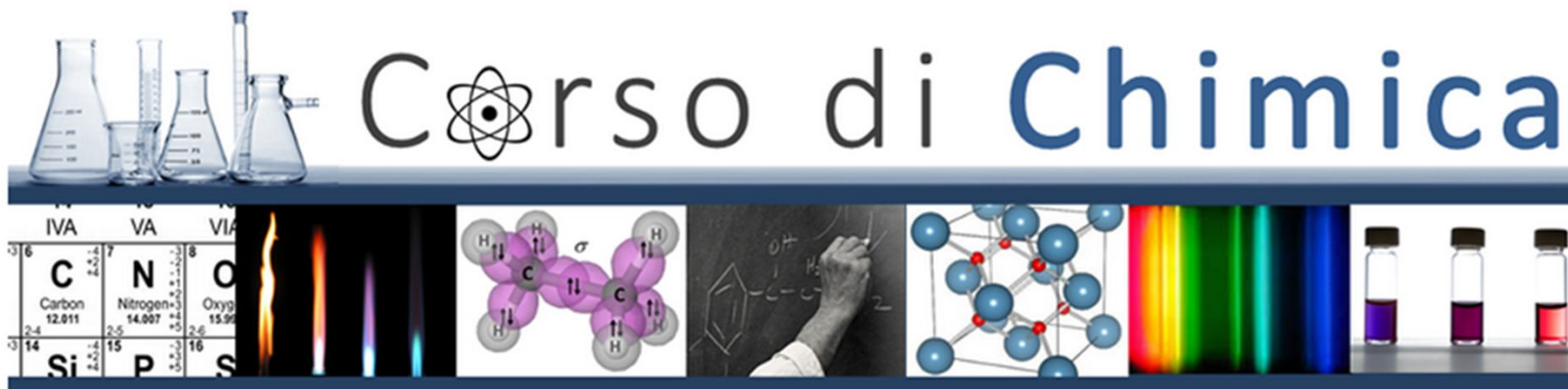




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Dipartimento di Ingegneria ed Architettura



docente

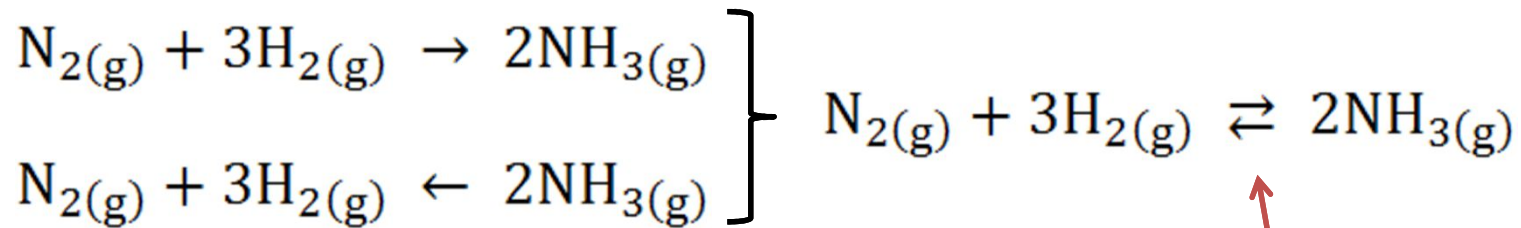
Alois Bonifacio

(abonifacio@units.it)

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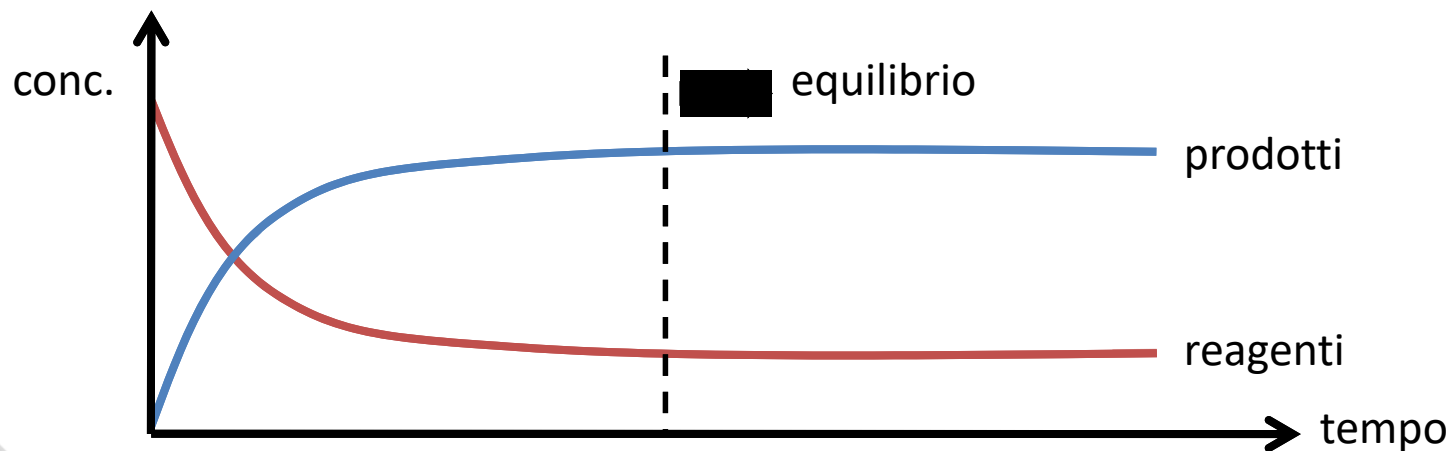
Equilibri chimici

