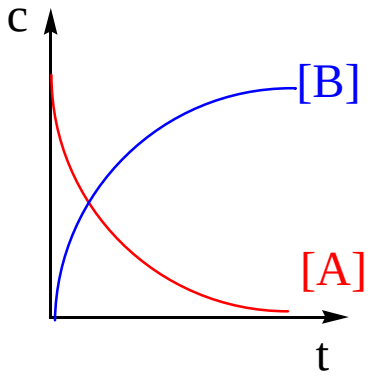
CINETICA CHIMICA

$HCl + NaOH \rightarrow H_2O + NaCl$ RAPIDA

$C_{DIAMANTE} \rightarrow C_{GRAFITE}$ LENTISSIMA

CINETICA CHIMICA:
-VELOCITA'
-MECCANISMO → COME AVVIENE

VELOCITA' → DEFINIZIONE



$A \rightarrow B$ $\qquad v = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$

$aA + bB \rightarrow cC + dD$ $\qquad v = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$ $\qquad v = -\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$

VELOCITA' DI REAZIONE $\rightarrow$ DIPENDE DA:

- CONCENTRAZIONE DEI REAGENTI
- TEMPERATURA
- RADIAZIONI, CATALIZZATORI

DIPENDENZA da CONC.

$A + B \rightarrow C + D$

$$v = k[A]^{\alpha}[B]^{\beta}$$

k = costante di velocità
α, β ordine di reazione
α, $\beta \neq a, b$

Reazione di ordine α in A
" di ordine β in B
" di ordine complessivo $\alpha + \beta$

α, β determinati sperimentalmente

Reazioni del I ordine

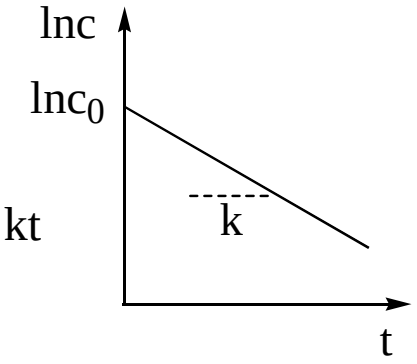
$A \rightarrow B$ $\qquad v = -\frac{d[A]}{dt} = k[A] \quad \rightarrow -\frac{d[A]}{[A]} = kdt$

$t = 0 \; [A] = c_0$

$t \quad [A] = c$ $\qquad \int_{c_0}^{c} \frac{d[A]}{[A]} = -\int_0^t kdt$

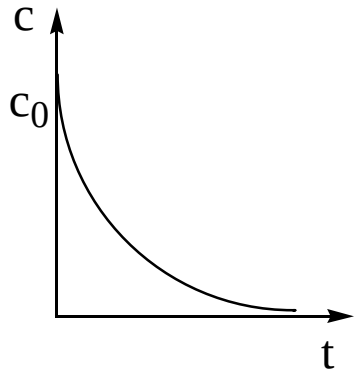
$\ln \frac{c}{c_0} = -kt$ $\qquad \ln c_0$

$\ln c = \ln c_0 - kt$



$\frac{c}{c_0} = e^{-kt}$ $\qquad c_0$

$c = c_0 \, e^{-kt}$



$^{14}C \rightarrow {}^{14}N + e^-$ decadimento nucleare τ= tempo di dimezzamento

$t = 0 \quad c = c_0$

$t = \tau \quad c = c_0/2$

$$\ln \frac{c}{c_0} = -kt \; \rightarrow \; \ln \frac{c/2}{c_0} = -\ln 2 = -k\tau$$

$$\tau = \frac{\ln 2}{k} = \frac{0{,}693}{k}$$

Reazioni del II ordine

$A + B \rightarrow C + D \qquad v = -\frac{d[A]}{dt} = k[A][B]$

$A \rightarrow B \qquad v = -\frac{d[A]}{dt} = k[A]^2$

$[A] = [B] = c \quad v = -\frac{dc}{dt} = kc^2 \quad \rightarrow \frac{dc}{c^2} = -kt$

$t = 0 \qquad c = c_0$

$$\int_{c_0}^{c} \frac{dc}{c^2} = -\int_0^t k\,dt$$

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

$t = \tau \quad c = c_0/2 \quad \rightarrow \quad \frac{2}{c_0} - \frac{1}{c_0} = \frac{1}{c_0} = k\tau \rightarrow \qquad \tau = \frac{1}{kc_0}$

MECCANISMO DI REAZIONE

REAZIONI → URTI ANELASTICI (TEORIA delle COLLISIONI)

MECCANISMO di REAZIONE → in uno STADIO SINGOLO

→ in PIU' STADI (ognuno con la sua k)

$NO_{(g)} + O_{3\,(g)} \rightarrow NO_{2\,(g)} + O_{2\,(g)}$ in uno stadio

$O_{3\,(g)} \rightarrow O_{2\,(g)} + O_{(g)}$

$O_{3\,(g)} + O_{(g)} \rightarrow 2\,O_{2\,(g)}$ in due stadi

$2\,O_{3\,(g)} \rightarrow 3\,O_{2\,(g)}$ reazione complessiva

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ B = intermedio di reazione

1) $NO_{2(g)} + F_{2\,(g)} \xrightarrow{k_1} NO_2F_{(g)} + F_{(g)}$ stadio lento $v_1 = k_1[NO_2][F_2]$

2) $F_{(g)} + NO_{2(g)} \xrightarrow{k_2} NO_2F_{(g)}$ stadio veloce $v_2 = k_2[NO_2][F]$

$2\,NO_{2(g)} + F_{2\,(g)} \rightarrow 2\,NO_2F_{(g)}$ $v_2 > v_1$ $v = v_1$

DIPENDENZA da T

TEORIA delle COLLISIONI $\rightarrow$
REAZIONE = URTO ANELASTICO

Perché due molecole reagiscano:
-devono collidere v = f(c, T)
- “ “ con <u>energia sufficiente</u> (KE) $\rightarrow$ urti efficaci

Es. $H_2 + Cl_2 \rightarrow 2\ HCl$

rottura vecchi legami (H-H, Cl-Cl) + formazione nuovi legami (H-Cl)

$\downarrow$

barriera energetica da superare = Energia di attivazione (E_{att})

Perché due molecole reagiscano devono avere

$KE > E_{att}$

Quante sono le molecole in grado di reagire (N_E?)

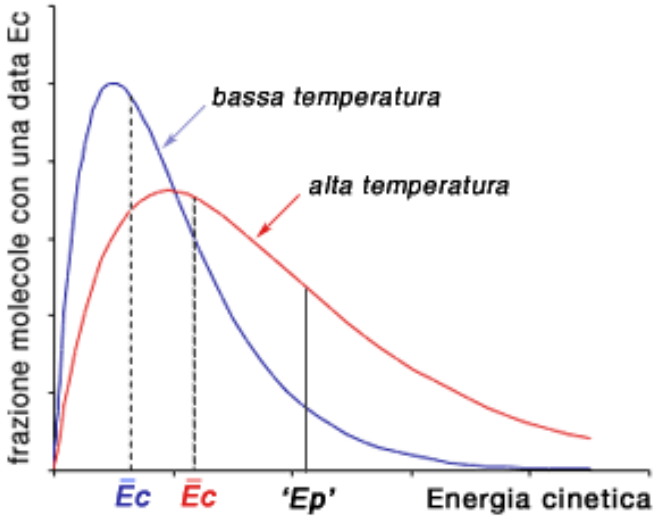
$$\frac{N_E}{N} = e^{-\frac{E_{att}}{RT}}$$

