{10^{-1} \cdot 10^{-5}}{1 + 10^{-5}} = 10^{-6} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = \frac{c_a [\text{H}^+]}{K_a + [\text{H}^+]} = \frac{10^{-1} \cdot 1}{10^{-5} + 1} = 10^{-1} \text{ M}$$

$\text{pH} = 1$ $[\text{H}^+] = 10^{-1} \text{ M}$

$$[\text{CH}_3\text{COO}^-] = \frac{10^{-1} \cdot 10^{-5}}{10^{-1} + 10^{-5}} = 10^{-5} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = \frac{10^{-1} \cdot 10^{-1}}{10^{-5} + 10^{-1}} = 10^{-1} \text{ M}$$

$\text{pH} = 2$ $[\text{H}^+] = 10^{-2} \text{ M}$

$$[\text{CH}_3\text{COO}^-] = \frac{10^{-1} \cdot 10^{-5}}{10^{-2}} = 10^{-4} \text{ M} \quad [\text{CH}_3\text{COOH}] = \frac{10^{-1} \cdot 10^{-2}}{10^{-2}} = 10^{-1} \text{ M}$$

$\text{pH} = 5$ $[\text{H}^+] = 10^{-5} \text{ M}$

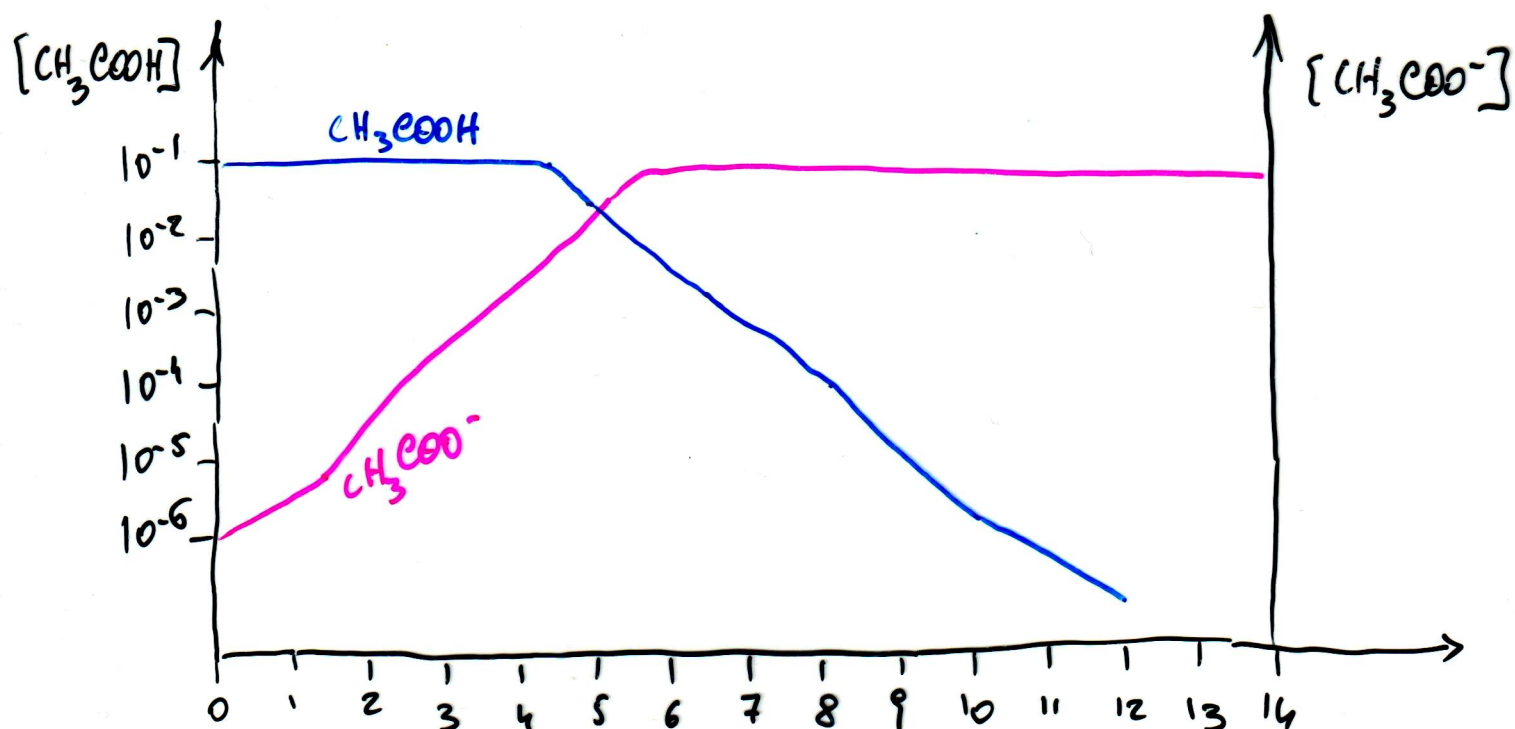
$$[\text{CH}_3\text{COO}^-] = \frac{10^{-1} \cdot 10^{-5}}{10^{-5} + 10^{-5}} = \frac{10^{-6}}{2 \cdot 10^{-5}} = 0,5 \cdot 10^{-1} = \underline{5 \cdot 10^{-2} \text{ M}}$$