definizione "cinetica" di equilibrio chimico

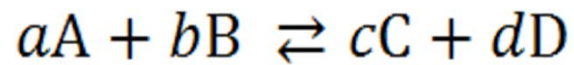


↑
doppia freccia

si ha **equilibrio** quando le velocità delle reazioni diretta ed inversa sono uguali ossia quando le **concentrazioni** di prodotti e reagenti **non cambiano** nel tempo



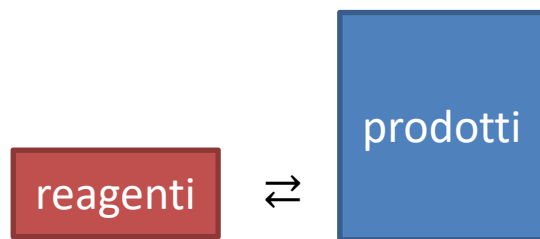
costante di equilibrio: legge azione massa



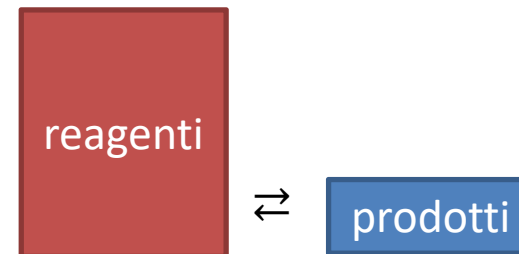
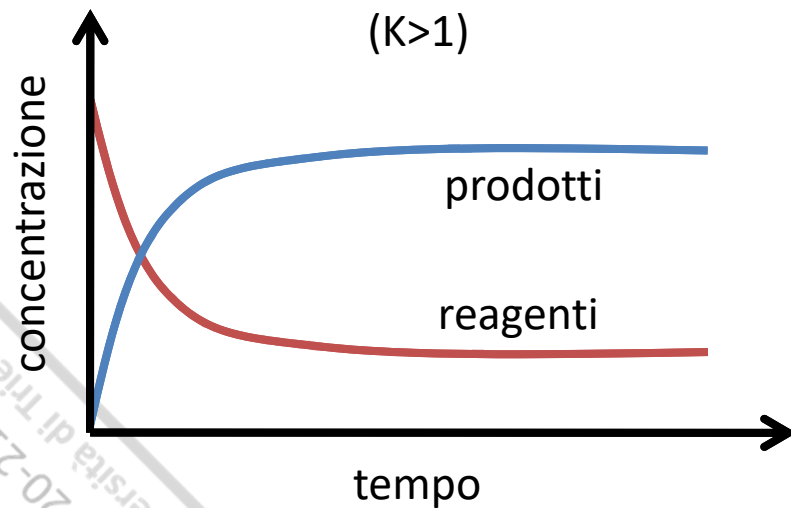
$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Legge dell'azione di massa (o di Guldberg e Waage)

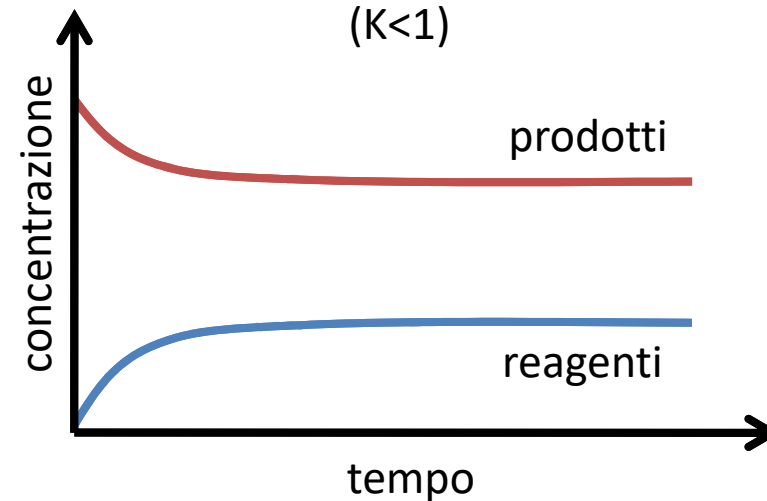
costante di equilibrio (a T cost)



($K > 1$)



($K < 1$)

