

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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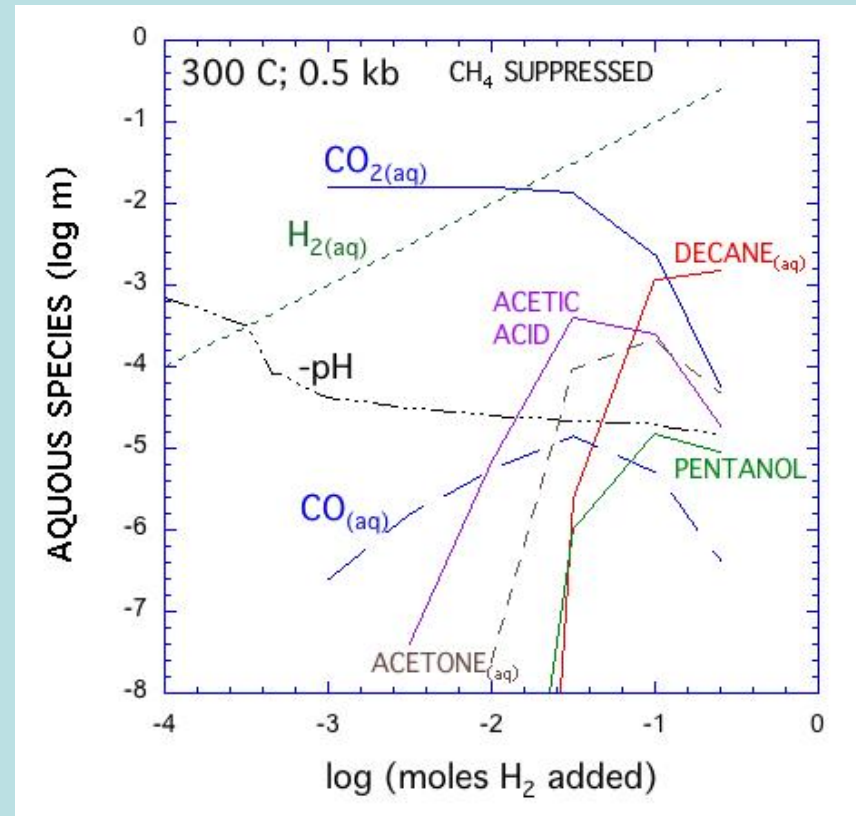
Model of the progressive reaction of CO₂ with H₂ at 300 C and 0.5 kb

In this calculation H₂ is added to an aqueous solution containing CO₂ 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.

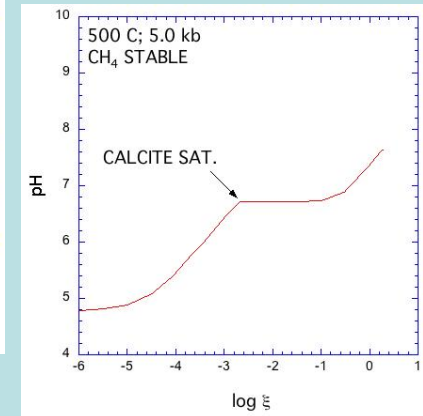
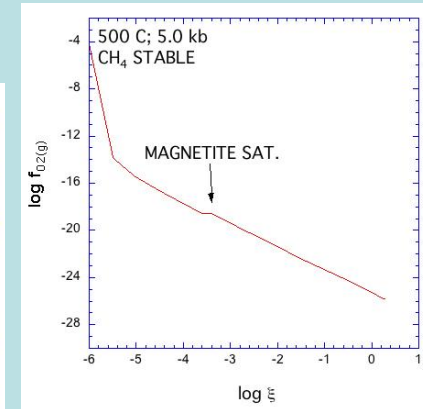
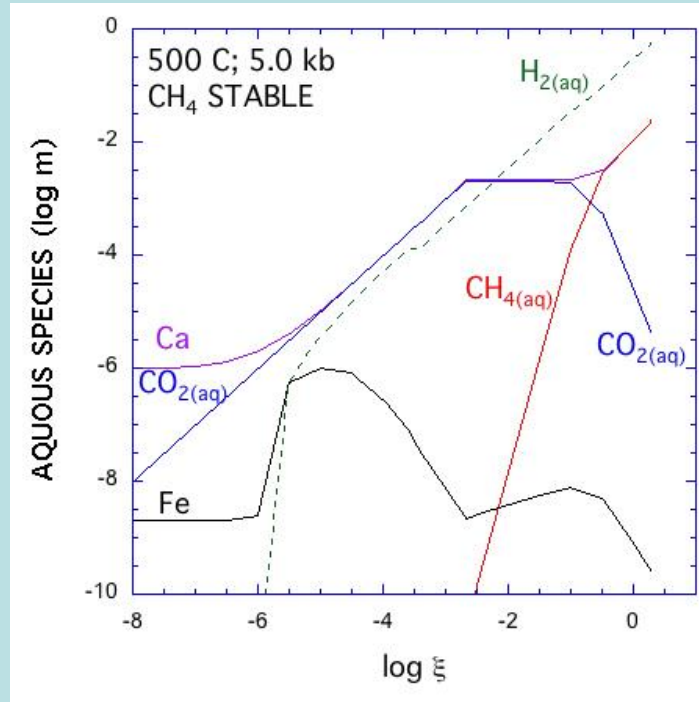
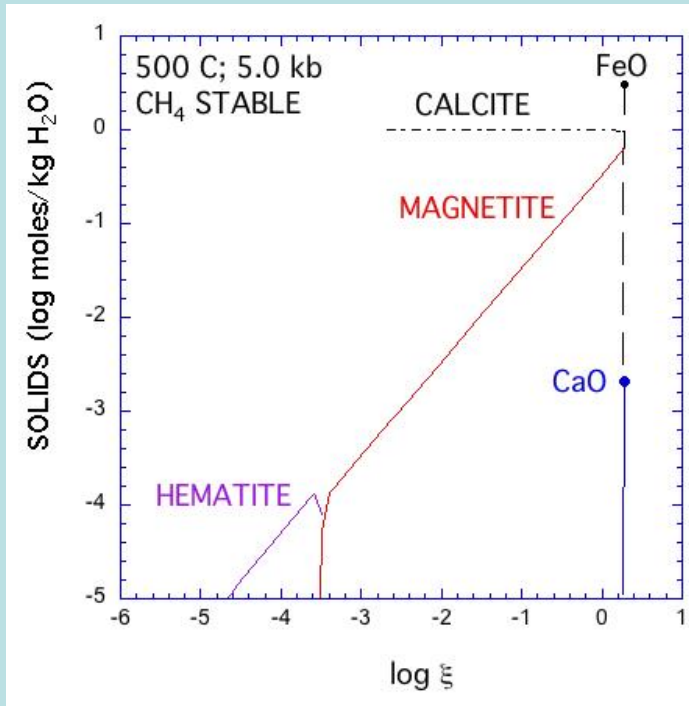
Enough H₂ is added to allow other reduced carbon-bearing species to form, eventually including decane.