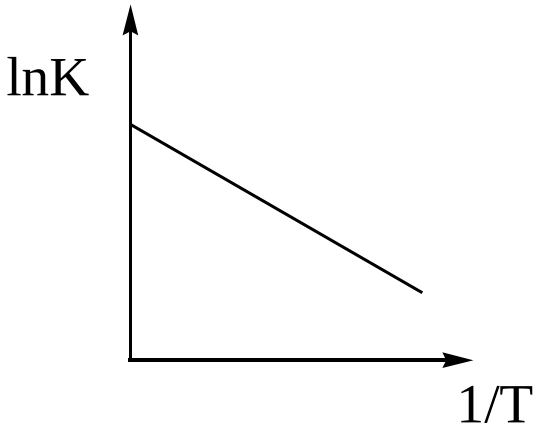
Equazione di Arrhenius

$$k = A \times e^{-\frac{E_{att}}{RT}}$$

A = fattore di frequenza

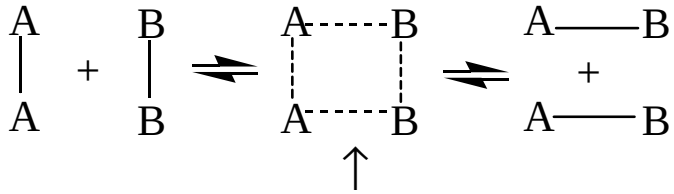
$$\ln k = c - \frac{E_{att}}{RT}$$





TEORIA DELLO STATO DI TRANSIZIONE

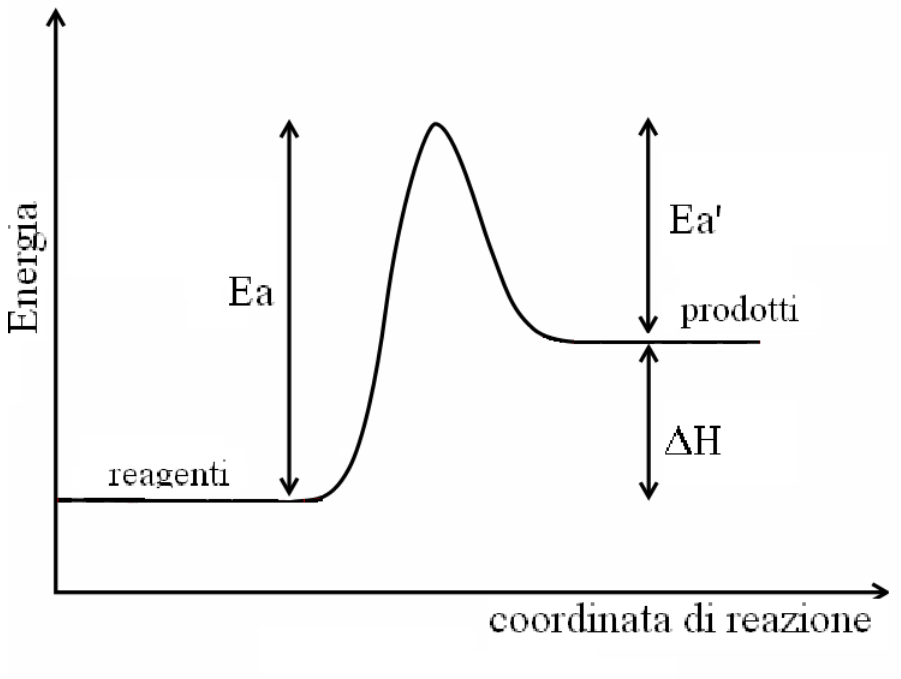
$A_2 + B_2 \leftrightarrows 2AB$



Complesso attivato

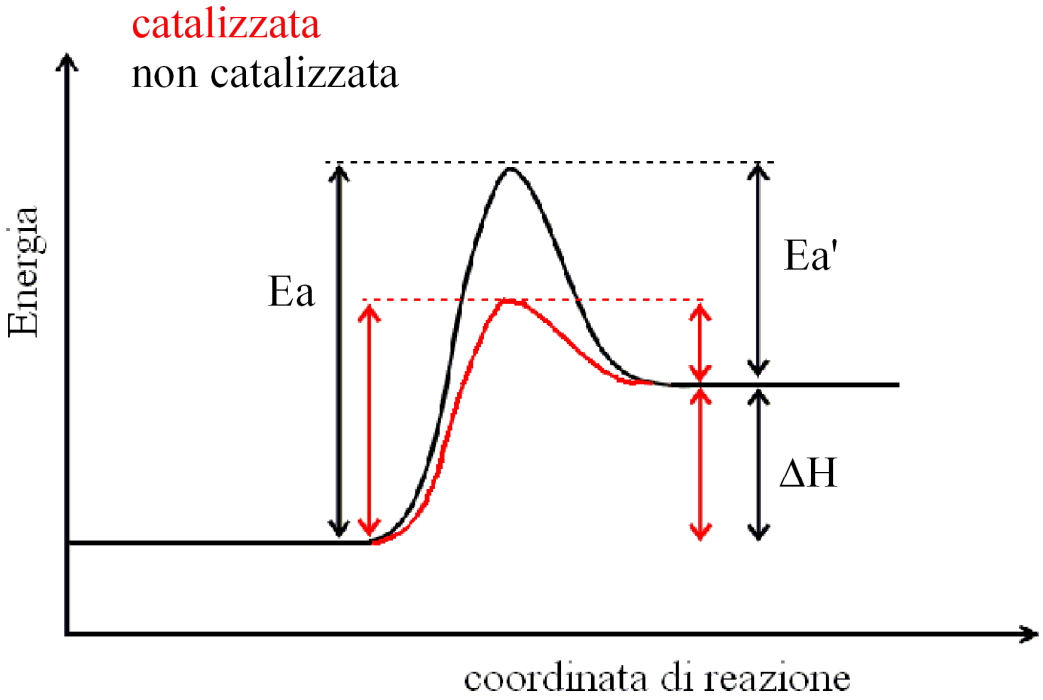
$k_d = A\, e^{-E_a/RT}$

$k_i = A' e^{-E_a'/RT}$



CATALIZZATORE

→ <u>fa variare la velocità di una reazione</u>
→ non influenza la natura dei prodotti
→ non figura nell'equazione stechiometrica
→ (non influenza la posizione dell'equilibrio)



Catalisi:
- omogenea
- eterogenea

Selettività

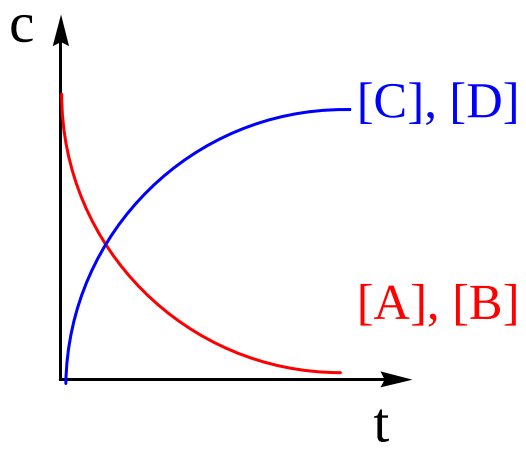
ENZIMI

COSTANTE DI EQUILIBRIO

$$A + B \underset{k_i}{\overset{k_d}{\leftrightarrows}} C + D$$

$$\vec{v} = k_d[A][B]$$

$$\overleftarrow{v} = k_i[C][D]$$



All'equilibrio

$$\vec{v} = \overleftarrow{v}$$

$$k_d[A]_{eq}[B]_{eq} = k_i[C]_{eq}[D]_{eq}$$

$$K_{eq} = \frac{k_d}{k_i} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}}$$

Derivazione termodinamica

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

$$\Delta G_{REAZ} = \sum_{i}^{PROD} \nu i\, G_i - \sum_{i}^{REAG} \nu i G_i = cG_C + dG_D - aG_A - bG_B$$

$$G_A = G°_A + RT \ln P_A \qquad G_B = G°_B + RT \ln P_B$$
$$G_C = G°_C + RT \ln P_C \qquad G_D = G°_D + RT \ln P_D$$

$$\Delta G_{REAZ} = c\,(G°_C + RT \ln P_C) + d\,(G°_D + RT \ln P_D) - a\,(G°_A + RT \ln P_A) - b\,(G°_B + RT \ln P_B)$$

$$\Delta G_{REAZ} = \overbrace{cG°_C + dG°_D - aG°_A - bG°_B}^{\Delta G°_{REAZ}} + cRT \ln P_C + dRT \ln P_D - aRT \ln P_A - bRT \ln P_B$$

$$\Delta G_{REAZ} = \Delta G°_{REAZ} + RT(c \ln P_C + d \ln P_D - a \ln P_A - b \ln P_B) =$$

$$= \Delta G°_{REAZ} + RT(\ln P_C^{\,c} + \ln P_D^{\,d} - \ln P_A^{\,a} - \ln P_B^{\,b}) =$$

$$= \Delta G°_{REAZ} + RT \ln \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}} = \Delta G_{REAZ}$$

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

$$\Delta G_{REAZ} = \Delta G°_{REAZ} + RT\ln\frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

REAZIONE SPONTANEA $\Delta G_{REAZ} < 0$

LA REAZIONE PROCEDE DA SINISTRA VERSO DESTRA

$\Delta G°_{REAZ}$ = cost $\Delta G_{REAZ} \rightarrow 0$

ALL' EQUILIBRIO: $\Delta G_{REAZ} = 0$

$\Rightarrow$ $\Delta G_{REAZ} = \Delta G°_{REAZ} + RT\ln\frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} = \Delta G°_{REAZ} + RT\ln K_P = 0$

$\Delta G°_{REAZ} = -\ RT\ln K_P$

ALL' EQUILIBRIO: $K_P = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$ = costante