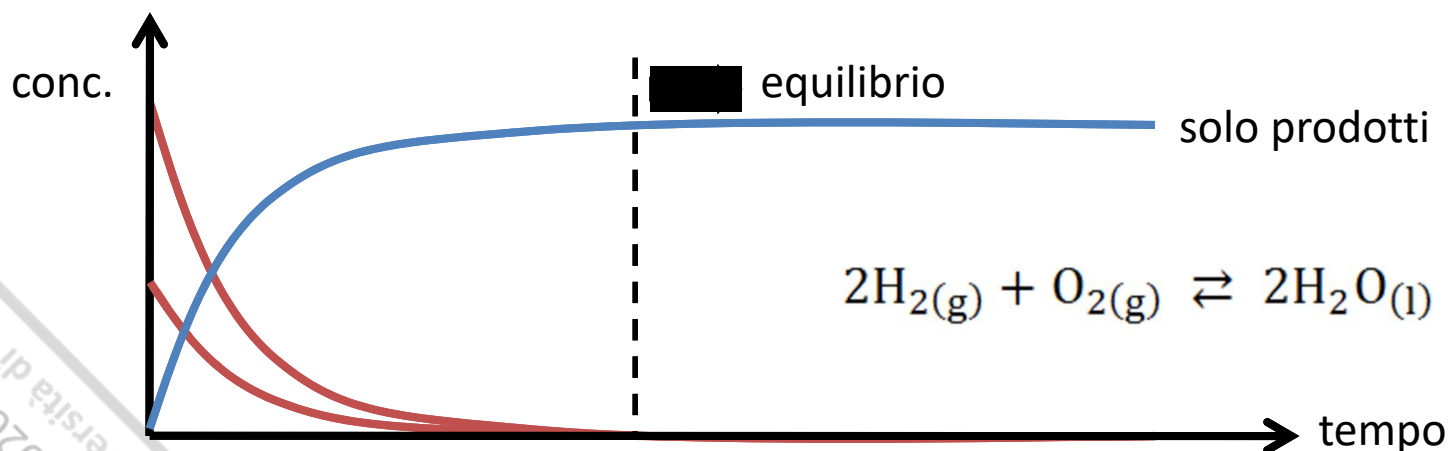


Valori numerici di K_c

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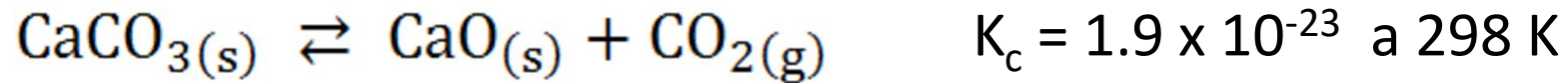
Reazione	Costante di equilibrio, K (a 25 °C)	Reazione spostata verso
<i>Reazione di combinazione di non metalli</i>		
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	4.2×10^{52}	$K > 1$; prodotti
$2 H_2(g) + O_2(g) \rightleftharpoons 2 H_2O(g)$	3.2×10^{81}	$K > 1$; prodotti
$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$	3.5×10^8	$K > 1$; prodotti
$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$	1.7×10^{-3} (a 2300 K)	$K < 1$; reagenti

per valori di K molto grandi, la reazione avviene
“completamente” (praticamente la reazione è “quantitativa”)



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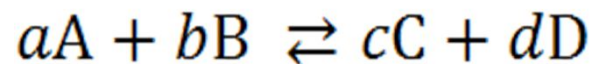
Valori numerici di K_c



Per K molto piccole in pratica non si formano prodotti in quantità apprezzabili

Sono presenti sia prodotti che reagenti all'equilibrio per K con valori **ne troppo grandi ne troppo piccoli**
(compresi tra da 10^{-10} a 10^{+10})

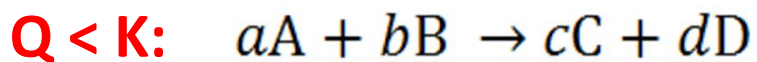
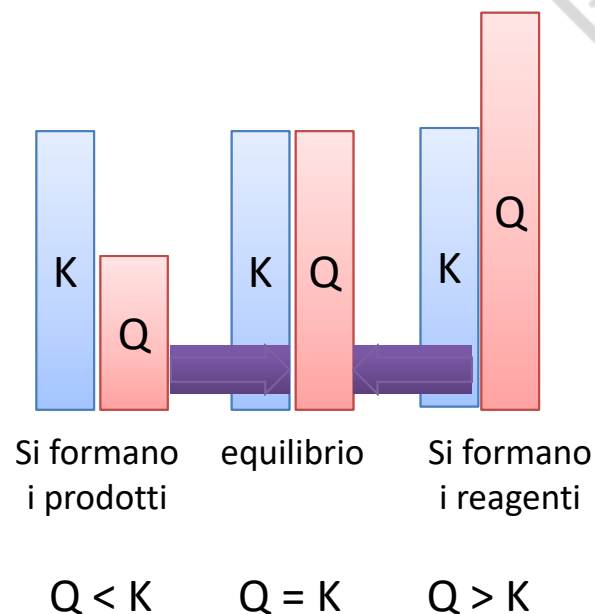
quoziente di reazione e K



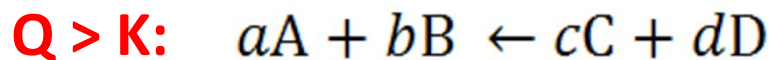
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Quoziente di
reazione

