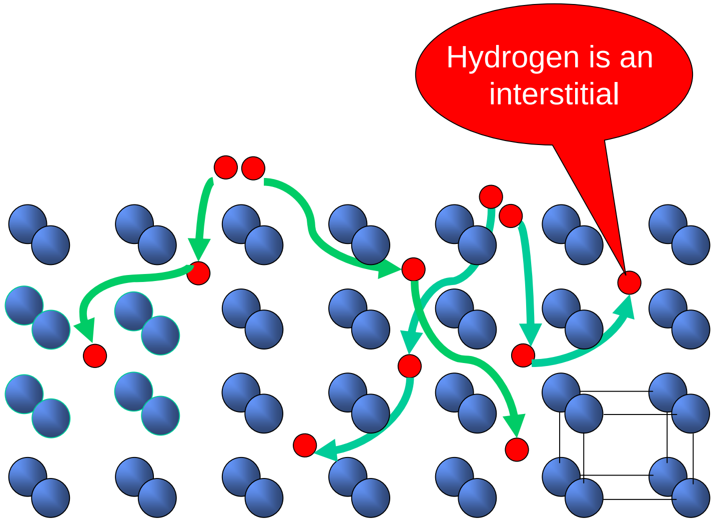
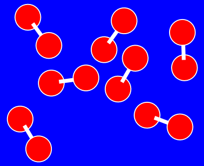
Reminder

Interstitial alloy



Statistical physics of the hydrogen gas

$$F = -kT\ln\sum_{n}\exp\left(-\frac{E_n}{kT}\right)$$



over all states of the gas containing N_H molecules.

$$\left(\sum_{\substack{n \\ \text{states of the gas}}} e^{-E_n/kT}\right) = \sum_{n} e^{-\sum_k \varepsilon_k/kT} = \left(\sum_{\substack{k \\ \text{molecular energies}}} e^{-\varepsilon_k/kT}\right)^{N_{H_2}} \frac{1}{N_{H_2}!}$$

where ε_k is the energy of the k-th molecule.

$$F = -kTN_{H_2}\ln\sum_{k} e^{-\varepsilon_k/kT} + kT\ln N_{H_2}!$$

Using Stirling’s formula

$$\ln N! \cong N\ln\frac{N}{e}$$

$$F = -kTN_{H_2}\ln\left(\frac{e}{N_{H_2}}\sum_{k} e^{-\varepsilon_k/kT}\right)$$

$$\varepsilon = \varepsilon_b + \frac{\mathbf{p}^2}{2m} + \frac{\mathbf{M}^2}{2\Theta_{H_2}}$$

ε_b is the binding energy of the H_2 molecule
M is the angular momentum and
Θ is the moment of inertia of the molecule.
The classical limit

$$F = -kTN_{H_2} \ln \frac{e}{N_{H_2}} \frac{1}{(2\pi\hbar)^r} \int e^{-\varepsilon(\mathbf{p},\mathbf{q})/kT}\, \mathbf{dpdq}$$

where **dp**=$dp_1,\ldots,dp_r$ and **dq=**$dq_1,\ldots,dq_r$ where r is the number of degrees of freedom of the molecule.

The free energy of a diatomic gas H_2

$$F_{H_2} = N_{H_2}\varepsilon_b + F_{translational} + F_{rotational}$$

$$= \left\{N_{H_2}\varepsilon_b\right\} + \left\{-N_{H_2} kT \ln\left[\frac{eV}{N_{H_2}}\left(\frac{m_{H_2} kT}{2\pi\hbar^2}\right)^{3/2}\right]\right\} + \left\{-N_{H_2} kT \ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)\right\}$$

from which we derive the chemical potential μ_{H_2}

$$\mu_{H_2} = \frac{\partial F_{H_2}}{\partial N_{H_2}} = \varepsilon_b - kT\ln\left[\frac{eV}{N_{H_2}}\left(\frac{m_{H_2} kT}{2\pi\hbar^2}\right)^{3/2}\right] + kT$$

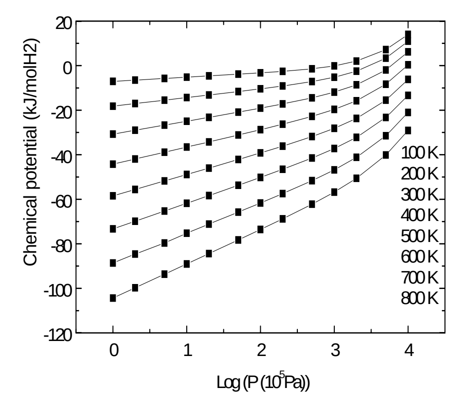
$$- kT\ln\left(\frac{kT\Theta_{H_2}}{\hbar^2}\right)$$

$$= \varepsilon_b - kT\ln\left[\frac{V}{N_{H_2}}\, kT\left(\frac{m_{H_2} kT}{2\pi\hbar^2}\right)^{3/2}\frac{\Theta_{H_2}}{\hbar^2}\right]$$

For an ideal gas $pV = N_{H_2} kT$

$$\mu_{H_2}(p,T) = \varepsilon_b - kT\ln\left[\frac{\Theta_{H_2}(kT)^2}{p\hbar^5}\left(\frac{m_{H_2} kT}{2\pi}\right)^{3/2}\right]$$

$$\mu_{H_2}(p,T) = \varepsilon_b - kT\ln\left[\frac{\Theta_{H_2}(kT)^2}{p\hbar^5}\left(\frac{m_{H_2} kT}{2\pi}\right)^{3/2}\right]$$



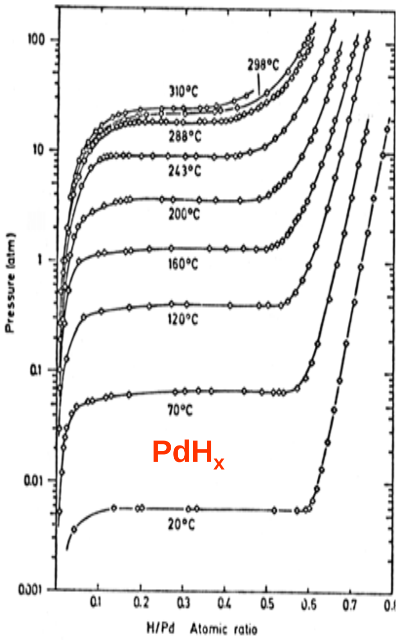
$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right]$$

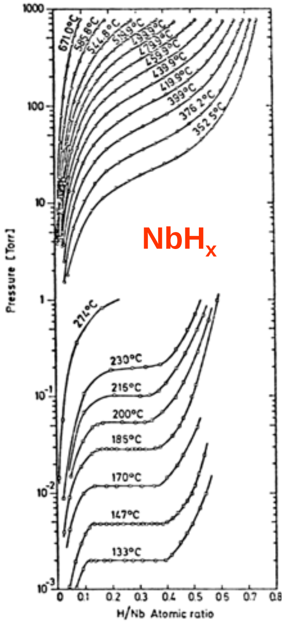
with

$$p_0(T) = \frac{(kT)^{7/2}\,\Theta_{H_2}\, m_{H_2}^{3/2}}{\hbar^5 (2\pi)^{3/2}}$$

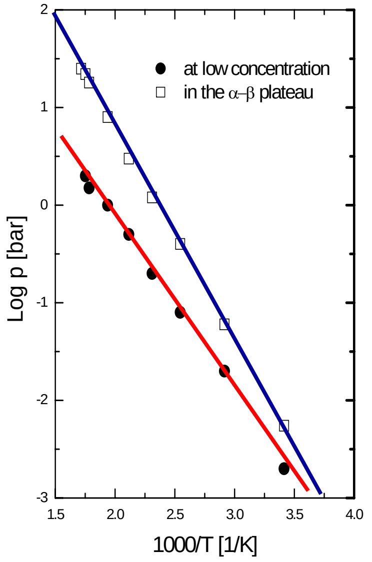
Thermodynamics of hydrogen in metals

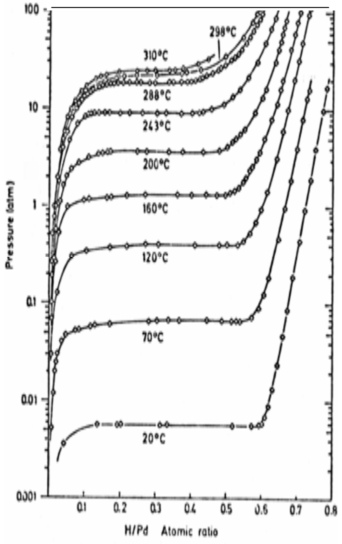
Ronald Griessen
Vrije Universiteit, Amsterdam
Feb. 2006



