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Thermodynamics of Gaseous Hydrogen and Hydrogen Transport in Metals

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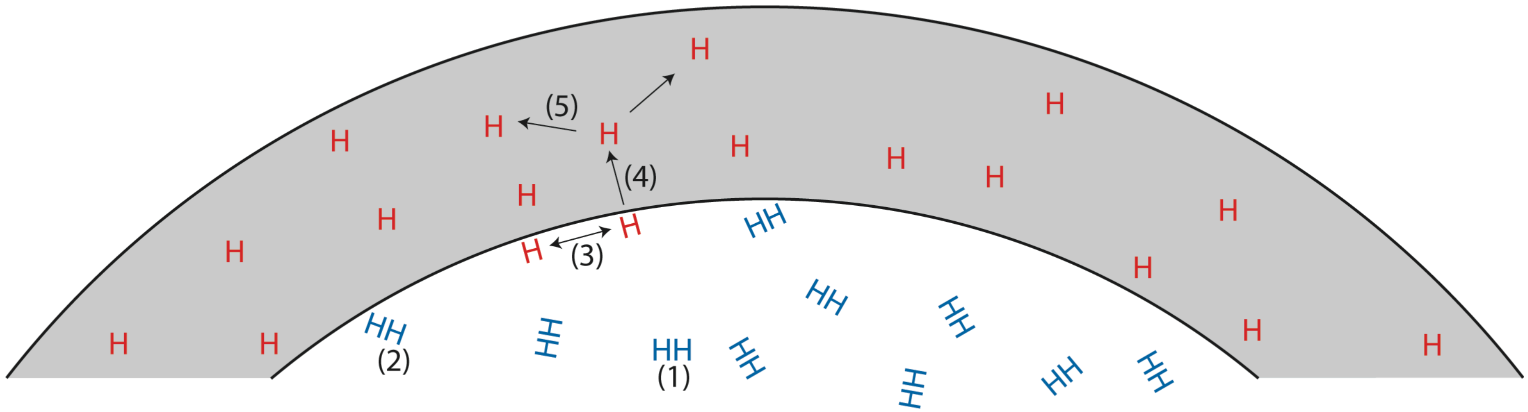
Hydrogen in Metals



Chemical Equilibrium: $\frac{1}{2}H_2 \leftrightarrow \underline{H}$

(1) Hydrogen gas

(2) Physisorption

(3) Dissociation

(4) Dissolution

(5) Diffusion

Solubility $K = \frac{c_o}{\sqrt{f}}$

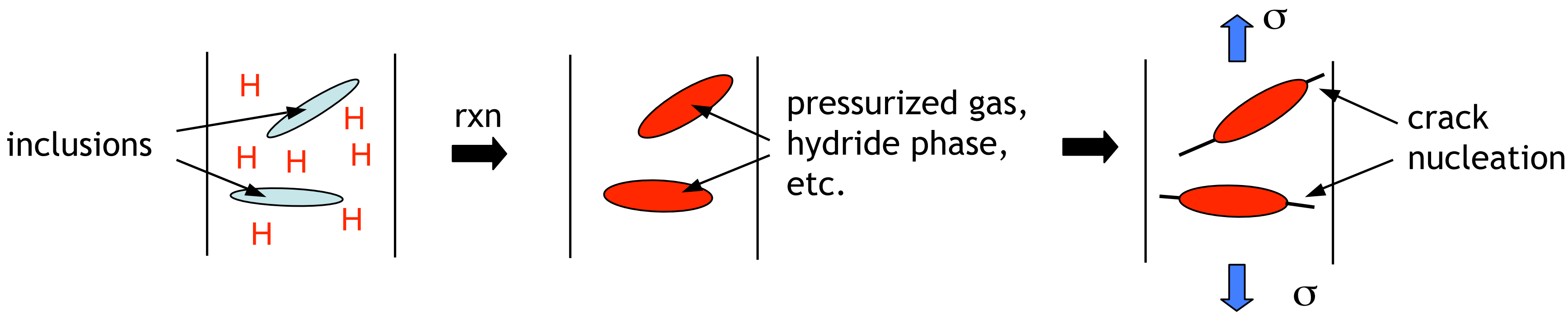
Diffusivity $J = -D\frac{dc}{dx}$

Permeability $\phi \equiv DK$

Hydrogen-Assisted Fracture Mechanisms in Metals

Hydrogen attack:

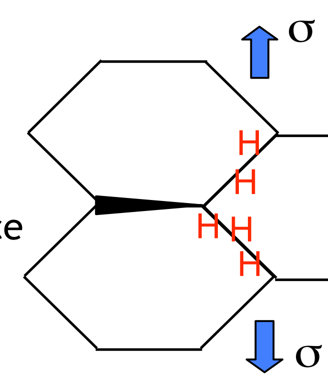
chemical reaction of atomic hydrogen with microstructural features

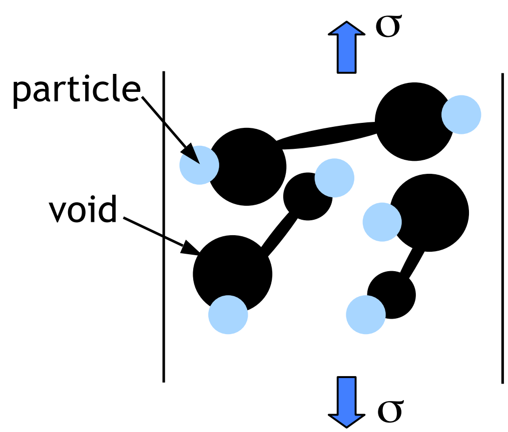


Hydrogen solute effects:

solute hydrogen enhanced failure of interfaces and deformation mechanisms

Hydrogen accumulation at interfaces affects strength of interface (grain boundaries, second phases, inclusions)



