

Fugacity, Simplifications, and Autoclave Experiments

Pressure effects on test solution composition and properties



OLI Systems Inc.

May 28, 2018

Agenda

- Summary statement
- Thermodynamic effect of simplification
- List of Autoclave Simplifications
- Effects of Simplification on Composition / Properties compared to real system
 - Use HPHT gas-condensate producer as a reference system
- Reconcile thermodynamics and autoclave recipe

Summary Statement

- Point 1 - Quantifying gas properties is transitioning from partial pressure to fugacity
- Point 2 – Lower pressure experiments affects the equilibrium constants
- Point 3 – Simplifying the test solution compositions affects fluid properties and speciation.

An alternative approach is to back calculate the gas fraction and inflow composition based on Test Solution targets and based on the test pressure to be used.

Thermodynamic effects of simplification

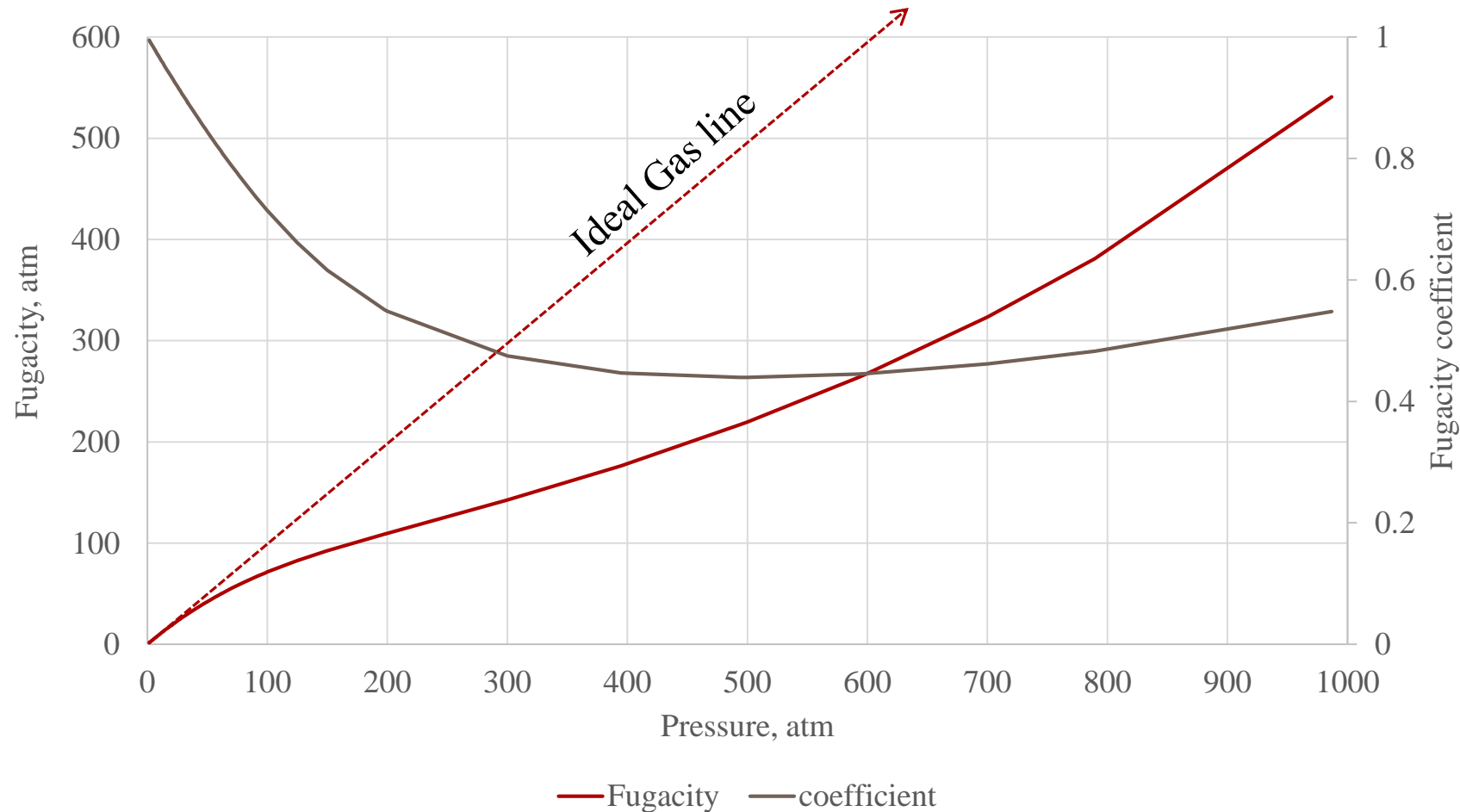
- Partial pressure deviates from real gas activity (fugacity) at elevated pressure
- Equilibrium constants are pressure dependent
 - An autoclave at low pressure overpredicts a gas solubility
 - $K_{CO_2,vap} = \frac{5e^{-3}}{3e^{-2}}$ @650 bar @1 bar
- Simplified compositions dismiss species complexation
 - Mg, Ca, Fe complex with HCO_3^{-1} , Acetate⁻¹, changing species activity

Simplification: NACE/ISO standards

- Run experiment at lower pressure. Fix pp or mole% of CO₂ / H₂S
- Gas phase (components)
 - CO₂, H₂S, CH₄, N₂
 - Replace CH₄ with N₂ (safety)
 - Limit HC gas to CH₄ (eliminate C₂+))
- Oil phase
 - Hexane, n-octane, n-decane, n-toluene, kerosene
- Electrolyte phase (components)
 - NaCl, NaHCO₃, NaAcetate, HCl, NaOH, CaCl₂

Point 1 - Fugacity

CO₂ fugacity using Soave-Redlich-Kwong



EOS's

van der Waals

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Soave Redlich-Kwong

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$

Peng Robinson + mods

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

Elliot, Suresh, Donohue

$$\frac{pV_m}{RT} = Z = 1 + Z^{\text{rep}} + Z^{\text{att}}$$

Virial EoS

$$\frac{pV_m}{RT} = A + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots$$