$Q = K$ all'equilibrio



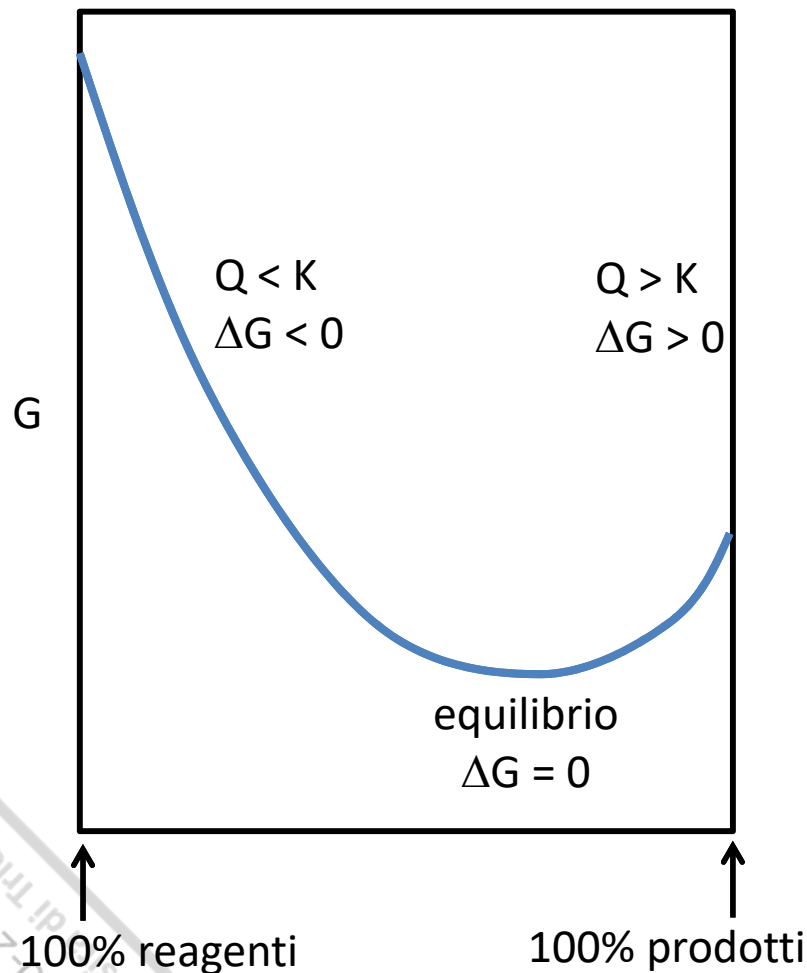
la reazione procede
formando prodotti



la reazione "retrocede"
formando reagenti

definizione “termodinamica” di equilibrio

si può dimostrare per via termodinamica che per una data reazione:



$$\Delta G = \Delta G_r^\circ + RT \ln Q$$

all' equilibrio $\Delta G = 0$ e $Q = K$:

$$\Delta G_r^\circ = -RT \ln K$$

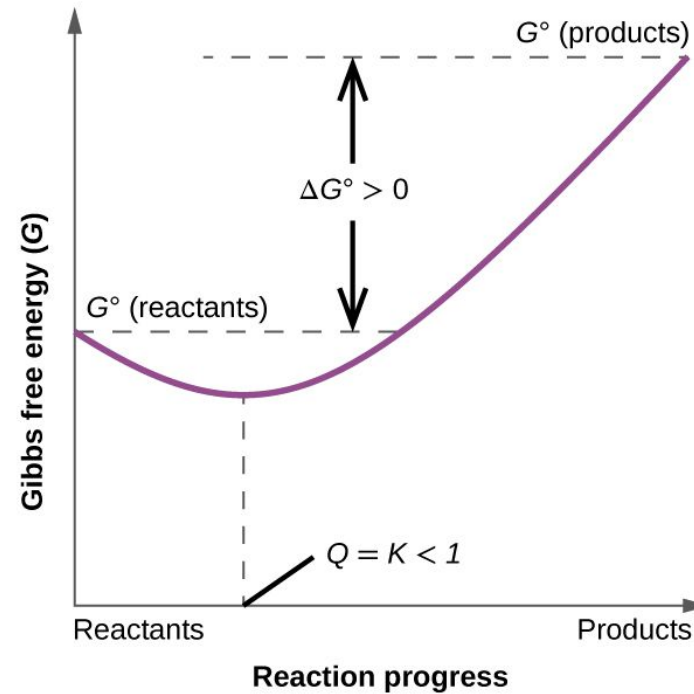
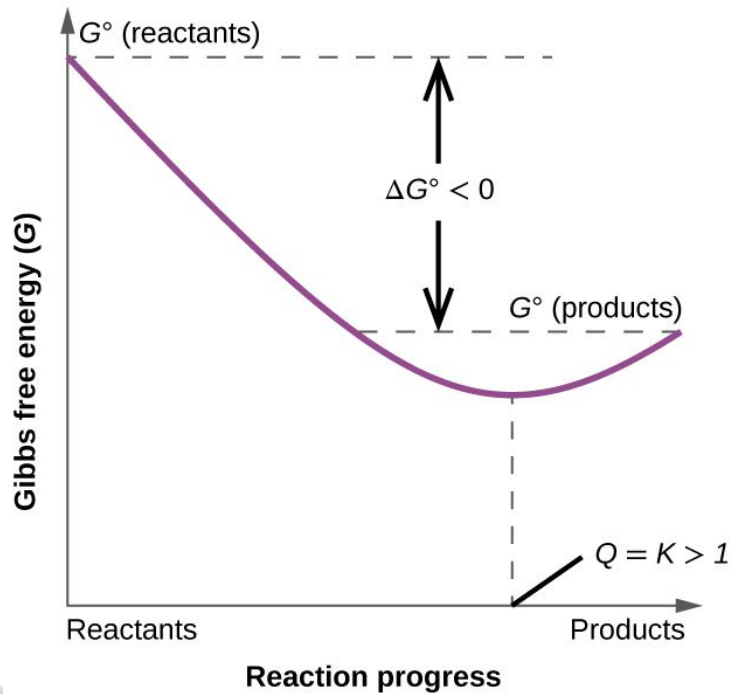
$$K > 1 \rightarrow \Delta G^\circ < 0$$

