THEORETICAL PREDICTION OF

HYDROCARBON-MINERAL-WATER REACTIONS AT ELEVATED T & P

How can we calculate their properties & what should be measured?

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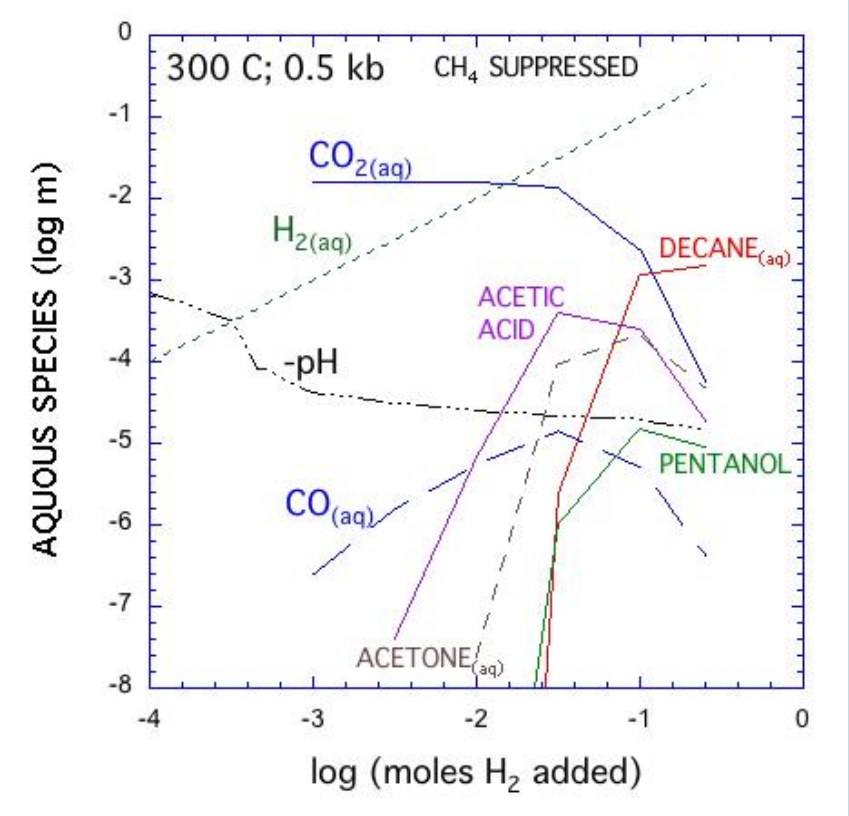
Model of the progessive reaction of CO_2 with H_2 at 300 C and 0.5 kb

In this calculation H_2 is added to an aqueous solution containing CO_2 and NaCl in the presence of magnetite.

The concentrations of the aqueous species are shown as a function of reaction progress.

In these calculations methane formation is suppressed.

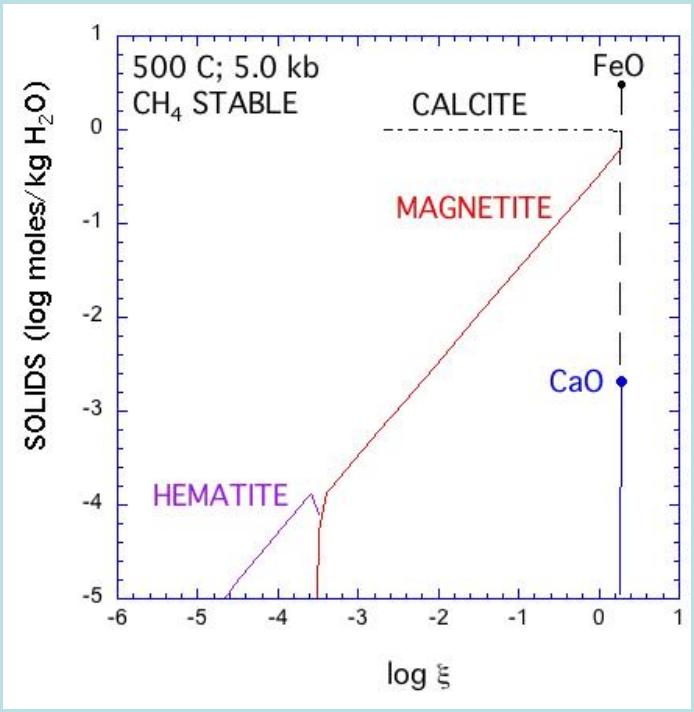
Enough H_2 is added to allow other reduced carbon-bearing species to form, eventually including decane.

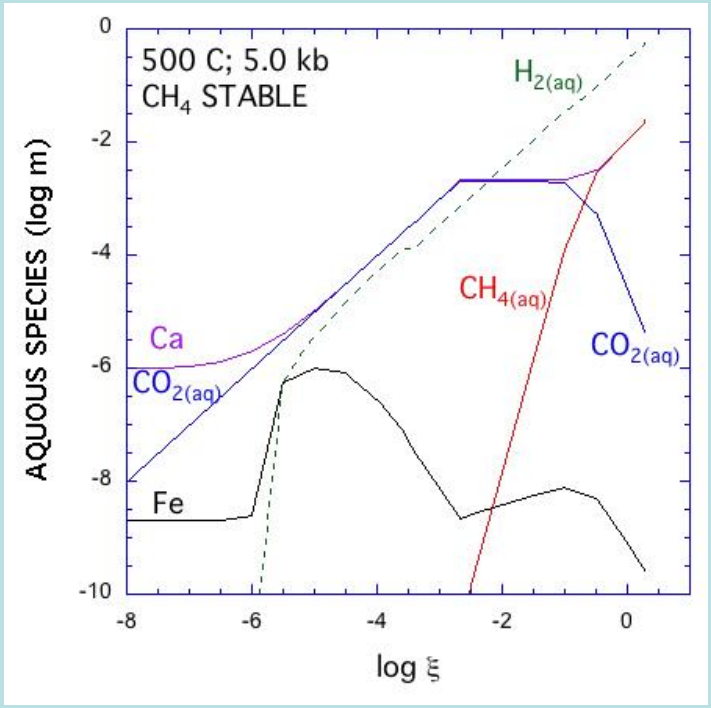


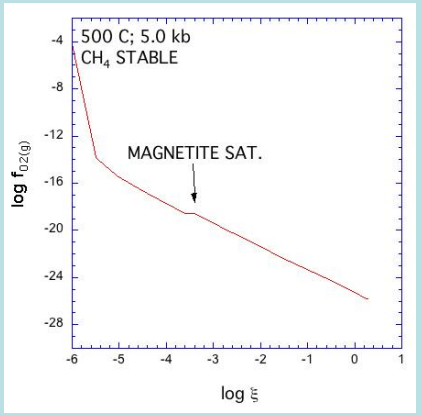
REACTION OF WATER + $CaCO_3$ + FeO at 500 C & 5.0 kb

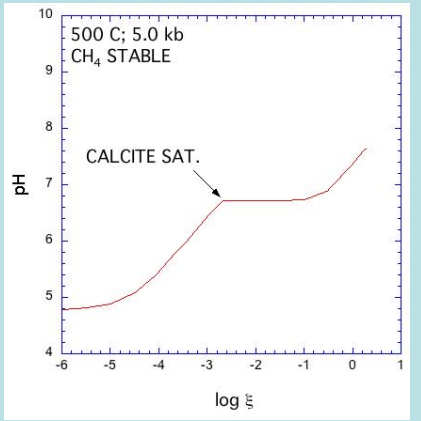
Stable equilibria

- methane present (Scott et al., 2004)









