

Computer Package

Fluids

version 2

a new jacket and improvements

Ronald J. Bakker
University of Leoben

Statement 1

Fluid inclusions cannot be understood or interpret without a thorough knowledge of the thermodynamic properties of fluids

Statement 2a

Every published Equation of State can be improved, and have to be checked on limitations and errors

Statement 2b

Reliability of Equations of State can only be judged by direct comparison to experimental data

Equation of State = $p(n, V, T)$ or $p(x, v, T)$
 $V(n, p, T)$ or $v(x, p, T)$
 $y(q)$
 $A(n, V, T)$ or $A_m(x, v, T)$

similarity
diversity
complexity
mathematics
computer modelling

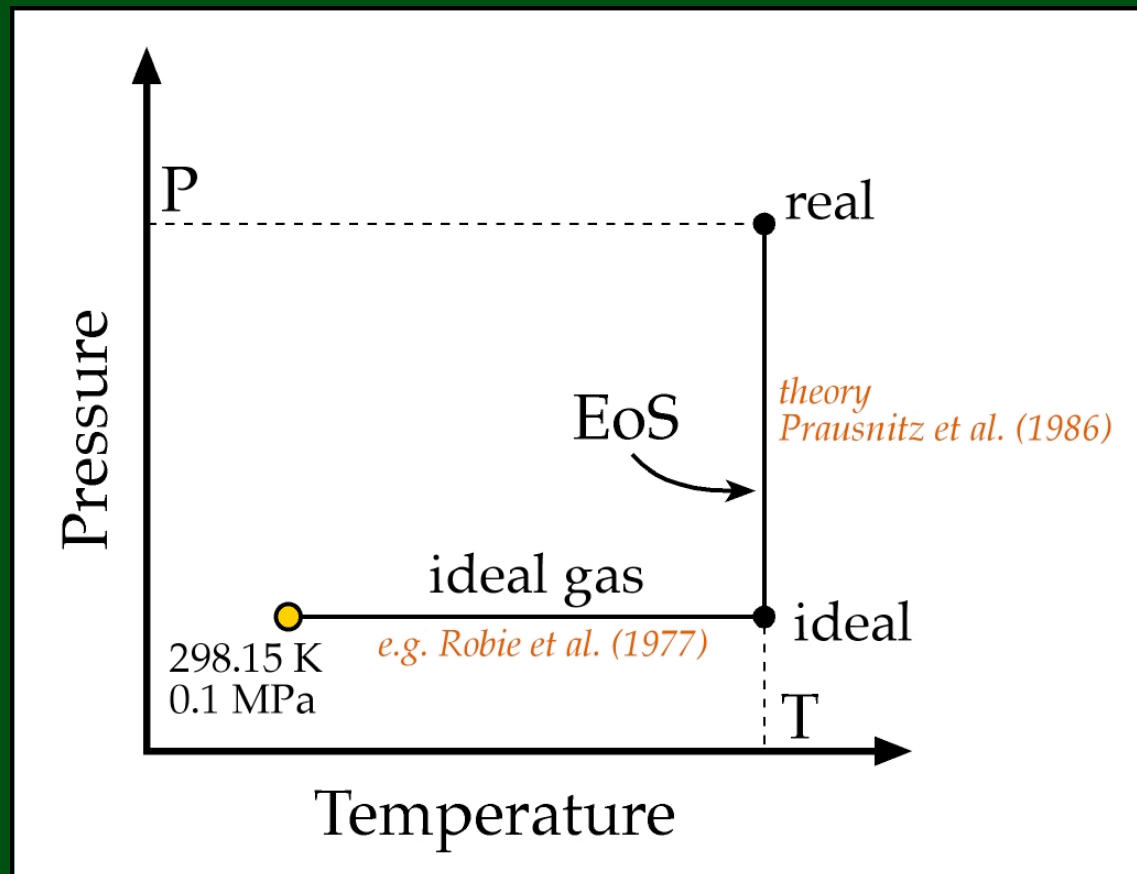
What can we do with the parameters:

$$n, V, T, p$$

Fluid Inclusion Research:	isochore calculation homogenization condition salinity calculations
---------------------------	---

