IMPACTS

Project no.:
308809

Project acronym:
IMPACTS

Project full title:
The impact of the quality of CO_2 on transport and storage behavior

Collaborative large-scale integrating project

FP7 - ENERGY.2012-1-2STAGE

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Duration: 3 years

D 3.2.1
New standard property model for CO_2 mixtures

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Actual delivery date: 2015-09-30

Organisation name of lead participant for this deliverable:
RUB

Project co-funded by the European Commission within the Seventh Framework Programme (2012-2015)		
Dissemination Level		
PU	Public	x
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential , only for members of the consortium (including the Commission Services)	

Deliverable number:	D 3.2.1
Deliverable name:	New standard property model for CO_2 mixtures
Work package:	WP 3.2 Technical knowledge base for CO_2 transport and storage
Lead participant:	RUB

Author(s)		
Name	**Organisation**	**E-mail**
Stefan Herrig	RUB	S.Herrig@thermo.rub.de
Roland Span	RUB	R.Span@thermo.rub.de

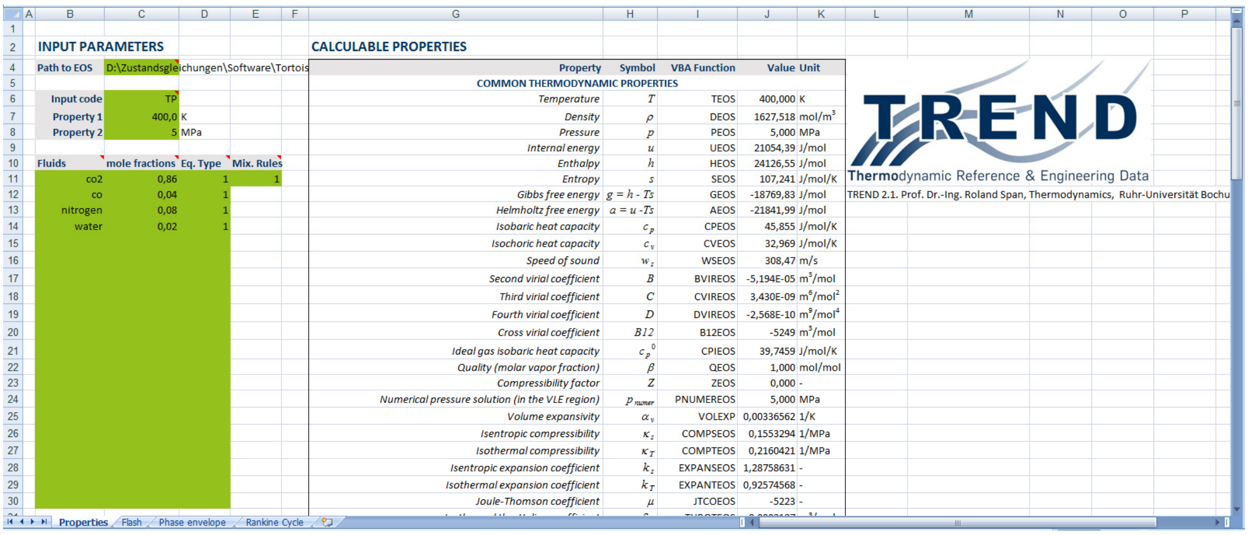
Abstract

Understanding the impact of impurities in CO_2-rich mixtures on the process chain of Carbon Capture and Storage (CCS) requires various interdisciplinary contributions to enable process simulations, geological research, material science, or safety analyses. At a certain point all these efforts demand the knowledge of thermodynamic properties of the involved mixtures. Within the research presented in this work, the thermodynamics group of RUB (Ruhr-Universität Bochum) is continuously developing a standard equation of state for CO_2-rich mixtures including components found to be relevant in CCS applications. In addition, new algorithms were developed to face the challenges of phase stability analyses and predictions of various phase equilibria including fluid phases as well as hydrates or solids of CO_2 and water. To enable straightforward calculations based on these complex thermodynamic models and algorithms RUB is providing the software package TREND (see *Span et al.*, *2015*) to the CCS community. The upcoming new version of TREND is supposed to be an important element of the IMPACTS Toolbox.

Public introduction (*)

The IMPACTS project was initiated to understand the impact of impurities in CO_2-rich mixtures on the process chain of Carbon Capture and Storage (CCS). This aim requires various interdisciplinary contributions resulting from, e.g., process simulations, geological research, material science, or safety analyses. However, at a certain point all these efforts demand the knowledge of thermodynamic properties of the involved mixtures. Nowadays, the most accurate way to determine these properties is by means of empirical multiparameter equations of state.

As a member of Work Package 1.2 (“Thermophysical behavior of CO_2 mixtures”) the thermodynamics group of RUB (Ruhr-Universität Bochum) is continuously developing an accurate equation of state for CO_2-rich mixtures including components found to be relevant in CCS applications. In addition, new algorithms were developed to face the challenges of phase stability analyses and predictions of various phase equilibria including fluid phases as well as hydrates or solids of CO_2 and water. It is not surprising that neither the application of these algorithms nor the calculation of thermodynamic properties from the equation of state can be individually handled by typical users. Consequently, a simple interface is needed that enables straightforward calculations based on these complex thermodynamic models and algorithms. Within Work Package 3.2 (“Technical knowledge base for CO_2 transport and storage”) RUB is providing the software package TREND (see *Span et al., 2015*) to the CCS community. Since 2009, this property package is continuously improved and extended. The latest version 2.0.1 will soon be distributed via the IMPACTS eRoom and is supposed to become an element of the IMPACTS Toolbox.