$$K < 1 \rightarrow \Delta G^\circ > 0$$

$$K = e^{-\frac{\Delta G_r^\circ}{RT}} \quad \begin{array}{l} \Delta G^\circ < 0 \rightarrow K > 1 \\ \Delta G^\circ > 0 \rightarrow K < 1 \end{array}$$

definizione “termodinamica” di equilibrio

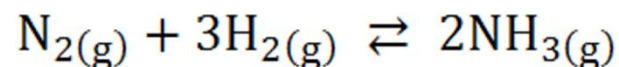
$$\Delta G = \Delta G_r^\circ + RT \ln Q \quad \left\{ \begin{array}{l} \Delta G_r^\circ = -RT \ln K \\ K = e^{-\frac{\Delta G_r^\circ}{RT}} \end{array} \right.$$



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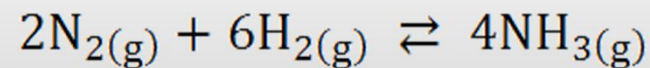
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relazione tra le K di reazioni diverse



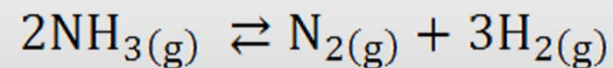
$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

variazione
coefficienti
stechiometrici



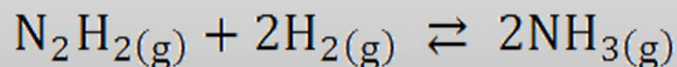
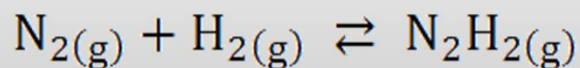
$$K'_C = \frac{[\text{NH}_3]^4}{[\text{N}_2]^2[\text{H}_2]^6} = K_C^2$$

reazioni
inverse



$$K'_C = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K_C}$$

somma di reazioni



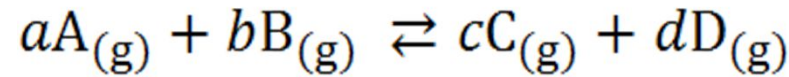
$$K'_C = \frac{[\text{N}_2\text{H}_2]}{[\text{N}_2][\text{H}_2]}$$

$$K''_C = \frac{[\text{NH}_3]^2}{[\text{N}_2\text{H}_2][\text{H}_2]^2}$$

$$K_C = K'_C \cdot K''_C$$

equilibri in fase gassosa: K_C e K_P

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$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \quad p_A^a = \frac{n_A}{V} RT = [A]RT$$

$$K_p = \frac{[C]^c (RT)^c \cdot [D]^d (RT)^d}{[A]^a (RT)^a \cdot [B]^b (RT)^b}$$

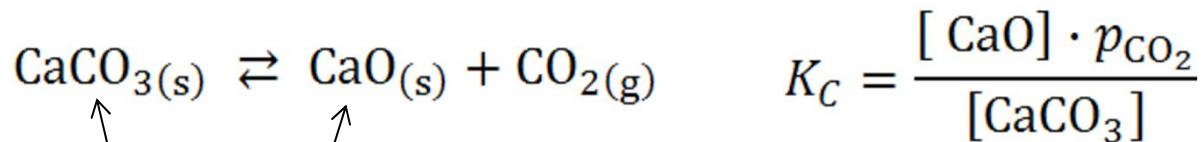
$$K_p = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} (RT)^{[(c+d)-(a+b)]}$$

$$K_p = K_C (RT)^{[(c+d)-(a+b)]} \quad \text{relazione tra } K_C \text{ e } K_P$$

se $(c+d) - (a+b) = 0$, $K_C = K_P$

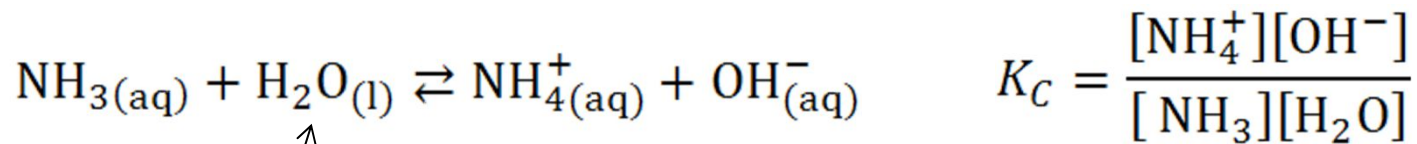
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solidi puri, liquidi puri e K