$\Delta G° < 0 \quad K > 1$

$\Delta G° > 0 \quad K < 1$

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

ALL'EQUILIBRIO $\boxed{\Delta G = 0 \quad \Delta G° = - RT \ln K_P}$

$T = cost \quad K_P = cost \qquad K_P = f(T)$

$$\boxed{K_c = \frac{P_C^c P_D^d}{P_A^a P_B^b}}$$

ALL'EQUILIBRIO

$K_P >> 1$ ⇨ FAVORITI i PRODOTTI ⇨ REAZIONE SPOSTATA verso DESTRA

$K_P << 1$ ⇨ FAVORITI i REAGENTI ⇨ REAZIONE SPOSTATA verso SINISTRA

$$G_A = G°_A + RT\ln c_A = G°_A + RT\ln[A]$$

$$\boxed{K_c = \frac{c_C^c c_D^d}{c_A^a c_B^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

$$a\,A + b\,B \leftrightarrows c\,C + d\,D$$

$$\boxed{K_P = \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}}} \qquad K_c = \frac{c_C^{\,c} c_D^{\,d}}{c_A^{\,a} c_B^{\,b}}$$

$$PV = nRT \qquad c = \frac{n}{V} \qquad P = \frac{nRT}{V} = c\,RT$$

$$P_A = c_A RT \qquad P_C = c_C RT$$

$$P_B = c_B RT \qquad P_D = c_D RT$$

$$K_P = \frac{P_C^{\,c} P_D^{\,d}}{P_A^{\,a} P_B^{\,b}} = \frac{(c_C RT)^c (c_D RT)^d}{(c_A RT)^a (c_B RT)^b} = \frac{c_C^{\,c} c_D^{\,d}}{c_A^{\,a} c_B^{\,b}} \frac{(RT)^c (RT)^d}{(RT)^a (RT)^b} = K_c (RT)^{\Delta\nu}$$

K_C

$$\Delta\nu = c+d-(a+b)$$

$$K_P = K_C \cdot (RT)^{\Delta\nu}$$

$$K_C = K_P \cdot (RT)^{-\Delta\nu}$$

$$3\,H_{2\,(g)} + N_{2(g)} \leftrightarrows 2\,NH_{3\,(g)} \qquad K_P = \frac{P_{NH_3}^2}{P_{H_2}^3 \cdot P_{N_2}} \qquad K_C = \frac{c_{NH_3}^2}{c_{H_2}^3 \cdot c_{N_2}}$$

$$\Delta\nu = -2 \quad K_P = K_C \cdot (RT)^{\Delta\nu} = K_C \cdot (RT)^{-2}$$

$$H_{2\,(g)} + I_{2(g)} \leftrightarrows 2HI_{\,(g)} \qquad K_P = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$$

$$\Delta\nu = 0 \quad K_P = K_C$$

$$SO_2 + \tfrac{1}{2}\,O_2 \leftrightarrows SO_3 \quad \Rightarrow \quad K_P = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{1/2}}$$

$$2\,SO_2 + O_2 \leftrightarrows 2\,SO_3 \quad \Rightarrow \quad K'_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 \cdot P_{O_2}}$$

$$K'_P = K_P^2$$

IN SOLUZIONE ⇨ K_C

$HClO \leftrightarrows H^+ + ClO^-$ $\qquad K_c = \frac{c_{H^+} c_{ClO^-}}{c_{HClO}} = \frac{[H^+][ClO^-]}{[HClO]}$

$Fe^{2+} + 6\ Cl^- \leftrightarrows FeCl_6^{4-}$ $\qquad K = \frac{[FeCl_6^{4-}]}{[Fe^{2+}][Cl^-]^6}$

EQUILIBRI IN FASE ETEROGENEA

$C_{(s)} + O_{2\ (g)} \leftrightarrows CO_{2(g)}$ $\qquad K_P = \frac{P_{CO_2}}{P_{O_2}}$

$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ $\qquad K = [Ag^+]\cdot[Cl^-]$

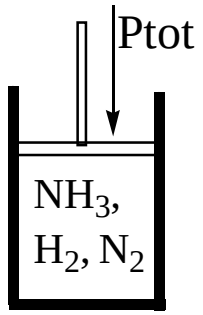
PRINCIPIO DI LE CHATELIER

$3\ H_{2\,(g)} + N_{2(g)} \leftrightarrows 2\ NH_{3\,(g)}$ $\quad K_P = \dfrac{P_{NH_3}^2}{P_{H_2}^3 \cdot P_{N_2}}$ $\quad K_C = \dfrac{c_{NH_3}^2}{c_{H_2}^3 \cdot c_{N_2}}$

$K_P, K_C = cost$

AUMENTO di P_{N_2}, P_{H_2} ⇨ l'EQUILIBRIO si sposta verso DESTRA

AUMENTO di P_{NH_3} ⇨ l'EQUILIBRIO si sposta verso SINISTRA



VARIAZIONE DI P_{tot}?

$P_{H_2} = x_{H_2} \cdot P_{tot}$

$P_{N_2} = x_{N_2} \cdot P_{tot}$

$P_{NH_3} = x_{NH_3} \cdot P_{tot}$

$$K_P = \frac{P_{NH_3}^2}{P_{H_2}^3 \cdot P_{N_2}} = \frac{(x_{NH_3} \cdot P_{tot})^2}{(x_{H_2} \cdot P_{tot})^3 \cdot (x_{N_2} \cdot P_{tot})} = \frac{x_{NH_3}^2}{x_{H_2}^3 \cdot x_{N_2}} \cdot \frac{(P_{tot})^2}{(P_{tot})^4} = K_x \cdot P_{tot}^{-2}$$

$$K_x = \frac{x_{NH_3}^2}{x_{H_2}^3 \cdot x_{N_2}}$$

<u>NON</u> E' UNA VERA COSTANTE TERMODINAMICA

$K_P = K_X \cdot P^{\Delta\nu}$ $\quad \Delta\nu = \sum_{PROD} \nu_i - \sum_{REAG} \nu_i$ $\quad \nu_i$ = coefficienti Stechiometrici

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$2\ H_{2\,(g)} + O_{2(g)} \leftrightarrows 2\ H_2O_{\,(g)}$

$\Delta\nu = -1 \qquad K_P = K_X \cdot P^{-1}$

$$K_P = \frac{P_{H_2O}^{\,2}}{P_{H_2}^{\,2} \cdot P_{O_2}}$$

REAZIONE FAVORITA DA AUMENTO P

$PCl_{5\,(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$

$\Delta\nu = 1 \quad K_P = K_X \cdot P$

$$K_P = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$$

REAZIONE SFAVORITA DA AUMENTO P

$C_{(s)} + O_{2(g)} \leftrightarrows CO_{2\,(g)} \qquad K_P = \frac{P_{CO_2}}{P_{O_2}}$

$\Delta\nu = 0 \quad K_P = K_X$

VARIAZIONI DI P NON HANNO EFFETTO SULL'EQUILIBRIO

N.B. per il calcolo di $\Delta\nu$ contano i coeff. delle <u>sostanze gassose</u>

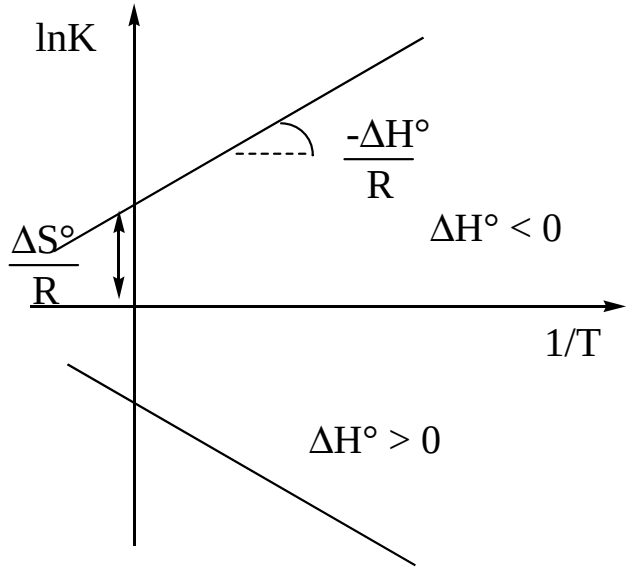
EFFETTO DELLA TEMPERATURA

$$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ \Rightarrow$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \Rightarrow \frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

$$\ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$



$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{\Delta H^\circ}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] = \frac{\Delta H^\circ \Delta T}{R T_2 T_1}$$

