

# Geological Fluids

## Thermodynamics and Computer Modelling

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Fluids are involved in most geological processes

Geological Fluids :

1.  $\text{H}_2\text{O}$
2. Gases ( $\text{CO}_2$ - $\text{CH}_4$ - $\text{N}_2$ - $\text{H}_2\text{S}$ , dissolved species)
3. Salts ( $\text{NaCl}$ - $\text{KCl}$ , dissolved species)
4. Ionic species

Properties of fluids: „Equation of State“

### *Statement 1a*

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

### *Statement 1b*

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

## *Statement 2*

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

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  $A_m(x, v, T)$

Problem = 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
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General Fluid Research:	a lot
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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:  $x_{\text{bulk}}, v, T, p$

spinodal:  $x, v$

critical point:  $x$

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

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

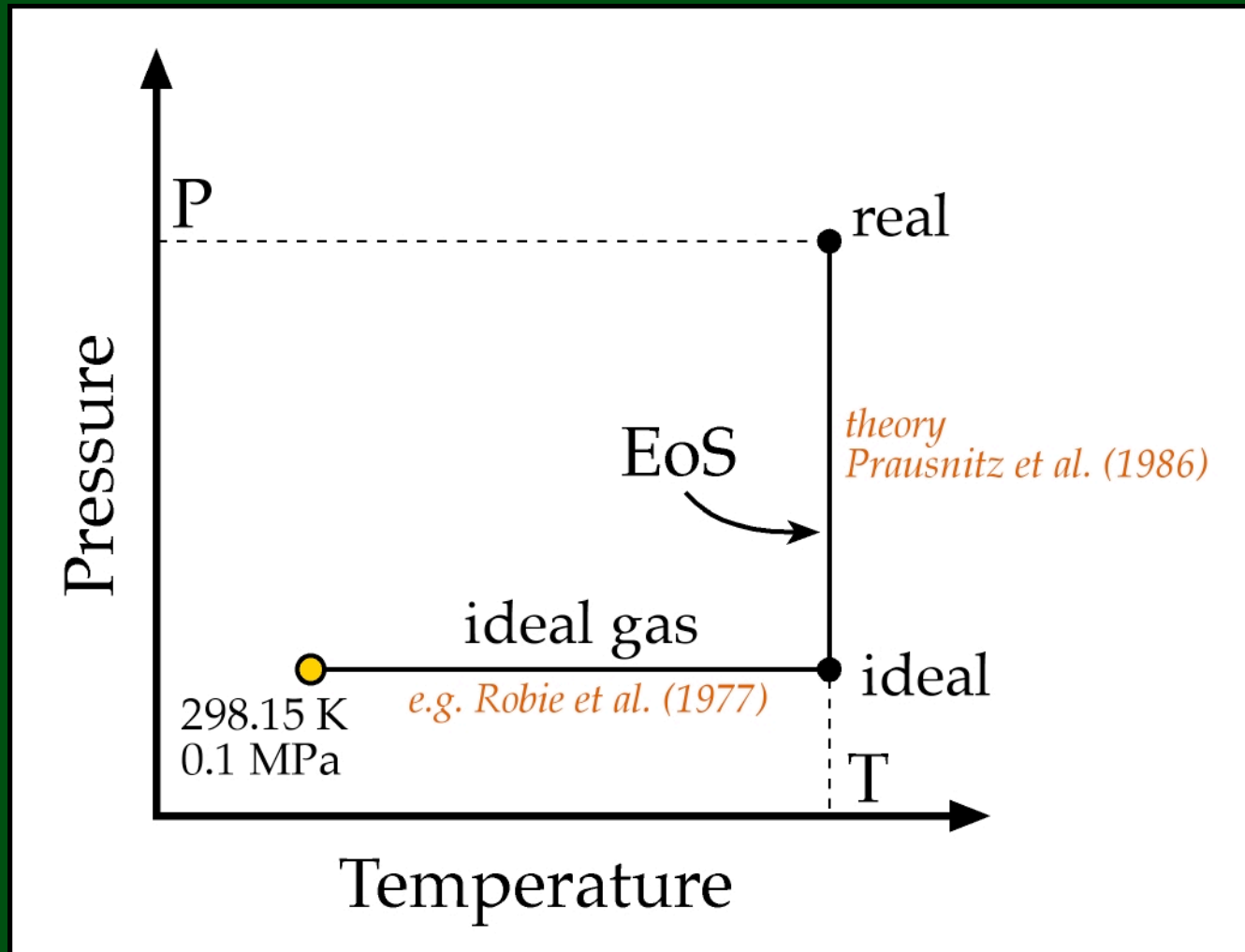
entropy:  $S(x,T,p)$

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

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

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

# From Equation of State to Thermodynamic properties







# Computer Modelling: „FLUIDS“

Example from

**Fluid Inclusion**

Waals, JD van der (1873) De ...  
Universiteit Leiden, pp 134.

a-values and b-values of indi

Fluid system:  
 $H_2O - CO_2 - CH_4 - N_2$

Fluid Compos  
amount-of-substance

H <sub>2</sub> O	0.8
CO <sub>2</sub>	0.1
CH <sub>4</sub>	
N <sub>2</sub>	0.1
C <sub>2</sub> H <sub>6</sub>	
H <sub>2</sub> S	
NH <sub>3</sub>	
H <sub>2</sub>	
O <sub>2</sub>	
CO	
sum:	1

Calcul

- ☐ M
- ☐ P
- ☐ T
- ☐ F
- ☐ A
- ☐ H
- ☐ L
- ☐ S
- ☐ C
- ☐ R
- ☐ R
- ☐ E
- ☐ R
- ☐ R
- ☐ C

Procedures

Molar Volumes

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	cm <sup>3</sup> /mol
Excess Molar Volume	4.73193	cm <sup>3</sup> /mol
Density	0.2638232	g/cm <sup>3</sup>

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													
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N2	0.0101903													
H2O	0.8													
