Working Group on H isotopes and He in Materials

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Thermodynamic Explanation for the Hysteresis in Metal-Hydrogen Systems

R. B. Schwarz(1) and A. G. Khachaturyan(2)

(1) Materials Science and Technology Division
Los Alamos National Laboratory, Mail Stop G755
Los Alamos, NM 87545

(2) Department of Ceramics and Materials Engineering
Rutgers University
P.O. Box 909, Piscataway, NJ 08855-0909

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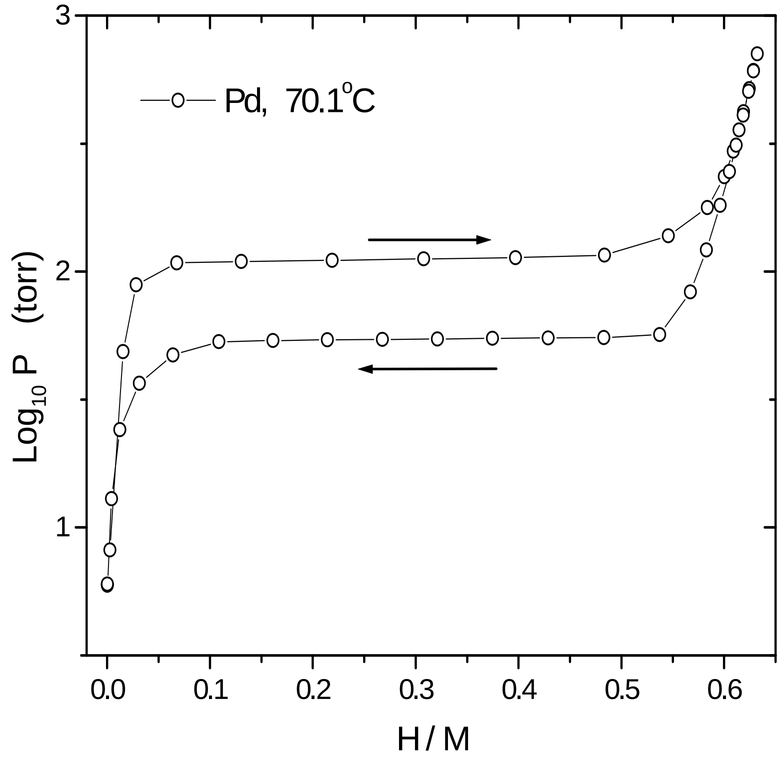
The Pressure-composition isotherms in Metal-H Systems often have Hysteresis



- Conventional thermodynamics cannot explain the hysteresis
- Hysteresis reflects a non-conservative (dissipative) mechanism
- Various dissipative mechanisms have been suggested (e.g., dislocation generation)

TEM: precipitates in the $\alpha + \beta$ region of Pd H [Ho et al. (1978)]

