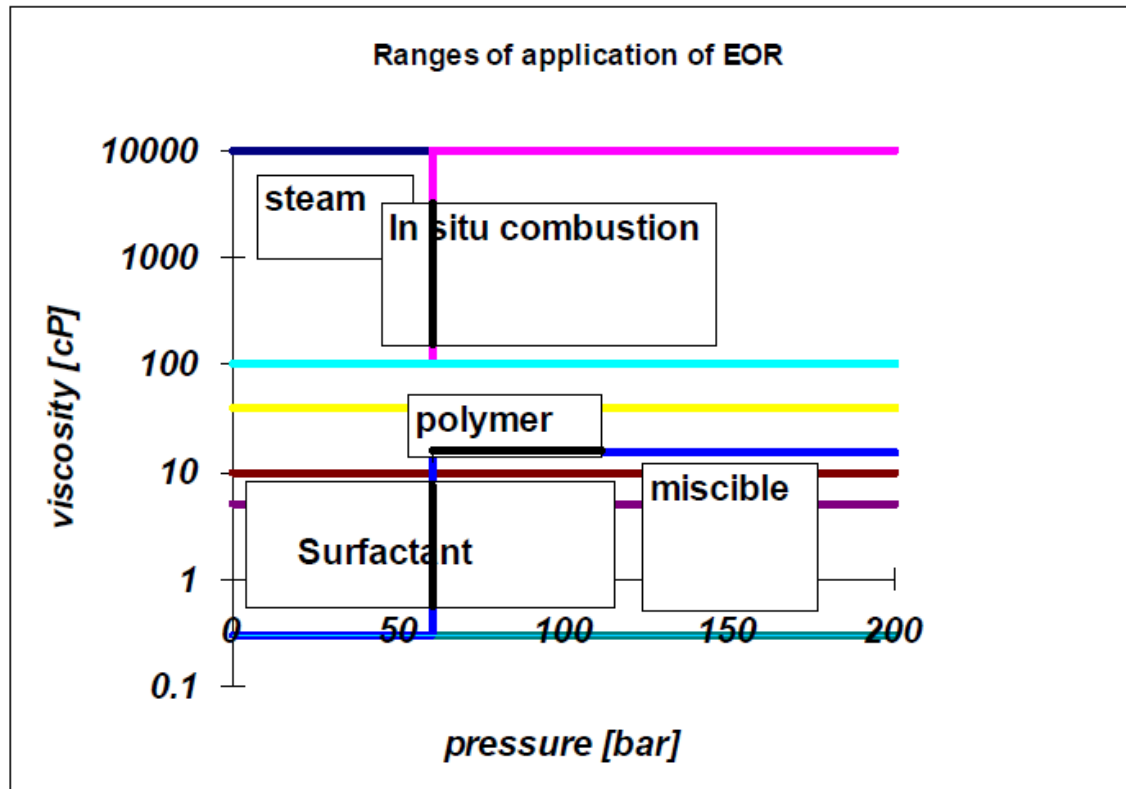# Geochemical Modeling of water flooding oil in calcite reservoirs at high carbon dioxide pressure

Rouhi Farajzadeh, Dan Marchesin, Cor van Kruijsdijk, Wanderson Lambert, Hua Guo, Ali Akbar Eftekhari, Vitor Matos, Hamidreza Salimi, Amaury Alvarez Cruz

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Ranges of application of EOR

RECOVERY OF OIL BECOMES INCREASINGLY CHALLENGING, WHAT ABOUT LOW/HIGH SALINITY WATER INJECTION?

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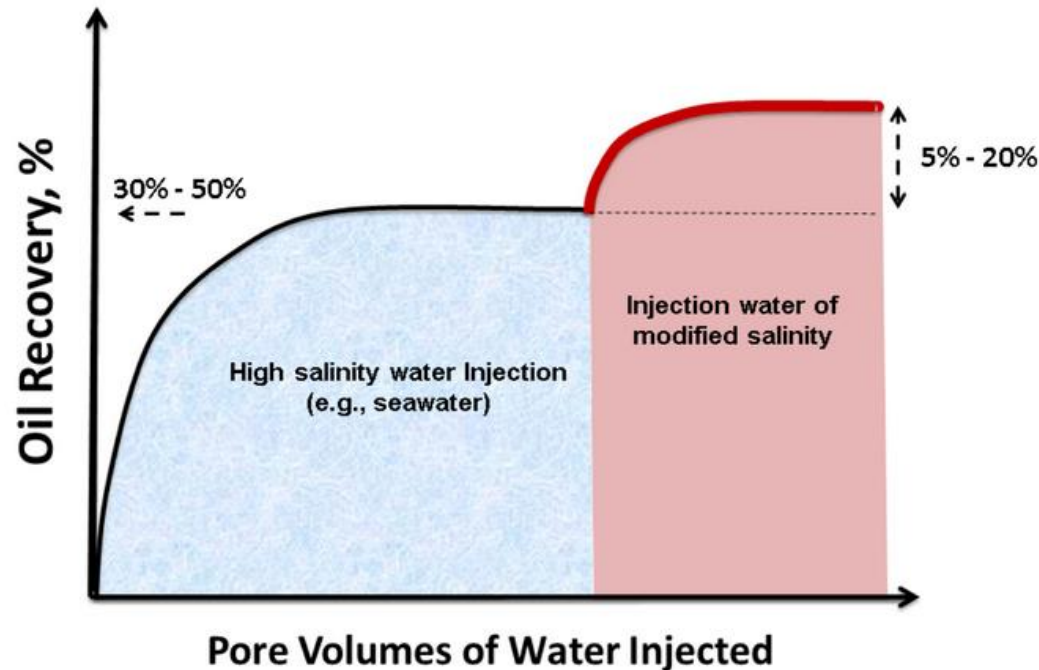# Other challenges: Incorporate geochemistry
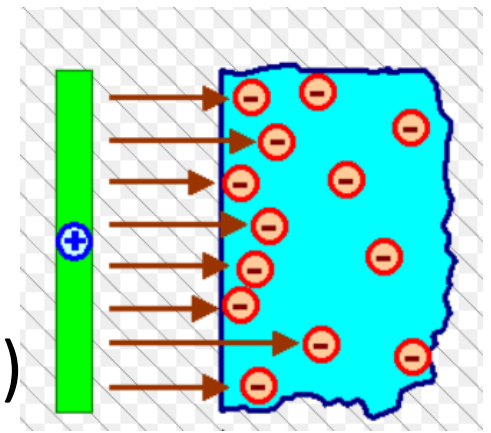
- High salinities (low-salinity water injection)

- Oil-wet- fractured calcite reservoirs

- High carbon dioxide content
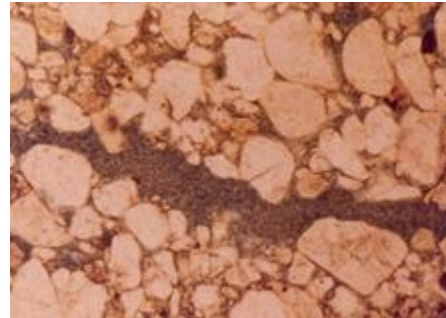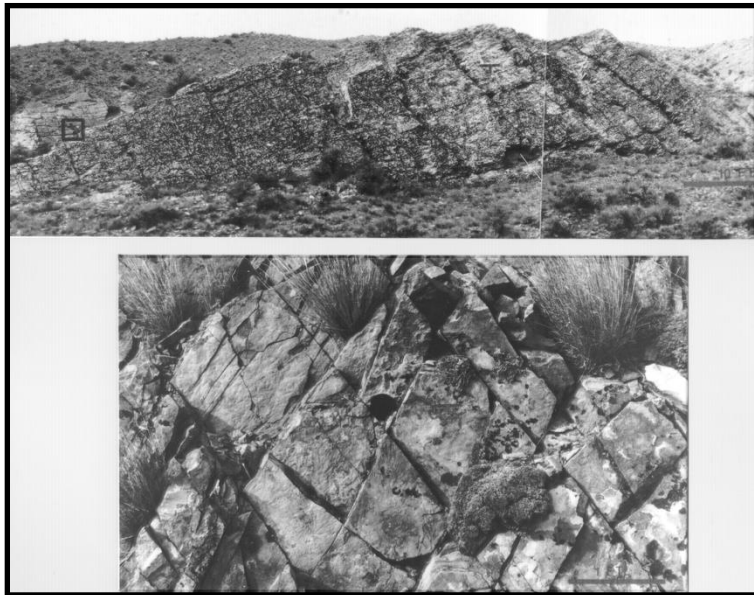
$$\log_{10} \gamma_{\pm} = -\frac{A z_+ z_- \sqrt{I}}{1 + aB\sqrt{I}} + CI$$

Before the turn of the century it was found by many researchers (Norman Morrow) that the water composition can effect oil recovery by some 10%

- **Yildiz, H.O., Valat, M., and Morrow, N.R.: "Effect of Brine Composition on Wettability and Oil Recovery of a Prudhoe Bay Crude Oil," J. Can. Pet. Tech, Jan. 1999, 38 (1) 26-31.**
- **Tang, G.Q. and Morrow, N.R.: "Salinity Temperature, Oil Composition and Oil Recovery by Waterflooding," SPE Reservoir Engineering, November 1997, 12, (4) 269-276.**
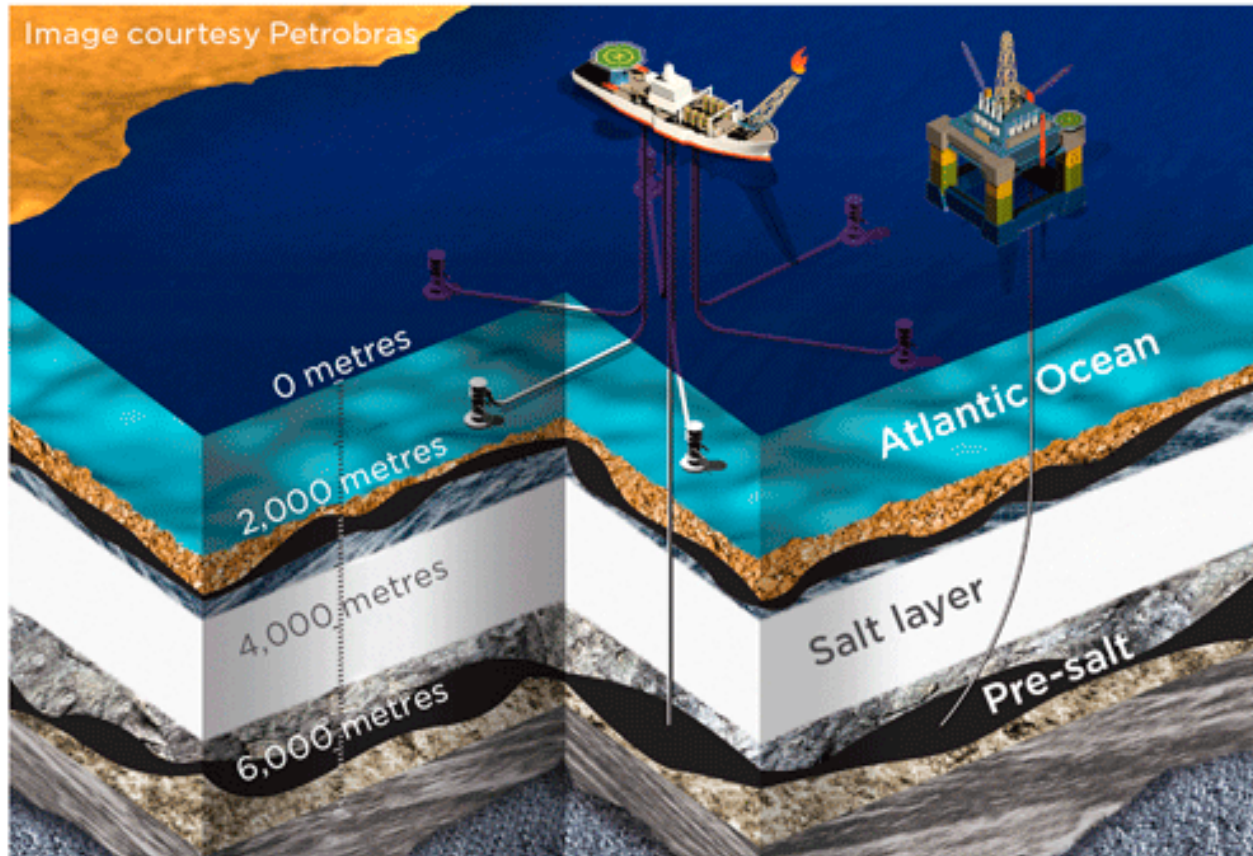
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presal