ENDOTERMICA	$\Delta H^\circ > 0$	$T_2 > T_1$	$K_2 > K_1$
ESOTERMICA	$\Delta H^\circ < 0$	$T_2 > T_1$	$K_2 < K_1$

$$A + B \underset{k_i}{\overset{k_d}{\leftrightarrows}} C + D$$

$$\vec{v} = k_d[A][B] \qquad \overleftarrow{v} = k_i[C][D]$$

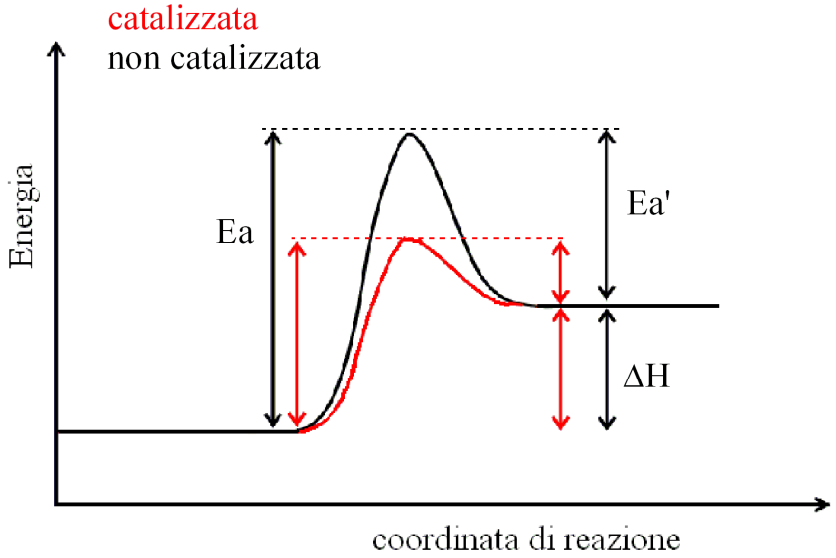
All'equilibrio $\vec{v} = \overleftarrow{v}$

$$k_d[A]_{eq}[B]_{eq} = k_{-i}[C]_{eq}[D]_{eq}$$

$$K_{eq} = \frac{k_d}{k_i} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}}$$

$$k_d = e^{-E_a/RT}$$

$$k_i = e^{-E_a'/RT}$$



$$K_{eq} = \frac{k_d}{k_i} = \frac{Ae^{-E_a/RT}}{A'e^{-E_a'/RT}} = \frac{A}{A'}e^{-(E_a - E_a')/RT} = Be^{-\Delta H/RT}$$

$$\ln K_{eq} = B' - \frac{\Delta H}{RT} \Rightarrow \frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2}$$

REAZIONI IN SOLUZIONE

- ACIDO-BASE ⇨ SCAMBIO DI PROTONI

$$HA + B \leftrightarrows A^- + BH^+$$

- REDOX ⇨ SCAMBIO DI ELETTRONI

$$A_{OX} + B_{RED} \leftrightarrows A_{RED} + B_{OX}$$

- REAZIONI DI SOLUBILIZZAZIONE

$$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$$

- REAZIONI DI COMPLESSAZIONE

$$Fe^{2+} + 6\ Cl^- \leftrightarrows FeCl_6^{4-}$$

REAZIONI ACIDO-BASE

ARRHENIUS

ACIDO ⇨ LIBERA IONI H^+
BASE ⇨ LIBERA IONI OH^-

$HCl \rightarrow H^+ + Cl^-$ ACIDO

$NaOH \rightarrow Na^+ + OH^-$ BASE

$NH_3 + H_2O \rightarrow NH_4OH$

$NH_4OH \leftrightarrows NH_4^+ + OH^-$

BRÖNSTED E LOWRY

ACIDO ⇨ SPECIE CAPACE DI DONARE IONI H^+
BASE ⇨ SPECIE CAPACE DI ACCETTARE IONI H^+

$HA \leftrightarrows A^- + H^+$
ACIDO BASE CONIUGATA

$B + H^+ \leftrightarrows BH^+$
BASE ACIDO CONIUGATO

$HA + B \leftrightarrows A^- + BH^+$
ACIDO 1 BASE 2 BASE 1 ACIDO 2

$HNO_2 + H_2O \leftrightarrows NO_2^- + H_3O^+$
acido1 base2 base1 acido2

H_3O^+ = IONE IDRONIO (OSSONIO)

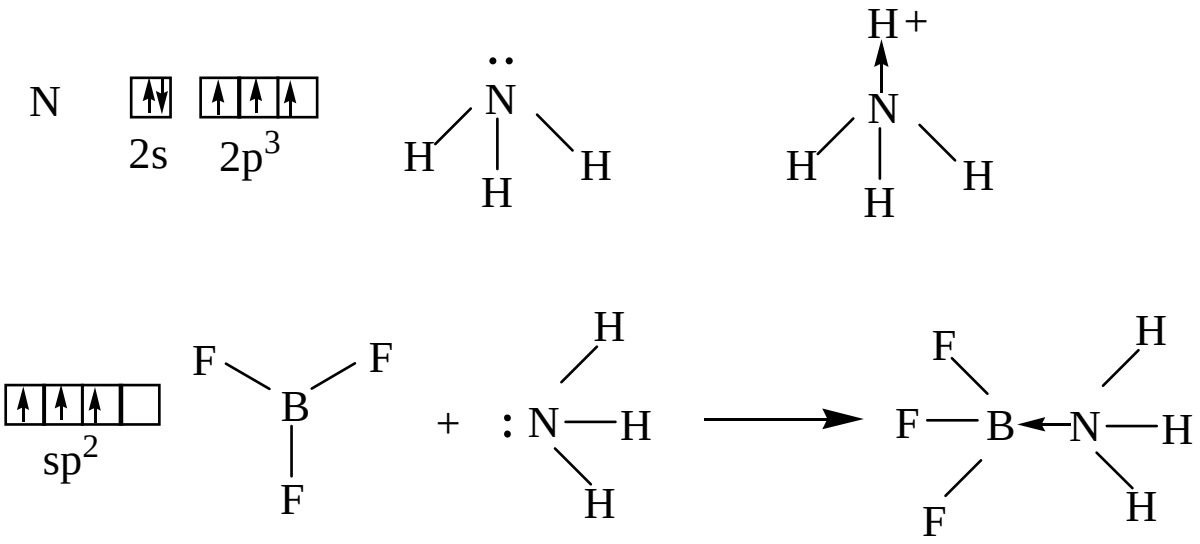
$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
base1 acido2 acido1 base2

OH^- = IONE OSSIDRILE

$NaOH \rightarrow Na^+ + OH^-$

LEWIS

ACIDO ⇨ SPECIE CAPACE DI ACCETTARE LONE PAIRS
BASE ⇨ SPECIE CAPACE DI DONARE LONE PAIRS



ACIDO DEBOLE

$$HA + H_2O \leftrightarrows A^- + H_3O^+ \quad \longleftarrow \quad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$HA \leftrightarrows A^- + H^+ \longleftarrow K_a = \frac{[A^-][H^+]}{[HA]}$$

$$HF + H_2O \leftrightarrows F^- + H_3O^+ \quad K_{HF} = \frac{[F^-][H_3O^+]}{[HF]} = 6{,}6 \times 10^{-4}$$

$$HCN + H_2O \leftrightarrows CN^- + H_3O^+ \qquad K_{HCN} = \frac{[CN^-][H_3O^+]}{[HCN]} = 6{,}17 \times 10^{-10}$$

ACIDO FORTE

$$HA + H_2O \rightarrow A^- + H_3O^+$$
$$HA \rightarrow A^- + H^+$$

BASE DEBOLE

$$B + H_2O \leftrightarrows BH^+ + OH^- \quad K_b = \frac{[BH^+][OH^-]}{[B]}$$

BASE FORTE

$NaOH \rightarrow Na^+ + OH^-$ ← MONOPROTICA

$Ba(OH)_2 \rightarrow Ba^{+2} + 2\ OH^-$ ← DIPROTICA

$2\,H_2O \leftrightarrows H_3O^+ + OH^-$ $\qquad K_W = [H_3O^+][OH^-] = 10^{-14}$

Acqua pura $[H_3O^+] = [OH^-] \Rightarrow K_W = [H_3O^+]^2 = 10^{-14}$

$\Rightarrow [H_3O^+] = \sqrt{K_W} = \sqrt{10^{-14}} = 10^{-7}$

$$pH = -\log [H_3O^+]$$

Acqua pura :
$[H_3O^+] = [OH^-] = 10^{-7} \Rightarrow pH = -\log [H_3O^+] = -\log 10^{-7} = 7$

SOLUZIONE ACIDA $\quad [H_3O^+] > [OH^-] \qquad [H_3O^+] > 10^{-7} \quad pH < 7$

SOLUZIONE BASICA $\quad [H_3O^+] < [OH^-] \qquad [H_3O^+] < 10^{-7} \quad pH > 7$

$$0 \leq pH \leq 14$$

$$pOH = -\log[OH^-] = -\log\left(\frac{K_W}{[H_3O^+]}\right) = -\log K_W + \log[H_3O^+] = 14 - pH$$

CALCOLO DEL pH

Acido forte: HCl 0,1 M pH = ?