↑ ↑
solidi puri

$$K'_C = K_C \frac{[\text{CaCO}_3]_{\text{cost}}}{[\text{CaO}]_{\text{cost}}} = p_{\text{CO}_2}$$



↑
liquido puro
(solvente)

$$K'_C = K_C \cdot [\text{H}_2\text{O}]_{\text{cost}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

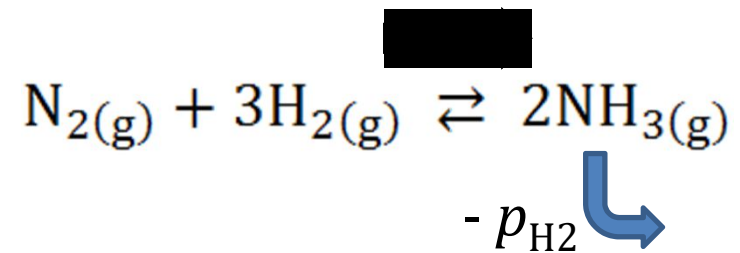
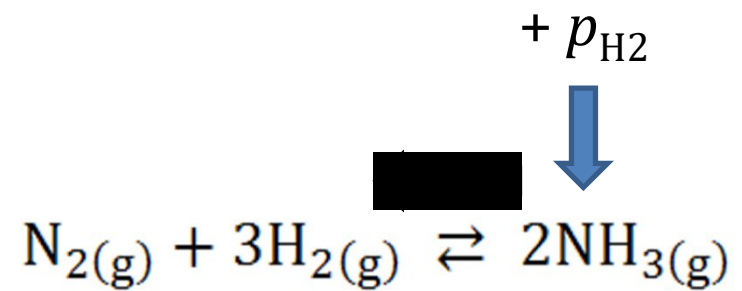
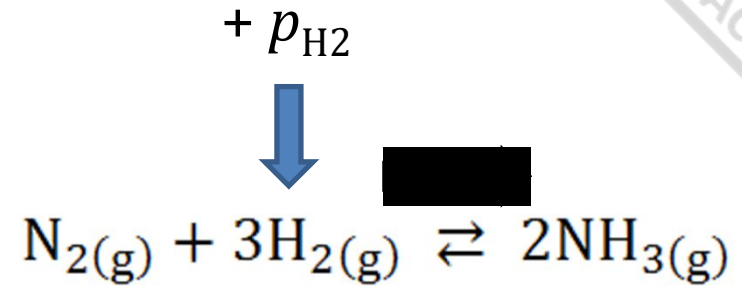
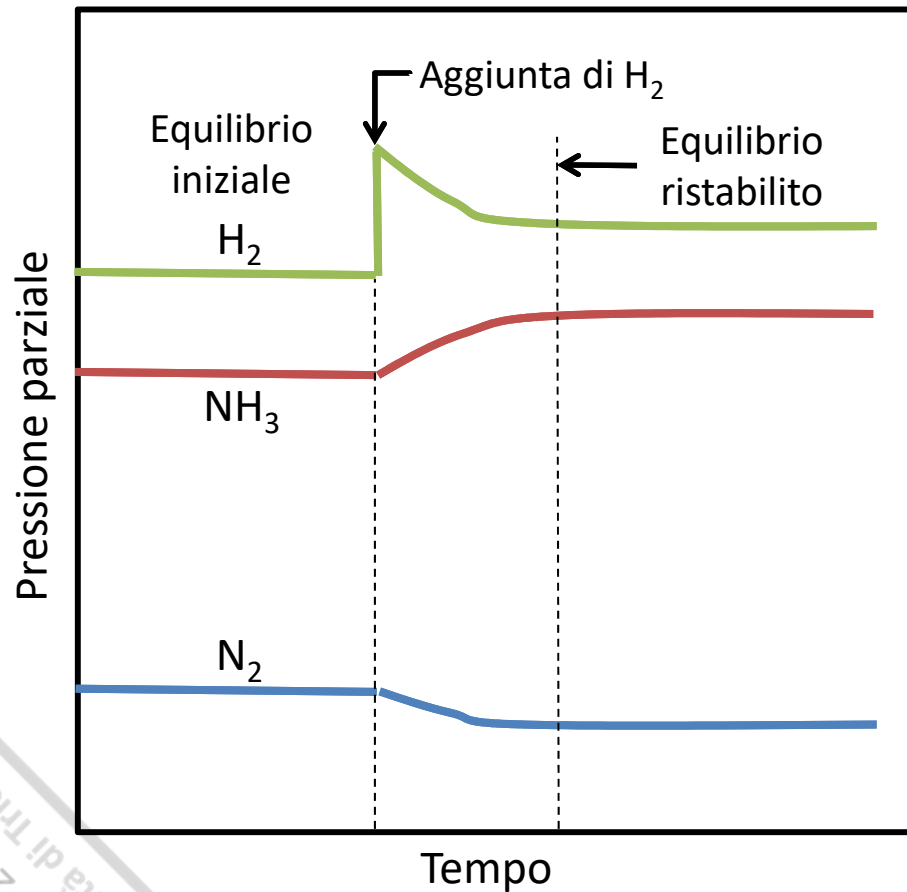
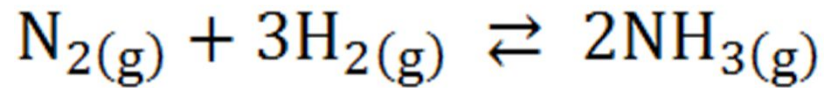
le concentrazioni dei solidi puri e dei liquidi puri e dei solventi (nelle soluzioni diluite) **non compaiono mai** nell'espressione di K

principio di Le Châtelier

quando un sistema all'equilibrio viene perturbato, il sistema reagisce in modo da **minimizzare l'effetto della perturbazione**, raggiungendo un nuovo stato di equilibrio