$$[\text{CH}_3\text{COOH}] = \frac{10^{-1} \cdot 10^{-5}}{10^{-5} + 10^{-5}} = \underline{5 \cdot 10^{-2} \text{ M}}$$

$\text{pH} = 8$ $[\text{H}^+] = 10^{-8} \text{ M}$

$$[\text{CH}_3\text{COO}^-] = \frac{10^{-1} \cdot 10^{-5}}{10^{-8} + 10^{-5}} = \frac{10^{-6}}{10^{-5}} = 10^{-1} \text{ M}$$

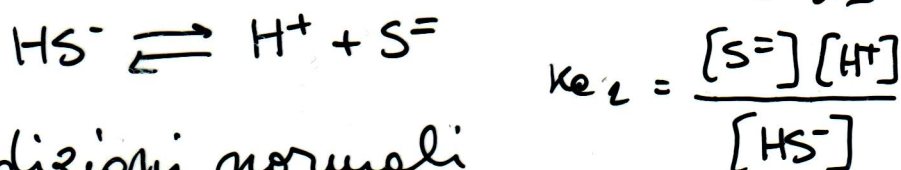
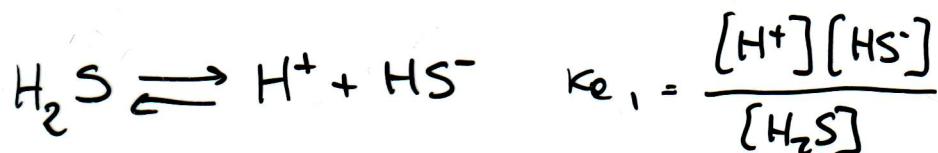
$$[\text{CH}_3\text{COOH}] = \frac{c_a [\text{H}^+]}{K_a + [\text{H}^+]} = \frac{10^{-1} \cdot 10^{-8}}{10^{-5} + 10^{-8}} = \frac{10^{-9}}{10^{-5}} = 10^{-4} \text{ M}$$



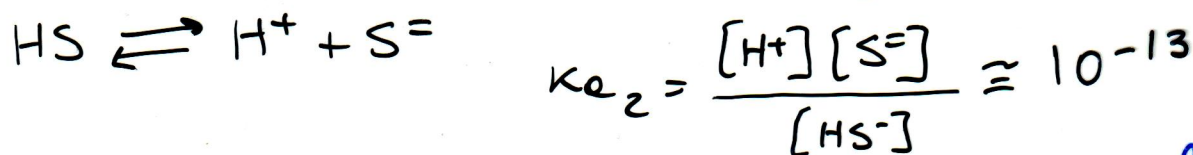
2.4) L'ACIDO SOLFIDRICO H_2S

- Stato dell' H_2S a condizioni normali.

A pressione e temperatura ordinarie (1 atm, 25°C) l' H_2S è un GAS. Una soluz. acquosa saturo in H_2S mostra una concentrat. di acido = 0,1 M.



Vediamo a condizioni normali di temp. e pressione le concentraz. delle varie specie dell' H_2S



Incognite: $[\text{H}_2\text{S}]$, $[\text{HS}^-]$, $[\text{S}^{2-}]$, $[\text{H}^+]$, $[\text{OH}^-]$ *le trascuriamo perché troppo piccole*

↓
li assumiamo
provenienti solo
della 1^a dissoc. H_2S
quindi $[\text{H}^+] = [\text{HS}^-]$