$HCl + H_2O \rightarrow Cl^- + H_3O^+$

0,1 M $\rightarrow$ 0,1 M 0,1 M

$[H_3O^+] = 0{,}1\ M = 10^{-1}\ M$ $pH = -\log [H_3O^+] = 1$

Base forte: NaOH 0,01 M pH = ?

$NaOH \rightarrow Na^+ + OH^-$

0,1 M $\rightarrow$ 0,1 M 0,1 M

$[OH^-] = 0{,}1\ M = 10^{-1}\ M$ $pOH = -\log [OH^-] = 1$

$$[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13} M$$

$pH = -\log [H_3O^+] = 14 - pOH = 13$

ACIDO DEBOLE

0,1 M HCN $K_a = 6{,}17 \times 10^{-10}$

$$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$$

c		10^{-7}	/
c-x		x	x

$$K_{HCN} = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{x^2}{c-x} \sim \frac{x^2}{c}$$

$K_a < 10^{-3}$ $\quad$ $c > 10^{-3}$

$$[H_3O^+] = x = \sqrt{K_a \times c} = \sqrt{0{,}1 \times 6{,}17 \times 10^{-10}} = 7{,}8 \times 10^{-6}$$

$$pH = -\log [H_3O^+] = -\log(7{,}8 \times 10^{-6}) = 5{,}11$$

$$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$$

c(1-α)		αc	αc

$$K_{HCN} = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{(\alpha c)^2}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha} \sim \alpha^2 c$$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{6{,}17 \times 10^{-10}}{0{,}1}} = 7{,}8 \times 10^{-5}$$

$$\alpha = \frac{[H_3O^+]}{c} = \frac{7{,}8 \times 10^{-6}}{0{,}1} = 7{,}8 \times 10^{-5}$$

BASE DEBOLE

0,1 M NH_3 K_B= 1,8 x 10^{-5}

$$\underset{c-x}{NH_3} + H_2O \leftrightarrows \underset{x}{NH_4^+} + \underset{x}{OH^-} \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{c-x} \sim \frac{x^2}{c}$$

$$[OH^-] = x = \sqrt{K_b} \times c = \sqrt{1{,}8 \times 10^{-5} \times 0{,}1} = 1{,}34 \times 10^{-3}$$

pOH = -log $[OH^-]$ = -log (1,34 x 10^{-3})= 2,87

pH = 14- pOH = 11,13

$$[H_3O^+] = \frac{K_W}{[OH^-]} = \frac{10^{-14}}{1{,}34 \times 10^{-3}} = 7{,}5 \times 10^{-12}\ M$$

pH = - log $[H_3O^+]$ = - log (7,5 x10^{-12}) = 11,13

ACIDI POLIPROTICI

$$H_2S + H_2O \leftrightarrows HS^- + H_3O^+ \qquad K_{a1} = \frac{[HS^-][H_3O^+]}{[H_2S]}$$

$$HS^- + H_2O \leftrightarrows S^{2-} + H_3O^+ \qquad K_{a2} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$$

$$K_{a1} > K_{a2}$$

$$H_3PO_4 + H_2O \leftrightarrows H_2PO_4^- + H_3O^+ \qquad K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$$

$$H_2PO_4^- + H_2O \leftrightarrows HPO_4^{2-} + H_3O^+ \qquad K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$

$$HPO_4^{2-} + H_2O \leftrightarrows PO_4^{3-} + H_3O^+ \qquad K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]}$$

$$K_{a1} > K_{a2} > K_{a3}$$

✸ $HNO_2 + H_2O \leftrightarrows NO_2^- + H_3O^+$

acido1 base2 base1 acido2

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

✵ $NO_2^- + H_2O \leftrightarrows HNO_2 + OH^-$

base1 acido2 acido1 base2

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

Lo ione NO_2^- è la base coniugata dell'acido HNO_2

$$K_a \times K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} \times \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = [H_3O^+][OH^-] = K_W$$

$$K_b = \frac{K_W}{K_a} \qquad K_a = \frac{K_W}{K_b}$$

IDROLISI SALINA

$NaNO_2 \rightarrow$ deriva da → $NaOH$ = base forte

$NaNO_2 \rightarrow$ deriva da → HNO_2 = acido debole

$NaNO_2 \rightarrow Na^+ + NO_2^-$

$NO_2^- + H_2O \leftrightarrows HNO_2 + OH^-$

~~$Na^+ + H_2O \leftrightarrows NaOH + H^+$~~

pH basico

$$K_i = K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = \frac{K_W}{K_a}$$

ACIDO FORTE + BASE DEBOLE

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

pH acido

$$K_i = K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_W}{K_b}$$

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

SOLUZIONE TAMPONE

ACIDO DEBOLE (HA) + un suo SALE con BASE FORTE (NaA)
Es. HF + NaF, HNO_2 + $NaNO_2$

$HA + H_2O \leftrightarrows A^- + H_3O^+$ dissociazione acido: parziale

$NaA \rightarrow Na^+ + A^-$ dissociazione sale: totale

$A^- + H_2O \leftrightarrows HA + OH^-$ idrolisi sale: parziale

c_A= conc. dell'acido c_S= conc. del sale

$$\begin{array}{ccc} HA + H_2O & \leftrightarrows & A^- + H_3O^+ \\ c_A & & c_S \end{array}$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \Rightarrow [H_3O^+] = K_a \text{ x } \frac{[HA]}{[A^-]} = K_a \text{ x } \frac{c_A}{c_S}$$

$$pH = -\log[H_3O^+] = -\log\left(K_a \frac{c_A}{c_S}\right) = -\log K_a - \log\frac{c_A}{c_S} = pK_a + \log\frac{c_S}{c_A}$$

$$pH = pK_a + \log\frac{c_S}{c_A} \qquad \Rightarrow \qquad c_S = c_A \qquad pH = pK_a$$

Aggiungiamo c_H moli di un acido forte HA_f ($c_H << c_S, c_A$)

$$HA_f + H_2O \rightarrow A_f^- + H_3O^+$$
$$c_H$$

$$HA + H_2O \leftrightarrows A^- + H_3O^+$$

c_A	c_S	c_H
$c_A + c_H$	$c_S - c_H$	?

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} = \frac{(c_S - c_H)[H_3O^+]}{(c_A + c_H)} \qquad [H_3O^+] = K_a\frac{(c_A + c_H)}{(c_S - c_H)}$$

$$pH = pK_a + \log\frac{c_S - c_H}{c_A + c_H} \cong pK_a + \log\frac{c_S}{c_A} \qquad c_A, c_S << c_H$$

BASE DEBOLE B (c_B)
+ suo SALE con ACIDO FORTE BHCl (c_S)

$$BHCl \rightarrow BH^+ + Cl^-$$

$$B + H_2O \leftrightarrows BH^+ + OH^-$$
$$c_B \qquad\qquad c_S$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad \Rightarrow \quad [OH^-] = K_b \frac{[B]}{[BH^+]} = K_b \frac{c_B}{c_S}$$

$$pOH = -\log[OH^-] = pK_b + \log\frac{c_S}{c_B}$$

pH=14-pOH

FATTORI CHE INFLUENZANO LA FORZA DEGLI ACIDI E DELLE BASI

IDRURI :LUNGO IL PERIODO

$LiH < BeH_2 < CH_4 < NH_3 < H_2O < HF$

CARATTERE ACIDO $\rightarrow$

LUNGO IL GRUPPO

$H_2O < H_2S < H_2Se < H_2Te$ $\quad HF < HCl < HBr < HI$

BASI : $NH_3 > H_2O > HF$

OSSIACIDI:

$HClO > HBrO > HIO$ $\quad$ Cl-O-H > Br-O-H > I-O-H

$HClO_4 > HClO_3 > HClO_2 > HClO$ $\quad H_2SO_4 > H_2SO_3$

$CF_3COOH > CH_3COOH$

SOSTANZE ANFOTERE - ANFOLITI

$Al(OH)_3 + 3\ H_3O^+ \leftrightarrows Al^{3+} + 6\ H_2O$
$Al(OH)_3 + OH^- \leftrightarrows Al(OH)_4^- \leftrightarrows AlO_2^- + 2\ H_2O$

$H_2O + NH_3 \leftrightarrows NH_4^+ + OH^-$
$H_2O + HCl \rightarrow \quad Cl^- \quad + \quad H_3O^+$

$H_2PO_4^- + H_3O^+ \rightarrow H_3PO_4 + H_2O$
$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

$NH_2\text{-}R\text{-}COOH$ AMINOACIDI

$NH_2\text{-}R\text{-}COOH + OH^- \rightarrow \ NH_2\text{-}R\text{-}COO^- + H_2O$