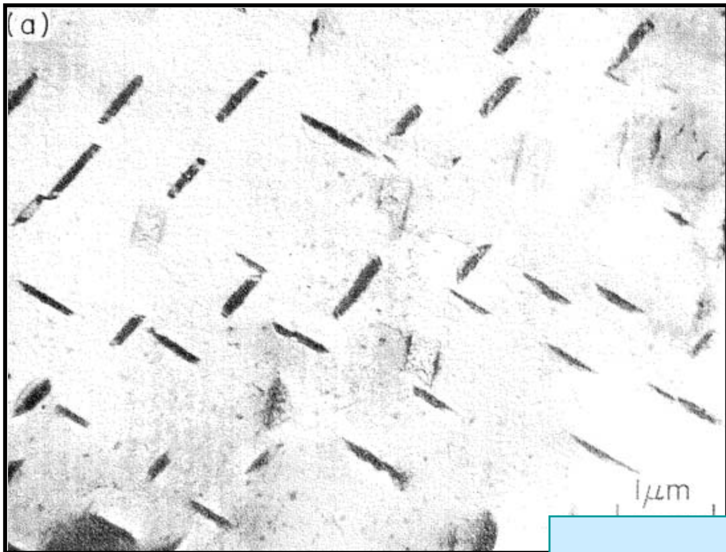


plate-shaped
β – phase
precipitates on
(100) planes
in the α matrix

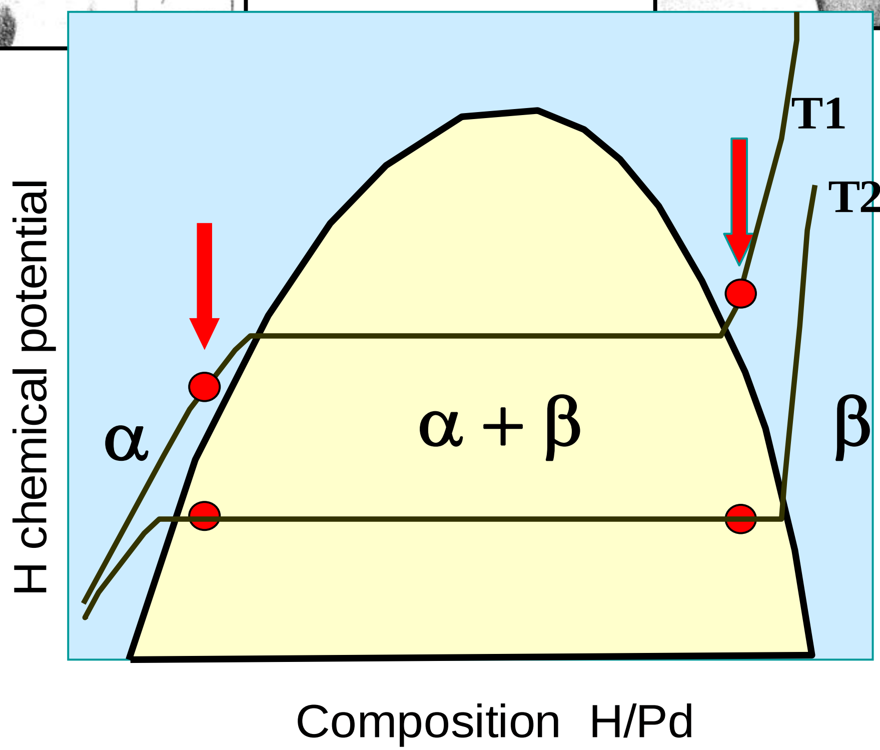


plate-shaped
α – phase
precipitates on
(100) planes
in the β matrix

Effects of Coherent Interfaces in Two-Phase Systems:

Roytburt (1984), Cahn and Larché (1984):

- Decomposition in an elastically isotropic system producing a 2-phase coherent mixture
- Assumed crystal lattice parameters of the two phases are different but *do not depend on composition*. This gives:

$$\text{Elastic strain} \propto \omega(1-\omega)$$

Important results emerged from these works:

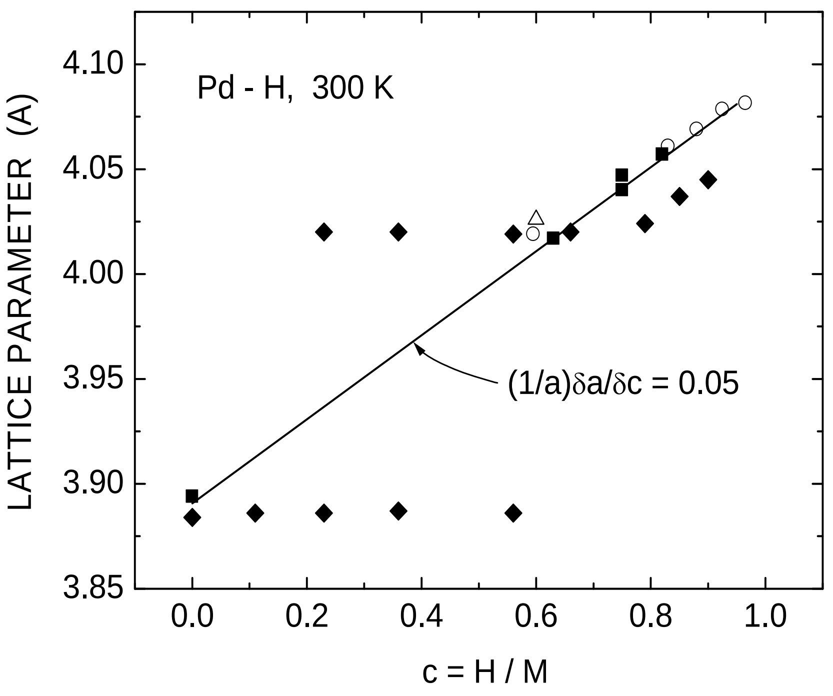
- Coherent equilibrium cannot be described by the common-tangent rule.
- Equilibrium fails to obey Gibbs thermodynamics.

Lee (1994)