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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
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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 cm<sup>3</sup>/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)

# Computer modelling: „FLUIDS“



## Example from the „AqSoVir“

Start

Fluid Inclusion Laboratory Leoben

**AqSoVir**  
Software Package Fluid

Purely empirical best-fits developed at the Vienna Institute of Mineralogy and Petrology, University of Leoben (1988 - 1993)

Ref.1: Hall DL, Sterner SM, Bodnar RJ (1988) Freezing point depression of NaCl-KCl-H<sub>2</sub>O solutions. Economic Geology, v.83, 197-202.  
Ref.2: Sterner SM, Hall DL, Bodnar RJ (1988) Synthetic fluid inclusions in the system NaCl-KCl-H<sub>2</sub>O 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-H<sub>2</sub>O. v.15, 19-41.  
Ref.4: Oakes CS, Bodnar RJ, Simonson JM (1990) The system NaCl-KCl-H<sub>2</sub>O: liquidus at 1 atm total pressure. Geochimica et Cosmochimica Acta, v.54, 1005-1015.  
Ref.5: Bodnar RJ (1993) Revised equation and table for determining the depression of H<sub>2</sub>O-NaCl solutions. Geochimica et Cosmochimica Acta, v.57, 1005-1015.

Fluid system:  $H_2O - NaCl - KCl - CaCl_2$  (partly)

Salinity: H<sub>2</sub>O - 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)  °C

Sylvite (-22.9 to 658-770 °C)  °C

phase diagram

continue

	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: H<sub>2</sub>O – 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

H<sub>2</sub>O

0

-21.2

+0.1

-22.9

-2.3

-10.7

cotectic line (halite + sylvite)

T<sub>1</sub>

isotherm

T<sub>2</sub>

490

658

800.08

801

NaCl

T<sub>1</sub>

490

489.81

658

770

772.33

KCl

T<sub>1</sub>

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 T<sub>1</sub> the “halite” crystal (with 5% KCl) is completely dissolved, whereas the remaining “sylvite” crystal contains about 15 % NaCl (anhydrous solvus-ratio at T<sub>1</sub>, this point is revealed in the calculation-window). During further heating both liquid and remaining crystal change their compositions. The intersection of the T<sub>2</sub> isotherm and the line between the T<sub>1</sub>-cotectic and T<sub>1</sub>-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>