Illustration of oil extraction from Brazil's pre-salt reservoirs

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Sleipner field

CO₂ separated from natural gas

ca. 800 meters

CO₂ is injected into the Utsira-formation

ca. 2500 meters

ca. 3000 meters

Natural gas with 8-9 % CO₂

Source: Statoil
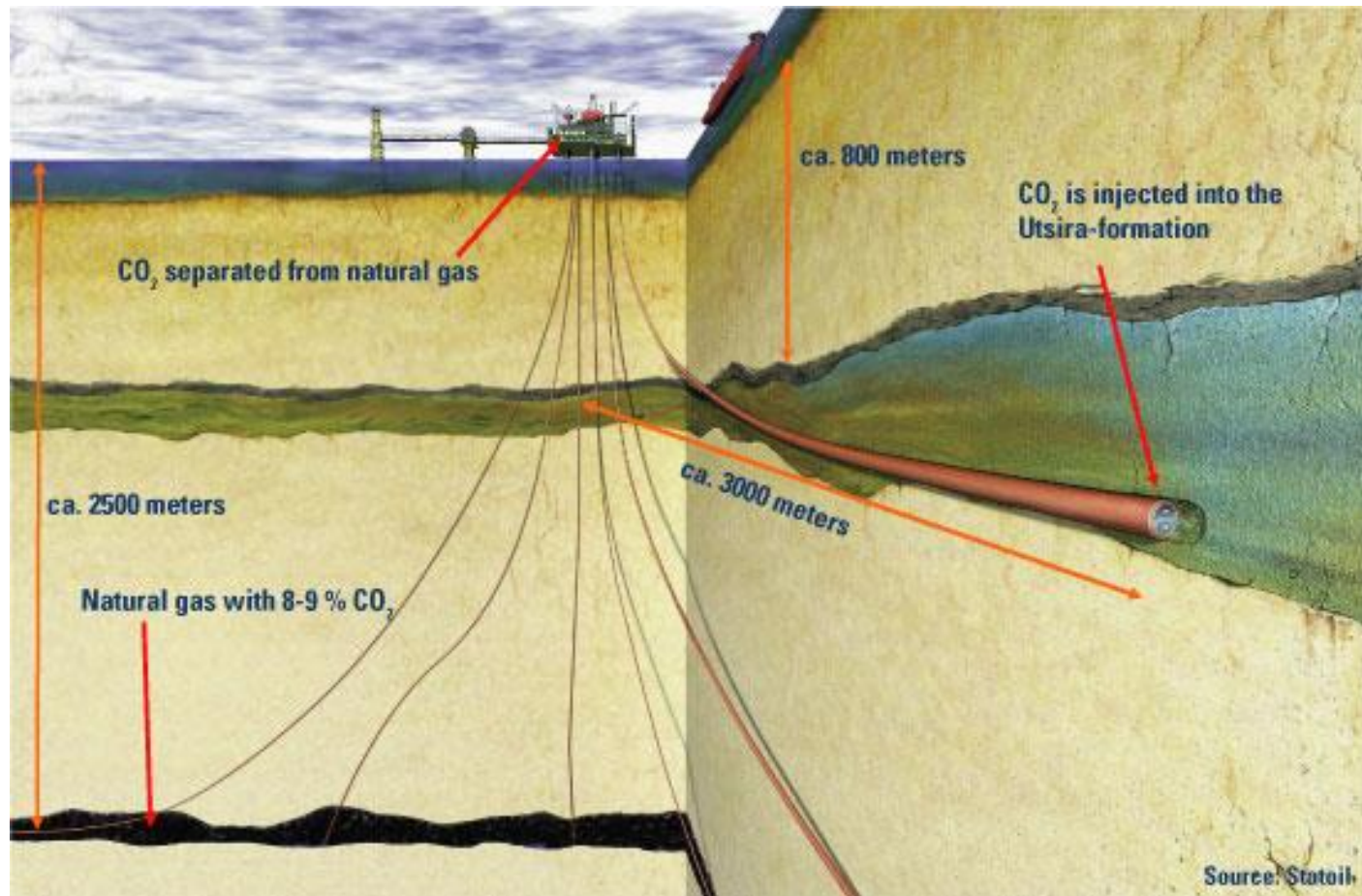
Hypotheses

- **1-Geochemistry can be incorporated in multiphase flow simulators by**
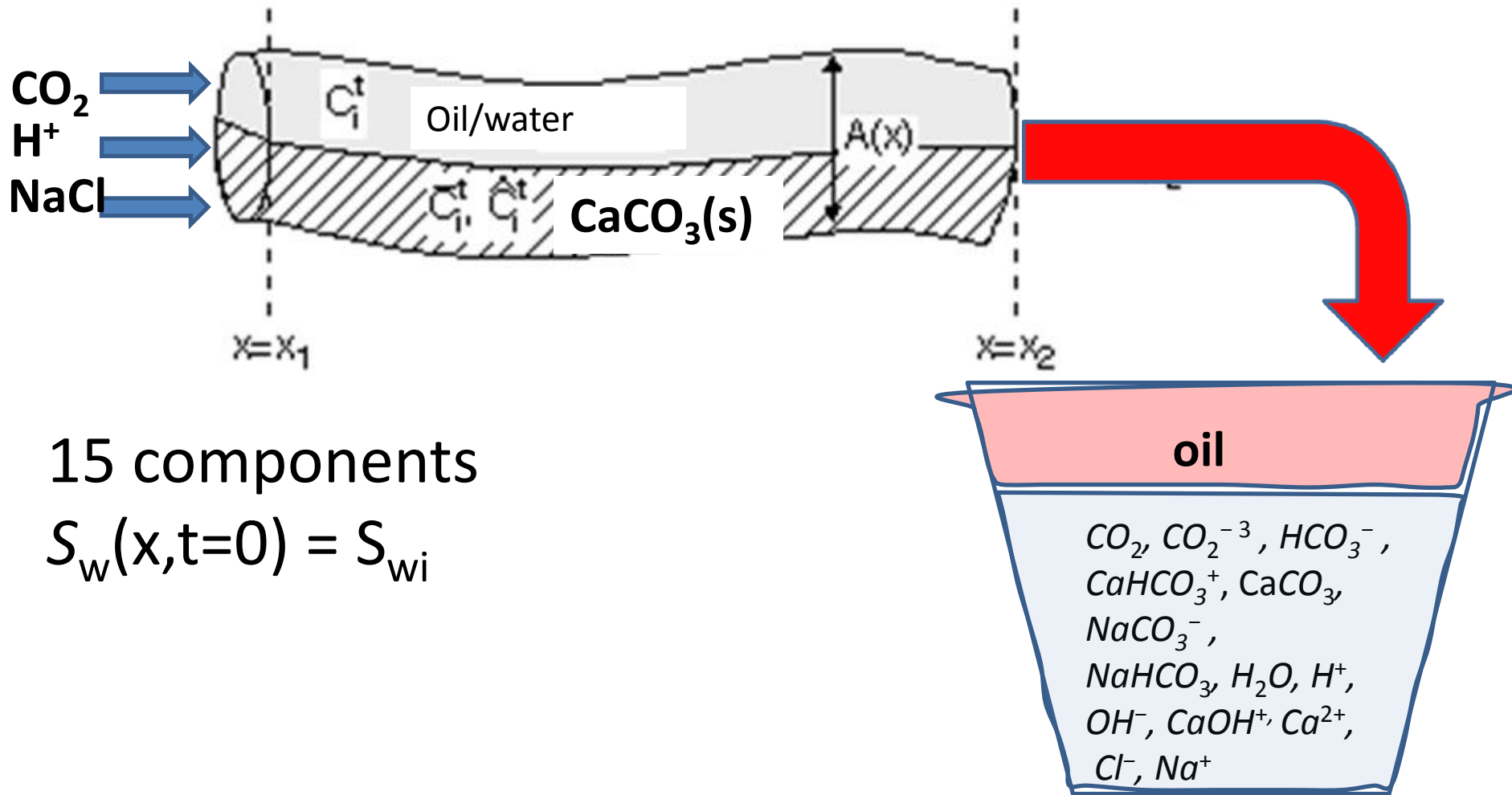 - a- Use of geochemical software to create look-up tables or regression formula and use of EUREQA statistical software
  - b- Simultaneous solution of all relevant equations
- **2- Oil recovery predictions require full incorporation of geochemistry**
  - a- e.g.: Aqueous Carbon dioxide dissolution depends on ionic strength
  - b- Wetting behaviour depends on surface charges and thus on adsorption of surface complexes
  - Positive effect on relative permeabilities not clear
- **The main challenge for petroleum engineers is to understand geochemistry, which is facilitated with the help of existing free software**
  - PHREEQC, MINTEQ
- **Dissolved Carbon dioxide, analogously to gaseous CO_2, main contributor to enhance oil recovery**
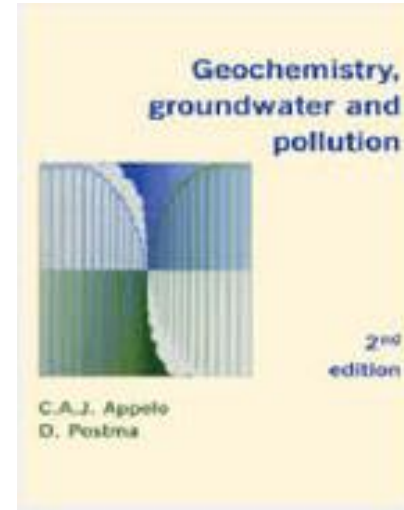
Low salinity water injection: 1-D setting

Figure adapted from geochemistry and fluid flow

CO_2

H^+

$NaCl$

C_i^t Oil/water

$A(x)$

C_i^t $\hat{C}_i^t$ $CaCO_3(s)$

$x=x_1$ $x=x_2$

15 components
$S_w(x,t=0) = S_{wi}$

oil

CO_2, CO_2^{-3}, HCO_3^-, $CaHCO_3^+$, $CaCO_3$, $NaCO_3^-$, $NaHCO_3$, H_2O, H^+, OH^-, $CaOH^+$, Ca^{2+}, Cl^-, Na^+
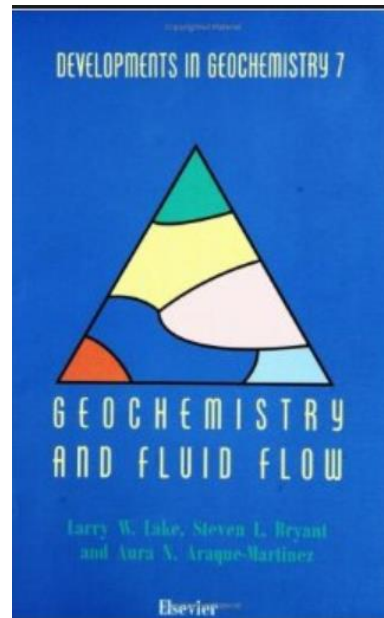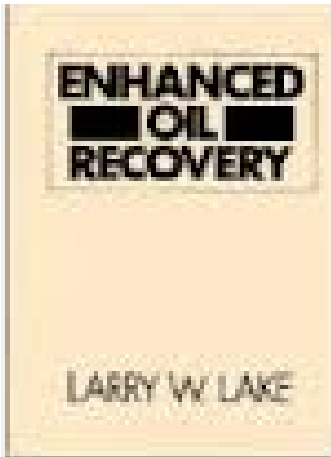
Traditional approach using geochemical software for "flash" calculation
MORES and PHREEQC (ETH))

MODELING MULTIPHASE FLOW INCLUDING GEOCHEMISTRY

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Main step in creation of look-up table Determine # of equations and unknowns

- **Assumption of local thermodynamic equilibrium: number of degrees of freedom N_f can be derived with extended Gibbs phase rule: $N_f = N_s - N_r - N_c - p + 2$ = # species - # reactions - # constraints - # phases + (T,P) = 15-8-2-3 = 2 +(T,P pm)**
  - *N_c = 2 for charge balance equation and NaCl equation, p = 3*

    We choose H^+ and Cl^-

- **For surface species $N_S - N_R - N_C = 0$ = # surface species - # reactions - # constraints (number of species – number of reactions – number of constraints = zero; see below)**

(1) C Anthony J Appelo and Dieke Postma. *Geochemistry, groundwater and pollution*. Taylor & Francis, 2005.
(2) David L Parkhurst and CAJ Appelo. *Description of Input and Examples for PHREEQC* US Geological Survey Denver, 2013.

Activities

EQUILIBRIUM RELATIONS
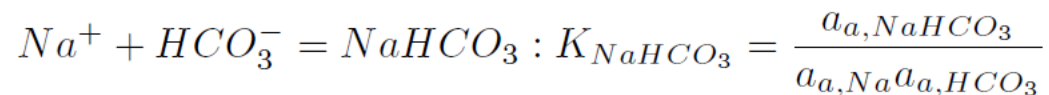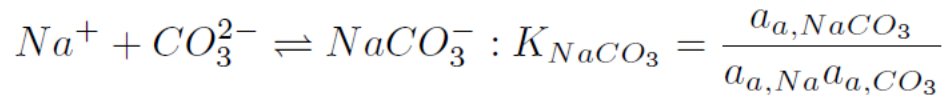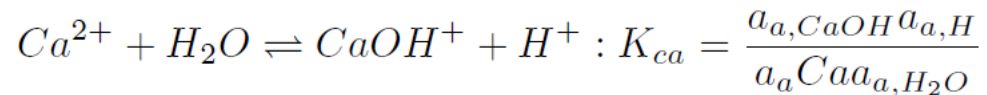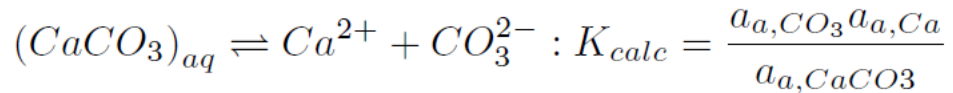
Eight equilibrium equations
(page 87 of EOR)

TABLE 3-7 SELECTED SOLUBILITY DATA AT 298 K FOR AQUEOUS AND SOLID SPECIES IN NATURALLY OCCURRING PERMEABLE MEDIA (ADAPTED FROM DRIA ET AL., 1988)

Aqueous species or complexes		Log K_r	ΔH° J/kg-mole
OH^-	$= H_2O - H^+$	14.00	-133.5
$CaOH^+$	$= Ca^{2+} + H_2O - H^+$	12.70	-173.2
$Ca(OH)_2$	$= Ca^{2+} + 2H_2O - 2H^+$	27.92	-267.2
$CaCO_3$	$= Ca^{2+} + CO_3^{2-}$	-3.23	44.1
$CaHCO_3^+$	$= Ca^{2+} + CO^{2-} + H^+$	-11.23	45.0
$Ca(HCO_3)_2$	$= Ca^{+2} + 2CO_3^{2-} + 2H^+$	-20.73	66.8
HCO_3^-	$= CO_3^{2-} + H^+$	-8.84	35.5
$CO_2(dissolved)$	$= CO_3^{2-} - H_2O + 2H^+$	-16.68	53.8