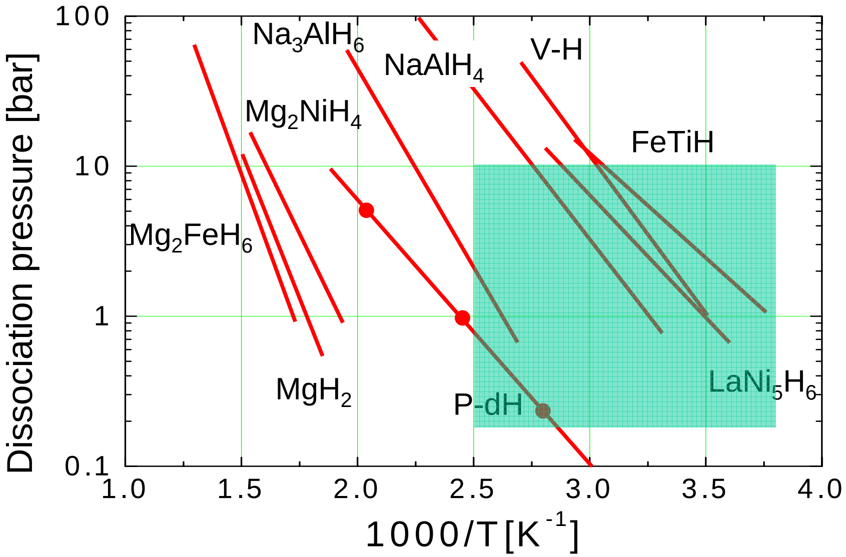


Van t'Hoff plots

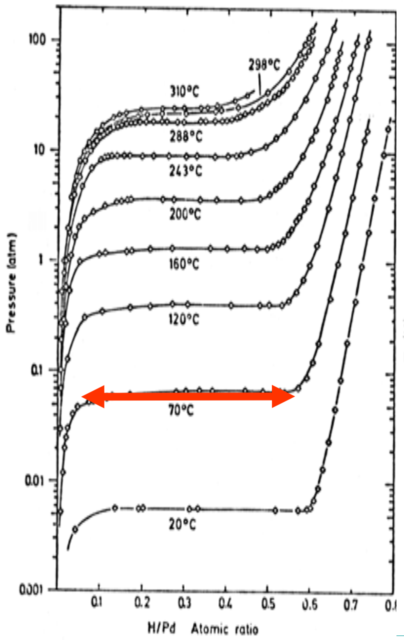


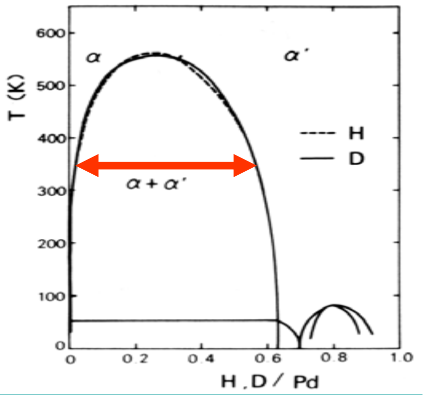


Van t'Hoff plots of some metal-hydrides

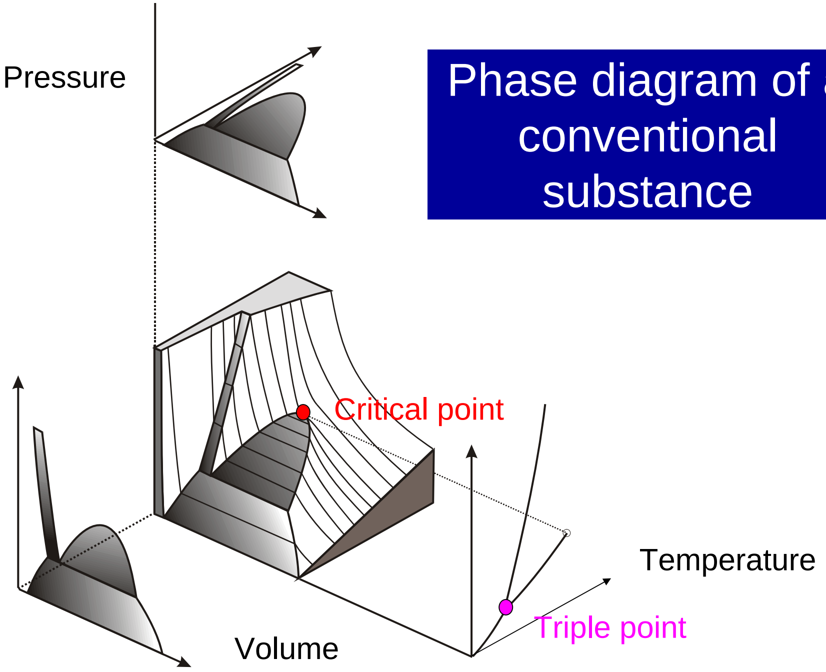


P-c isotherms and phase diagram

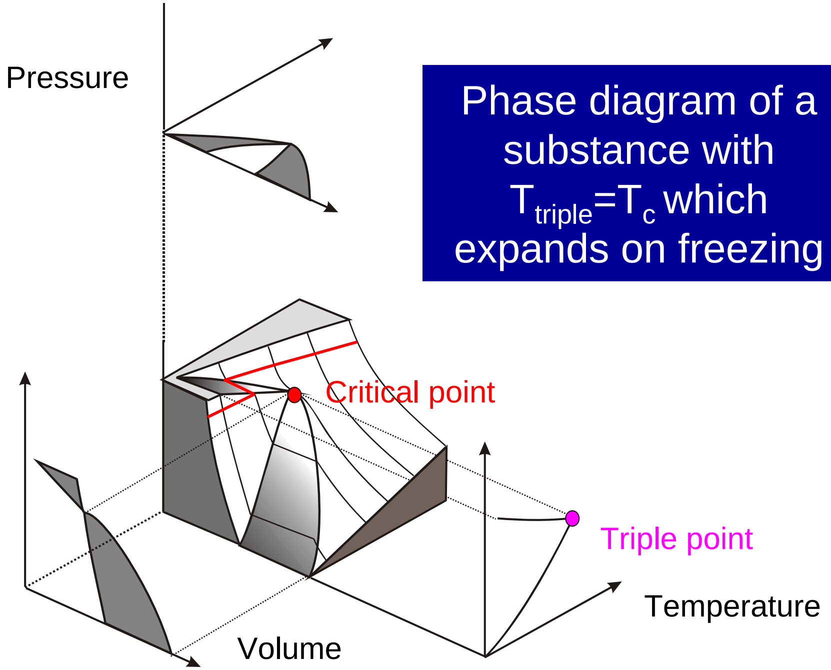




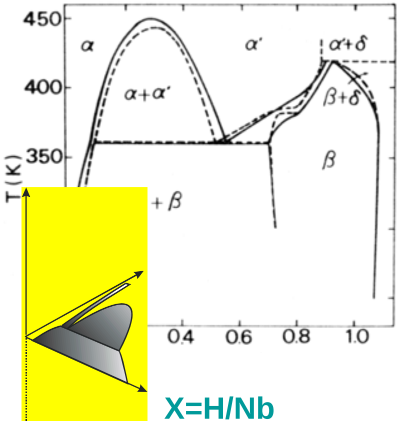
Phase diagram of a conventional substance



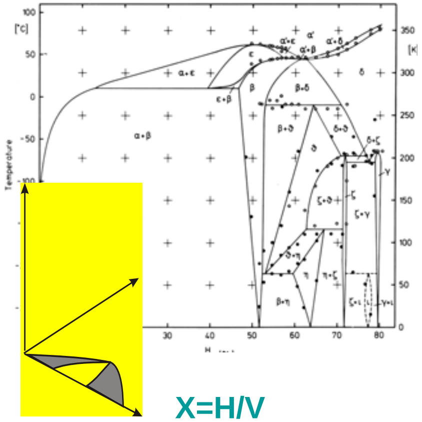
Phase diagram of a substance with $T_{triple}=T_c$ which expands on freezing



