

New developments of the software package FLUIDS:

program PURES and LonerAP

Ronald J. Bakker  
Resource Mineralogy  
Montanuniversität Leoben  
Austria

Start

Fluid Inclusion Laboratory Leoben

FILL

© R. J. Bakker, 2011

modification 01/2022

developed with XOJO 2021 r2.1

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

Pures

"Pure Gases"

Software Package Fluids 6.0

Helmholtz energy functions for pure gases

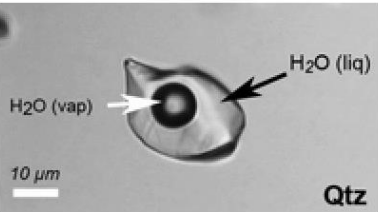
surface tensions and viscosity models

$$A(\rho, T) = A_{Basis}(\rho, T) + A_{Residual}(\rho, T) + A_{Ideal Gas}(\rho, T)$$

$$a(\rho, T) = a^o(\rho, T) + a^r(\rho, T)$$

where  $o$  = ideal, and  $r$  = residual

Water, Carbon dioxide, Methane, Nitrogen, Ethane, Oxygen,  
 Ammonia, Carbon monoxide, Hydrogen, Heavy water, Argon,  
 Propane, Sulfur dioxide, Hydrogen sulfide, Helium



application example: fluid inclusion in quartz

next

Start

Fluid Inclusion Laboratory Leoben

FILL

© R. J. Bakker, 2008

modification 04/2023

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

Loner AP

Software Package Fluids

Fluid system: H<sub>2</sub>O – CO<sub>2</sub> – CH<sub>4</sub> – NaCl – KCl

Temperature limit: > 300 °C
 

note limits

Equation (Helmholtz energy function):

$$a(T, v, x) = a^{ideal gas}(T, v, x) + a^{reference}(T, v, x) + a^{perturbation}(T, v, x)$$

$$a^{reference}(T, v, x) = a^{repulsive}(v, x) + a^{dipolar}(T, v, x)$$

note definitions

Andrzej Anderko, Kenneth S Pitzer (1993a)  
 Equation-of-state representation of phase equilibria and volumetric properties of the system NaCl-H<sub>2</sub>O above 573 K. *Geochimica et Cosmochimica Acta*, vol. 57, 1657-1680.

Andrzej Anderko, Kenneth S Pitzer (1993b)  
 Phase equilibria and volumetric properties of the systems KCl-H<sub>2</sub>O and NaCl-KCl-H<sub>2</sub>O above 573 K: Equation of state representation. *Geochimica et Cosmochimica Acta*, 57, 4885-4897.
 

note Anderko

Zhenhao Duan, Nancy Moller, John H Weare (1995)  
 Equation of state for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> system: Prediction of phase equilibria and volumetric properties. *Geochimica et Cosmochimica Acta*, 59, 2869-2882.

Z Duan, N Moller, JH Weare (2003)  
 Equation of state for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system and the NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system: Phase equilibria and volumetric properties above 573 K. *Geochimica et Cosmochimica Acta*, 67, 671-680.
 

note Duan

Extra: quartz solubility according to Akin'fiev and Diamond (2009) and Manning (1994)

next

# program *PURES*

review of eos of pure gases for most relevant gas components that are found in fluid inclusions

Cf.

GERG-2004 (and 2008)  
(Groupe Européen de  
Recherches Gazières)

Kunz et al. (2007)  
Kunz and Wagner (2012)

NIST Chemistry WebBook  
Thermophysical Properties of Fluid  
Systems

Procedures

Select Component

☐ H2O, Haar et al. (1984)

☒ H2O, Wagner and Pruss (2002)  
IAPWS R6-95 (2018)

☐ CO2, Span and Wagner (1996)

☐ CH4, Setzmann and Wagner (1991)

☐ N2, Jacobsen et al. (1986)

☐ N2, Span et al. (2000)

☐ C2H6, Friend et al. (1991)

☐ C2H6, Bücker and Wagner (2006)

☐ O2, Stewart et al. (1991)

☐ NH3, Haar and Gallagher (1978)

☐ NH3, Tillner-Roth and Baehr (1993)

☐ CO, Goodwin (1985)

☐ CO, Lemmon and Span (2006)

☐ D2O, Hill et al. (1982)

☐ D2O, Herrig et al. (2018)  
IAPWS R16-17 (2018)

☐ H2 (normal), Leachman et al. (2009)

☐ H2 (para), Leachman et al. (2009)

☐ H2 (ortho), Leachman et al. (2009)

☐ C3H8, Miyamoto and Watanabe (2000)

☐ C3H8, Lemmon et al. (2009)

☐ SO2, Lemmon and Span (2006)

☐ SO2, Gao et al. (2016)

☐ H2S, Sakoda and Uematsu (2004)

☐ H2S, Lemmon and Span (2006)

☐ Ar, Tegeler et al. (1999)

☐ He, Ortiz-Vega (2013)

Select Calculation

☒ Pressures (T, V)

☐ Molar Volumes (T, P)

☐ Temperatures (P, V)

☐ Isochores

☐ Isotherms

☐ Fugacities (T, P, V)

☐ Homogenization conditions

☐ Liquid-Vapour Equilibrium

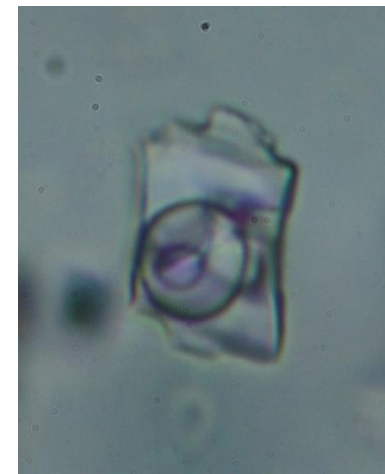
☐ Thermodynamic Properties

next

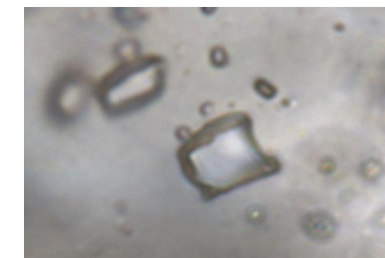
Reference:

Wagner W, Pruss A (2002)  
  
The IAPWS Formulation 1995 for the Thermodynamic  
Properties of Ordinary Water Substance for General  
and Scientific Use.  
  