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Equilibrium reactions: PHREEQC (US-geological survey) input concentrations: NaCl, CO_2 equilibrate with calcite (Appelo / Parkhurst)

$$(CO_2)_{aq} + H_2O \rightleftharpoons HCO_3^- + H^+ : \quad K_a = \frac{a_{HCO_3^-} a_{H^+}}{a_{(CO_2)_{aq}} a_{H_2O}}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ : K_b = \frac{a_{a,CO_3} a_{a,H}}{a_{a,HCO_3}}$$

$$H_2O \rightleftharpoons OH^- + H^+ : K_w = \frac{a_{a,OH} a_{a,H}}{a_{a,H_2O}}$$

USGS Software determines:

(1) 15 Relevant species
(2) 10 Equilibrium reactions
(3) Equilibrium calculations
(4) Equilibrium compositions

$$(CaCO_3)_{aq} \rightleftharpoons Ca^{2+} + CO_3^{2-} : K_{calc} = \frac{a_{a,CO_3} a_{a,Ca}}{a_{a,CaCO3}}$$

$$Ca^{2+} + H_2O \rightleftharpoons CaOH^+ + H^+ : K_{ca} = \frac{a_{a,CaOH} a_{a,H}}{a_a Ca a_{a,H_2O}}$$

Eureqa software determines convenient regression expressions; choice between accuracy and simplicity

$$CO_3^{2-} + Ca^{2+} + H^+ \rightleftharpoons CaHCO_3^+ : K_{hca} = \frac{a_{a,CaHCO_3}}{a_{a,CO_3} a_{a,Ca} a_{a,H}}$$

$$Na^+ + CO_3^{2-} \rightleftharpoons NaCO_3^- : K_{NaCO_3} = \frac{a_{a,NaCO_3}}{a_{a,Na} a_{a,CO_3}}$$

$$Na^+ + HCO_3^- = NaHCO_3 : K_{NaHCO_3} = \frac{a_{a,NaHCO_3}}{a_{a,Na} a_{a,HCO_3}}$$

$(CaCO3)_r = (CaCO3)_{aq}$ $(CO2)o \ (CO2)aq$

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Some theory to obtain activity coefficients (a = γc)

- The chemical potential of a component does not depend on whether the concentrations are measured in molar, molal or mole fractions.

- $\mu = \mu_{0X} + RT \ln (\gamma_x X) = \mu_{0m} + RT \ln (\gamma_m m) = \mu_{0c} + RT \ln (\gamma_c c) = \mu_0 + RT \ln a$

  where μ_{0X} is the chemical potential of pure solute having the properties of an infinitely dilute solution, μ_{0m} is the chemical potential of the solute in the ideal one molal solution

  and μ_{0c} is the chemical potential of the ideal one molar solution.

- Anderson and Crerar show that difference between the activity coefficients γ except for very high concentrations are extremely small, e.g.,

  $\ln \gamma_x = \ln \gamma_m + \Gamma = \ln \gamma_m + \ln (1 + 0.0180153m)$

- Greg M Anderson and David A Crerar. *Thermodynamics in geochemistry: The equilibrium model*. Oxford University Press, USA, 1993.

Activity coefficients

- The chemical potential does not depend on whether the concentrations are expressed in mole fractions X, molalities m, or molarities c or activities a.

- The equations require a reference concentration: $X=1$, concentration / sum of concentrations, $m =$ *concentration of one mol / kg-water (molal) or one mol / liter solution (molar)*

$$\mu = \mu_X^0 + RT \ln (\gamma_{H,x} X)$$
$$= \mu_m^0 + RT \ln (\gamma_{H,m} m)$$
$$= \mu_c^0 + RT \ln (\gamma_{H,c} c)$$
$$= \mu^0 + RT \ln a$$

The reference activity is the activity of one molal of substance if it were to behave ideally.

$\ln \gamma_{H,x} = \ln \gamma_{H,m} + \Gamma = \ln \gamma H; m + \ln (1 + 0.0180153m)$

Activity coefficients $\gamma = a / c$

The extended Debye-H¨uckel theory for calculating the activity coefficient $\gamma_j(\mu)$ of an ion reads (A = 1.1709, B = 0.3281,

ionic strength = $\mu = \frac{1}{2}c_i z_i^2 = \frac{1}{2}a_i / \gamma_i(\mu) z_i^2$)

$$ln\ \gamma_i(\mu) = - Az_i^2 \sqrt{\mu}/ (1 + B\ a_i\sqrt{\mu}) + b_i\mu$$

In the absence of data for the ionic radius a_j and the active fraction coefficient b_j, the formula of Davies is often used

$$ln\ \gamma_j(\mu) = - Az_j^2 \sqrt{\mu}/ (1 + B\sqrt{\mu}) + 0.3\ \mu$$

Equilibrium constants are expressed in activities not concentrations

Activity coefficients

There is a variety of models for the activity coefficient. Data difficult to find

Debye-Huckel model:

$\ln \gamma_j (\mu) = - A z_j^2 \sqrt{\mu} / (1 + B \,°a_j \sqrt{\mu}) + b_j \mu$

$B_\gamma = (8\pi N_A q_e^2 \rho_0 / 1000 \varepsilon_r k_B T))^{1/2} =$
$50.29158649 \, \rho_0^{1/2} / (\varepsilon_r T)^{1/2}$

$A_\gamma = (2\pi N_A q_e^6 \rho_0 / (1000 (\varepsilon_r RT)^3))^{1/2} =$
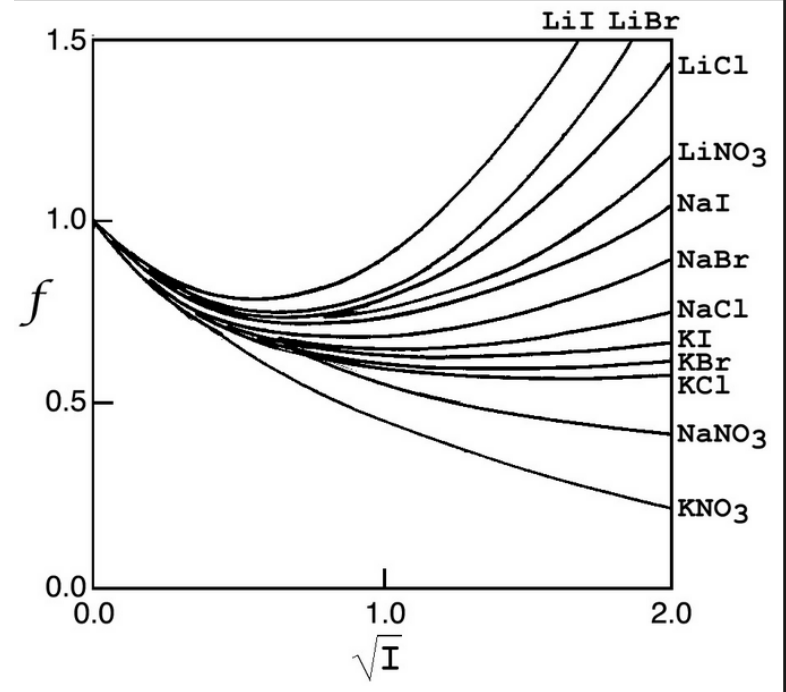$\qquad = 1824829.238 \, \rho_0^{1/2} / (\varepsilon_r T)^{3/2}$

[mol/kg]^(1/2), °a_j in Angstrom

at where A = 1.17 08, B = 0.3281 <small>B=0.3281   1.1...708</small>

Davies made an equation that does not require ion specific data

$\ln \gamma_j (\mu) = - A z_j^2 \sqrt{\mu} / (1 + \sqrt{\mu}) + 0.3 \, \mu,$

$$[\alpha_{Ca^{2+}}][\alpha_{CO_3^{2-}}] = K_{sp} = 4.47 \times 10^{-9}$$

$$[Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}} = K_{sp} = 4.47 \times 10^{-9}$$

$$[Ca^{2+}](0.405)[CO_3^{2-}](0.37) = 4.47 \times 10^{-9}$$

$$X^2 = \frac{4.47 \times 10^{-9}}{(0.405)(0.37)} = 2.98 \times 10^{-8}$$

$$X = \sqrt{2.98 \times 10^{-8}} = 1.73 \times 10^{-4}$$

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Activity coefficients for neutral molecules

The Setch´enow coefficient k_S relates the activity coefficient of interest to the ionic strength of the solution, e.g., for carbon dioxide
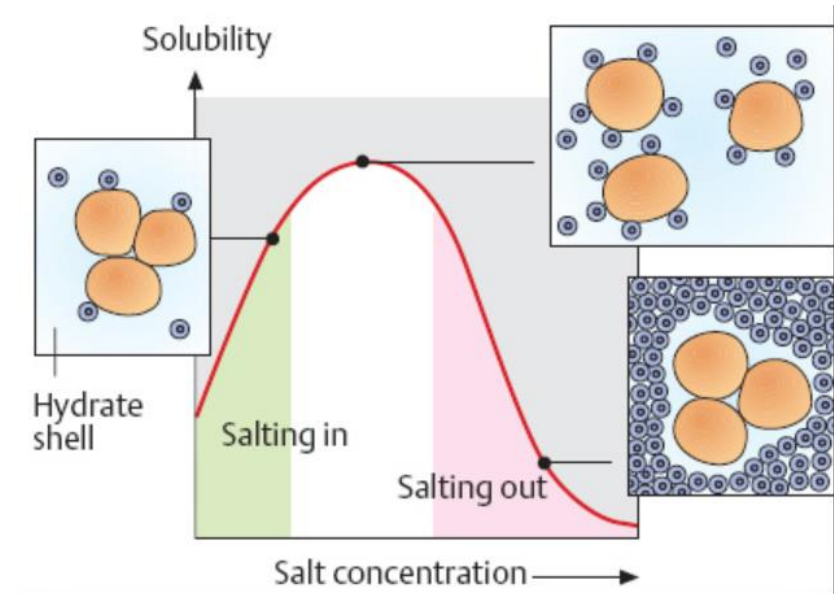
$$\log \gamma_{CO2(aq)} = k_S \, \mu,$$

where the logarithm has base ten. Similar relations hold for the other noncharged components.
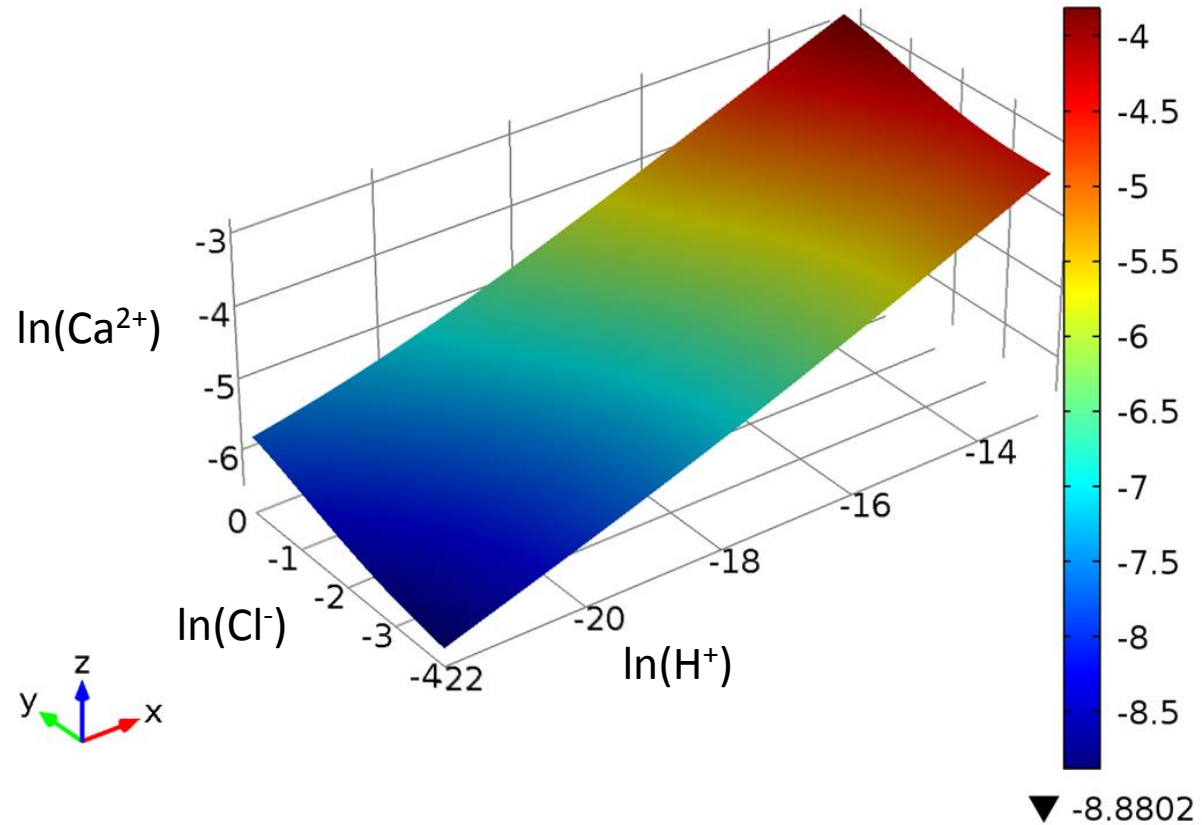
For single salt solutions, values can be found in [98]. Byrne et al. [21] use the equation