$NH_2\text{-}R\text{-}COOH + H_3O^+ \rightarrow NH_3^+\text{-}R\text{-}COOH + H_2O$

EQUILIBRI DI SOLUBILITA'

$C_6H_{12}O_{6(S)} \xrightarrow{H_2O} C_6H_{12}O_{6(aq)}$

$NaCl_{(S)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$

s = solubilità = M_{MAX}

$s_{C_6H_{12}O_6} = [C_6H_{12}O_6]_{MAX}$

$s_{NaCl} = [Na^+]_{MAX} = [Cl^-]_{MAX}$

$AgCl_{(S)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ $\quad K_S = [Ag^+][Cl^-]$

$Ag_2S \leftrightarrows 2Ag^+ + S^{2-}$ $\quad K_S = [Ag^+]^2[S^{2-}]$

$Mg(OH)_2 \leftrightarrows Mg^{2+} + 2OH^-$ $\quad K_S = [Mg^{2+}][OH^-]^2$

$Ca_3(PO_4)_2 \leftrightarrows 3Ca^{2+} + 2PO_4^{3-}$ $\quad K_S = [Ca^{2+}]^3[PO_4^{3-}]^2$

$s = f(T)$ $\qquad K_S = f(T)$

$AgCl_{(S)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ $\quad K_S = [Ag^+][Cl^-] = 2{,}8 \times 10^{-10}$

$\quad\quad s \quad\quad s \quad\quad s = [Ag^+] = [Cl^-]$

$K_S = [Ag^+][Cl^-] = s^2$ $\quad s = \sqrt{K_s} = \sqrt{2{,}8 \times 10^{-10}} = 1{,}7 \times 10^{-5}\,M$

$Ag_2S \leftrightarrows 2Ag^+ + S^{2-}$ $\quad K_S = [Ag^+]^2[S^{2-}] = (2s)^2(s) = 4s^3$

$\quad\quad 2s \quad\quad s$

$$s = \sqrt[3]{\frac{K_s}{4}}$$

$Al(OH)_3 \leftrightarrows Al^{3+} + 3OH^-$ $\quad K_S = [Al^{3+}]\,[OH^-]^3 = s(3s)^3 = 27s^4$

$\quad\quad s \quad\quad 3s$

$$s = \sqrt[4]{\frac{K_s}{27}}$$

EFFETTO DELLO IONE A COMUNE

Soluzione satura AgCl da solo

$AgCl_{(S)} \leftrightarrows \underset{s}{Ag^+_{(aq)}} + \underset{s}{Cl^-_{(aq)}}$

$K_S = [Ag^+][Cl^-] = s^2$

$s = \sqrt{K_s} = 1{,}7 \times 10^{-5}$ M

Soluzione satura AgCl + 0,1 M NaCl

$NaCl \rightarrow Na^+ + Cl^-$

$\underset{c_{NaCl}}{} \quad \underset{c_{NaCl}}{}$

$AgCl_{(S)} \leftrightarrows \underset{s}{Ag^+_{(aq)}} + \underset{s + c_{NaCl}}{Cl^-_{(aq)}}$

$K_S = [Ag^+][Cl^-] = s(s+c_{NaCl})$

$c_{NaCl} >> s \qquad s + c_{NaCl} \approx c_{NaCl}$

$K_S = s \cdot c_{NaCl} \qquad c_{NaCl} = 0{,}1$ M

$s = K_S / c_{NaCl} = 2{,}8 \times 10^{-10} / 0{,}1 = 2{,}8 \times 10^{-9}$ M

EFFETTO DEL PH SULLA SOLUBILITA’

IDROSSIDI $Mg(OH)_2 \leftrightarrows Mg^{2+} + 2OH^-$

$K_S = [Mg^{2+}][OH^-]^2$ $\qquad s = [Mg^{2+}] = \dfrac{K_S}{[OH^-]^2}$

$Ag_2S \leftrightarrows 2Ag^+ + S^{2-}$ $\qquad K_S = [Ag^+]^2[S^{2-}]$

in ambiente acido $\qquad S^{2-} + H^+ \rightarrow HS^-$

$HS^- + H^+ \rightarrow H_2S$

$CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}$ $\qquad K_S = [Ca^{2+}][CO_3^{2-}]$

$CO_3^{2-} + 2\,H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$

$NaCl \rightarrow Na^+ + Cl^-$

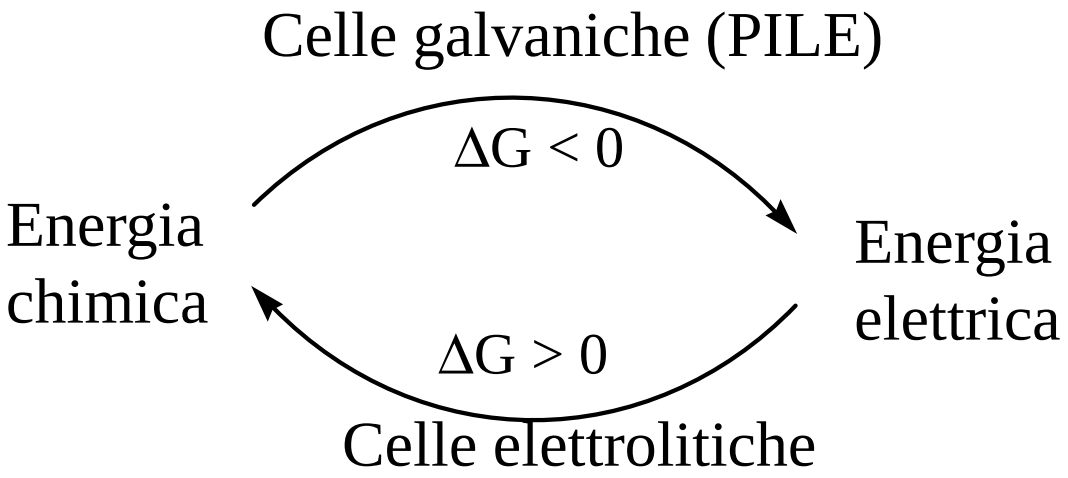
$AgNO_3 \rightarrow Ag^+ + NO_3^-$

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$ $\qquad K_S = [Ag^+]_{sat}[Cl^-]_{sat}$

$[Ag^+]\,[Cl^-] > K_S$ si ha precipitazione

$[Ag^+]\,[Cl^-] < K_S$ non si ha precipitazione

ELETTROCHIMICA



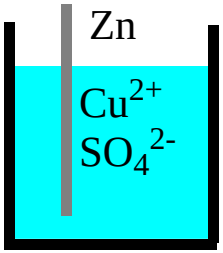
PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA ($\Delta G < 0$) per produrre ENERGIA ELETTRICA

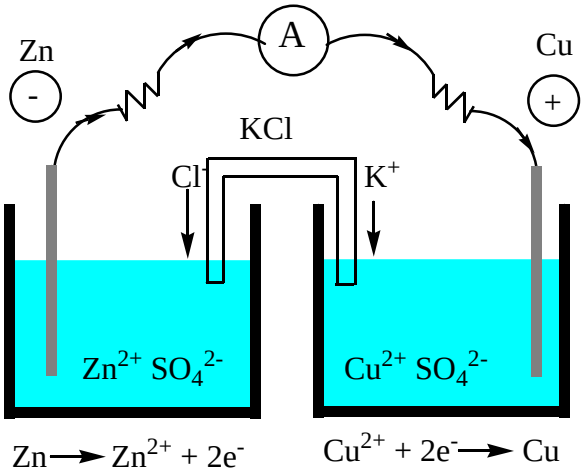
Energia chimica → Energia elettrica

$Cu^{2+} + Zn^0 \rightarrow Cu^0 + Zn^{2+}$

$Cu^{2+} + 2\ e^- \rightarrow Cu^0$

$Zn^0 \rightarrow Zn^{2+} + 2\ e^-$





$E_{PILA} = E_+ - E_- > 0$

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$

$E_{PILA} = E_+ - E_-$

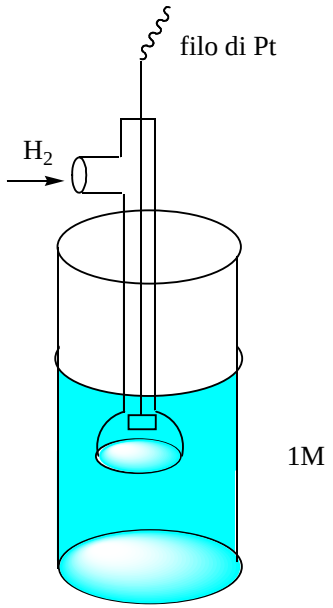
E_+ , E_- dipendono :

- dalla concentrazione delle specie ossidate e ridotte
- dalla loro natura chimica