INPUT PARAMETERS

Path to EOS D:\Zustandsgleichungen\Software\Tortois

Input code TP
Property 1 400,0 K
Property 2 5 MPa

Fluids	mole fractions	Eq. Type	Mix. Rules
co2	0,86	1	1
co	0,04	1	
nitrogen	0,08	1	
water	0,02	1	

CALCULABLE PROPERTIES

Property	Symbol	VBA Function	Value	Unit
COMMON THERMODYNAMIC PROPERTIES				
Temperature	T	TEOS	400,000	K
Density	ρ	DEOS	1627,518	mol/m³
Pressure	p	PEOS	5,000	MPa
Internal energy	u	UEOS	21054,39	J/mol
Enthalpy	h	HEOS	24126,55	J/mol
Entropy	s	SEOS	107,241	J/mol/K
Gibbs free energy	$g = h - Ts$	GEOS	-18769,83	J/mol
Helmholtz free energy	$a = u - Ts$	AEOS	-21841,99	J/mol
Isobaric heat capacity	c_p	CPEOS	45,855	J/mol/K
Isochoric heat capacity	c_v	CVEOS	32,969	J/mol/K
Speed of sound	w_s	WSEOS	308,47	m/s
Second virial coefficient	B	BVIREOS	-5,194E-05	m³/mol
Third virial coefficient	C	CVIREOS	3,430E-09	m⁶/mol²
Fourth virial coefficient	D	DVIREOS	-2,568E-10	m⁹/mol⁴
Cross virial coefficient	$B12$	B12EOS	-5249	m³/mol
Ideal gas isobaric heat capacity	c_p^0	CPIEOS	39,7459	J/mol/K
Quality (molar vapor fraction)	β	QEOS	1,000	mol/mol
Compressibility factor	Z	ZEOS	0,000	-
Numerical pressure solution (in the VLE region)	p_{numer}	PNUMEREOS	5,000	MPa
Volume expansivity	α_v	VOLEXP	0,00336562	1/K
Isentropic compressibility	κ_s	COMPSEOS	0,1553294	1/MPa
Isothermal compressibility	κ_T	COMPTEOS	0,2160421	1/MPa
Isentropic expansion coefficient	k_s	EXPANSEOS	1,28758631	-
Isothermal expansion coefficient	k_T	EXPANTEOS	0,92574568	-
Joule-Thomson coefficient	μ	JTCOEOS	-5223	-

Figure 1: Example calculations of several relevant state properties within the TREND Excel interface for a multicomponent CO -rich mixture at given temperature and pressure.

(*) According to Deliverables list in Annex I, all restricted (RE) deliverables will contain an introduction that will be made public through the project WEBsite

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1 INTRODUCTION

The IMPACTS project was initiated to understand the impact of impurities in CO_2-rich mixtures on the process chain of Carbon Capture and Storage (CCS). This aim requires various interdisciplinary contributions resulting from, e.g., process simulations, geological research, material science, or safety analyses. However, at a certain point all these efforts demand the knowledge of thermodynamic properties of the involved mixtures. Nowadays, the most accurate way to determine these properties is by means of empirical multiparameter equations of state.

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To emphasize the need for property packages such as TREND, some of the main challenges of calculating thermodynamic properties from multiparameter equations of state are discussed briefly in chapter 2 of this report. In the third chapter some options of TREND are demonstrated and results of exemplary calculations are shown. A short overview of the models included in the upcoming version of TREND is given in chapter 4. The report concludes with a summary of the results and outlook to future work.

2 CHALLENGES OF CALCULATING THERMODYNAMIC PROPERTIES FROM ACCURATE EQUATIONS OF STATE

Over the last decades, various research groups put extensive efforts into the development of highly accurate multiparameter equations of state describing the thermodynamic properties of pure fluids and mixtures. The most commonly used form of these property models is explicit in the Helmholtz free energy. This kind of equations of state is categorized as “fundamental equation of state”. The advantage of such a fundamental model is that all thermodynamic properties can be calculated by combining derivatives of its functional form. In contrast, obtaining caloric properties from so-called “thermal equations of state” (e.g. explicit in pressure) requires complex integrations. However, since the mathematical structure of Helmholtz equations of state includes different term types with a large number of parameters, calculating their derivatives easily turns into a quite challenging and time-consuming problem. This aspect can be emphasized by the exemplary calculations of two technical relevant properties. Equation (2.1) highlights that calculating the pressure p at a given temperature T and density ρ from an equation of state explicit in the reduced Helmholtz energy α is comparably simple

$$p = \rho RT\left(1+\delta\alpha_{\delta}^{\mathrm{r}}\right). \tag{2.1}$$

Besides the reduced density δ and the gas constant R, only the first derivative of the residual Helmholtz energy with respect to δ (written as $\alpha_{\delta}^{\mathrm{r}}$) is required. In contrast, if the isobaric heat capacity c_p is needed, the following equation has to be solved

$$c_p = R\left[-\tau^2\left(\alpha_{\tau\tau}^{\mathrm{o}}+\alpha_{\tau\tau}^{\mathrm{o}}\right)+\frac{\left(1+\delta\alpha_{\delta}^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{1+2\delta\alpha_{\delta}^{\mathrm{r}}-\delta^2\alpha_{\delta\delta}^{\mathrm{r}}}\right]. \tag{2.2}$$

Calculating this property obviously requires various different derivatives of the reduced ideal and residual part of the Helmholtz energy (written as α^{o} and α^{r}), e.g., the second mixed derivative of α^{r} with respect to the reduced temperature τ and density δ (written as $\alpha_{\delta\tau}^{\mathrm{r}}$).

It may be recognized from the required derivatives in the two exemplary calculations above that the independent variables of equations of state explicit in the Helmholtz energy are the inverse reduced temperature, the reduced density, and – in case of mixture calculations – the composition. However, in practical applications other input parameters such as temperature and pressure or pressure and enthalpy are often more convenient. This poses the additional challenge that the original equation of state parameters need to be iterated. Consequently, the implementation of so-called “density solver” algorithms is essential to calculate thermodynamic state properties. The algorithm implemented in TREND was developed with a main focus on its stability, which is demanding target, since these models often have multiple density roots at a given temperature, pressure, and composition. These different roots need to be evaluated with regard to plausibility and stability in order to identify the correct solution.