$$\log m_0 / m_s = \Sigma \, k_{m,i} \, \mu$$

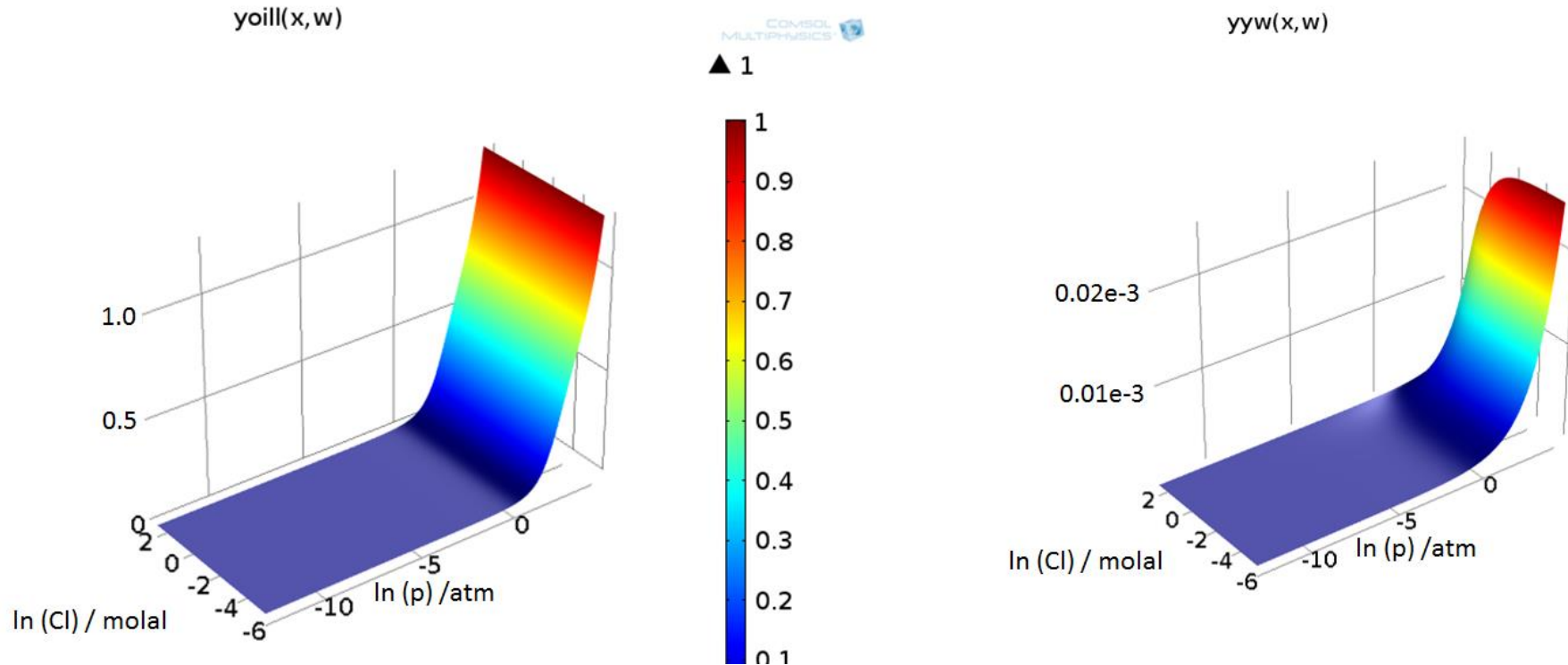where m and m_0 are the solubilities in salt solutions and distilled water

Solubility

Hydrate shell

Salting in

Salting out

Salt concentration

Ln(Ca^{2+} (hp = x=ln(H$^+$), cl = y= ln Cl$^-$)

$$\ln(Ca^{2+}) = 1.93 + 0.467 \ln(H^+) - 0.00927 \ln(H^+) \ln(Cl^-) - 0.0893 \ln(Cl^-)(Cl^-)$$

Comparison of carbon dioxide dissolution in oil and water

Decane versus pressure

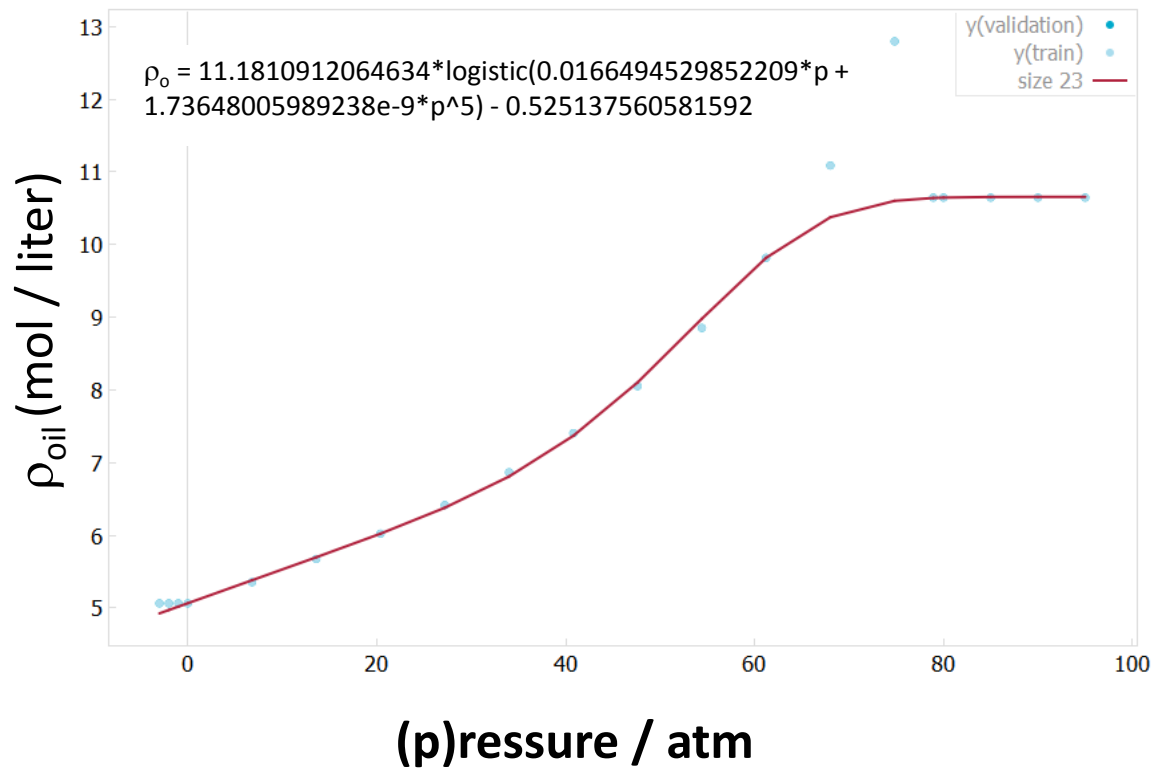T = 100° F

decane = -0.499660001029639*erfc(p - 76.8684480220767)*asinh(p - 77.6044420017854)
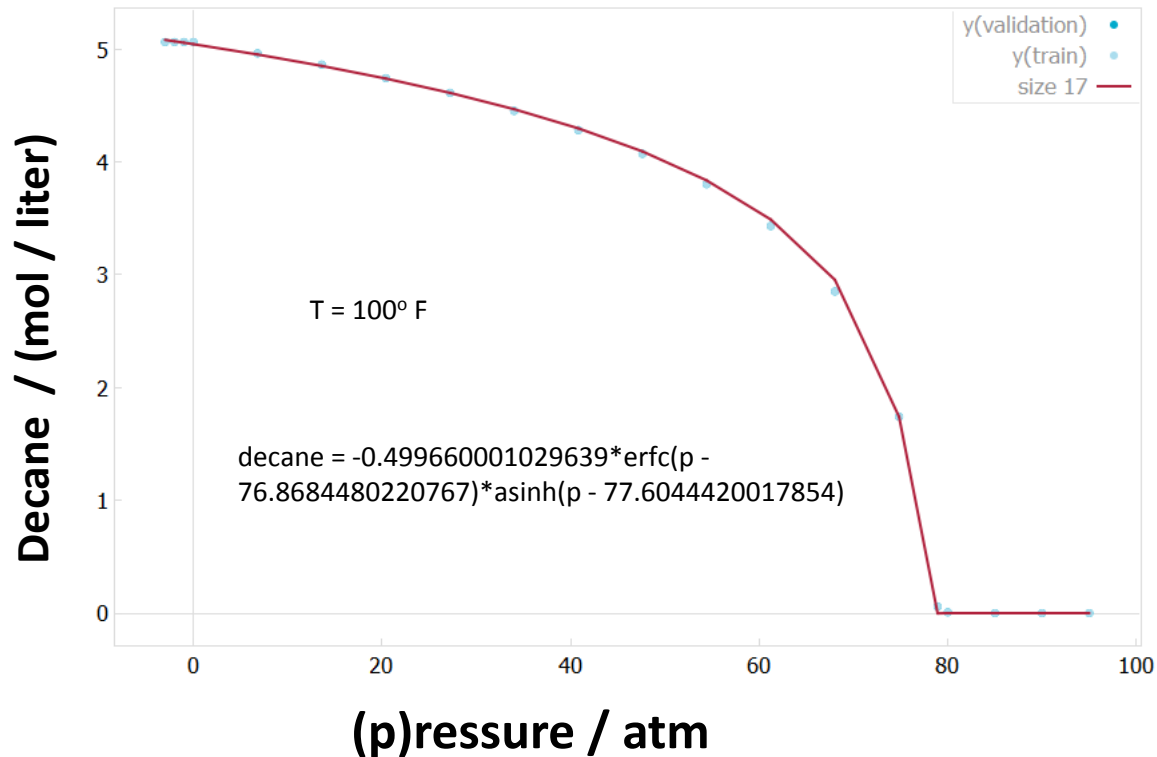
Oleic phase density versus pressure

$\rho_o = 11.1810912064634 * logistic(0.0166494529852209*p + 1.73648005989238e\text{-}9*p\text{^}5) - 0.525137560581592$

Axis label (y): ρ_{oil} (mol / liter)

Axis label (x): **(p)ressure / atm**

Legend: y(validation), y(train), size 23

Example necessity of incorporation of geochemistry

CARBON DIOXIDE DISSOLUTION DEPENDS ON IONIC STRENGTH

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Carbon dioxide dissolution

At this boundary we use Henry's law to relate the gas pressure to the carbon dioxide concentration in the liquid, i.e.,

$$K_{w-g}^{H} = a_{w,CO_2}/a_{g,CO_2} = m_{w,CO_2}\, \gamma_{w,CO_2}/f_{g,CO_2}\,,$$

$$6$$

where m_{w,CO_2} is the molality of carbon dioxide in the water phase, γ_{w,CO_2} the activity coefficient, and $f_{g,CO_2(g)}$ is the fugacity of carbon dioxide in the gas phase. We use PHREEQC (Parkhurst and Appelo, 2013) for the computations. The procedure to get activities in neutral molecules is given in (Randall and Failey, 1927)