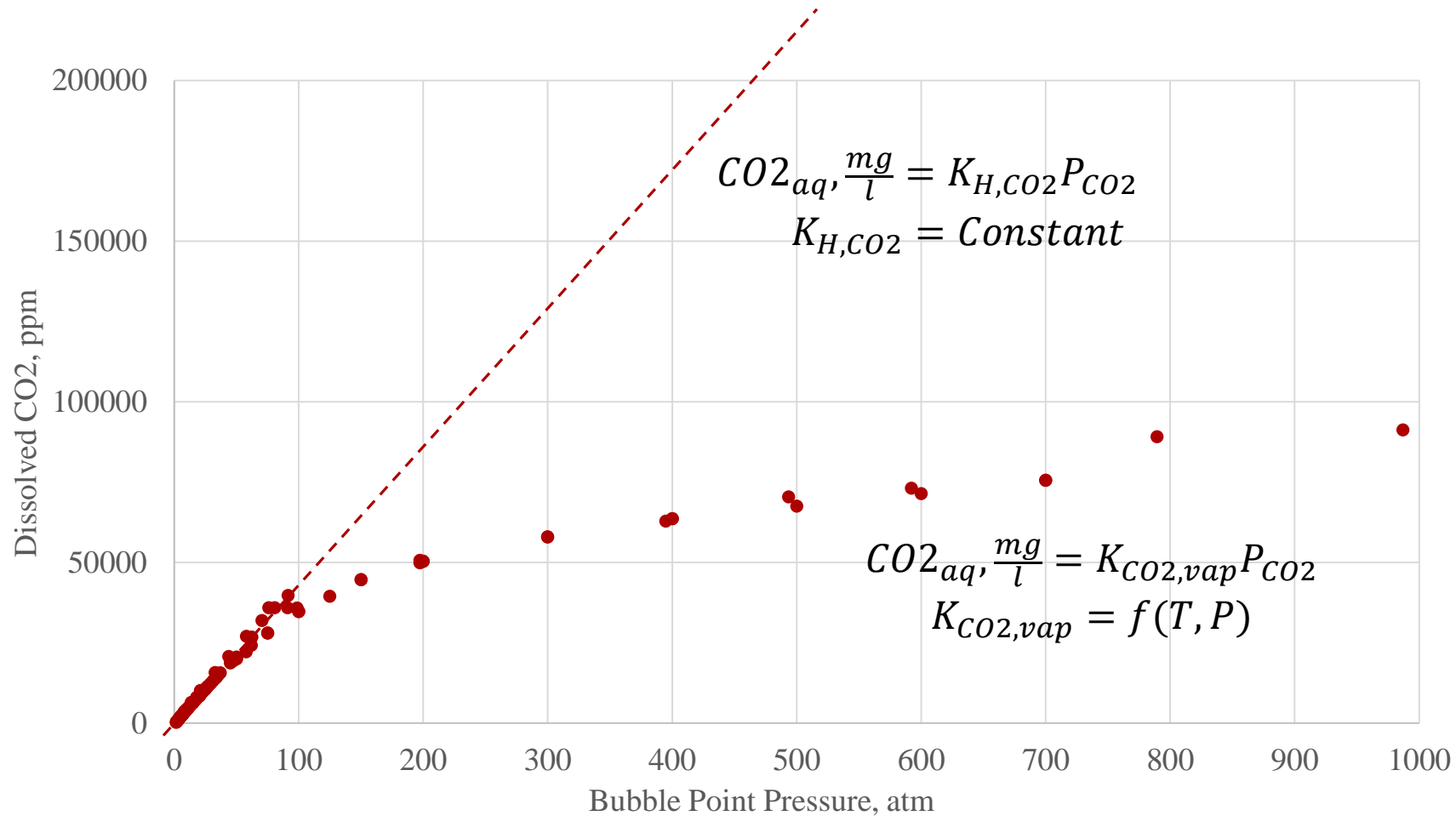
Cubic

SAFT

At 650 bar, effective pressure (fugacity) is about 50% lower than partial pressure

Point 2 – Pressure effects on K_{vap}

CO2 solubility at bubble point pressure

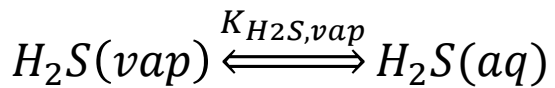
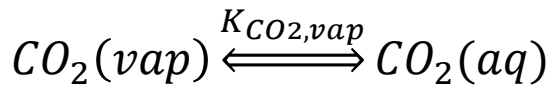
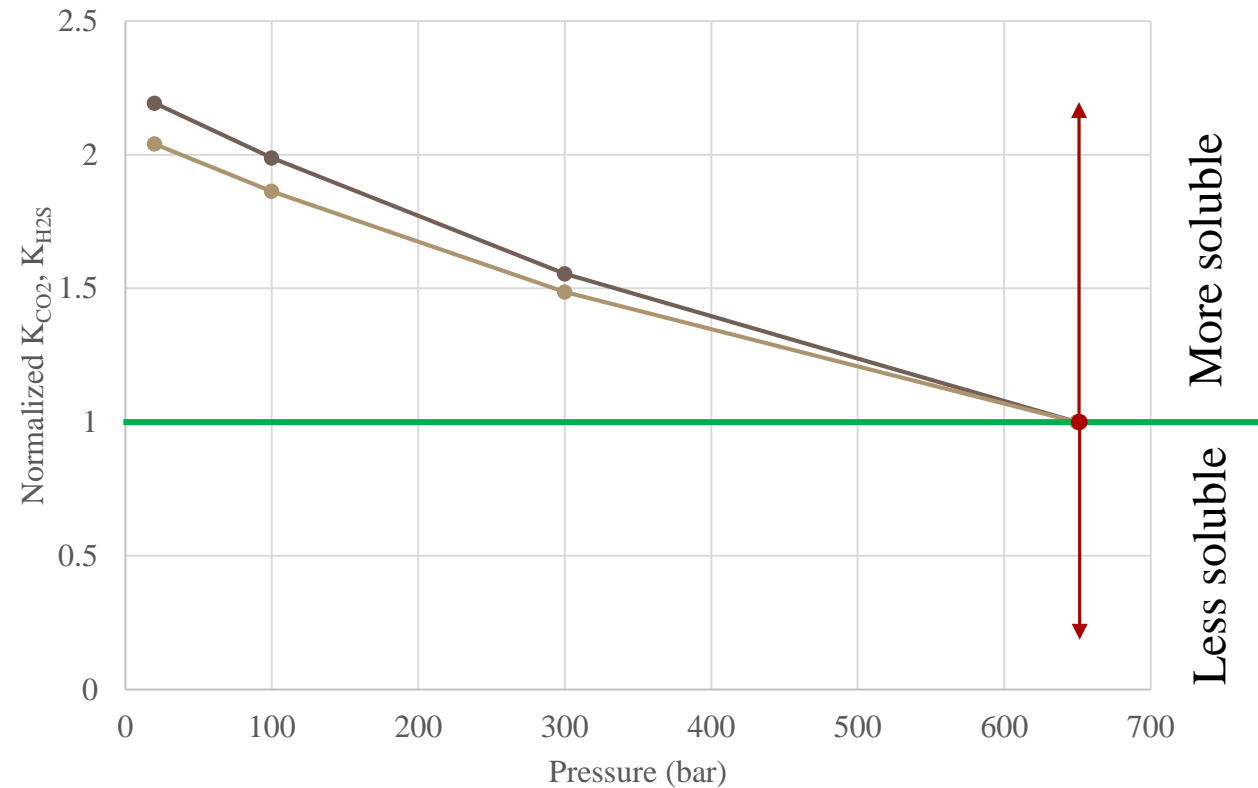


when isolating solubility constant
(ignoring fugacity effects)