J. Phys. Chem. Ref. Data, vol. 31, 387  
  
The International Association for the Properties of  
Water and Steam  
<http://www.iapws.org>  
  
from the melting curve to 1273 K at pressures to  
1000 MPa

what is the application of  
properties of pure gases to fluid  
inclusion research?



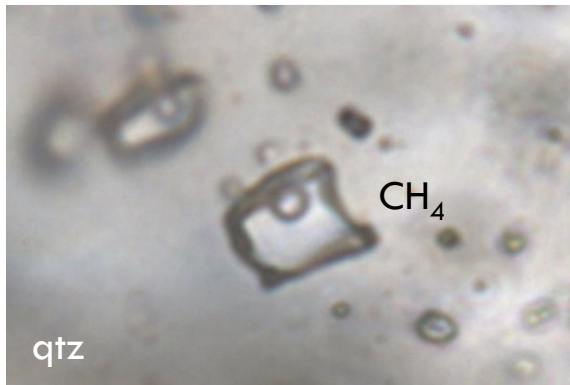
CO<sub>2</sub>-H<sub>2</sub>O-NaCl



CH<sub>4</sub>

# program *PURES*

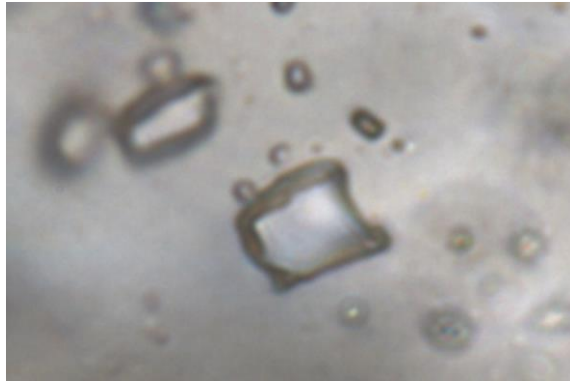
special application to fluid inclusion research



homogenization

LV → L

-126.1 °C



Isochore

Fluid: CH4 (Setzmann and Wagner, 1991)

Molar Volume  cm<sup>3</sup>/mol

corresponding density = 363.7194 kg/m<sup>3</sup>

clear

Vol. Unit  
☒ cm<sup>3</sup>/mol  
☐ kg/m<sup>3</sup>

Fluid Inclusions: Isochore Correction

density correction for fluids ☐ no  
entrapped in inclusions in quartz (expansivity and compressibility) ☒ yes

explanation

Molar Volume is defined at: > -126.1 °C

temperature  °C

corresponding pressure: 125.8837 MPa

Fluid Inclusions: Homogenization conditions

intersection isochore and liquid-vapour curve

Calculate

homogenization temperature -126.1 °C

homogenization pressure 0.9076724 MPa

Isochore definition

pressure calculation between lower and upper temperature limits

lower temperature  °C

upper temperature  °C

temperature interval  degree

calculate

Temperature (°C)	Pressure (MPa)
100	180.1768
150	214.1035
200	246.5547
250	277.7477
300	307.8316
350	336.8876
400	364.9306
450	391.9102

export file

data is available in:  
44.10763.txt

## program *Loner AP*

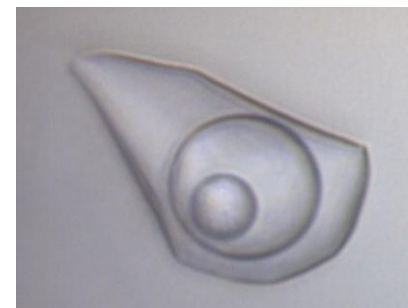
H<sub>2</sub>O – CO<sub>2</sub> – CH<sub>4</sub> – NaCl – KCl mixtures

Helmholtz energy function:  $\alpha(T, v, x)$

1. position of solvus
2. liquid – vapour equilibrium conditions
3. homogenization conditions
4. isochore calculations

main equations:

$$-p = \left( \frac{\partial A}{\partial V} \right)_{T, n_i, n_j, \dots}$$
$$\mu_i = \left( \frac{\partial A}{\partial n_i} \right)_{T, P, n_j, \dots}$$



fluid inclusion  
CO<sub>2</sub>-H<sub>2</sub>O-NaCl

Fluid

Composition

clear all

select unit

☒ mass%

☐ as%

☐ molality

as% = amount-of-substance percentage  
(alternative: "mole" percentage)

mass% = mass percentage  
(alternative: "weight" percentage)

mass %

H<sub>2</sub>O

CO<sub>2</sub>

CH<sub>4</sub>

NaCl

KCl

Recalculated Composition

	mass %	as %	molality
H <sub>2</sub> O	<input type="text"/>	<input type="text"/>	
CO <sub>2</sub>	<input type="text"/>	<input type="text"/>	<input type="text"/>
CH <sub>4</sub>	<input type="text"/>	<input type="text"/>	<input type="text"/>
NaCl	<input type="text"/>	<input type="text"/>	<input type="text"/>
KCl	<input type="text"/>	<input type="text"/>	<input type="text"/>

Calculation Procedure

☐ Pressures

☐ Molar Volumes

☐ Temperatures

☐ Isochores

☐ Fugacities

☐ Activities

☐ Spinodal

☐ Critical Point

☐ Homogenization conditions

☐ Liquid-Vapour equilibria

☐ Quartz Solubility

☐ Helmholtz Energy

next

program *Loner AP*

what else can we do with this equation of state?