Density of carbon dioxide solutions
(ex 22, PHREEQC)
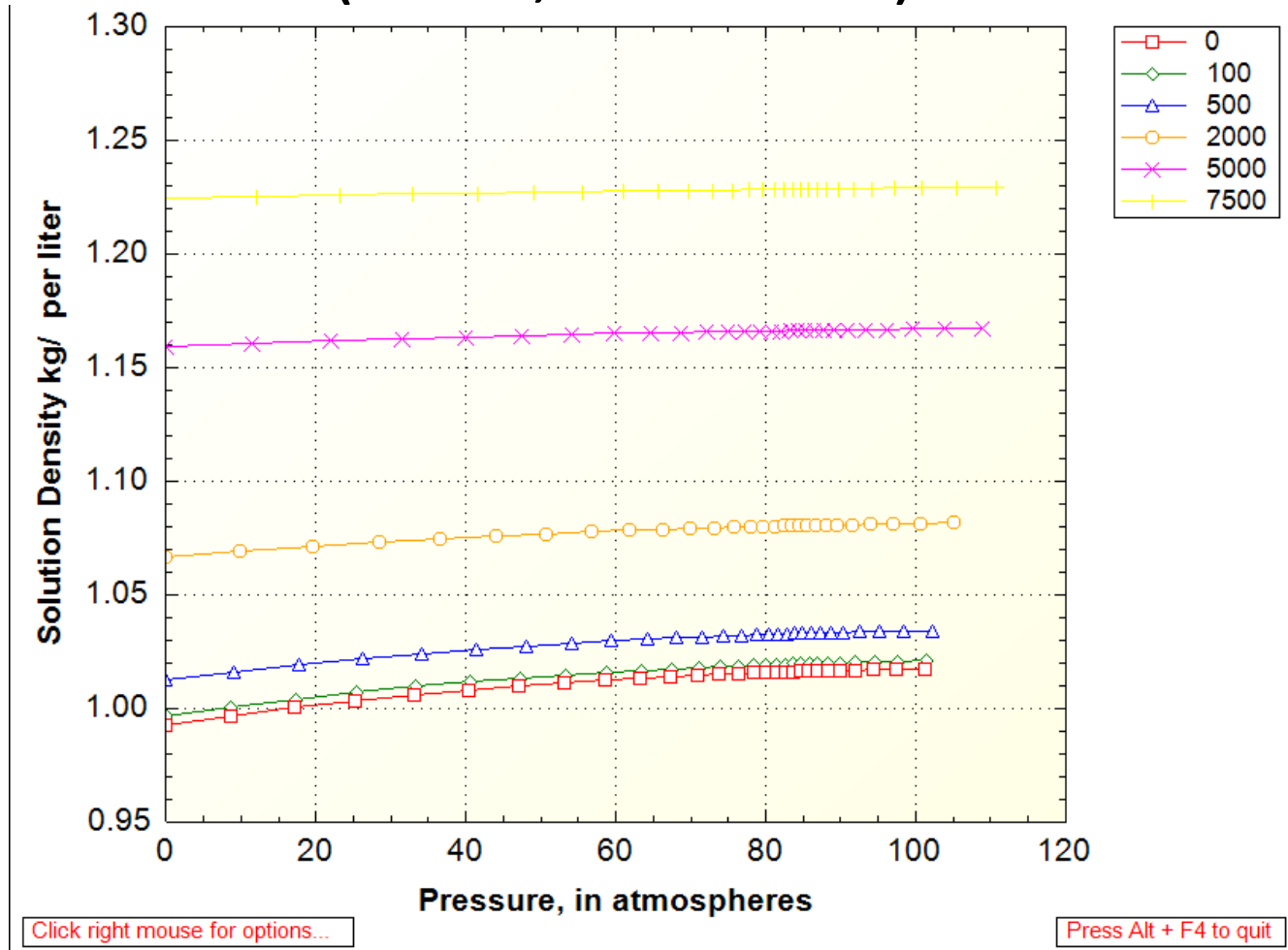
Henry coefficient P=Hc
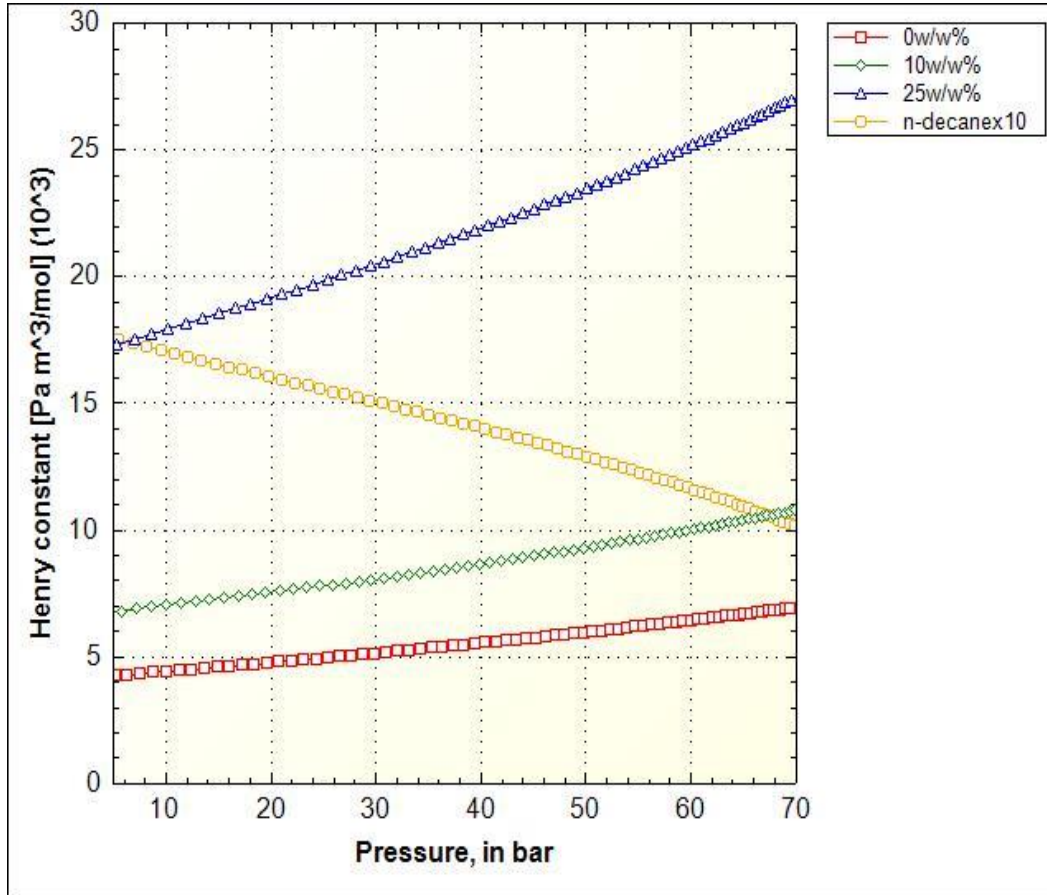
$K_H = aCO2(g)/aCO2(aq) = f_{CO2(g)} / c_{CO2(aq)}\gamma_{CO2(aq)}$
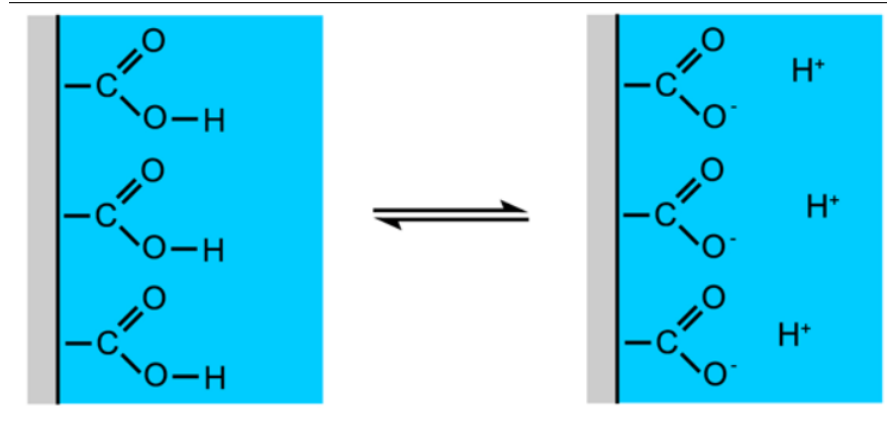
$K = a_{CO2(aq)}/a_{CO2(g)}$ and fresh/salt = $K/K_s = \gamma$

Setchenov-coefficients C

$$\log_{10} \gamma_{\pm} = -\frac{Az_+ z_- \sqrt{I}}{1 + aB\sqrt{I}} + CI$$

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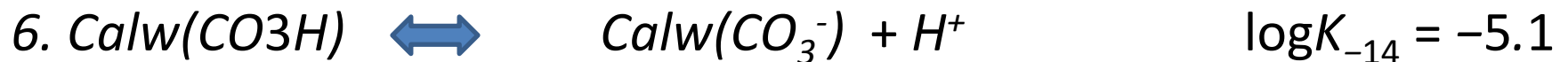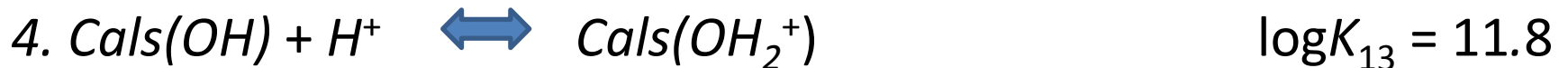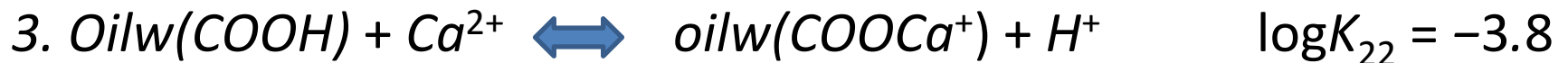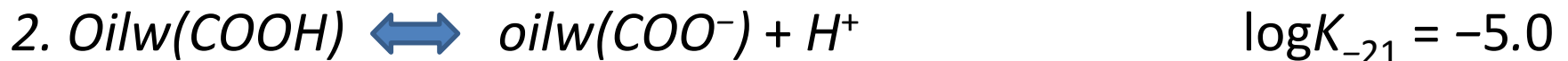
- Adsorbed species determine surface charge

Charge on calcite and oil surface can be obtained with phreeqc

- **Importance of surface complexes**

Wetting behaviour depends on surface charges and thus on adsorption of surface complexes

Surface complexes (after Brady)

1. *oils(NH$^+$)* $\longleftrightarrow$ *oils(N) + H+* $\qquad$ $\log K_{-11} = -6.0$

2. *Oilw(COOH)* $\longleftrightarrow$ *oilw(COO$^-$) + H$^+$* $\qquad$ $\log K_{-21} = -5.0$

3. *Oilw(COOH) + Ca^{2+}* $\longleftrightarrow$ *oilw(COOCa$^+$) + H$^+$* $\qquad$ $\log K_{22} = -3.8$

4. *Cals(OH) + H$^+$* $\longleftrightarrow$ *Cals(OH$_2^+$)* $\qquad$ $\log K_{13} = 11.8$

5. *Cals(OH)+ HCO$_3^-$* $\longleftrightarrow$ *Cals(CO$_3^-$) + H$_2$O* $\qquad$ $\log K_{33} = 5.8$

6. *Calw(CO3H)* $\longleftrightarrow$ *Calw(CO$_3^-$) + H$^+$* $\qquad$ $\log K_{-14} = -5.1$

7. *Calw(CO3H) + Ca^{2+}* $\longleftrightarrow$ *Calw(CO3Ca$^+$) + H+* $\qquad$ $\log K_{24} = -2.6,$
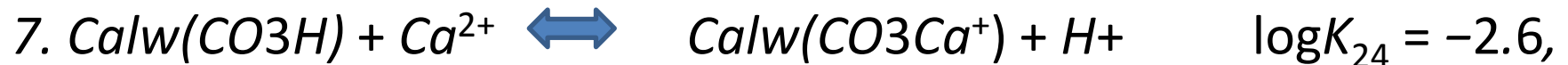
# 4- Constraints

$$oil_s(NH^+) \quad + \ oil_s(N) \ = x_1 \, c_1$$

$$Oil_w(COOH) \ + \ oil_w(COO^-) \ + oil_w(COOCa^+) \ = x_2 c_2$$

$$Cal_s(OH) + \ Cal_s(OH_2^+) + Cal_s(CO_3^-) \quad = x_3 c_3$$

$$Cal_w(CO3H) \quad + \quad Cal_w(CO_3^-) \ + Cal_w(CO3Ca^+) = x_4 c_4$$

Calculation of charge densities

- **The charge density in the domain of fixed ions is given by $\sigma = F/(AS)\, \Sigma_s (c_s v_s)$, F = Faraday constant, c_s, v_s = concentration and charge of surface species. Solid concentration S = g/L, A[m²/g]**

- $\sigma = sign\,(\psi_0)\,\sqrt{(4000RT\epsilon_r\epsilon_0)}\,\Sigma_i\,S_{bulk;i}\,(\exp\,-z_i F\psi_0\,/(RT)\,-1)\,\rightarrow\psi_0$

- $\Delta G_{0Total} = \Delta G_{0intrinsic} + \Delta G_{0Coulombic} = \Delta G_{0intrinsic} + \Delta ZF\psi_0$

- $K_{app} = \exp{-\Delta G_{0intrinsic}} + \Delta ZF\psi_0/(RT) := K_{int}\,\exp(\Delta ZF\psi_0 / RT)$
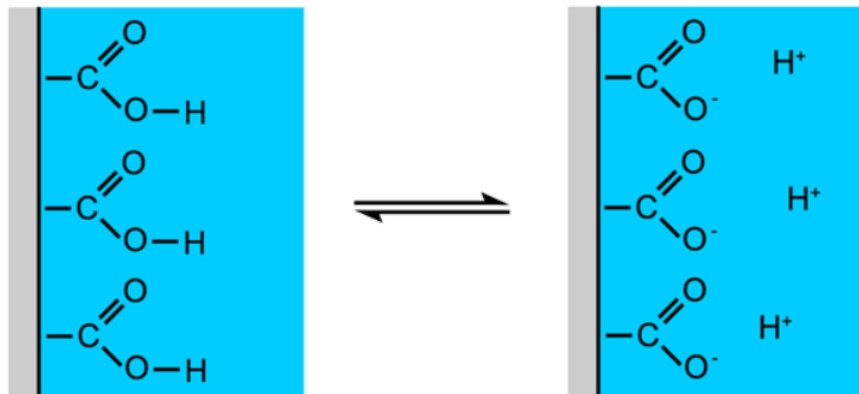
Surface concentrations; effect of ionic strength (PHREEQC)
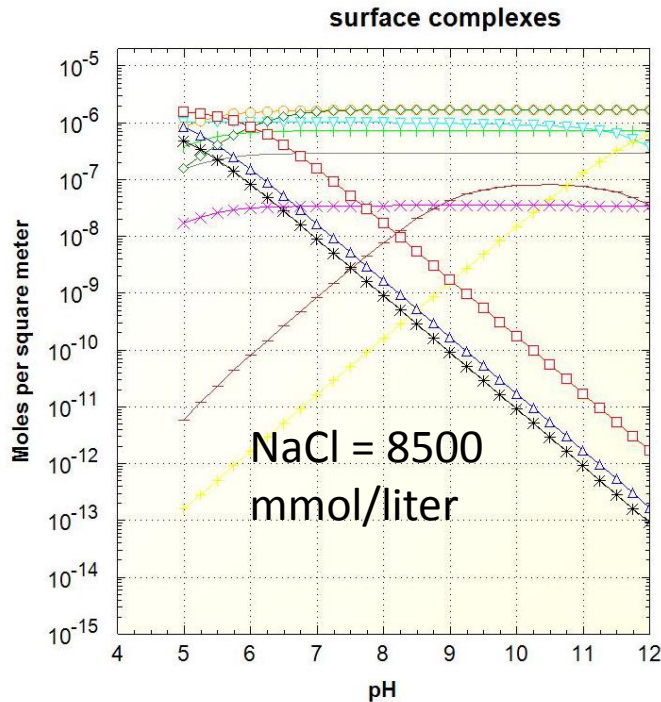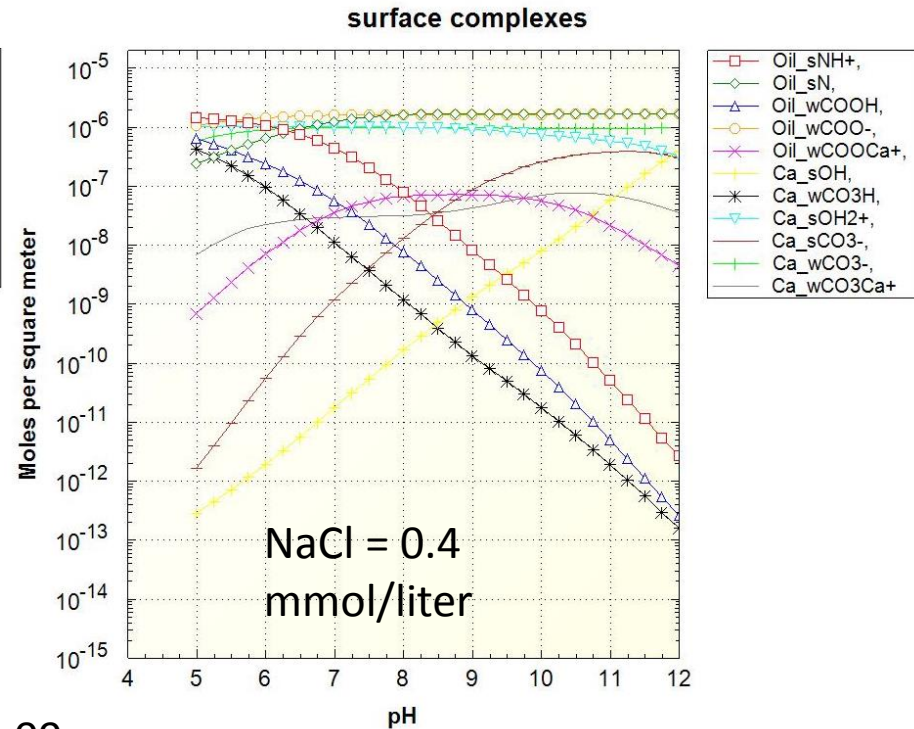