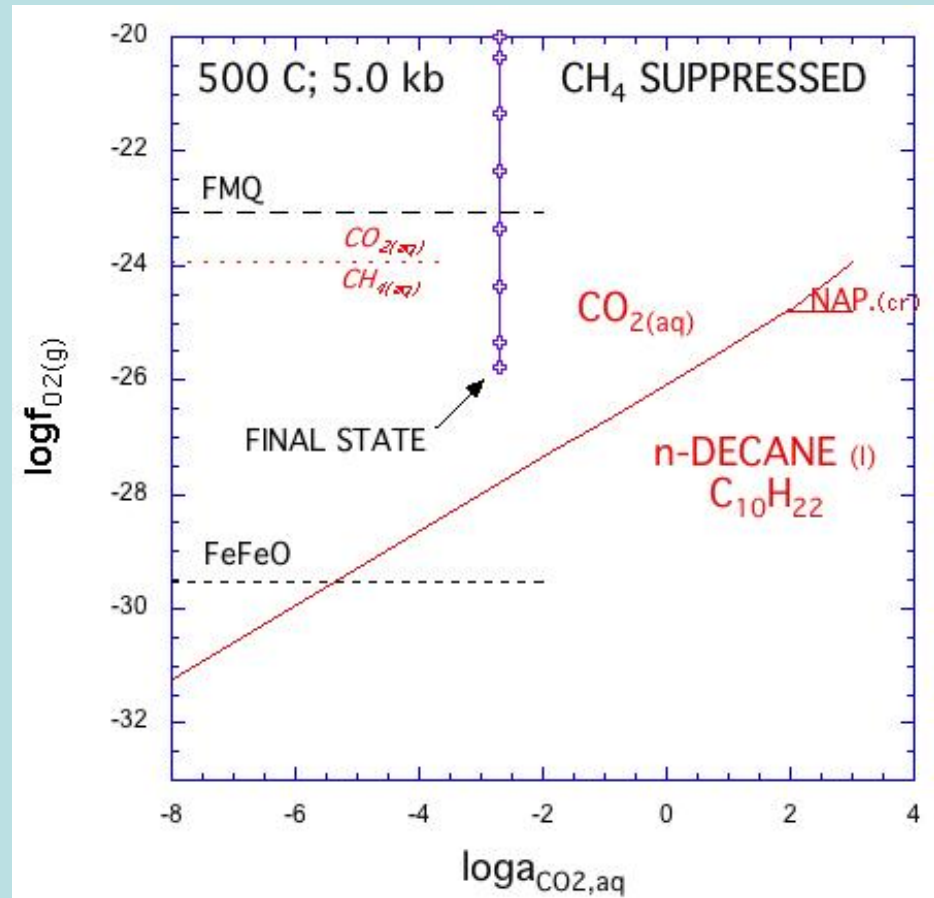
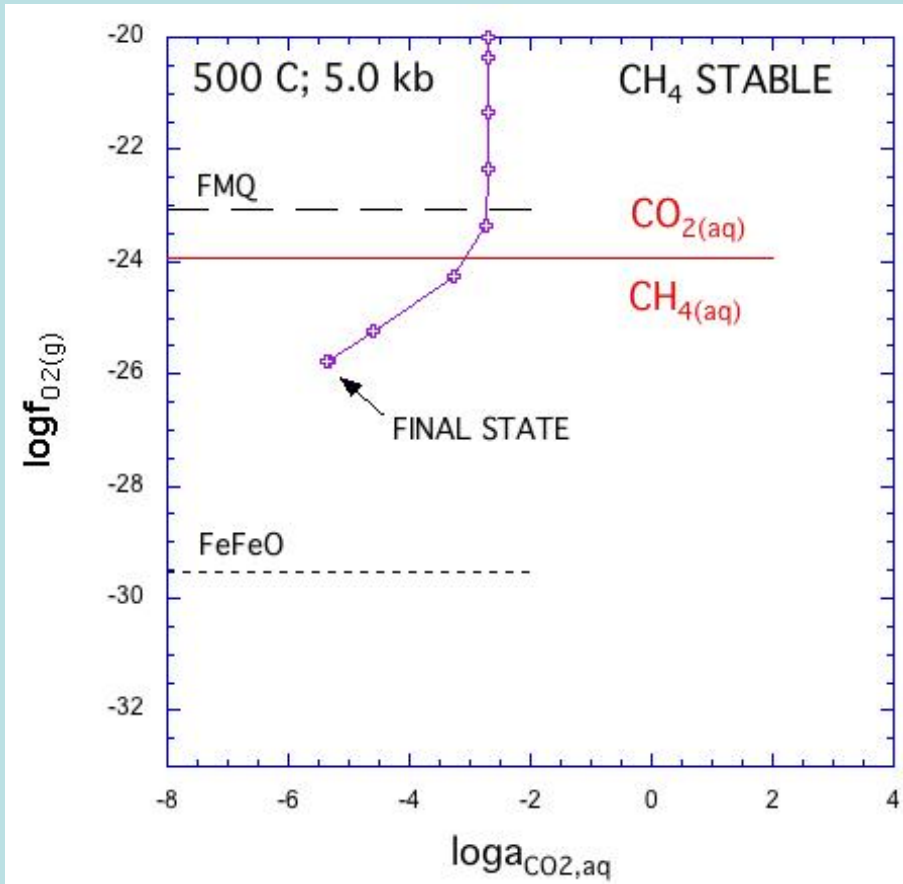
REACTION OF WATER + CaCO₃ + FeO at 500 C & 5.0 kb

Stable equilibria

- methane present (Scott et al., 2004)