**Spinodal**

$$Det_{spin} = \begin{vmatrix} A_{VV} & A_{n_1V} & A_{n_2V} \\ A_{n_1V} & A_{n_1n_1} & A_{n_1n_2} \\ A_{n_2V} & A_{n_1n_2} & A_{n_2n_2} \end{vmatrix} = 0$$

$A = \text{Helmholtz energy}$

e.g.  $A_{VV} = \left( \frac{\partial^2 A}{\partial V^2} \right)_{n_1, n_2}$

$$Det_{spin} = A_{VV} \cdot A_{n_1n_1} \cdot A_{n_2n_2} - (A_{n_2V})^2 \cdot A_{n_1n_1} + A_{n_1V} \cdot A_{n_1n_2} \cdot A_{n_2V} - (A_{n_1n_2})^2 \cdot A_{VV} + \\ A_{n_2V} \cdot A_{n_1V} \cdot A_{n_1n_2} - (A_{n_1V})^2 \cdot A_{n_2n_2} = 0$$

$$Det_{spin} = A_{n_2V} \cdot C_{A_{n_2V}} + A_{n_1n_2} \cdot C_{A_{n_1n_2}} + A_{n_2n_2} \cdot C_{A_{n_2n_2}} = 0$$



program Loner AP

what else can we do with this equation of state?

## Critical Point

$$Det_{crit} = \begin{vmatrix} A_{VV} & A_{n_1V} & A_{n_2V} \\ A_{n_1V} & A_{n_1n_1} & A_{n_1n_2} \\ D_V & D_{n_1} & D_{n_2} \end{vmatrix} = 0$$

e.g.

$$A_{VVV} = \left( \frac{\partial^3 A}{\partial V^3} \right)_{n_1, n_2}$$

matrix of cofactors

$$\text{e.g. } D_V = \frac{\partial Det_{spin}}{\partial V} = \begin{vmatrix} A_{VVV} & A_{n_1VV} & A_{n_2VV} \\ A_{n_1VV} & A_{n_1n_1V} & A_{n_1n_2V} \\ A_{n_2VV} & A_{n_1n_2V} & A_{n_2n_2V} \end{vmatrix} \times \begin{vmatrix} C_{A_{VV}} & C_{A_{n_1V}} & C_{A_{n_2V}} \\ C_{A_{n_1V}} & C_{A_{n_1n_1}} & C_{A_{n_1n_2}} \\ C_{A_{n_2V}} & C_{A_{n_1n_2}} & C_{A_{n_2n_2}} \end{vmatrix}$$

$$Det_{crit} = C_{A_{n_2V}} \times \frac{\partial Det_{spin}}{\partial V} + C_{A_{n_1n_2}} \times \frac{\partial Det_{spin}}{\partial n_1} + C_{A_{n_2n_2}} \times \frac{\partial Det_{spin}}{\partial n_2} = 0$$

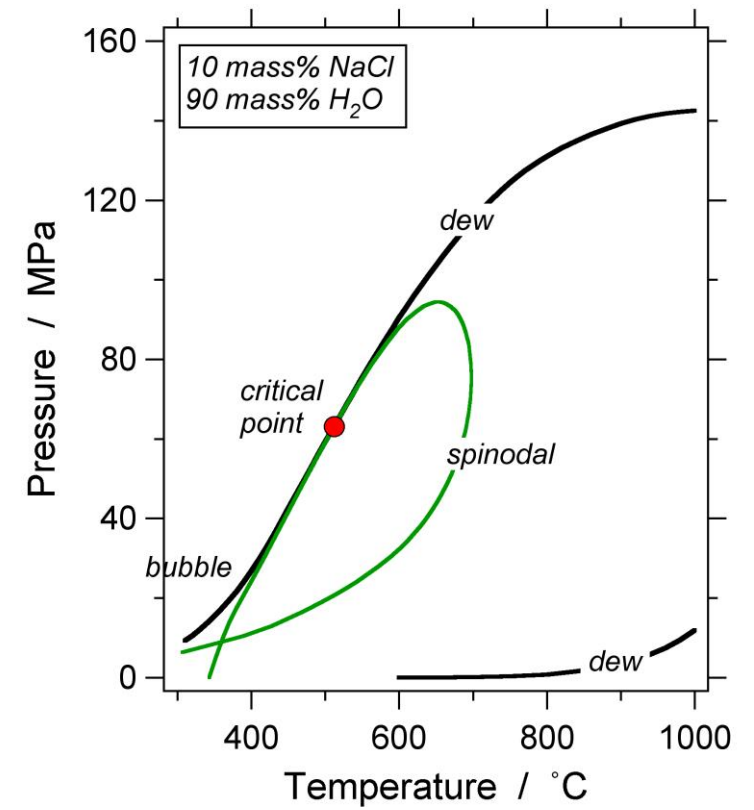
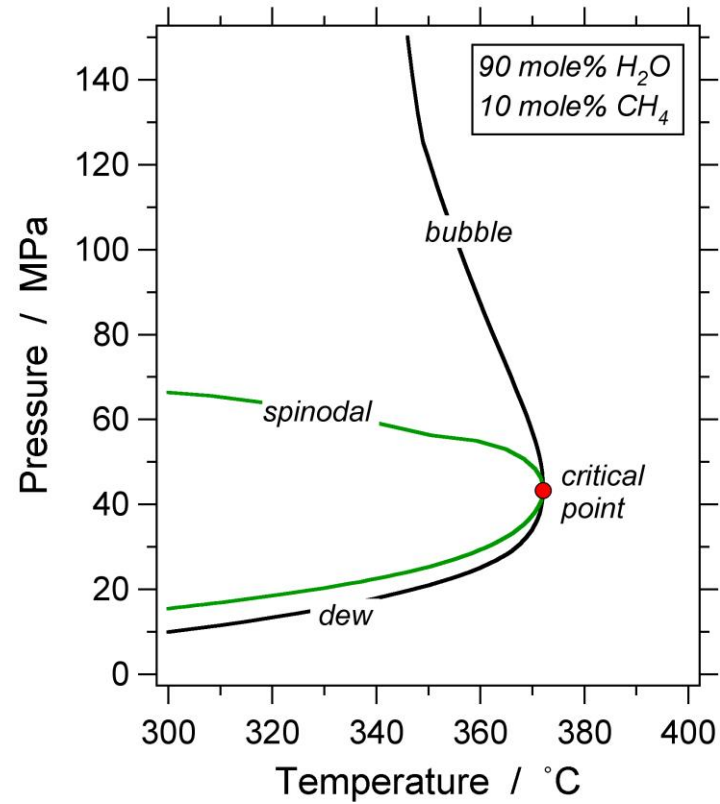
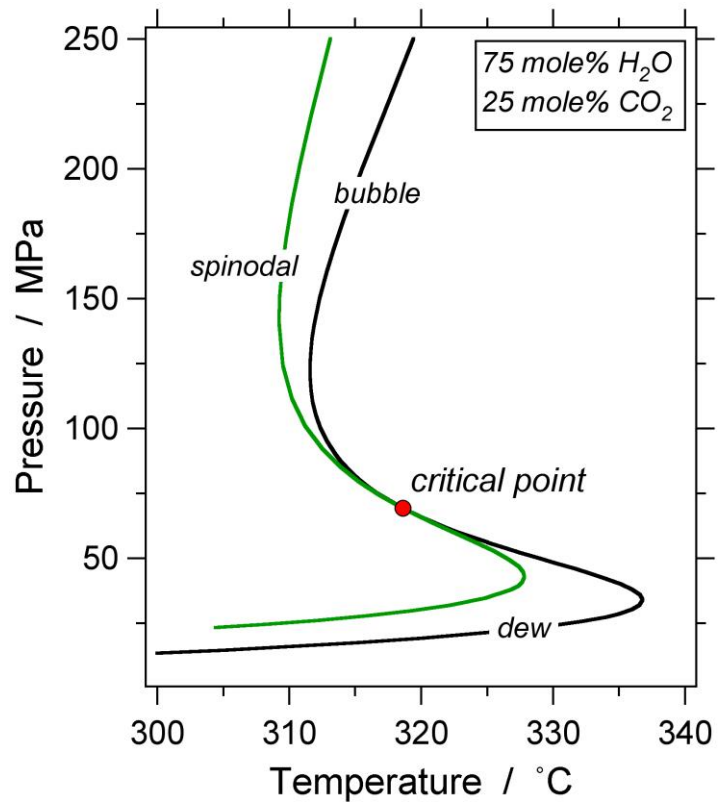