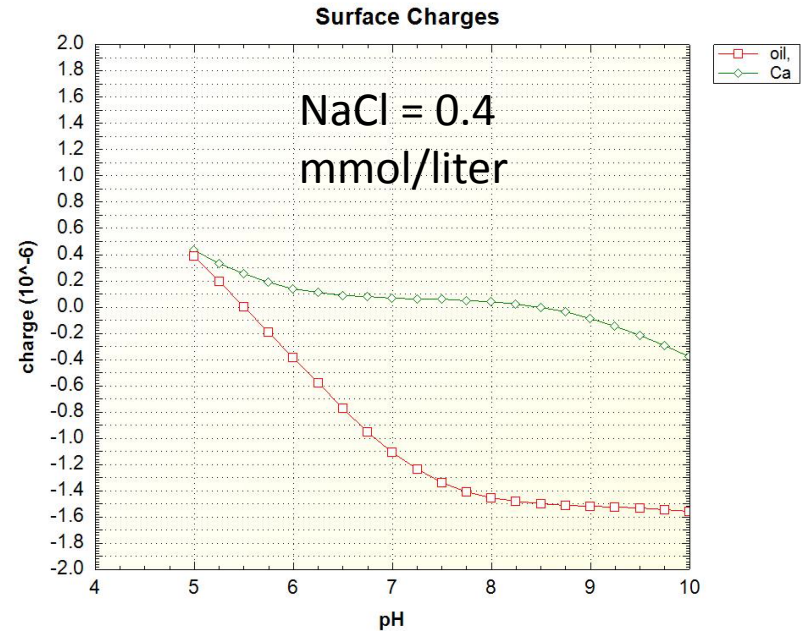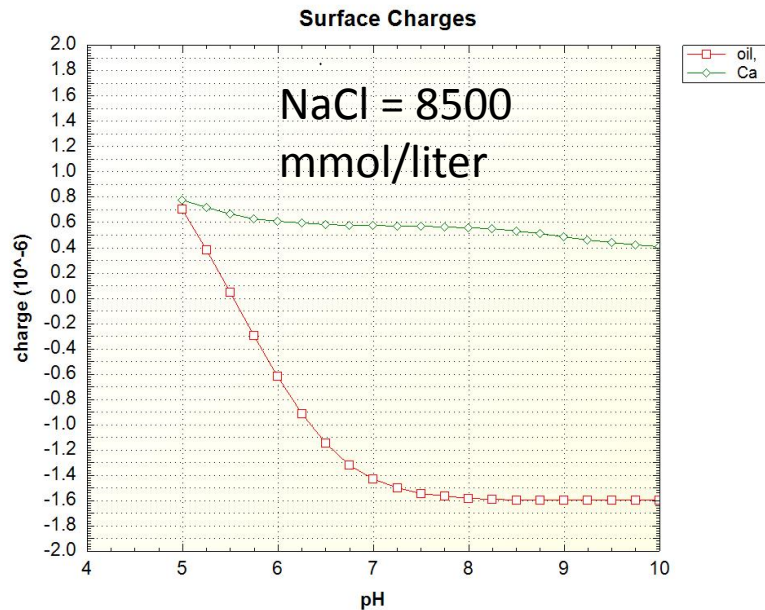Oil_sNH+ 1.67e-6 600. 0.09
Oil_wCOOH 1.67e-6
Ca_sOH   1.0e-6   600. 0.09
Ca_wCO3H 1.0e-6

Surface charge

NaCl = 8500 mmol/liter

NaCl = 0.4 mmol/liter

Oil_sNH+ 1.67e-6 600. 0.09
Oil_wCOOH 1.67e-6
Ca_sOH   1.0e-6   600. 0.09
Ca_wCO3H 1.0e-6

Surface charge
independent of amount of oil; depends on fraction active sites

NaCl = 8500 mmol/liter

NaCl = 8500 mmol/liter

Oil_sNH+ 1.67e-6 600. 0.009
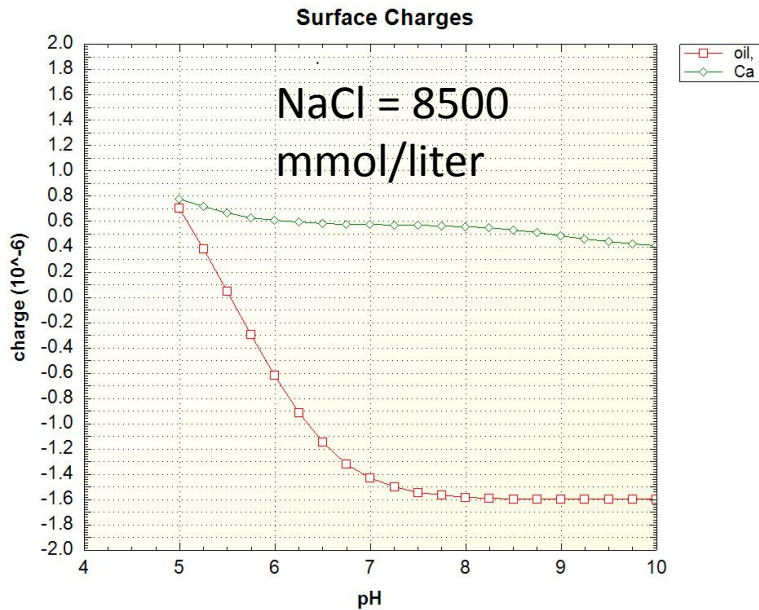Oil_wCOOH 1.67e-6
Ca_sOH   1.0e-6   600. 0.009
Ca_wCO3H 1.0e-6

Oil_sNH+ 1.67e-5 600. 0.09
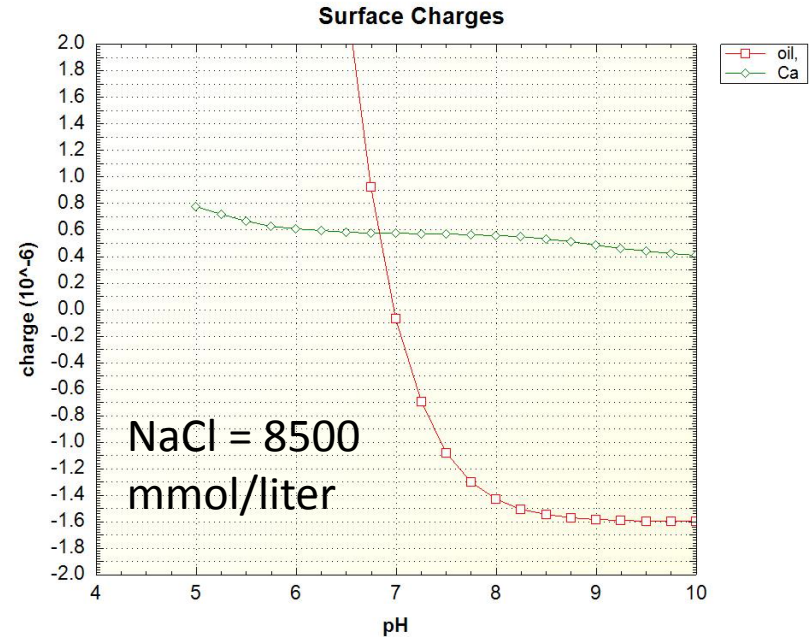Oil_wCOOH 1.67e-6
Ca_sOH   1.0e-6   600. 0.09
Ca_wCO3H 1.0e-6

Reservoir Engineering Course, *12-16 January 2015*

Interface interaction (SPE 17367, Hirasaki)

Van der Waals attraction

$A_z = \frac{3}{4} kT (\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)$
$/((\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)12\,\pi D^2)$
+ high frequency terms

Double layer repulsion

$P(\kappa D \gg 1) \rightarrow (\varepsilon_0\,\varepsilon)^{-1}\,\sigma_1\,\sigma_2\,e^{-\kappa D}$

$\kappa = 0.304\,e{-}9\,/\,\sqrt{I}$ (mol/liter)

Hydration forces

(Repulsive or attractive, very small range)

Disjoining pressure Π

$\Pi = \partial_r U$; $P_c = \Pi - 2 H \gamma$, H = curvature
Unstable water films at high P_c

- ## Calcite-H$_2$O-oil

$\varepsilon_2\,\sigma_2$ $\varepsilon_3\,\sigma_3$ $\varepsilon_1\,\sigma_1$ oil

Cal-cite   **water**
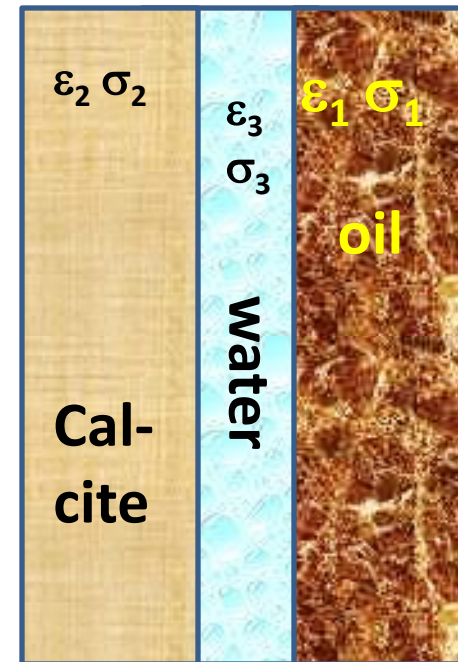
Repulsion is ↓ requirement for stability of water-film
Water film is requirement for water-wet behavior

Charges on surface complexes

EFFECT ON RELATIVE PERMEABILITIES?

Relative permeabilities

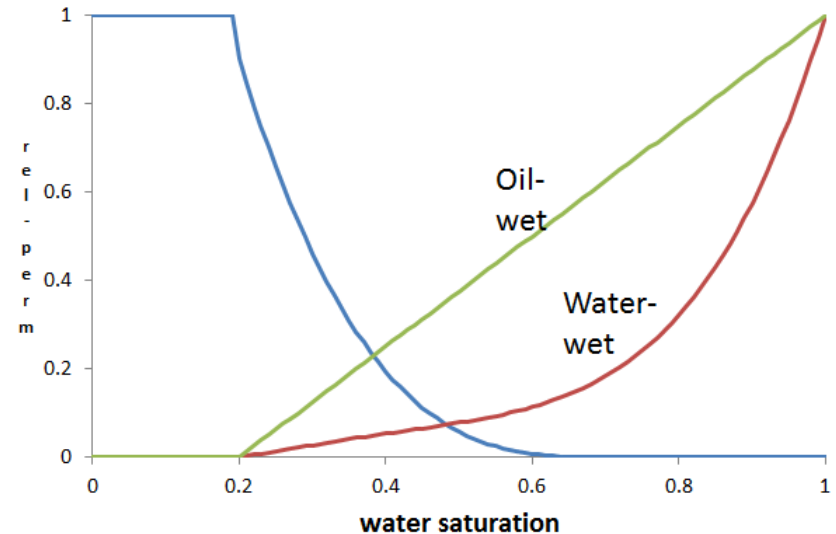- **Relative oil permeabilities of strongly water-wet systems remain close to one, when the oil saturation is 5-10% above one minus connate water saturation**

- **At residual oil saturation $S_{or} \approx 0.25$ the relative permeability to water can be 10% of the single phase permeability.**

- **The cross-over point, i.e. the saturation at which the relative oil permeability and relative water permeability are equal is above 50% water saturation.**

Relative permeabilities

- **For strongly oil-wet systems the oil permeability starts to reduce when the water saturation becomes higher than the connate water saturation.**

- **The relative permeability of water at residual oil saturation is greater than 50% and approaching 100%.**