CO2-H2O System @ 100C
Experimental data from eleven citations

Pressure effects on K_{vap} values for CO_2 , H_2S , H_2O

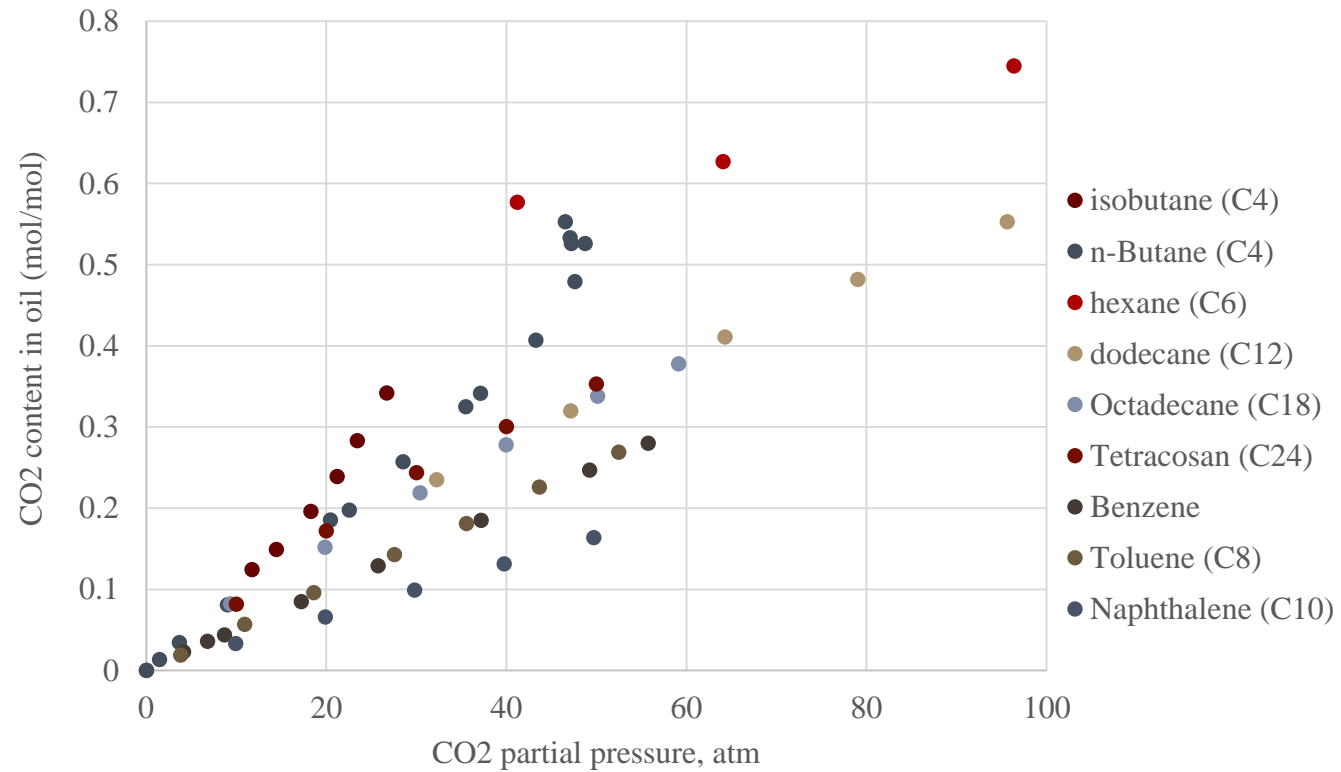
$K_{CO_2,vap}$, $K_{H_2S,vap}$ normalized to 1 @ 650bar



K-values computed using the Helgeson-Kirkham-Flowers-Tanger and Soave-Redlich-Kwong equations of state

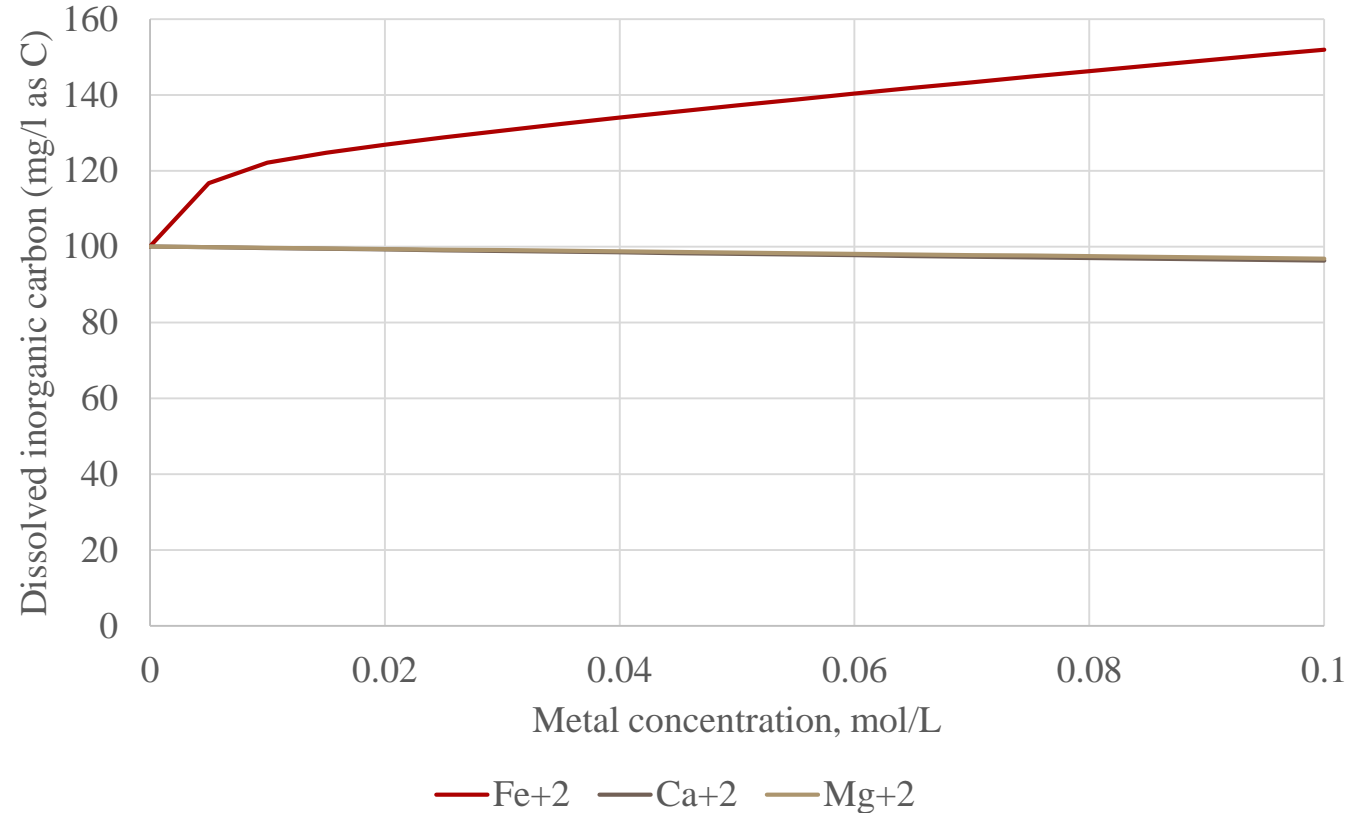
CO_2 , H_2S are intrinsically more soluble at lower pressures

