Jafnvægi efnahvarfa

Skrifum efnahvörf sem

$$\sum_j \nu_j A_j = 0$$

T.d. verður

$$H_2 + Cl_2 = 2HCl$$

þá táknað með

$A_1 = H_2$ $\quad \nu_1 = 1$

$A_2 = Cl_2$ $\quad \nu_2 = 1$

$A_3 = HCl$ $\quad \nu_3 = -2$

Í jafnvægi hefur frjálsa orka Gibbs lággildi m.t.t. hlutfalls efnanna

$$dG = \sum_j \mu_j dN_j - \sigma d\tau + V dp$$

Venjulega gildir í hvörfum

$$d\tau = 0, \quad dp = 0$$

$$\rightarrow dG = \sum_j \mu_j dN_j$$

með

$$\mu_j \equiv \left(\frac{\partial G}{\partial N_j}\right)_{\tau, p}$$

Stilgreinum

fjöldi hvarfa

$$dN_j = \nu_j \, d\hat{N}$$

$$dG = \left\{ \sum_j \nu_j \mu_j \right\} d\hat{N}$$

í jafnvægi

$$\boxed{\sum_j \nu_j \mu_j = 0} \quad (*)$$

Kjörgas

Notum

$$\mu = \tau \left\{ \ln\left(\frac{n}{n_Q}\right) - \ln Z_{int} \right\}$$

$$\downarrow$$

$$\mu_j = \tau \left\{ \ln n_j - \ln c_j \right\}$$

með

$$c_j \equiv n_{Qj} \, Z_j^{int}$$

fall af τ en ekki n_j

Umritum $(*)$ því sem

$$\sum_j \nu_j \ln n_j = \sum_j \nu_j \ln c_j$$

og því sem

$$\sum_j \ln n_j^{\nu_j} = \sum_j \ln c_j^{\nu_j} = \ln\left\{\prod_j c_j^{\nu_j}\right\} \equiv \ln K(\tau)$$

$$= \ln\left\{\prod_j n_j^{\nu_j}\right\}$$

jafnvægis fasti

$$K(\tau) = \prod_j n_{Qj}^{\nu_j} \exp\left\{-\nu_j F_j^{int}/\tau\right\}$$

því $F_j^{int} = -\tau \ln\left\{Z_j^{int}\right\}$

skrifum sem

$$\boxed{\prod_j n_j^{\nu_j} = K(\tau)}$$

Lögmál massaverkunar

breyting á einum þætti hefur áhrif á alla hina.

þegar $K(\tau)$ er reiknað
þarf að stilla saman
alla viðmiðunarpunkta

T.d. í

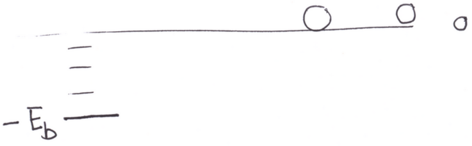
$$H_2 \longleftrightarrow 2H$$

veljum 0-ið fyrir innri
orkuna fyrir H_2 til að
falla saman við orkuna
fyrir tvö kyrr ótengd H

$$\downarrow$$

Grunnástand $H_2 = -E_B$

þ.s. E_b er minnsta orka
sem þarf til að rjúfa H_2



Dæmi

$$H_2 \longleftrightarrow 2H$$

$$\rightarrow H_2 - 2H = 0$$

$$\prod_j n_j^{\nu_j} = K(\tau)$$

$$\rightarrow [H_2][H]^{-2} = \frac{[H_2]}{[H]^2} = K(\tau)$$

[...] : styrkur ...

$$\rightarrow \frac{[H]}{[H_2]} = \frac{1}{\sqrt{[H_2]}\,\sqrt{K}}$$

Hlutfallið er háð $\frac{1}{\sqrt{[H_2]}}$

$E_B = 4.476$ eV at $T = 0$

Orkan og bindiorkan keppast hér

Í hreinu vatni mælist styrkur

$[H^+] = [OH^-] = 10^{-7}$ mol/l

Skilgreint

$$pH \equiv -\log_{10}[H^+]$$

Hreyfilíkan fyrir massavirkni

$$A + B \leftrightarrow AB$$

Hraðajafna fyrir n_{AB}

$$\frac{dn_{AB}}{dt} = C\, n_A n_B - D\, n_{AB}$$

myndunar-stuðull

rofnunar-stuðull

Í jafnvægi er $\frac{dn_{AB}}{dt} = 0$

$$\rightarrow \quad C\, n_A n_B = D\, n_{AB}$$

$$\rightarrow \quad \frac{n_A n_B}{n_{AB}} = \frac{D}{C}$$

(**) principle of detailed balance

milli-ástand

$A + E \leftrightarrow AE$

$AE + B \leftrightarrow AB + E$

hvati $\leftrightarrow$ E

breytir ekki (**)