REACTION OF WATER + CaCO₃ + FeO at 500 C & 5.0 kb



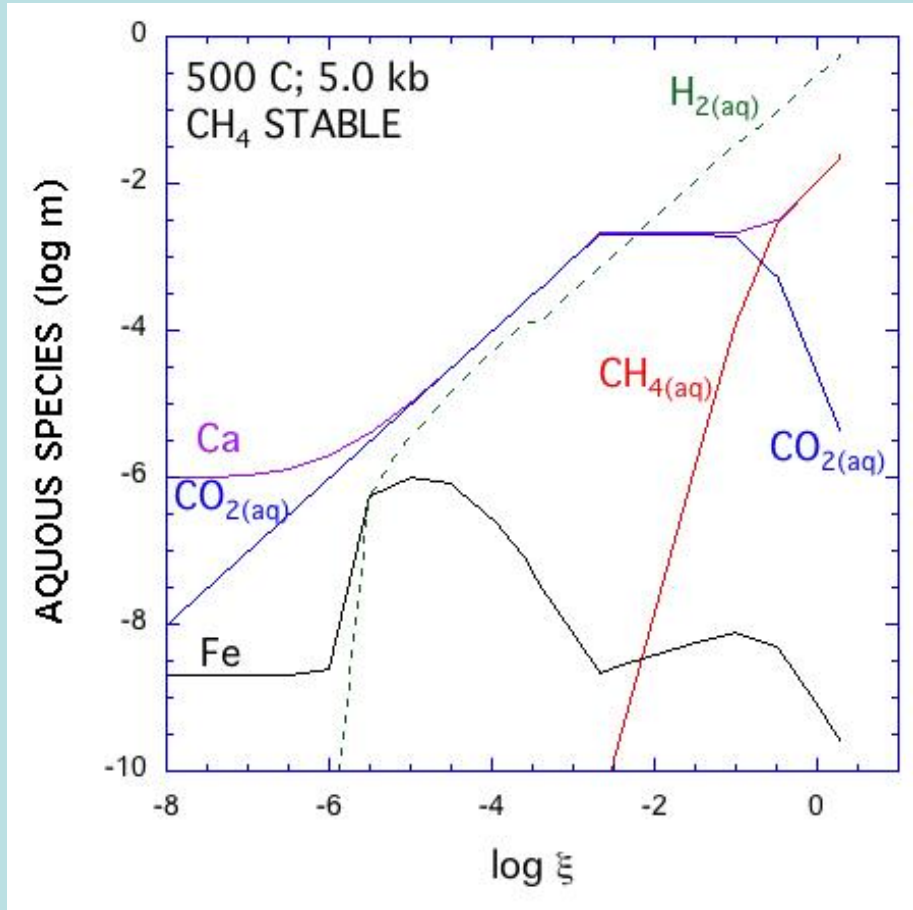
Stable equilibria

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Metastable equilibria

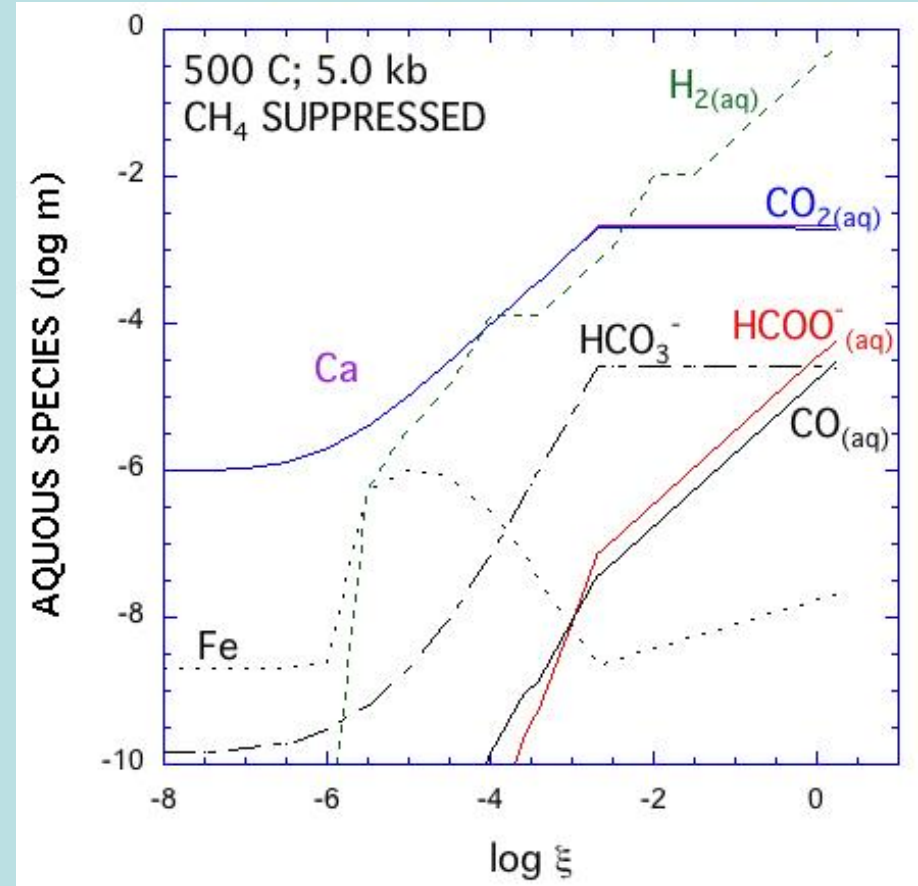
- methane prevented from forming

REACTION OF WATER + CaCO₃ + FeO at 500 C & 5.0 kb



Stable equilibria

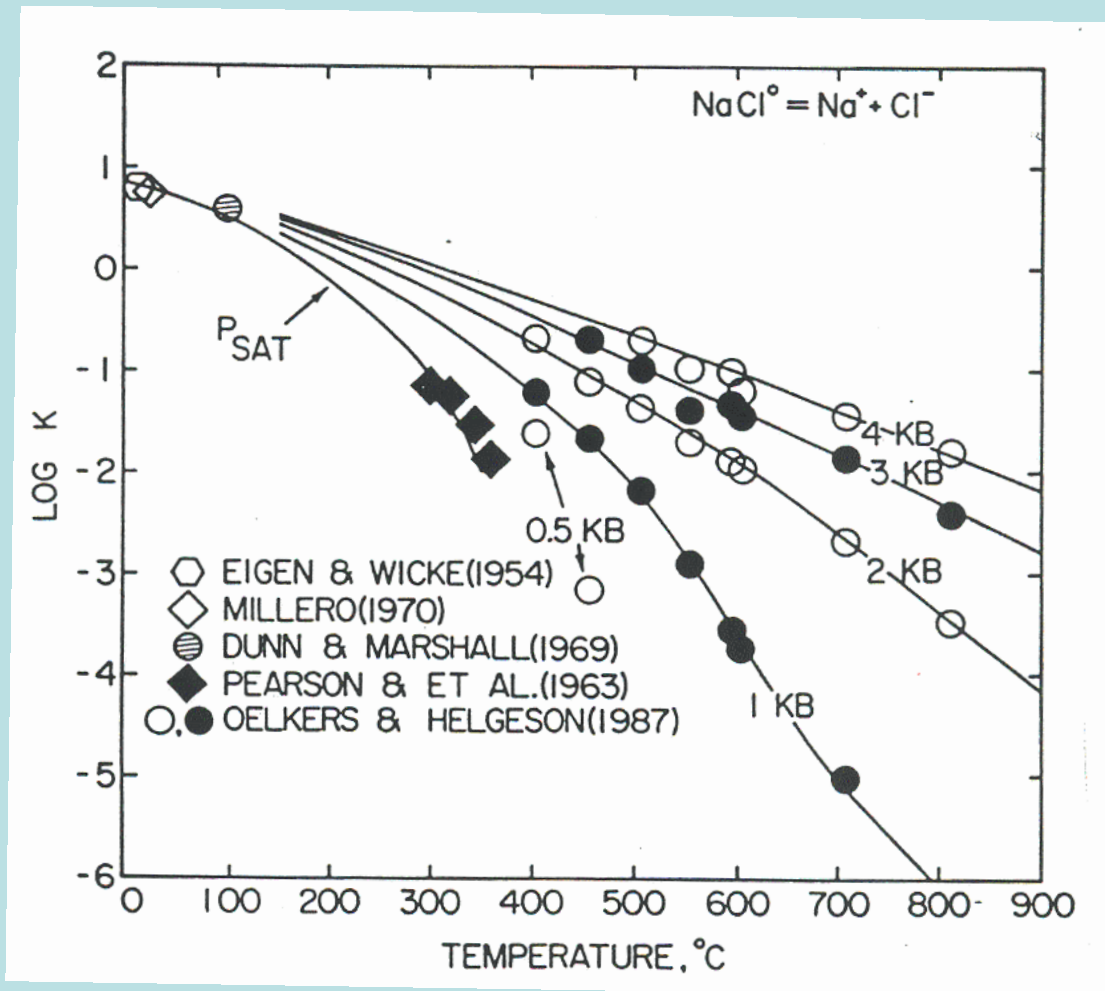
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Metastable equilibria