## program *Loner AP*

examples:

binary mixtures: solvus, spinodal, critical point



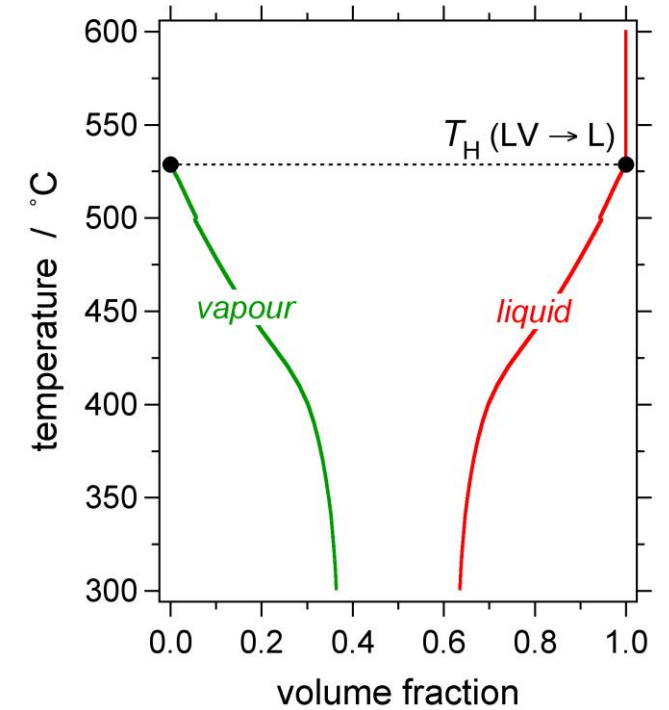
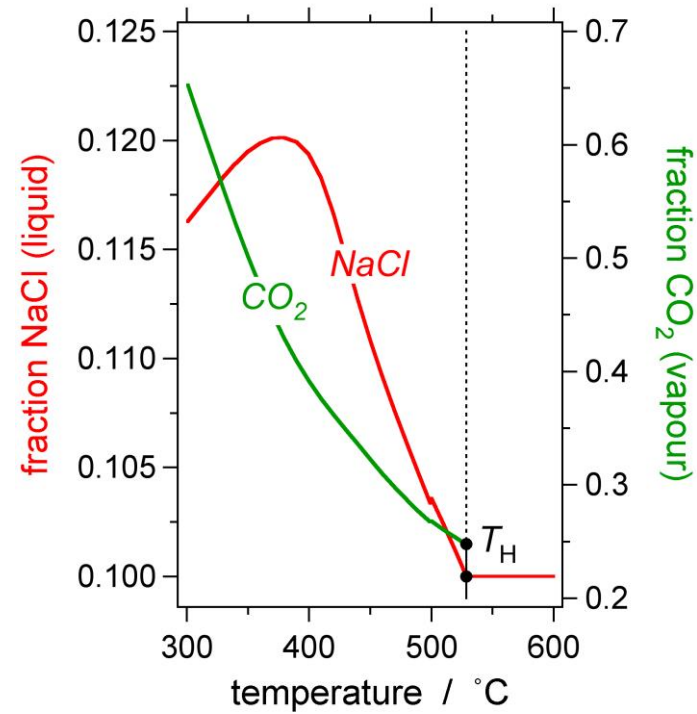
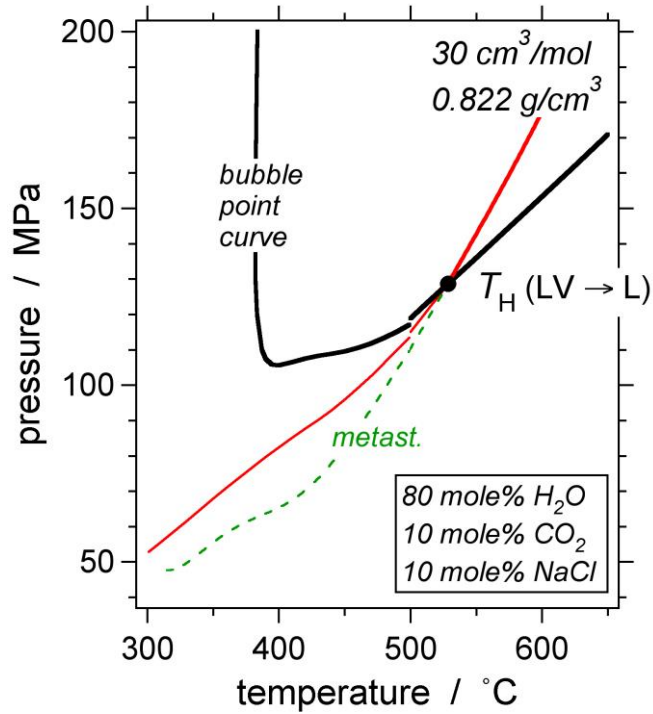
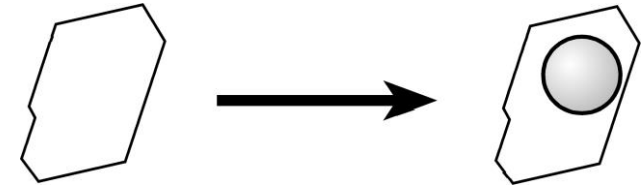