POTENZIALE STANDARD di un semielemento

→Tutte le specie hanno attività unitaria

Si può misurare la f.e.m. di una pila
non il potenziale dei singoli semielementi



Elettrodo standard a idrogeno

$2H^+ + 2\ e^- \rightarrow H_{2\ (g)}$

(Pt) H_2(g) (1atm) | H^+ (1M)

$[H^+]$= 1 M P_{H_2} = 1 atm

E_{H^+/H_2}= 0

specie ossidata	*specie ridotta*	E^0 *(V)*
$F_{2\ (g)} + 2e \leftrightarrows 2F^-_{(aq)}$		+2.87
$H_2O_{2\ (aq)} + 2H^+_{(aq)} + 2e \leftrightarrows 2H_2O_{(l)}$		+1.77
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e \leftrightarrows Mn^{2+}_{(aq)} + 4H_2O_{(l)}$		+1.51
$Au^{3+}_{(aq)} + 3e \leftrightarrows Au_{(s)}$		+1.50
$Cl_{2\ (g)} + 2e \leftrightarrows 2Cl^-_{(aq)}$		+1.36
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e \leftrightarrows 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$		+1.33
$O_{2\ (g)} + 4H^+_{(aq)} + 4e \leftrightarrows 2H_2O_{(l)}$		+1.23
$ClO_4^-{}_{(aq)} + 2H^+_{(aq)} + 2e \leftrightarrows ClO_3^-{}_{(aq)} + H_2O_{(l)}$		+1.23
$Pt^{2+}_{(aq)} + 2e \leftrightarrows Pt_{(s)}$		+1.20
$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e \leftrightarrows NO_{(g)} + H_2O_{(l)}$		+0.96
$Ag^+_{(aq)} + e \leftrightarrows Ag_{(s)}$		+0.80
$Cu^{2+}_{(aq)} + 2e \leftrightarrows Cu_{(s)}$		+0.34
$2H^+_{(aq)} + 2e \leftrightarrows H_{2(g)}$		**+0.00**
$Fe^{2+}_{(aq)} + 2e \leftrightarrows Fe_{(s)}$		-0.44
$Cr^{3+}_{(aq)} + 3e \leftrightarrows Cr_{(s)}$		-0.74
$Zn^{2+}_{(aq)} + 2e \leftrightarrows Zn_{(s)}$		-0.76
$Al^{3+}_{(aq)} + 3e \leftrightarrows Al_{(s)}$		-1.66
$Mg^{2+}_{(aq)} + 2e \leftrightarrows Mg_{(s)}$		-2.36
$Na^+_{(aq)} + e \leftrightarrows Na_{(s)}$		-2.71
$K^+_{(aq)} + e \leftrightarrows K_{(s)}$		2.93
$Li^+_{(aq)} + e \leftrightarrows Li_{(s)}$		-3.05

$E_{PILA} = E_+ - E_-$ E_+ , E_- dipendono :

- dalla natura chimica delle specie ossidate e ridotte $\rightarrow$ E°
- dalla loro concentrazione

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n} \log \frac{a_{ox}}{a_{red}}$$ Equazione di Nernst

R = 0,0821 atm·l·K^{-1}= 8,31 J ·K^{-1} T = 298 K

F= 96500 C 2,3 conversione da ln a log

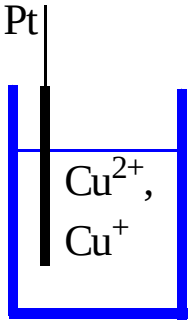
a = attività ↗ per le specie in soluzione: concentrazione (M)
→ per i gas: pressione P
↘ per i solidi puri: 1

$2H^+ + 2e^- \rightarrow H_2$ $\quad$ $Pt, H_2 | H^+$

$$E_{H^+/H_2} = E^0_{H^+/H2} + \frac{0{,}0592}{2}\log\frac{a^2_{H^+}}{a_{H_2}} = \frac{0{,}0592}{2}\log\frac{[H^+]^2}{P_{H_2}}$$

$Cu^{2+} + e^- \rightarrow Cu^+$ $\quad$ $Pt \mid Cu^{2+}, Cu^+$

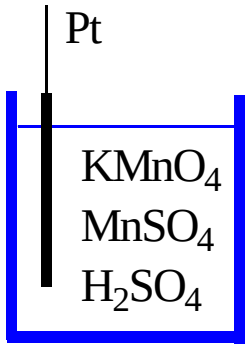
$$E_{Cu^{2+}/Cu^+} = E^0_{Cu^{2+}/Cu^+} + 0{,}0592\log\frac{[Cu^{2+}]}{[Cu^+]}$$



$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

$Pt \mid KMnO_4, MnSO_4, H_2SO_4$

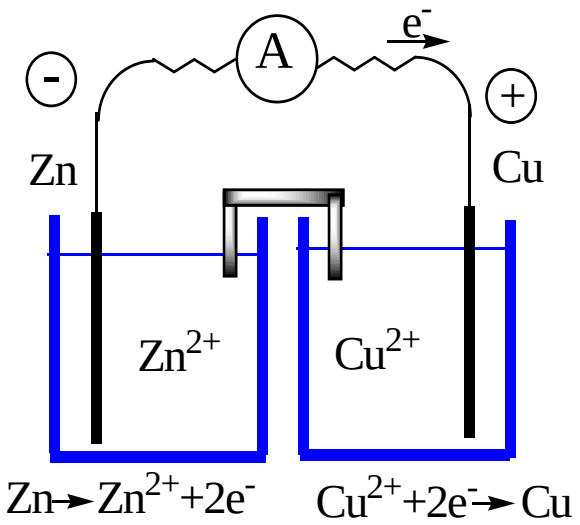
$$E_{MnO_4^-/Mn^{2+}} = E^0_{MnO_4^-/Mn^{2+}} + \frac{0{,}0592}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$



$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} = E^0 + \frac{0{,}0592}{n}\log\frac{a_{ox}}{a_{red}}$$

$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$

$E_{PILA} = E_+ - E_-$



+ $Cu^{2+} + 2\,e^- \rightarrow Cu^0$ $\quad E_+ = E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0{,}0592}{2}\log[Cu^{2+}]$

- $Zn^0 \rightarrow Zn^{2+} + 2\,e^-$ $\quad E_- = E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} + \frac{0{,}0592}{2}\log[Zn^{2+}]$

PILA → dispositivo che utilizza una REAZIONE REDOX SPONTANEA ($\Delta G < 0$) per produrre ENERGIA ELETTRICA
Energia chimica → Energia elettrica

$G = H - TS \Rightarrow dG = dH - TdS - SdT$

$H = E + PV \Rightarrow dG = dE + PdV + VdP - TdS - SdT$

T= costante $SdT = 0$ P= costante $VdP = 0$

$dG = dE + PdV - TdS$

$dE = \delta Q - \delta W$ $\delta Q = TdS$ (reversibile)

$dG = \delta Q - \delta W + TdS - PdV = -\delta W + PdV$

$\delta W = PdV + \delta W_{elettr} \Rightarrow dG = -\delta W_{elettr}$ $\Delta G = -W_{elettr} = -nFE_{pila}$

$\Delta G° = -nFE°_{PILA} = -nF(E°_{+} - E°_{+})$ $-\frac{\Delta G^0}{nF} = E^0_{PILA} = E^0_{+} - E^0_{-}$

$\Delta G° = -RT\ln K = nFE°$ $E^0_{PILA} = -\frac{\Delta G^0}{nF} = -\frac{RT}{nF}\ln K$

$\Delta G = nFE_{pila}$ $E_{PILA} = E_+ - E_-$ $E_1 = E_+$ $E_2 = E_-$ $E_1 > E_2$

$Ox_1 + n_1e^- \leftrightarrows Red_1$ x n_2

$Red_2 \leftrightarrows Ox_2 + n_2e^-$ x n_1 $n = n_1n_2$

$n_2\,Ox_1 + n_1Red_2 \leftrightarrows n_2\,Red_1 + n_1Ox_2$

$G = G° + RT \ln a$ $\Delta G_{REAZ} = \Sigma_{i\,PROD} \nu i\, G_i - \Sigma_{i\,REAG} \nu i G_i$

$$\Delta G_{REAZ} = n_2 (G°_{Red_1} + RT \ln a_{Red_1}) + n_1 (G°_{Ox_2} + RT \ln a_{Ox_2})$$
$$- n_2 (G°_{Ox_1} + RT \ln a_{Ox_1}) - n_1 (G°_{Red_2} + RT \ln a_{Red_2}) =$$

$$n_2 (G°_{Red_1} - G°_{Ox_1} + RT \ln \frac{a_{Red_1}}{a_{Ox_1}}) - n_1 (G°_{Red_2} - G°_{Ox_2} + RT \ln \frac{a_{Red2}}{a_{Ox2}}) =$$

$$n_2 (\Delta G°_1 - RT \ln \frac{a_{Ox_1}}{a_{Red_1}}) - n_1 (\Delta G°_2 - RT \ln \frac{a_{Ox2}}{a_{ox2}}) = \Delta G$$