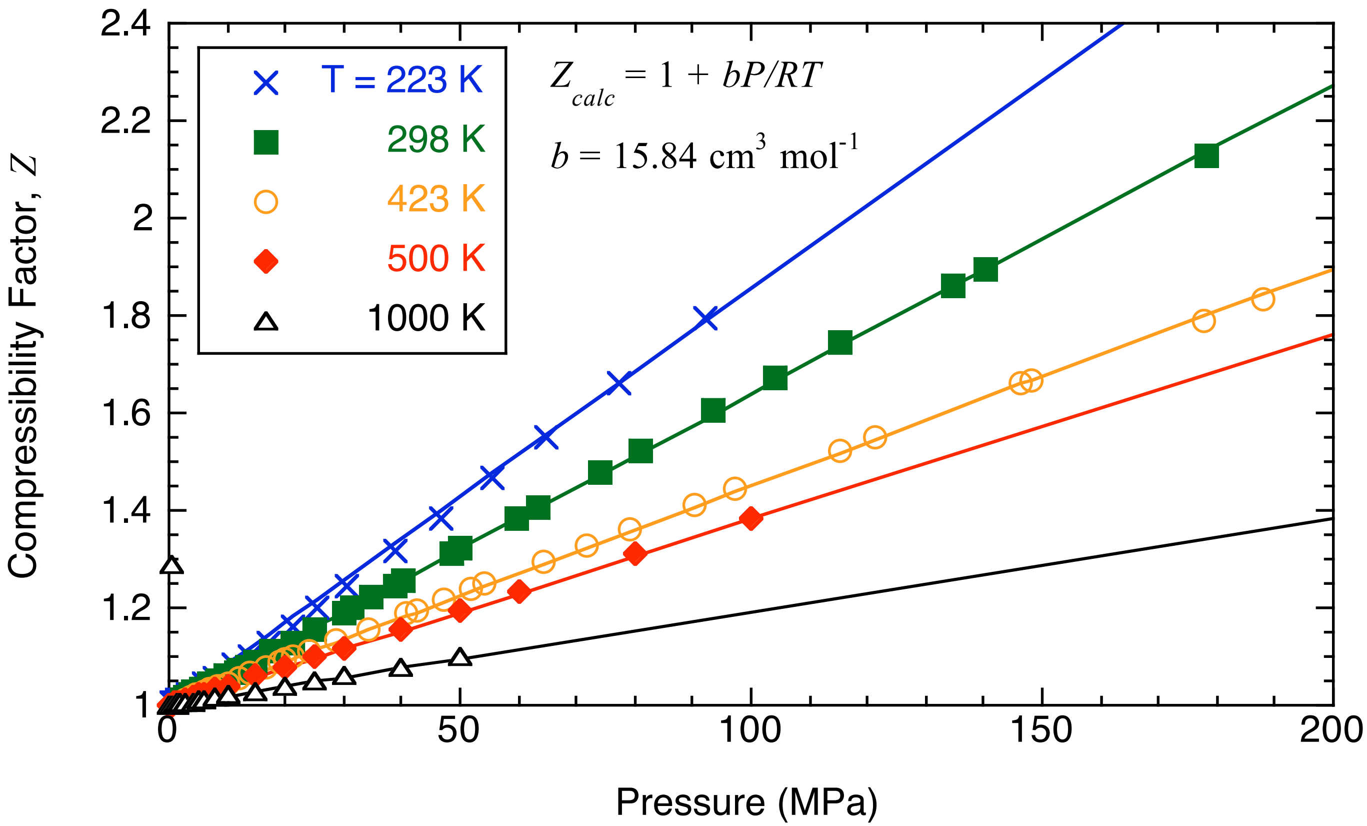


Hydrogen enhanced shear localization

Outline

- Thermodynamics of high-pressure hydrogen
  - Equation of state for hydrogen
  - Fugacity in gas mixtures containing hydrogen
- Equilibrium hydrogen content in metals (thermodynamics)
  - Sievert's Law
  - Stress
  - Hydrogen trapping
- Hydrogen transport in metals, diffusivity (kinetics)
  - Stress
  - Hydrogen trapping

Non-Ideal Behavior of High-Pressure Hydrogen Described by Abel-Noble EOS: $V_m = RT/P + b$



Fitting data of Michels et al (1955) for
$223 < T < 473$ K
$P < 200$ MPa

$b = 15.84\ cm^3\ mol^{-1}$

- Compressibility factor $Z = PV_m/RT$
  - for ideal gas $Z = 1$ Ideal gas EOS $V_m^o = RT/P$
  - at high pressure $Z > 1$ Abel-Noble EOS $V_m = V_m^o + b$

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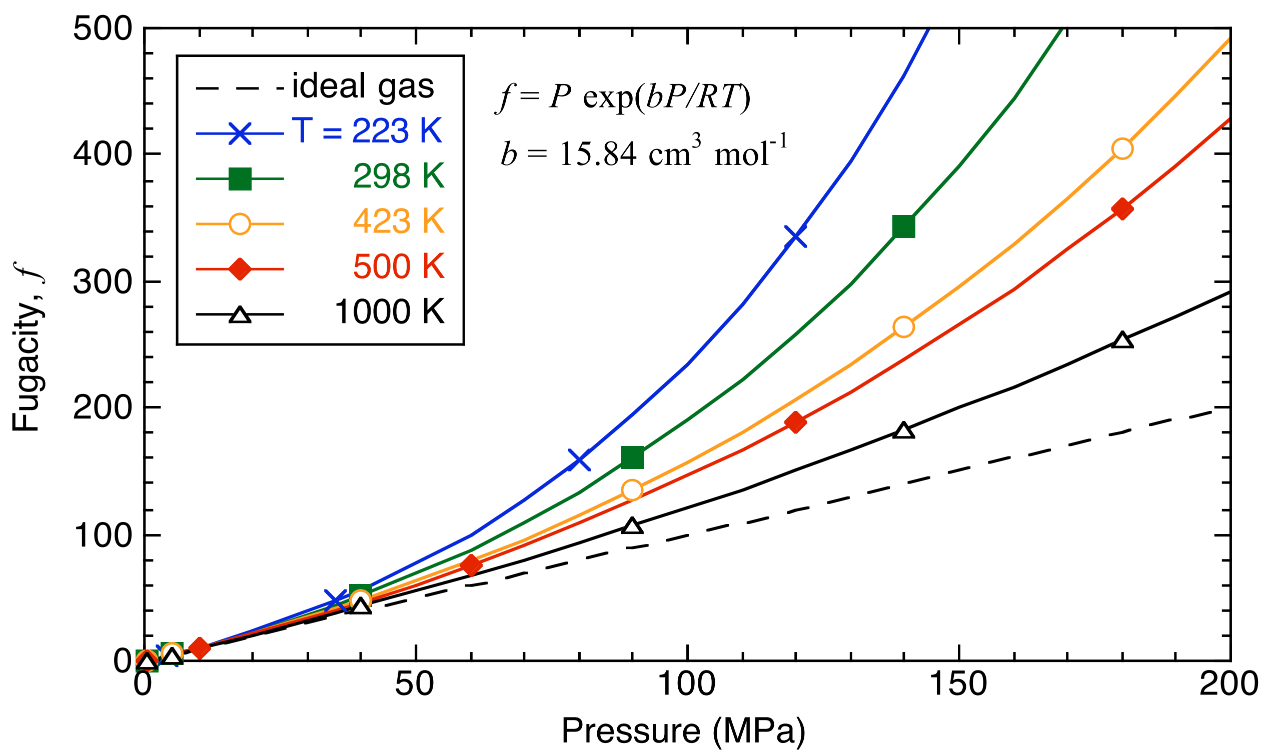
Fugacity of Hydrogen Gas