- methane prevented from forming

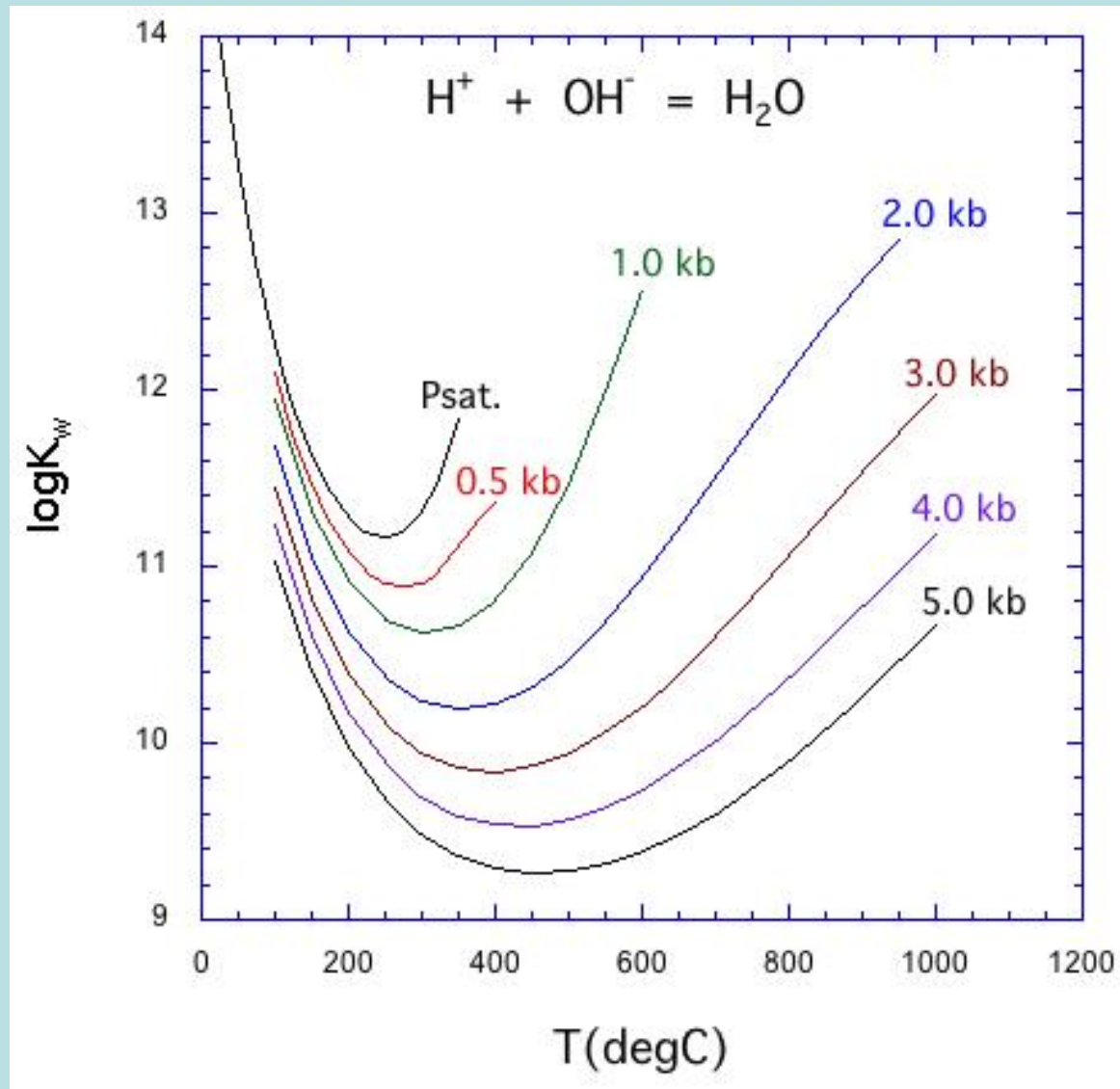
ION ASSOCIATION AT ELEVATED P & T



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

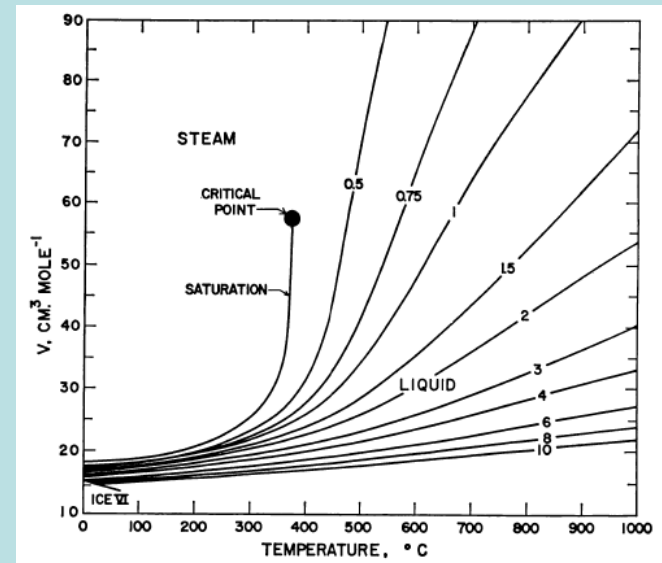
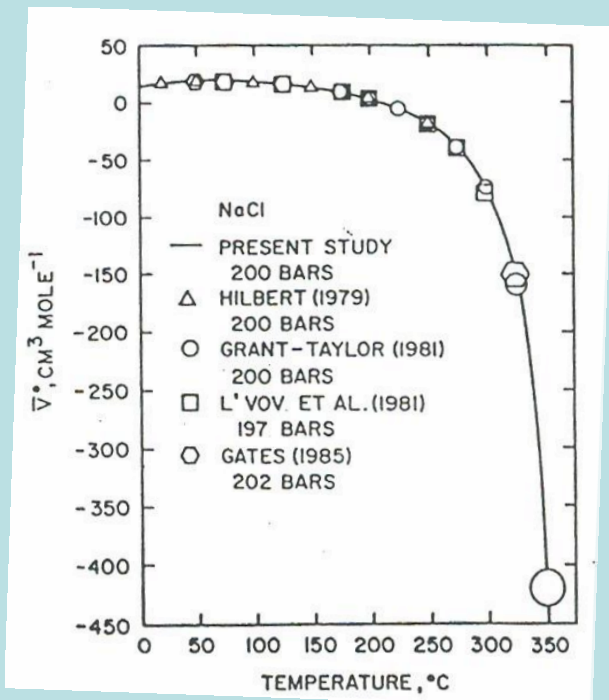
$$\Delta G_{r;P,T}^0 = \sum_j \nu_j \Delta \bar{G}_{f,j;P,T}^0$$

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

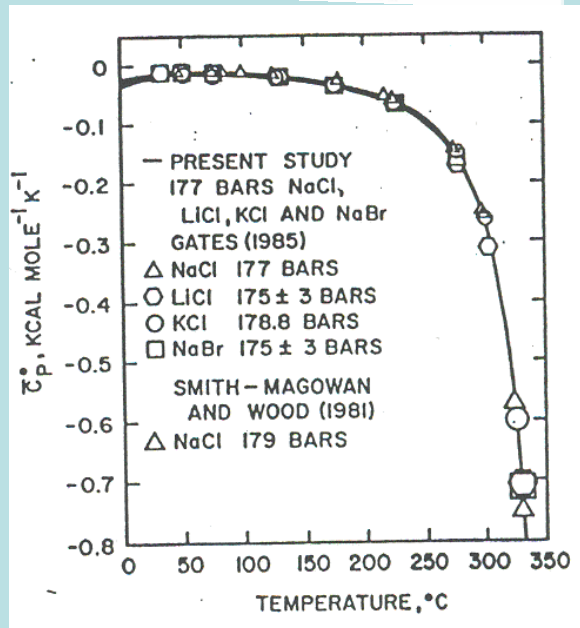
$$\Delta \bar{G}_{j;P_r,T_r \rightarrow P,T}^0 = -\bar{S}_{j;T_r}^0 (T - T_r) + \int_{P_r,T_r}^{P_r,T} C_{P_r;j}^0 dT - T \int_{P_r,T_r}^{P_r,T} \frac{C_{P_r;j}^0}{T} dT + \int_{P_r,T}^{P,T} V_{T;j}^0 dP$$