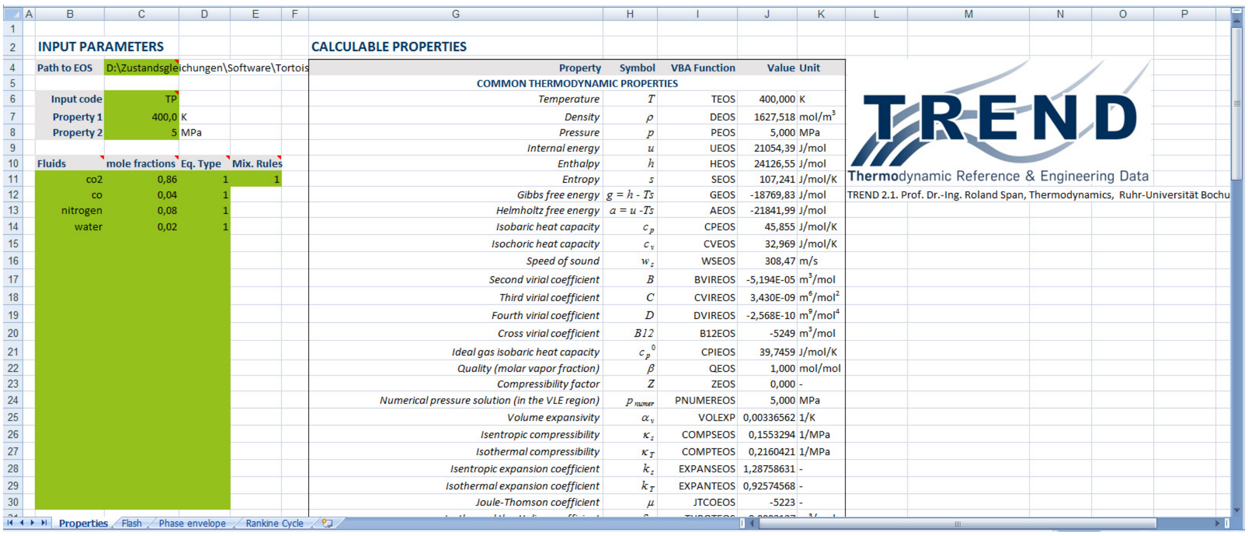
Although calculating the required derivatives based on different input parameters can be demanding, these problems are still relatively simple as long as the given state point is at a homogeneous state. The task becomes significantly more complex when a specified mixture splits into two or more phases. Stability analyses and phase equilibrium calculations still belong to the most challenging numerical problems in thermodynamics, often leading to large and complex systems of equations. Additional problems occur when the involved phases do not only include liquids or gases but also solids or hydrates. Since these phases cannot be described with the same equations as the fluid phases, such phase equilibrium calculations require a consistent interaction of different types of models.

The challenges exemplary described in this section should highlight that for most users even highly accurate equations of state are almost worthless without a software package providing the required algorithms. For this reason, TREND is a valuable tool for the CCS community and an important contribution to the IMPACTS Toolbox.

3 SELECTED FEATURES OF THE PROPERTY PACKAGE TREND

The calculation of thermophysical properties with the software package TREND is explained in detail in the TREND manual including all provided functions. However, to demonstrate the functionality of the software, some of its features are exemplary shown in this section. All TREND routines can be used by compiling the FORTRAN source code or calling the dynamic link library (dll) in other programming environments. Since it makes things easier to visualize, this description is focused on the Excel interface of the property package.

When opening the Excel interface the first worksheet that appears is entitled "Properties" (see Figure 3.1)



INPUT PARAMETERS

Path to EOS	D:\Zustandsgleichungen\Software\Tortois	
Input code	TP	
Property 1	400,0	K
Property 2	5	MPa

Fluids	mole fractions	Eq. Type	Mix. Rules
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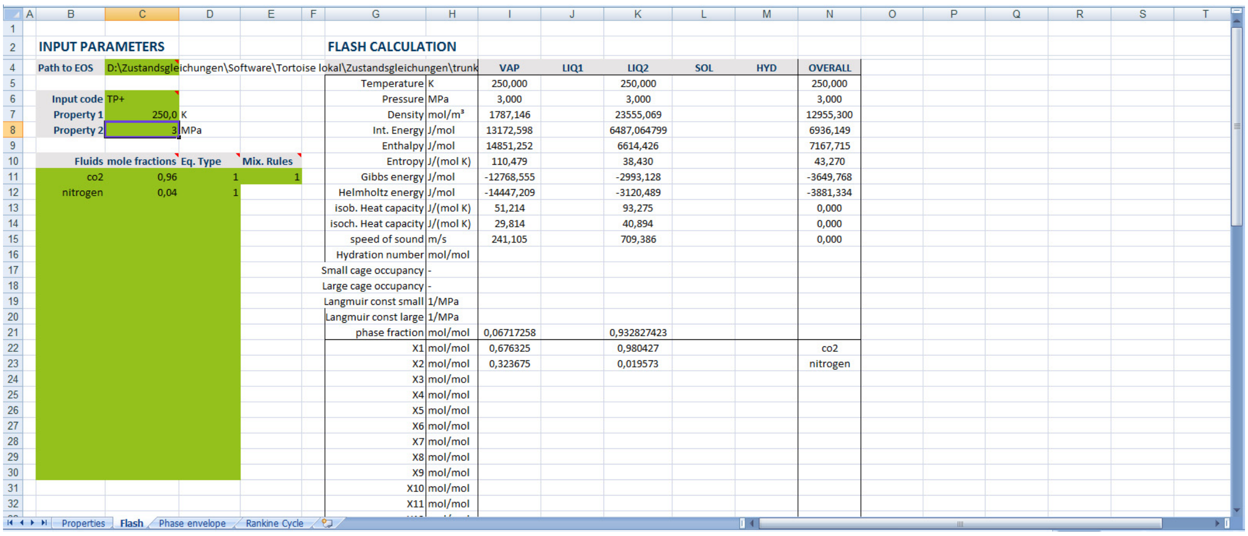
Isothermal expansion coefficient	k_T	EXPANTEOS	0,92574568	-
Joule-Thomson coefficient	μ	JTCOEOS	-5223	-

Figure 3.1: Screenshot of the "Properties" worksheet in TREND.