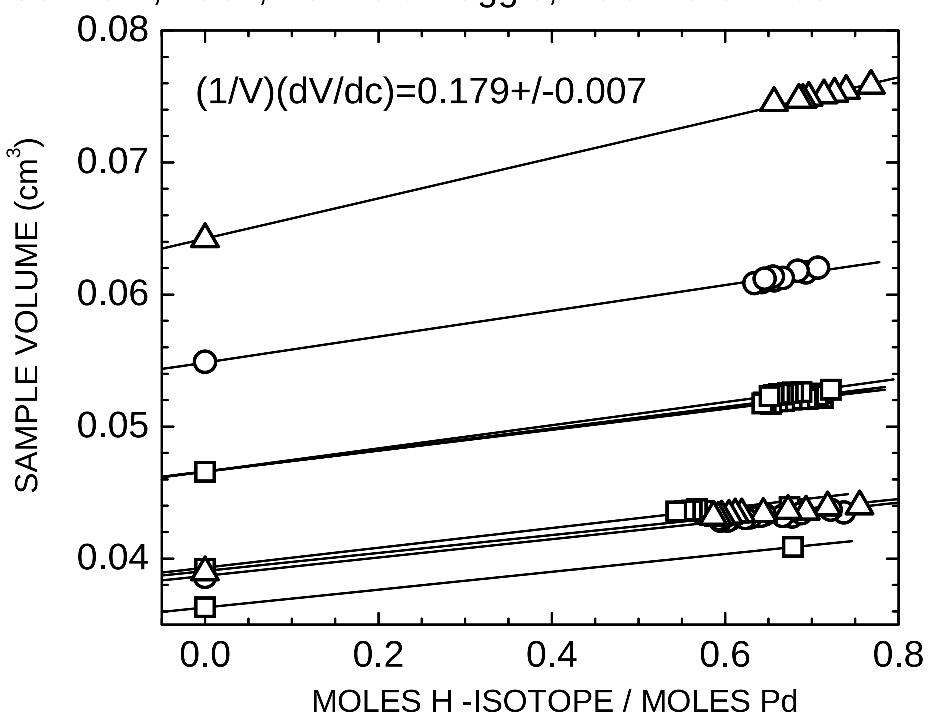
- If crystal lattice parameters do NOT follow Vegard's law, unusual effects expected for coherent interfaces should vanish.

H interstitial acts as dilatational center

Old literature data:



Schwarz, Bach, Harms & Tuggle, Acta Mater. 2004



Δ Protium

O Deuterium

□ Tritium

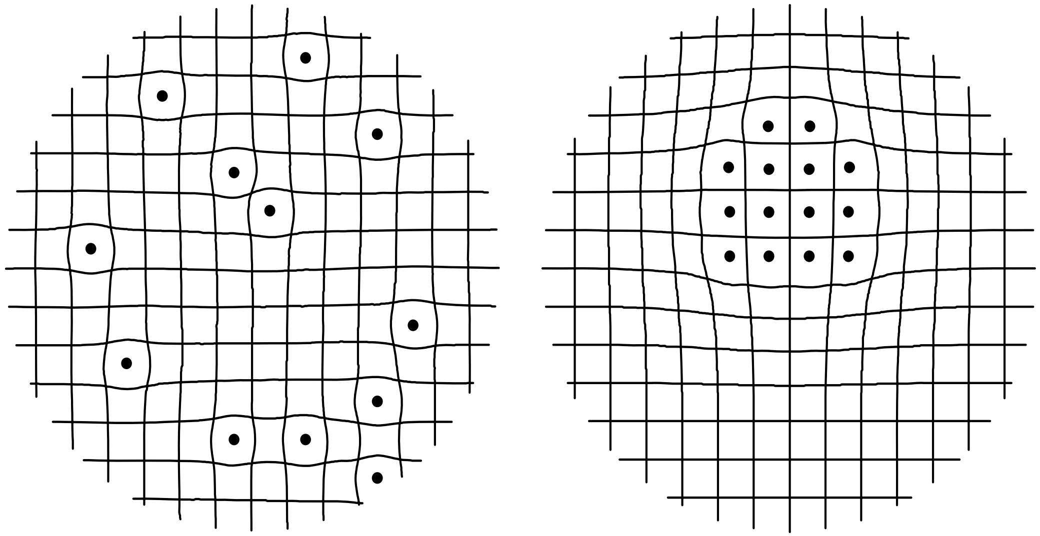
Vegard's law is a good approx. for the lattice parameter change

Elastic energy due to dilatational centers

Eshelby (1956):

(1) Elastic energy due to a concentration *c* of substitutional dilatational centers

$$E_{el} = N\, v_o G\, \frac{1+\sigma}{1-\sigma}\, \varepsilon_o^2\; c\,(1-c) \qquad\qquad \varepsilon_o = \frac{1}{a}\,\frac{\partial a}{\partial c}$$



(a) (b)