Equazioni: $K_{a1} = \frac{[\text{H}^+]^2}{[\text{H}_2\text{S}]} \approx 10^{-7}$; $K_{a2} = [\text{S}^{2-}] \approx 10^{-13}$

$$c_a = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]$$

poiché, a c.m. $[\text{H}_2\text{S}] = 0,1 \text{ M}$ in soluzione acquosa saturata,

$$[\text{H}^+]^2 = [\text{HS}^-]^2 = K_{a1} \cdot [\text{H}_2\text{S}] = 10^{-7} \cdot 10^{-1} = 10^{-8} \text{ M}$$

$$[\text{HS}^-] = [\text{H}^+] \approx 10^{-4} \quad ; \quad [\text{S}^{2-}] = K_{a2} \approx 10^{-13}$$

$$c_a = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] = 0,1 + 10^{-4} + 10^{-13} \approx 0,1 \text{ M}$$

$$c_a \approx 10^{-1} \text{ M}$$

noti ma trascurabili

a c.m. l' H_2S è quasi tutto indissociato *perché troppo piccoli*
cioè (quindi è nelle forme H_2S)

• **VARIATIONE DELLE VARIE SPECIE DI H_2S IN FUNZIONE DEL pH.**

Incognite: $[\text{H}_2\text{S}]$, $[\text{HS}^-]$, $[\text{S}^{2-}]$

Equazioni: $K_{a1} = \frac{[H^+][HS^-]}{[H_2S]} \approx 10^{-7}$

$$K_{a1,2} = \frac{[H^+][S^{2-}][H^+][HS^-]}{[H_2S][HS^-]} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \approx 10^{-20}$$

$$C_a = [H_2S] + [HS^-] + [S^{2-}]$$

Per sapere come varia H_2S in funzione del pH, esprimiamo HS^- e S^{2-} in funzione di H_2S :

\downarrow dal K_{a1} \swarrow dal $K_{a1,2}$

$$[HS^-] = \frac{K_{a1} \cdot [H_2S]}{[H^+]}, \quad [S^{2-}] = \frac{K_{a1,2} \cdot [H_2S]}{[H^+]^2}$$

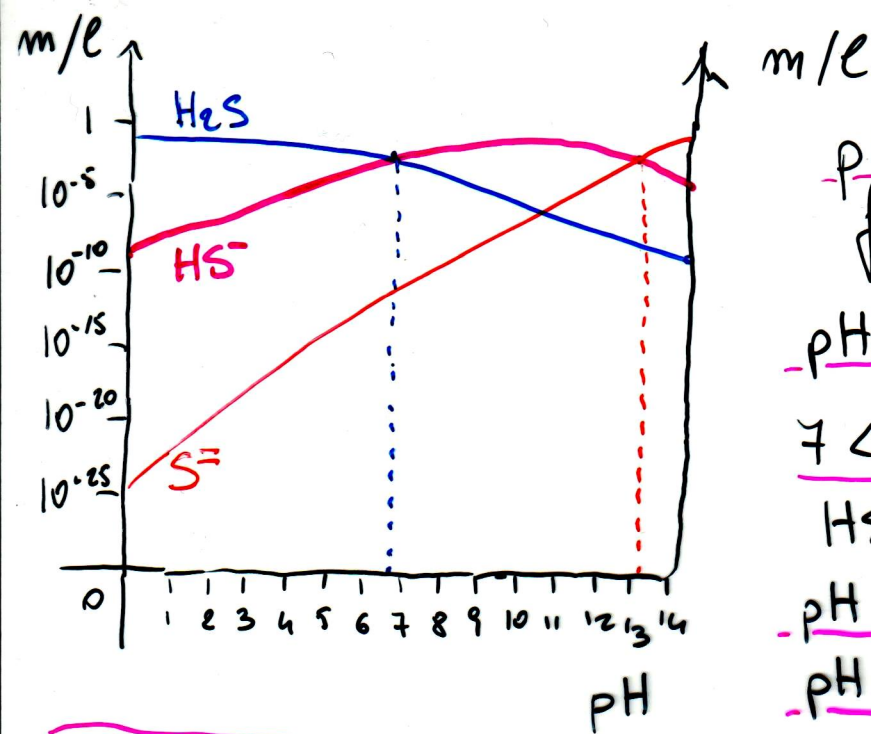
$$C_e = [H_2S] + \frac{K_{a1} [H_2S]}{[H^+]} + \frac{K_{a1,2} [H_2S]}{[H^+]^2} \quad \text{da cui:}$$

$$[H_2S] = \frac{C_a}{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1,2}}{[H^+]^2}}$$

allo stesso modo ci ricaviamo le altre formule

$$[HS^-] = \frac{C_e}{1 + \frac{[H^+]}{K_{a1}} + \frac{K_{a2}}{[H^+]}}$$

$$[S^{2-}] = \frac{C_e}{1 + \frac{[H^+]}{K_{a1}} + \frac{[H^+]^2}{K_{a1,2}}}$$



pH acido: prevale la forma indissociata H_2S

pH = 7: abbiamo $[H_2S] = [HS^-]$

$7 < pH < 13$: prevale la forma HS^-

pH = 13: abbiamo $[HS^-] = [S^{2-}]$

pH > 13: prevale la forma S^{2-}

pH = 0

$$K_{e1,2} = \frac{[H^+]^2 \cdot [S^{2-}]}{[H_2S]} \approx 10^{-20}, \quad [S^{2-}] = \frac{10^{-20} \cdot 10^{-1}}{1} = 10^{-21} \text{ M}$$