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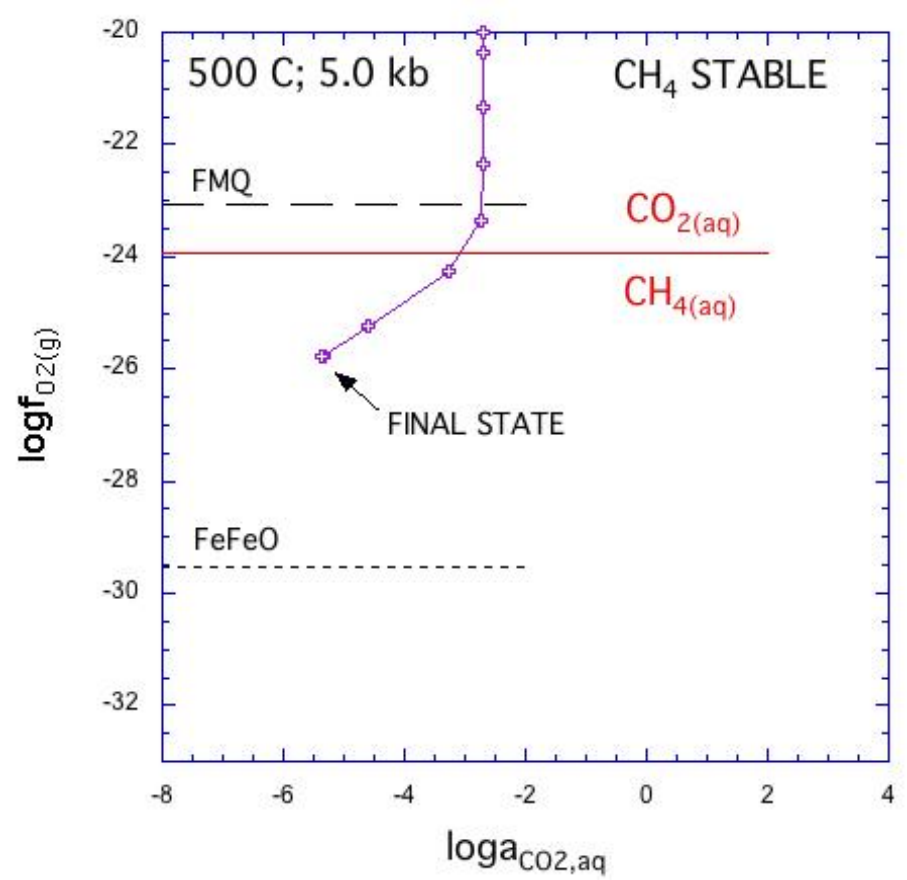

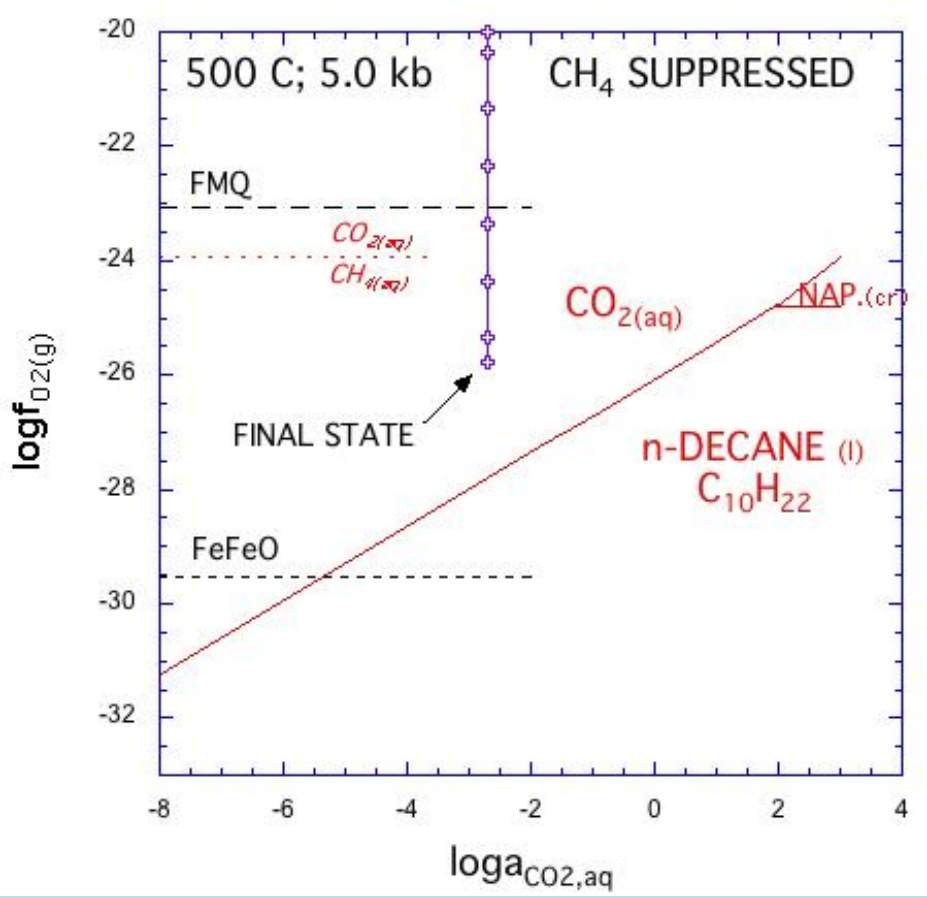

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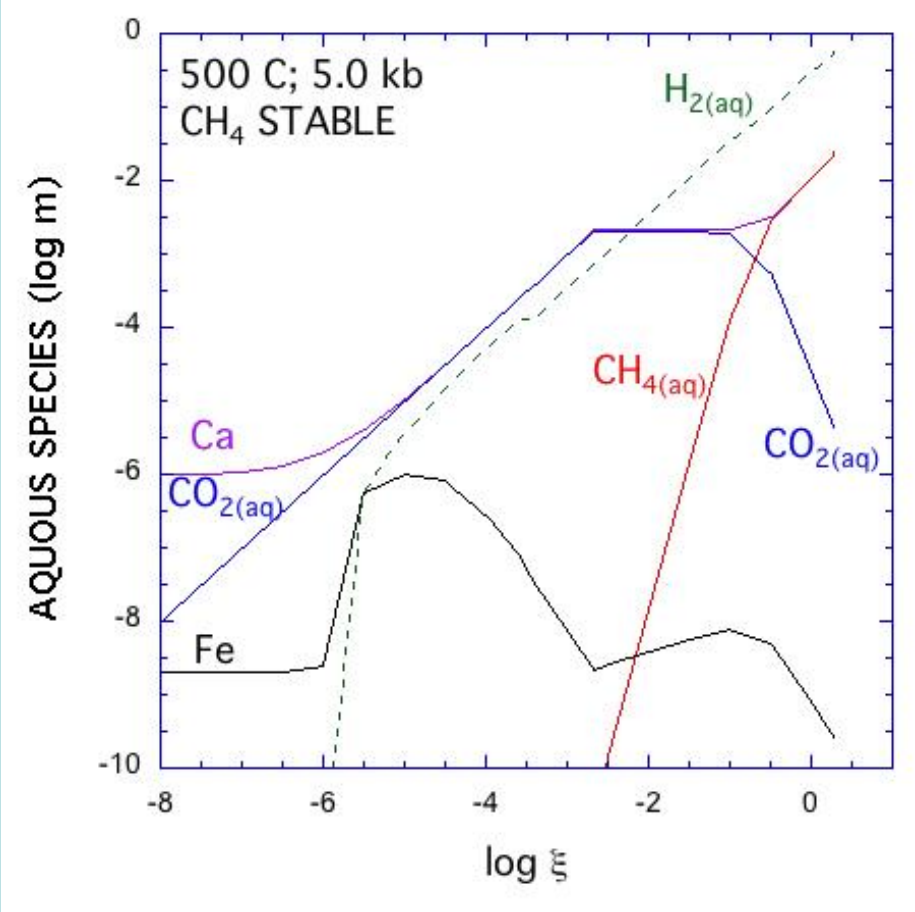