(2) E_{el} is configurationally independent

Free energy for a two-phase system of α and β phases

Gibbs free energies of the α and β phases in their single-phase states

$$G_\alpha(\mathrm{p}, \mathrm{T}, c_\alpha) = g_\alpha(\mathrm{p}, \mathrm{T}, c_\alpha) + \mathrm{A}\, c_\alpha (1 - c_\alpha)$$

$$G_\beta(\mathrm{p}, \mathrm{T}, c_\beta) = g_\beta(\mathrm{p}, \mathrm{T}, c_\beta) + \mathrm{A}\, c_\beta (1 - c_\beta)$$

where $$A = v_{\mathrm{o}}\; G\; \frac{1+\sigma}{1-\sigma}\varepsilon_o^2$$

Incoherent interfaces:

$$G^{\mathrm{incoh}}(\mathrm{p}, \mathrm{T}, \mathrm{c}_\alpha, \mathrm{c}_\beta, \omega) = (1 - \omega)\,[g_\alpha(\mathrm{p}, \mathrm{T}, \mathrm{c}_\alpha) + \mathrm{A}\, \mathrm{c}_\alpha (1 - \mathrm{c}_\alpha)] + \omega\,[g_\beta(\mathrm{p}, \mathrm{T}, \mathrm{c}_\beta) + \mathrm{A}\, \mathrm{c}_\beta (1 - \mathrm{c}_\beta)]$$

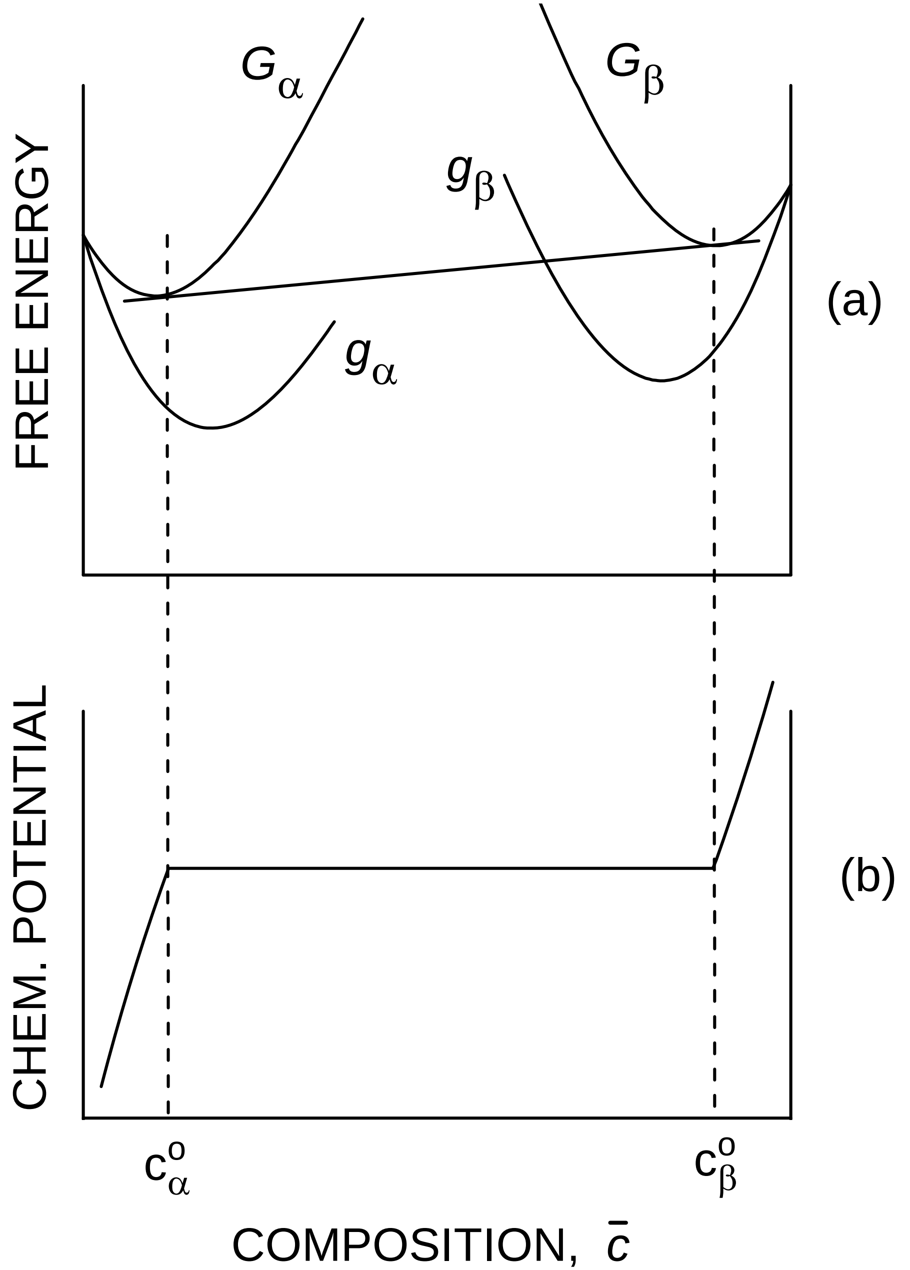
Coherent interfaces:

$$G^{\mathrm{coh}}(\mathrm{p}, \mathrm{T}, \mathrm{c}_\alpha) = (1 - \omega)\,[g_\alpha(\mathrm{p}, \mathrm{T}, \mathrm{c}_\alpha) + \mathrm{A}\, \mathrm{c}_\alpha (1 - \mathrm{c}_\alpha)] + \omega\,[g_\beta(\mathrm{p}, \mathrm{T}, \mathrm{c}_\beta) + \mathrm{A}\, \mathrm{c}_\beta (1 - \mathrm{c}_\beta)] + A\,(\mathrm{c}_\alpha - \mathrm{c}_\beta)^2\, \omega\, (1 - \omega)$$