Thermodynamic Quantity Describing Non-Ideal Behavior

- Chemical potential of gas: $\mu = \mu_o + RT\ln\left(\frac{f}{f_o}\right)$
- Definition of fugacity: $\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{V_m}{RT} - \frac{1}{P}\right)dP$

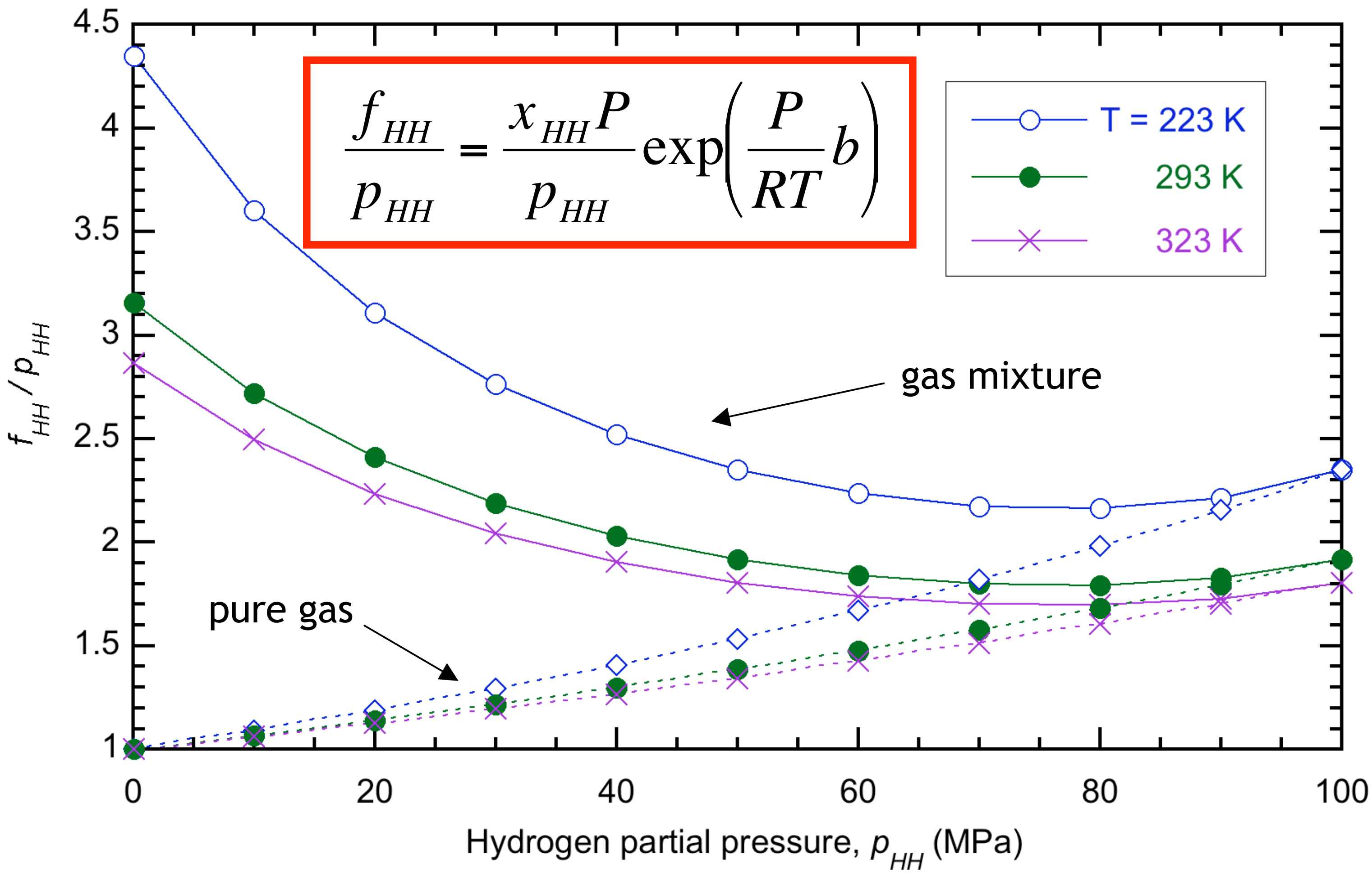


For Abel-Noble equation of state

$$\frac{f}{P} = \exp\left(\frac{P}{RT}b\right)$$

Fugacity of Hydrogen in Ideal Gas Mixtures