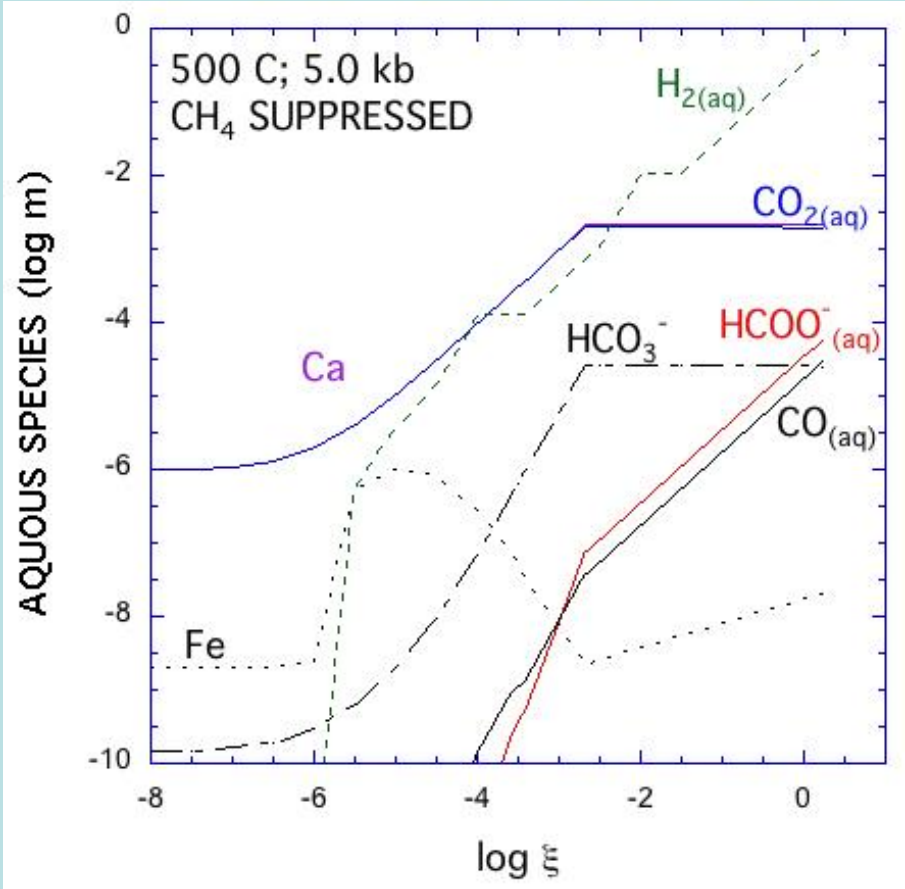

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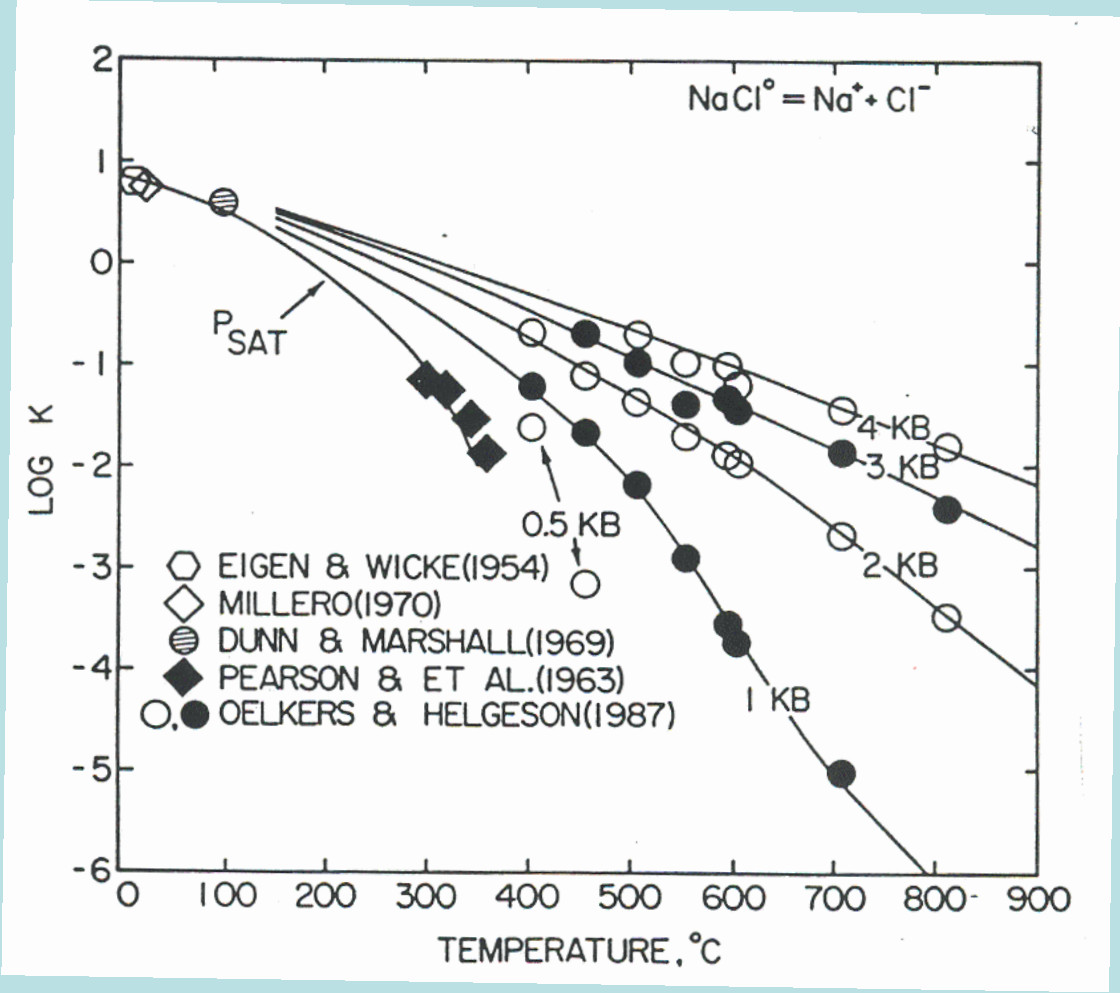
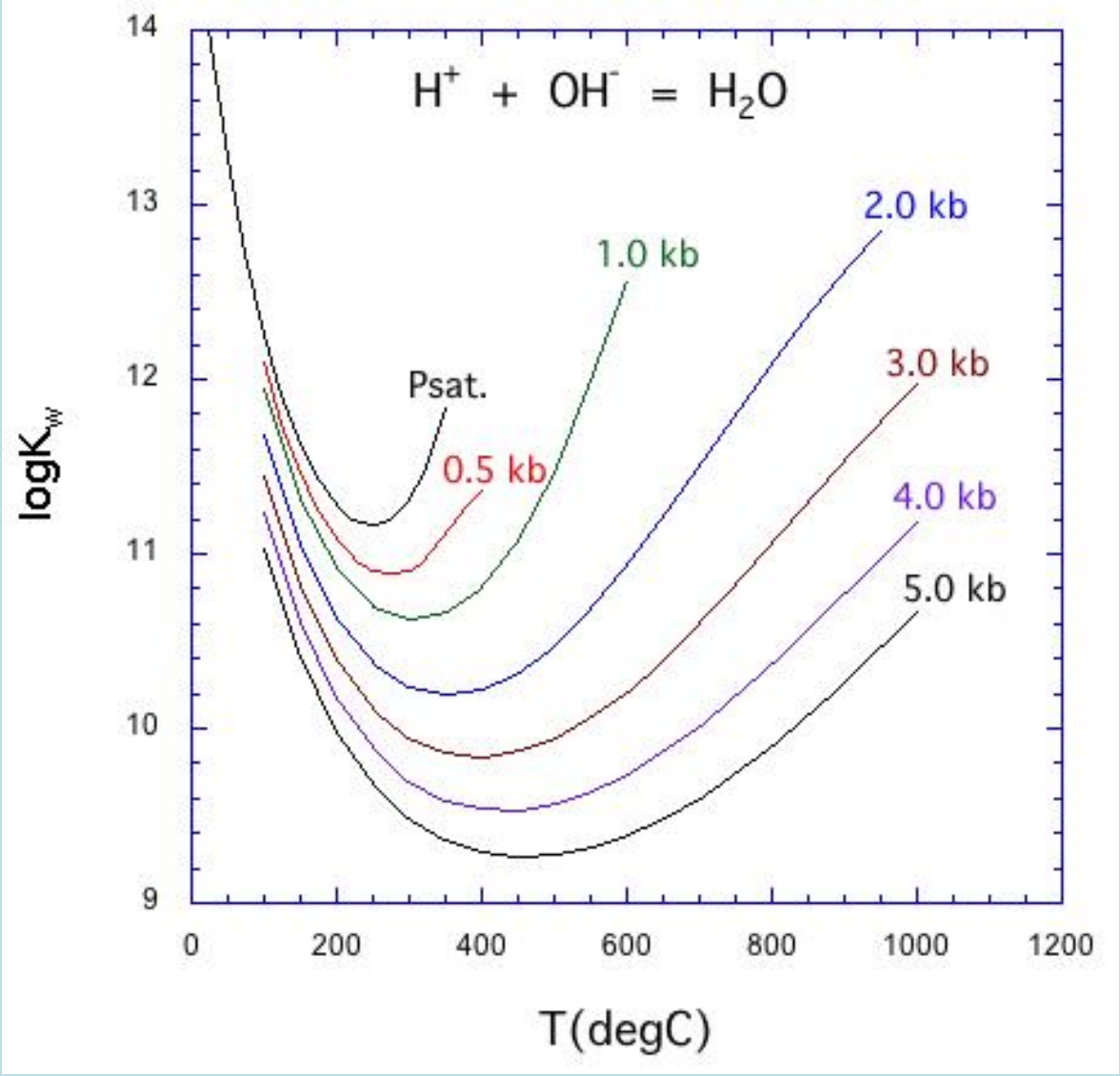
ION ASSOCIATION AT ELEVATED P & T



