

PVTxy properties of CO₂ mixtures relevant for CO₂ capture, transport and storage: Review of available experimental data and theoretical models

Hailong Li^{a,b,*}, Jana P. Jakobsen^a, Øivind Wilhelmsen^a, Jinyue Yan^{b,c}

^a SINTEF Energy, Kolbjørn Hejes vei 1A, 7465 Trondheim, Norway

^b Energy Process, Royal Institute of Technology, 10044 Stockholm, Sweden

^c School of Sustainable Development of Society and Technology, Mälardalen University, Västerås, Sweden

ARTICLE INFO

Article history:

Received 29 October 2010

Received in revised form 8 March 2011

Accepted 31 March 2011

Available online 11 May 2011

Keywords:

CO₂ mixtures

Thermodynamic property

VLE

Density

Equation of state

CO₂ capture and storage

ABSTRACT

The knowledge about pressure–volume–temperature–composition (PVTxy) properties plays an important role in the design and operation of many processes involved in CO₂ capture and storage (CCS) systems. A literature survey was conducted on both the available experimental data and the theoretical models associated with the thermodynamic properties of CO₂ mixtures within the operation window of CCS. Some gaps were identified between available experimental data and requirements of the system design and operation. The major concerns are: for the vapour–liquid equilibrium, there are no data about CO₂/COS and few data about the CO₂/N₂O₄ mixture. For the volume property, there are no published experimental data for CO₂/O₂, CO₂/CO, CO₂/N₂O₄, CO₂/COS and CO₂/NH₃ and the liquid volume of CO₂/H₂. The experimental data available for multi-component CO₂ mixtures are also scarce. Many equations of state are available for thermodynamic calculations of CO₂ mixtures. The cubic equations of state have the simplest structure and are capable of giving reasonable results for the PVTxy properties. More complex equations of state such as Lee–Kesler, SAFT and GERG typically give better results for the volume property, but not necessarily for the vapour–liquid equilibrium. None of the equations of state evaluated in the literature show any clear advantage in CCS applications for the calculation of all PVTxy properties. A reference equation of state for CCS should, thus, be a future goal.

© 2011 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	3568
2. Operating windows of CO ₂ conditioning and transport	3568
2.1. Temperature and pressure windows	3568
2.2. Possible impurities	3568
3. Available experimental data	3570
3.1. Summary of measurements	3570
3.2. Knowledge gaps	3570
3.3. The precision, consistency and reliability of the experimental data	3570
4. Existing models	3573
4.1. Cubic EOS	3573
4.2. Benedict–Webb–Rubin (BWR) EOS [79]	3575
4.3. Statistical Associating Fluid Theory EOS	3576
4.4. Predictive EOS	3577
4.5. The GERG equation [92]	3577
5. Discussion	3577
6. Conclusions	3578
Acknowledgement	3578
References	3578

* Corresponding author. Present address: Mälardalen University, PO Box 883, 72123 Västerås, Sweden. Tel.: +46 21 103159; fax: +46 21101480.

E-mail address: lihailong@gmail.com (H. Li).

Nomenclature

α	Helmholtz energy
k_{ij}	binary interaction parameter
ρ	density
P	pressure
R	gas constant
T	temperature
V, v	molar volume
x	mole fraction in liquid phase
X	total mole fraction
y	mole fraction in vapour phase

Abbreviation:

BWR	Benedict–Webb–Rubin
CCS	CO ₂ capture and storage
Comp	compressibility
CPA	cubic plus association
EOS	equation of state
GERG	Group Européen de Recherche Gazières
HV	Huron–Vidal

ISRK	improved Soave–Redlich–Kwong
LK	Lee–Kesler
MPR	modified Peng–Robinson
MSRK	modified Soave–Redlich–Kwong
PR	Peng–Robinson
PPR	predictive–Peng–Robinson
PSRK	predictive Redlich–Kwong–Soave
PT	Patel–Teja
PVTxy	pressure–volume–temperature–composition
RK	Redlich–Kwong
SAFT	Statistical Associating Fluid Theory
SRK	Soave–Redlich–Kwong
VLE	vapour–liquid equilibrium

Subscript:

g	gas
i, j	component labels
l	liquid

1. Introduction

Currently, there are several running commercial projects about CO₂ capture, transport and storage (CCS). For example, the Snøhvit project (Northern Norway) operated by Statoil runs a 153 km offshore pipeline transporting liquid CO₂ from an LNG plant to a sub-sea well. In the Sleipner project (North Sea) which is also operated by Statoil, the CO₂ is transported a short distance near the critical point between two connected offshore platforms. Here, the CO₂ capture unit is on one platform, while the wellhead is connected to the other [1]. From those projects, many Research & Development requests have been raised to improve the Health, Safety and Environment and reduce the costs in existing and future CCS chains.

Carbon dioxide captured from an energy conversion process always contains impurities. Previous work has revealed that the existences of impurities will clearly impact the design and operation of CCS systems [2,3]. Therefore, the knowledge of thermodynamic properties, especially the pressure–volume–temperature–composition (PVTxy) properties, is essential to the design and operation of CO₂ conditioning and transport. The knowledge of the behaviour of the mixture under the conditions of the particular process will allow (as shown in Fig. 1):

- Identification of possibly encountered problems.
- Specification of safe concentration limits for the involved impurities.
- Definition of the requirements for purification if necessary.
- Designing efficient, safe and economic processes.

A typical CO₂ capture and storage (CCS) chain normally consists of four main steps: CO₂ capture, CO₂ conditioning (dehydration, non-condensable gas separation and/or liquefaction, and compression/pumping), CO₂ transport and CO₂ storage. Fig. 2 illustrates how these steps are linked together.

The vapour–liquid–equilibrium (VLE) of CO₂ mixtures is, for example, one of the basic parameters to design the capture of CO₂ and also to design non-condensable gas separation processes. The volume property is important in the design and operation of compression, transportation and storage. It could be said that the development and technical breakthrough of new CCS systems relies on a deeper understanding of the thermodynamic properties

of CO₂ mixtures. PVTxy properties can be measured directly. However, because CCS processes cover a large range of operation conditions from atmospheric pressure to supercritical states, and involve multi-component mixtures, experiments alone cannot satisfy the requirements of engineering applications. In order to exceed the limitations of the experiments, theoretical models have been developed based on the experimental data.

This work contains a review of both the experimental data and the thermodynamic models for PVTxy properties of CO₂ mixtures with impurities. The purpose of the work is to summarize and evaluate the available experimental data, identify knowledge gaps and investigate the available theoretical models that have been proposed and tested in the literature. The work will also provide suggestions for future research on the PVTxy properties of CO₂ mixtures.

2. Operating windows of CO₂ conditioning and transport

The operating windows of the process determine the relevant ranges of temperature, pressure and composition, in which experimental data are required and property models should preferably be validated to minimize the uncertainties in the design criteria of the different processes.

2.1. Temperature and pressure windows

The operating conditions of CO₂ capture, transport and storage (CCS) are estimated in Table 1 [4,5]. Some sub-processes or options for these are indicated in Table 1 as well. The table shows that the CCS chain covers pressures from ~0 MPa to 50 MPa and temperatures from 218 K to 1620 K.

2.2. Possible impurities

The type and amount of the impurities introduced into the CO₂ depend on the fuels used and the type of capture technology. The CO₂ streams captured from post-combustion with an amine solution are relatively clean, with H₂O as the main impurity. However, relative high levels of impurities are expected in the CO₂ streams captured from oxy-fuel combustion, and a more complicated composition of the CO₂ stream is expected in the cases with

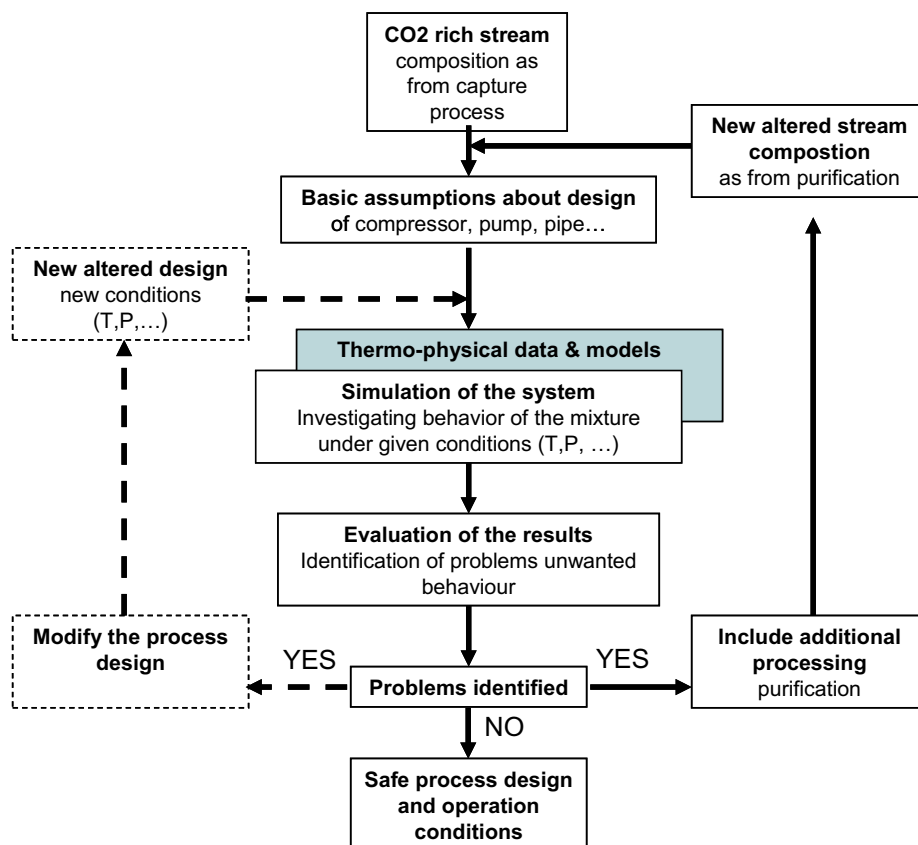


Fig. 1. Importance of the knowledge of CO₂ mixture properties and behaviour for design and operation of safe and cost and energy efficient processes.

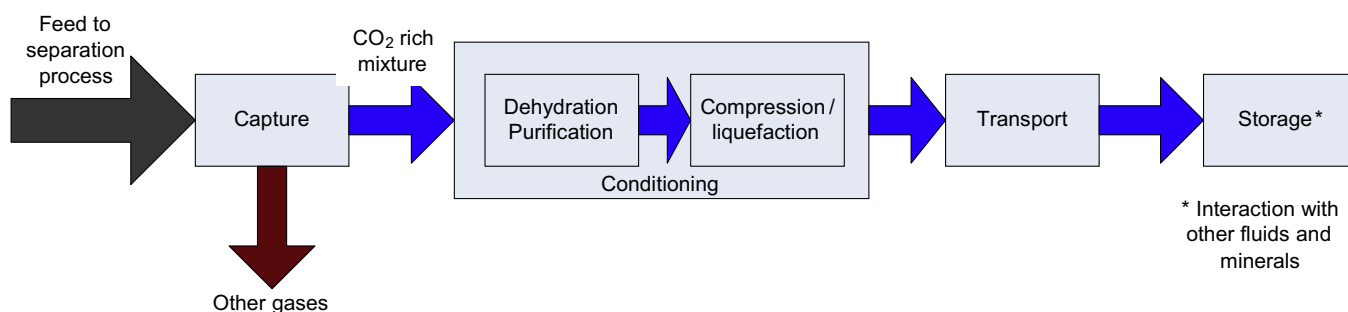


Fig. 2. Main components of the CCS chain.