STANDARD VOLUMES & HEAT CAPACITIES OF AQUEOUS IONS

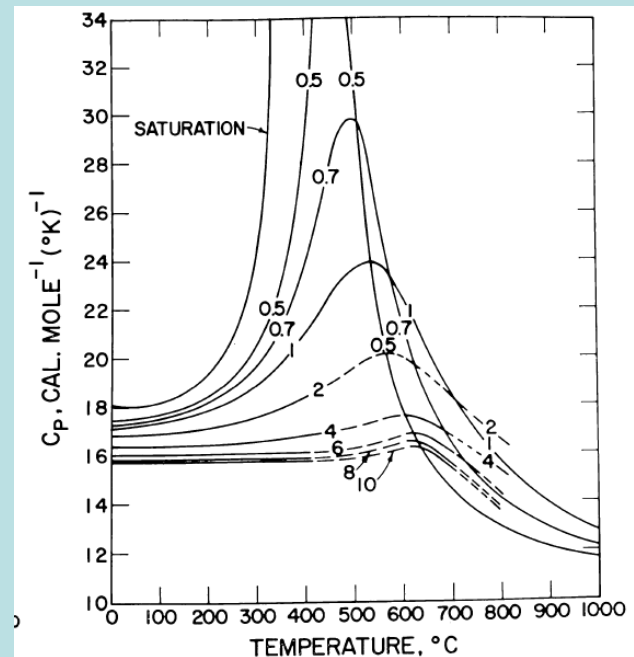
and WATER



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

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

Standard Gibbs free energy at T & P depends on

- * Free energy at 25 C & 1 bar

 - **KNOWN!**

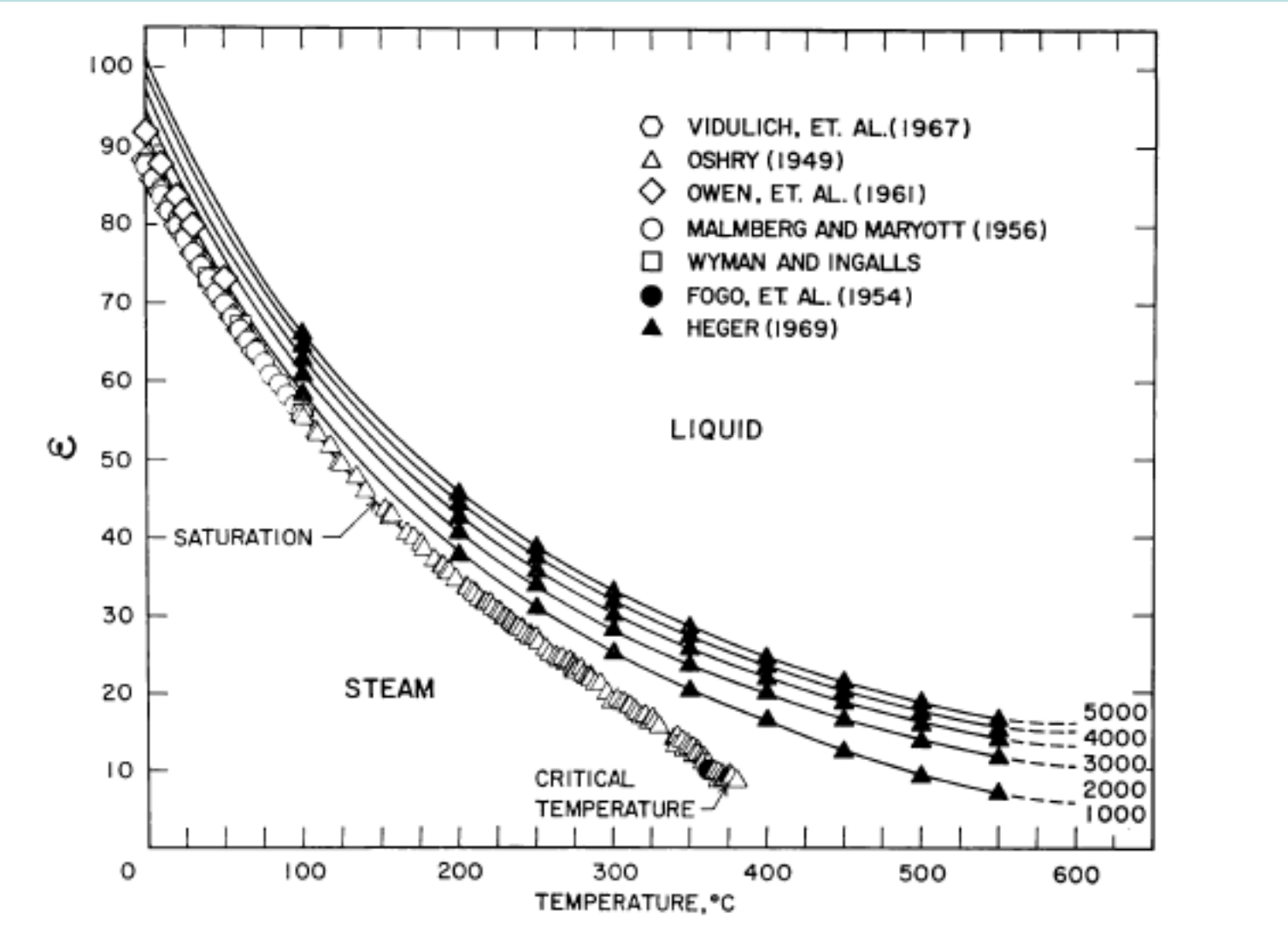
- * Equation of state coefficients for each ion

 - **KNOWN FOR HUNDREDS OF IONS!**

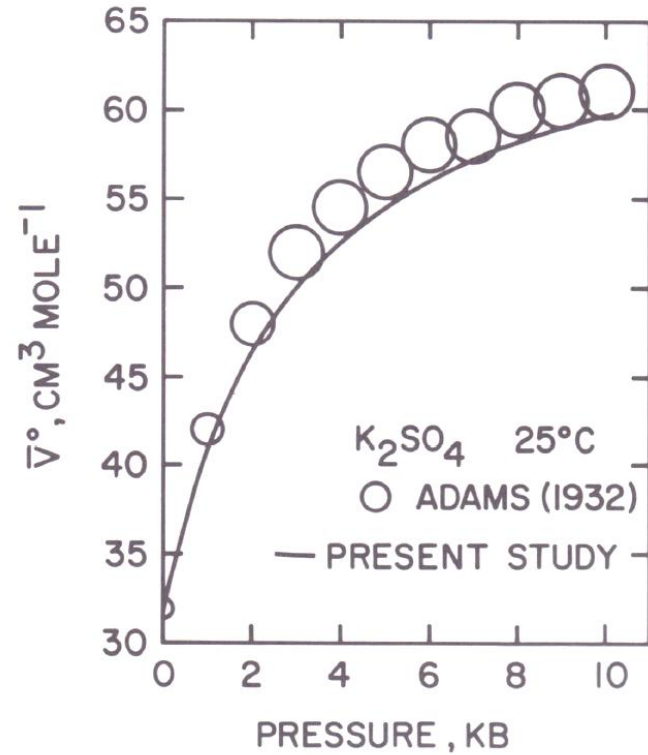
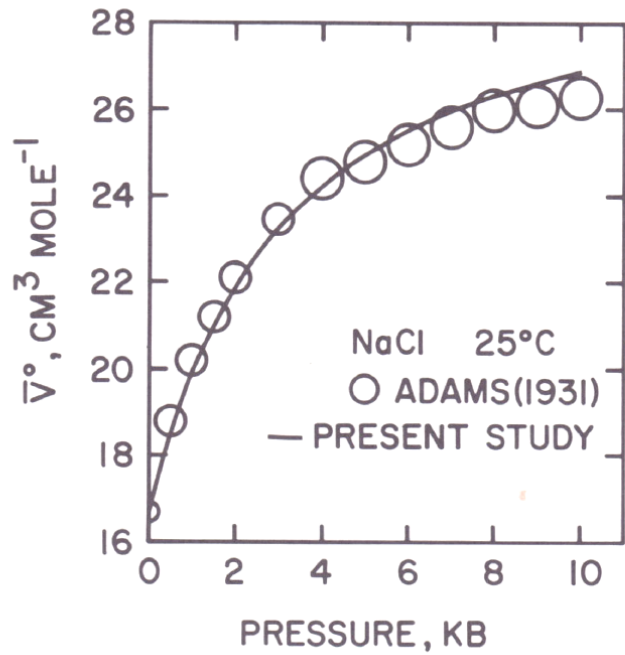
- * Dielectric constant of water