# program *Loner AP*

examples:

ternary mixtures

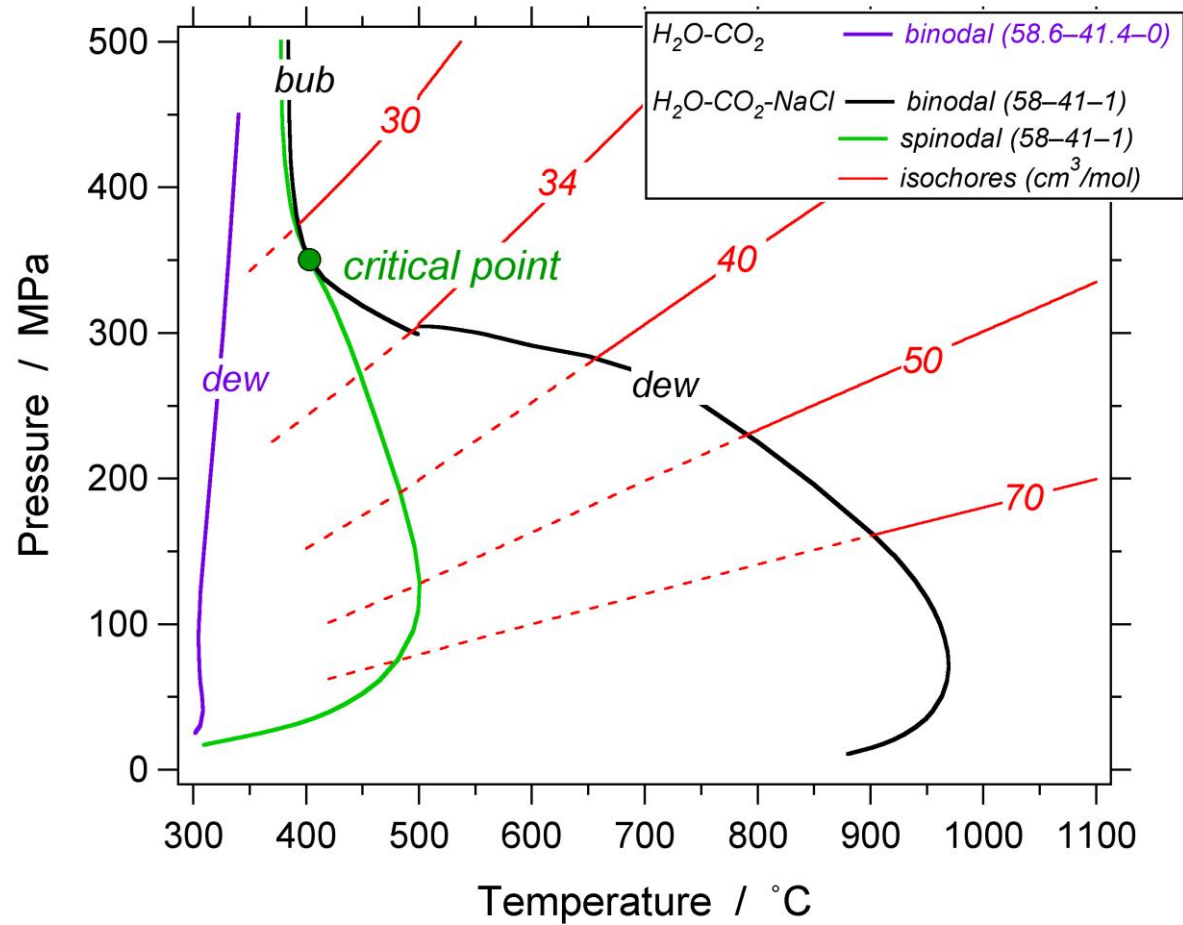
isochores, homogenization conditions fluid inclusions



program *Loner AP*

examples:

adding a little bit NaCl: major effect on immiscibility



# program Loner AP

examples:

critical points

Fluid

Composition

as %

H<sub>2</sub>O

95

CO<sub>2</sub>

3

CH<sub>4</sub>

NaCl

2

KCl

select unit

☐ mass%

☒ as%

☐ molality

as% = amount-of-substance percentage  
(alternative: "mole" percentage)

mass% = mass percentage  
(alternative: "weight" percentage)

clear all

Recalculated Composition

	mass %	as %	molality
H <sub>2</sub> O	87.30088	95	
CO <sub>2</sub>	6.734799	3	1.752898
CH <sub>4</sub>			
NaCl	5.964323	2	1.168599
KCl			