Point 3 – CO₂ solubility in aromatic and aliphatic HC



Point 3 – Metal Complexation effects on speciation

Fe²⁺, Ca²⁺, Mg²⁺ sequestering HCO₃⁻¹ in an open system



when isolating solubility constant
(ignoring fugacity effects)

CO₂-H₂O System @ 100C
Experimental data from eleven citations

Reference system: High P, Multi-component production

Brine Analysis

Cations (mg/L)	
Na ⁺¹	56000
K ⁺¹	360
Ca ⁺²	1720
Mg ⁺²	315
Sr ⁺²	84
Ba ⁺²	11
Fe ⁺²	18
Anions (mg/L)	
Cl ⁻¹	89800
SO ₄ ⁻²	760
HCO ₃ ⁻¹	101
HCOO ⁻¹	0.7
C ₂ H ₃ O ₂ ⁻¹	165
C ₃ H ₅ O ₂ ⁻¹	28
C ₄ H ₇ O ₂ ⁻¹	21
Br ⁻¹	340
Neutrals (mg/L)	
SiO ₂	17
B(OH) ₃	120
pH	6.7

Gas Analysis

component	mole%
H2O	0.15
N2	0.2
H2S	0.5
CO2	2.5
CH4	91
C2H6	3
C3H8	1
i-C4H10	0.2
n-C4H10	0.3
i-C5H12	0.13
n-C5H12	0.12
C6+	0.8

Condensate Analysis

component	mole%
CH4	5
C2H6	1.4
C3H8	2.4
i-C4H10	1.3
n-C4H10	2.6
i-C5H12	2.2
n-C5H12	2.3
C6-C10	35.2
C11-C15	21.8
C16-C20	11.6
C21-C25	5.3
C26-C30	4.8
C31-C35	1.3

3.43 mmol/l or
282 mg/l as NaAcetate

Red variables are inputs to the test solution or headspace composition

Computed Reservoir composition and properties

Variable	Value
Res T (C)	100
Res P (bar)	650
GWR sE ³ m ³ /m ³	10
CGR sm ³ /sE ³ m ³	0.29
pH	4.66
Cl- (ppm)	91880
X _{CO2} (mole%)	2.5
f _{CO2} (bar)	11.3
X _{H2S} (mole%)	0.5
f _{H2S} (bar)	1.4

Acid	ppm	Anion	ppm
CO2	1238	HCO ₃ ⁻¹	207
H ₂ S	425	HS ⁻¹	11.4
Acetic acid	104	Acetate ⁻¹	32
Formic acid	0.15	Formate ⁻¹	0.57
Propanoic acid	17	Propanate ⁻¹	3.3
Butanoic acid	6	Butyrate ⁻¹	.02

Simulate case in an Autoclave

NaCl 14.5%
 NaHCO₃ 0.015
 NaAcetate 0.025
 HCl to 6 pH

 P_{CO2} 16.25 bar
 P_{H2S} 3.25 bar
 P_{CH4} balance

 PT₁ 650 bar
 PT₂ 300 bar
 PT₃ 100 bar
 PT₄ ~20 bar
 T 100 C

1 L autoclave
 500 ml test solution
 500 ml headspace

P (bar)	650	650	300	100	20.5
T (C)	100	100	100	100	100
pH	4.66	4.61	4.54	4.44	4.38
Cl ⁻ (ppm)	91880	95136	93977	93330	92978
f _{CO2} (bar)	11.1	11.7	11.6	13.7	15.5
f _{H2S} (bar)	1.4	1.6	1.8	2.5	3.0
P _{CO2} (bar)	16.25	16.25	16.25	16.25	16.25
P _{H2S} (bar)	3.25	3.25	3.25	3.25	3.25
Acid (ppm)					
CO ₂	1238	1456	2113	3112	3851
H ₂ S	425	551	946	1646	2211
Acetic acid	127	166	151	148	149
Anion (ppm)					
HCO ₃ ⁻¹	207	204	182	174	171
HS ⁻¹	11.4	13.2	16	19	22
Acetate ⁻¹	36	45	55	55	53

0.755x

0.378x

Reconciliation

Parameters	Targets
pH	4.65
Cl-1	90600
H2S, aq	470
HS-1	12.8
CO2, aq	1389
HCO3-1	216
HAc	126
Ac-1	36

Inputs	Value	Parameters	values
NaCl		pH	
		Cl-1	
NaAcetate		H2S, aq	
Set pH		HS-1	
PCO2		CO2, aq	
PH2S		HCO3-1	
Pressure		HAc	
		Ac-1	