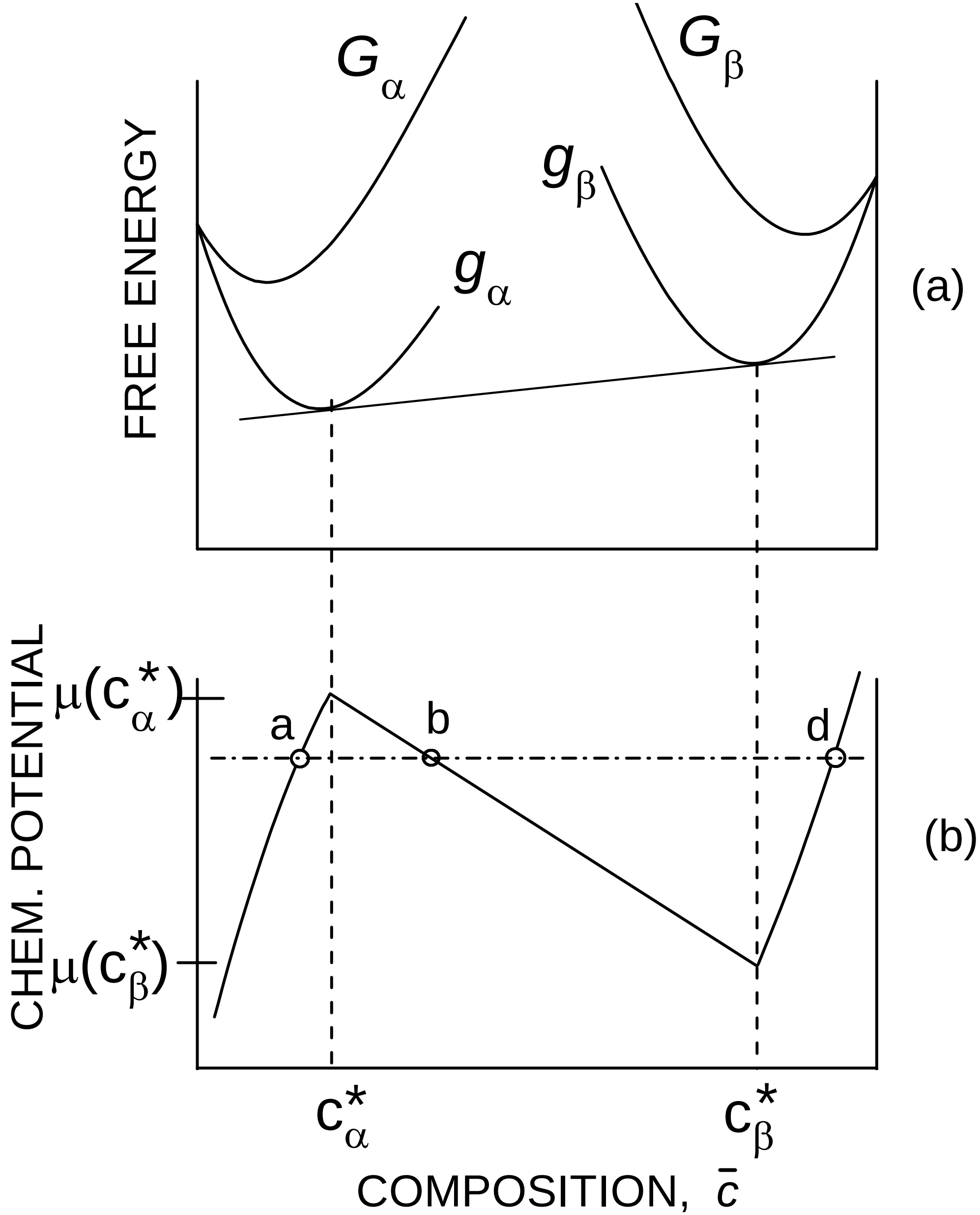
After some algebra we obtain:

$$G^{\mathrm{coh}}(\mathrm{p},\mathrm{T}, \mathrm{c}_{\alpha,}\, \mathrm{c}_{\beta,}\omega) = (1-\omega)\, g_\alpha(\mathrm{p}, \mathrm{T}, \mathrm{c}_\alpha) + \omega\, g_\beta(\mathrm{p}, \mathrm{T}, \mathrm{c}_\beta) + A\,[\mathrm{c}(1 - \mathrm{c})]$$