Phase diagrams of NbH_x and VH_x



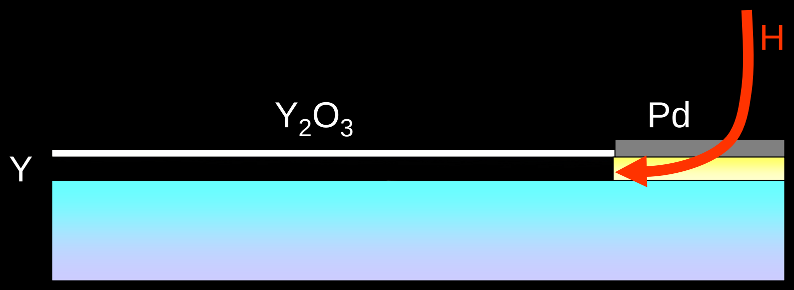
X=H/Nb



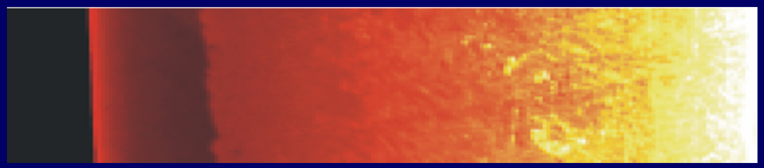
X=H/V

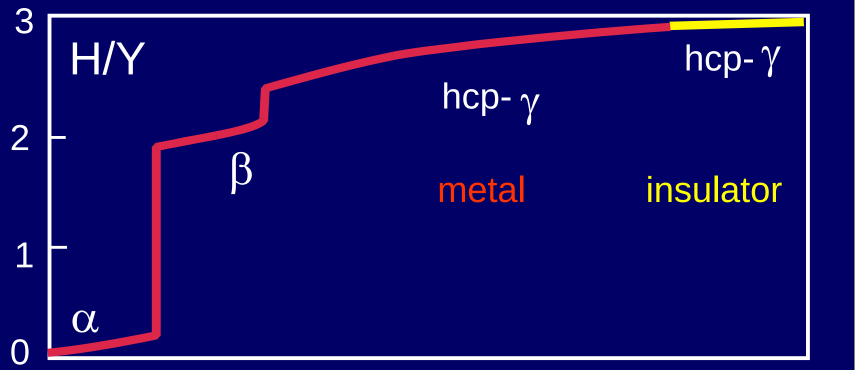
Seeing a lattice gas moving in a metal

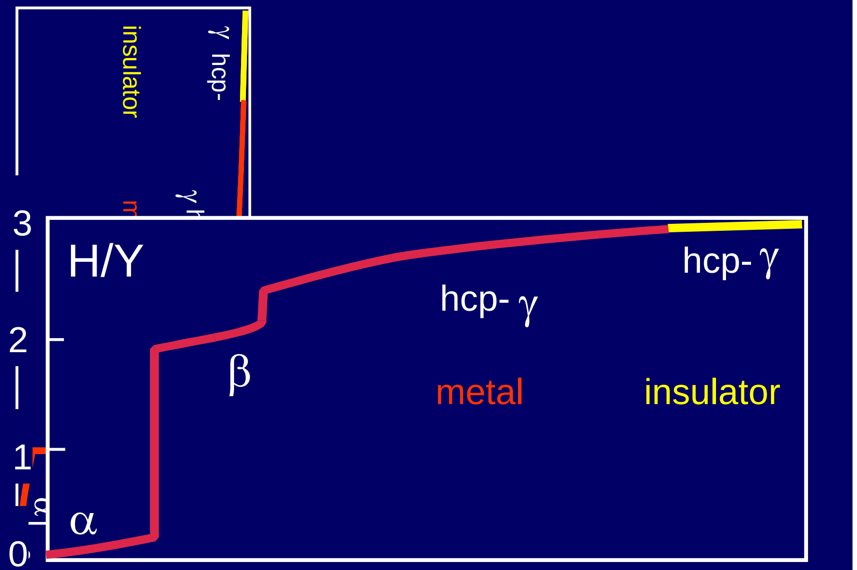
H diffusion in Y

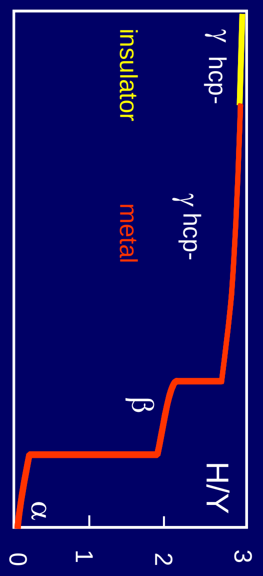


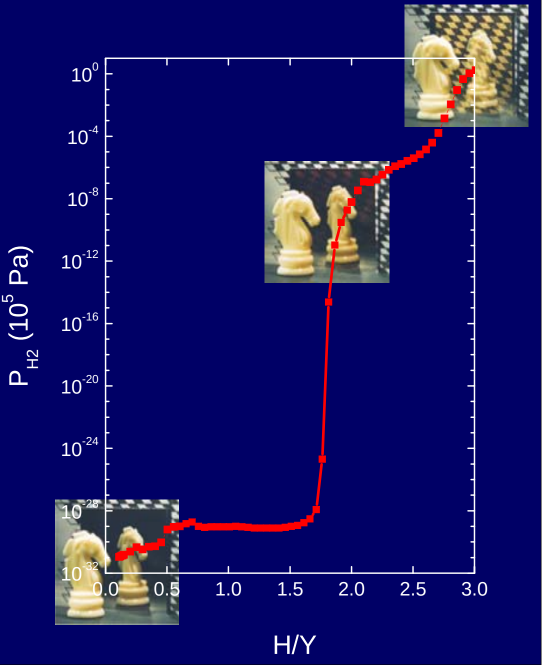
Den Broeder, van der Molen et al, Nature 394 (1998) 656



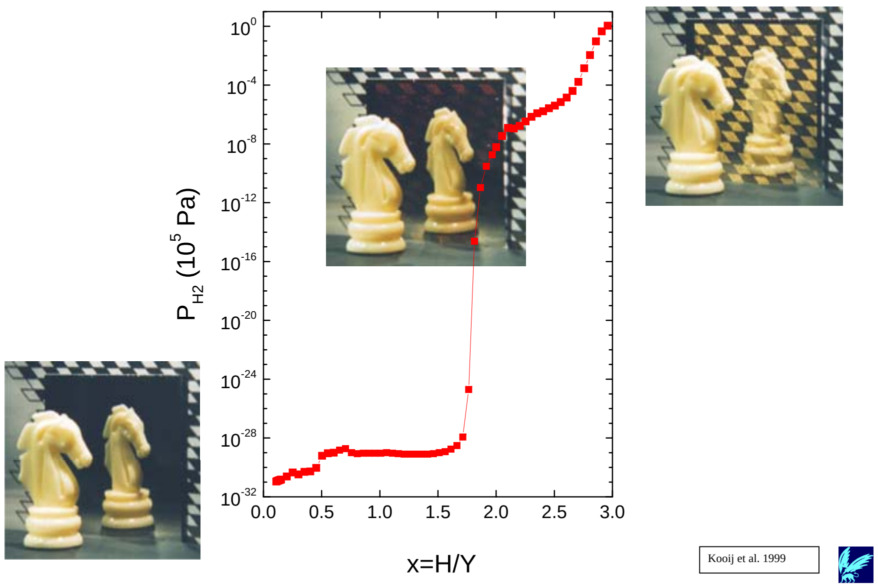






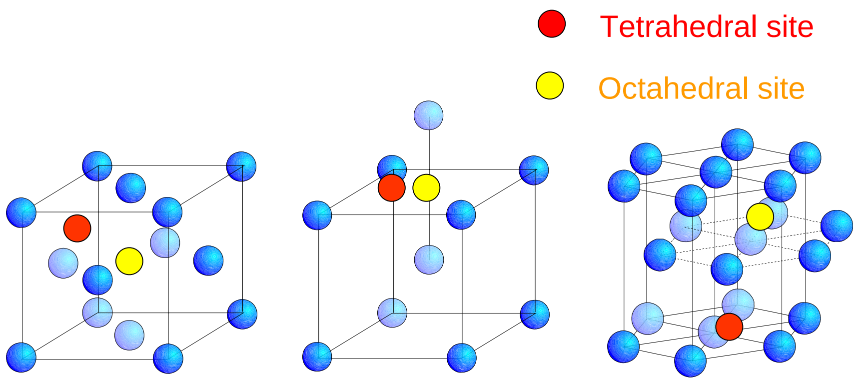


Pressure-composition isotherm of YH_x at T=293 K

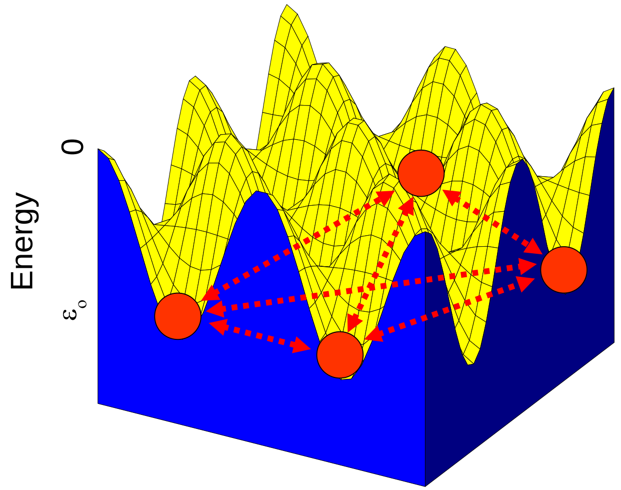


Kooij et al. 1999

Interstitial sites in FCC, BCC and HCP lattices



Theory of the lattice gas



Definition of a lattice gas

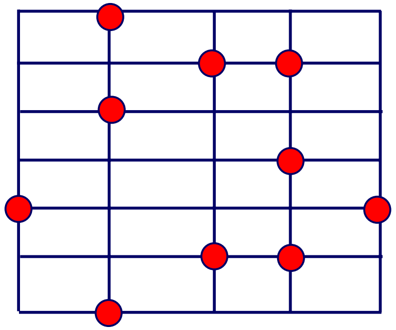
A lattice gas is a monoatomic gas with the interaction

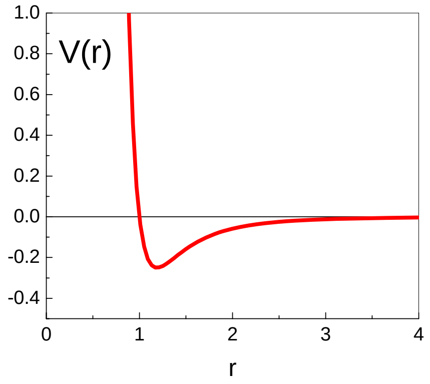
$$U = \sum_{i,j} U(|\mathbf{R}_i - \mathbf{R}_j|)$$

where $\mathbf{R}_i$ indicates the position of the i-th atom and

a) the atoms have a finite impenetrable core of diameter a, so that U(r)= ∞ for r<a
b) the interaction has a finite range, so that U(r)=0 for r>b
c) U(r) is nowhere -∞

Definition of a lattice gas





Energy of hydrogen atoms dissolved in a metal

$$E = N_H \varepsilon_o + N_{HH} \varepsilon$$

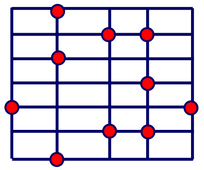
N_{HH} : number of nearest neighbour H-pairs
ε : strength of H-H pair interaction energy
N : total number of sites
N_H : number of H

The free energy $F=U-TS$ is

$$F = -kT \ln \sum \exp\left[-\frac{N_H \varepsilon_o + N_{HH} \varepsilon}{kT} \right]$$

where the sum is taken over all configurations of N_H atoms distributed over N sites.

The Bragg-William approximation



In this approximation

$$N_{HH} = N_H n \frac{N_H}{N} \frac{1}{2}$$

n = number of nearest neighbours interstitial sites

$\frac{N_H}{N}$ = probability of finding a n. n. around a given H

The energy E of a configuration is

$$E = \varepsilon_o N_H + \frac{\varepsilon}{2} n \frac{N_H^2}{N}$$

$$F = -kT\ln\sum\exp\left[-\frac{N_H\varepsilon_o + N_{HH}\varepsilon}{kT}\right]$$

$$F = -kT\ln\left[\frac{N!}{N_H!(N-N_H)!}e^{-\left(\varepsilon_o N_H + \frac{\varepsilon}{2}n\frac{N_H^2}{N}\right)/kT}\right]$$

$$= -kT\left[\ln N! - \ln N_H! - \ln(N-N_H)!\right] - \left(N_H\varepsilon_o + \varepsilon\frac{n}{2}\frac{N_H^2}{N}\right)$$

With Stirling's formula

$\ln N! \cong N\ln N - N$ and $c_H = \frac{N_H}{N}$

$$F_H = kTN[c_H\ln c_H + (1-c_H)\ln(1-c_H)] + N[\varepsilon_o c_H + \varepsilon\frac{n}{2}c_H{}^2]$$