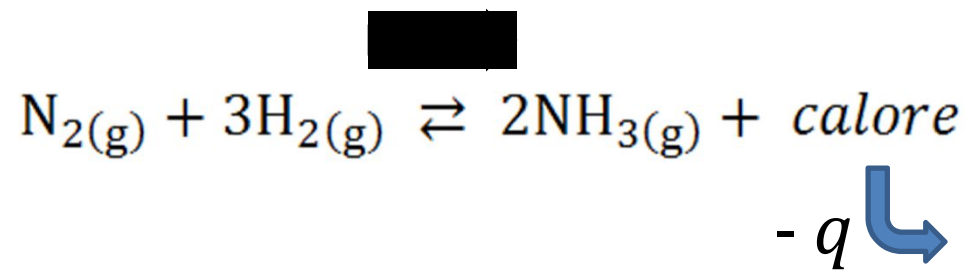
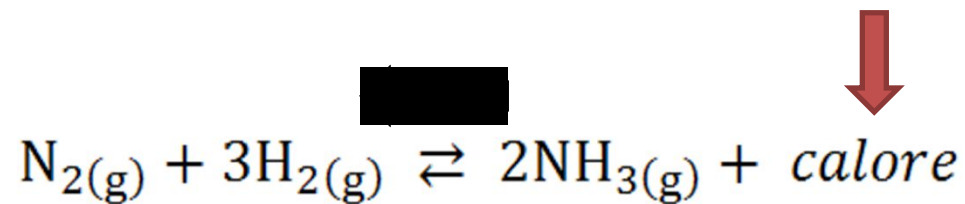
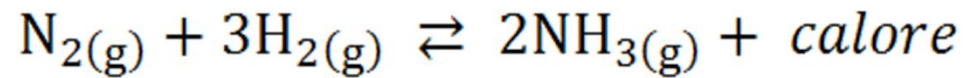
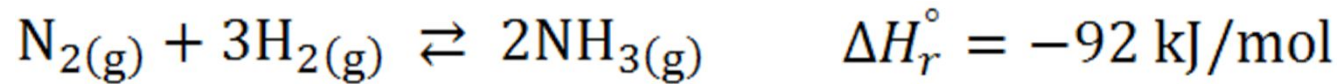
principio di Le Châtelier – variazione conc.



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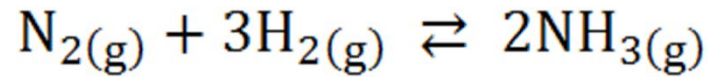
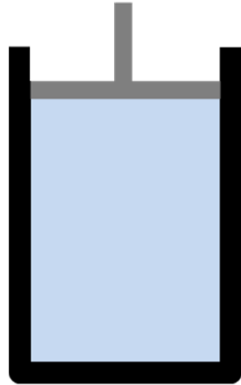
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principio di Le Châtelier – variazione T



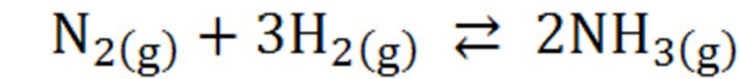
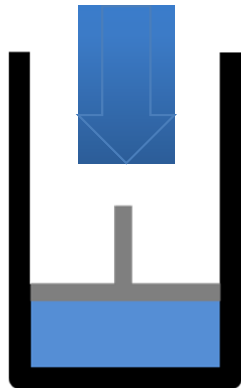
principio di Le Châtelier – variazione P/V

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$$P V = n R T$$

aumento pressione diminuzione volume



totale moli reagenti

4

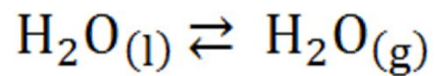
totale moli prodotti

2

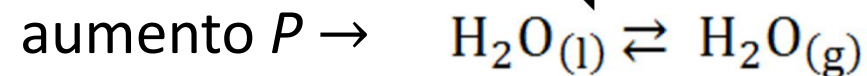
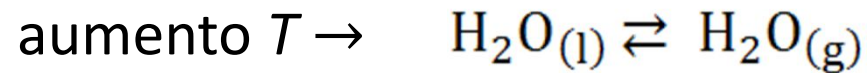
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principio di Le Châtelier – processi fisici

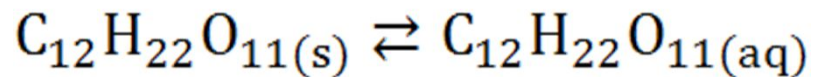
anche ai processi fisici si applica il principio di Le Chatelier



$$K_p = p_{\text{H}_2\text{O}}$$

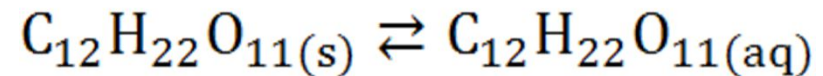


solvatazione saccarosio (processo endotermico $\Delta H > 0$)