The worksheet provides a list of the most relevant thermophysical properties – in this case for a given mixtures of carbon dioxide, carbon monoxide, nitrogen, and water. Thus, it is a useful example to become familiar with the calling sequence of the property functions. Besides commonly relevant properties, such as density, enthalpy, heat capacity, or speed of sound, the worksheet includes less known properties like the Grueneisen coefficient, phase identification parameter or various derivatives of the Helmholtz free energy. Although these properties are most likely not relevant for most users, they are extremely helpful when fitting and analyzing equations of state or validating algorithms based on these models.

The functions included in the "Property" worksheet provide overall properties in case of a phase equilibrium state. More detailed information about the present phases are given in the "Flash" Worksheet as shown in Figure 3.2.



INPUT PARAMETERS

Path to EOS	D:\Zustandsgleichungen\Software\Tortoise lokal\Zustandsgleichungen\trunk
Input code	TP+
Property 1	250,0 K
Property 2	3 MPa

Fluids	mole fractions	Eq. Type	Mix. Rules
co2	0,96	1	1
nitrogen	0,04	1	

FLASH CALCULATION

		VAP	LIQ1	LIQ2	SOL	HYD	OVERALL
Temperature	K	250,000		250,000			250,000
Pressure	MPa	3,000		3,000			3,000
Density	mol/m³	1787,146		23555,069			12955,300
Int. Energy	J/mol	13172,598		6487,064799			6936,149
Enthalpy	J/mol	14851,252		6614,426			7167,715
Entropy	J/(mol K)	110,479		38,430			43,270
Gibbs energy	J/mol	-12768,555		-2993,128			-3649,768
Helmholtz energy	J/mol	-14447,209		-3120,489			-3881,334
isob. Heat capacity	J/(mol K)	51,214		93,275			0,000
isoch. Heat capacity	J/(mol K)	29,814		40,894			0,000
speed of sound	m/s	241,105		709,386			0,000
Hydration number	mol/mol						
Small cage occupancy	-						
Large cage occupancy	-						
Langmuir const small	1/MPa						
Langmuir const large	1/MPa						
phase fraction	mol/mol	0,06717258		0,932827423			
X1	mol/mol	0,676325		0,980427			co2
X2	mol/mol	0,323675		0,019573			nitrogen
X3	mol/mol						
X4	mol/mol						
X5	mol/mol						
X6	mol/mol						
X7	mol/mol						
X8	mol/mol						
X9	mol/mol						
X10	mol/mol						
X11	mol/mol						

Figure 3.2: Screenshot of the "Flash" worksheet in TREND. The specified state point is in the vapor-liquid equilibrium region of the binary system CO_2 + nitrogen.

The example shows a *Tp*-flash calculation of a binary mixture of CO_2 and nitrogen ($x_{CO2} = 0.96$, $x_{N2} = 0.04$) at $T_1 = 250$ K and $p_1 = 3$ MPa. With regard to a *p*, *T* - diagram of this mixtures (as given in Figure 3.3), it becomes apparent that the specified state point "1" is in the vapor-liquid equilibrium region. The screenshot of the Excel interface shows that TREND does not only predict the correct phases but additionally provides the corresponding compositions, fractions, and state properties as well as the properties of the overall system.

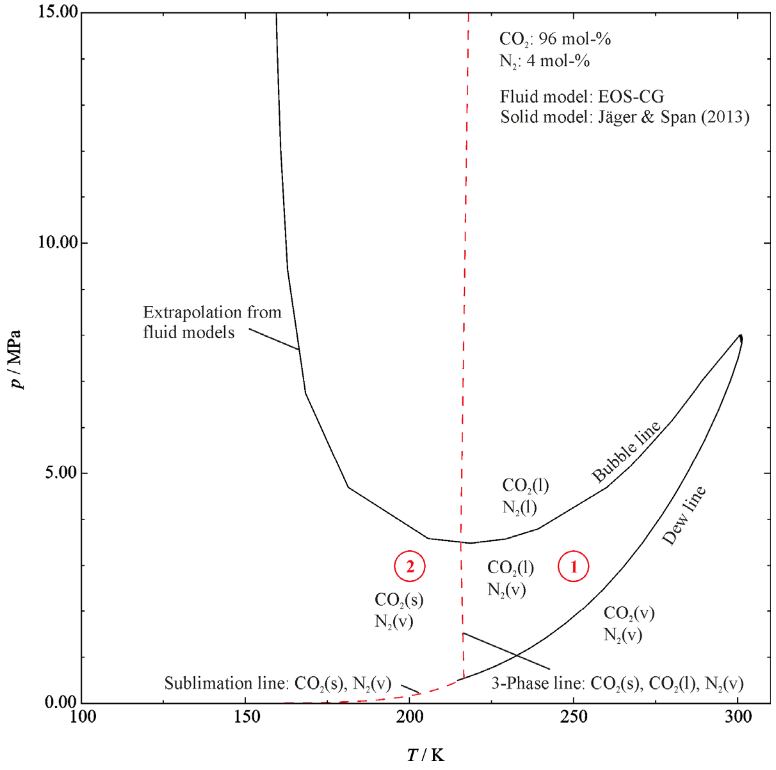
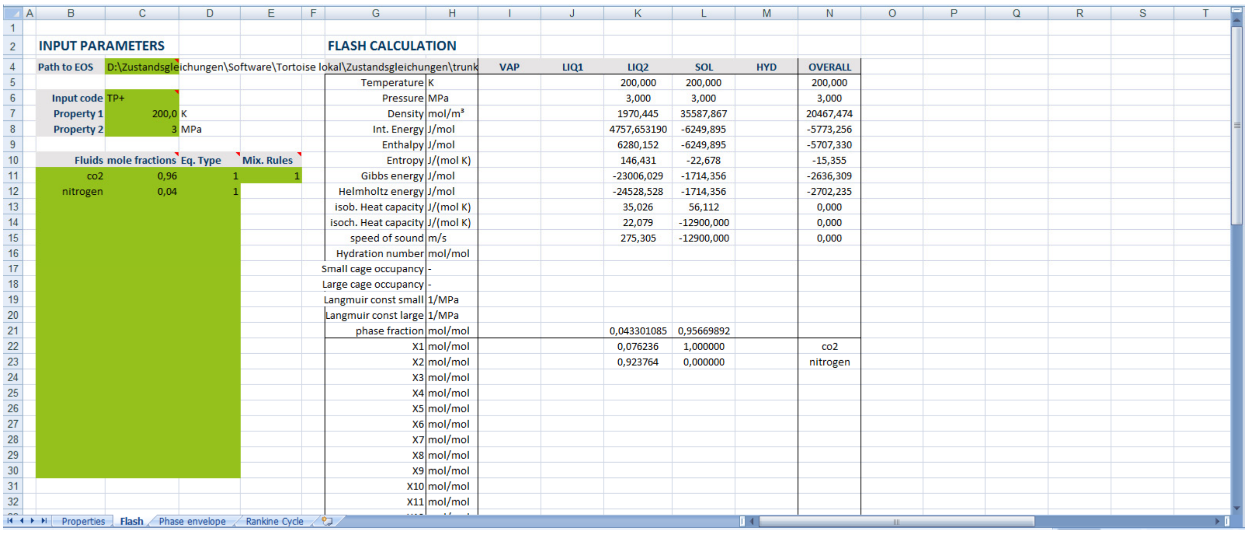