General Fluid Research:	a lot
-------------------------	-------

From Equation of State to Thermodynamic properties



a lot =

molare volume: $v(x,T,p)$

pressure: $p(x,v,T)$

temperature: $T(x,v,p)$

fugacity: $f(x,T,p)$

activity: $a(x,T,p)$

bubble-dew point: T_h, P_h, V_h

liquid-vapour equilibrium: x_{bulk}, v, T, p

spinodal: x, v

critical point: x

internal energy: $U(x,T,p)$

enthalpy: $H(x,T,p)$

entropy: $S(x,T,p)$

Helmholtz energy: $A(x,T,p)$

Gibbs Free energy: $G(x,T,p)$

chemical potentials: $\mu(x,T,p)$

Example from the „Loner“ group



Fluid Inclusion

amount-of-substance

Fluid Compos

H₂O 0.8

CO₂ 0.1

CH₄

N₂ 0.1

C₂H₆

H₂S

NH₃

H₂

O₂

CO

sum: 1

Procedures

Pressure 25 MPa

Temperature 300 °Celsius

☐ in K

☒ in °C

calculate

mathematical solutions

☒ 81.92816

☐ 70.60935 and -51.3133-i

☐ 70.60935 and 51.3133-i

Molar Volume 81.92816 cm³/mol

Excess Molar Volume 4.73193 cm³/mol

Density 0.2638232 g/cm³

continue



Bubble-Dew point

Select

☒ Homogenization Temperature °Celsius ☐ in K ☒ in °C

☐ Homogenization Pressure MPa

Mode

☒ Vapour ☐ Liquid

calculate first approach

First Approach

Homogenization Pressure MPa

Composition	Phase X	Phase Y
H2O	0.9941949	0.8
CO2	0.0036473	0.1
N2	0.0021578	0.1

calculate

Homogenization Pressure 12.22109 MPa

	Phase X	Phase Y												
Molar Volume	<input type="text" value="49.8137"/>	<input type="text" value="253.4525"/>												
Density	<input type="text" value="0.3795964"/>	<input type="text" value="0.0852805"/>												
Composition	<table><tbody><tr><td>H2O</td><td>0.9593441</td></tr><tr><td>CO2</td><td>0.0304656</td></tr><tr><td>N2</td><td>0.0101903</td></tr></tbody></table>	H2O	0.9593441	CO2	0.0304656	N2	0.0101903	<table><tbody><tr><td>H2O</td><td>0.8</td></tr><tr><td>CO2</td><td>0.1</td></tr><tr><td>N2</td><td>0.1</td></tr></tbody></table>	H2O	0.8	CO2	0.1	N2	0.1
H2O	0.9593441													
CO2	0.0304656													
N2	0.0101903													
H2O	0.8													
CO2	0.1													
N2	0.1													
Fugacity (MPa)	<table><tbody><tr><td>H2O</td><td>7.099916</td></tr><tr><td>CO2</td><td>1.118073</td></tr><tr><td>N2</td><td>1.473502</td></tr></tbody></table>	H2O	7.099916	CO2	1.118073	N2	1.473502	<table><tbody><tr><td>H2O</td><td>7.099916</td></tr><tr><td>CO2</td><td>1.118073</td></tr><tr><td>N2</td><td>1.473502</td></tr></tbody></table>	H2O	7.099916	CO2	1.118073	N2	1.473502
H2O	7.099916													
CO2	1.118073													
N2	1.473502													
H2O	7.099916													
CO2	1.118073													
N2	1.473502													

Solution after 43 iterations



Helmholtz Energy

Differential Form $\left(\frac{\partial A}{\partial V}\right)_T = -p$
see Prausnitz et al. (1986)

Pressure MPa

Temperature °Celsius ☐ in K ☒ in °C

calculate molar volume

mathematical solutions
☒ 350.62
☐ 41.375 and -35.42855*i*
☐ 41.375 and 35.42855*i*

Molar Volume 350.62 cm³/mol

Δ Helmholtz Energy -358491.3 J /mol

Ideal Helmholtz Energy	-358457.1	J /mol
Excess Helmholtz Energy	-34.25653	J /mol

Standard state conditions: 298.15 K and 0.1 MPa
between 298.15 and T (at 0.1 MPa): Ideal Gas Mixture
Thermodynamic data Robie et al. (1979)

Example from the „AqSo“ group



Start

Fluid Inclusion Laboratory Leoben

AqSoVir

Software Package Fluid Inclusions

Purely empirical best-fits developed at the Vienna University of Technology and State University (1988 - 1993)