Conclusions

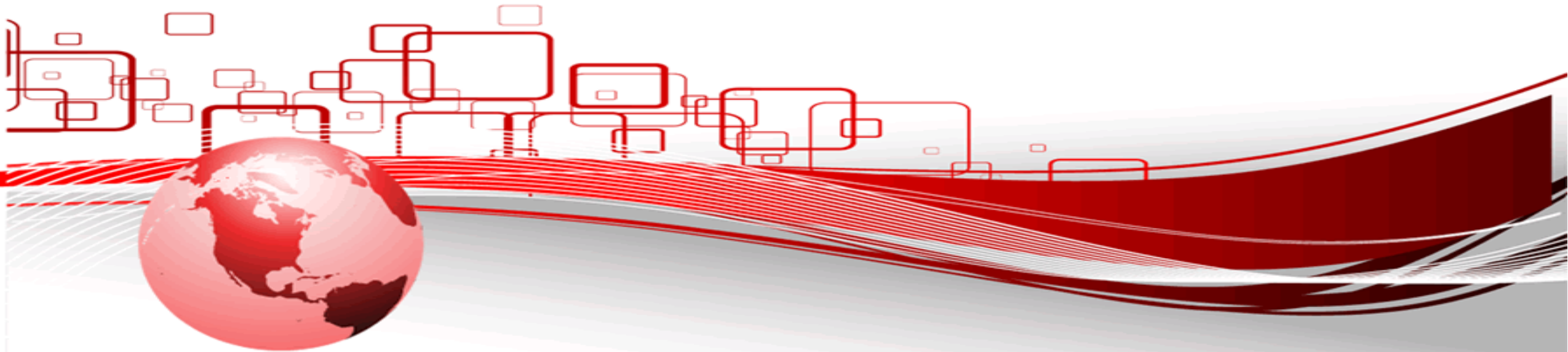
- Simplifications to autoclave experiments or written into standards can be tested for their thermodynamic impact.
- Predicting this impact requires
 - EoS for T / P -dependent equilibrium constants,
 - Activity model for computing non-ideal, chemical interactions (including fugacity coefficients), and
 - chemical reaction / speciation models for quantifying concentrations and properties.
- Subsequent prediction of ionization and activity coefficients at the high pressure, can be used as refinements targets, so that the aqueous species activities (and pH) match the higher-pressure conditions.

Acknowledgements

- People that helped us understand what is needed or provided key documents
 - Brent Sherar (Blade / Honeywell)
 - Rudy Hausler (Blade)
 - Jose Vera (DNV)
 - Tracey Jackson (BHGE)
 - Giuseppe Mortali (C-S-M)
 - Floriant Thebault (Vallourec)
 - Florent Boucher (SWRI)
 - Many others...



Backup slides



Gas Pressure physical effects

$$y_{H_2S}P_T = P_{H_2S}$$

$$V = \frac{nRT}{N_A P} = 4e^{-26} \text{ m}^3 @ 1 \text{ atm (25 C)}$$

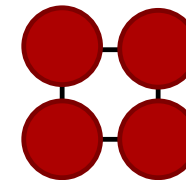
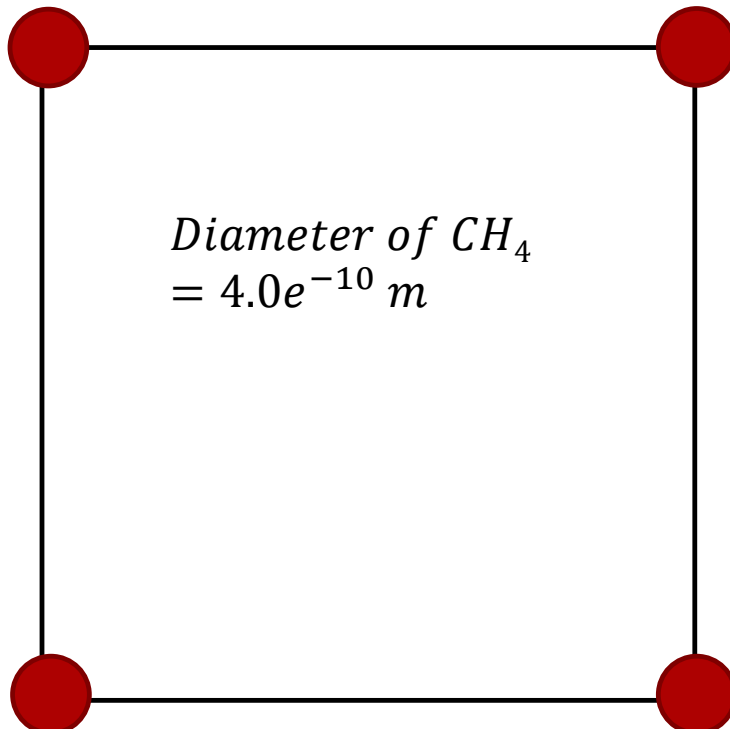
$$\text{Intermolecular distance} = V^{1/3} = 3.4e^{-9} \text{ m}$$

$$\text{mean free path} = 6.0e^{-8} \text{ m}$$

$$\phi_{H_2S} y_{H_2S} P_T = f_{H_2S}$$

$$V = \frac{nRT}{N_A P} = 4e^{-26} \text{ m}^3 @ 1000 \text{ atm}$$

$$\text{Intermolecular distance} = V^{1/3} = 4.3e^{-10} \text{ m}$$



Using partial pressure instead of fugacity

Show the EOS here – show the white paper details

Low pressures, gases modeled as interacting through perfect elastic collisions
– intermolecular interactions do not contribute significantly to the gas particle's energetics

$$PV = nRT$$

Molecular volume no longer insignificant

$$P(V - nb) = P(V - 4N_A * \frac{4}{3}\pi r^3)nRT$$

High pressures and low temperatures, intermolecular forces (repulsive and attractive). 1873 vdW introduced

$$(P + \frac{an^2}{V^2})(V - nb) = P(V - 4N_A * \frac{4}{3}\pi r^3)nRT$$

“a” is magnitude of intermolecular attraction (high value, more attraction between molecules)

Dipole-dipole

Debye-forces - Dipole-induced dipole

London dispersion forces - Instantaneous dipole-induced dipole – when the mass of a gas molecule increases heavy refrigerants), more electrons are present. The electron clouds of the colliding molecules can repel each other – creating an instantaneous dipole. This can induce further dipoles in neighboring molecules. This is significant at HP and LT.

Using partial pressure instead of fugacity

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = P\left(V - 4N_A * \frac{4}{3}\pi r^3\right)nRT$$

Limited predictions near condensation point, near critical point, or at high pressures

Real gases – compressibility factor, critical point, isotherm, specific heat

Molecular volume no longer insignificant

$$P(V - nb) = P\left(V - 4N_A * \frac{4}{3}\pi r^3\right)nRT$$

High pressures and low temperatures, intermolecular forces (repulsive and attractive). 1873
vdW introduced

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = P\left(V - 4N_A * \frac{4}{3}\pi r^3\right)nRT$$

No way to form a liquid or solid at high pressure. Ideal gas does not describe or allow for phase transition. Need a more complex EOS. Real gas models needed near the condensation point, critical point at high pressures. Redlich-Kwong allows this.

$$RT = P(V_m - b) + a \left[\frac{V_m - b}{V_m(V_m + b)T^{\frac{1}{2}}} \right]$$

Other models: Berthelot, Dieterici, Clausius, Virial, Peng Robinson, Wohl, Beattie-Bridgeman, Benedict

Acentric factor

Its value is defined at the reference temperature of $T_r = 0.7$

$$\omega = -\log(P_r^{sat}) - 1 \quad \text{at } T_r = 0.7$$

Soave expanded the T-dependent attractive parameter

$$a = a(T, \omega)$$

$$\left[P + \frac{\alpha a}{\bar{v}(\bar{v} + b)} \right] (\bar{v} + b) = RT$$

$$\alpha = \left[1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - \sqrt{T_r}) \right]^2$$

Influence of acentric factor and T on attractive term is through a.