Helium-Hydrogen gas mixtures: $P = 100\text{MPa} = p_{HH} + p_{He}$



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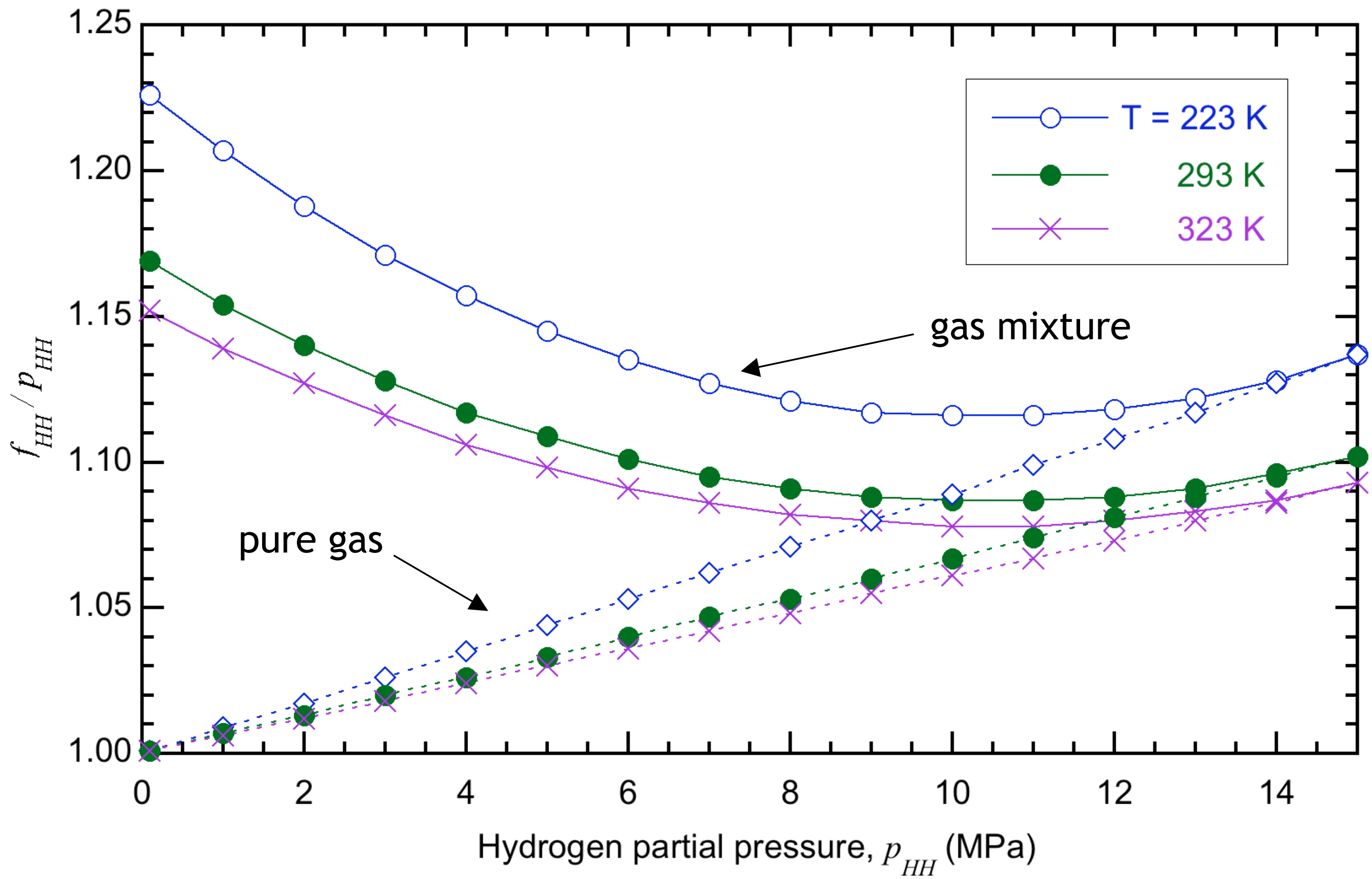
Fugacity of Hydrogen in Ideal Gas Mixtures

Helium-Hydrogen gas mixtures: $P = 15\text{MPa} = p_{HH} + p_{He}$



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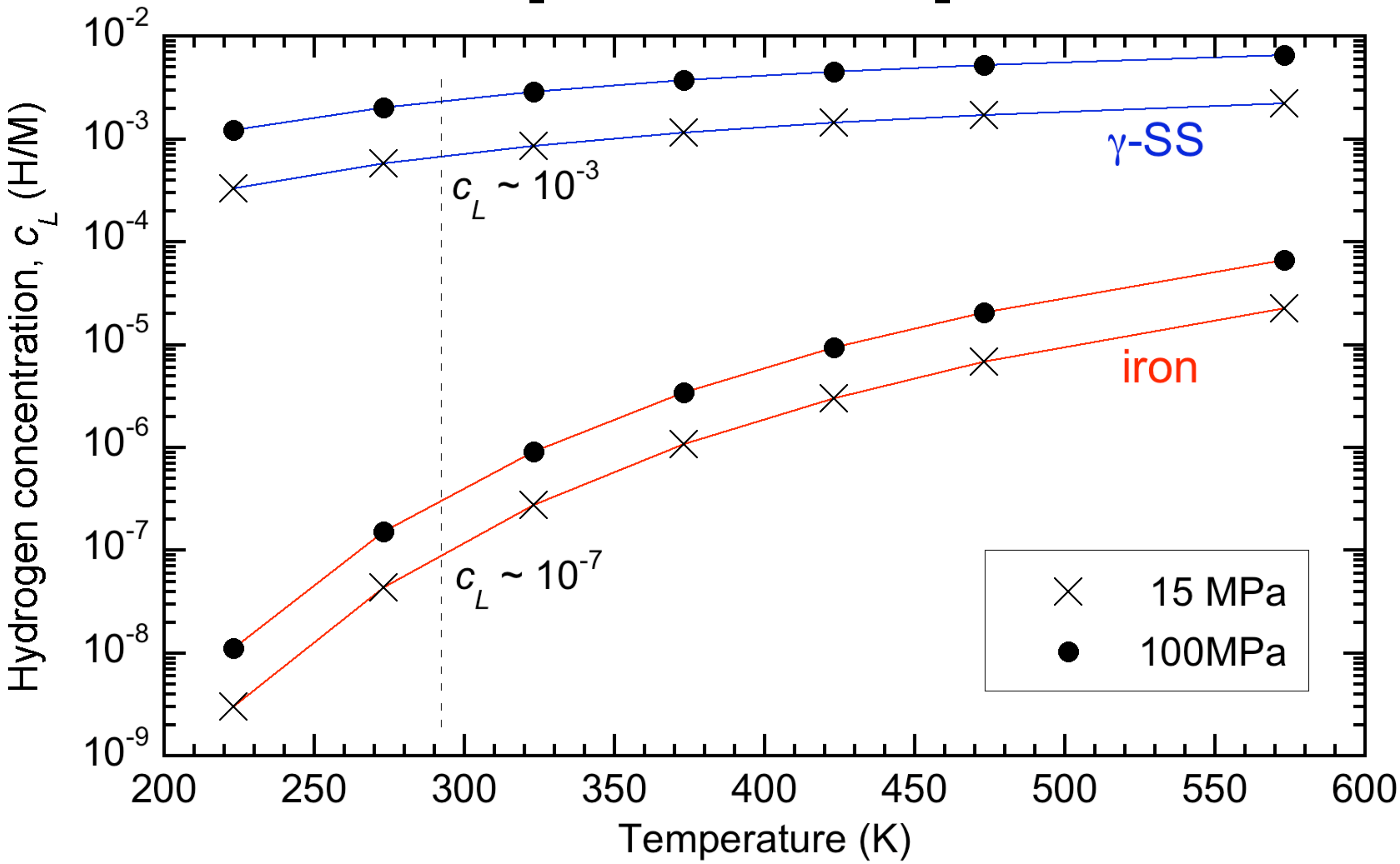
Concentration of Hydrogen in Metals