Chemical potential

$$F_H = kTN[c_H\ln c_H + (1-c_H)\ln(1-c_H)] + N[\varepsilon_o c_H + \varepsilon\frac{n}{2}c_H{}^2]$$

$$\mu_H(c_H,T) = \left.\frac{\partial F}{\partial N_H}\right|_{T,V} = \frac{1}{N}\left.\frac{\partial F}{\partial c_H}\right|_{T,V}$$

$$\mu_H = kT\,ln\frac{c_H}{1-c_H} + \varepsilon_o + \varepsilon n c_H$$

Solubility isotherms

$$\mu_{H_2} = \varepsilon_b + kT\ln\left[\frac{p}{p_0(T)}\right]$$

$$\mu_H = kT\,ln\frac{c_H}{1-c_H} + \varepsilon_o + \varepsilon n c_H$$

$$p_0(T) = \left(\frac{(kT)^{7/2}\Theta_{H_2}m_{H_2}^{3/2}}{\hbar^5(2\pi)^{3/2}}\right)$$

$$p_0(T) = \left(\frac{T}{9.13}\right)^{7/2}$$

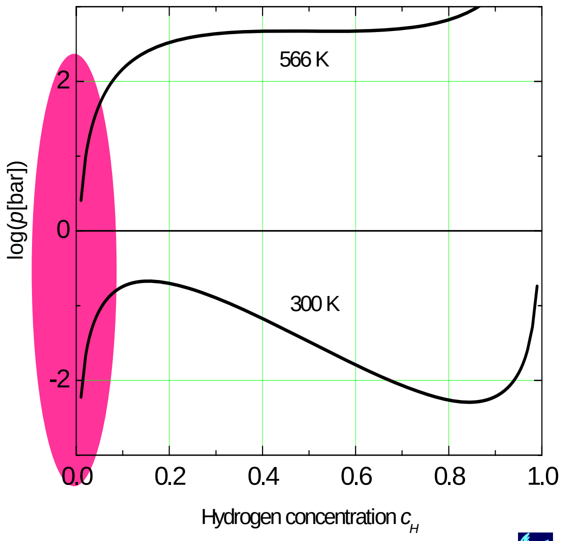
with p_o
expressed in bar
and T in Kelvin.

$$\frac{1}{2}\left(\varepsilon_b + kT\,ln\frac{p}{p_0(T)}\right) = kT\,ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

Example of isotherms

$$\frac{1}{2}\left(\varepsilon_b + kT\ln\frac{p}{p_0(T)}\right) = $$
$$= kT\ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

ε_o= -228 kJ/molH
εn = -19 kJ/molH and
ε_b = -436 kJ/molH$_2$

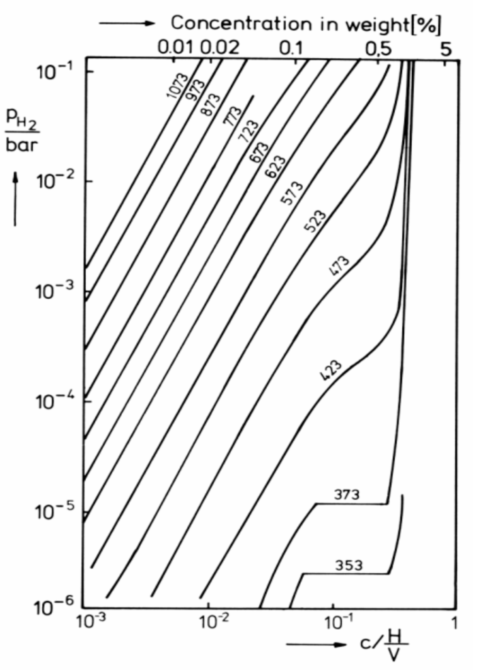


Sievert's law

$$\frac{1}{2}\left(\varepsilon_b + kT\,ln\frac{p}{p_0(T)}\right) = kT\,ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

$$\frac{1}{2}\ln p = kT\ln c_H$$

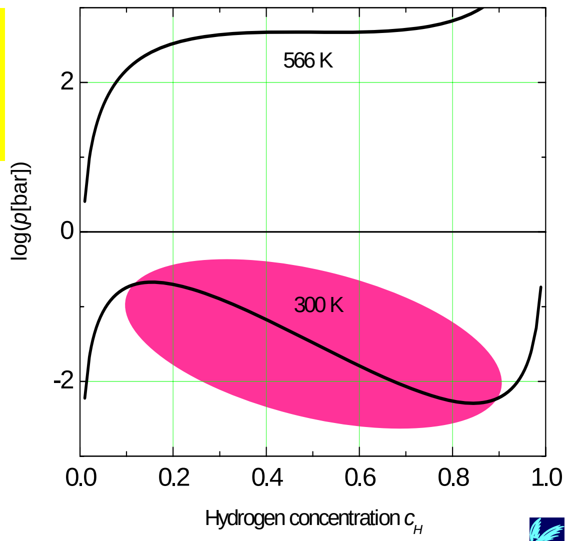
$\lim\limits_{\delta p \to 0}$ $\lim\limits_{\delta c_H \to 0}$



Example of isotherms

$$\frac{1}{2}\left(\varepsilon_b + kT\ln\frac{p}{p_0(T)}\right) = \\ = kT\ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

ε_o = -228 kJ/molH
εn = -19 kJ/molH and
ε_b = -436 kJ/molH_2

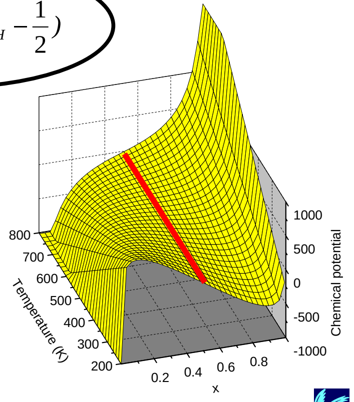


To ease the discussion

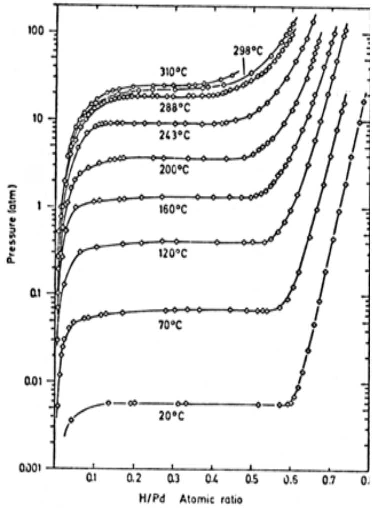
$$\frac{1}{2}\left(\varepsilon_b + kT\,ln\frac{p}{p_0(T)}\right) = kT\,ln\frac{c_H}{1-c_H} + \varepsilon_0 + \varepsilon n c_H$$

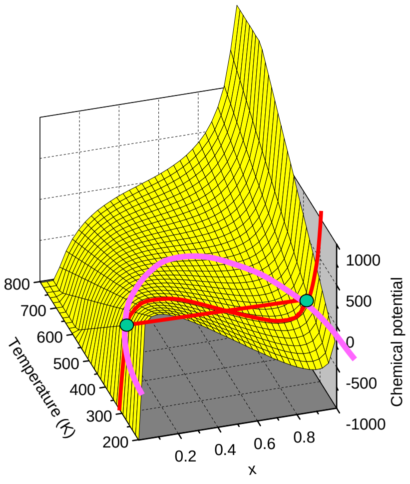
$$\frac{1}{2}\left(\varepsilon_b - \varepsilon n + kT\,ln\frac{p}{p_0(T)} - 2\varepsilon_0\right) = kT\,ln\frac{c_H}{1-c_H} + \varepsilon n(c_H - \frac{1}{2})$$

$$f(c_H) = kT\,ln\frac{c_H}{1-c_H} + \varepsilon n(c_H - \frac{1}{2})$$

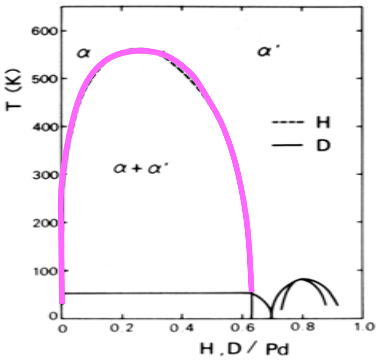


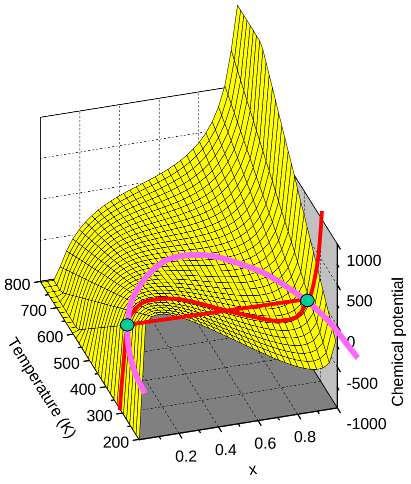
Maxwell construction





P-c isotherms and phase diagram



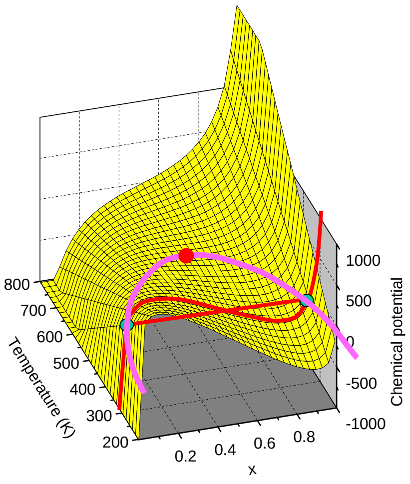


Coexistence curve

$$kT\ln\frac{c_i}{1-c_i}+\varepsilon n(c_i-\tfrac{1}{2})=0$$

$$T_c=-\frac{\varepsilon n}{4k}$$

For PdH$_x$
T_c= 566 K
εn= -0.20 eV
T_c=566 K

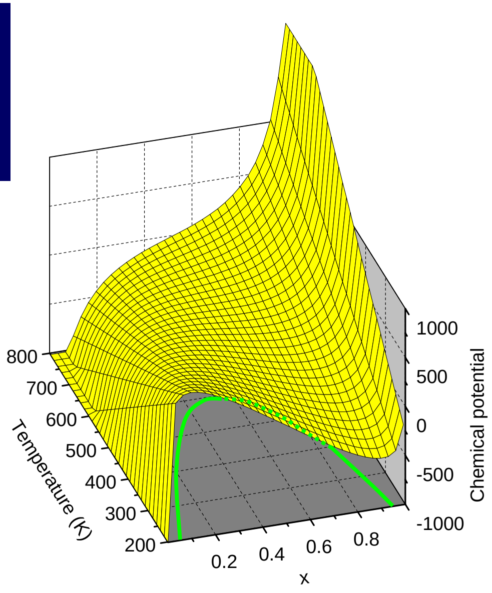


The spinodal is the locus of the points with

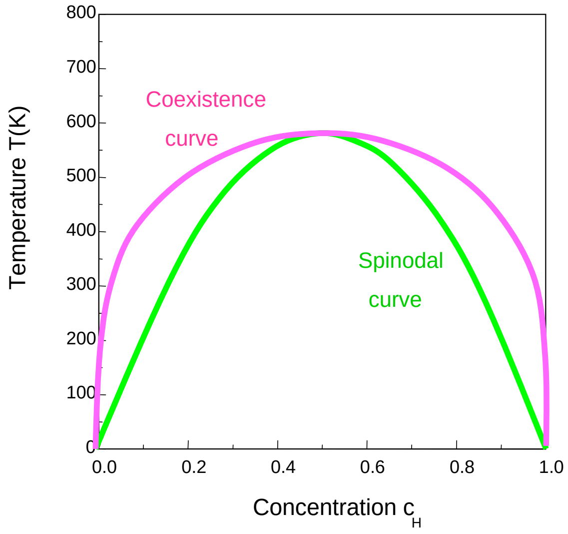
$$\frac{\partial \mu_H}{\partial c_H}=0$$