Table 1
Estimated operating conditions (P and T) of CCS processes.

CCS process	P (MPa)	T (K)
CO ₂ capture	0.05–8	298.15–1620
Post-combustion	0.05–0.3	313–410
Oxy-fuel combustion	0.1	298.15–333
Pre-combustion	0.1–8	298.15–1620
CO ₂ conditioning	0–11	219.15–423.15
Initial compression	0–3	293.15–423.15
Dehydration	2–3	283.15–303.15
Non-condensable gas separation	2–5	219.15–248.15
Further compression/pumping	5–11	283.15–303.15
CO ₂ transport	0.5–20	218.15–303.15
Pipeline	7.5–20	273.15–303.15
Small tanks	1.5–2.5	238.15–248.15
Large tanks	0.5–0.9	218.15–228.15
CO ₂ storage	0.1–50	277.15–423.15

Integrated Gasification Combined Cycles. Based on the different oil industry and fuel conversion processes, the possible impurities are summarized in Table 2. Recently, comprehensive reviews on the experimental PVTxy-data of CO₂/H₂O and CO₂/amines have been published [6–12]. In addition, an extensive review of the available experimental data and models for CO₂ hydrates has been presented previously [13]. Therefore, this work will review the available experimental data and models for the impurities which have not yet been thoroughly treated in the literature, namely: CH₄, H₂S, N₂, O₂, CO, H₂, COS, Ar, SO_x, NO_x, NH₃ and SO₂.

In general, there are no strong technical barriers to provide high purity CO₂ from the flue gas of fossil fuel fired power plants. However, high purity requirements are likely to induce additional costs and energy requirements resulting in a high loss of power plant efficiency. It is, thus, of importance to find an optimal balance between the requirements with respects to safety, legal and environmental aspects of transport and storage and the costs

Table 2
Possible impurities [4].

#	Description	Possible impurities
1	CO ₂ captured from natural gas sweetening	CH ₄ , amines, H ₂ O
2	CO ₂ captured from heavy oil production and upgrading	H ₂ S, N ₂ , O ₂ , CO, H ₂ O, H ₂ , COS, Ar, SO _x , NO _x
3	CO ₂ captured from power plants using post-combustion capture	N ₂ , amines, H ₂ O, O ₂ , NH ₃ , SO _x , NO _x
4	CO ₂ captured from power plants using oxy-combustion capture	N ₂ , O ₂ , SO ₂ , H ₂ S, Ar
5	CO ₂ captured from power plants using pre-combustion capture	H ₂ , CO, N ₂ , H ₂ S, CH ₄

Table 3
Impurity concentrations [5,14].

Component	Min mol%	Max mol%
CO ₂	75	99
N ₂	0.02	10
O ₂	0.04	5
Ar	0.005	3.5
SO ₂	<0.0001	1.5
H ₂ S + COS	0.01	1.5
NO _x	0.0002	0.3
CO	0.0001	0.2
H ₂	0.06	4
CH ₄	0.7	4

concerning CO₂ sequestration. The possible concentration ranges of the impurities in the captured CO₂ streams are given in Table 3. These estimates are based on previous studies [5,14].

3. Available experimental data

3.1. Summary of measurements

The PVTxy properties of CO₂ mixtures have attracted the interest of researchers for over a century. Many experiments have been conducted. However, experimental studies have mainly focused on impurities such as water, hydrocarbons, nitrogen and hydrogen sulphide due to their importance for producing and processing natural gas resources and for using the CO₂ mixture for enhanced oil recovery processes. As a result, there are many available experimental data about the mixtures CO₂/H₂O, CO₂/N₂, CO₂/CH₄ and CO₂/H₂S, which cover a wide range of temperatures and pressures. The experimental data of the CO₂ mixtures containing O₂, Ar, SO₂, CO, H₂ and other impurities are limited, although such impurities will be important for CCS processes, in particular for the oxy-fuel combustion technology. Available experimental PVTxy-data of CO₂ mixtures are summarized in Table 4, with their corresponding ranges in temperature and pressure and the reported uncertainty. The reported uncertainties are typically smaller in newer work due to more accurate measuring techniques.

3.2. Knowledge gaps

The ranges of *T*, *P*, *x* and *y* for the experimental data of the VLE and the volume are summarized in Tables 5 and 6 and illustrated in Figs. 3 and 4 respectively. Compared to the operating windows given in Table 1, there are, obviously, some gaps between the available experimental data and the requirements with respect to design and operation in CCS.

For the VLE property, there are no data about CO₂/COS, and quite few data about CO₂/N₂O according to Table 5. For the CO₂/SO₂ mixture, few experimental data are available at temperatures below 290 K; while few experimental data are available at pressures below 4.4 MPa for CO₂/Ar and few experimental data are available at pressures over 0.7 MPa for CO₂/N₂O₄. For CO₂/CO, the quantity of data is rather small. In addition, only few experimental

data are available for multi-component CO₂ mixtures, such as CO₂/CH₄/N₂, CO₂/N₂/O₂, CO₂/CH₄/H₂S and CO₂/CO/H₂.

The saturation line of pure CO₂ is illustrated by the solid black curve in Fig. 3. The range of the VLE data for some of the mixtures, such as CO₂/SO₂, differs considerably from pure CO₂, illustrating that the VLE behaviour of the mixture may be quite different from pure CO₂. The relevant *T/P* range for the VLE data will thus change from mixture to mixture. Since the amount of impurities in CCS is modest according to Table 3 (<10%), it is reasonable to assume that the *T/P* range of available VLE data (the coloured boxes in Fig. 3) should ideally cover most of the CO₂ saturation line to satisfy the requirements of CCS applications. For some mixtures, such as CO₂/CH₄ and CO₂/N₂, the range of the VLE data covers the whole curve, but for mixtures such as CO₂/Ar, CO₂/CO and CO₂/SO₂, the boxes cover little of the phase envelope, which clearly displays the need of more data. According to the figure, the *T/P* range of the CO₂/NH₃ system is very different from all the other binary systems. This can be explained by the chemical reactions which occur in addition to the VLE [39], with formation of ammonium carbamate at temperatures less than ~400 K and urea and water at larger temperatures, making it a complex system with five components. The *T/P* range of future VLE experiments, for example for the mixtures CO₂/H₂S, CO₂/CO and CO₂–SO₂ may easily be identified using Fig. 3.

For the volume property, the situation of the experimental measurements is even worse than for the VLE property. There are no published experimental data on the volume of CO₂/O₂, CO₂/CO, CO₂/N₂O₄, CO₂/COS and CO₂/NH₃ and the liquid volume of CO₂/H₂. For CO₂/H₂S and CO₂/N₂O, some experimental data are available, but only for saturated phases. For multi-component CO₂ mixtures, the situation is similar for the volume as for the VLE property, with very few data available. Fig. 4 shows the *T/P* range of the available experiments for the volume property. The binary mixtures containing CH₄ and N₂ cover a decent part of the *T/P* space, while it is not true for the mixtures containing Ar, H₂ and H₂S. Another concern is that few volume measurements are conducted at temperatures higher than 400 K. But it is significant to have sufficient experimental data to span the whole *T/P* range relevant for CCS applications (218–1620 K and ~0–50 MPa).

3.3. The precision, consistency and reliability of the experimental data

As experimental measurements are used for model calibration and parameter fitting, it is of great importance to have reliable measurements in order to develop high accuracy models. Table 4 shows that many of the measurements are published before 1980. In order to check the precision, consistency and reliability of the published literature, experimental data available in the same ranges of composition, pressure and temperature have been compared, and the comparison is displayed in the Figs. 5–9.

Fig. 5 presents the comparison regarding the VLE of CO₂/CH₄. According to the comparison, the measured data agree better for the bubble points than for the dew points. Some larger inconsistencies were observed (>5%). For example, as shown in Fig. 5b, the deviations between Donnelly's data [23] and Mraw's data [42] can be up to 20% for the CO₂ concentration in the vapour phase

Table 4Available PVTX experimental data for CO₂ mixtures.