$$c_o = \left[K_o \exp\left(-\Delta H /_{RT}\right)\right] f_{HH}^{\;1/2}$$



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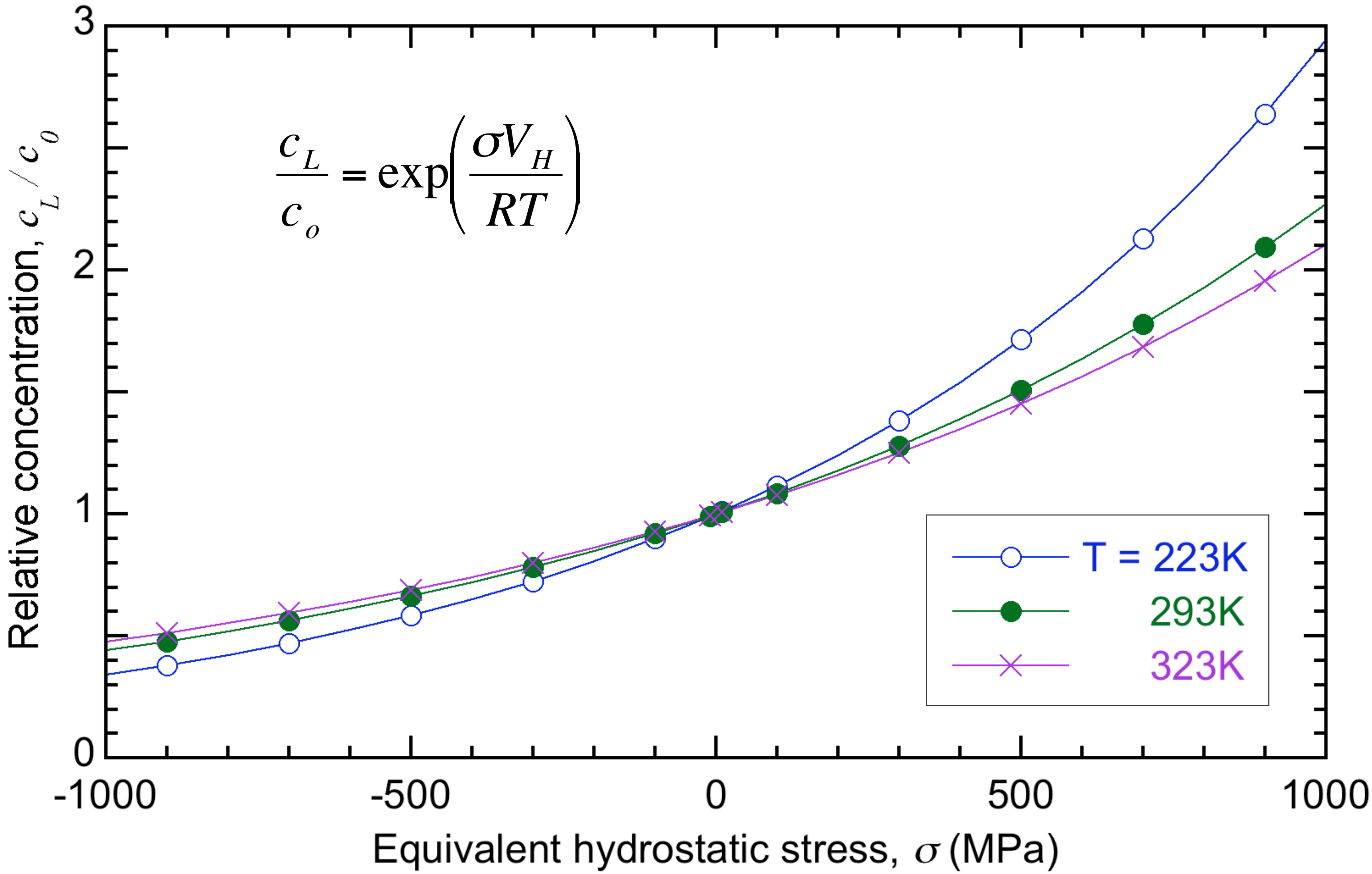
Stress affects hydrogen content in metals