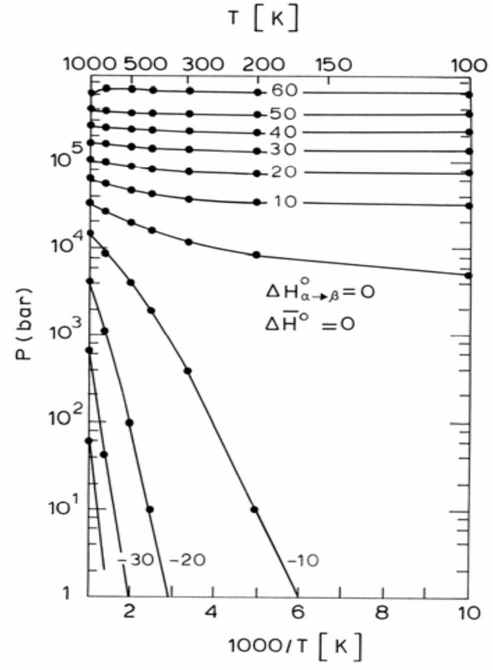
$$\frac{\partial \mu_H}{\partial c_H}=kT_{sp.}\frac{1}{c_H(1-c_H)}+\varepsilon n=0$$

$$T_{sp.}=-\frac{\varepsilon n}{k}c_H(1-c_H)$$



Coexistence and spinodal curves





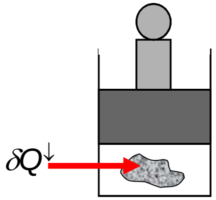
Plateau pressure of a metal-hydride with
V_H =1. 7 cm^3/molH
Θ_E= 850 K

Heat of solution (reaction)

$\delta Q^{\downarrow}$ is the amount of heat received by the system during the reaction

$$\frac{x}{2}H_2 + M \rightarrow MH_x + \delta Q^{\downarrow}$$

$\delta Q^{\downarrow}$ < 0 for exothermic reactions
$\delta Q^{\downarrow}$ > 0 for endothermic reactions.



At constant pressure and at constant temperature T=T$_0$. δN_H hydrogen atoms are transferred from the gas to the metal

$$\delta Q^{\downarrow} = T_0 \delta S = \delta H$$

since $H = U + pV$

Along the coexistence line

$$\tfrac{1}{2}\mu_{H_2}(p,T) = \mu_H(p,T,c_H)$$

$$\frac{1}{2}\left.\frac{\partial(\mu_{H_2}/T)}{\partial(1/T)}\right|_p + \frac{1}{2}\left.\frac{\partial(\mu_{H_2}/T)}{\partial p}\right|_T \left.\frac{\partial p}{\partial(1/T)}\right|_{c_H}$$
$$= \left.\frac{\partial(\mu_H/T)}{\partial(1/T)}\right|_{p,c_H} + \left.\frac{\partial(\mu_H/T)}{\partial p}\right|_T \left.\frac{\partial p}{\partial(1/T)}\right|_{c_H}$$

Using the general relations

$$\left.\frac{\partial(\mu/T)}{\partial(1/T)}\right|_{p,n} = \left.\frac{\partial H}{\partial n}\right|_{p,T} \equiv \overline{H}$$

$$\left.\frac{\partial \mu}{\partial p}\right|_{n,T} = \left.\frac{\partial^2 G}{\partial p \partial n}\right|_T = \left.\frac{\partial V}{\partial n}\right|_{p,T} \equiv \overline{V}$$

Partial molar heat of solution

$$\Delta\overline{H} = \overline{H}_H - \tfrac{1}{2}\overline{H}_{H_2} = \left(\overline{V}_H - \tfrac{1}{2}\overline{V}_{H_2}\right)\left.\frac{\partial p}{\partial \ln T}\right|_{c_H}$$

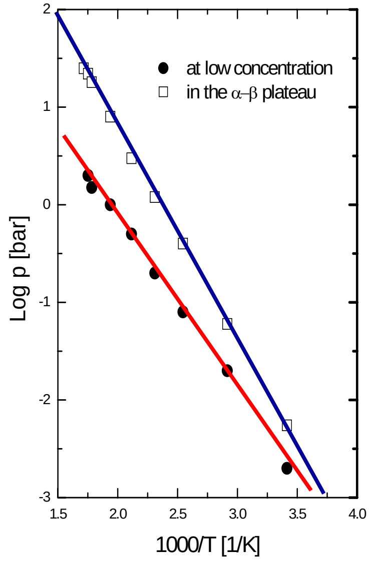
At low and moderate pressures

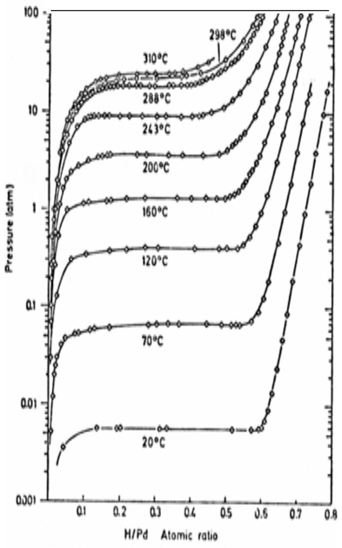
$$\Delta\overline{H} = \overline{H}_H - \tfrac{1}{2}\overline{H}_{H_2} = \left(\overline{V}_H - \tfrac{1}{2}\overline{V}_{H_2}\right)\left.\frac{\partial p}{\partial \ln T}\right|_{c_H}$$

$$p\overline{V}_{H_2} = RT$$

$$\Delta\overline{H} = \overline{H}_H - \tfrac{1}{2}\overline{H}^0_{H_2} \cong \frac{R}{2}\left.\frac{\partial \ln p}{\partial(1/T)}\right|_{c_H}$$

Van t'Hoff plots





One-phased MH$_x$ Two-phased MH$_x$

$$M+\frac{x}{2}H_2\rightarrow MH_x$$

$$MH_{c_\alpha}+\tfrac{1}{2}\left(c_\beta-c_\alpha\right)H_2\rightarrow MH_{c_\beta}$$

$$\frac{\bar{H}_H-\frac{1}{2}\bar{H}_{H_2}}{\left(\bar{V}_H-\frac{1}{2}\bar{V}_{H_2}\right)}=\left.\frac{\partial p}{\partial \ln T}\right|_{c_H}$$

$$\frac{H_\beta-H_\alpha-\frac{1}{2}\left(c_\beta-c_\alpha\right)\bar{H}_{H_2}}{\frac{1}{2}\left(c_\beta-c_\alpha\right)\bar{V}_{H_2}-\left(V_\beta-V_\alpha\right)}=\frac{dp}{d\ln T}$$

$$\Delta\bar{H}=\bar{H}_H-\tfrac{1}{2}\bar{H}$$

$$\Delta H_{\alpha\rightarrow\beta}=\frac{H_\beta-H_\alpha}{c_\beta-c_\alpha}-\tfrac{1}{2}\bar{H}_{H_2}$$

$$\Delta\bar{H}=\left(\bar{V}_H-\tfrac{1}{2}\bar{V}_{H_2}\right)\left.\frac{\partial p}{\partial \ln T}\right|_{c_H}$$

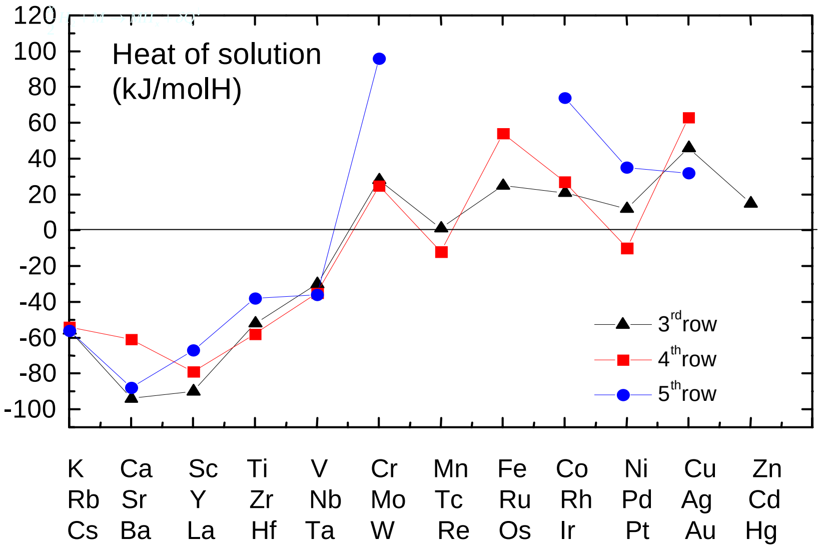
$$p\bar{V}_{H_2}=RT$$

$$\Delta H_{\alpha\rightarrow\beta}\cong\left(\bar{V}_H-\tfrac{1}{2}\bar{V}_{H_2}\right)\frac{dp}{d\ln T}$$

$$\Delta\bar{H}\cong\frac{R}{2}\left.\frac{\partial \ln p}{\partial\left(1/T\right)}\right|_{c_H}$$

$$\Delta H_{\alpha\rightarrow\beta}\cong\frac{R}{2}\left.\frac{\partial \ln p}{\partial\left(1/T\right)}\right|_{c}$$