pH = 2,2

$$[S^{2-}] \approx \frac{10^{-21}}{10^{-4}} \approx 10^{-17} \text{ M}$$

pH = 9

$$[S^{2-}] \approx \frac{10^{-21}}{10^{-9}} \approx 10^{-12} \text{ M}$$

$$Ag_2S = 8 \cdot 10^{-50} \quad K_{ps}$$

$$HgS = 10^{-53}$$

$$CuS = 10^{-37}$$

$$PbS = 10^{-28}$$

$$CdS = 10^{-27}$$

$$SnS = 10^{-26}$$

$$ZnS = 2 \cdot 10^{-24}$$

$$CoS = 5 \cdot 10^{-22}$$

$$NiS = 4 \cdot 10^{-20}$$

$$MnS = 3 \cdot 10^{-11}$$

solub (s)

$$\sim 10^{-17} \text{ M}$$

$$\sim 10^{-27} \text{ M}$$

$$\sim 10^{-19} \text{ M}$$

$$\sim 10^{-14} \text{ M}$$

$$\sim 10^{-13} \text{ M}$$

$$\sim 10^{-13} \text{ M}$$

$$\sim 10^{-12} \text{ M}$$

$$\sim 10^{-10} \text{ M}$$

$$\sim 10^{-9} \text{ M}$$

$$\sim 10^{-5} \text{ M}$$

1° GRUPPO SIST. CAT.

2° GRUPPO

(pH 0-2,2)

4° GRUPPO (pH 9-10)

PH e dissociazione

H_2S (GAS ; Tamb. $p=1 \text{ atm}$)

UNA SOLUZIONE AQUEA SATURA IN H_2S
MOSTRA UNA CONCENTRAZIONE DI ACIDO 0.1 M



$$[H^+] = [HS^-]$$



$$\Rightarrow K_{a1} = \frac{[H^+]^2}{[H_2S]}$$

$$\Rightarrow [H^+]^2 = K_{a1} \cdot [H_2S]$$

$$\Rightarrow K_{a2} = [S^{2-}]$$

$$\text{a c.m. } [H_2S] = 0.1 \text{ M}$$

$$[S^{2-}] \approx 10^{-13}$$

$$C_{\text{ov}} = [H_2S] + [HS^-] + [S^{2-}]$$

$0.1 \quad 10^{-4} \quad 10^{-13}$

$$[H^+]^2 = [HS^-]^2 = \underbrace{10^{-7} \cdot 10^{-1}}_{10^{-8} \text{ M}}$$

$$\underbrace{[H^+] = [HS^-]}_{\approx 10^{-4} \text{ M}}$$

a c.m. H_2S è quasi tutto INDISSOCIATO

$$pH = 0 \Rightarrow [H^+] = 1 \Rightarrow \frac{[HS^-]}{[H_2S]} = \frac{10^{-7}}{1} \Rightarrow [H_2S] \gg [HS^-]$$