Figure 3.3: *p*, *T* - diagram of the binary system $CO_2 + N_2$ with two exemplary state points.

When decreasing the temperature down to $T_2 = 200$ K at a constant pressure $p_2 = p_1 = 3$ MPa, the phase diagram in Figure 3.3 indicates that the flash calculation has to result in a phase equilibrium of a N_2-rich gas phase and solid CO_2. Figure 3.4 shows the results of the specified *Tp*-flash. It can be noted that TREND provides a correct description of the expected phase equilibrium.



INPUT PARAMETERS

Path to EOS D:\Zustandsgleichungen\Software\Tortoise lokal\Zustandsgleichungen\trunk

Input code TP+
Property 1 200,0 K
Property 2 3 MPa

Fluids	mole fractions	Eq. Type	Mix. Rules
co2	0,96	1	1
nitrogen	0,04	1	

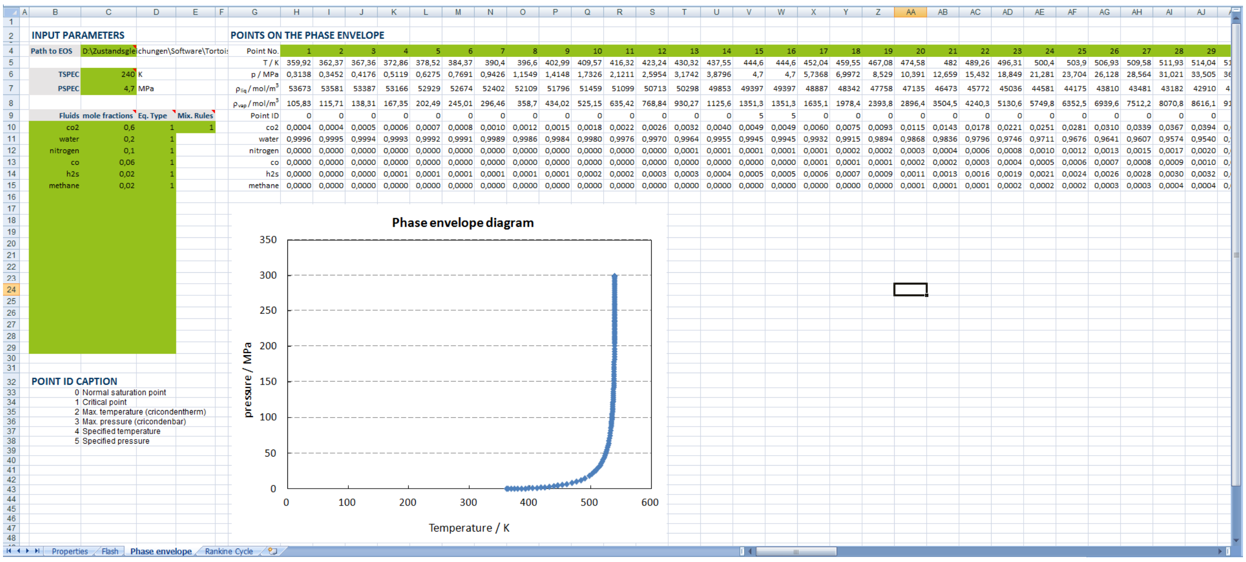
FLASH CALCULATION

		VAP	LIQ1	LIQ2	SOL	HYD	OVERALL
Temperature	K			200,000	200,000		200,000
Pressure	MPa			3,000	3,000		3,000
Density	mol/m³			1970,445	35587,867		20467,474
Int. Energy	J/mol			4757,653190	-6249,895		-5773,256
Enthalpy	J/mol			6280,152	-6249,895		-5707,330
Entropy	J/(mol K)			146,431	-22,678		-15,355
Gibbs energy	J/mol			-23006,029	-1714,356		-2636,309
Helmholtz energy	J/mol			-24528,528	-1714,356		-2702,235
isob. Heat capacity	J/(mol K)			35,026	56,112		0,000
isoch. Heat capacity	J/(mol K)			22,079	-12900,000		0,000
speed of sound	m/s			275,305	-12900,000		0,000
Hydration number	mol/mol						
Small cage occupancy	-						
Large cage occupancy	-						
Langmuir const small	1/MPa						
Langmuir const large	1/MPa						
phase fraction	mol/mol			0,043301085	0,95669892		
X1	mol/mol			0,076236	1,000000		co2
X2	mol/mol			0,923764	0,000000		nitrogen
X3	mol/mol						
X4	mol/mol						
X5	mol/mol						
X6	mol/mol						
X7	mol/mol						
X8	mol/mol						
X9	mol/mol						
X10	mol/mol						
X11	mol/mol						

Figure 3.4: Screenshot of the “Flash” worksheet in TREND. The specified state point is in the vapor-solid equilibrium region of the binary system CO_2 + nitrogen.