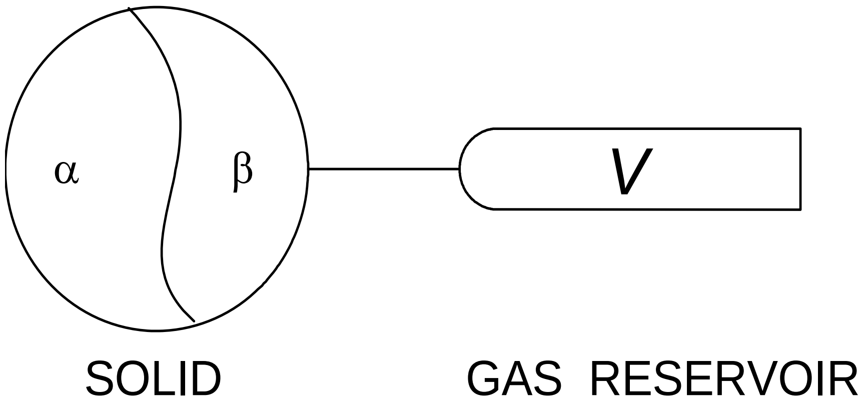
Incoherent Decomposition:



Coherent Decomposition:



Equilibrium in a two-phase coherent system in equilibrium with a source of interstitials



Open system:

$$V \rightarrow \infty$$

Pressure remains ≈ constant when solid exchanges interstitials with reservoir

Minimization of $G^{coh}(p,T, c_{a,}\ c_{b,}\omega)$ has no solution for range of c

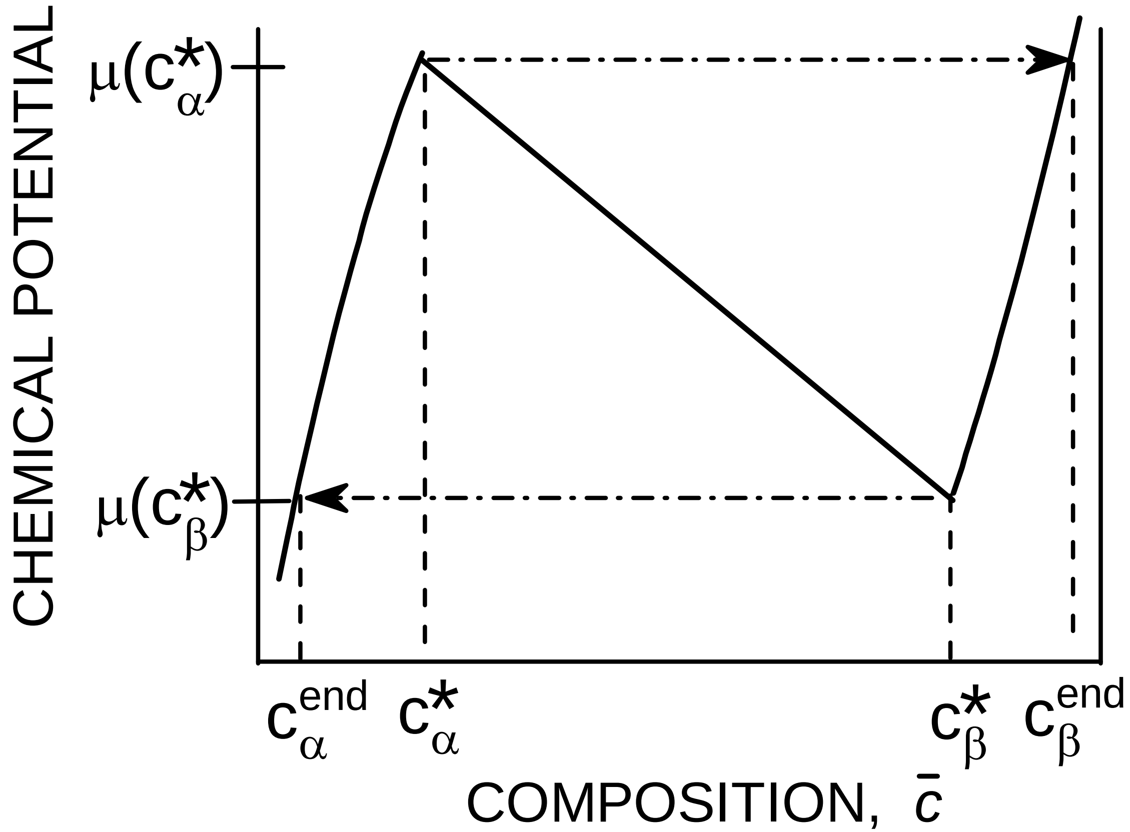
Closed system:

$$V \rightarrow 0$$

Total number of interstitials in the solid is constant

Minimization of G^{coh}(p,T, ca, cb,ω) has a solution for any value of c

Hysteresis for a coherent two-phase system in equilibrium with a source of interstitials at constant chemical potential (open system)