Heat of solutions of some metal-hydrides



Inclusion of thermal and steric effects

$$\mu_H=RT\,ln\left(\frac{c_H}{1-c_H}\right)+\varepsilon_0+\varepsilon n c_H$$
$$+\bar{V}_H\,p+\tfrac{3}{2}R\theta_E+3RT\,ln\left(1-e^{-\theta_E/T}\right)$$

$$\bar{H}_H=\varepsilon_0+\varepsilon n c_H+\bar{V}_H\,p+\tfrac{3}{2}R\theta_E+3R\theta_E\,\frac{1}{e^{\theta_E/T}-1}$$

$$\bar{H}_{H_2}=\bar{H}^0_{H_2}+\frac{7}{2}RT$$

$$\Delta\bar{H}=\bar{H}^0_H-\tfrac{1}{2}\bar{H}^0_{H_2}$$

A simple but useful relation

$$\mu_H = RT\,ln\left(\frac{c_H}{1-c_H}\right)+\varepsilon_0+\varepsilon n c_H$$

$$\overline{H}_H=\varepsilon_0+\varepsilon n c_H$$

$$\overline{S}_H=-R\ln\left(\frac{c_H}{1-c_H}\right)$$

$$\tfrac{1}{2}\mu_{H_2}(p,T)=\mu_H(p,T,c_H)$$

$$\Delta\overline{H}=T\overline{S}_H-\tfrac{1}{2}T\overline{S}_{H_2}$$

$$\overline{S}_{H_2}=\overline{S}^0_{H_2}-R\ln p$$

with $\frac{S^0_{H_2}}{2R}=7.87$

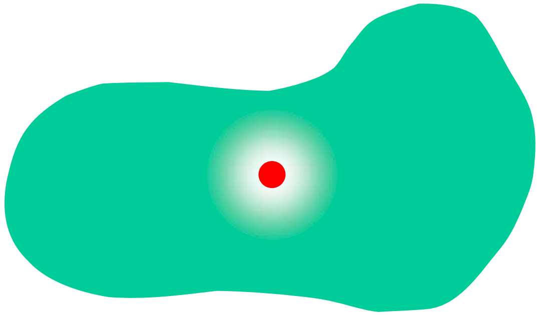
$$\tfrac{1}{2}\ln p=\frac{\Delta\overline{H}}{RT}+\frac{S^0_{H_2}}{2R}$$

The interaction cannot be electronic

Potential of charge Ze
in vacuum

$$V_0(r)=\frac{Ze^2}{r}$$

Potential of charge Ze
in a metal



$$V_0(r)=\frac{Ze^2e^{-\frac{r}{r_{TF}}}}{r}$$

$$r_{TF}=\left(\frac{2\varepsilon_0E_F}{3e^2N^*}\right)^{\frac{1}{2}}$$ = typically 0.1 nm

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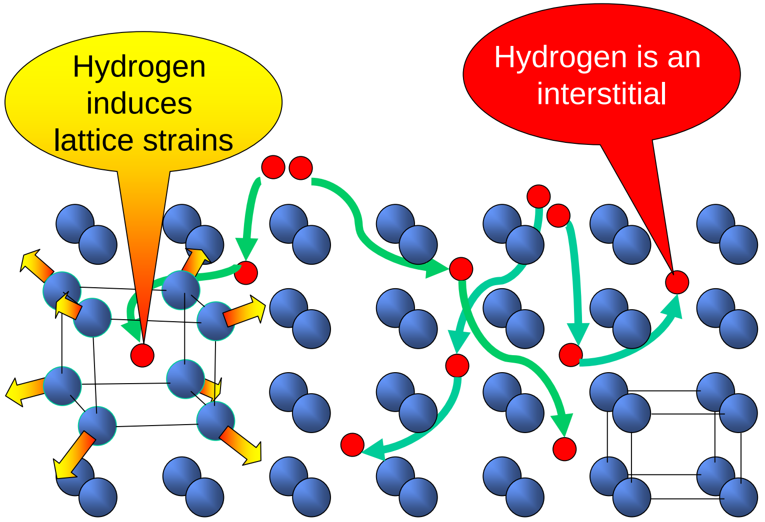
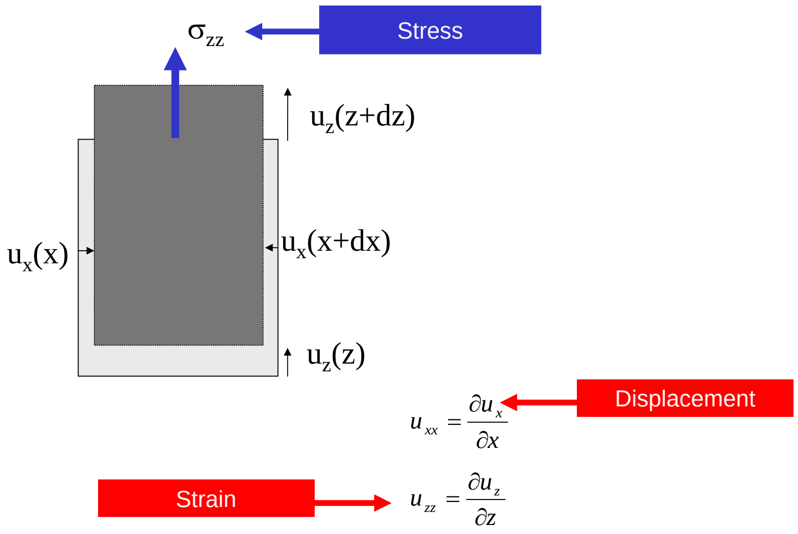
Elastic H-H interaction



Displacements, strains and stresses



$$u_{xx}=\frac{\partial u_x}{\partial x}$$

$$u_{zz}=\frac{\partial u_z}{\partial z}$$

Hookes's law

$$u_{xx} = \frac{1}{E}\left[\sigma_{xx} - \nu\left(\sigma_{yy} + \sigma_{zz}\right)\right]$$

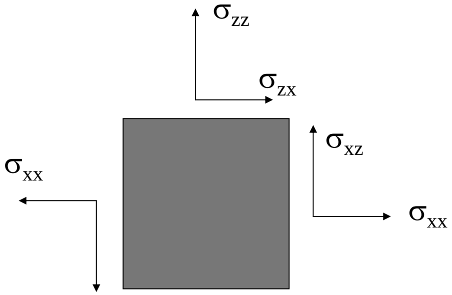
$$u_{yy} = \frac{1}{E}\left[\sigma_{yy} - \nu\left(\sigma_{xx} + \sigma_{zz}\right)\right]$$

$$u_{zz} = \frac{1}{E}\left[\sigma_{zz} - \nu\left(\sigma_{xx} + \sigma_{yy}\right)\right]$$

$$u_{zy} = \frac{(1+\nu)}{E}\sigma_{zy}$$

$$u_{zx} = \frac{(1+\nu)}{E}\sigma_{zx}$$

$$u_{xy} = \frac{(1+\nu)}{E}\sigma_{xy}$$



Hookes's law

$$u_{xx} = \frac{1}{E}\left[\sigma_{xx} - \nu\left(\sigma_{yy} + \sigma_{zz}\right)\right]$$

$$u_{yy} = \frac{1}{E}\left[\sigma_{yy} - \nu\left(\sigma_{xx} + \sigma_{zz}\right)\right]$$

$$u_{zz} = \frac{1}{E}\left[\sigma_{zz} - \nu\left(\sigma_{xx} + \sigma_{yy}\right)\right]$$

$$u_{zy} = \frac{(1+\nu)}{E}\sigma_{zy}$$

$$u_{zx} = \frac{(1+\nu)}{E}\sigma_{zx}$$

$$u_{xy} = \frac{(1+\nu)}{E}\sigma_{xy}$$

$$\sigma_{xx} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{xx} + \nu\left(u_{yy} + u_{zz}\right)\right]$$

$$\sigma_{yy} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{yy} + \nu\left(u_{xx} + u_{zz}\right)\right]$$

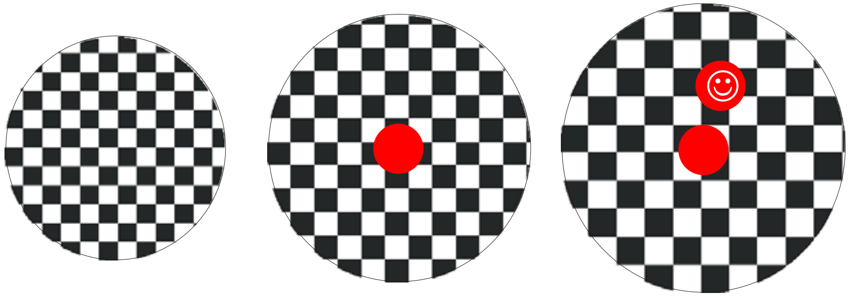
$$\sigma_{zz} = \frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{zz} + \nu\left(u_{xx} + u_{yy}\right)\right]$$

$$\sigma_{zy} = \frac{E}{(1+\nu)}u_{zy}$$

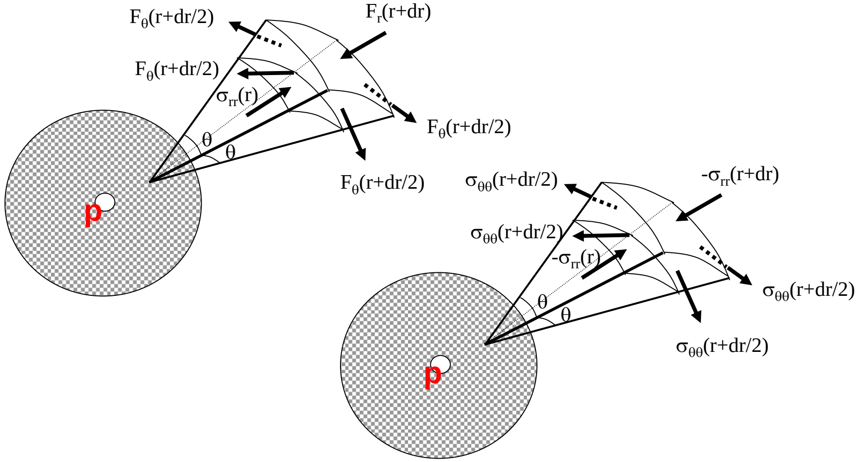
$$\sigma_{zx} = \frac{E}{(1+\nu)}u_{zx}$$

$$\sigma_{xy} = \frac{E}{(1+\nu)}u_{xy}$$

Long range attractive elastic interaction



Equilibrium of forces



$$-\sigma_{rr}\left[r+dr\right]\times\theta^2\left(r+dr\right)^2 + 4\sigma_{\theta\theta}\left[r+{dr}/{2}\right]\times\theta\times r\times\frac{\theta}{2}dr + \sigma_{rr}\left[r\right]\times\theta^2\times r^2 = 0$$