This example highlights one of the most remarkable achievements of recent works on the software development at RUB. In contrast to most other property packages, TREND enables the description of the fluid phases in equilibrium with solids (of water and CO_2) by means of Helmholtz equations of state. Additionally, the user does not have to decide whether the calculation of a specified state point requires a hydrate or solid phase model, but the flash algorithms automatically employ the adequate equations.

Another important feature for the CCS community might be the easy calculation of phase envelopes as provided in the worksheet “Phase envelope”. An example of the functionality of the corresponding algorithms is shown in Figure 3.5. It has to be noted that the phase envelope routines in the Excel interface only consider vapor-liquid equilibria. The construction of phase diagrams including other types of equilibria and possible three phase lines (see for instance the $p, T-$diagram given in Figure 3.3) has to be carried out manually by the user. However, the algorithms implemented in TREND do enable such calculations since equilibria of up to three phases were considered in the stability analyses and phase equilibrium routines.



INPUT PARAMETERS

Path to EOS	D:\Zustandsgleichungen\Software\Tortoi		
TSPEC	240	K	
PSPEC	4,7	MPa	
Fluids	mole fractions	Eq. Type	Mix. Rules
co2	0,6	1	1
water	0,2	1	
nitrogen	0,1	1	
co	0,06	1	
h2s	0,02	1	
methane	0,02	1	

POINTS ON THE PHASE ENVELOPE

Point No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
T / K	359,92	362,37	367,36	372,86	378,52	384,37	390,4	396,6	402,99	409,57	416,32	423,24	430,32	437,55	444,6
p / MPa	0,3138	0,3452	0,4176	0,5119	0,6275	0,7691	0,9426	1,1549	1,4148	1,7326	2,1211	2,5954	3,1742	3,8796	4,7
ρ_{liq} / mol/m³	53673	53581	53387	53166	52929	52674	52402	52109	51796	51459	51099	50713	50298	49853	49397
ρ_{vap} / mol/m³	105,83	115,71	138,31	167,35	202,49	245,01	296,46	358,7	434,02	525,15	635,42	768,84	930,27	1125,6	1351,3
Point ID	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5
co2	0,0004	0,0004	0,0005	0,0006	0,0007	0,0008	0,0010	0,0012	0,0015	0,0018	0,0022	0,0026	0,0032	0,0040	0,0049
water	0,9996	0,9995	0,9994	0,9993	0,9992	0,9991	0,9989	0,9986	0,9984	0,9980	0,9976	0,9970	0,9964	0,9955	0,9945
nitrogen	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0001	0,0001	0,0001
co	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000
h2s	0,0000	0,0000	0,0000	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0,0002	0,0002	0,0003	0,0003	0,0004	0,0005
methane	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000

Point No.	16	17	18	19	20	21	22	23	24	25	26	27	28	29
T / K	444,6	452,04	459,55	467,08	474,58	482	489,26	496,31	500,4	503,9	506,93	509,58	511,93	514,04
p / MPa	4,7	5,7368	6,9972	8,529	10,391	12,659	15,432	18,849	21,281	23,704	26,128	28,564	31,021	33,505
ρ_{liq} / mol/m³	49397	48887	48342	47758	47135	46473	45772	45036	44581	44175	43810	43481	43182	42910
ρ_{vap} / mol/m³	1351,3	1635,1	1978,4	2393,8	2896,4	3504,5	4240,3	5130,6	5749,8	6352,5	6939,6	7512,2	8070,8	8616,1
Point ID	5	0	0	0	0	0	0	0	0	0	0	0	0	0
co2	0,0049	0,0060	0,0075	0,0093	0,0115	0,0143	0,0178	0,0221	0,0251	0,0281	0,0310	0,0339	0,0367	0,0394
water	0,9945	0,9932	0,9915	0,9894	0,9868	0,9836	0,9796	0,9746	0,9711	0,9676	0,9641	0,9607	0,9574	0,9540
nitrogen	0,0001	0,0001	0,0002	0,0002	0,0003	0,0004	0,0006	0,0008	0,0010	0,0012	0,0013	0,0015	0,0017	0,0020
co	0,0000	0,0001	0,0001	0,0001	0,0002	0,0002	0,0003	0,0004	0,0005	0,0006	0,0007	0,0008	0,0009	0,0010
h2s	0,0005	0,0006	0,0007	0,0009	0,0011	0,0013	0,0016	0,0019	0,0021	0,0024	0,0026	0,0028	0,0030	0,0032
methane	0,0000	0,0000	0,0000	0,0000	0,0001	0,0001	0,0001	0,0002	0,0002	0,0002	0,0003	0,0003	0,0004	0,0004

POINT ID CAPTION

0	Normal saturation point
1	Critical point
2	Max. temperature (cricondentherm)
3	Max. pressure (cricondenbar)
4	Specified temperature
5	Specified pressure

