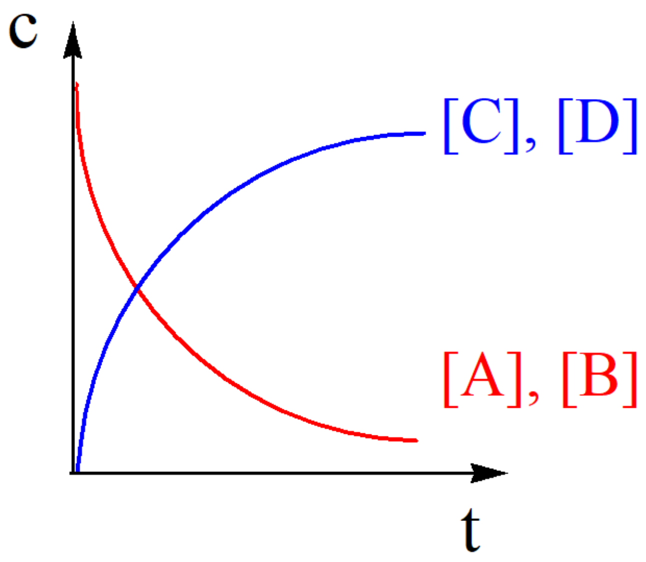
REAZIONI DI EQUILIBRIO

$$A + B \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftarrows}} C + D$$

$$\overrightarrow{v} = \overrightarrow{k}[A][B]$$

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



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

$$\overrightarrow{k}[A]_{eq}[B]_{eq} = \overleftarrow{k}[C]_{eq}[D]_{eq}$$

$$\frac{\overrightarrow{k}}{\overleftarrow{k}} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = K$$

$$A + B \rightleftarrows C + D$$

$$K = \frac{[C][D]}{[A][B]}$$

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

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

Derivazione termodinamica

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

$$\Delta G_{REAZ} = \sum_i \nu_i G_i - \sum_i \nu_i G_i = cG_C + dG_D - aG_A - bG_B$$

PROD REAG

$G_A = G°_A + RT \ln P_A$ $G_B = G°_B + RT \ln P_B$ $G = G° + RT \ln M$

$G_C = G°_C + RT \ln P_C$ $G_D = G°_D + RT \ln P_D$ soluzione

$$\Delta G_{REAZ} = cG°_C + cRT \ln P_C + dG°_D + dRT \ln P_D$$

$$- aG°_A - aRT \ln P_A - bG°_B - bRT \ln P_B$$

$$\Delta G°_{REAZ} = cG°_C + dG°_D - aG°_A - bG°_B$$

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

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

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

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

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

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

LA REAZIONE PROCEDE DA SINISTRA VERSO DESTRA

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

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

$\Delta G° < 0$	$K > 1$
$\Delta G° > 0$	$K < 1$

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

ALL'EQUILIBRIO

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

ALL'EQUILIBRIO

$K \gg 1$ ⇨ FAVORITI i PRODOTTI ⇨ REAZIONE SPOSTATA verso DESTRA

$K \ll 1$ ⇨ FAVORITI i REAGENTI ⇨ REAZIONE SPOSTATA verso SINISTRA

$$\Delta G° = -RT \ln K$$

T = cost K= cost K = f(T)

⬇

$$K=e^{-\frac{\Delta G°}{RT}}$$

$\Delta G° < 0$ ⇨ $K>1$ ⇨ FAVORITI i PRODOTTI

$\Delta G° > 0$ ⇨ $K<1$ ⇨ FAVORITI i REAGENTI

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

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

Soluzioni, gas

$$K_P = \frac{P_C^c\,P_D^d}{P_A^a\,P_B^b}$$

gas

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

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

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

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

$\uparrow$ K_C

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

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

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

$$3\,H_{2\,(g)} + N_{2(g)} \rightleftarrows 2\,NH_{3\,(g)}$$

$$\Delta\nu = 2-4 = -2 \quad K_P = K_C \cdot (RT)^{\Delta\nu} = K_C \cdot (RT)^{-2}$$

$$K_P = \frac{P_{NH_3}^{\,2}}{P_{H_2}^{\,3} \cdot P_{N_2}} \qquad K_C = \frac{c_{NH_3}^{\,2}}{c_{H_2}^{\,3} \cdot c_{N_2}}$$