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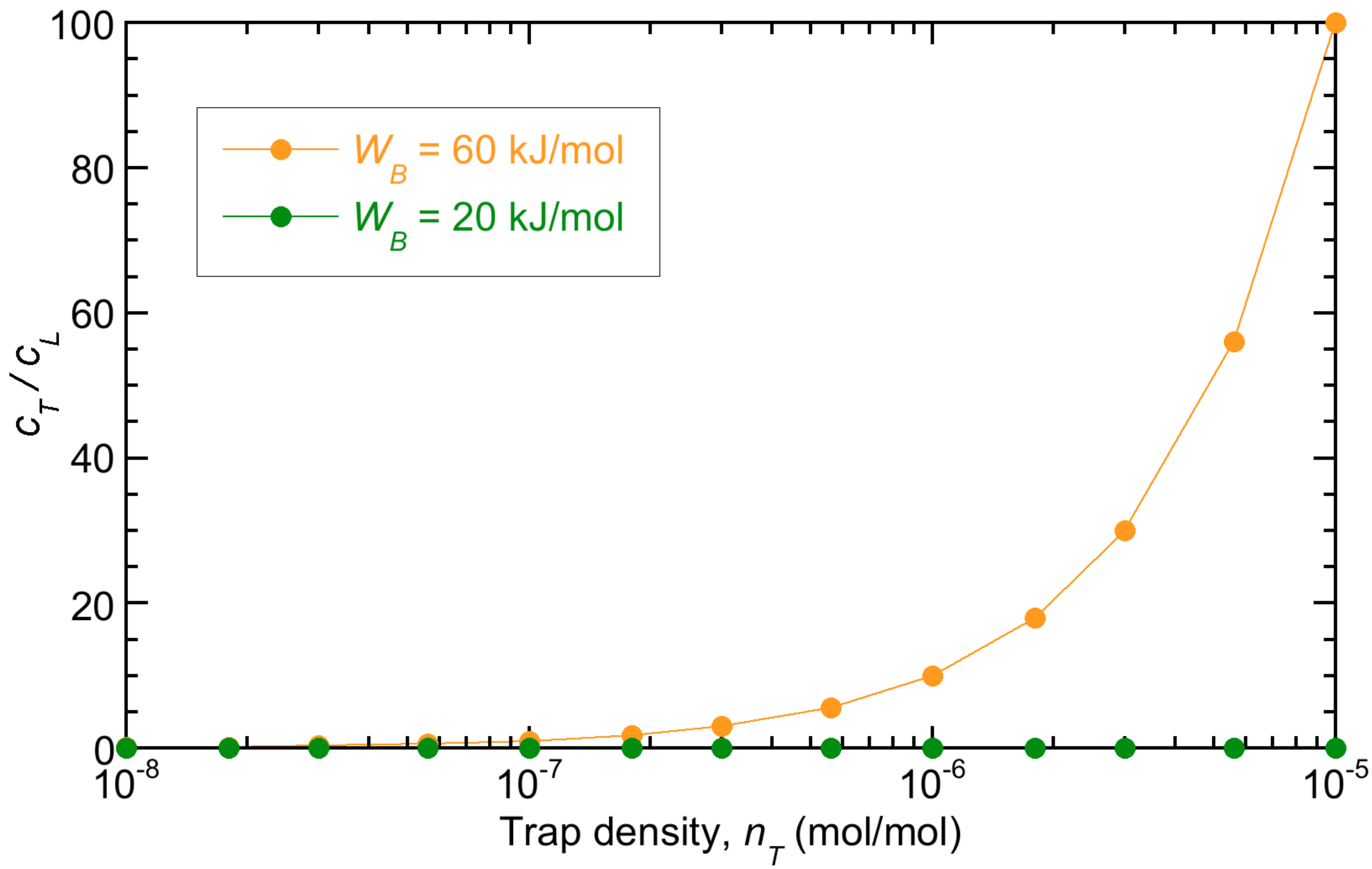
Trapped hydrogen can be much larger than lattice hydrogen



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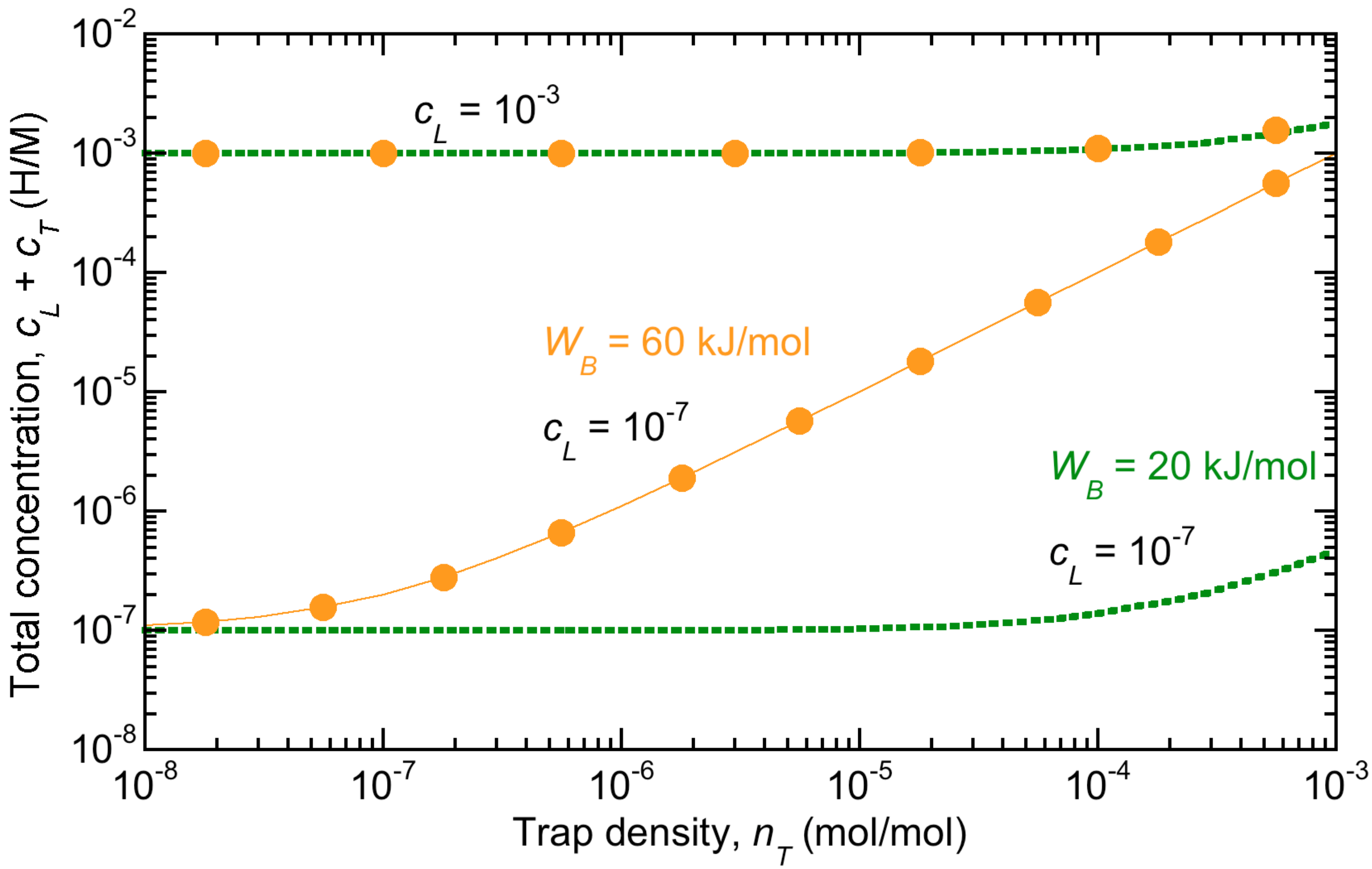
Trapped hydrogen can be much larger than lattice hydrogen