Calculation Procedure

☐ Pressures

☐ Molar Volumes

☐ Temperatures

☐ Isochores

☐ Fugacities

☐ Activities

☐ Spinodal

☒ Critical Point

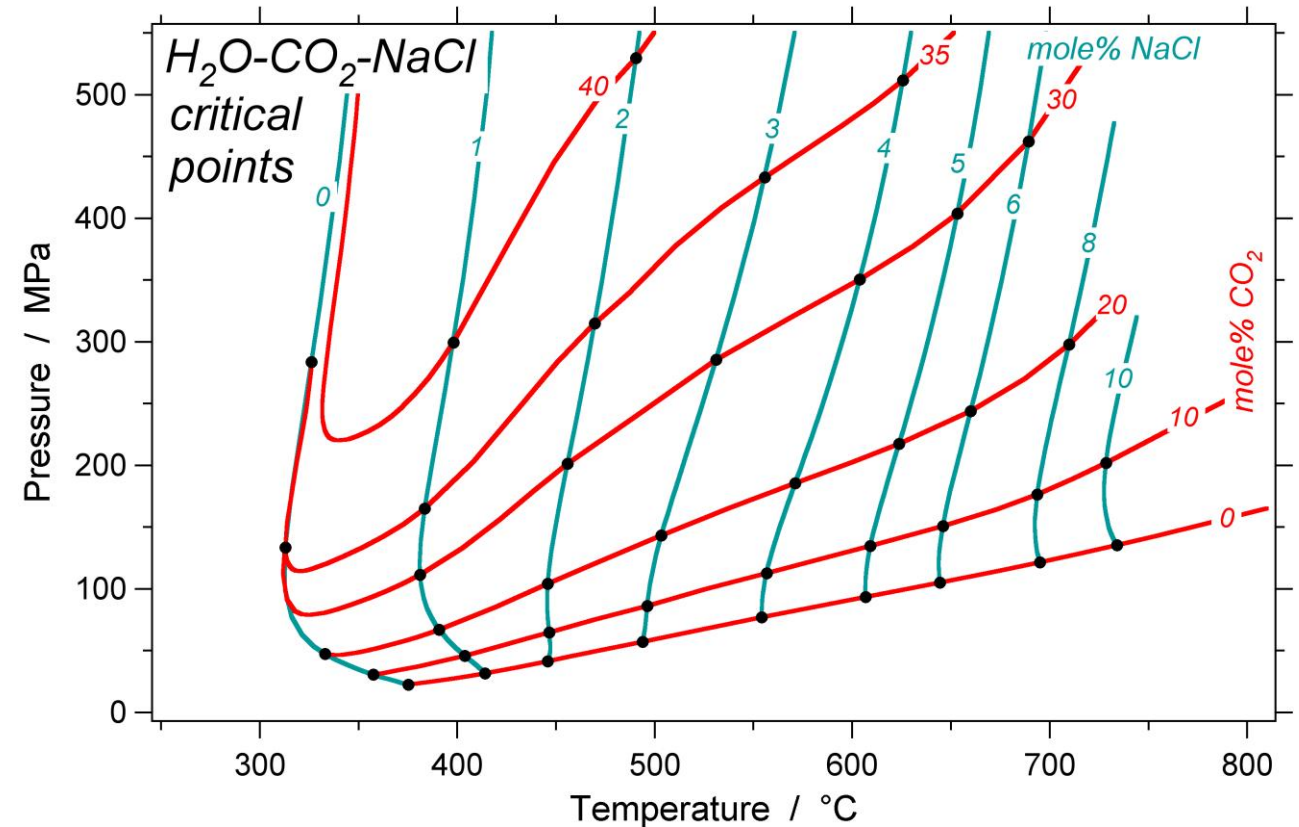
☐ Homogenization conditions

☐ Liquid-Vapour equilibria

☐ Quartz Solubility

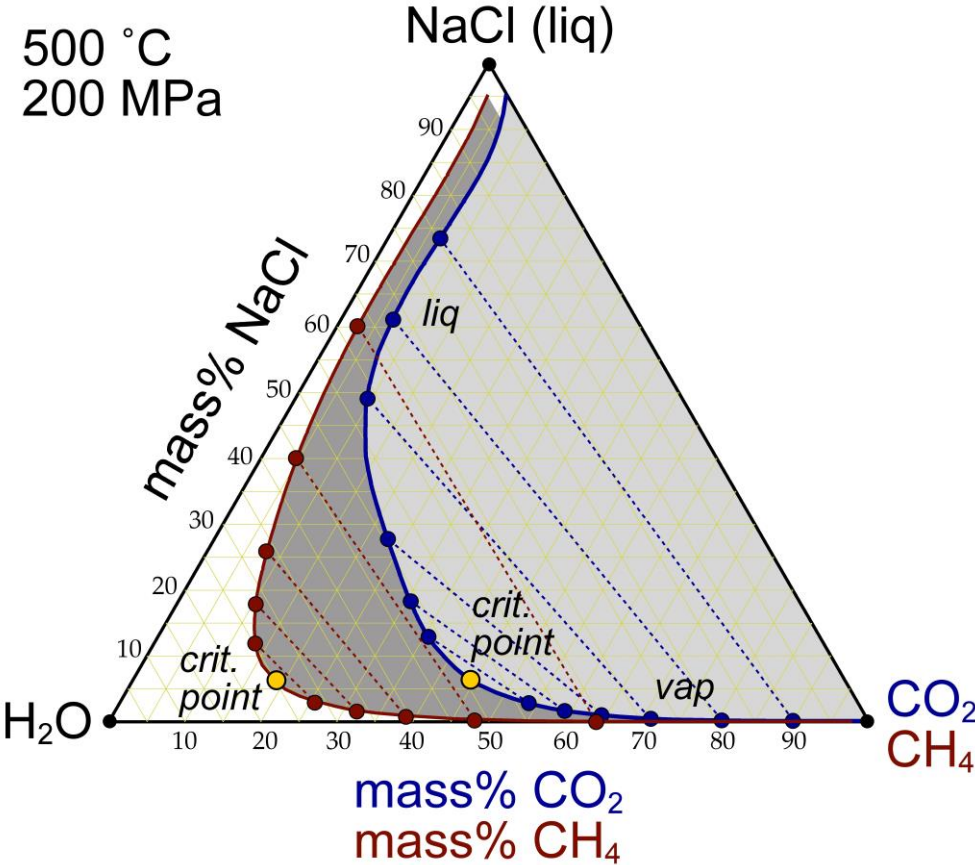
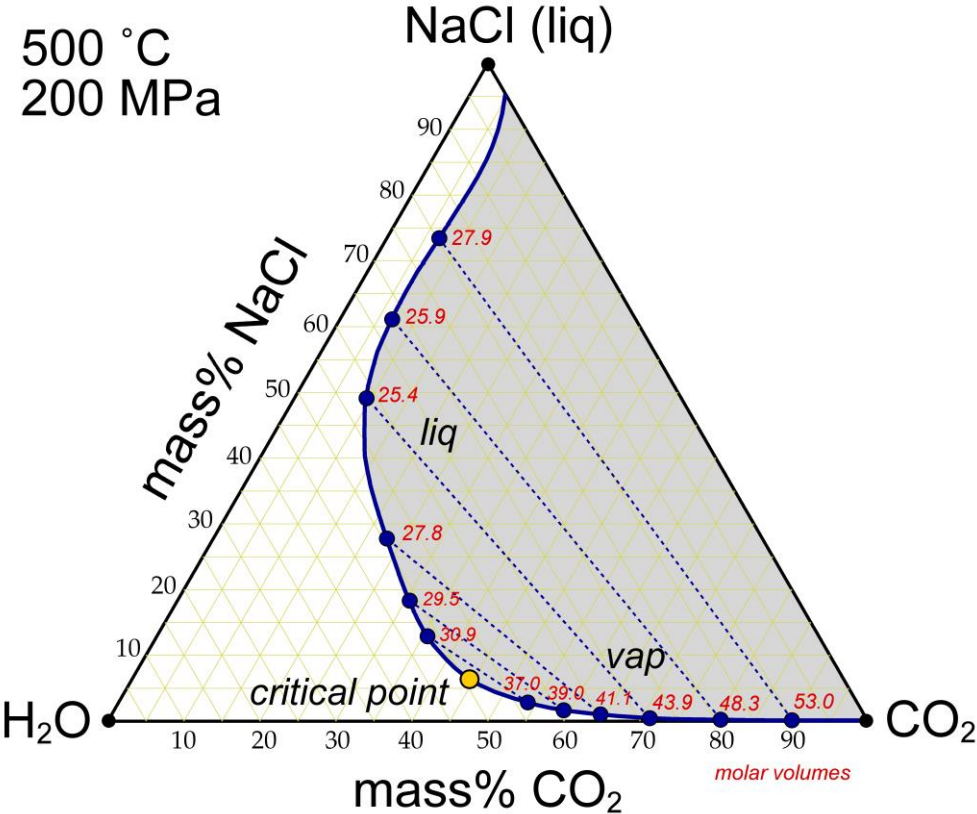
☐ Helmholtz Energy