Equation for displacements *u(r)*

$$-\sigma_{rr}[r+dr]\times\theta^2(r+dr)^2+4\sigma_{\theta\theta}\left[r+{dr}/{2}\right]\times\theta\times r\times\frac{\theta}{2}dr+\sigma_{rr}[r]\times\theta^2\times r^2=0$$

Keeping terms to first order only we obtain $r^2\frac{d\sigma_{rr}}{dr}+2r\sigma_{rr}-2r\sigma_{\theta\theta}=0$

$$\sigma_{rr}=\frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{rr}+\nu(u_{\theta\theta}+u_{\theta\theta})\right]$$

$$\sigma_{\theta\theta}=\frac{E}{(1+\nu)(1-2\nu)}\left[(1-\nu)u_{\theta\theta}+\nu(u_{rr}+u_{\theta\theta})\right]$$

$$u_{rr}=\frac{du}{dr}$$

$$u_{\theta\theta}=\frac{u}{r}$$

$$r^2\frac{d^2u}{dr^2}+2r\frac{du}{dr}-2u=0$$

Solution for displacements *u(r)*

The general solution of $r^2\frac{d^2u}{dr^2}+2r\frac{du}{dr}-2u=0$

The displacement is of the form $u(r)=ar+\frac{b}{r^2}$

and the strains

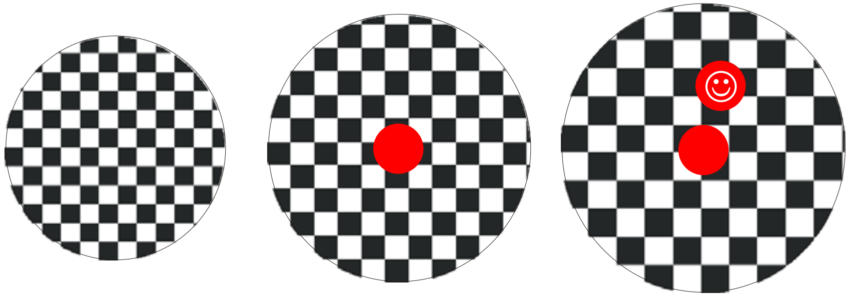
$$u_{rr}=\frac{du}{dr}=a-\frac{2b}{r^3}$$

$$u_{\theta\theta}=\frac{u}{r}=a+\frac{b}{r^3}$$

and the local volume dilation

$$\left.\frac{\Delta V}{V}\right|_{matrixl}=u_{rr}+2u_{\theta\theta}=3a=P\frac{2(1-2\nu)^2}{E(1-\nu)}$$

Long range attractive elastic interaction



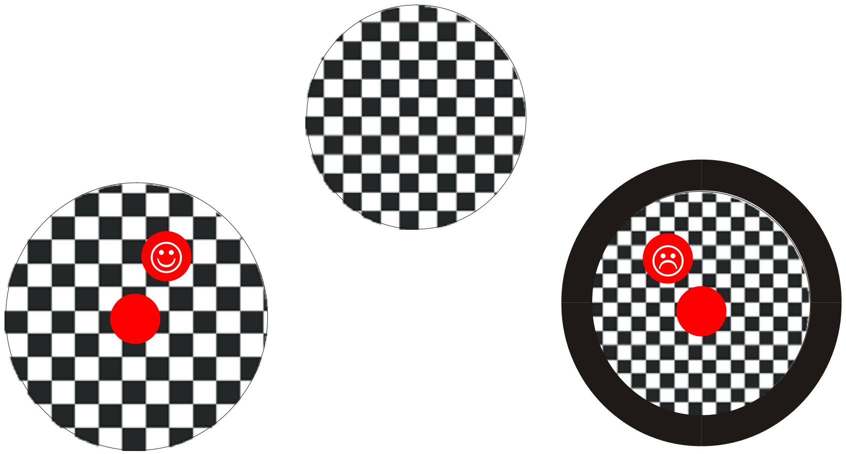
$$\left.\frac{\partial(\mu/T)}{\partial(1/T)}\right|_{p,n}=\left.\frac{\partial H}{\partial n}\right|_{p,T}\equiv\bar{H}$$

$$\frac{\partial}{\partial p}\left(\left.\frac{\partial(\mu/T)}{\partial(1/T)}\right|_{p,n}\right)=\frac{\partial}{\partial(1/T)}\left(\left.\frac{\partial(\mu/T)}{\partial p}\right|_{T,n}\right)=\bar{V}=\left.\frac{\partial\bar{H}}{\partial p}\right|_{n,T}$$

$$\left(-\frac{\partial\bar{H}}{\partial\ln V}\right)=B\bar{V}$$

For PdH_x: $\delta\left(\Delta\bar{H}\right)=-324\frac{\mathrm{kJ}}{\mathrm{molH}}\left(\frac{\delta V}{V}\right)$

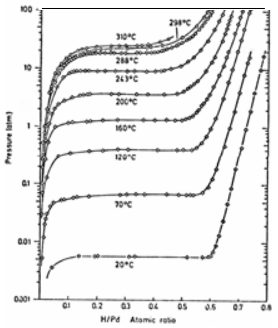
Effect of boundary conditions on H-H interaction

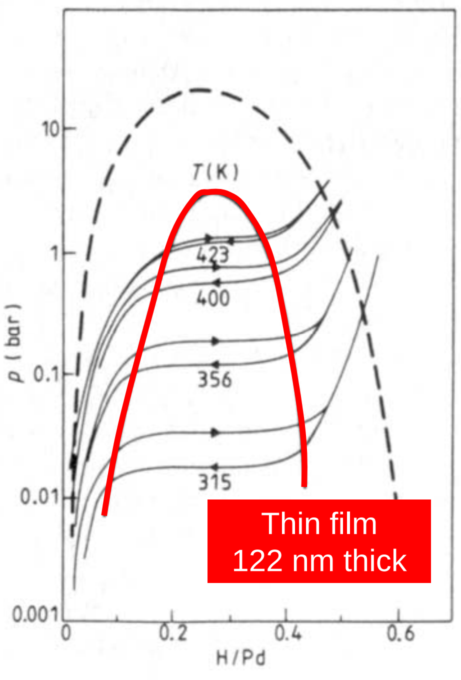


attractive

repulsive

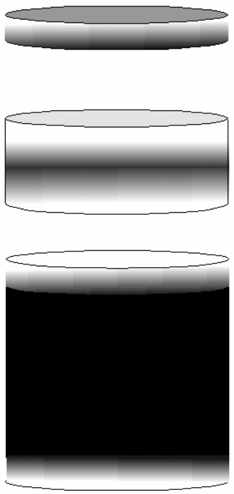
T_c lowering in PdH_x films

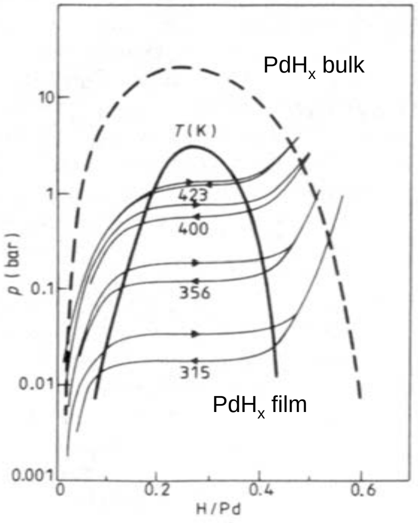




Thin film
122 nm thick

Shape dependence of macroscopic hydrogen density modes





PdH_x bulk

PdH_x film

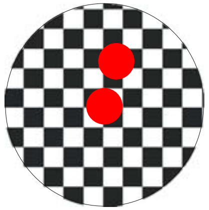
H in alloys and compounds II

$$\mu_H = kT\ln\left(\frac{c_H}{1-c_H}\right)+\varepsilon_0+\varepsilon n c_H$$

leads to Fermi statistics for H in M

$$c_H = \frac{1}{e^{\frac{\varepsilon_0+\varepsilon n c_H-\mu_H}{kT}}+1}$$

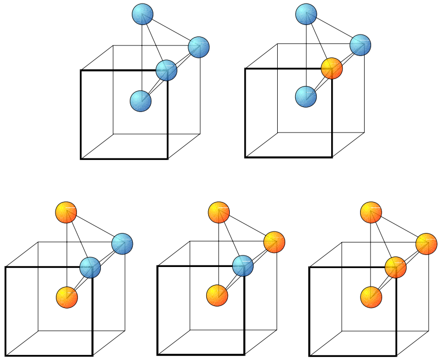
$$c = \sum g_j c_j$$



Elastic interaction not site dependent ⇒ depends only on total concentration c

$$c_j = \frac{1}{e^{\frac{\varepsilon_j+f(c,T)-\mu_H}{kT}}+1}$$

H in alloys and compounds

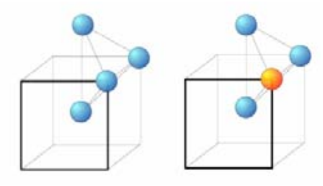


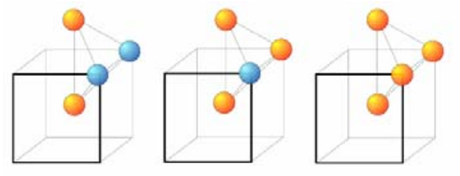
$$c = \sum g_j c_j$$

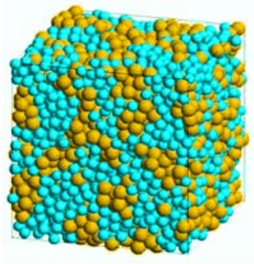
$$c_j = ?$$

Multi-site lattice-gas model

H occupies tetrahedral sites formed of (4-j)-Mg and j-V atoms.
There are 5 clusters $1 \le j \le 5$