ef AE er stammlift

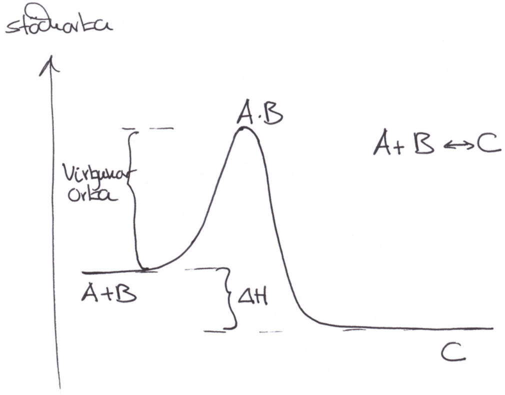
og með hverfandi styrk

Aðeins upplýsingar um

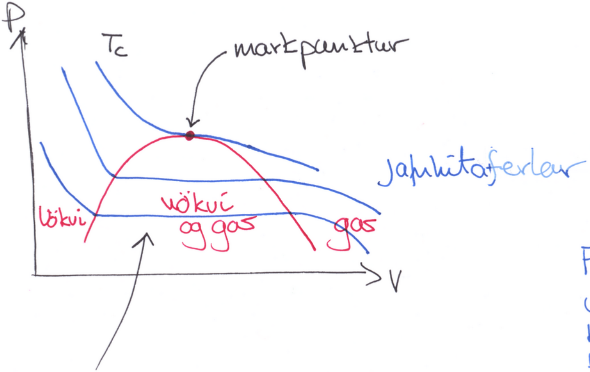
jafnvægis eiginleika

hvartsins í (**)

ekki hraða



Fasabreytingar



fyrir ofan T_c er aðeins einn fasi

$$T_c^{H_2O} = 647.1 \text{ K}$$

Markhitastig

Fasabreytingar í raungasi ... eru vegna víxlverkunar milli atóma. Kjörgaslíkanið sýnir enga fasabreytingar

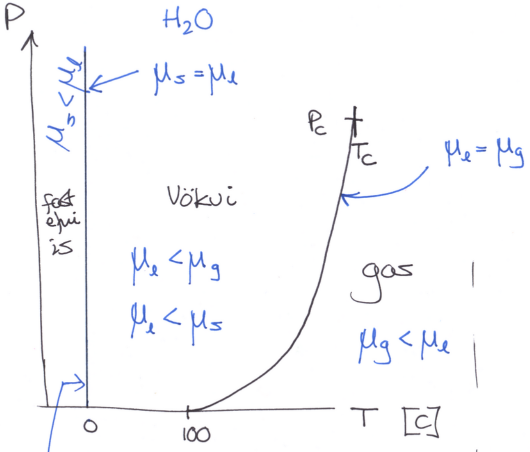
Tveir fasar í jafnvægi

$\longrightarrow$

$$\tau_1 = \tau_2 \qquad \tau_l = \tau_g$$

$$\mu_1 = \mu_2 \qquad \mu_l = \mu_g \qquad \longrightarrow \qquad \boxed{\mu_l(p,\tau) = \mu_g(p,\tau)}$$

$$p_1 = p_2 \qquad p_l = p_g$$



jafnvægisferill fyrir vökva og gas

jafnvægisferill fyrir ís og vökva

skilgreining jafnvægisferils

$$\mu_g(p_0, \tau_0) = \mu_l(p_0, \tau_0)$$

í vissum punkti (p_0, τ_0)

Ef fasarnir eru líka í jafnvægi í $(p_0 + dp, \tau_0 + d\tau)$

$$\rightarrow \mu_g(p_0 + dp, \tau_0 + d\tau) = \mu_l(p_0 + dp, \tau_0 + d\tau)$$

línuleg nálgun

$$\mu_g(p_0,\tau_0) + \left(\frac{\partial \mu_g}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_g}{\partial \tau}\right)_p d\tau + \cdots = \mu_l(p_0,\tau_0) + \left(\frac{\partial \mu_l}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_l}{\partial \tau}\right)_p d\tau + \cdots$$

$$\hookrightarrow \left(\frac{\partial \mu_g}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_g}{\partial \tau}\right)_p d\tau = \left(\frac{\partial \mu_l}{\partial p}\right)_\tau dp + \left(\frac{\partial \mu_l}{\partial \tau}\right)_p d\tau$$

$$\hookrightarrow \frac{dp}{d\tau} = \frac{\left(\frac{\partial \mu_l}{\partial \tau}\right)_p - \left(\frac{\partial \mu_g}{\partial \tau}\right)_p}{\left(\frac{\partial \mu_g}{\partial p}\right)_\tau - \left(\frac{\partial \mu_l}{\partial p}\right)_\tau}$$

Afleiðujafna fyrir jafnvægisferil tveggja fasa

Munum

$$G = N\mu(p,\tau), \qquad \left(\frac{\partial G}{\partial p}\right)_{N\tau} = V, \qquad \left(\frac{\partial G}{\partial \tau}\right)_{Np} = -\sigma$$

$$\to \quad \frac{1}{N}\left(\frac{\partial G}{\partial p}\right)_{N\tau} = \frac{V}{N} = v = \left(\frac{\partial \mu}{\partial p}\right)_{\tau}$$

$$\frac{1}{N}\left(\frac{\partial G}{\partial \tau}\right)_{Np} = -\frac{\sigma}{N} = -s = \left(\frac{\partial \mu}{\partial \tau}\right)_{p}$$

$$\to \quad \boxed{\frac{dp}{d\tau} = \frac{s_g - s_l}{v_g - v_l}}$$

aukning óreiðu kerfisins þ. ein sameind fer úr vökva í gas

aukning rúmmáls kerfisins þ. ein sameind fer úr vökva í gas

$$N = N_l + N_g$$

$$đQ = \tau(s_g - s_\ell)$$: varmimin sem setja verður í kerfið til að flytja eina sameind jafngengt frá vökva í gas við fast τ

$$\equiv L$$

uppgufunarvarmi

setjum $\Delta v = v_g - v_\ell$

$$\boxed{\frac{dp}{d\tau} = \frac{L}{\tau \Delta v}}$$

Clausius-Clapeyron-
eða
Gufuþrýstings-jafnan

Báðar hliðar jöfnunnar eru ómoldar og vel ~~staðþ~~ ~~þ~~ stær