 - **ϵ_{H_2O} - KNOWN TO 5.0 kb ONLY.....**

Dielectric constant of water - current limits



from Helgeson and Kirkham (1974)



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

**New Proposal to DOE (Cohen, Fei, Wu, & Sverjensky):
Measurements and theory to obtain volumes of H₂O, CO₂ and H₂O-CO₂ mixtures**

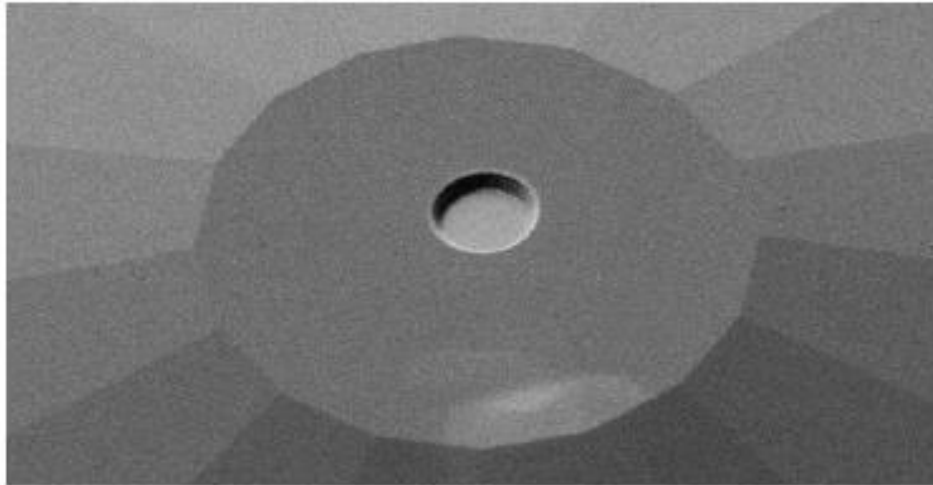
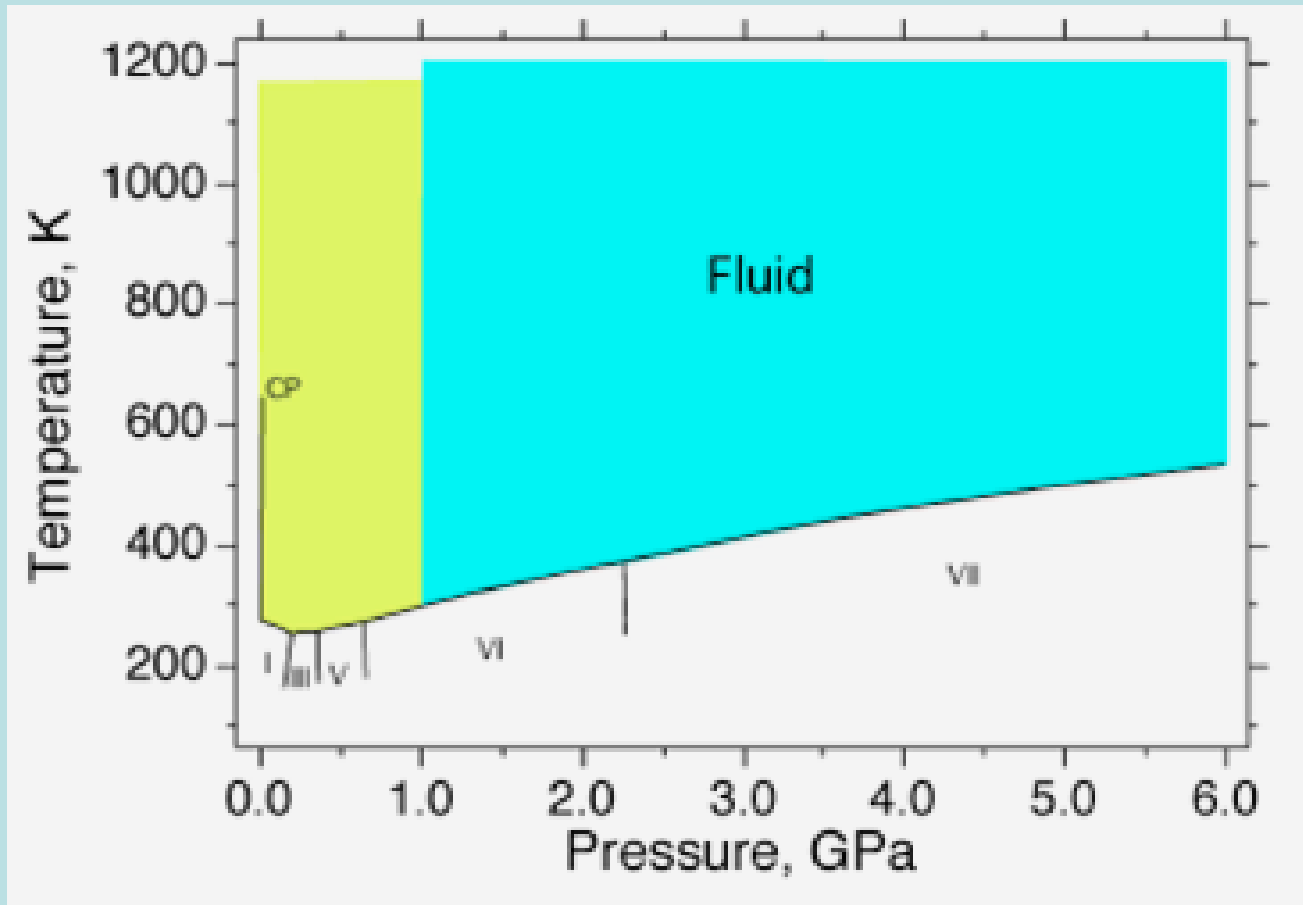


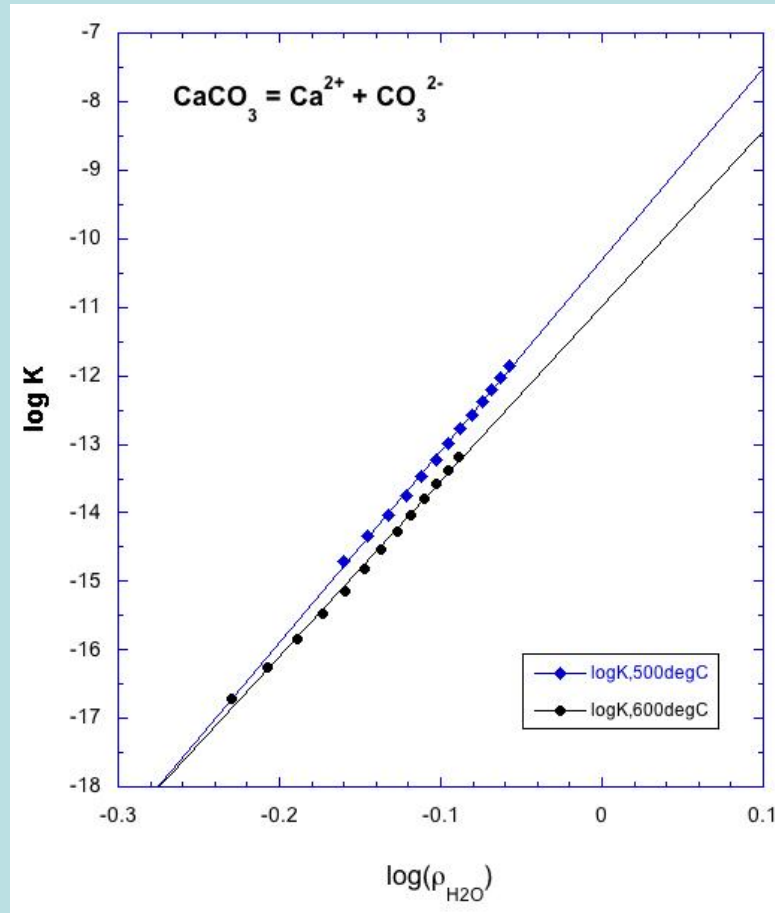
Fig. 2. Sample chamber in the diamond anvil fabricated by focused ion beam (FIB) milling. The anvil could be coated with Pt (or Au) to contain fluid H₂O. The sample chamber will be 150 μ m diameter by 40 μ m depth.