Applying the critical conditions from above we get:

$$a = 0.427480 \frac{R^2 T_c^2}{P_c} \quad b = 0.086640 \frac{RT_c}{P_c}$$

Soave introduced a mixing rule modification using a binary interaction parameter. There is no analytical, science-based derivation to justify it. They are heuristics, and a measure of interaction between a pair of dislike molecules

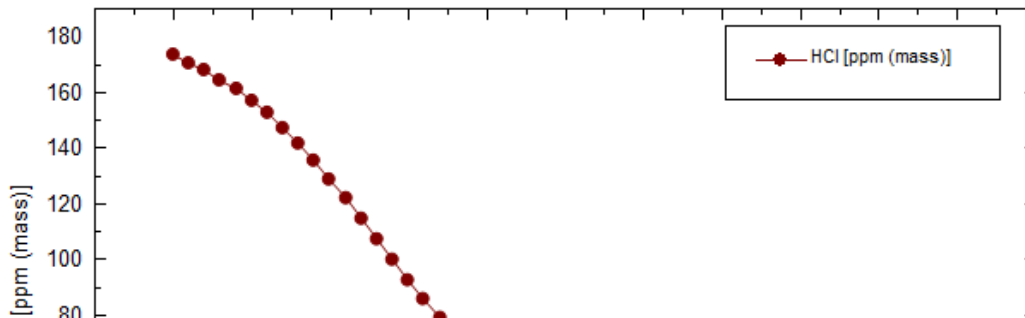
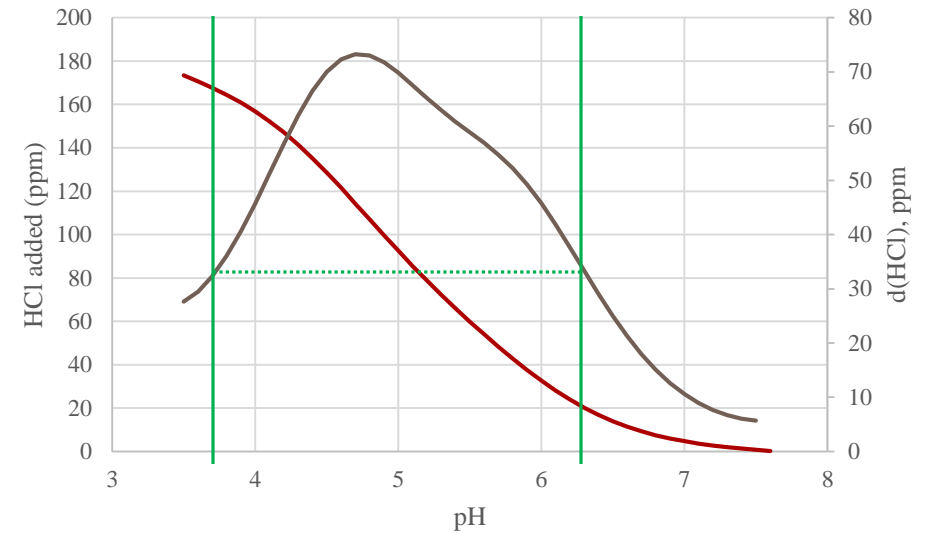
$$(\alpha a)_m = \sum_i \sum_j y_i y_j (\alpha a)_{ij} = \sum_i \sum_j y_i y_j \sqrt{(\alpha a)_i (\alpha a)_j} (1 - k_{ij})$$

Simulate above case using an Autoclave

NaCl 14.5%
NaHCO₃ 0.015
NaAcetate 0.025
HCl to ?? pH

P_{CO2} 16.25 bar
P_{H2S} 3.25 bar
P_{CH4} balance

PT₁ 650 bar
PT₂ 300 bar
PT₃ 100 bar
PT₄ ~20 bar
T 100 C



Simplifications (summary)

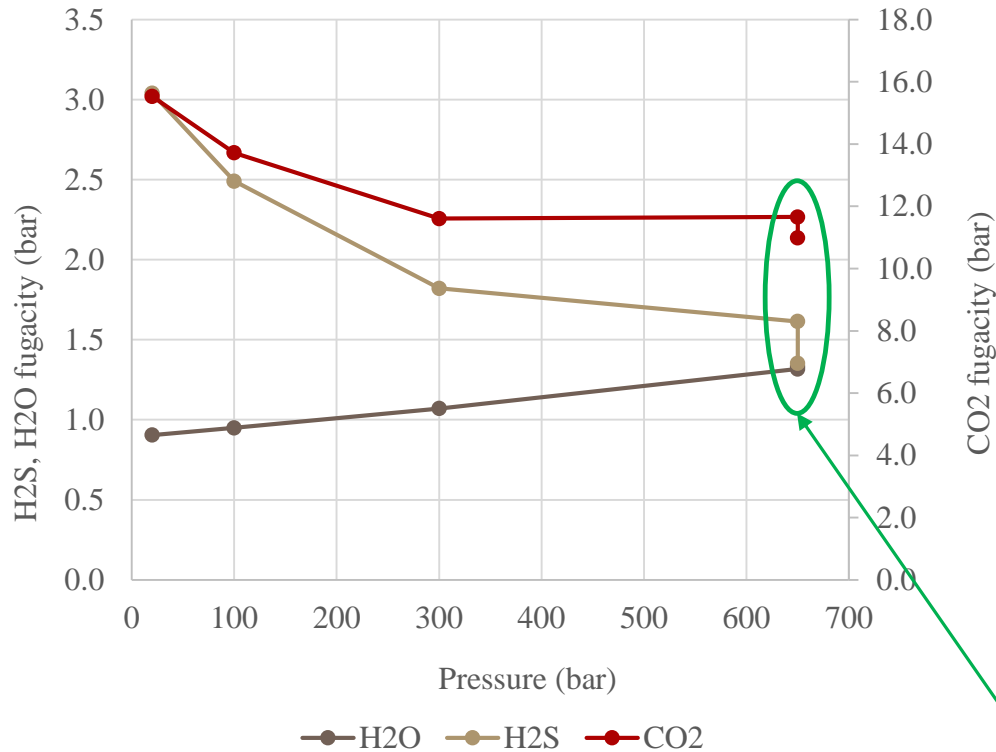
Simplifying action	Components ignored	Argument for simplification	Argument against simplification
Eliminate Conservative species	K, Li, Br, B(OH) ₃	Salinity estimated using NaCl	
Eliminate Reactive species	Mg ⁺² , Sr ⁺² , Ba ⁺² , SO ₄ ⁻²	Salinity estimated using NaCl	Ion-pairing, complexation, and precipitation
Eliminate some pH buffers	HCO ₃ ⁻¹ , HCOO ⁻¹ , CH ₃ COO ⁻¹ , C ₂ H ₅ COO ⁻¹	Organic acids represented using acetic acid	pH buffering
Eliminate precipitating species	CaCO ₃ , FeCO ₃ , FeS		Alkaline precipitates
Limit gas composition	Ethane+		Molecular interactions on gas Fugacity
Limit oil composition	Alkanes, alkenes, aromatics, naphthenic acids		H ₂ S, CO ₂ , organic acid solubility in polar oils
Low Pressure	CH ₄ /N ₂ (reduce amount to reduce pressure)	Reduces risk, enables experimental work	Fugacity and equilibrium constant changes