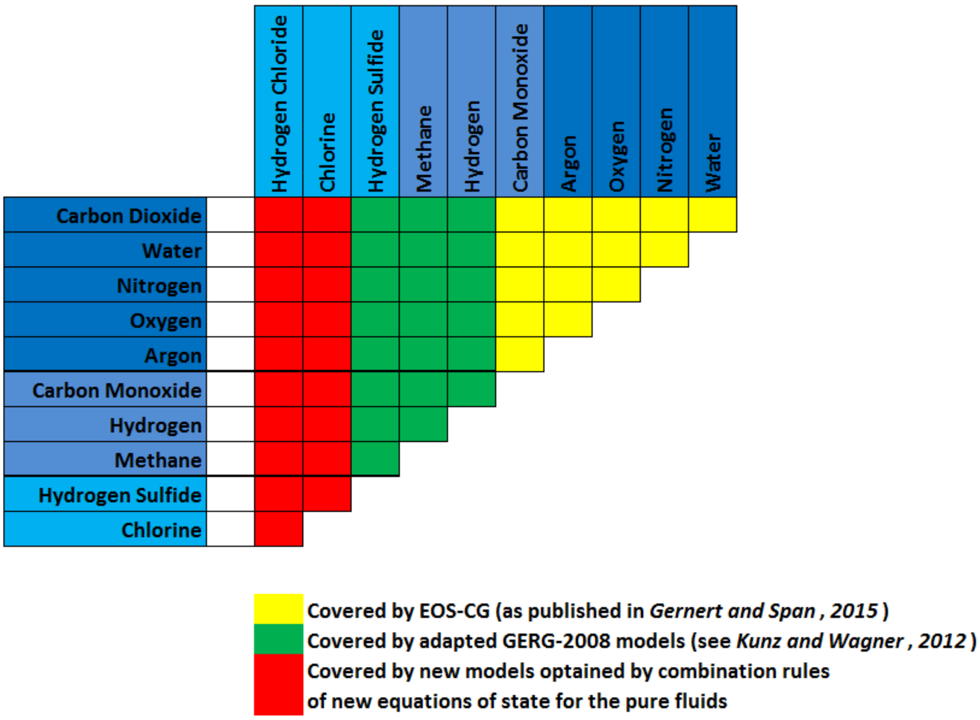
Figure 3.5: Screenshot of the "Phase envelope" worksheet in TREND. The *p*, *T* - diagram shows the phase envelope of an exemplary CO_2-rich mixture.

The functions provided in the worksheets of the Excel interface enable straight-forward calculations of individual state points. In addition, these worksheets should be understood as examples of the correct calling sequence. This should help inexperienced users to set up own spreadsheets in order to calculate different state points at various input parameters.

4 INCLUDED THERMODYNAMIC MODELS

Although the development of models for mixtures of CCS relevant components is focused on highly accurate equations of state explicit in the reduced Helmholtz free energy, TREND additionally provides various other types of models, namely the cubic equations of state of *Soave (1972)* (SRK) and *Peng and Robinson (1976)* (which is not implemented for mixtures), the formulation of *Plöcker et al. (1978)* (LKP), and the Costald equation of *Thomson et al. (1982)*. However, these models will not be discussed within this report. Additional information can be found in the TREND manual.

For mixtures, Helmholtz equations of state were presented within the GERG-2008 package (see *Kunz and Wagner*, *2012*) for natural gases and the EOS-CG model for "combustion gases and combustion gas like mixtures" of *Gernert and Span (2015)*. This recently published status of the EOS-CG model already included mixtures of carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide. To extend the mixture model established models for binary mixtures with hydrogen, methane, and hydrogen sulfide were adapted from the GERG-2008 package. Furthermore, new models for binary systems with chlorine and hydrogen chloride were added. Figure 4.1 shows systems considered in the most current version of the property model.



		Hydrogen Chloride	Chlorine	Hydrogen Sulfide	Methane	Hydrogen	Carbon Monoxide	Argon	Oxygen	Nitrogen	Water
Carbon Dioxide		🟥	🟥	🟩	🟩	🟩	🟨	🟨	🟨	🟨	🟨
Water		🟥	🟥	🟩	🟩	🟩	🟨	🟨	🟨	🟨	
Nitrogen		🟥	🟥	🟩	🟩	🟩	🟨	🟨	🟨		
Oxygen		🟥	🟥	🟩	🟩	🟩	🟨	🟨			
Argon		🟥	🟥	🟩	🟩	🟩	🟨				
Carbon Monoxide		🟥	🟥	🟩	🟩	🟩					
Hydrogen		🟥	🟥	🟩	🟩						
Methane		🟥	🟥	🟩							
Hydrogen Sulfide		🟥	🟥								
Chlorine		🟥									

🟨 Covered by EOS-CG (as published in *Gernert and Span*, *2015*)
🟩 Covered by adapted GERG-2008 models (see *Kunz and Wagner*, *2012*)
🟥 Covered by new models optained by combination rules of new equations of state for the pure fluids

Figure 4.1: Currently available models for mixtures of components relevant in CCS applications.

It should be noted that the models for the binary systems with chlorine and hydrogen chloride were not fitted to experimental data, since the data situation was not sufficient for a nonlinear multiparameter fit. These systems were described by means of linear or quadratic combinations of the equations of state for the pure fluids.

For numerical reasons, the GERG-2008 package includes special, shorter equations of state for the pure components of the mixture model. In the EOS-CG model, pure fluids are described by means of highly accurate reference equations of state where such equations are available. Thus, the transition from mixture to pure fluid calculations is consistent and it is ensured that the best available model is used. The reference equations of state included in the EOS-CG mixture model are given in Table 4.1.

Table 4.1: Equations of state used for the pure fluid components in the EOS-CG mixture model.