Source	Year	Type	Mixture	T (K)	P (Mpa)	Uncertainty
Caubet [15]	1901	PVTX	CO ₂ /SO ₂	291–416	2.7–10.5	
Booth and Carter [16]	1930	TPxy	CO ₂ /O ₂	213–260	3.7–14.5	P: 0.1 atm T: 0.03 K
Cummings [17]	1931	TPxy	CO ₂ /SO ₂	313–403	0.6–9.5	
Reamer et al. [18]	1944	Comp	CO ₂ /CH ₄	311–511	1.4–69	
Haney and Bliss [19]	1944	Comp	CO ₂ /N ₂	298.15–398.15	3–50	T: ±0.05 K
von Steckel [20]	1945	TPxy	CO ₂ /H ₂ S	221–288.15	0.1–3.6	
Bierlein et al. [21]	1953	PVTX	CO ₂ /H ₂ S	273–370	1.5–8.5	V: ±0.02% T: ±0.02 K P: ±0.01 atm T: ±0.01 K
Cook [22]	1953	TPxy	CO ₂ /N ₂ O	293.15–307.15	5–7.3	
Donnelly et al. [23]	1954	TPxy	CO ₂ /CH ₄	167–301	2.0–7.4	
Sobocinski and Kurata [24]	1959	TPxy	CO ₂ /H ₂ S	224.8–363.71	0.7–8.3	P: ±1–2 lb./sq T: ±0.1–0.2F T: 0.02 K P: ±0.1%
Hensel et al. [25]	1964	TPxy	CO ₂ /CH ₄ /H ₂ S	222–238.75	2.1–4.8	
Muirbrook et al. [26]	1965	TPxy	CO ₂ /O ₂ , CO ₂ /N ₂ , CO ₂ /N ₂ /O ₂	273.15	5.5–12	P: ±0.1%
Zenner and Dana [27]	1965	TPxy	CO ₂ /O ₂ , CO ₂ /N ₂ , CO ₂ /N ₂ /O ₂	218.15–273.15	1.3–15	
Kestin et al. [28]	1966	PVTX	CO ₂ /Ar	293.15–303.15	0.101–2.58	P: ±0.5% T: ±1 K
Kaminishi et al. [29]	1968	TPxy	CO ₂ /CO, CO ₂ /Ar, CO ₂ /CH ₄ , CO ₂ /CO/H ₂	223.15–283.15	2.4–20	
Neumann and Walch [30]	1968	TPxy	CO ₂ /CH ₄	208.45–219.85	44–69	
Spano et al. [31]	1968	TPxy	CO ₂ /H ₂	219.9–289.9	1.1–2012	
Fredenslund et al. [32]	1970	TPxy	CO ₂ /O ₂	223.15–283.15	1–13	P: ±0.5% T: ±0.02 K P: ±0.01 atm T: ±0.01 K
Arai et al. [33]	1971	PVTX	CO ₂ /N ₂ , CO ₂ /CH ₄	253–288	5–15	
Chang et al. [34]	1971	Solubility	CO ₂ /N ₂ O ₄	262.15–293.15	0.02–0.07	
Lemkowitz et al. [35]	1971	Bubble Point	CO ₂ /NH ₃	413.3–468.2	4.2–17.5	P: ±0.1 atm T: ±0.1 K
Sarashina et al. [36]	1971	PVTX	CO ₂ /Ar	288.15	5.69–9.77	P: ±0.01 atm T: ±0.01 K
Sarashina et al. [37]	1971	PVTX	CO ₂ /CH ₄ /N ₂	233.15–273.15	6–10	P: ±0.01 atm T: ±0.01 K
Fredenslund et al. [38]	1972	TPxy	CO ₂ /O ₂	223.75	0.9–14.1	P: ±0.015 atm T: ±0.01 K
Lemkowitz et al. [39]	1972	Bubble Point	CO ₂ /NH ₃	418–531	7.8–81	P: ±0.1 atm T: ±0.1 K
Davalos et al. [40]	1976	TPxy	CO ₂ /CH ₄	230–250	0.9–8.5	
Altunin et al. [41]	1977	Comp	CO ₂ /Ar	303.15	0.29–10.75	
Mraw et al. [42]	1978	TPxy	CO ₂ /CH ₄	89–208	0.5–6.3	
Somait et al. [43]	1978	TPxy	CO ₂ /CH ₄ , CO ₂ /N ₂	270	3–12	P: ±0.015 atm T: ±0.02 K P: ±0.5% T: ±0.02 K P: ±0.1% T: ±0.02 K
Tsang and Streett [44]	1981	TPxy	CO ₂ /H ₂	220–290	14–172	
Al-Sahhaf [45]	1983	TPxy	CO ₂ /N ₂ , CO ₂ /CH ₄ , CO ₂ /CH ₄ /N ₂	219.26–270	0.58–16.15	
Dorau et al. [46]	1983	TPxy	CO ₂ /N ₂	223.15–273.15	3–20	
Yorizane et al. [47]	1985	TPxy	CO ₂ /N ₂	273.2–298.2	4.5–8.14	P: ±0.5% T: ±0.1 K
Mallu et al. [48]	1987	Comp and 2nd Virial coefficient	CO ₂ /CO	323.15–423.15	0–6.50	
Hacura et al. [49]	1988	PVTX	CO ₂ /N ₂	323–348	500–2500	P: ±2.5 bar T: ±0.5 K
Magee and Ely [50]	1988	PVTX	CO ₂ /CH ₄	225–400	2–35	P: ±0.01% T: ±0.05 K P: ±0.015% T: ±0.002 K
Brugge et al. [51]	1989	Comp	CO ₂ /CH ₄ , CO ₂ /N ₂	300 and 320	0.1–10.6	P: ±0.01% T: ±0.001 K
Ely et al. [52]	1989	PVTX	CO ₂ /CH ₄ , CO ₂ /N ₂	250–330	2.3–32	P: ±0.01% T: ±0.001 K
Esper et al. [53]	1989	PVTX	CO ₂ /N ₂	205–320	0.1–48	P: ±0.015% T: ±0.01 K
McElory et al. [54]	1989	Comp	CO ₂ /CH ₄ /N ₂	303.15–333.2	3.79–12.64	P: ±0.1% T: ±0.01 K
Trappehl and Knapp [55]	1989	TPxy	CO ₂ /CH ₄ /N ₂	220	2–12	
Al-Sahhaf [56]	1990	TPxy	CO ₂ /CH ₄ /N ₂	230–250	6.21–10.34	P: ±0.1% T: ±0.02 K
Xu et al. [57]	1992	TPxy	CO ₂ /N ₂ , CO ₂ /CH ₄ , CO ₂ /CH ₄ /N ₂	288 and 293	5.11–9.11	P: ±0.02 Mpa T: ±0.01 K
Seitz et al. [58]	1996	PVTX	CO ₂ /CH ₄ /N ₂	323.15–523.15	19.9–99.9	
Bezanehtak et al. [59]	2002	PVTX	CO ₂ /H ₂	278.15–290.15	4.8–19.2	

at high pressures. Taking into account the more up to date measuring techniques, the data by Mraw et al. [42] should be preferred. Fig. 5a shows a comparison amongst the sources [40,43,45], where

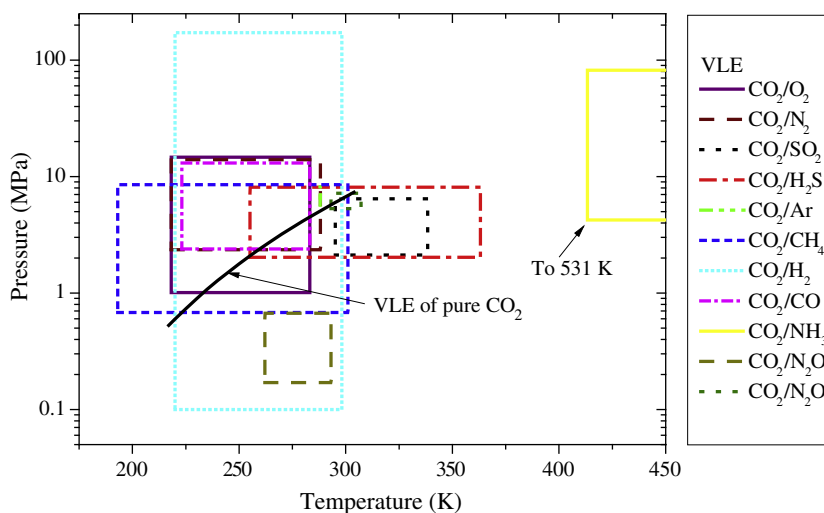
the newer data by Somait et al. and Al-Sahhaf et al. agree well and should be preferred. Fig. 5c shows a comparison of the data by Xu et al. and Arai et al. These data agree well on the dew points, but

Table 5Summary of the TPxy ranges of the VLE experimental data for CO₂ mixtures.

Mixtures	T (K)	P (Mpa)	$x_{\text{CO}_2}^a$	$y_{\text{CO}_2}^a$	No. of exp. point
CO ₂ /O ₂	218.15–283.15	1.01–14.70	0.0–0.999	0.0–0.95	>100
CO ₂ /N ₂	218.15–403.15	0.60–13.95	0.43–1.00	0.153–1.00	>100
CO ₂ /SO ₂	295.15–338.45	2.12–6.43	–	0.75–0.93	91
CO ₂ /H ₂ S	255.15–363.15	2.03–8.11	0.01–0.97	0.05–0.97	>100
CO ₂ /Ar	233.15–288.15	4.4–11.6	0.69–0.967	0.266–0.94	25
CO ₂ /CH ₄	193.15–301	0.68–8.5	0.026–0.99	0.026–0.96	>100
CO ₂ /H ₂	220–298.15	0–172	0.444–0.988	0.067–0.898	>300
CO ₂ /CO	223.15–283.15	2.39–13.08	0.631–0.957	0.213–0.827	22
CO ₂ /NH ₃	413.35–531.15	4.25–81.67	0.023–0.333	–	62
CO ₂ /COS	NA				
CO ₂ /N ₂ O ₄	262.15–293.15	0.17–0.67	0.005–0.021	–	8
CO ₂ /N ₂ O	293.15–307.15	5.3–7.2	0.258–0.881	0.258–0.881	>100
CO ₂ /CH ₄ /N ₂	220–293.45	6–10	0.543–0.989	0.266–0.974	>100
CO ₂ /O ₂ /N ₂	218.15–273.15	5.1–13	0–0.925	0–0.611	80
CO ₂ /CO/H ₂	233.15–283.15	2–20	0.527–0.977	0.174–0.726	31
CO ₂ /CH ₄ /H ₂ S	222.15–238.75	2.07–4.83	0.108–0.776	0.024–0.543	16

^a Mole fraction.**Table 6**Summary of TPxy ranges of the experimental volume data for CO₂ mixtures.

	Phase	T (K)	P (Mpa)	$x_{\text{CO}_2}^a$	$y_{\text{CO}_2}^a$	No. of exp. point
CO ₂ /O ₂	V_g	NA				
	V_l	NA				
CO ₂ /N ₂	V_g	253.15–398.15	2.35–250		0.25–1	>200
	V_l	250–300	2.43–32	0.85–1		80
CO ₂ /SO ₂	V_g	287.15–347.35	0.10–7.60		0.125–0.927	120
	V_l	299.15–341.15	5.67–10.64	0.125–0.927		36
CO ₂ /H ₂ S ^b	V_g	278.05–304.86	3.50–6.99		0.83–0.90	16
	V_l	275.07–306.27	3.50–6.99	0.83–0.90		16
CO ₂ /Ar	V_g	293.15–303.15	0.10–2.50		0.84–0.92	16
	V_l	288.15	7.51–9.78	0.83–0.94		4
CO ₂ /CH ₄	V_g	219.7–400	0.1–35		0.1–0.98	>300
	V_l	220–300	6–35	0.56–0.98		80
CO ₂ /CO	V_g	NA				
	V_l	NA				
CO ₂ /N ₂ O ^b	V_g	293–307.15	5.3–7.1		0.258–0.881	25
	V_l	293–307.15	5.3–7.1	0.258–0.881		25
CO ₂ /H ₂	V_g	NA				
	V_l	278.15–290.15	4.8–19.2	0.8429–0.9912		42
CO ₂ /CH ₄ /N ₂	V_g	303.15–523.15	3.79–99.9		0–1	100
	V_l	NA				

^a Mole fraction.^b Saturated volume.**Fig. 3.** T/P ranges of the experimental data about the VLE of CO₂ mixtures.

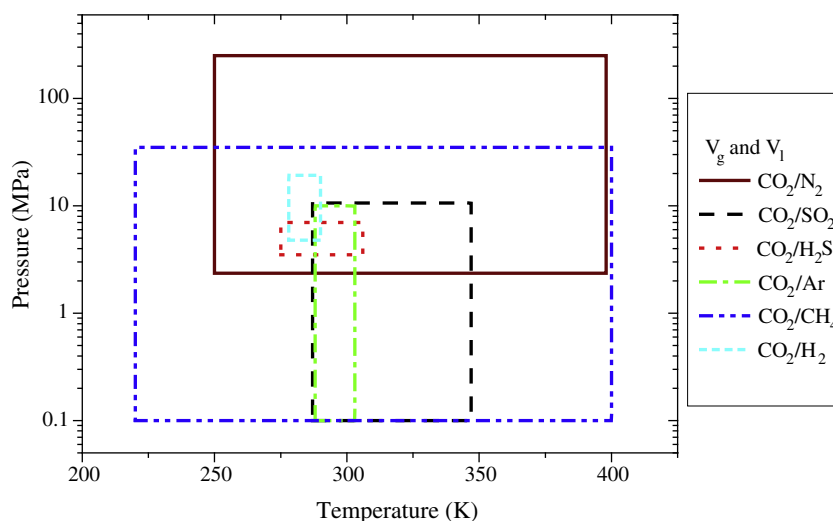


Fig. 4. The T/P range of the experimental data for the volume of CO_2 mixtures.

show different trends for the bubble points. Here, the newer data by Xu et al. [57] should be more reliable.