next



program *Loner AP*

examples:



program *Loner AP*

*but ...*

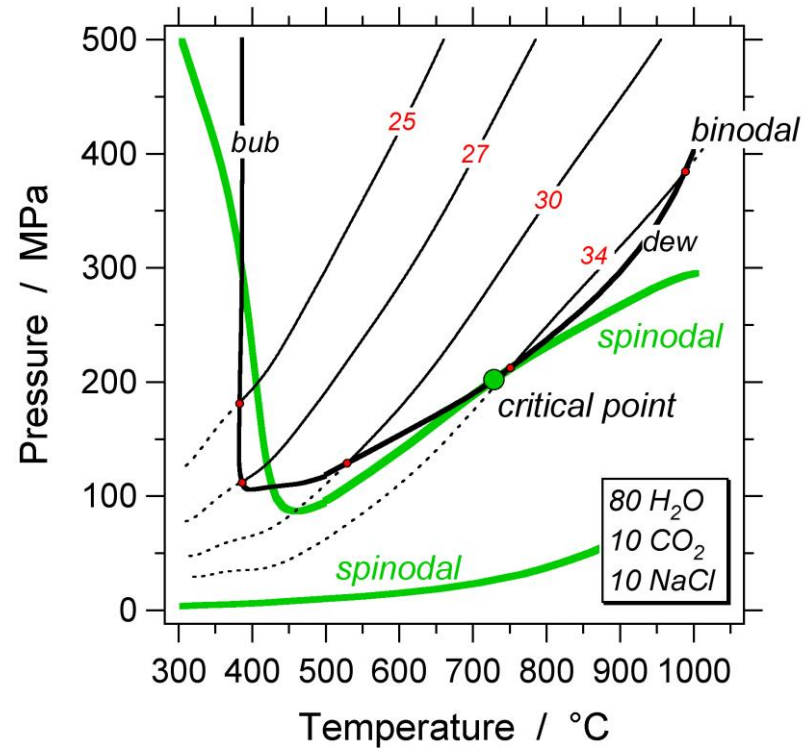
this equation of state has abundant serious problems  
which are only popping up after using this software

abundant mistakes in original papers  
literature provides many manipulated images  
tables and images in literature cannot be reproduced  
multiple mathematical solutions (e.g. critical points)  
accuracy (significant misfits)

## program *Loner AP*

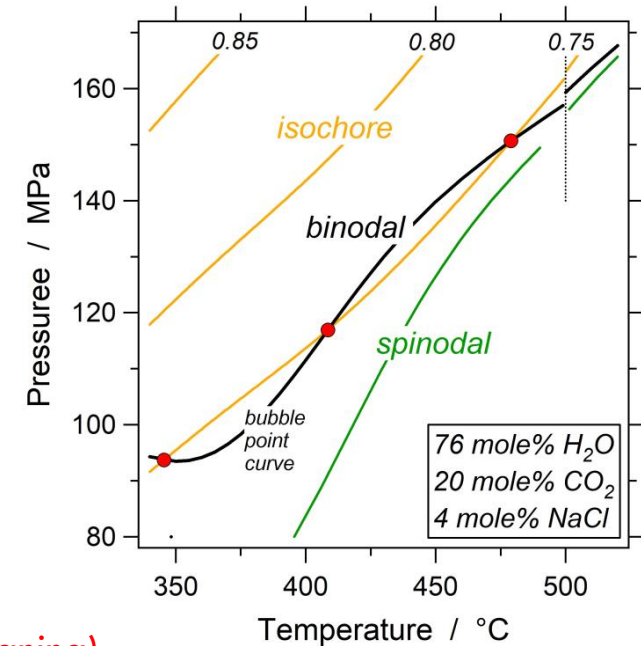
*but ....*

For example:



- multiple intersections isochore – bubble-dew-point curve ?
- spinodal exceeds binodal (solvus) ?

e.g.  
Frantz et al. (1992)  
Diamond (1996)