Component	Formula	Pure fluid equation used in EOS-CG mixture model
Carbon dioxide	CO_2	Reference equation of state by *Span und Wagner (1996)*
Water	H_2O	Reference equation of state by *Wagner and Pruß (2002)*
Nitrogen	N_2	Reference equation of state by *Span et al. (2000)*
Oxygen	O_2	Reference equation of state by *Schmidt and Wagner (1985)*
Argon	Ar	Reference equation of state by *Tegeler et al. (1999)*
Carbon monoxide	CO	Short industrial equation of state by *Lemmon and Span (2006)*
Hydrogen	H_2	Reference equation of state by *Leachman et al. (2009)*
Methane	CH_4	Reference equation of state by *Setzmann and Wagner (1991)*
Hydrogen sulfide	H_2S	Short industrial equation of state by *Lemmon and Span (2006)*
Chlorine	Cl_2	New equation of state developed by *Herrig et al. (2016)*
Hydrogen Chloride	HCl	New equation of state developed by *Thol et al. (2016)*

The list of components given in Table 4.1 is currently going to be extended by two equations of state for monoethanolamine and diethanolamine. These equations will most likely be included in the upcoming version 2.0.1 of TREND.

Adding new pure fluids and mixtures

As already indicated, the structure of the mixture models requires two different elements: equations of state for the pure components and additional functions for all possible binary combinations. Since the standard property model is continuously extended by new components, a simple implementation of new pure fluids and binary mixtures is important. The “EOS_CG” folder within the TREND software package includes two folders: “BINARY_MIX_FILES” containing files for all binary mixtures and “FLUIDS” including files for all pure fluid components. This file structure is illustrated in Figure 4.2.

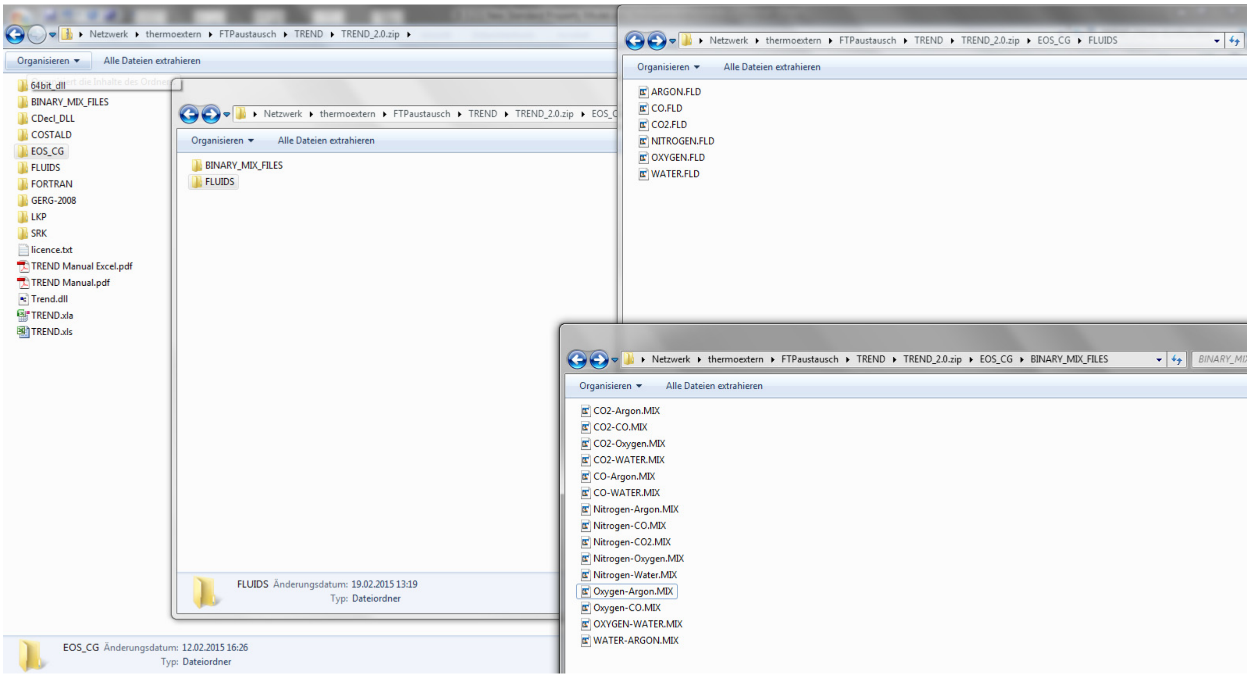


Figure 4.2: File structure within TREND (here illustrated for version 2.0).

If new models become available, the property model can easily be updated by adding the corresponding files. The folders “BINARY_MIX_FILES” and “FLUIDS” can also be found in the main folder of the software package. These two folders should always contain the most current files available for all pure fluids or binary mixtures. Thus, new files should also be added to these folders.

5 CONCLUSION AND OUTLOOK

This report presents the current status of the standard property model for CO_2-rich mixtures developed at RUB within Work Package 1.2 of the IMPACTS project. Within Work Package 3.2, all developed equations of state are implemented into the software package TREND (see *Span et al.*, *2015*) to be provided to the CCS community. TREND enables straightforward calculations by means of a simple interface. Calculating state properties for mixtures using highly accurate multiparameter equations of state additionally requires complex phase equilibrium calculations and stability analyses. The algorithms implemented in TREND allow for calculations of equilibria of up to three phases including hydrates as well as solid phases of CO_2 and water.

After adding new models and completing last thorough validations, TREND 2.0.1 will soon be distributed via the IMPACTS eRoom and is supposed to be an element of the IMPACTS Toolbox. The included equations of state will continuously be updated until the end of the IMPACTS project.

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- E.ON AG for awarding the E.ON International Research Award 2007 to the project EOS-CG
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TABLE OF SYMBOLS

Latin Symbols

c	Heat capacity
p	Pressure
R	Molar gas constant
T	Temperature
x	Mole fraction of one component in the mixture

Greek Symbols

α	Reduced Helmholtz free energy
δ	Reduced density
ρ	Density
τ	Inverse reduced temperature

Subscripts

δ	Derivative with respect to the reduced density
τ	Derivative with respect to the reduced temperature
p	Constant pressure

Superscripts

o	Ideal part of the Helmholtz free energy
r	Residual part of the Helmholtz free energy

Abbreviations

CCS	Carbon capture and storage
l	Liquid
s	Solid
v	Vapor

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