Sverjensky et al. (1997)

Equation of state prediction of K_w

$$K_w = \frac{a_{H_2O}}{a_{H^+} a_{OH^-}}$$



What happens to K_w at higher pressures?

EXPERIMENTS NEEDED! FUNDAMENTAL MOLECULAR THEORY NEEDED

CALCULATION OF

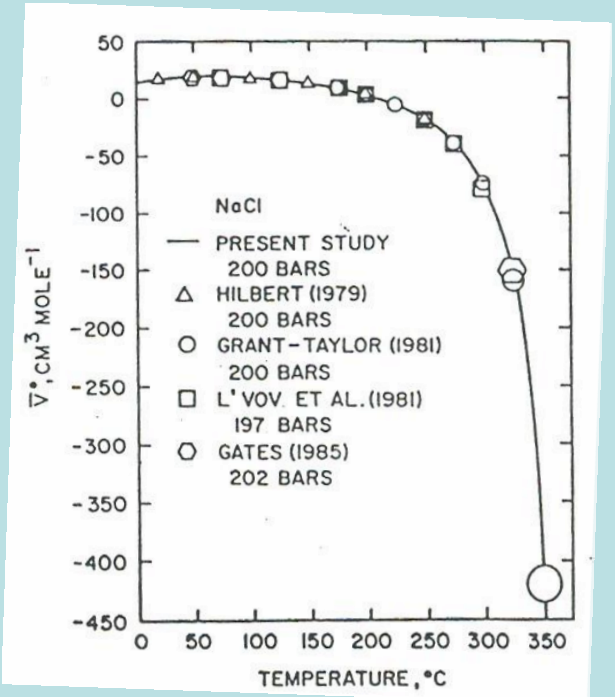
STANDARD GIBBS FREE ENERGIES OF REACTION AT P AND T

$$\Delta G^{0}_{r;P,T} = \sum_{j} \nu_{j} \Delta \overline{G}^{0}_{f,j;P,T}$$

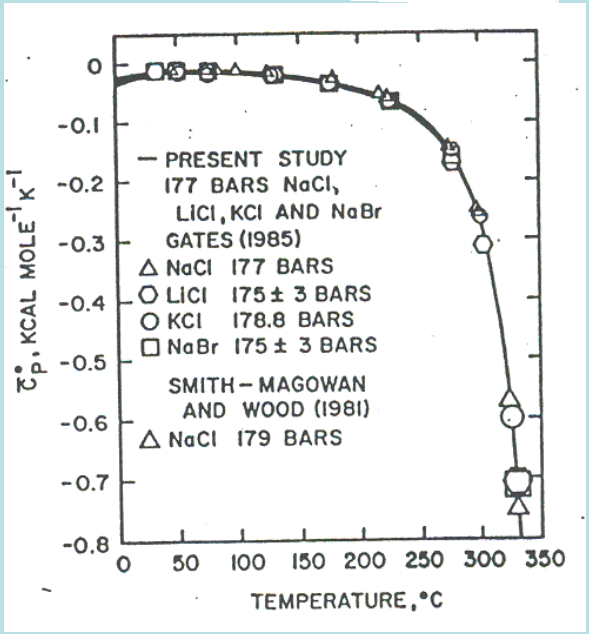
$$\Delta \overline{G}^{0}_{f,j;P,T} = \Delta \overline{G}^{0}_{f,j;P_r,T_r} + \Delta \overline{G}^{0}_{j;P_r,T_r \rightarrow P,T}$$

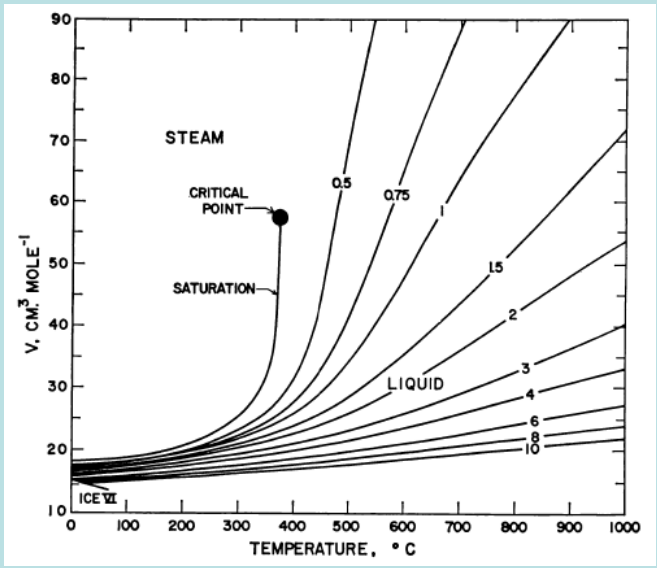
$$\Delta \overline{G}^{0}_{j;P_r,T_r \rightarrow P,T} = -\overline{S}^{0}_{j;T_r}\left(T - T_r\right) + \int_{P_r,T_r}^{P_r,T} C^{0}_{P_r;j}\,dT - T\int_{P_r,T_r}^{P_r,T} \frac{C^{0}_{P_r;j}}{T}\,dT + \int_{P_r,T}^{P,T} V^{0}_{T;j}\,dP$$

STANDARD VOLUMES & HEAT CAPACITIES OF AQUEOUS IONS and WATER

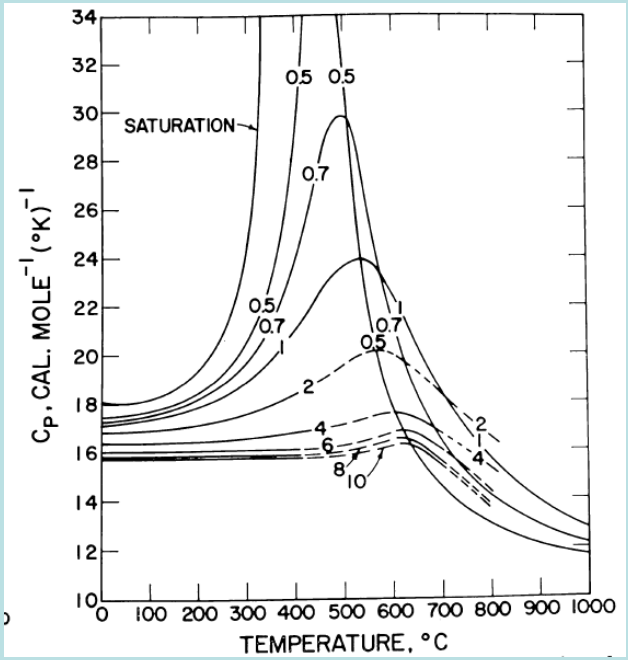


Tanger & Helgeson (1988)





Helgeson & Kirkham (1974a)



WHY THE DIELECTRIC CONSTANT OF WATER?