Ref.1: Hall DL, Sterner SM, Bodnar RJ (1988) Freezing point depression of NaCl-KCl-H₂O solutions. *Economic Geology*, v.83, 197-202.
 Ref.2: Sterner SM, Hall DL, Bodnar RJ (1988) Synthetic fluid inclusions in the system NaCl-KCl-H₂O under vapor-saturated conditions. *Cosmochimica Acta*, v.52, 989-1005.
 Ref.3: Bodnar RJ, Sterner SM, Hall DL (1989) SALTY: a FORTRAN program for the calculation of fluid inclusion compositions in the system NaCl-KCl-H₂O. *Geochimica et Cosmochimica Acta*, v.53, 19-41.
 Ref.4: Oakes CS, Bodnar RJ, Simonson JM (1990) The system NaCl-KCl-H₂O: liquidus at 1 atm total pressure. *Geochimica et Cosmochimica Acta*, v.54, 19-41.
 Ref.5: Bodnar RJ (1993) Revised equation and table for determination of fluid inclusion compositions in the system NaCl-KCl-H₂O. *Geochimica et Cosmochimica Acta*, v.57, 19-41.

Fluid system:

Salinity: H₂O - NaCl - KCl

Dissolving Phases

☐ Ice + Hydrohalite
☐ Ice + Sylvite
☐ Hydrohalite + Halite
☐ Hydrohalite + Sylvite
☒ Halite + Sylvite

Cotectic Line

☐ Best-Fit formulas (ref.3)
☒ Exact Intersections of Isotherms (© R. J. Bakker, 2003)

Dissolution Temperatures

Limits cotectic line: from -2.3 to 489.8 °C

Halite (-2.3 to 658-801 °C) °C

Sylvite (-22.9 to 658-770 °C) °C

	cotectic mass%	anhydrous solvus-ratio	final mass%	molality (mole/kg)
NaCl	18.43756	0.9997604	41.28681	12.02814
KCl	16.29109	0.0002396	17.42668	3.609921



Salinity: H₂O – NaCl – KCl

Dissolving Phases

☐ Ice + Hydrohalite

☐ Ice + Sylvite

☐ Hydrohalite + Halite

☐ Hydrohalite + Sylvite

☒ Halite + Sylvite

Cotectic Line

☐ Best-Fit formulas (ref.3)

☒ Exact Intersections of Isotherms (© R. J. Bakker, 2003)

clarification

Dissolution Temperatures

Limits cotectic line: from -2.3 to 489.8 °C

Halite (-2.3 to 658-801 °C)

420 °C

Sylvite (-22.9 to 658-770 °C)

60 °C

phase diagram

calculate

	cotectic mass%	anhydrous solvus-ratio	final mass%	molality (mole/kg)
NaCl	18.43756	0.9997604	41.28681	12.02814
KCl	16.29109	0.0002396	17.42668	3.609921

Calculation Cotectic Lines

"exact" intersection

isotherm

Liquid + Ice Field

Liquid

Anhydrous Solvus – Ratio

H₂O

0

-21.2

+0.1

-22.9

-2.3

-10.7

cotectic line (halite + sylvite)

T₁

isotherm

T₂

490

658

800.08

801

NaCl

T₁

490

489.81

772.33

770

KCl

T₁

anhydrous solvus-ratio

+ vapour

The use of "t" in a significant intersection software offers these intersections.

The limits of temperature phase) always

Example:

Fluid inclusion with two daughter crystals (halite and sylvite) at room temperature and a vapour bubble. At T₁ the "halite" crystal (with 5% KCl) is completely dissolved, whereas the remaining "sylvite" crystal contains about 15 % NaCl (anhydrous solvus-ratio at T₁, this point is revealed in the calculation-window). During further heating both liquid and remaining crystal change their compositions. The intersection of the T₂ isotherm and the line between the T₁-cotectic and T₁-anhydrous solvus-ratio defines the bulk salinity of this inclusion. (see Ref.2 and 3).

Note: yellow dots indicate temperatures on the NaCl-KCl solvus (maximum at 490 °C). White dots are specific temperatures on cotectic lines. Temperatures are given in °C.

Note (© R. J. Bakker, 2003): the numbers in red are based on the polynomials given in Ref.2 and 3. The azeotropic point in the NaCl-KCl binary (minimum melting point at 658 °C and 43.9 mass% NaCl) cannot be obtained according to these polynomials. The "exact intersection" calculation results in a maximum temperature of the cotectic at 655.68 °C for 43.09 mass% NaCl and 56.44 mass% KCl.

Computer Package

Fluids

version 2

MacOS

Windows

Linux (Unix)

<http://fluids.unileoben.ac.at>