$\Delta G°_1 = G°_{Red_1} - G°_{Ox_1}$ $\Delta G°_2 = G°_{Red_2} - G°_{Ox_2}$

$$\Delta G = n_2(\Delta G°_1\text{-}RT\ln\frac{a_{Ox1}}{a_{Red1}}) - n_1(\Delta G°2 - RT\ln\frac{a_{Ox2}}{a_{Red2}}) = -nFE_{pila}$$

$$n = n_1 n_2$$

$$E_{PILA} = -\frac{\Delta G}{nF} = -n_2\left(\frac{\Delta G_1^0}{nF} - \frac{RT}{nF}\ln\left[\frac{a_{Ox_1}}{a_{Red1}}\right]\right) + n_1\left(\frac{\Delta G_2^0}{nF} - \frac{RT}{nF}\ln\left[\frac{a_{Ox_2}}{a_{Red2}}\right]\right) =$$

$$= -E_1^0 + \frac{RT}{n_1F}\ln\left[\frac{a_{Ox_1}}{a_{Red_1}}\right] - E_2^0 + -\frac{RT}{n_2F}\ln\left[\frac{a_{Ox_2}}{a_{Red_2}}\right] = E_{PILA}$$

$$E_1 = E_1^0 + \frac{RT}{nF}\ln\left[\frac{a_{Ox_1}}{a_{Red_1}}\right]$$

$$E_2 = E_2^0 + \frac{RT}{nF}\ln\left[\frac{a_{Ox2}^d}{a_{Red2}^b}\right]$$

$$E^0_{PILA} = -\frac{\Delta G^0}{nF} = \frac{RT}{nF}\ln K$$

$$-\frac{\Delta G^0}{nF} = E^0_{PILA} = E^0_{+} - E^0_{-}$$

$Ox_1 + n_1 e^- \leftrightarrows Red_1 \quad \times n_2$

$Red_2 \leftrightarrows Ox_2 + n_2 e^- \quad \times n_1$

$n = n_1 n_2$

$n_2 Ox_1 + n_1 Red_2 \leftrightarrows n_2 Red_1 + n_1 Ox_2$

$E_{PILA} = 0 \quad \rightarrow \quad \Delta G_{REAZ} = 0$

$$E_{PILA} = -\frac{\Delta G_{REAZ}}{nF} = -\frac{\Delta G^0}{nF} - \frac{RT}{nF}\ln\left[\frac{a^{n_2}_{Red_1} a^{n_1}_{Ox_2}}{a^{n_2}_{Ox_1} a^{n_1}_{Red_2}}\right] = 0$$

$$\Delta G^0 = -RT\ln\left[\frac{a^{n_2}_{Red_1} a^{n_1}_{Ox_2}}{a^{n_2}_{Ox_1} a^{n_1}_{Red_2}}\right] \qquad \left[\frac{a^{n_2}_{Red_1} a^{n_1}_{Ox_2}}{a^{n_2}_{Ox_1} a^{n_1}_{Red_2}}\right] = K$$

$\Delta G° = -RT\ln K = nFE°$

$$K = e^{\frac{nFE°}{RT}}$$

PILE A CONCENTRAZIONE

- $Cu \mid [Cu^{2+}]_- \mid\mid [Cu^{2+}]_+ \mid Cu$ +

$Cu^{2+} + 2\ e^- \rightarrow Cu^0$ $\qquad E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0,0592}{2}\log[Cu^{2+}]$

$+\ Cu^{2+} + 2\ e^- \rightarrow Cu^0$ $\qquad E_+ = E^0_{Cu^{2+}/Cu} + \frac{0,0592}{2}\log[Cu^{2+}]_+$

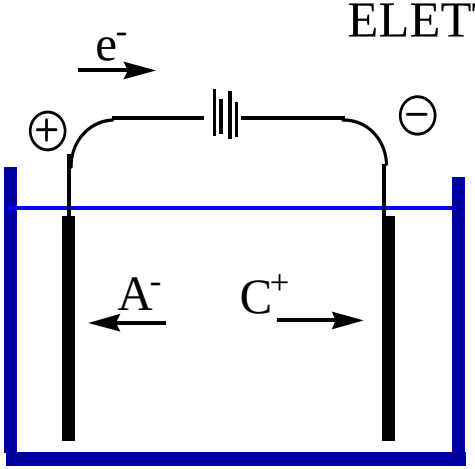
$-\ Cu^0 \rightarrow Cu^{2+} + 2\ e^-$ $\qquad E_- = E^0_{Cu^{2+}/Cu} + \frac{0,0592}{2}\log[Cu^{2+}]_-$

$$E_{PILA} = E_+ - E = \frac{0,0592}{2}(\log[Cu^{2+}]_+ - \log[Cu^{2+}]_-) = \frac{0,0592}{2}\log\frac{[Cu^{2+}]_+}{[Cu^{2+}]_-}$$

$[Cu^{2+}]_+ > [Cu^{2+}]_-$ $\qquad E_{PILA} > 0$

Driving force: ΔG_{MIX}

ELETTROLISI



Energia elettrica → Energia chimica

Reazioni non spontanee ($\Delta G>0$)

Elettrolisi di NaCl

Sale fuso

$C^+ = Na^+$ $A^- = Cl^-$

Polo - $Na^+ + e^- \rightarrow Na$

Polo + $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

$NaCl \rightarrow \frac{1}{2}Cl_2 + Na$

Soluzione acquosa

$C^+ = Na^+, H^+$ $A^- = Cl^-, OH^-$

Polo - ~~$Na^+ + e^- \rightarrow Na$~~

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

Polo + $Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$

$2OH^- \rightarrow \frac{1}{2}O_2 + 2e^- + H_2O$

LEGGI DI FARADAY

-La quantità di sostanza che viene ossidata o ridotta ad un elettrodo è proporzionale alla quantità di elettricità passata

$w = w_e \cdot Q = w_e \cdot I \cdot t$ w_e = equivalente elettrochimico

-Uguali quantità di carica Q determinano la deposizione di un uguale numero di equivalenti di specie ossidate o ridotte.

$P_{EQ} = PM/z$ $P_{EQ} = PA/z$

1F = 96500 C ⇨ 1 equivalente $F = N_A \cdot e^-$

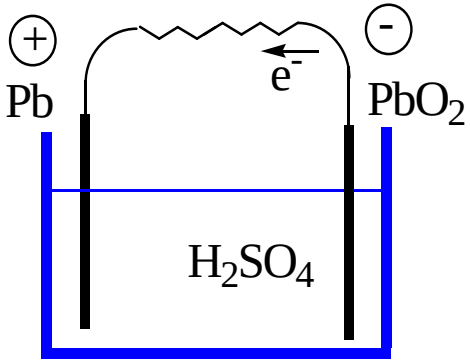
$H^+ + e^- \rightarrow 1/2\ H_2$	1 eq = 1 mole → 1F = N_A e^-
$Fe^{2+} + 2e^- \rightarrow Fe$	1 eq = 1/2 mole → 1F = N_A e^-
$Al^{3+} + 3e^- \rightarrow Al$	1 eq = 1/3 mole → 1F = N_A e^-

ACCUMULATORI

$Pb \mid PbSO_4, H_2SO_4 \mid PbO_2$

$E°_{PbO_2/Pb^{2+}} > E°_{Pb^{2+}/Pb}$

Carica: elettrolisi

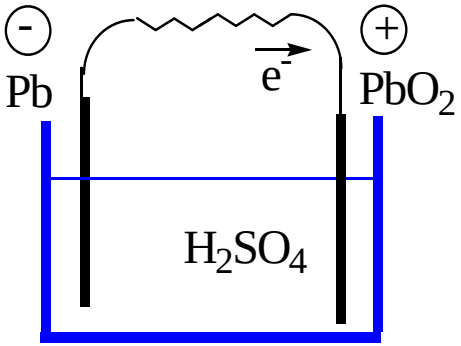


$+ \quad Pb^{2+} + 2e^- \rightarrow Pb$

$- \quad Pb^{2+} + 2H_2O \rightarrow PbO_2 + 2e^- + 4H^+$

$2Pb^{2+} + 2H_2O \rightarrow PbO_2 + Pb + 4H^+$

Scarica: pila



$+ \quad PbO_2 + 2e^- + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

$- \quad Pb \rightarrow Pb^{2+} + 2e^-$

$PbO_2 + Pb + 4H^+ \rightarrow 2Pb^{2+} + 2H_2O$