Equation of state for the standard Gibbs free energy of an aqueous ion

(Helgeson et al., 1981)

e.g. the OH^- ion

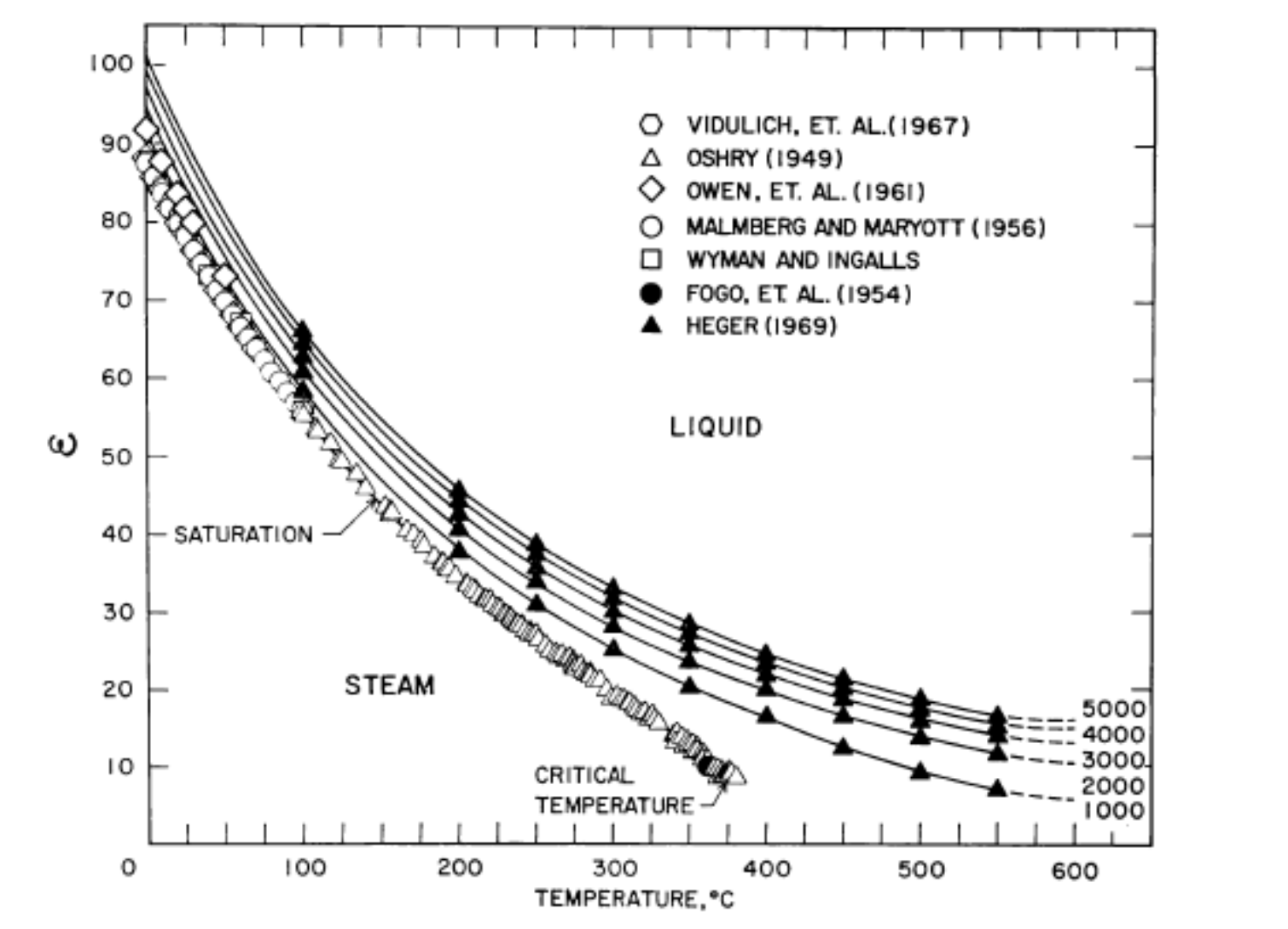
$$\Delta\overline{G}^{0}_{f,OH^-;P,T} = \Delta\overline{G}^{0}_{f,OH^-;P_r,T_r} + f(T,P) + \omega\left(\frac{1}{\varepsilon_{H_2O}} - 1\right)$$

Standard Gibbs free energy at T & P depends on

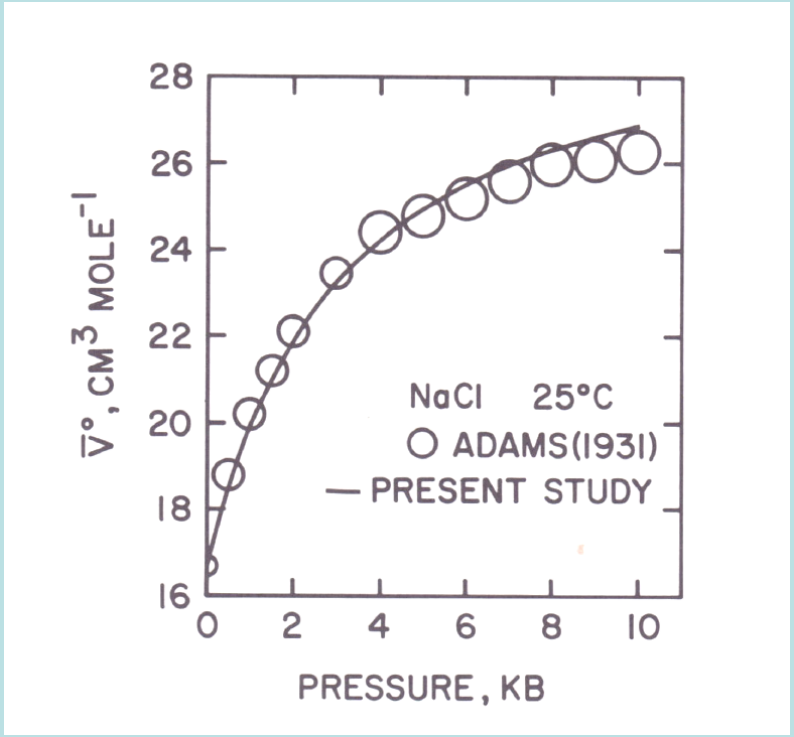
* Free energy at 25 C & 1 bar
  - KNOWN!
* Equation of state coefficients for each ion
  - KNOWN FOR HUNDREDS OF IONS!
* Dielectric constant of water

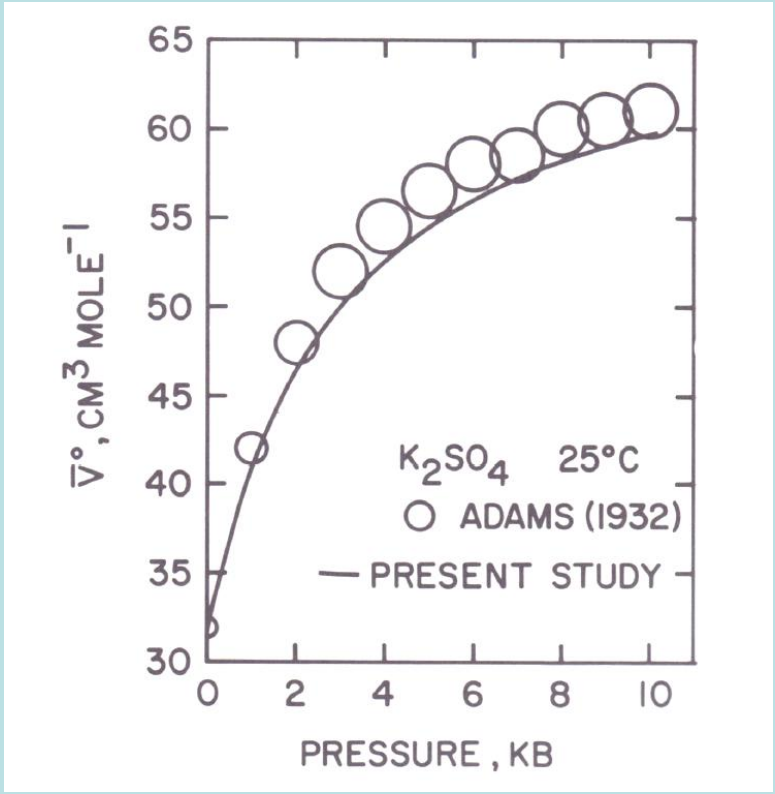
ε_{H_2O} - KNOWN TO 5.0 kb ONLY……

Dielectric constant of water - current limits



from Helgeson and Kirkham (1974)





$$\overline{V}_j^0 = a_{1,j} + \frac{a_{2,j}}{\psi + P} + \left(a_{3,j} + \frac{a_{4,j}}{(\psi + P)}\right)\left(\frac{1}{T - \theta}\right) - \omega_j Q_{P,T}$$