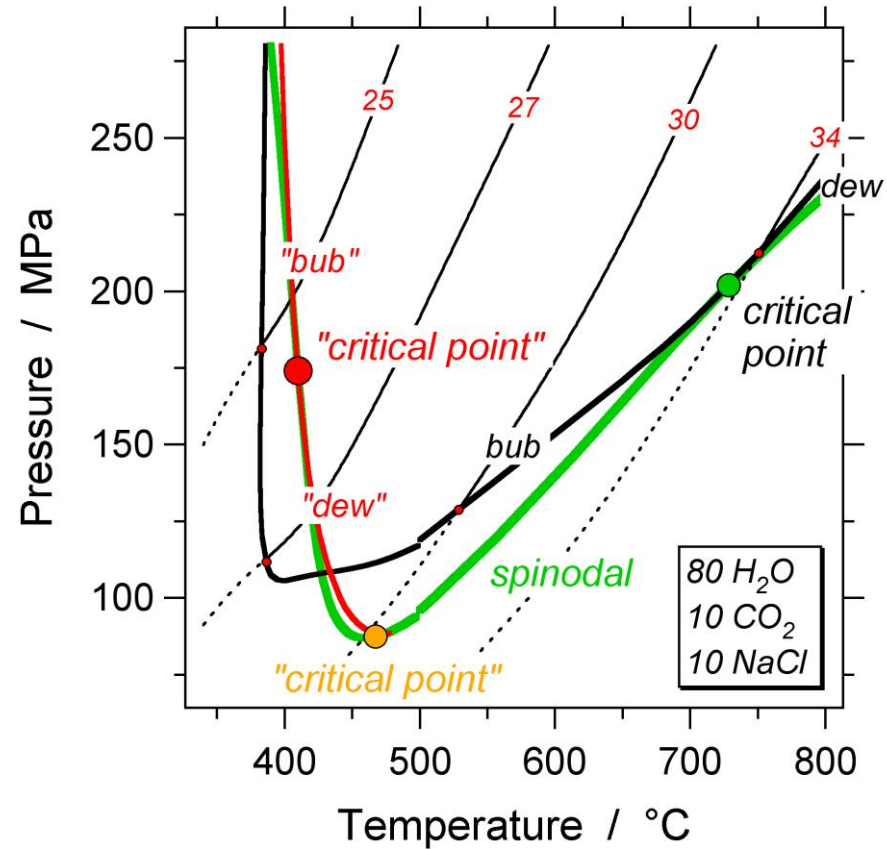
*irrelevant  
mathematical  
solutions  
(no physical meaning)*



## program *Loner AP*

*but ....*

in more detail:



- multiple critical points ?
- multiple dew-point curves ?
- multiple bubble-point curves ?

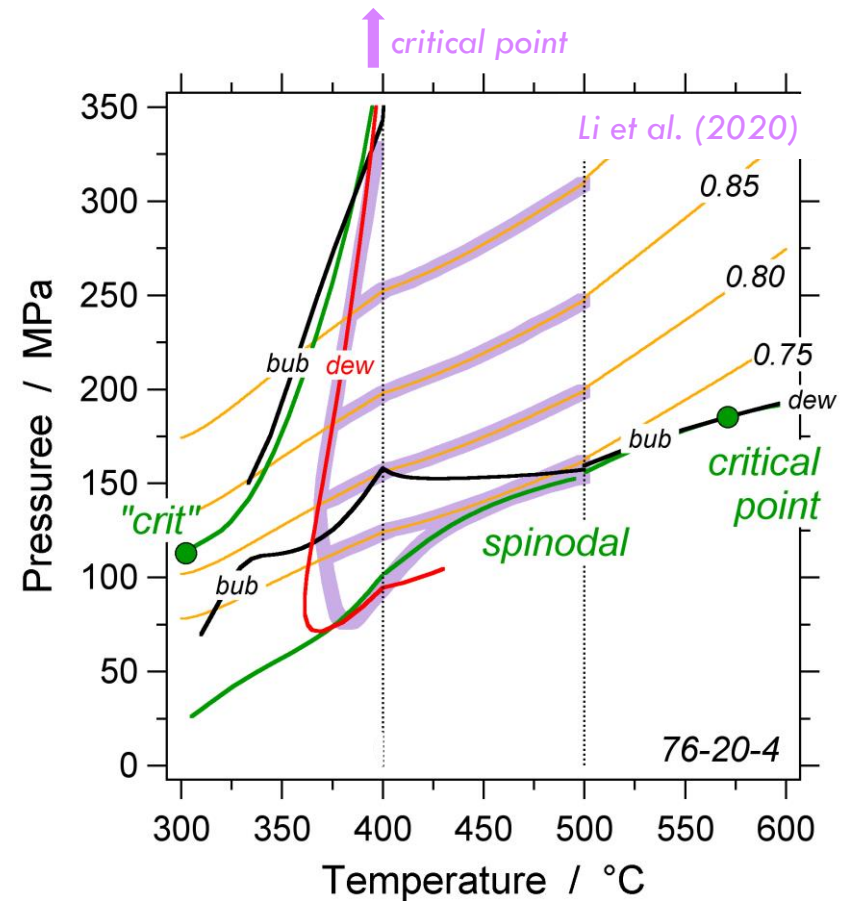
several irrelevant mathematical solutions  
(no physical meaning)



undesirable consequence of multiple mathematical solutions:

selecting the wrong critical point and solvus

- critical point above 350 MPa ?
- solvus below 400 °C ?
- solvus coincide with part of spinodal ?
- solvus coincide with wrong dew-point curve ?
- isochores correct ?



## program *Loner AP*

application of this software:

this equation of state is a very rough first approach of fluid properties of  
 $\text{H}_2\text{O} - \text{CO}_2 - \text{CH}_4 - \text{NaCl} - \text{KCl}$  mixtures

*but please: do not take Duan et al. (1995, 2003) as a standard reference for fluid immiscibility*

and it needs a lot of improvements/corrections

software offers the possibilities to detect deceptive mathematical solutions

software illustrates all the misleading applications presented in literature

formulations of critical points and spinodal offers the possibility to improve solvus models

thank you for your attention

software will be available on the websites

*or you can ask me for a copy during this conference*

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

<https://rohmin.unileoben.ac.at>