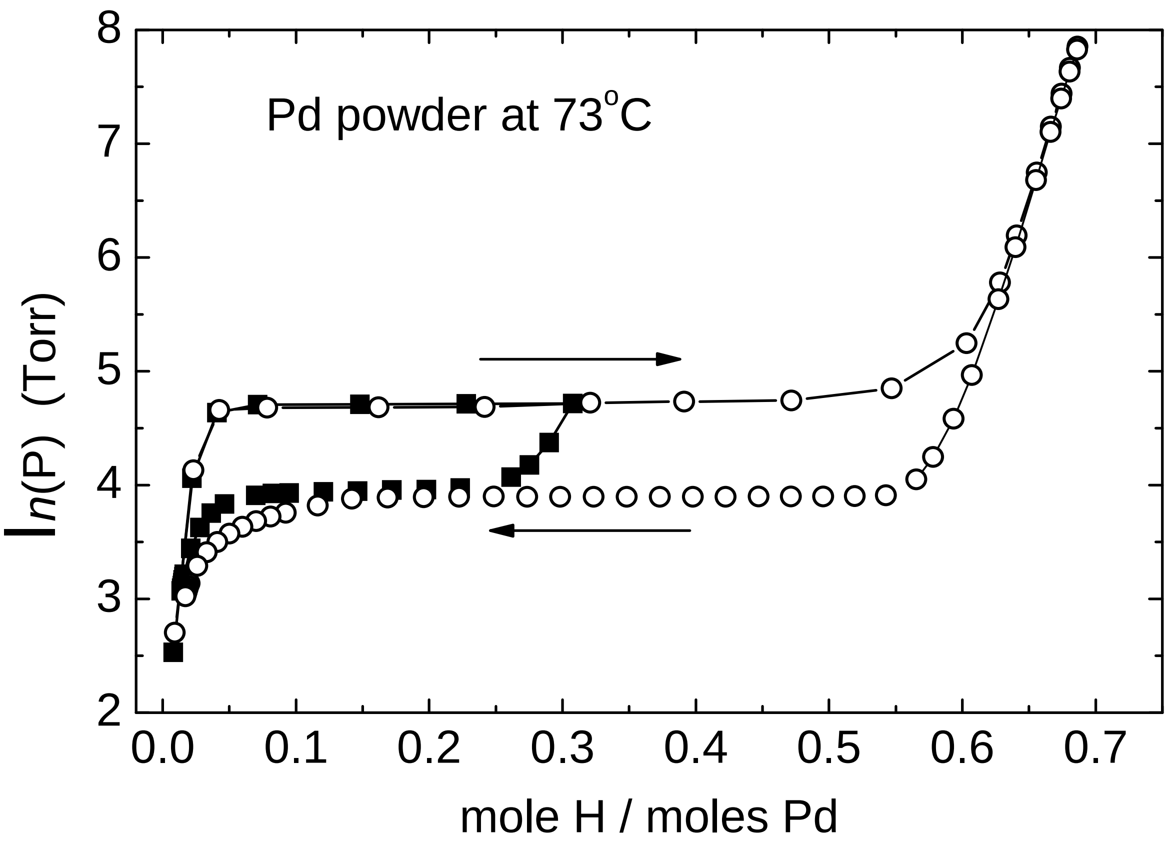
Model predicts that the hysteresis vanishes at a critical point:

$$\ell n \frac{P_1}{P_2} = \frac{4 v_o G \dfrac{1+\sigma}{1-\sigma} \varepsilon_o^2 (c_\beta^* - c_\alpha^*)}{kT}$$

Estimate for Pd crystal at 70 oC:

v_o = (a-Pd)³ / 4
G = C' = 25 GPa
σ = 0.44
εo = 0.058
c_β*-c_α* = 0.52
kT = 1.38E-23 x 340 J