New Proposal to DOE (Cohen, Fei, Wu, & Sverjensky):

Measurements and theory to obtain volumes of H_2O, CO_2 and H_2O-CO_2 mixtures

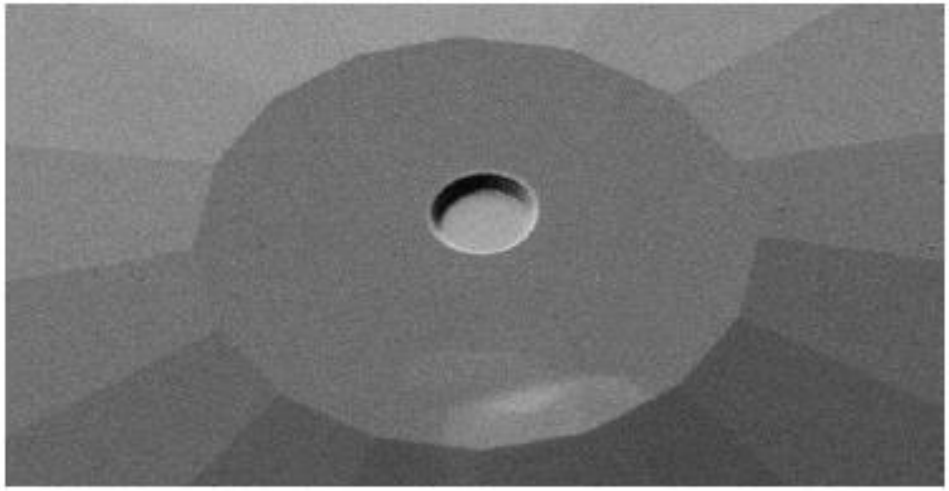
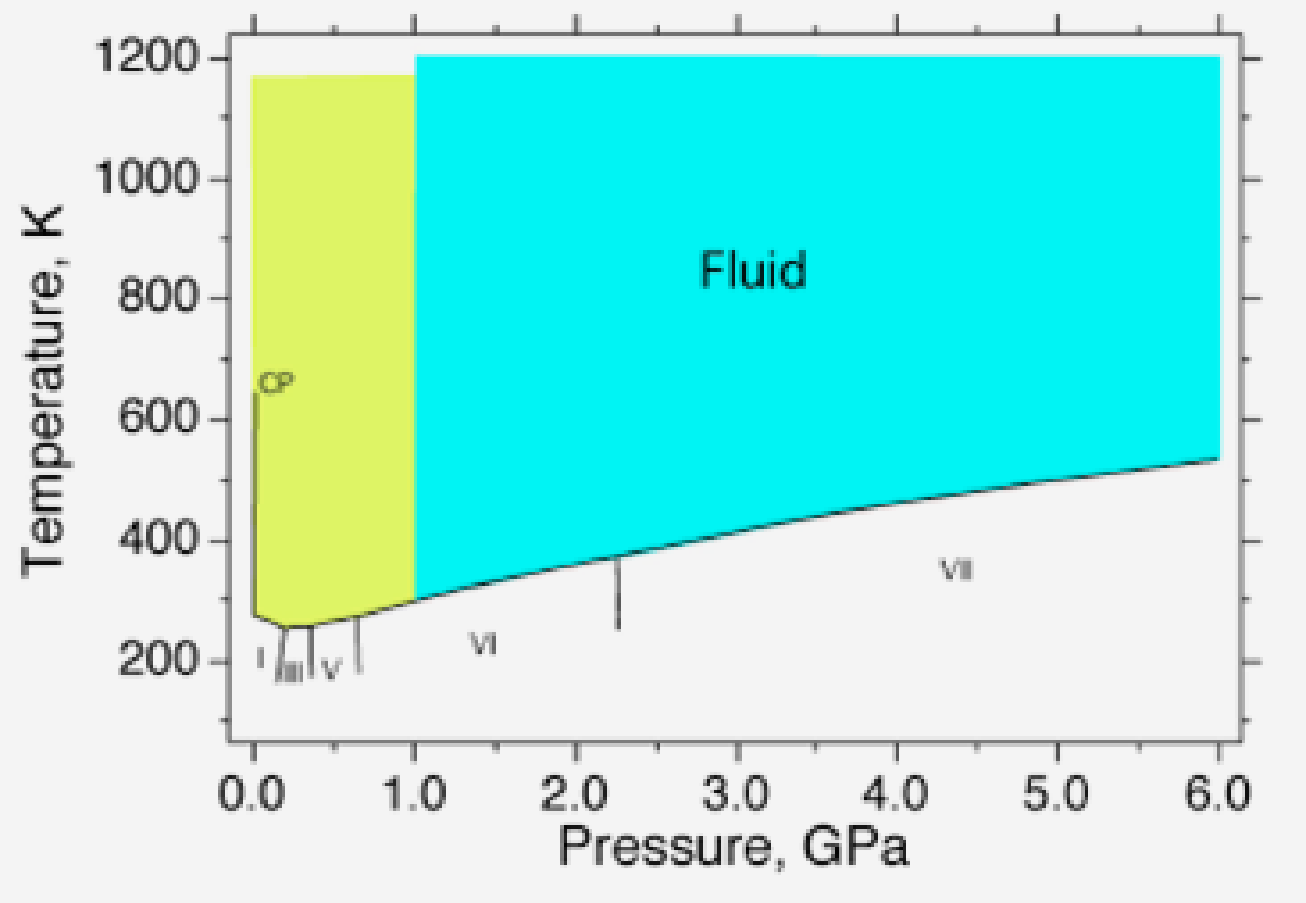


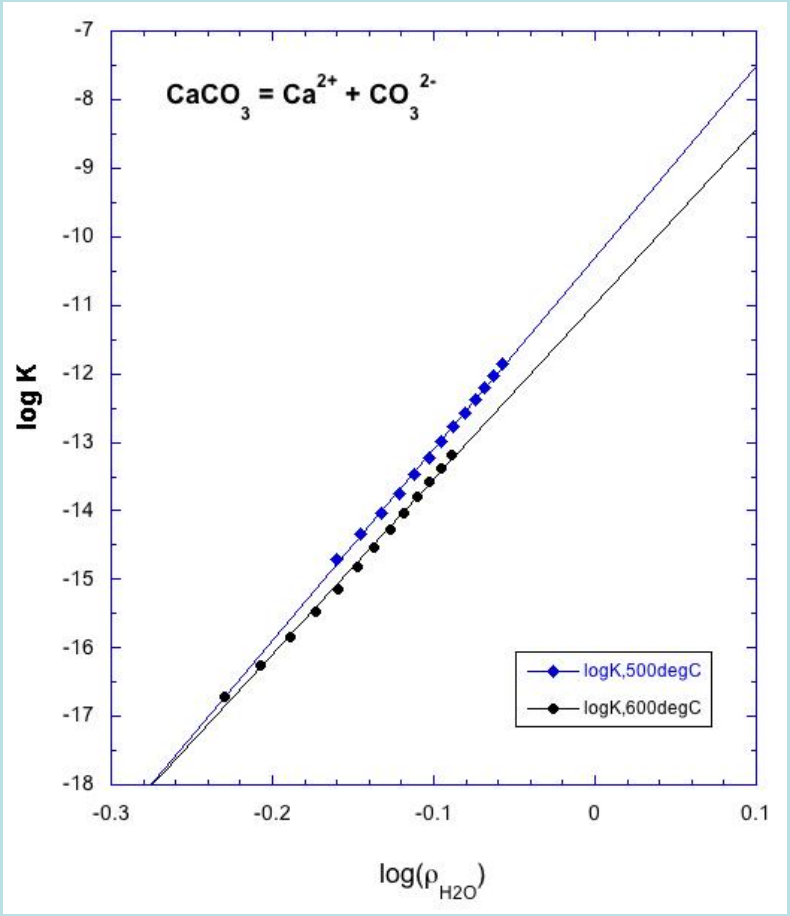
Fig. 2. Sample chamber in the diamond anvil fabricated by focused ion beam (FIB) milling. The anvil could be coated with Pt (or Au) to contain fluid H_2O. The sample chamber will be 150μm diameter by 40μm depth.