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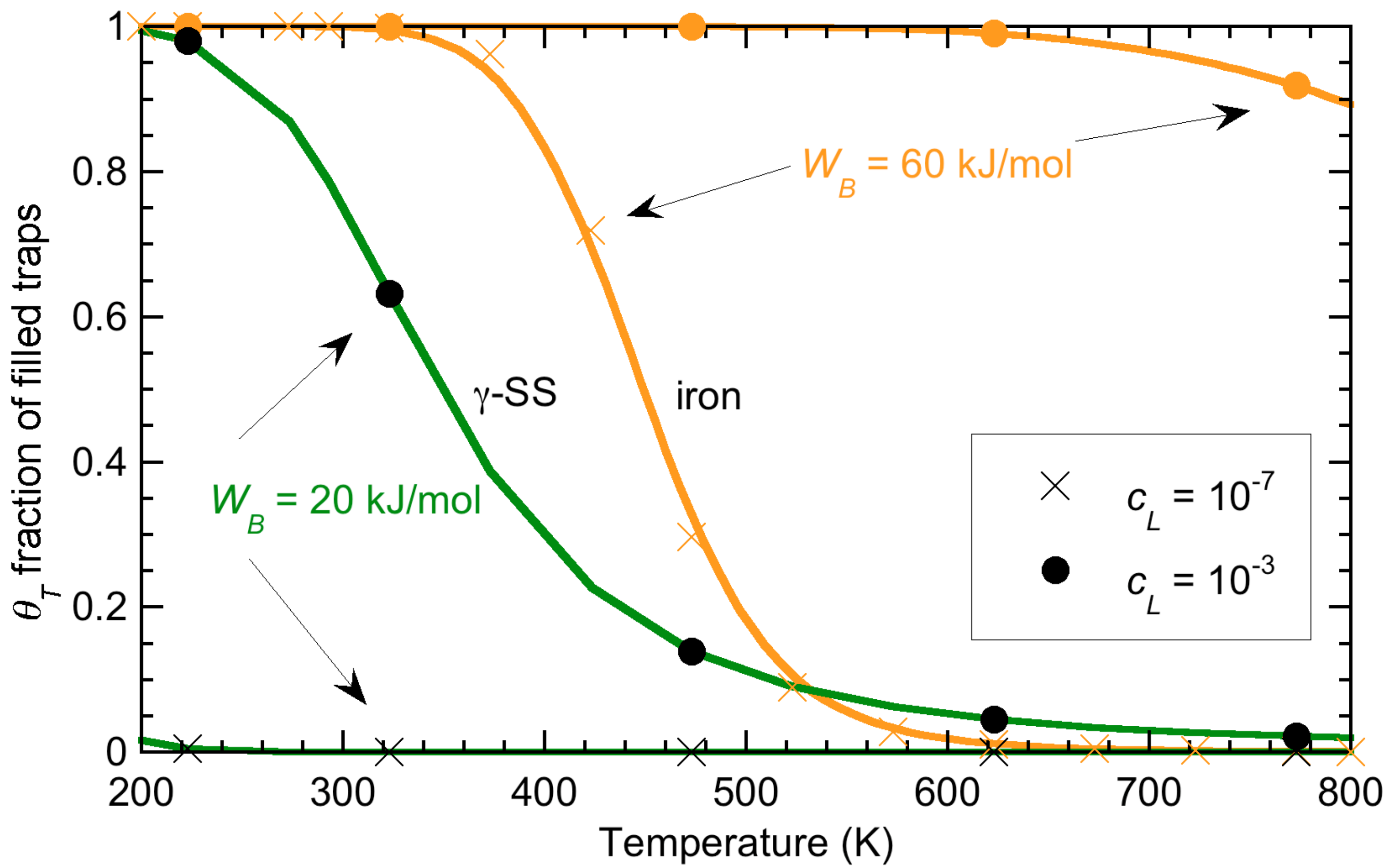
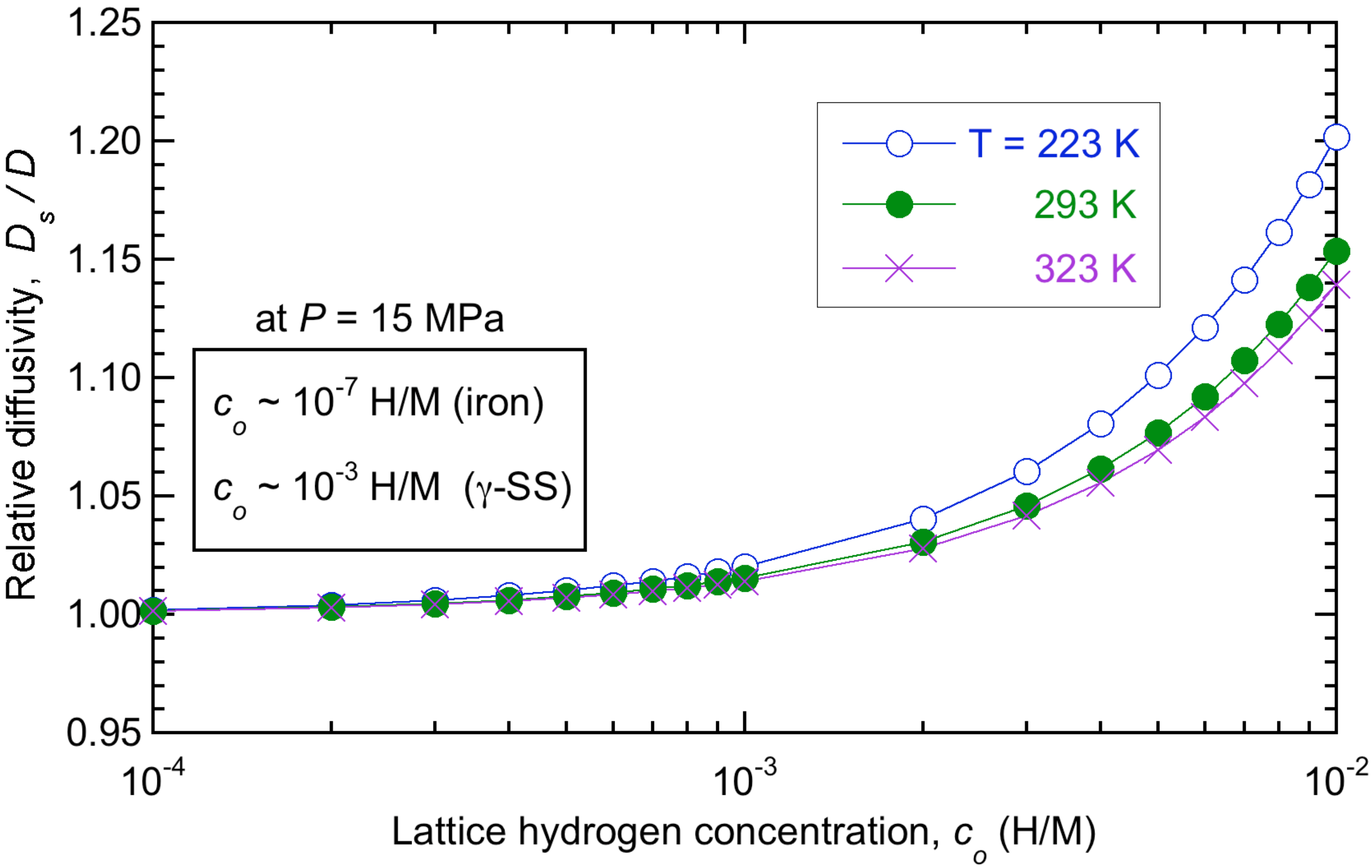
Trapping is characterized by trap energy and lattice hydrogen concentration