Fig. 6 presents the comparison regarding the VLE of $\text{CO}_2/\text{H}_2\text{S}$. According to Fig. 6, the data from Bierlein [21] and Sobocinski [24] agree well. Bierlein [21] compared his measurements with Steckel's data. The scatter around the mean curve, shown in Fig. 4 of [21], is as large as 0.5 atmospheres for some points. Steckel's value for the vapour pressure of pure carbon dioxide deviates almost 1 atmosphere from the generally accepted value. Therefore, Steckel's data are not recommended in future model development or verification.

Fig. 7 presents the comparison regarding the VLE of CO_2/O_2 . Large inconsistencies may be observed between Fredenslund's data [32] and Zenner and Dana's data [27] (Fig. 7a). Since the measurements conducted by Fredenslund et al. in 1970 [32] and 1972 [38] agree quite well, as shown in Fig. 7b, the data by Fredenslund et al. [32,38] should be preferred.

Fig. 8 presents the comparison regarding the VLE and density of CO_2/N_2 . Even though the VLE measurements ([32] and [38]) were published by the same author, Fredenslund, the data published in different years are not consistent for CO_2/N_2 , even though the author shows consistent measurements for CO_2/O_2 (Fig. 7). Inconsistency was also identified between the density data from Haney [19] and Brugge [51]. Additional experiments are required to verify the accuracy of these data.

Fig. 9 presents the comparison regarding the VLE of CO_2/H_2 . Here, it is evident that the inconsistencies become larger at higher temperatures, for example at 290 K (Fig. 9a). There is no good agreement among the three available data sources [31,44,59], except the data of Bezhanetak [59] and Tsang [44] concerning the bubble point curve at high CO_2 concentrations. The reason for this may be the high saturated pressures, which may be over 18 MPa for CO_2 concentrations around 60 mol%.

4. Existing models

An equation of state (EOS) is a mathematical relation connecting the volume, pressure, temperature and composition of a mixture. From the interrelationships provided by classical thermodynamics, departure functions from ideal gas behaviour and phase equilibria can be calculated. The thermodynamic properties for both the vapour and liquid phases can be calculated with a minimum amount of component data, typically being critical tempera-

tures, pressures and acentric factors. An equation of state may be valid for a wide range of temperatures and pressures, including sub-critical and supercritical regions.

According to the origin, equations of state may be classified into several families. The van der Waals family of cubic equations and the family of extended virial equations are examples. It has been shown that the performances of different models vary for different properties, components and conditions [60–62]. The most commonly encountered EOS relevant for CCS are discussed below, with particular focus on those which already have been tested in the literature. The performance of the EOS is summarized in Table 7.

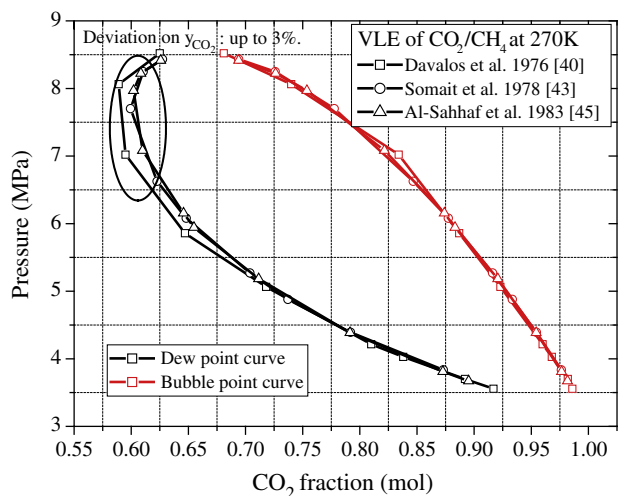
4.1. Cubic EOS

The cubic equations are, probably, the simplest EOS which predict the existence of a critical point and yield a quantitative representation of vapour-liquid equilibria. Their simple structure makes them popular in engineering applications. Since van der Waals proposed his EOS in 1873, numerous modified versions of cubic EOS with two or more parameters have been developed to improve the predictions of volumetric and phase equilibrium properties of fluids. Examples are the Redlich–Kwong EOS [63] (RK), the Soave–Redlich–Kwong EOS [64] (SRK), the Peng–Robinson EOS [65] (PR) and many others. It is well established that cubic EOS can model phase equilibrium satisfactorily.

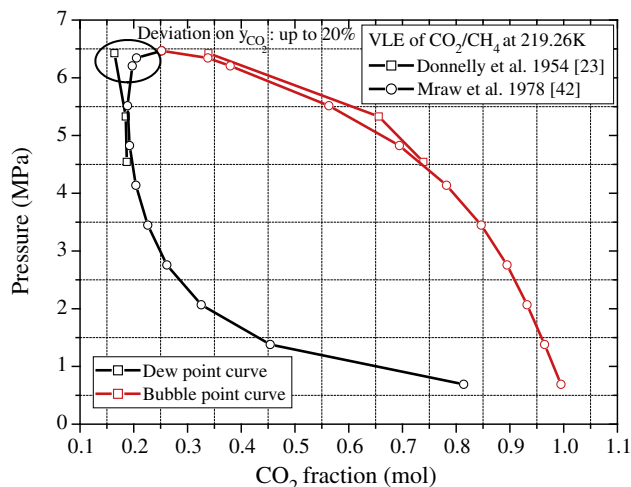
The PR and the Patel–Teja (PT) [66] EOS were investigated by Al-Sahhaf et al. [56] for the VLE of the ternary system $\text{N}_2/\text{CO}_2/\text{CH}_4$. PR was first used with generalized parameters and then with fluid-specific temperature-dependent parameters. The three methods gave similar results with no significant advantage of using the fluid-specific temperature-dependent parameters.

Thiery et al. [67] evaluated the SRK EOS for VLE and volume calculations of CO_2/N_2 , CO_2/CH_4 and $\text{CO}_2/\text{CH}_4/\text{N}_2$. Their results showed that with the SRK EOS, the average deviation for the saturated pressures is around 1% in the temperature range of 208.45–270 K for the CO_2/CH_4 system, 4% in the temperature range of 218.15–273.15 K for the CO_2/N_2 system, and 2–3% for the $\text{CO}_2/\text{CH}_4/\text{N}_2$ system.

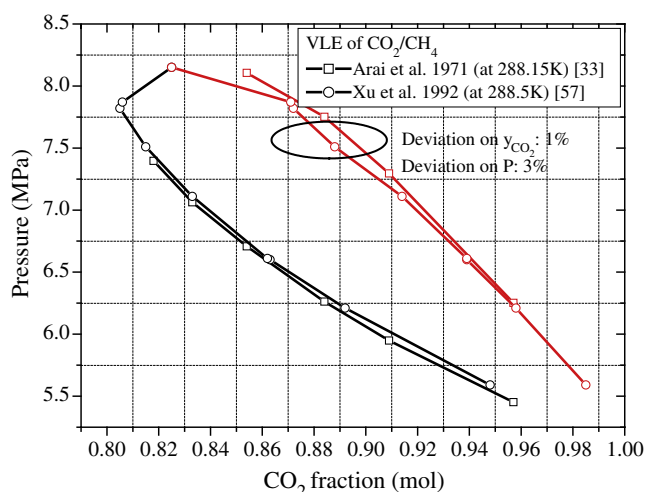
Duan et al. [68] extended a general EOS, which was developed for pure non-polar systems to polar systems and mixtures. They claimed that the EOS had an average error of 1.6% in density calculations for $\text{CO}_2/\text{H}_2\text{O}$, CO_2/N_2 , CO_2/CH_4 and $\text{CO}_2/\text{N}_2/\text{CH}_4$. Comparisons with commonly used EOS for supercritical fluids show that the studied EOS covers far more TPX space with higher accuracy.



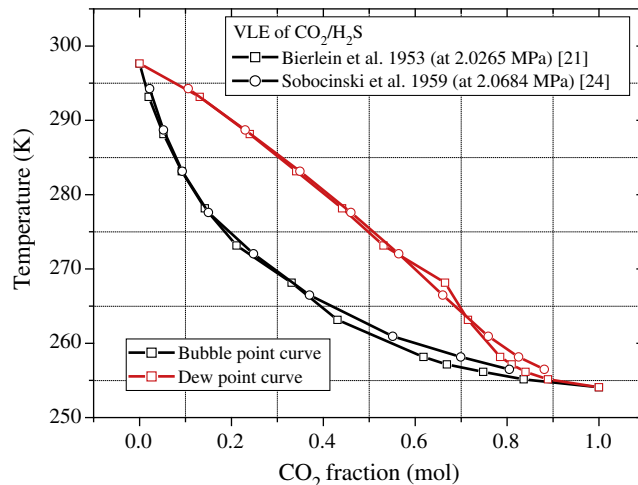
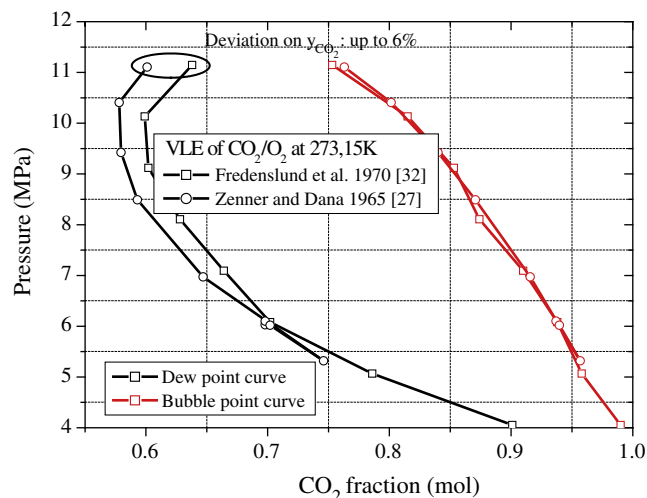
(a) 270K



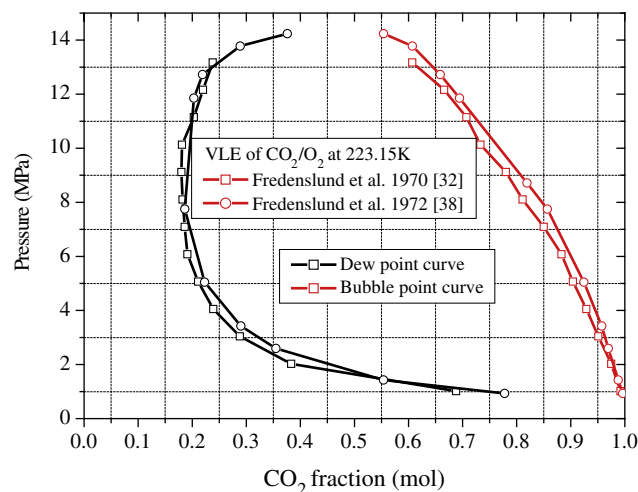
(b) 219.26K



(c) 288.15K

Fig. 5. Comparison of different experiments about the VLE of CO₂/CH₄.Fig. 6. Comparison of different experiments about the VLE of CO₂/H₂S.