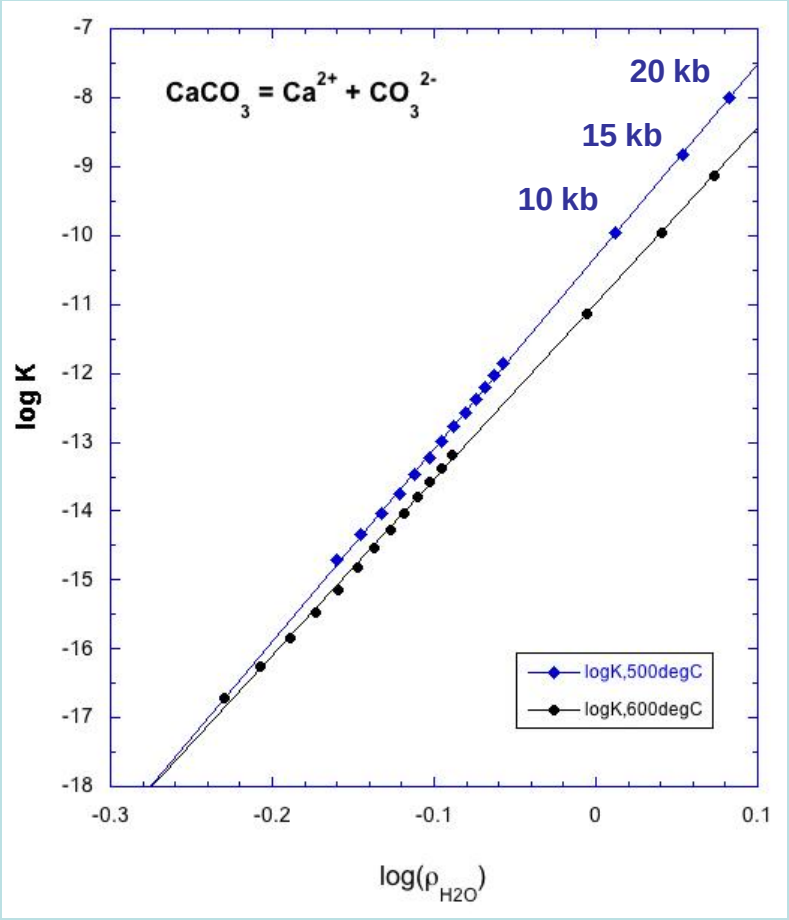
Blue Area: Proposal to measure volumes of H_2O, CO_2 and H_2O-CO_2 mixtures

What can be done now?

Calculated with SUPCRT (EOS)