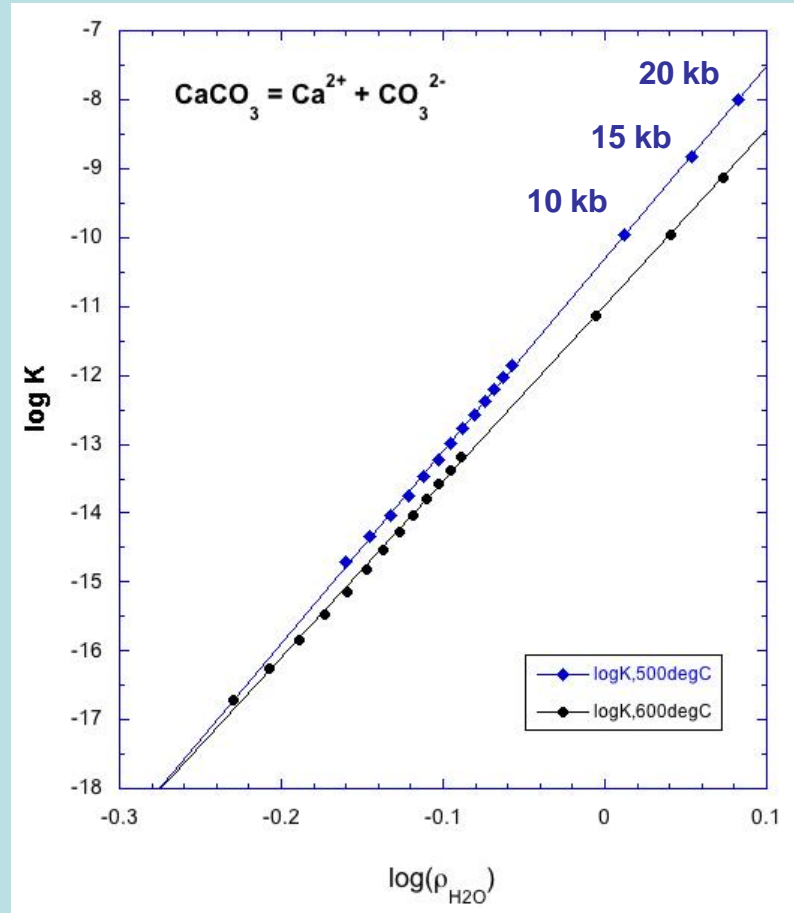
Blue Area: Proposal to measure volumes of H₂O, CO₂ and H₂O-CO₂ mixtures

What can be done now?

Calculated with SUPCRT (EOS)

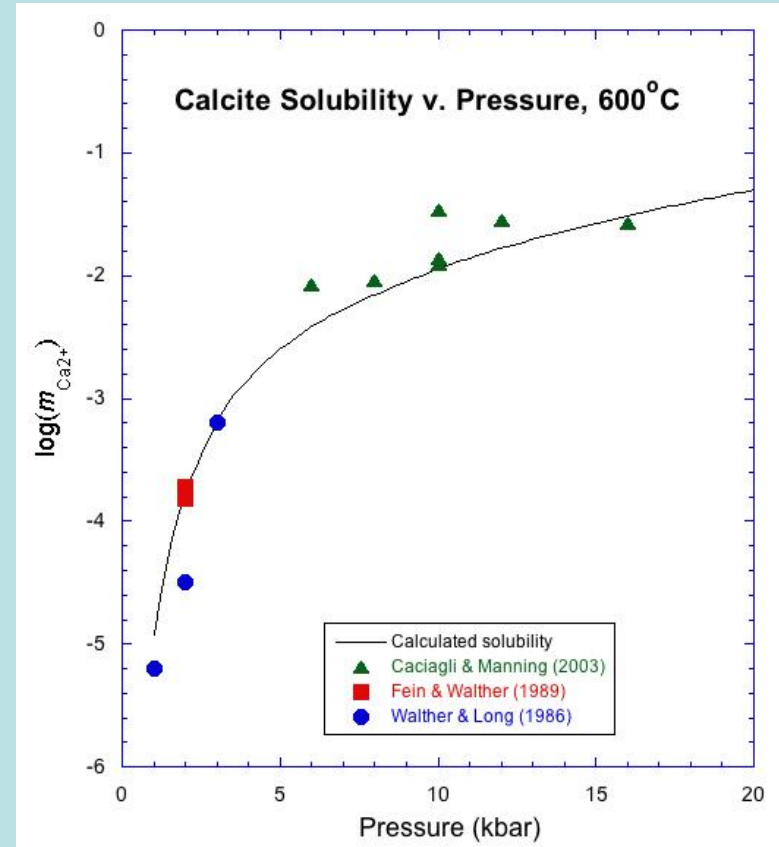
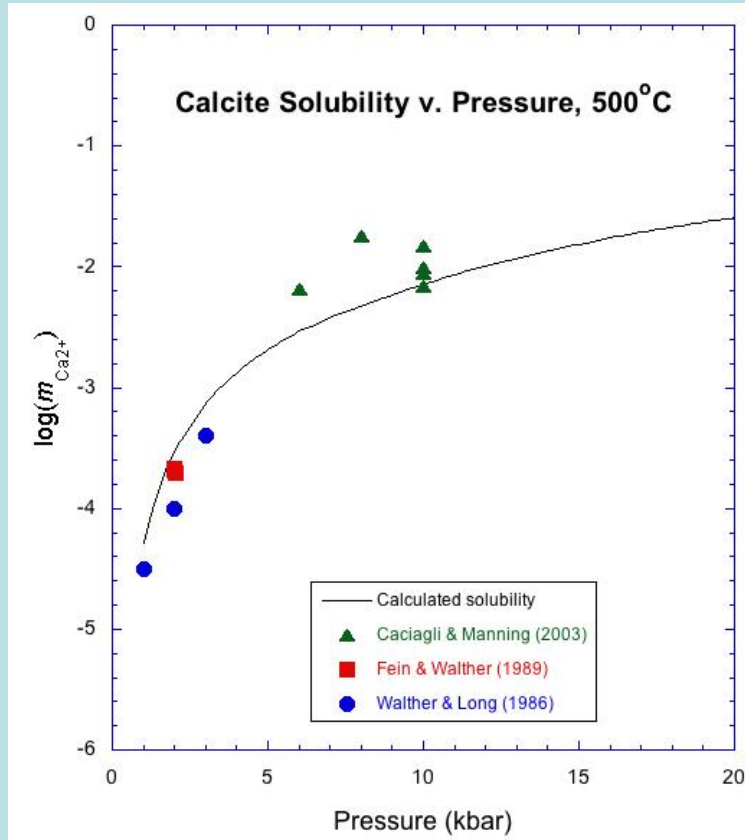