Thermodynamic basis

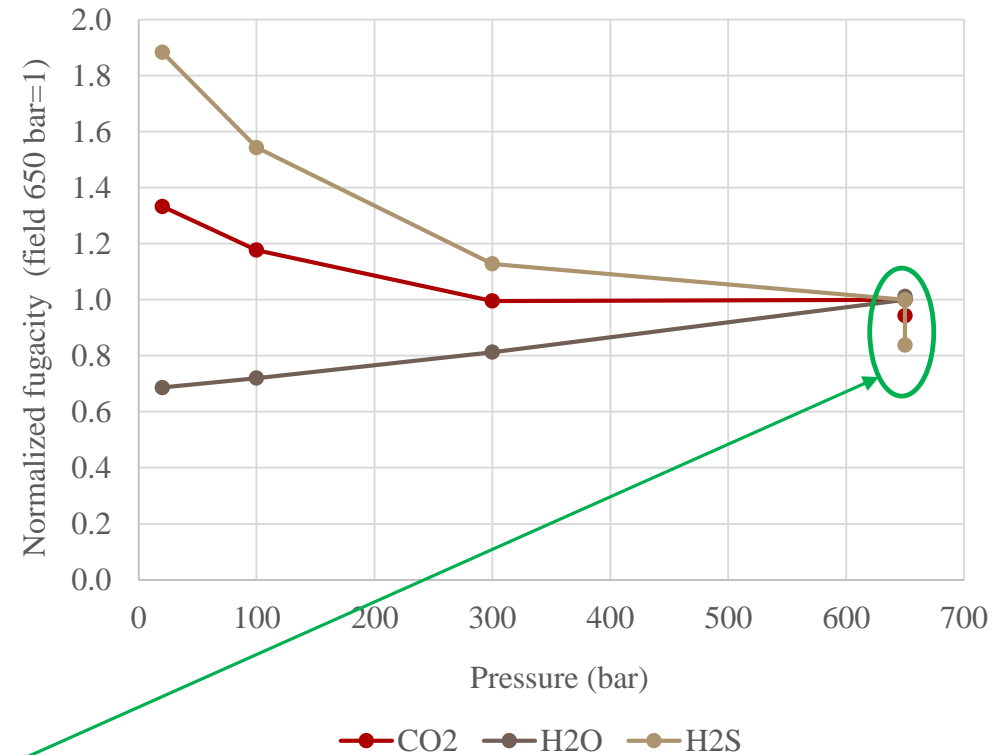
- Input parameters of a test solution, ~~T~~, P, Composition
 - Broad chemical reactions:
 - Electrolyte Speciation
 - Precipitation-dissolution
 - Water-vapor-oil partitioning
 - Adsorption on surfaces
 - REDOX
 - ~~Rate limitations (not equilibrium thermodynamics)~~
 - ~~Diffusion limitations (mass flux)~~
 - ~~Activation limits (all types)~~
 - ~~Hydrodynamic limitations~~
 - ...
- Effects of Pressure and Composition simplifications on these reactions
-

Pressure effects on CO₂, H₂S, H₂O Fugacity

Based on $P_{\text{CO}_2}=16.25 \text{ bar}$ $P_{\text{H}_2\text{S}}=3.25 \text{ bar}$