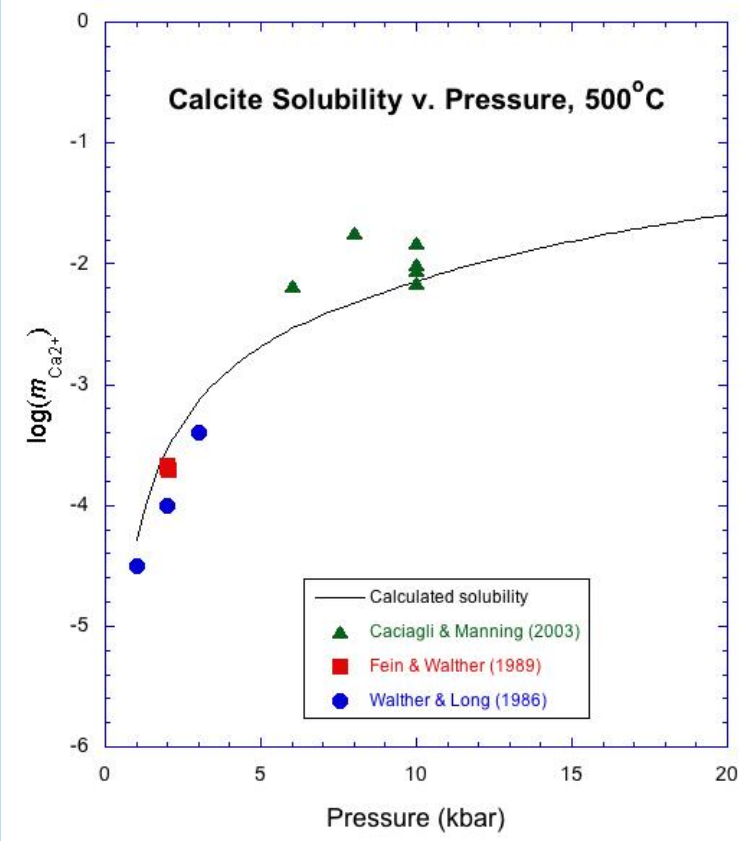


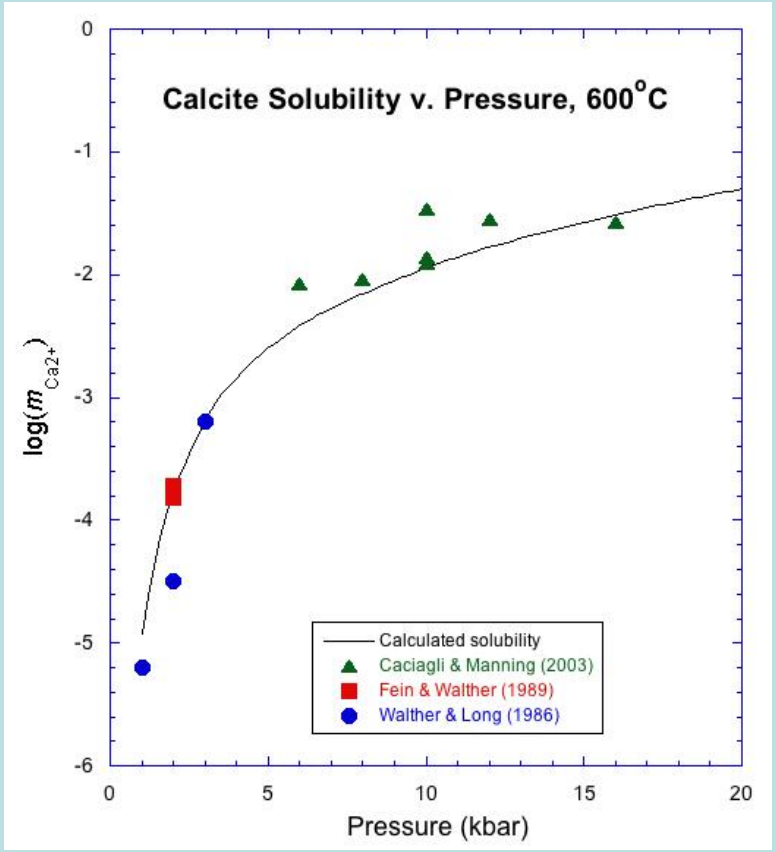
Extrapolated to 10, 15 & 20 Kb



Extrapolations carried out for all equilibria in the calcite-water system

Prediction of calcite solubility at elevated T & P





Similar calculations possible for hydrocarbon-mineral-water systems…

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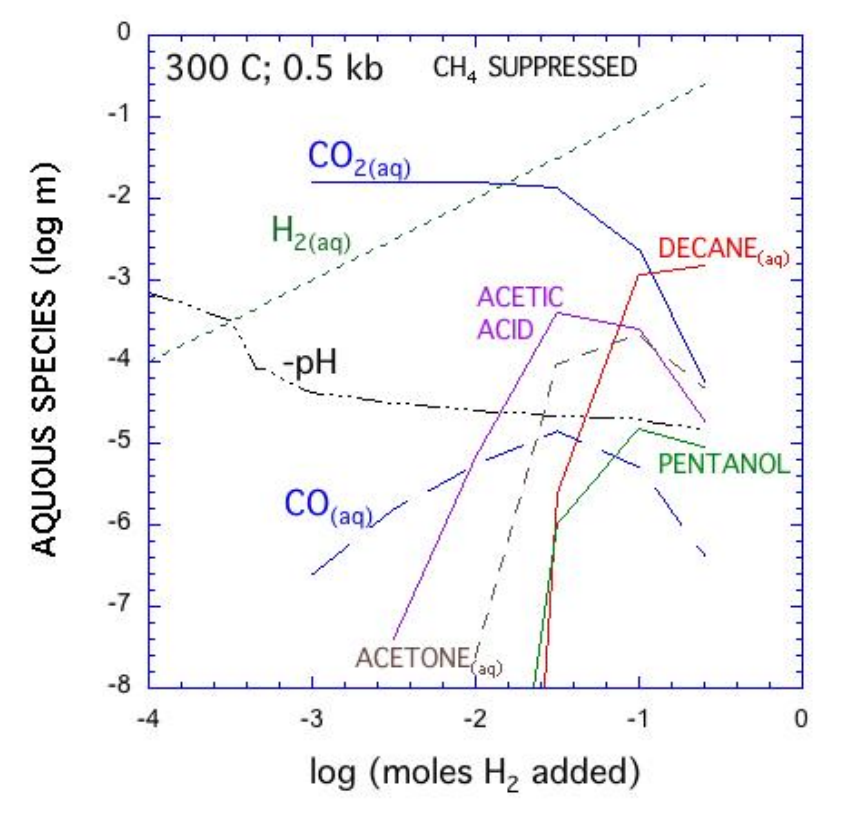

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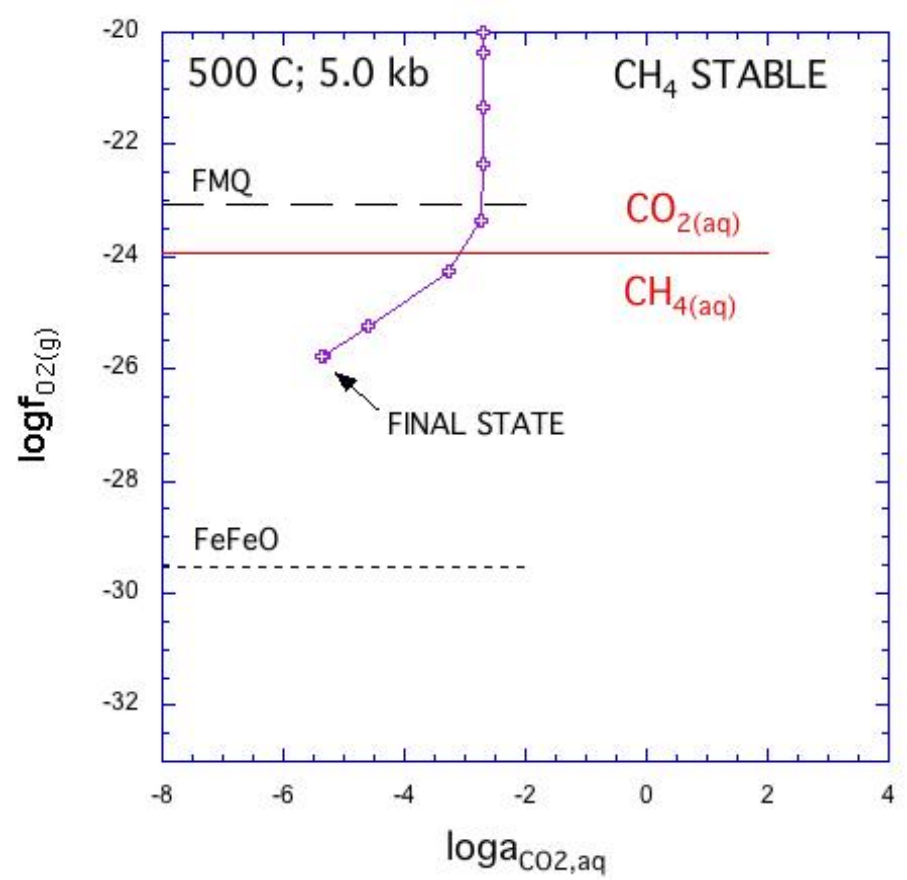

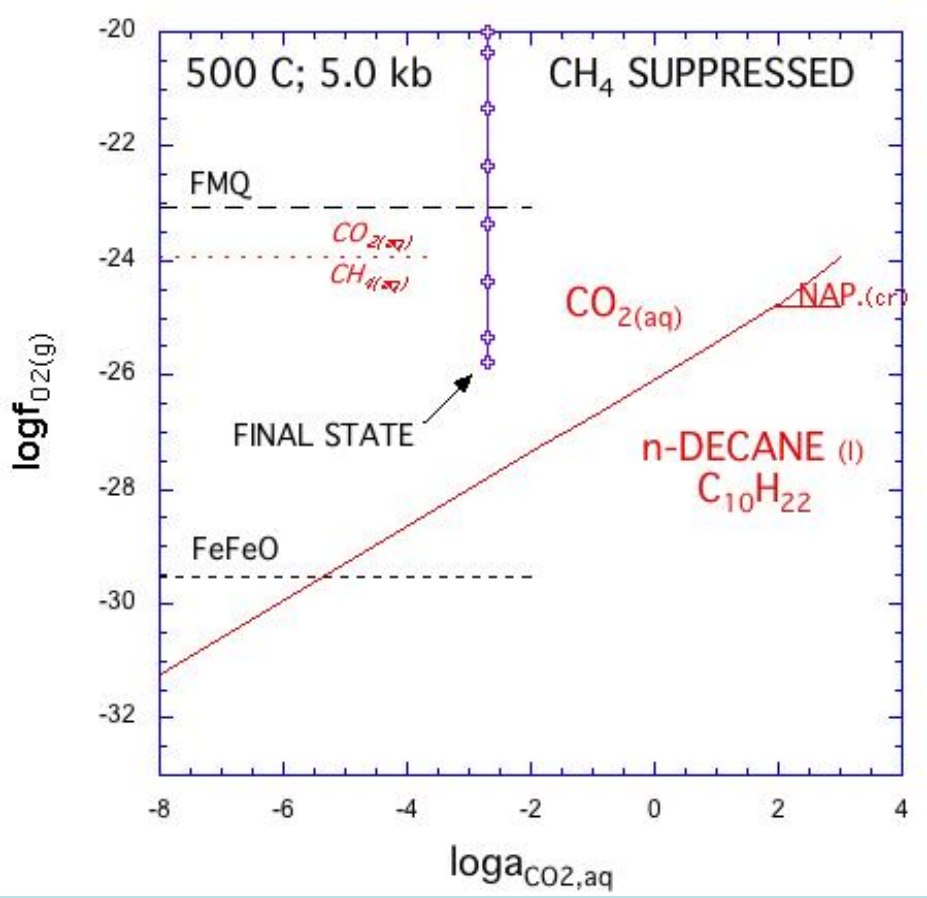

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Summary of Experiments & Theory Needed

At pressures up to 60.0 kbars:

Expts. & Theory

(1) Volumes of H_2O, CO_2 and mixtures

- leads to partial molal volume of solute CO_2
- constrain equation of state for partial molal volumes of aqueous solutes (e.g. CO_2)

Theory

(2) Dielectric constant of water (ε_{H_2O})

- extend equation of state calculations in P & T

Theory

(3) Association constant of water (K_w)

- a direct test of equation of state for aqueous ions at high pressures

Expts. & Geochem. Thermo.

(4) Solubilities of minerals (e.g. calcite, quartz, corundum)

- a direct test of equation of state for aqueous ions at high pressures