Extrapolated to 10, 15 & 20 Kb



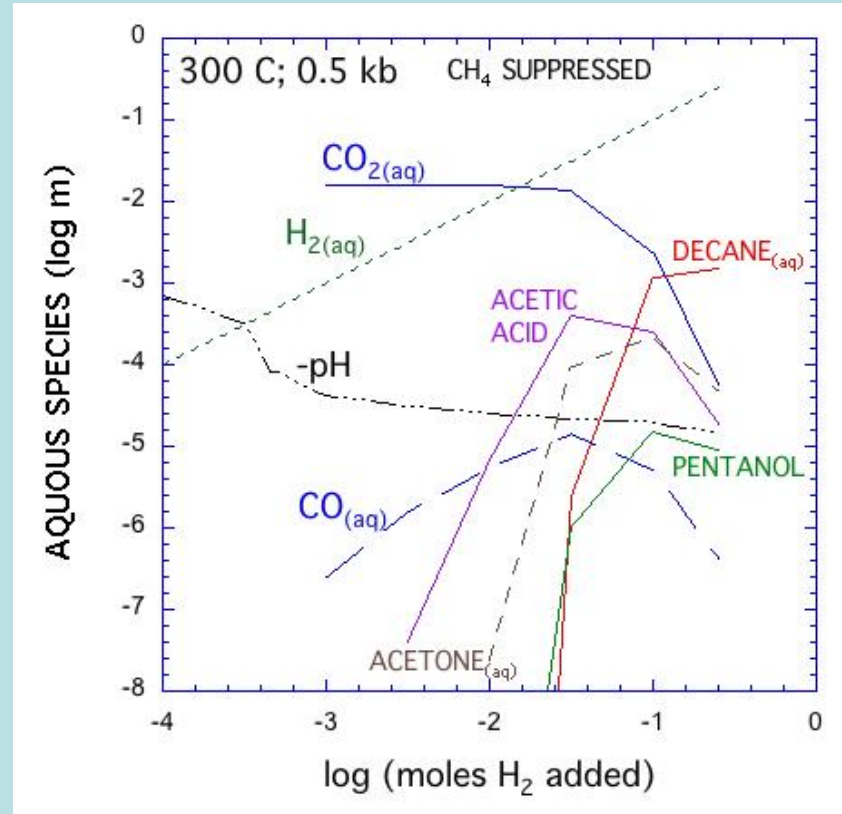
Extrapolations carried out for all equilibria in the calcite-water system

Prediction of calcite solubility at elevated T & P

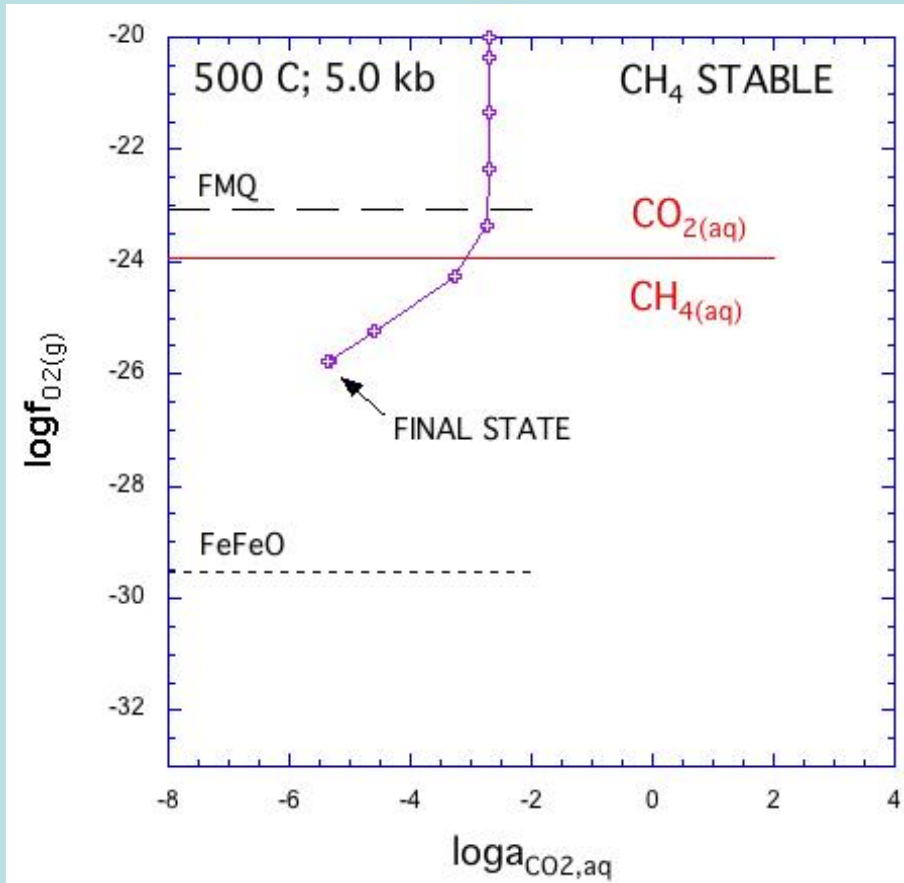


Similar calculations possible for hydrocarbon-mineral-water systems...

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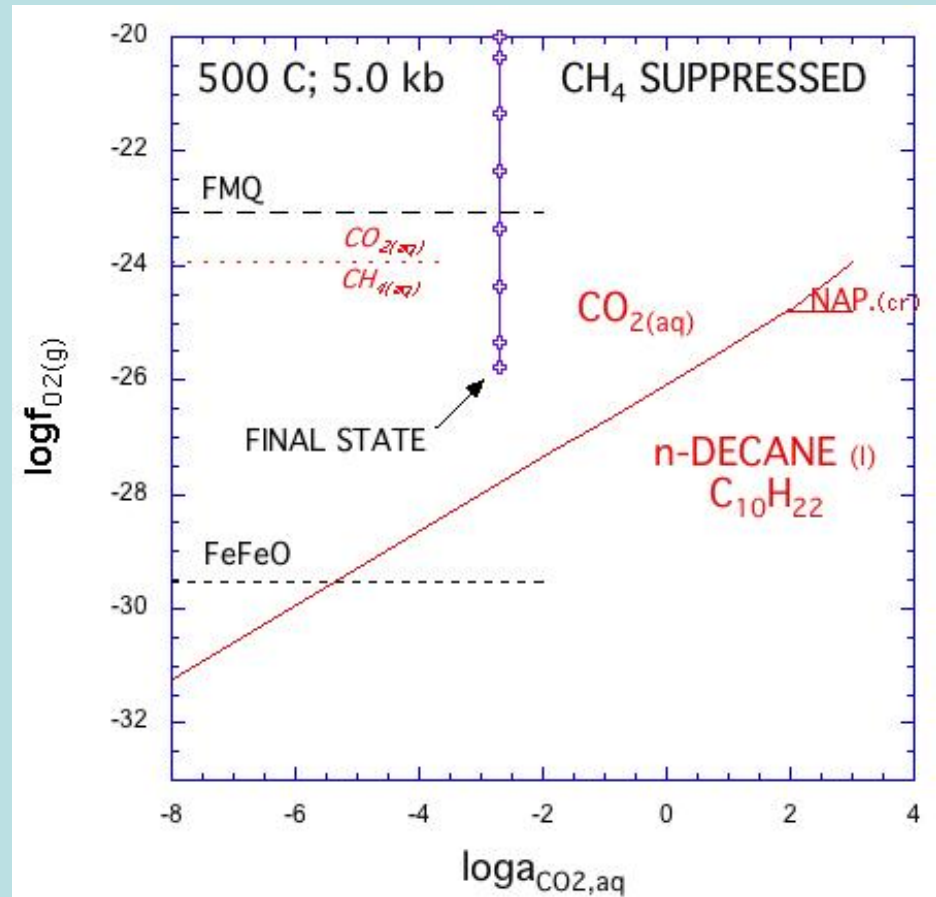


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Summary of Experiments & Theory Needed

At pressures up to 60.0 kbars:

Expts.
&
Theory

(1) Volumes of H₂O, CO₂ and mixtures

- leads to partial molal volume of solute CO₂
- constrain equation of state for partial molal volumes of aqueous solutes (e.g. CO₂)

Theory

(2) Dielectric constant of water ($\epsilon_{\text{H}_2\text{O}}$)

- 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