$$H_{2\,(g)} + I_{2(g)} \rightleftarrows 2HI_{\,(g)}$$

$$\Delta\nu = 2-2 = 0 \quad K_P = K_C$$

$$K_P = \frac{P_{HI}^{\,2}}{P_{H_2} \cdot P_{I_2}}$$

$$SO_2 + ½\,O_2 \rightleftarrows SO_3 \quad \Rightarrow \quad K_P = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{1/2}}$$

$$K'_P = K_P^2$$

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

$$\Delta G°' = 2\,\Delta G°$$

EQUILIBRI IN FASE ETEROGENEA

$$C_{(s)} + O_{2\,(g)} \rightleftarrows CO_{2(g)}$$

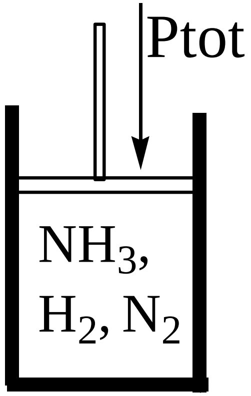
$$K_P = \frac{P_{CO_2}}{P_{O_2}}$$

$$\Delta\nu = 1-1 = 0$$

PRINCIPIO DI LE CHATELIER

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

K_P= cost T= 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}? $P_{H_2} = x_{H_2} \cdot P_{tot}$
$P_{N_2} = x_{N_2} \cdot P_{tot}$
$P_{NH_3} = x_{NH_3} \cdot P_{tot}$

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

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

NON E' UNA VERA COSTANTE TERMODINAMICA

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

ν_i = coefficienti Stechiometrici

$\Delta\nu = \sum_i \nu_i - \sum_i \nu_i$ (PROD, REAG)

$\Delta\nu>0$ sfavorita aumento P
$\Delta\nu<0$ favorita aumento P
$\Delta\nu=0$ indifferente aumento P

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

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

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

REAZIONE FAVORITA DA AUMENTO P

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

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

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

REAZIONE SFAVORITA DA AUMENTO P

$C_{(s)} + O_{2(g)} \leftrightarrows CO_{2\,(g)}$

$$K_P = \frac{P_{CO_2}}{P_{O_2}}$$

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

VARIAZIONI DI P NON HANNO EFFETTO SULL'EQUILIBRIO

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

EFFETTO DELLA TEMPERATURA

$$\Delta G° = - RT \ln K = \Delta H° - T\Delta S°$$

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

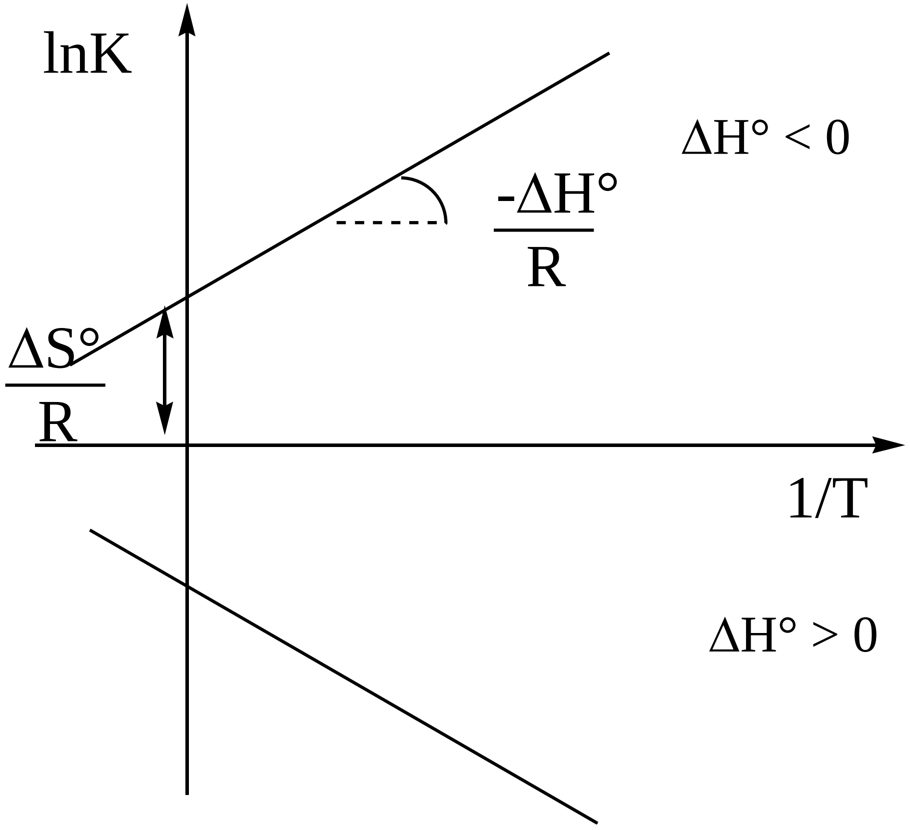
$$\frac{d\ln K}{dT} = \frac{\Delta H°}{RT^2}$$