Model: ln(*P1/P2*) = 2.6
Data: ln(*P1/P2*) = 0.9



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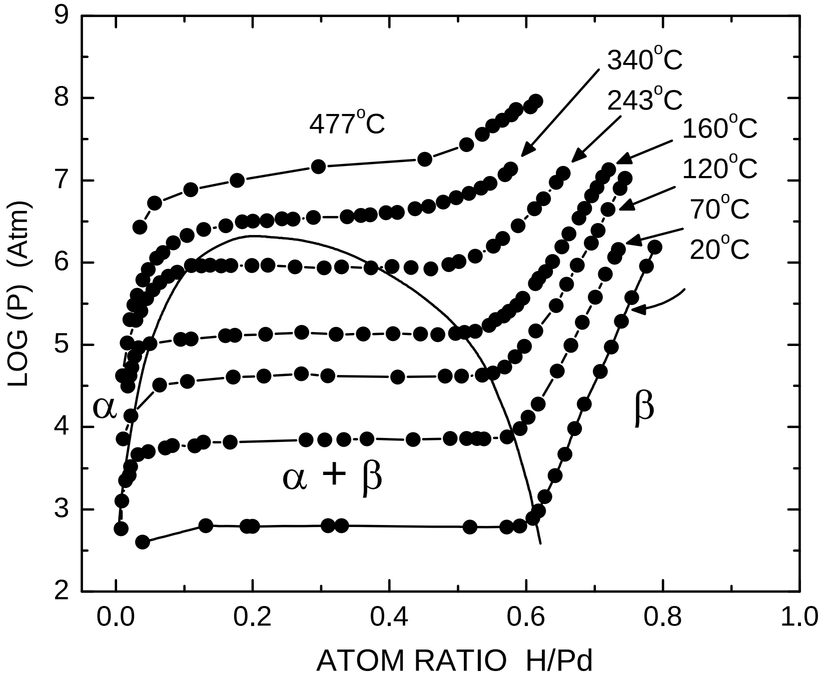
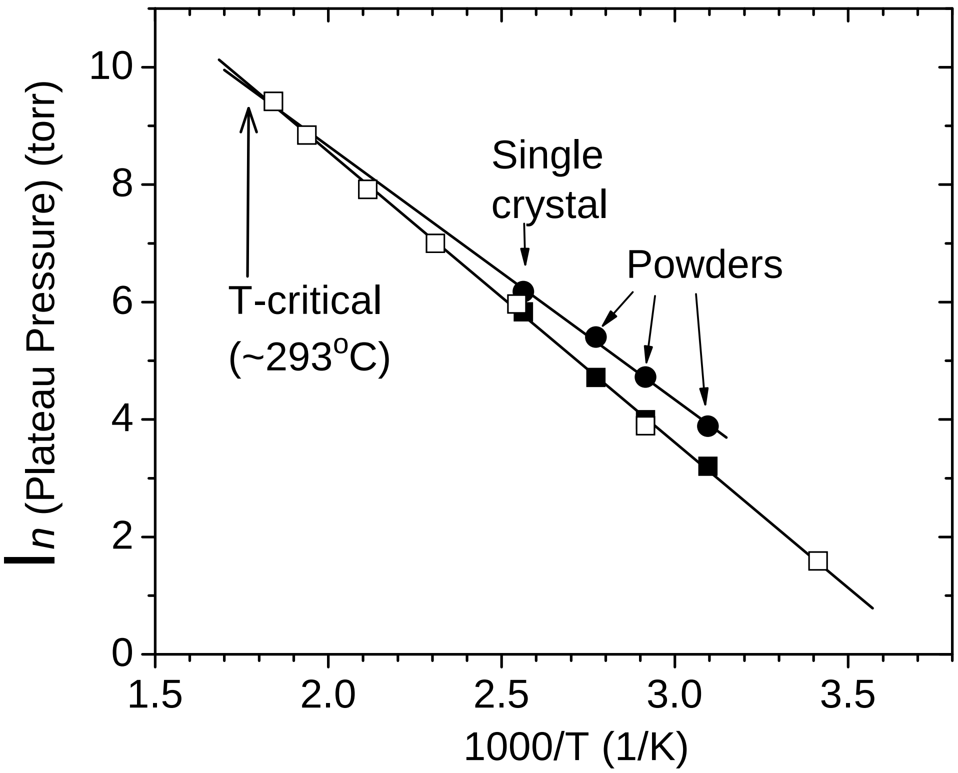
Model correctly predicts the miscibility-gap "critical point"

$$\ell n\ \frac{P_1}{P_2} = \frac{4 v_o G \dfrac{1+\sigma}{1-\sigma}\ \varepsilon_o^2 \,(c_\beta^* - c_\alpha^*)}{kT}$$





CONCLUSIONS:

- The coherency strain between the decomposing phases has a profound effect on the thermodynamics of the two-phase system.

- The coherency strain introduces a *macroscopic* thermodynamic barrier that cannot be surmounted by thermal fluctuations.

- The chemical potential for interstitials in a the two-phase region of a system with coherent interfaces depends on the average composition.

- In Metal-Hydrogen systems, the thermodynamic barrier causes hysteresis between the plateau pressures for absorption and desorption. We derive a quantitative expression for the hysteresis.

- For a metal-hydrogen system, the effects of the coherency strain depend on whether the system is open or closed

 Open system: the α and β phases cannot coexist.

 Closed system: Coexistence of the α and β phases is possible but then The chemical potential of the interstitials, μ, is a function of ω.