(a) 273.15 K



(b) 223.15 K

Fig. 7. Comparison of different experiments about the VLE of CO₂/O₂.

It is believed to be accurate from supercritical temperatures to 2000 K and from 0 to 25,000 bar or higher with an average error in the density of less than 2% for both pure components and

mixtures in the system H₂O/CO₂/CH₄/N₂/CO/H₂/O₂/H₂S/Ar, with possible extension to additional gases.

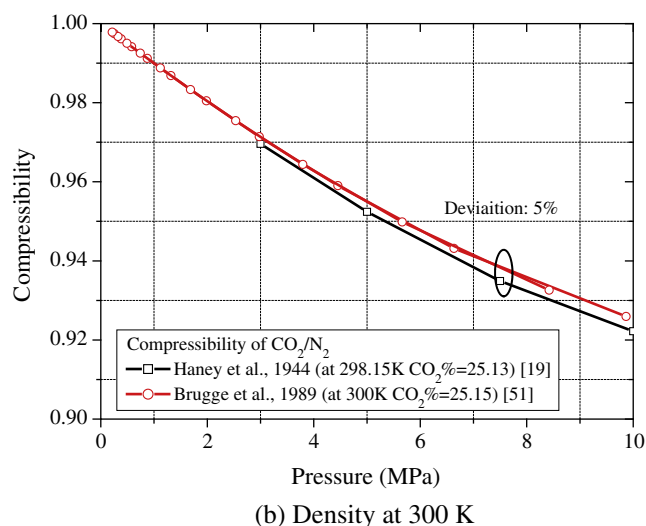
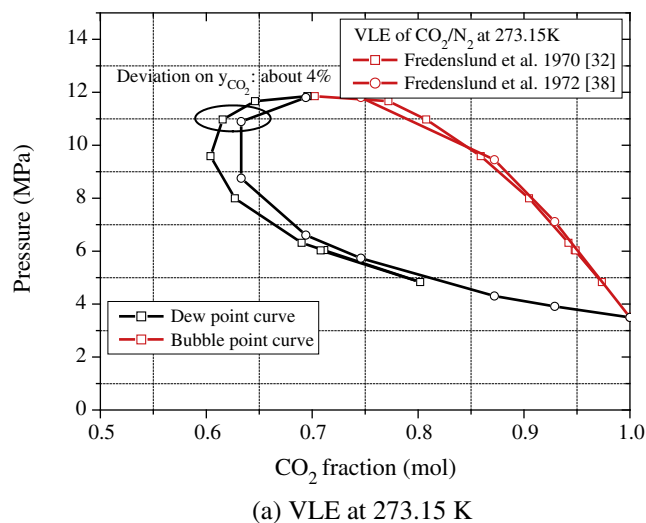


Fig. 8. Comparison of different experiments about the VLE and density of CO₂/N₂.

Later, Duan et al. [69] developed a new cubic EOS modelling the VLE and volumetric properties of natural fluids, such as CO, CO₂, N₂, O₂, NH₃, H₂O, inert gases and hydrocarbons. For CO₂ mixtures, it was tested regarding CO₂/CH₄ and CO₂/N₂. They claimed that the calculations of the VLE are in good agreement with experiments; however, the concrete accuracy was not given. It was also concluded that the new cubic EOS had about the same accuracy as Lee–Kesler [70] EOS (LK) for volumetric calculations.

Boyle and Carroll [71] investigated PR, SRK, PT, PR–Peneloux, SRK–Peneloux and PR–Mathisa EOS for the density calculations of CO₂/H₂S. The results showed that PT is the most accurate EOS in the liquid area, the supercritical area and overall with an Absolute Average Deviation (AAD) of 2.16%, 2.26% and 1.82% respectively; while SRK is the most accurate EOS in the vapour area with an AAD of 0.51%.

Austegard et al. [9] evaluated several EOS regarding the mutual solubilities in H₂O/CO₂/CH₄, including the second order SRK–Huron–Vidal (SRK–HV), the SRK–vdW and the cubic plus association (CPA), which uses a cubic equation, normally SRK, and adds the association term from the Statistical Associating Fluid Theory (SAFT) equation. The results show that SRK–HV is superior to the other two for the mixtures investigated.

Seven cubic equations of state were evaluated concerning the VLE and the density of CO₂ mixtures including CH₄, N₂, O₂, H₂S,

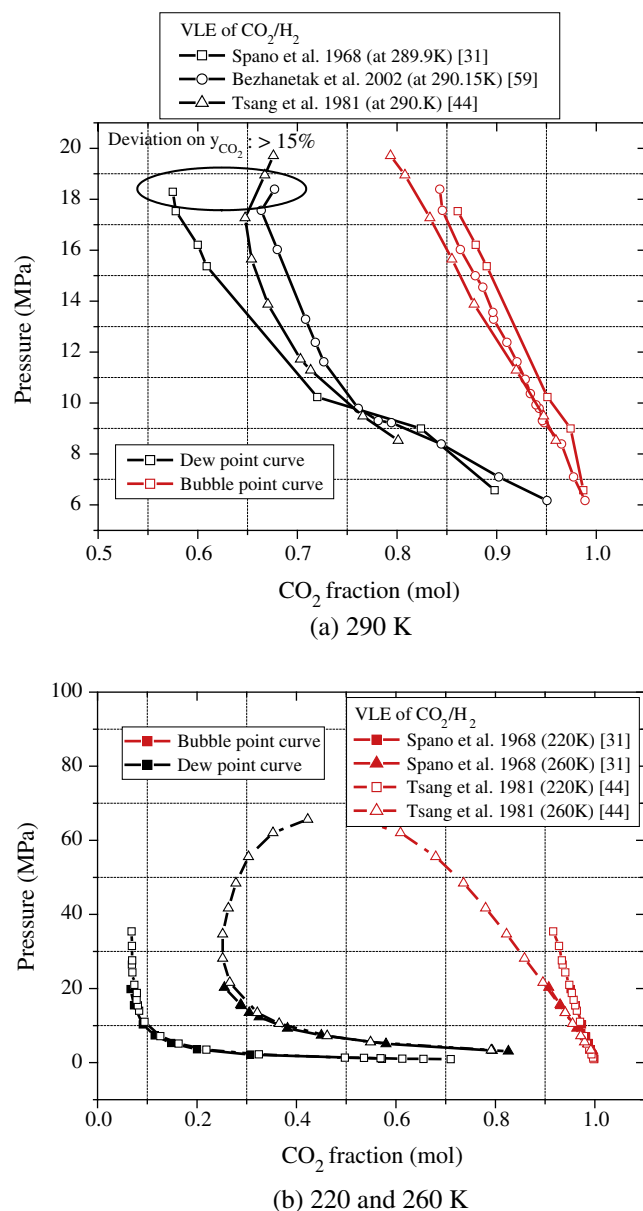


Fig. 9. Comparison of different experiments about the VLE of CO₂/H₂.

SO₂ and Ar using many of the experimental data presented in this work [5,72,73]. The EOS evaluated were PR, RK, SRK, PT, 3P1T [74], PR–Peneloux [75], SRK–Peneloux [76] and the improved SRK [77]. The binary interaction parameters, k_{ij} , were calibrated with respect to the VLE data available. In general, with calibrated k_{ij} , the cubic EOS gave an AAD within 5% for VLE calculations, and 6% for calculations of the density, except for the CO₂/SO₂ mixture.

Vrabec et al. [78] proposed to use the PR EOS combined with a model based on Henry's law constants for the ternary mixture CO₂/N₂/O₂ at low temperatures (218–251 K). Their results show that the PR EOS describes both binary and ternary experimental data well, except at high pressures close to the critical region.

4.2. Benedict–Webb–Rubin (BWR) EOS [79]

Virial and extended virial equations of state are used when high accuracy is needed in the calculation of thermodynamic properties and phase behaviour. These multi-parameter equations often require large amount of high accuracy data for parameter

Table 7Summary of the performance of different EOS for the calculation of PVTxy properties of CO₂ mixtures.

EOS	Author	T/P/X _{CO2}	Mixtures	Accuracy (Absolute Average Deviation %)		
				VLE	Density	
					V _g	V _l
BWR	Li [80]	216–363 K/5.2–145 bar/0–1	CO ₂ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	2.7–9.7	0.8–9.2	>9
Duan96	Duan [68]	<2000 K/<25,000 bar	H ₂ O, CO ₂ , CH ₄ , N ₂ , CO, H ₂ , O ₂ , H ₂ S, Ar	–	<2	–
Duan04	Duan [69]	230–288 K/10–160 bar/0–1	CO ₂ /CH ₄ , CO ₂ /N ₂	–	–	–
GERG 2004	GERG [92]	90–450 K/<350 bar	H ₂ O, CO ₂ , O ₂ , N ₂ , CO, CH ₄ , C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀ , i-C ₄ H ₁₀ , n-C ₅ H ₁₂ , i-C ₅ H ₁₂ , n-C ₆ H ₁₄ , n-C ₇ H ₁₆ , n-C ₈ H ₁₈ , Ar, H ₂ , He	1–3	0.2–0.5	0.1–0.5
LK	Li [80]	216–363 K/5.2–145 bar/0–1	CO ₂ , N ₂ , O ₂ , Ar	2.2–10.4	0.5–5.7	3.8–18.4
	Al-Sahhaf [45]	220–270 K/6–167 bar/0.3–1	CO ₂ , CH ₄ , N ₂	3–3.9	–	–
	Thiery [67]	220–273 K/20–120 bar	CO ₂ , CH ₄ , N ₂	–	<5 ^a	<5 ^a
PR	Al-Sahhaf [56]	220–270 K/<158 bar	CO ₂ , CH ₄ , N ₂	2.1–3.3	–	–
	Boyle and Carroll [71]	250–450 K/0–200 bar/0.5–0.94	CO ₂ /H ₂ S	–	1.26 (2.76 ^b)	2.81
	Li [72]	193–363 K/1–143 bar/0–1	CH ₄ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	1.22–6.04	1.58–13.02	1.74–9.43
PR-Peneloux	Vrabec [78]	218–253 K	CO ₂ , N ₂ , O ₂	–	–	–
	Boyle and Carroll [71]	250–450 K/0–200 bar/0.5–0.94	CO ₂ /H ₂ S	–	1.39 (3.24 ^b)	3.53
	Li [73]	220–347 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , H ₂ S, SO ₂ , Ar	–	2.85–11.64	3.79–10.51
PT	Al-Sahhaf [56]	220–270 K/<15 8 bar	CO ₂ , CH ₄ , N ₂	1.6–3.2	–	–
	Boyle and Carroll [71]	250–450 K/0–200 bar/0.5–0.94	CO ₂ /H ₂ S	–	1.02 (2.26 ^b)	2.16
	Li [72]	193–363 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	2.32–10.82	0.98–13.06	1.77–9.28
Predictive-PR	Vitu [87]	165.2–673 K/3–490 bar/0–1	CO ₂ , n-alkanes	–	–	–
RK	Li [72]	193–363 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	5.25–14.17	1.47–14.26	4.86–11.96
SAFT	Belkadi [85]	298–328 K	CO ₂ + NO ₂ /N ₂ O ₄	0.003–2.2	–	–
SRK	Boyle and Carroll [71]	250–450 K/0–200 bar/0.5–0.94	CO ₂ /H ₂ S	–	0.51 (2.79 ^b)	9.23
	Li [72]	193–363 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	1.32–11.28	1.50–14.00	4.18–10.84
	Austegard [9]	245–383 K/1–3500 bar	H ₂ O, CO ₂ , CH ₄	3–9.3 ^c	–	–
SRK-HV	Boyle and Carroll [71]	250–450 K/0–200 bar/0.5–0.94	CO ₂ /H ₂ S	–	0.65 (2.89 ^b)	5
SRK-Peneloux	Li [73]	220–347 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , H ₂ S, SO ₂ , Ar	–	2.59–12.76	4.97–12.15
Improved SRK	Li [73]	220–347 K/1–143 bar/0–1	CO ₂ , CH ₄ , N ₂ , H ₂ S, SO ₂ , Ar	–	5.17–8.83	4.64–13.21
Predictive SRK	Li [80]	216–363 K/5.2–145 bar/0–1	CO ₂ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	1.4–16.2	0.6–9.2	>9
3P1T	Li [72]	193–363 K/5–140 bar/0–1	CO ₂ , CH ₄ , N ₂ , O ₂ , H ₂ S, SO ₂ , Ar	3.32–25.75	–	–