ENDOTERMICA

$$\Delta H° > 0 \qquad \frac{d\ln K_P}{dT} > 0$$

ESOTERMICA

$$\Delta H° < 0 \qquad \frac{d\ln K_P}{dT} < 0$$



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

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

$$T_2 > T_1$$

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\Delta H°}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

ENDOTERMICA	$\Delta H° > 0$	$T_2 > T_1$	$\ln\frac{K_2}{K_1} > 0$	$K_2 > K_1$
ESOTERMICA	$\Delta H° < 0$	$T_2 > T_1$	$\ln\frac{K_2}{K_1} < 0$	$K_2 < K_1$

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

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

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

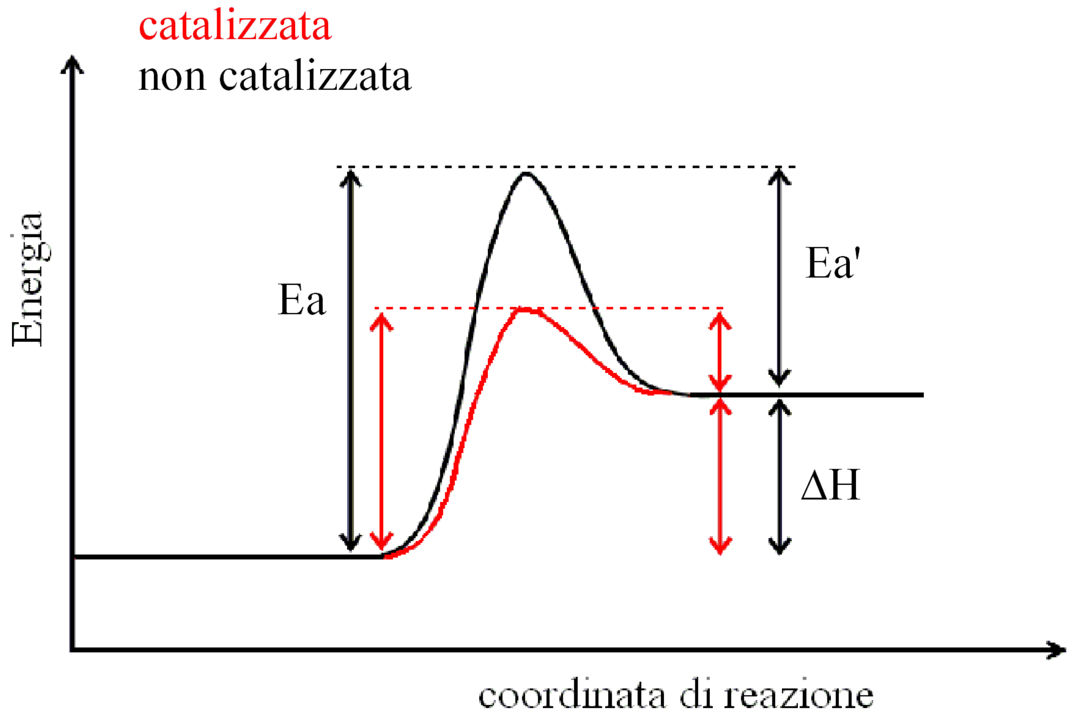
All'equilibrio $\overrightarrow{v} = \overleftarrow{v}$

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

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

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

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



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

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