- **The cross-over point when water and oil permeability are equal is less than 50%.**
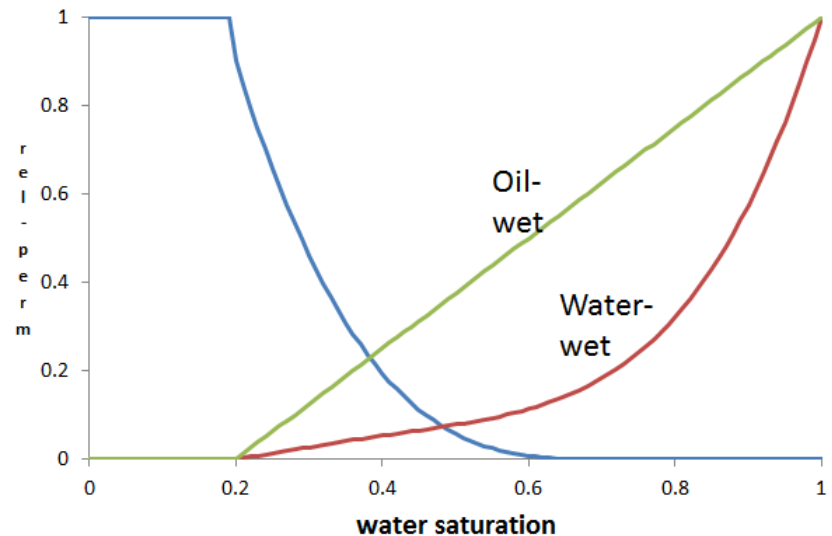
Water-wet/ oil wet
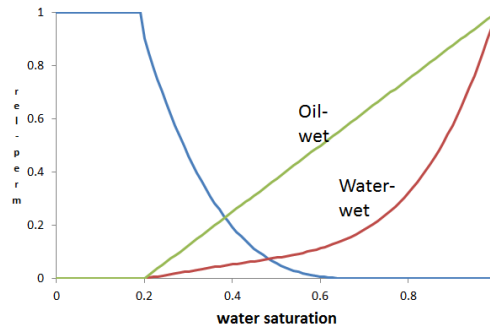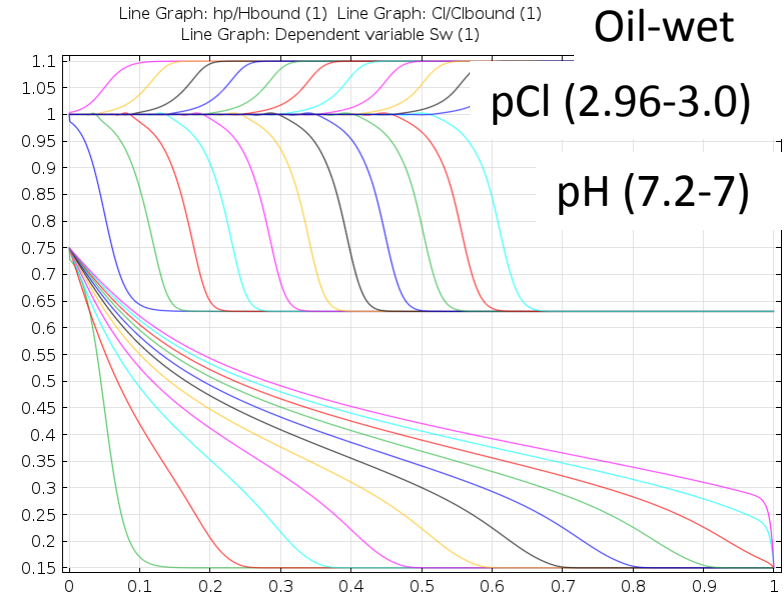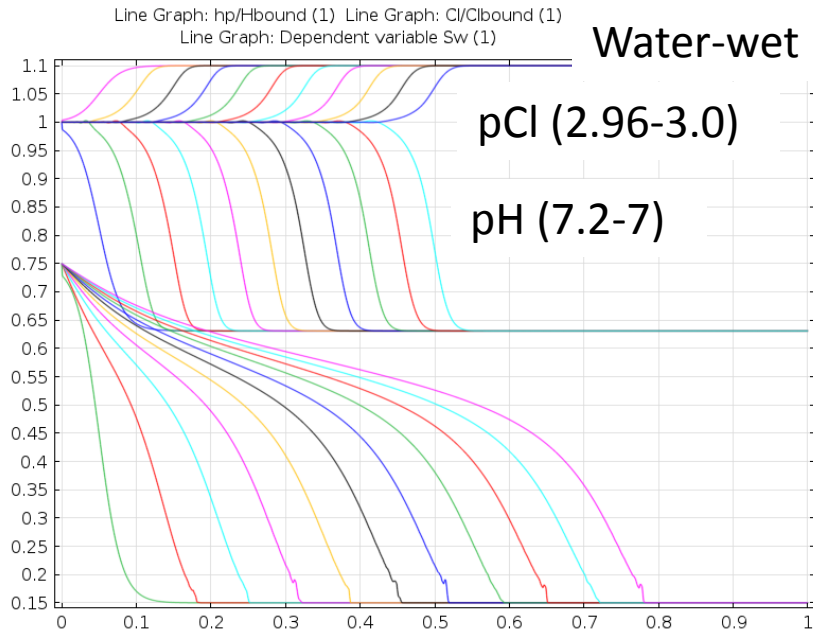
Conservation of master species

DERIVATION OF MODEL EQUATIONS

Enumeration of master species,
(Consult geochemical software, e.g. Appelo)

- Master species are C(+ 4), C(-4), H(1), O(-2), Ca(2), Na(1), Cl(-1)
    - C(4) = {CO_2+ HCO_3 ,etc.}, C(-4) = $C_7 H_{16}$
    - H(1) = {H^++ H_2O, etc}
    - O(-2) = {CO_2+ HCO_3 ,etc.}
    - Ca(2) = {Ca^{2+} + $CaOH^+$, etc}
    - Na(1) = {Na^+ + Na_2CO_3 + $NaHCO_3^-$}
    - Cl(-1) = {Cl^-}
    - C(-4) = {$C_{10}H_{22}$}
- $\varphi\Sigma_\alpha (\partial_t(c_\alpha x_{\alpha i} S_\alpha + \partial_x(u c_\alpha x_{\alpha i} f_\alpha) = $ diffusion terms, i=1..N_c) (EOR, pp 29)

Equations

We are trying to find the solution of the total inorganic carbon equation

$$\partial_t \left(\varphi S_w c_{a,C(4)}. \right) + \partial_t \left(\varphi S_o c_{o,CO_2}. \right) + \partial_x \left(u f_w c_{a,C(4)}. \right) + \partial_x \left(u f_o c_{o,CO_2}. \right) = 0, \quad (42)$$

the total hydrogen equation

$$\partial_t \left(\varphi S_w c_{a,H(1)}. \right) + \partial_x \left(u f_w c_{a,H(1)}. \right) = 0, \quad (43)$$

the total oxygen equation

$$\partial_t \left(\varphi S_w c_{a,O(2)}. \right) + 2 \partial_t \left(\varphi S_o c_{o,CO_2}. \right) + \partial_x \left(u f_w c_{a,O(2)}. \right) + 2 \partial_x \left(u f_o c_{o,CO_2}. \right) = 0, \quad (44)$$

and the organic carbon equation

$$\partial_t \left(\varphi S_o c_{o,C(-4)}. \right) + \partial_x \left(u f_o c_{o,C(-4)}. \right) = 0, \quad (45)$$

where $c_{w,j}$ and $c_{o,j}$ are the mole fractions times the molar density $\overline{\rho}_w$ in the water and $\overline{\rho}_o$ oleic phase respectively. The molar density of water is given by

$$\overline{\rho}_w = \frac{1}{\sum_{i=1}^{6} x_i \overline{V}_i}, \quad (46)$$

where x_i is the mole fraction in the solution of component i, and $\overline{V}_i$ is the molar volume of component i.

Partial molar volume V_i and molar concentration c

The partial molar volume is a mol-based (n_i) average of the partial molar volume (V_i) of each *constituent.*

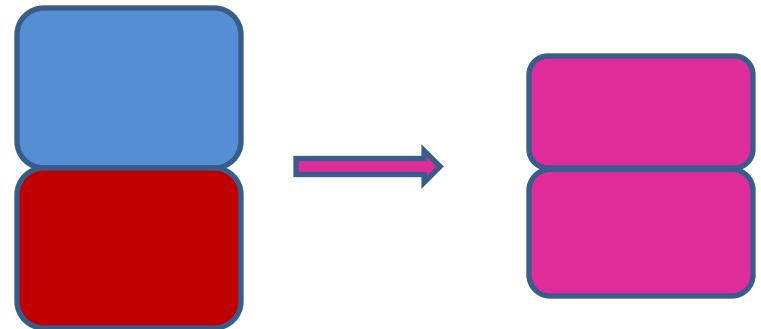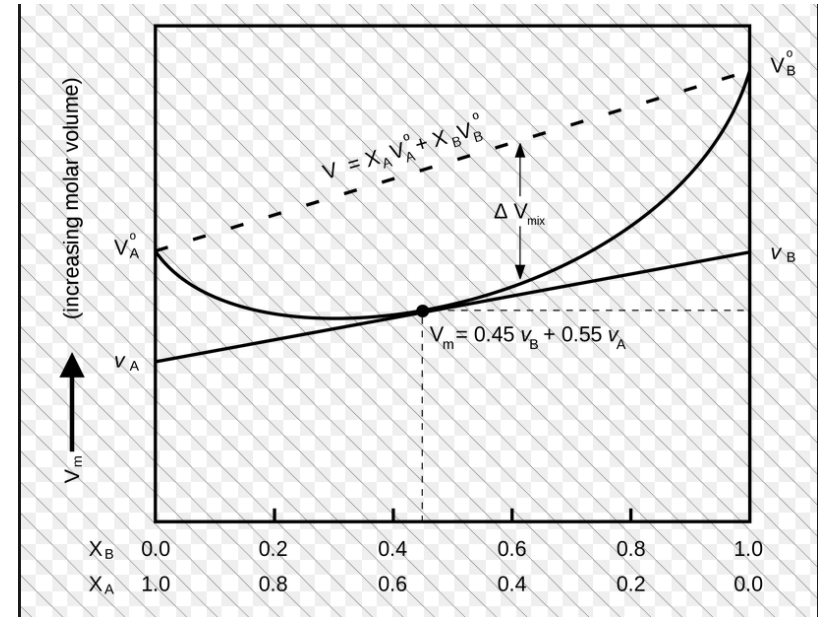$V_A = \partial V / \partial n_A$; $V_B = \partial V / \partial n_B$

$dV = \partial V / \partial n_A \, dn_A + \partial V / \partial n_B \, dn_B$

Gibbs-Duhem: $V = V_A \, n_A + V_B \, n_B$

$1 = V_A \, c_A + V_B \, c_B = c \, (V_A \, x_A + V_B \, x_B)$ →

$c = 1/(V_A \, x_A + V_B \, x_B)$

Generalized: $c = 1 / (\Sigma_i \, x_i \, V_i)$

Partial molar volume V_i
HKF model (see PHREEQC data base)
(Helgeson, Kirkham, Flowers)

N_A = Avogadro number, q_e = 4.803 e-10 is charge of electron (esu), ε_r relative dielectic constant of water, ρ_0 density of pure water , P pressure in atm and κ_0 is compressibility of puer water

There are regression expressions for the partial molar volume of ions in water.
At infinite dilution

$V_i^0 = 41.84\,(a_1/10 + 100a_2 / (2600 + P_b) - WQ_{Born}$
$+ a_3 / (T_K - 228) + 10000a_4 / ((2600 + Pb)(T_K - 228)))$

The parameters a_i, i_i are to be found in the data base of Phreeqc, Born constant: $Q_{Born} = -\partial_P(1/\varepsilon r) = -0.615e\text{-}06(/bar)$.

$V_k(\mu) - V_k^0 = Z_i^2 A_V \sqrt{\mu} / (1 + °a\, B_\gamma \sqrt{\mu}) + \beta_i\, \mu^{i4},$

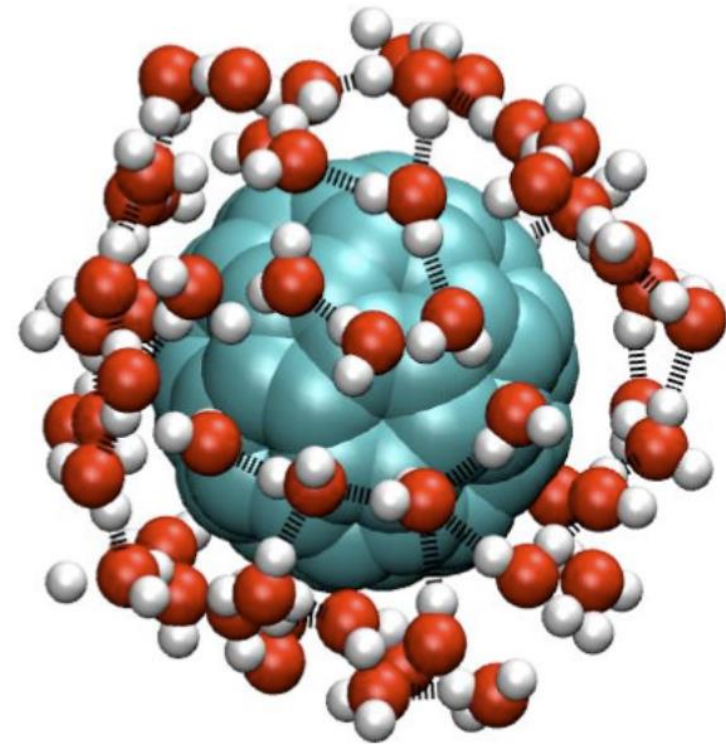where μ is the ionic strength, and $°a$ is the ionic radius (Angstrom)