^a 10–20% in the critical and the retrograde regions.^b In supercritical area.^c Solubility.

estimation, and there may be problems in determining unique values for these parameters. With a slight loss in accuracy, these problems could be solved by using the extended virial equations in a corresponding state form.

With the commercial software Aspen Plus, a virial type EOS was evaluated regarding the calculations of VLE and density of CO₂ mixtures containing CH₄, N₂, O₂, H₂S, SO₂ and Ar [80]. The results showed that BWR could give a better accuracy than cubic EOS for some mixtures like CO₂/SO₂, CO₂/N₂ and CO₂/O₂. However, the difference in the accuracy of the saturated pressures is usually less than 3%.

The EOS by Lee–Kesler [70] (LK) is a modified form of the BWR EOS. The performance of LK for the CO₂/CH₄/N₂ system does not show any advantages compared to cubic EOS, such as PR and PT, except in the calculations of volumes. Al-Sahhaf et al. [45] compared the multi-fluid reference corresponding states method proposed by Teja and Rice [81], LK and the PR EOS for the system CO₂/CH₄/N₂. The multi-fluid model and LK gave comparable results for the CO₂/CH₄/N₂ system. However, the multi-fluid model predictions were slightly better than the predictions of LK for the ternary system. The cubic PR EOS was found to be better than both corresponding states methods in VLE calculations for both binary and ternary mixtures. In addition, none of the methods provided a good representation near the critical points.

Thiery et al. [67] also calculated the thermodynamic properties of the CO₂/CH₄/N₂ system with the LK EOS. For the calculations of molar volumes of the mixture, the relative deviations for the LK EOS were smaller than 5%, except in the critical and the retrograde condensation regions, where the relative errors could reach 10–20%.

4.3. Statistical Associating Fluid Theory EOS

Molecular-based equations of state which also have a foundation in statistical mechanics are also very attractive EOS for CO₂ mixtures. Among them, the Statistical Associating Fluid Theory (SAFT) EOS has become very popular because of its capability of successfully predicting thermodynamic properties of several complex fluids, including chain, aromatic and chlorinated hydrocarbons, esters, alkanols, carboxylic acids, and many others. SAFT was envisioned as an application of Wertheim's theory [82] of association through the use of a first-order thermodynamic perturbation theory to formulate a physically based EOS. The original SAFT EOS was first introduced by Chapman et al. in 1990 [83] and has inspired much derived work on the modelling of polymer–solvent systems. An advantage of SAFT-type equations compared to other approaches is that, as they are based on statistical mechanics, parameters have a clear physical meaning. When carefully fitted they can be used with predictive power to explore other regions of the phase diagram far from the data and operating conditions used in the parameter regression. They typically perform better than other models for interacting compounds, and have found to yield better results than for example activity coefficient models [83,84].

Belkadi et al. [86] evaluated the soft-SAFT EOS regarding the VLE of CO₂/NO_x. The soft-SAFT EOS is a modification of the original SAFT equation, where the main difference is the use of the Lennard–Jones intermolecular potential for the reference fluid in the soft-SAFT equation, with dispersive and repulsive forces into the same term, while the original SAFT EOS has a perturbation scheme based on a hard sphere reference fluid plus dispersive

contributions to it. A recent modelling work on the VLE of CO₂–perfluoroalkanes mixtures using the soft-SAFT equation of state showed that no binary interaction parameters are needed when the quadrupolar moment of CO₂ is explicitly included and the involved molecules do not differ substantially in size. In that case, the quadrupolar effect on the phase equilibrium is not hidden in the binary parameter value, but explicitly described. This increases the extrapolation capability of the model. Belkadi et al. [85] concluded that the soft-SAFT model was successfully able to capture the non-ideal behaviour of the CO₂ + NO₂/N₂O₄ system.

4.4. Predictive EOS

Predictive EOS is a type of EOS which combines a cubic EOS with a group contribution method. They typically use the UNIFAC method to calculate the mixture parameters. The main advantage is that the VLE can be predicted for a large number of systems without introducing new model parameters which must be fitted to experimental VLE data [86].

The predictive-SRK EOS [86] was evaluated with Aspen Plus regarding the calculations of VLE and density of CO₂ mixtures containing impurities [77]. PSRK is similar but slightly less accurate than the BWR EOS. However, both BWR and PSRK have a much more complicated structure than cubic EOS. Their calculation procedure and applications, consequently, are not as straightforward as cubic EOS.

The predictive-PR (PPR) EOS was evaluated by Vitu et al. [87] regarding the phase equilibria of CO₂ + *n*-alkanes. The authors claimed that their applications of PPR always leads to better results than PSRK, SAFT-VR [88], PC-SAFT [89], soft-SAFT, GC-SAFT [90] and PRSV-WS [91], without giving any details from their calculations of the CO₂/CH₄ system. The PPR EOS has also been extended to any mixture containing hydrocarbons + CO₂ + H₂S + N₂.

4.5. The GERG equation [92]

This EOS was adopted under the name GERG 2004 by the GERG (Group Européen de Recherche Gazières) as the international reference equation of state for natural gases. The EOS may be used to calculate a number of thermodynamic properties of mixtures containing natural gas components. It is thus suitable for all technical applications using natural gas, e.g. pipeline transport and processes with liquefied natural gas. The GERG EOS is principally different from the other EOS discussed above because its formulation is based on a multi-fluid approximation, which is explicit in the reduced Helmholtz energy depending on the density, the temperature and the composition. The equation was developed by the Lehrstuhl für Thermodynamik at the Ruhr-Universität Bochum. It covers the whole fluid region (gas, liquid, supercritical region, liquid–vapour phase boundaries) of natural gas mixtures including the 18 most relevant components (methane, nitrogen, carbon dioxide, ethane, propane, *n*-butane, isobutene, *n*-pentane, isopentane, *n*-hexane, *n*-heptane, *n*-octane, hydrogen, oxygen, carbon monoxide, water, helium and argon). Since GERG is explicit in the reduced Helmholtz energy, all thermodynamic properties can be calculated from combinations of the derivatives. This is feasible, since it eliminates the need of integrating pressure explicit relations in the calculation of caloric properties.

The accuracy of the GERG EOS claims to be very high and the normal range of validity covers temperatures between 90 K and 450 K and pressures less than 35 MPa. This covers a large part of the *T/P* range for CCS applications, except regions with large temperatures or large pressures. The reported uncertainty of the EOS regarding gas phase density and the speed of sound is less than 0.1% from 250 K/270 K to 450 K and pressures up to 35 MPa. In the liquid phase of many binary and multi-component mixtures,

the uncertainty of the equation regarding the density is less than 0.1–0.5%. Based on the poor data situation, the VLE should be described as accurately as possible.

For solutions with large amounts of methane, GERG 2004 has a better accuracy than other EOS, because it was calibrated based on a tremendous amount of experimental data. However, since many impurities, such as NO_x, COS, H₂S and SO₂, were not involved in the database which GERG was based on, its applications are limited to mixtures not containing sulphur. Moreover, there are some differences between the uncertainties given by its manual and accuracy testes performed for CO₂ rich mixtures. The accuracy claimed by the GERG manual [92] was not obtained neither for the volume nor VLE calculations of CO₂ rich mixtures [80]. The AAD of the liquid volume of CO₂ mixtures could reach up to 18%, which is considerably larger than the AAD reported by the GERG manual [80] (for details, see Table 7).

5. Discussion

This work has summarized the experimental PVTxy-data available for CO₂ rich mixtures relevant for CCS. Some knowledge gaps were identified between available experimental data and requirements, and some inconsistencies were pointed out among the existing experimental data. Moreover, the accuracy of old data sources is questionable, such as the data available for the CO₂/SO₂ mixture. These data were obtained 100 years ago, when equipment and laboratory routines were not comparable with the standard today. Therefore, it is of importance to provide new data with a higher accuracy for many of the mixtures. This is also in correspondence with the investigations of the industrial requirements for thermodynamic and transport properties performed by Hendriks et al. [93] Their results showed that quality is considered more important than quantity. In their work, they conclude that both experimental data and models applicable to CCS obtain more and more focus in the industry.

Although the application of cubic EOS has been verified to be able to give satisfactory results, Vidal [94] argued that it may not be possible to build a cubic EOS which is able to reproduce all the thermodynamic properties of a fluid. They imply that instead of using only one EOS, two or more EOS may be applied for property calculations. The industry on the other hand, has expressed the need of more predictive EOS such as SAFT rather than correlative EOS with limited interpolation capabilities [93].

Meanwhile, many types of EOS have been reviewed concerning thermodynamic property calculations of CO₂ mixtures, but the evaluation results of the EOS performance have not pointed to one particular EOS. The cubic EOS still show advantages over more complicated EOS in the calculation of VLE, while for volume calculations they cannot compete with equations such as LK and SAFT. Of these reasons, more effort should be spent on evaluating and developing EOS for CCS applications. Considering the properties of semi-empirical models, more work on parameter regression for already established models, and also development of new models should be done as soon as new high quality experimental data is available.

Furthermore, it is no doubt that more accurate models are always preferable. However, in order to improve the accuracy, more parameters will have to be included in the EOS, which may reduce the predictive ability. Complicated structures may reduce the applicability of the EOS, for example by increasing the computation time and making the EOS less transparent and harder to implement correctly for the industry [93]. However, the accuracy of thermodynamic models may not be the bottleneck in many engineering applications. Therefore, it is important to identify an acceptable accuracy for the calculation of thermodynamic properties and subsequently develop criteria Regarding EOS selection.