Multi-site lattice-gas model

H occupies tetrahedral sites formed of (4-j)-Mg and j-V atoms.
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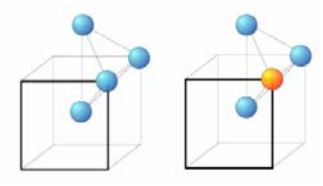
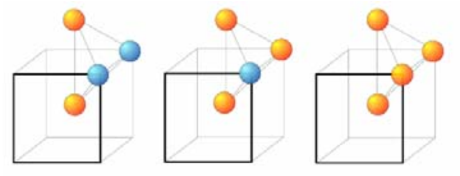
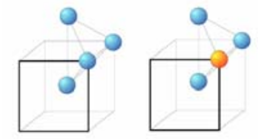


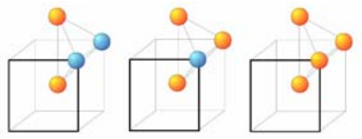


$$c = \sum g_j x_j$$

$$x_j = \frac{N_j^H}{N_j}$$

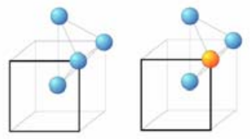
Pair probabilities in a Mg_yV_{1-y} alloy

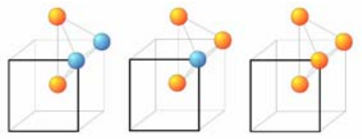




$$P_{V\text{-}V} = (1-y)$$
$$P_{V\text{-}Mg} = y$$
$$P_{Mg\text{-}V} = (1-y)$$
$$P_{Mg\text{-}Mg} = y$$

Chemical Short Range Order Parameter S





$$P_{V\text{-}V} = (1-y) + ys$$
$$P_{V\text{-}Mg} = y - ys$$
$$P_{Mg\text{-}V} = (1-y) - (1-y)s$$
$$P_{Mg\text{-}Mg} = y + (1-y)s$$

$S = 0$	random alloy
$S = 1$	fully segregated

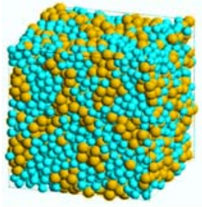
Limiting cases of the CSRO parameter

random alloy

S=0

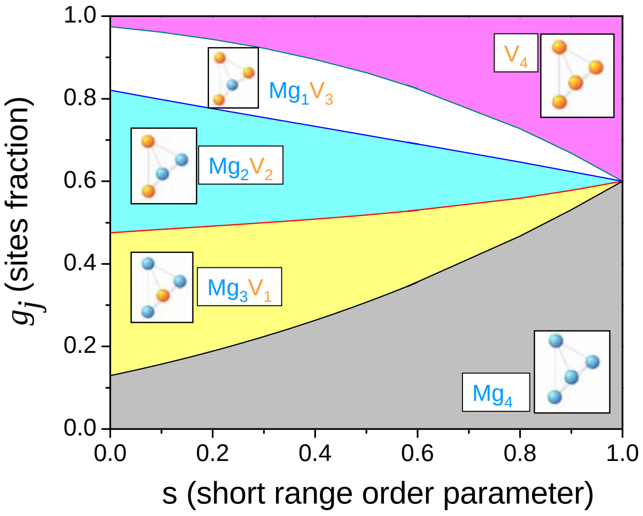
fully segregated

S=1

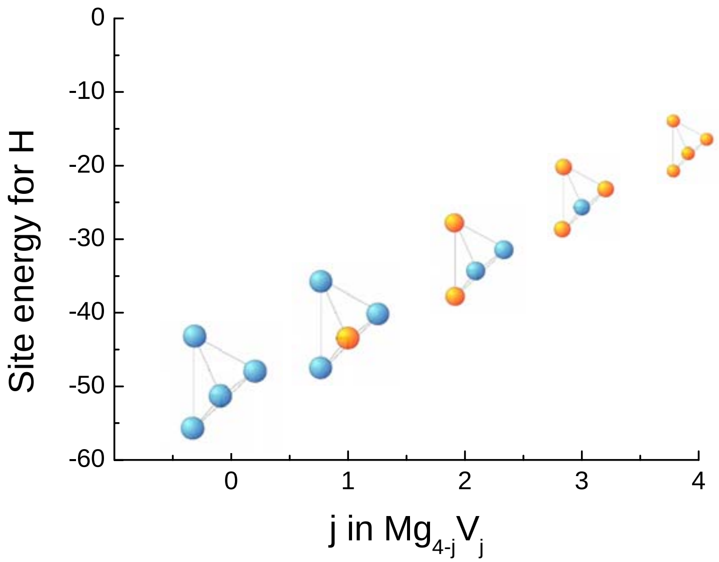


Site fraction in a $Mg_{60}V_{40}$ alloy

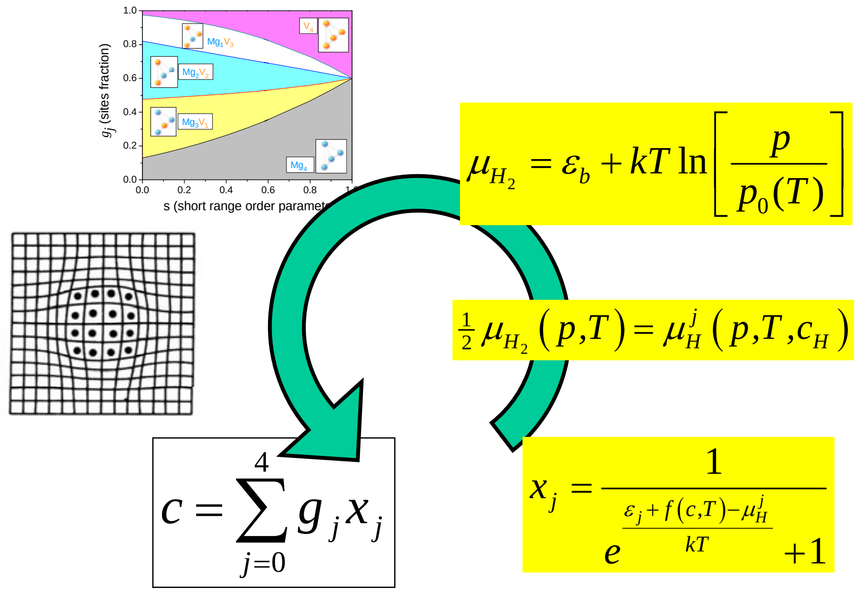
g_j = Fraction of sites of type *j* as a function of s (chemical short range order) for a certain composition.



Site energy for H in a free cluster



H in alloys

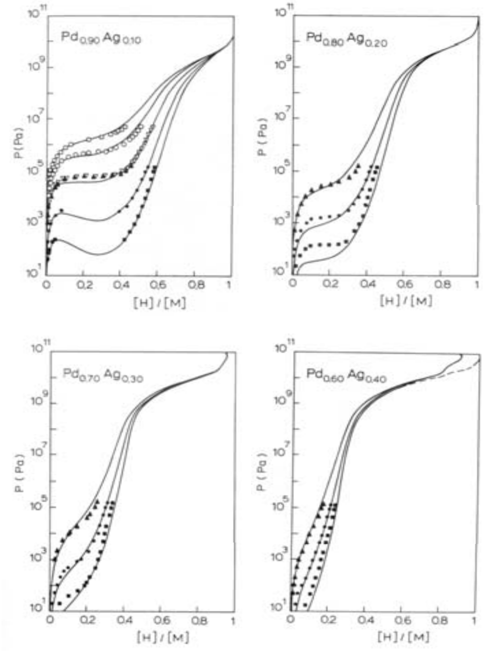


$$\mu_{H_2} = \varepsilon_b + kT \ln\left[\frac{p}{p_0(T)}\right]$$

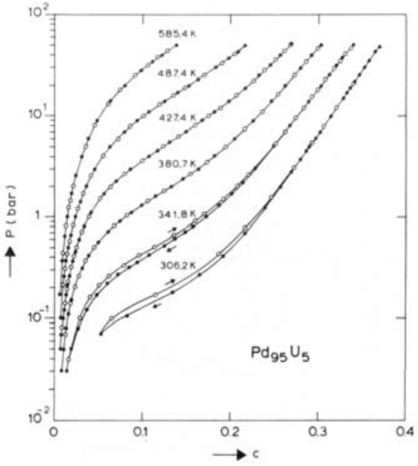
$$\tfrac{1}{2}\mu_{H_2}(p,T) = \mu_H^j(p,T,c_H)$$

$$x_j = \frac{1}{e^{\frac{\varepsilon_j + f(c,T) - \mu_H^j}{kT}} + 1}$$

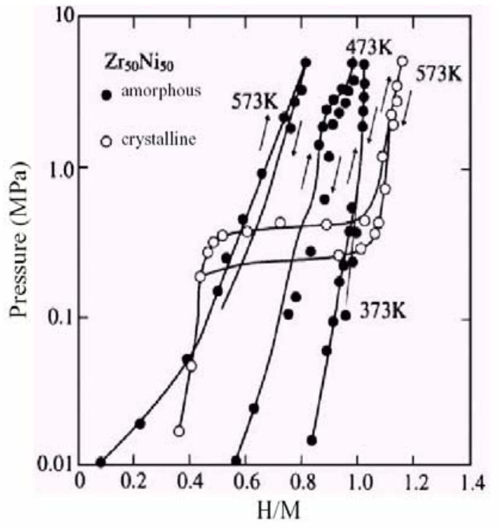
$$c = \sum_{j=0}^{4} g_j x_j$$



Sloping isotherms in alloys



H in amorphous metals



In amorphous materials there is a continuous distribution of site energies and the plateaus disappear completely

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