The Debye Limiting slope A_V

$A_V = (8\pi N_A^4 q_e^6 \rho_0 /(\varepsilon_r^3 RT))^{1/2} \;(\partial_P \ln \varepsilon_r - \kappa_0 /3))$
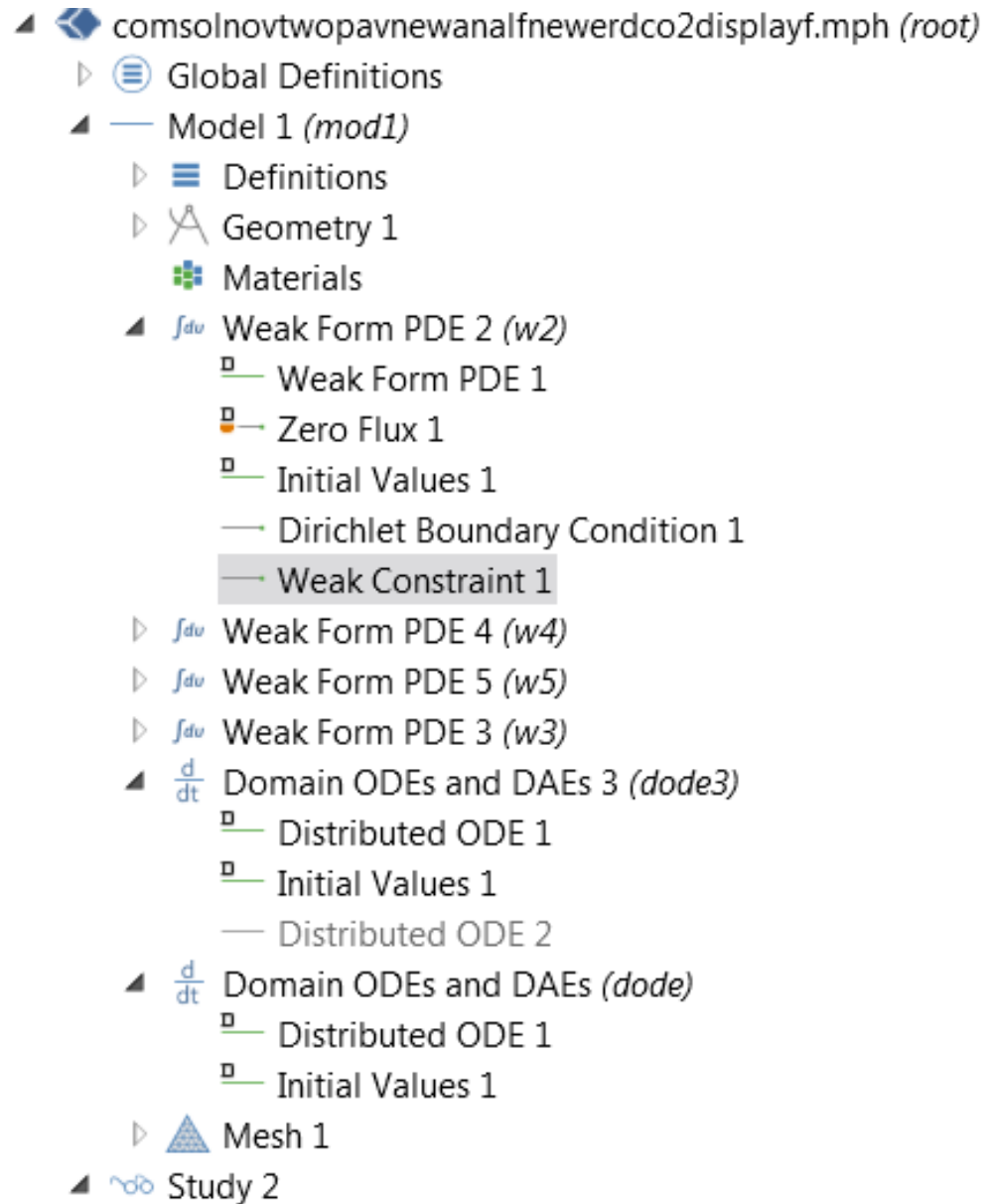
$\beta_i = i_1 + i_2/(T_K - 228) + i_3(T_K - 228)$

$B_\gamma = (8\pi N_A q_e^2 \rho_0 / 1000\varepsilon_r k_B T))^{1/2} =$
$50.29158649\, \rho_0^{1/2} / (\varepsilon_r T)^{1/2}$

Use equation based software to solve pde's and algebraic equations

(a) Define constants

(b) Define concentrations with regression expressions

(c) Formulate eqs. in weak form

(d) IC's and BC's

(e) Define mesh

(f) Study = solve

- ◢ ◈ comsolnovtwopavnewanalfnewerdco2displayf.mph *(root)*
  - ▷ ⊜ Global Definitions
  - ◢ — Model 1 *(mod1)*
    - ▷ ≣ Definitions
    - ▷ ⟁ Geometry 1
    - ⊞ Materials
    - ◢ ∫ᵈᵛ Weak Form PDE 2 *(w2)*
      - ᵈ— Weak Form PDE 1
      - ᵈ— Zero Flux 1
      - ᵈ— Initial Values 1
      - — Dirichlet Boundary Condition 1
      - — Weak Constraint 1
    - ▷ ∫ᵈᵛ Weak Form PDE 4 *(w4)*
    - ▷ ∫ᵈᵛ Weak Form PDE 5 *(w5)*
    - ▷ ∫ᵈᵛ Weak Form PDE 3 *(w3)*
    - ◢ $\frac{d}{dt}$ Domain ODEs and DAEs 3 *(dode3)*
      - ᵈ— Distributed ODE 1
      - ᵈ— Initial Values 1
      - — Distributed ODE 2
    - ◢ $\frac{d}{dt}$ Domain ODEs and DAEs *(dode)*
      - ᵈ— Distributed ODE 1
      - ᵈ— Initial Values 1
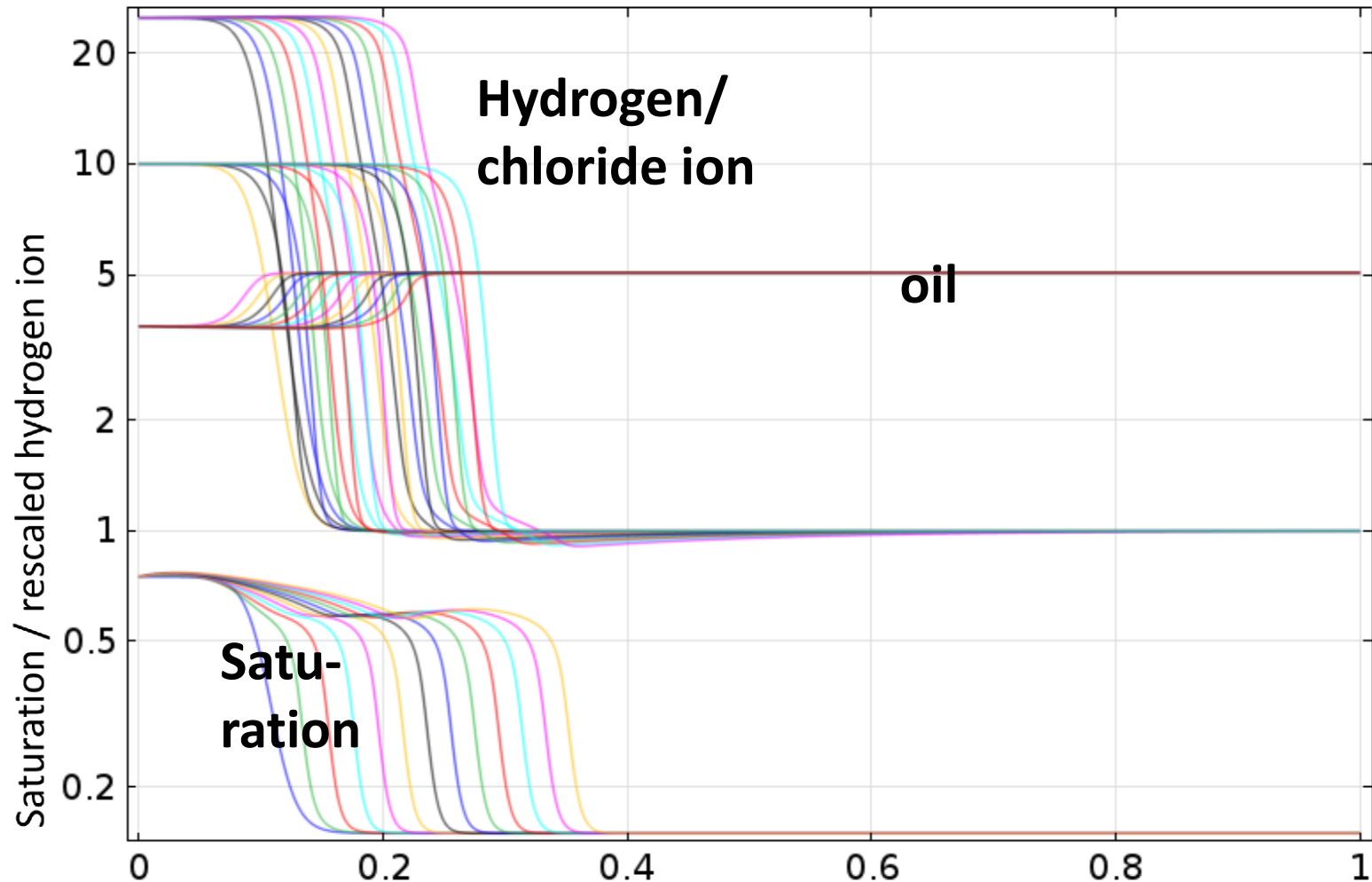   - ▷ △ Mesh 1
  - ◢ ∞ Study 2

Eigenvalue analysis

- When we perform an eigenvalue analysis we observe that $\lambda=0$ is one of the cahracteristic speeds

- Determination of the eigenvector shows that the corresponding eigenvector is associated with the porosity φ

- We can conclude that the porosity wave travels with zero speed, i.e. stays at the entrance and therefore a porosity change does not need to be considered.

Procedure of solving equations

- Determine activities from the equilibrium equations ($N_f = N_s(=15) - N_r(=8) - N_c(=1) - p(=3) = 3$ *(and we use [Na] = [Cl] as constraint)*

- (a) Determine ionic strength from $\mu = \frac{1}{2}c_i\, z_i^2 = \frac{1}{2}a_i\, / \gamma_i\, (\mu)\; z_i^2$), which is a non-linear algebraic equation

- (b) Express charge equation in terms of concentrations, which is a non-linear algebraic equation
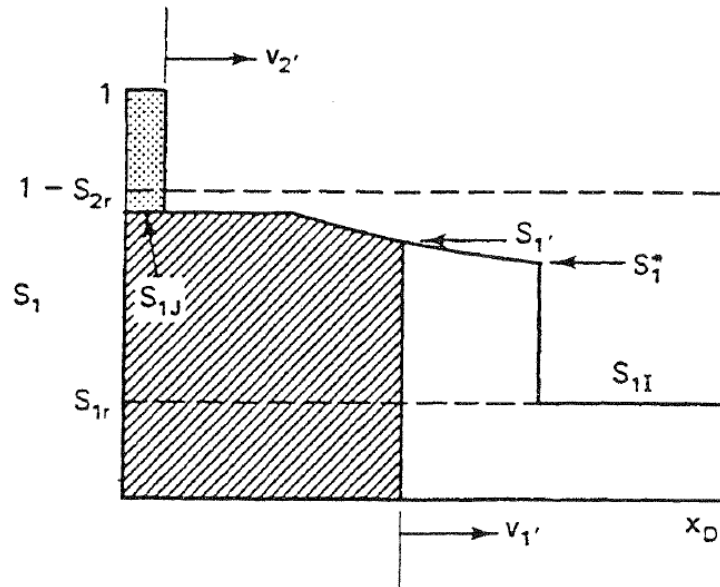
- All concentrations now depend on CO_3^-, Cl^-

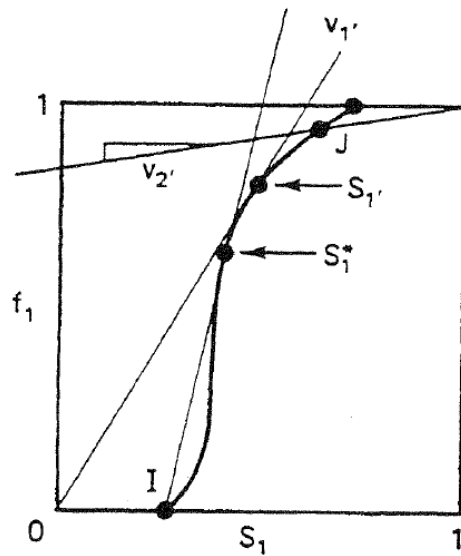Line Graph: Dependent variable Sw (1)
Line Graph: AH/(3.0e-5) (1)   Line Graph: Cl/2e-5 (1)
Line Graph: rhomoldecane(log(AH))

Hydrogen/chloride ion

oil

Saturation

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Fractional flow computations
EOR pp 155

Conclusions

- **1-Geochemistry can be accounted for by**
  - **a- Use of geochemical software to create look-up tables or regression formula; but solutions appear to be unstable**
  - **b- Simultaneous solution of all relevant equations; appears to have much better performance but validation needed**
- **2- Oil recovery predictions require full incorporation of geochemistry**
  - **a- Carbon dioxide dissolution depends on ionic strength; geochemical behaviour essential for understanding Low salinity waterflood**
  - **b- Wetting behaviour depends on surface charges and thus on adsorption of surface complexes and can be found with PHREEQC**
    - **Ionic strength not the only wetting modifying characteristic**
    - **Surfactants modify surface behaviour (carboxylic acids)**
    - **Virtue of water-wet relative permeabilities is not clear**
- **3- CO_2 presence is important reason for enhancing oil recovery**
- **Understanding geochemistry is facilitated with the help of the books "EOR" and "Geochemistry and Fluid flow"**
  - **The main problem is understanding fluid flow with geochemistry; not the programming**

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end

QUESTIONS?