6. Conclusions

This work has reviewed both the available experimental data and the theoretical models presented in the literature regarding thermodynamic properties (PVTxy) of CO₂ mixtures with impurities. It was shown that:

- (1) Compared to the operating windows of CO₂ capture, transport and storage, there are still some gaps between available experimental data and the requirements in design and operation. The major problems are: for the VLE property, there are no data about CO₂/COS and quite few data about CO₂/N₂O₄, and only a few of the experimental data are available for multi-component CO₂ mixtures. For the volume property, there are no experimental data on the volume of CO₂/O₂, CO₂/CO, CO₂/N₂O₄, CO₂/COS and CO₂/NH₃ and also not the liquid volume of CO₂/H₂. Also for multi-component CO₂ mixtures, experimental data for the volume property are scarce.
- (2) Among the available experimental data, some inconsistencies have been identified. For example, at high pressures, the deviations between Donnelly's data [23] and Mraw's data [42] for CO₂/CH₄ can be up to 20% for the CO₂ concentration in the vapour phase; and there is no good agreement among the three available data sources for the dew points of CO₂/H₂ at high temperatures (290 K). Therefore, more experiments should be planned to verify the accuracy of these measurements.
- (3) Among the existing thermodynamic models, cubic equations of state have the simplest structure and are capable of giving reasonable results for the PVTxy properties of CO₂ mixtures, if the binary interaction parameters k_{ij} are calibrated. EOS with complicated structures, such as BWR and SAFT, have shown to give a better accuracy than cubic EOS for volume calculations, but cubic EOS on the other hand, show an advantage in VLE calculations. GERG, according to its claimed accuracy, should give the best results. The equation is however intended for natural gas components, and not CO₂ rich mixtures and its applications are limited to certain impurities.
- (4) Currently, none of the EOS evaluated in the literature show any clear advantage in CCS applications for both VLE and volume calculations. Because of this situation, we suggest that more experimental measurements about the PVTxy properties of CO₂ rich mixtures should be conducted, including both binary and multi-component mixtures in order to ensure sufficient data for proper development of future EOS. In addition, it is also of importance to identify the accepted accuracy according to the demands of process design and operation before a proper model could be developed for CCS applications. A reference EOS for CCS should be a goal for the future.

Acknowledgement

This publication has been produced with support from the BIG-CCS Centre, performed under the Norwegian research program Centres for Energy Efficient Research. The authors acknowledge the following partners for their contributions: Aker Solutions, ConocoPhillips Skandinavia AS, Det Norske Veritas AS, Gassco AS, Hydro Aluminium AS, Shell Technology AS, Statkraft Development AS, StatoilHydro Petroleum AS, TOTAL E&P Norge AS, and the Research Council of Norway.

References

- [1] de Koeijer G, Borch JH, Drescher M, Li H, Wilhelmssen Ø, Jakobsen J. CO₂ transport – depressurization, heat transfer and impurities. In: Proceedings of 10th international conference on greenhouse gas technologies, Amsterdam (The Netherlands); September 19–23, 2010.
- [2] Li H, Yan J. Impact of impurities in CO₂ –fluids on CO₂ transport process. In: Proceedings of GT2006, ASME turbo expo 2006: power for land, sea and air, Barcelona, Spain; May 8–11, 2006.
- [3] Li H, Yan J, Yan J, Anheden M. Impurity impacts on the purification process in oxy-fuel combustion Based CO₂ capture and storage system. *Appl Energy* 2009;86(2):202–13.
- [4] Intergovernmental Panel on Climate Change (IPCC). IPCC special report on carbon dioxide capture and storage. Cambridge (United Kingdom, New York, USA): Cambridge University Press; 2005.
- [5] Li H. Thermodynamic properties of CO₂ mixtures and their applications in advanced power cycles with CO₂ capture processes. Stockholm, Sweden: Doctoral thesis of Royal Institute of Technology; 2008.
- [6] Spycher N, Pruess K, Ennis-King J. CO₂–H₂ O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar. *Geochim Cosmochim Acta* 2003;67(16):3015–31.
- [7] Chapoy A, Mohammadi AH, Chareton A, Tohidi B, Richon D. Measurement and modelling of gas solubility and literature review of the properties for the carbon dioxide–water system. *Ind Eng Chem Res* 2004;43:1794–802.
- [8] Poplsteinova J. Absorption of carbon dioxide – modeling and experimental characterization. Doctor thesis, Trondheim, Norway: Norwegian University of Science and Technology; 2004.
- [9] Austegard A, Solbraa E, de Koeijer G, Mølnvik MJ. Thermodynamic models for calculating mutual solubilities in H₂O–CO₂–CH₄ mixtures. *Chem Eng Res Des* 2006;84(A9):781–94.
- [10] Hu J, Duan Z, Zhu C, Chou I. PVTx properties of the CO₂–H₂O and CO₂–H₂O–NaCl systems below 647 K: assessment of experimental data and thermodynamic models. *Chem Geol* 2007;238:249–67.
- [11] Bottinger W, Maiwald M, Hasse H. Online NMR spectroscopic study of species distribution in MEA–H₂O–CO₂ and DEA–H₂O–CO₂. *Fluid Phase Equilib* 2008;263:131–43.
- [12] Faramarzi L, Kontogeorgis GM, Thomsen K, Stenby EH. Extended UNIQUAC model for thermodynamic modeling of CO₂ absorption in aqueous alkanolamine solutions. *Fluid Phase Equilib* 2009;282:121–32.
- [13] Li H, Jakobsen JP, Stang J. Predicting water concentration at equilibrium with CO₂ hydrates. *Int J Greenhouse Gas Control*, in press.
- [14] Visser E, Hendriks C, Barrio M, Mølnvik MJ, de Koeijer G, Liljemark S, et al. Dynamis CO₂ quality recommendations. *Int J Greenhouse Gas Control* 2008;2:478–87.
- [15] Caubet F. Liquéfaction des mélanges gazeux. Université de Bordeaux; 1901.
- [16] Booth HS, Carter JM. The critical constants of carbon dioxide–oxygen mixtures. *J Phys Chem* 1930;34:2801–25.
- [17] Cummings LWT. High-pressure rectification. I. Vapor–liquid equilibrium relations at high pressures. *Ind Eng Chem* 1931;23(8):900–2.
- [18] Reamer HH, Olds RH, Sage BH, Lacey WN. Phase equilibria in hydrocarbon systems: methane–carbon dioxide system in the gaseous region. *Ind Eng Chem* 1944;35(1):88–90.
- [19] Haney RED, Bliss H. Compressibilities of nitrogen–carbon dioxide mixtures. *Ind Eng Chem* 1944;36(11):985.
- [20] von Steckel F. Dampf-Flüssigkeits-Gleichgewichte einiger binärer, schwefelwasserstoffhaltiger systeme unter Druck. *Svensk Kemisk Tidskrift* 1945;9:209–16.
- [21] Bierlein JA, Kay WB. Phase equilibrium properties of system carbon dioxide–hydrogen sulphide. *Ind Eng Chem* 1953;45(3):618–24.
- [22] Cook D. The carbon–dioxide–nitrous–oxide system in the critical region. *Proc Roy Soc Lond* 1953;A219:245.
- [23] Donnelly HG, Katz DL. Phase equilibria in the carbon dioxide–methane system. *Ind Eng Chem* 1954;46(3):511–7.
- [24] Sobocinski DP, Kurata F. Heterogeneous phase equilibria of the hydrogen sulfide–carbon dioxide system. *AIChE J* 1959;5(4):545–51.
- [25] Hensel WE, Massoth FE. Phase equilibria for the ternary system: CH₄–CO₂–H₂S. *J Chem Eng Data* 1964;9:352.
- [26] Muirbrook NK, Prausnitz JM. Multicomponent vapor–liquid equilibria at high pressures. Part I. Experimental study of the nitrogen–oxygen–carbon dioxide system at 0 °C. *AIChE J* 1965;1(6):1097–102.
- [27] Zenner GH, Dana LI. Liquid–vapor equilibrium compositions of carbon dioxide–oxygen–nitrogen mixtures. *Chem Eng Prog Symp Ser* 1965;59.
- [28] Kestin J, Kobayashi Y, Wood RT. The viscosity of four binary gaseous mixtures at 20 °C and 30 °C. *Phys Amsterdam* 1966;32:1065–89.
- [29] Kaminishi G, Arai Y, Saito S, Maeda S. Vapor–liquid equilibria for binary and ternary systems containing carbon dioxide. *J Chem, Eng Jap* 1968;1(2):109–16.
- [30] Neumann PNA, Walch W. Dampf/Flüssigkeits-Gleichgewicht CH₄–CO₂ in bereich tiefer temperaturen und kleiner CO₂–molenbrüche. *Chem Ing Technol* 1968;40:241–4.
- [31] Spano JO, Heck CK, Barrick PL. Liquid–vapor equilibria of the hydrogen–carbon dioxide system. *J Chem Eng Data* 1968;13:168–71.
- [32] Fredenslund A, Sather GA. Gas–liquid equilibrium of the oxygen–carbon dioxide system. *J Chem Eng Data* 1970;15(1):17–22.