Equilibrium between lattice hydrogen and traps $$\frac{\theta_T}{(1-\theta_T)} = \theta_L \exp\left(\frac{W_B}{RT}\right)$$



Stress has minimal effect on Diffusivity

$$\frac{D_s}{D} = 1 + \frac{c_o}{V_M}\left(\frac{2}{9}\frac{E}{(1-\nu)}\frac{V_H{}^2}{RT}\right)$$



$V_M = 7.1\ cm^3/mol$

$V_H = 2\ cm^3/mol$

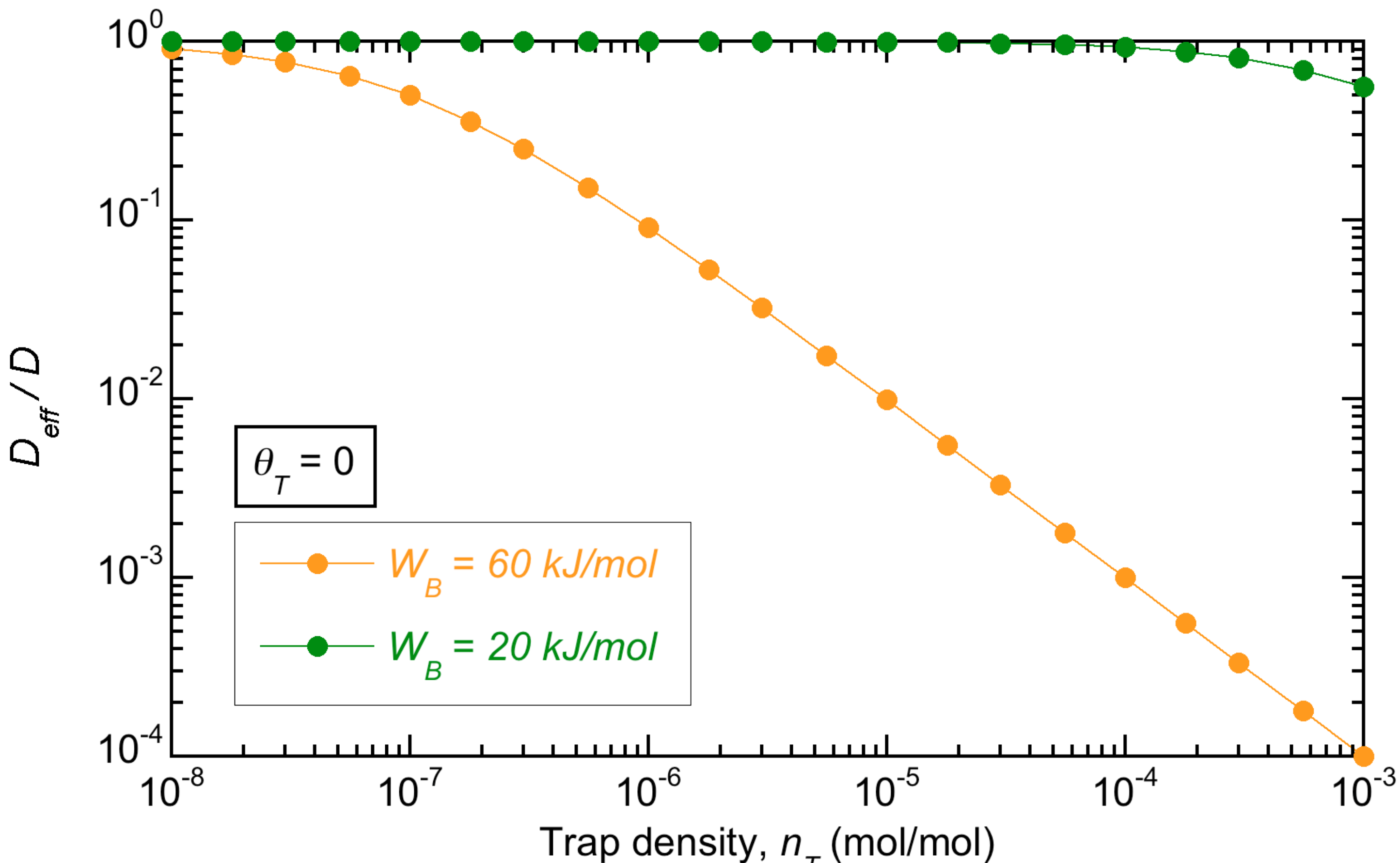
E = 200 GPa

v = 0.33

Diffusivity is Decreased by Trapping

Trapping affected diffusivity (D_{eff}) is a function of hydrogen concentration:

$$\frac{D_{eff}}{D} = \frac{c_L}{c_L + c_T(1 - \theta_T)}$$



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Summary

- Hydrogen fugacity
  - Abel-Noble EOS for hydrogen
  - Gas mixtures increase fugacity
- Stress
  - Tensile stress increases hydrogen dissolved in metals (compressive stress decreases hydrogen content)
  - Hydrogen diffusivity is indirectly increased by stress
- Hydrogen trapping
  - Low trap energy (γ-SS): essentially no effect on hydrogen and hydrogen transport
  - High trap energy (iron and steels):
    - Substantial increases in dissolved hydrogen content
    - Large decreases in apparent hydrogen diffusivity