$$pH = 3 \Rightarrow [H^+] = 10^{-3}$$

$$\frac{10^{-7}}{10^{-3}}$$

$$[H_2S] > [HS^-]$$

$$pH = 7 \quad [H^+] = 10^{-7}$$

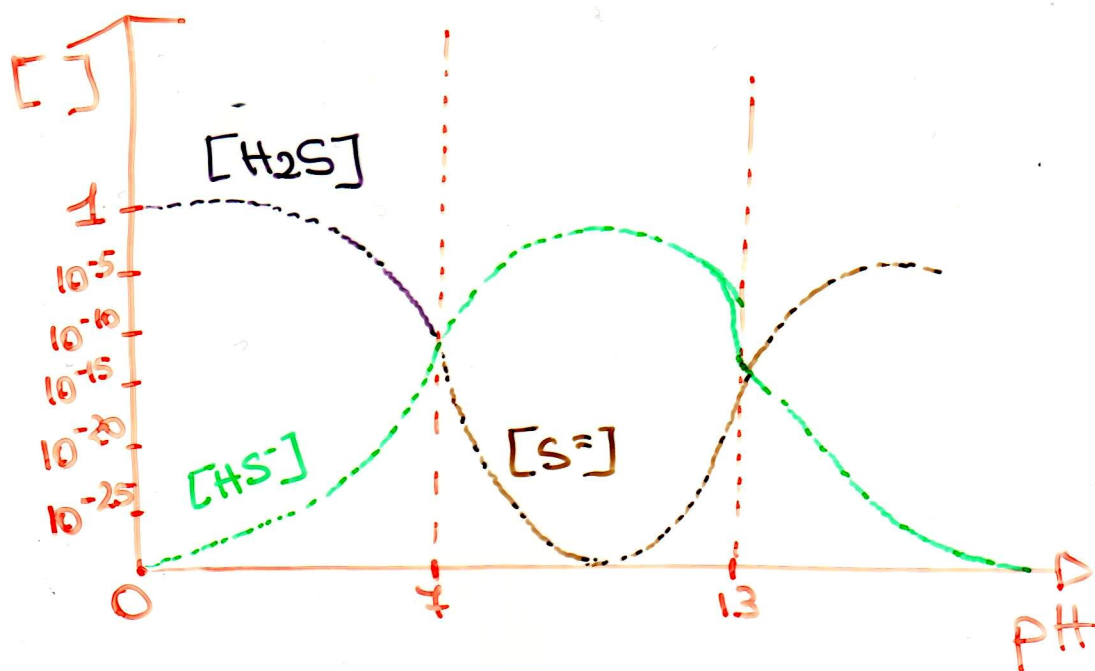
$$\frac{10^{-7}}{10^{-7}}$$

$$[H_2S] = [HS^-]$$

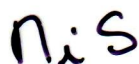
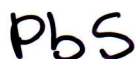
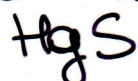
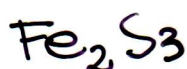
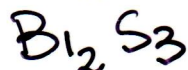
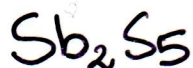
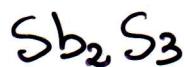
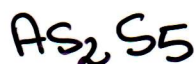
$$pH = 9 \quad [H^+] = 10^{-9} \quad [HS^-] \gg [S^{2-}] \Rightarrow \frac{[S^{2-}]}{[HS^-]} = \frac{10^{-13}}{10^{-9}}$$

$$pH = 13 \quad [H^+] = 10^{-13} \Rightarrow \frac{[S^{2-}]}{[HS^-]} = \frac{10^{-13}}{10^{-13}} \Rightarrow [S^{2-}] = [HS^-]$$

$$pH = 14 \quad [H^+] = 10^{-14} \quad \frac{10^{-13}}{10^{-14}} \quad [S^{2-}] > [HS^-]$$



SOLFURI



K_{ps}

10⁻¹²⁴

10⁻¹⁵⁰

10⁻⁹³

10⁻¹⁰⁰

10⁻¹²¹

10⁻⁸⁸

10⁻⁴⁰

10⁻⁵²

10⁻⁵¹

10⁻⁴⁹

10⁻²⁸

10⁻²⁴

II

10⁻²²

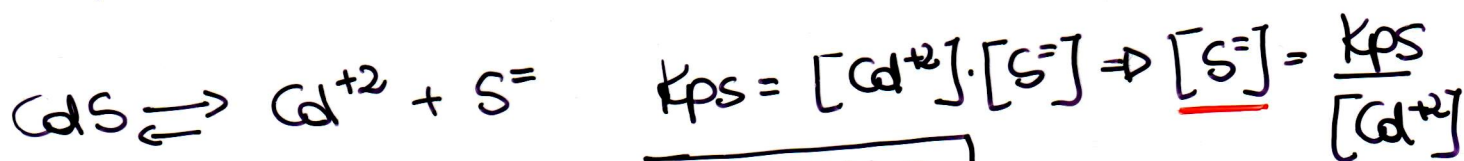
10⁻²¹

10⁻²⁰

10⁻¹⁸

10⁻¹⁰

IV



$$\Rightarrow \frac{10^{-24}}{10^{-5}} = \underline{10^{-22}} \Rightarrow \boxed{p.i \geq K_{ps}}$$

$$\text{ZnS} \Rightarrow 10^{-5} \cdot 10^{-22} < K_{ps}(10^{-22})$$

$$K_a^{10^{-22}} = \frac{[\text{H}^{+}]^2 \cdot [\text{S}^{=}] }{[\text{H}_2\text{S}]} \Rightarrow [\text{H}^{+}] = \sqrt{\frac{K_a^{10^{-22}} \cdot [\text{H}_2\text{S}] 10^{-1}}{[\text{S}^{=}] 10^{-22}}} = 0.312$$

⇓
pH = 0.5