- [33] Arai Y, Kaminishi G, Saito S. The experimental determination of the P – V – T – X relations for the carbon dioxide–nitrogen and the carbon dioxide–methane system. *J Chem Eng Jap* 1971;4(2):113–22.
- [34] Chang ET, Gokcen NA, Poston TM. Thermodynamic properties of gases in propellants. Solubilities of gaseous ammonia, carbon monoxide, carbon dioxide, and sulfur hexafluoride. *J Chem Eng Data* 1971;16(4):404–8.
- [35] Lemkowitz SM, Goedegebuur J, Van den Berg PJ. Bubble-point measurements in the ammonia–carbon dioxide system. *J Appl Chem Biotechnol* 1971;21:229–32.
- [36] Sarashina E, Arai Y, Saito S. The P – V – T – X relation for the carbon dioxide – system. *J Chem Eng Jap* 1971;4(4):379–81.
- [37] Sarashina E, Arai Y, Saito S. Vapor–liquid equilibria for the nitrogen–methane–carbon dioxide system. *J Chem Eng Jap* 1971;4(2):377.
- [38] Fredenslund A, Møllerup J, Persson O. Gas–liquid equilibrium of oxygen–carbon dioxide system. *J Chem, Eng Data* 1972;17(4):440–3.
- [39] Lemkowitz SM, Zuidam J, Van den Berg PJ. Phase behavior in the ammonia–carbon dioxide system at and above urea synthesis conditions. *J Appl Chem Biotechnol* 1972;22:727–37.
- [40] Davalos J, Anderson WR, Phelps RE, Kldnay AJ. Liquid–vapor equilibria at 250.00 K for systems containing methane, ethane, and carbon dioxide. *J Chem Eng Data* 1976;21(1):81–4.
- [41] Altunin VV, Koposhev OD. An experimental study of thermal properties of gaseous mixtures of carbon dioxide with argon. *Teploenergetika* 1977;24(8):80–3.
- [42] Mravac SC, Hwang S, Kobayashi R. Vapor–liquid equilibrium of the CH_4 – CO_2 system at low temperature. *J Chem Eng Data* 1978;23(2):135–9.
- [43] Somait FA, Kidnay AJ. Liquid–vapor equilibria at 270.00 K for system containing nitrogen, methane, and carbon dioxide. *J Chem Eng Data* 1978;23(4):301–5.
- [44] Tsang CY, Streett WB. Phase equilibria in the H_2/CO_2 system at temperatures from 20 to 290 K and pressures to 172 MPa. *Chem Eng Sci* 1981;36:993–1000.
- [45] Al-Sahhaf TA, Kidnay AJ, Sloan ED. Liquid + vapour equilibria in the nitrogen + carbon dioxide + methane system. *Ind Eng Chem Fundamen* 1983;22(4):372–80.
- [46] Dorau WI, Al-Wakeel M, Knapp H. VLE data for CO_2 – CF_2Cl_2 , N_2 – CO_2 , N_2 – CF_2Cl_2 and N_2 – CO_2 – CF_2Cl_2 . *Cryogen* 1983;29:35.
- [47] Yorzane M, Yoshimura S, Masuoka H, Miyano Y, Kakimoto Y. New procedure for vapour–liquid equilibria. Nitrogen + carbon dioxide, methane + Freon 22, and methane + Freon 12. *J Chem Eng Data* 1985;30:174–6.
- [48] Mallu BV, Natarajan G, Viswanath DS. Compression factors and second virial coefficients of CO_2 , CO_2 and $\{x\text{CO} + (1-x)\text{CO}_2\}$. *J Chem Thermodynamics* 1987;19:549–54.
- [49] Hacura A, Yoon JH, Baglin FG. Density values of carbon dioxide and nitrogen mixtures from 500 to 2500 bar at 323 and 348 K. *J Chem Eng Data* 1988;33(2):152–4.
- [50] Magee JW, Ely JF. Isochoric (P , V , T) measurements on CO_2 and (0.98 CO_2 + 0.02 CH_4) from 225 to 400 K and pressures to 35 MPa. *Int J Thermophys* 1988;9(4):547–57.
- [51] Brugge HB, Hwang CA, Gogers WJ, Holste JC, Hall KR, Lemming W, et al. Experimental cross virial coefficients for binary mixtures of carbon dioxide with nitrogen, methane and ethane at 300 and 320 K. *Physica A* 1989;156:382–416.
- [52] Ely JF, Haynes WM, Bain BC. Isochoric (p , V , T) measurements on CO_2 and on (0.982 CO_2 + 0.018 N_2) from 250 to 330 K at pressures to 35 MPa. *J Chem Thermodynamics* 1989;21:879–94.
- [53] Esper GJ, Bailey DM, Holste JC, Hall KR. Volumetric behavior of near-equimolar mixtures for CO_2 + CH_4 and CO_2 + N_2 . *Fluid Phase Equilib* 1989;49:35–47.
- [54] McElroy PJ, Battino R, Dowd MK. Compression-factor measurements on methane, carbon dioxide, and (methane + carbon dioxide) using a weighing method. *J Chem Thermodynamics* 1989;21:1287–300.
- [55] Trappehl G, Knapp H. Vapor–liquid equilibria in the ternary mixture N_2 + CH_4 + CO_2 and the quaternary mixture N_2 + CH_4 + C_2H_6 + C_3H_8 . *Cryogen* 1989;29:42–50.
- [56] Al-Sahhaf TA. Vapor–liquid equilibria for the ternary system N_2 – CO_2 – CH_4 at 230 and 250 K. *Fluid Phase Equilib* 1990;55:159–72.
- [57] Xu N, Dong J, Wang Y, Shi J. High pressure vapor–liquid equilibrium at 293 K for system containing nitrogen, methane and carbon dioxide. *Fluid Phase Equilib* 1992;81:175–86.
- [58] Seitz JC, Blencoe JG, Bodnar RJ. Volumetric properties for $x_1\text{CO}_2$ + $x_2\text{CH}_4$ + $(1-x_1-x_2)\text{N}_2$ at the pressures (19.94, 39.94, 59.39, 99.39) MPa and temperatures (323.15, 373.15, 473.15, 573.15) K. *J Chem Thermodynamics* 1996;28:539–56.
- [59] Bezahehtak K, Combes GB, Dehghani F, Foster NR. Vapor–liquid equilibrium for binary systems of carbon dioxide + methanol, hydrogen + methanol, and hydrogen + carbon dioxide at high pressures. *J Chem Eng Data* 2002;47:161–8.
- [60] Abbott MM. Cubic equations of state: an iterative review. *Am Chem Soc Adv Chem Ser* 1979;182:47–70.
- [61] Danesh A, Xu D-H, Todd AC. Comparative study of cubic equations of state for predicting phase behavior and volumetric properties of injection gas–reservoir oil systems. *Fluid Phase Equilib* 1991;63:259–78.
- [62] Yang J, Griffiths PR, Goodwin ARH. Comparison of methods for calculating thermodynamic properties of binary mixtures in the sub and super critical state: Lee–Kesler and cubic equations of state for binary mixtures containing either CO_2 and H_2S . *J Chem Thermodynamics* 2003;35:1521.
- [63] Redlich O, Kwong JNS. On the thermodynamics of solutions. *Chem Rev* 1949;44:233–44.
- [64] Soave G. Equilibrium constants for modified Redlich–Kwong equation of state. *Chem Eng Sci* 1972;27:1196–203.
- [65] Peng DY, Robinson DB. A new two-constant equation of state. *Ind Eng Chem Fundam* 1976;15:59–64.
- [66] Patel NC, Teja AS. A new cubic equation of state for fluids and fluid mixtures. *Chem Eng Sci* 1982;37(3):463–73.
- [67] Thiery R, Vidal J, Dubessy J. Phase equilibria modelling applied to fluid inclusions: Liquid–vapor equilibria and calculation of the molar volume in the CO_2 – CH_4 – N_2 system. *Geochim Cosmochim Acta* 1994;58(3):1073–82.
- [68] Duan Z, Møller N, Weare JH. A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture PVTX properties. *Geochim Cosmochim Acta* 1996;60(7):1209–16.
- [69] Duan Z, Hu J. A new cubic equation of state and its applications to the modelling of vapour–liquid equilibria and volumetric properties of natural fluids. *Geochim Cosmochim Acta* 2004;68(14):2997–3009.
- [70] Lee BI, Kesler MG. A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE J* 1975;21:510.
- [71] Boyle TB, Carroll JJ. Study determines best methods for calculating acid-gas density. *Oil Gas J* 2002(Jan 14):45.
- [72] Li H, Yan J. Evaluating cubic equations of state for calculation of vapour–liquid equilibrium of CO_2 and CO_2 mixtures for CO_2 capture and storage processes. *Appl Energy* 2009;86(6):826–36.
- [73] Li H, Yan J. Impacts of equations of state (EOS) and impurities on the volume calculation of CO_2 mixtures in the applications of CO_2 capture and storage (CCS) processes. *Appl Energy* 2009;86(12):2760–70.
- [74] Yu J, Lu BC, Iwai Y. Simultaneous calculations of VLE and saturated liquid and vapor volumes by means of a 3PIT cubic EOS. *Fluid Phase Equilib* 1987;37:207–22.
- [75] Mathias PM, Naheiri T, Oh EM. A density correction for Peng–Robinson equation of state. *Fluid Phase Equilib* 1989;47:77–87.
- [76] Peneloux A, Rauzy E. A consistent correction for Redlich–Kwong–Soave volumes. *Fluid Phase Equilib* 1982;8:7–23.
- [77] Ji W, Lempe DA. Density improvement of the SRK equation of state. *Fluid Phase Equilib* 1997;130(1–2):49–63.
- [78] Vrabec J, Kedia GK, Buchhauser U, Meyer-Pittroff R, Hasse H. Thermodynamic models for vapor–liquid equilibria of nitrogen + oxygen + carbon dioxide at low temperatures. *Cryogenics* 2009;49:72–9.
- [79] Benedict M, Webb GB, Rubin LC. An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. *J Chem Phys* 1940;8:334.
- [80] Li H, Yan J, Yan J, Anheden M. Evaluation of existing methods for the thermodynamic properties calculation of CO_2 mixtures. Technical report, KTH; 2007.
- [81] Teja AS, Rice P. A multifluid corresponding states principle for the thermodynamic properties of fluid mixtures. *Chem Eng Sci* 1981;36:1–6.
- [82] Wertheim MS. Thermodynamic perturbation theory of polymerization. *J Chem Phys* 1987;73:23–31.
- [83] Chapman WG, Gubbins KE, Jackson G, Radosz M. New reference equation of state for associating liquids. *Ind Eng Chem Res* 1990;29:1709–21.
- [84] Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules: extension to fluid mixtures. *Ind Eng Chem Res* 1991;30:1994–2005.
- [85] Belkadi A, Llovel F, Gerbaud V, Vega LF. Modeling the vapor–liquid equilibrium and association of nitrogen dioxide/dinitrogen tetroxide and its mixtures with carbon dioxide. *Fluid Phase Equilib* 2008;266:154–63.
- [86] Holderbaum T, Gmehling J. PSRK: a group contribution equation of state based on UNIFAC. *Fluid Phase Equilib* 1991;70:251–65.
- [87] Vitu S, Privat R, Jaubert JN, Mutelet F. Predicting the phase equilibria of CO_2 + hydrocarbon systems with the PPR78 model (PR EOD and k_{ij} calculated through a group contribution method). *J Supercritical Fluid* 2008;45:1–26.
- [88] Galindo A, Blas FJ. Theoretical examination of the global fluid phase behavior and critical phenomena in carbon dioxide + n -alkanes binary mixtures. *J Phys Chem* 2002;B106:4503–15.
- [89] Garcia J, Lugo L, Fernandez J. Phase equilibria, PVT behavior, and critical phenomena in carbon dioxide + n -alkane mixtures using the Perturbed-Chain Statistical Associating Fluid Theory. *Ind Eng Chem Res* 2004;43:8345–53.
- [90] Le Thi C, Tamouza S, Passarello JP, Tobaly P, de Hemptinne JC. Modeling phase equilibrium of H_2 + n -alkane and CO_2 + n -alkane binary mixtures using a Group Contribution Statistic Association Fluid Theory Equation of State (GC-SAFT EOS) with a k_{ij} Group Contribution Method. *Ind Eng Chem Res* 2006;45:6803–10.
- [91] Lopez JA, Cardona CA. Phase equilibrium calculations for carbon dioxide + n -alkanes binary mixtures with the Wong–Sandler mixing rules. *Fluid Phase Equilib* 2006;239:206–12.
- [92] GERG2004. <http://www.ruhr-unibochum.de/thermo/Software/Seiten/GERG_2004-eng.htm>.
- [93] Hendriks E, Georgios M, Dohrn R, de Hemptinne J-C, Economou IG, Zilkni FL, et al. Industrial requirements for thermodynamics and transport properties. *Ind Eng Chem Res* 2010;49:11131–41.
- [94] Vidal J. Equations of state – reworking the old forms. *Fluid Phase Equilib* 1983;13:15–33.