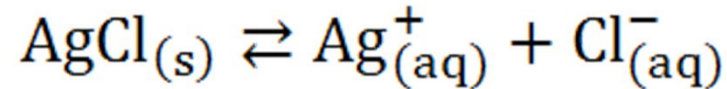
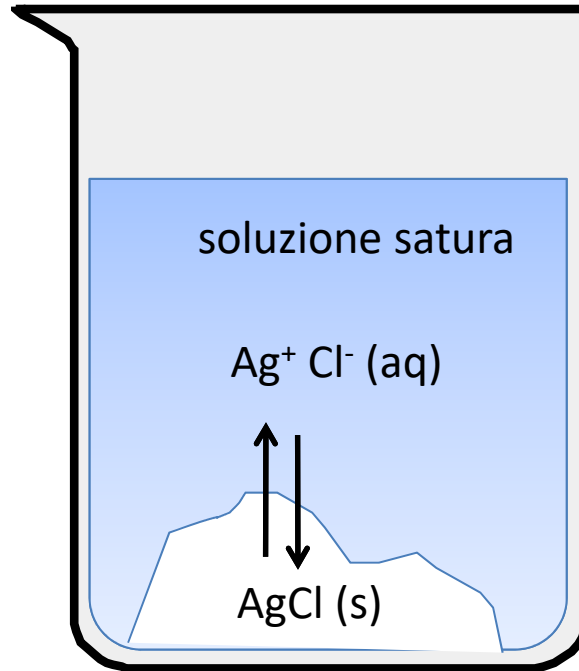
$$K_C = [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

aumento T



equilibrio in sistemi solido-liquido: K_{ps}

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prodotto di
solubilità

$$K_{ps} = [\text{Ag}^+][\text{Cl}^-] \cong 10^{-10}$$

↑ ↑
concentrazioni molari degli ioni
in soluzione, all' equilibrio con il
corpo di fondo

**concentrazioni molari degli ioni
in soluzione satura
= SOLUBILITA'**

**attenzione ai coefficienti !!!
(provare con CaCl_2)**

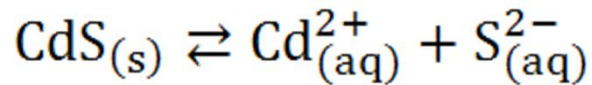
$$\text{solubilità } S = [\text{Ag}^+] = [\text{Cl}^-]$$

$$K_{ps} = [\text{Ag}^+][\text{Cl}^-] = S \cdot S = S^2$$

$$S = \sqrt[2]{S^2} = \sqrt[2]{10^{-10}} = 10^{-5} \text{ M}$$

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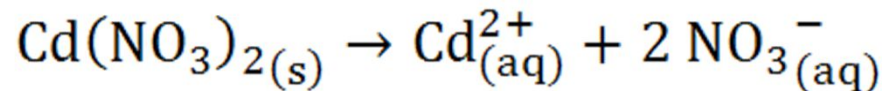
K_{ps} ed effetto dello "ione comune"



solido giallo
insolubile

$$K_{ps} = [\text{Cd}^{2+}][\text{S}^{2-}] = 3.6 \cdot 10^{-29}$$

$$[\text{Cd}^{2+}]^{\text{CdS}} = \sqrt[2]{K_{ps}}$$



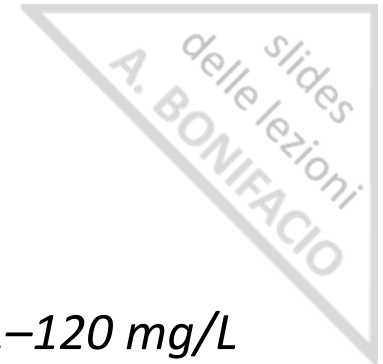
solido bianco
solubile

cosa accade se aggiungo
una soluzione diluita di
 $\text{Cd}(\text{NO}_3)_2$ ad una soluzione
satura di CdS?

$$[\text{Cd}^{2+}]^{\text{tot}} = [\text{Cd}^{2+}]^{\text{CdS}} + [\text{Cd}^{2+}]^{\text{Cd}(\text{NO}_3)_2}$$

$$[\text{Cd}^{2+}]^{\text{tot}} \cdot [\text{S}^{2-}] > K_{ps}$$

Durezza dell'acqua



misura della durezza

- gradi FRANCESI ($1^\circ\text{F} = 10\text{mg/L CaCO}_3$)
- gradi TEDESCHI ($1^\circ\text{dH} = 10\text{mg/L CaO}$)

acque...

mediamente dure 61–120 mg/L

dure 121–180 mg/L

molto dure ≥ 181 mg/L

residuo fisso

“quantità di sostanza solida perfettamente secca, residua dopo l'evaporazione di tutta l'acqua”

acque meteoriche: compreso tra 10 e 80 mg/L

acque oligominerali: compreso tra 80 e 200 mg/L

acque mediominerali: compreso tra 200 e 1.000 mg/L

acque minerali: superiore a 1.000 mg/L

acque salate: superiore a 30.000 mg/L.