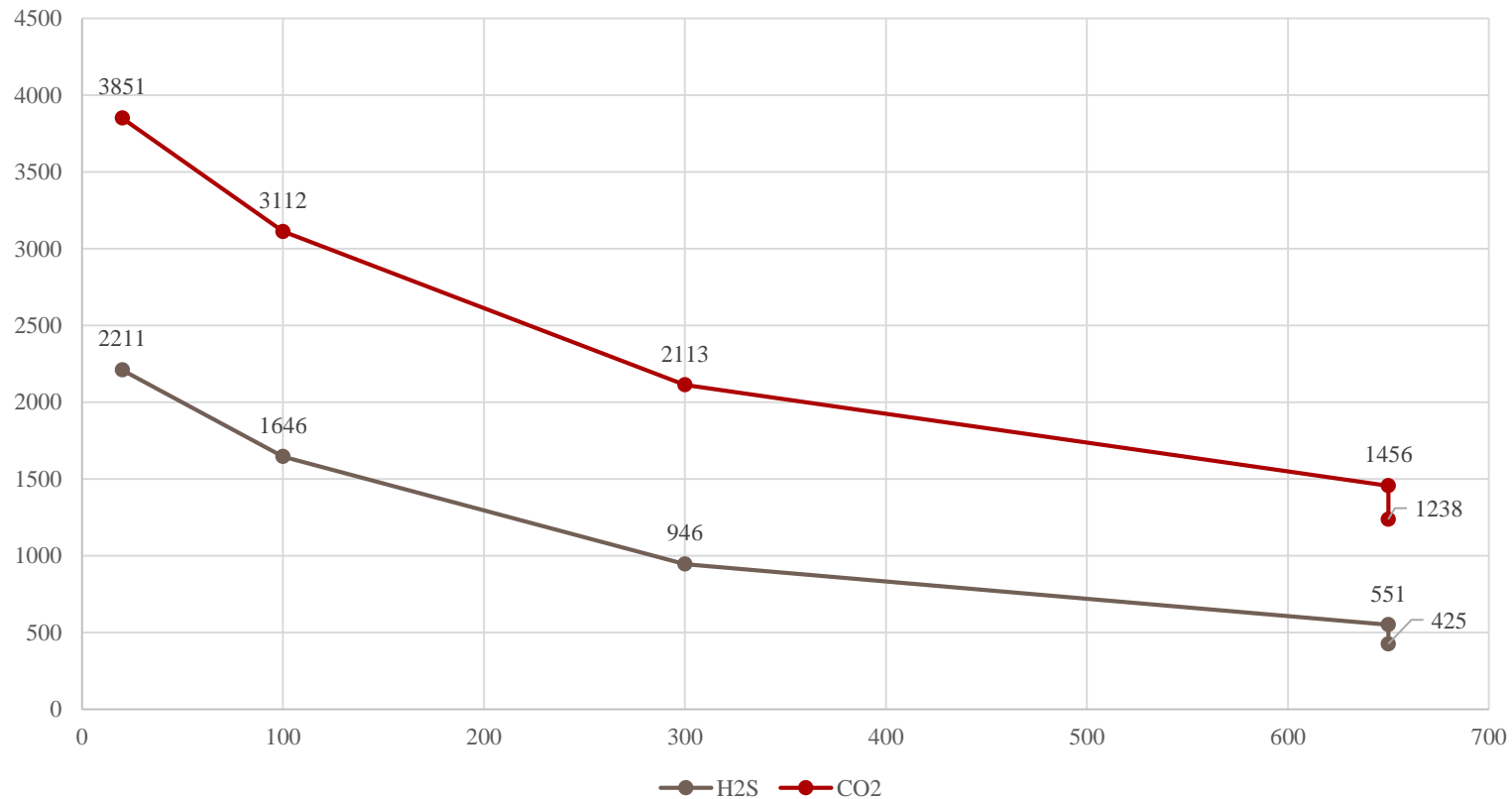
Normalized to 1.0 @ 650 bar autoclave



Vertical shift at 650 bar is solubility in condensate effects

Impact of Fugacity and K_{vap} on Dissolved Gas

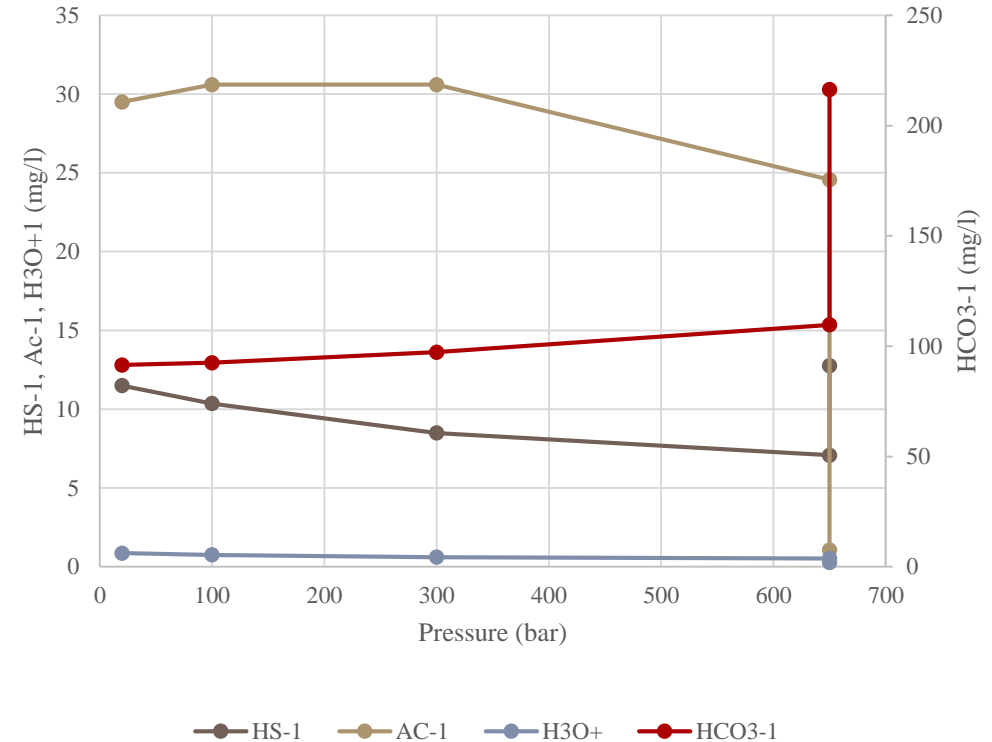
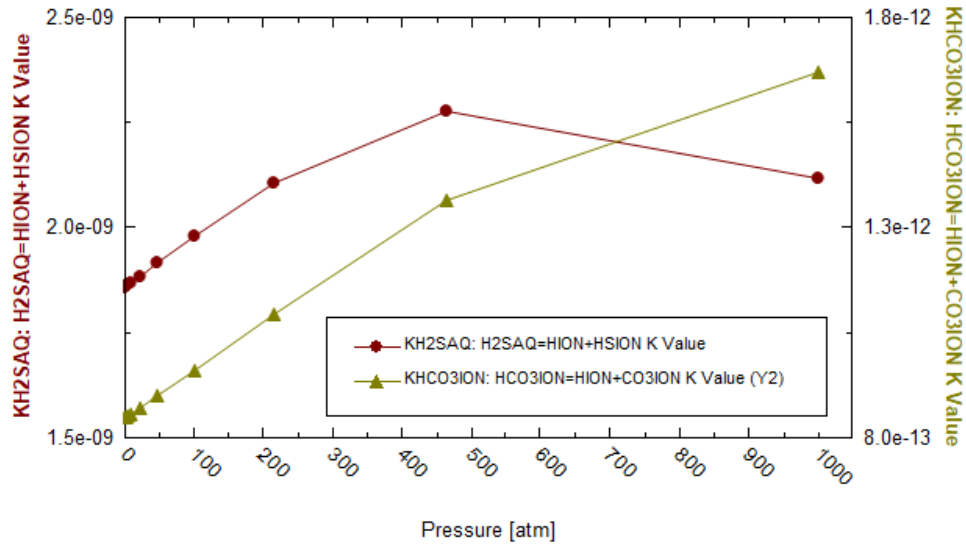
Partial pressures fixed at 16.25 bar CO_2 and 3.25 bar H_2S .
250 mg/l NaAcetate, 150 mg/l NaHCO_3 , 6 pH



Vertical shift at 650 bar is from difference between full-system pH and autoclave pH

Simplifications

Translating low P autoclaves to High P



- $H_2S = HS^{-1} + H^+$ ionization constant is computed to increase ~50% between 100 and 1000 bar (at 100 C).
- The net effect is increasing total H_2S solubility, HS^{-1} activity, and decreasing pH; each of which affect directly corrosion rates.

Comparison of key corrodants

Property	Field simulation	Lab @650 bar	Lab @300 bar	Lab @100 bar	Units
pH	4.65	4.34	4.27	4.17	
Cl-1	90600	95200	94020	93314	mg/l
H2S, aq	470	551	946	1646	mg/l
HS-1	12.8	7.1	8.5	10.4	mg/l
CO2, aq	1389	1456	2113	3113	mg/l
HCO3-1	216	110	97	93	mg/l
HAc	104+16+6	167	157	155	
Ac-1	33+3+.02	25	31	31	

CO2 5.567e-4 mol/mol
H2S 2.433e-4 mol/mol