

Calculation of Solid-Vapor Equilibria for Cryogenic Carbon Capture

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Abstract

This work deals with the thermodynamic modelling of phase equilibria calculations in the presence of solid carbon dioxide. The proposed model is based on the classical approach for this type of phase equilibrium calculations, namely on the equality of components' fugacities in the different phases and on the use of an expression for the fugacity of the freezing component in the solid phase, which is derived by relating it to its fugacity in the vapor phase. The results obtained with the proposed method are validated on the basis of other results reported in the literature and of those obtained using another tool that makes use of Gibbs free energy minimization. The good agreement between the results obtained with the different methods suggests that the proposed approach can be used for determining suitable operating conditions for processes aimed at separating CO₂ out of flue gas by freezing it out.

Keywords: CO₂, carbon capture, solid-vapor equilibria, cryogenic gas separation, flue gas

1. Introduction

In recent years, the world has experienced an increase in the carbon dioxide (CO₂) concentration emitted to the atmosphere, which is considered to be responsible for the climate change. Carbon dioxide capture and storage (CCS) is a technology that involves capturing the CO₂ produced by large industrial plants, compressing it for transportation and, then, injecting it deep into a rock formation at a carefully selected and safe site for its storage (Global CCS Institute, 2019). The analyses carried out by the Intergovernmental Panel on Climate Change (IPCC) and by the International Energy Agency (IEA) have shown that CCS is an essential part of the path towards meeting climate change

and is one of the few technologies that can deliver negative emissions on a large enough scale to limit temperature rises to 1.5 °C (IPCC, 2018). This has boosted an intense research on CO₂ capture technologies. For example, when considering the CO₂ capture from flue gases produced by power plants (De Guido et al., 2018), novel technologies have been proposed to accomplish that, as alternatives to the conventional removal by means of amine scrubbing. Some of these novel technologies (*e.g.*, the CCC-ECL process (Jensen et al., 2015), the CO₂ anti-sublimation process (Clodic et al., 2005), the technology based on dynamically operated packed beds (Tuinier et al., 2010), the CO₂ capture and compression unit (CO₂CCU) (Zanganeh et al., 2009), the cryogenic CO₂ capture system based on Stirling coolers (Song et al., 2012)) are operated at low/cryogenic temperatures and involve the formation of dry ice.

CO₂ is also present in natural gas and, together with hydrogen sulphide and other components, is responsible for its acidity. In order to produce a sales gas, CO₂ removal is required down to a concentration that depends on the natural gas final use. Typically, 2 mol% CO₂ is the specification for a pipeline-quality natural gas, whereas 50 ppm is the commonly accepted specification if natural gas has to be transported as LNG (Pellegrini et al., 2015b). Several technologies have been developed for natural gas/biogas purification (Kohl and Nielsen, 1997). The conventional technology is based on chemical absorption into aqueous amines solutions. However, this has been proven to be high energy-demanding when the content of CO₂ in raw natural gas is higher than 8-9 mol% (Langè et al., 2015). This is the case of natural gases extracted from reservoirs located in South-East Asia, Central USA and other regions (Pellegrini et al., 2019), and also of biogas, which is a mixture of methane and typically 35-40 mol% CO₂, depending on the biogas source (Pellegrini et al., 2015a). To make the development of these low-quality natural gas reserves and the upgrading of biogas economically viable, novel low-temperature/cryogenic technologies have been developed (De Guido et al., 2015; Qyyum et al., 2020) as well. Some of them are based on distillation and involve (*e.g.*, the Controlled-Freeze-ZoneTM - CFZTM process (Kelley et al., 2011)) or not (*e.g.*, the Ryan-Holmes process (Holmes and Ryan, 1982), the DCCDTM technology (Pellegrini, 2014; Pellegrini et al., 2017)) the formation of dry ice. Other technologies (*e.g.*, Cryocell[®] (Hart and Gnanendran, 2009), CCCTM (Fazlollahi et al., 2017), cryogenic packed beds (Tuinier and van Sint Annaland, 2012), GPP[®] (Bauer et al., 2013), Cryopur (Cryopur, 2020), *etc.*) are not based on distillation, but on other concepts to make the CO₂ freeze out from natural gas or biogas.

As reported by Jensen and Kurata (Jensen and Kurata, 1971), the full potential of cryogenic processing cannot be realized until reliable cryogenic phase behavior data become as available to plant designers as are data at higher temperatures. Moreover, failure to account for solid formation could lead to incorrect process design and clogged process equipment and resultant plant shutdowns

and safety hazards in processes where the formation of solids has to be avoided. Therefore, this requires being able to satisfactorily predict the thermodynamic behaviour of the system of interest, also in the presence of solid(s).

This work focuses on the modelling of phase equilibria in the presence of solid CO₂, with particular attention devoted to solid-vapour equilibrium (SVE) conditions for flue gas mixtures. Indeed, phase equilibria in the presence of dry ice for flue gas are less investigated in the literature with respect to natural gas and biogas mixtures, as proved by the lack of experimental data for the former system at SVE conditions. This is why, for assessing the reliability of the proposed thermodynamic approach, which is presented in Section 2, its results are discussed in Section 3) on the basis of the results reported in the literature (Baxter et al., 2009) and of those obtained by using another tool that is based on a different approach, i.e. Gibbs free energy minimization.

2. Thermodynamic framework

This section deals with the thermodynamic framework of this work. A key point for modeling SVE conditions is how to express the fugacity in the solid phase if a cubic Equation of State (EoS) is used to represent the volumetric behavior in the fluid phases, which does not directly take into account the solid phase. The expressions typically reported in the literature are summarized in Section 2.1, while the following Section 2.2 focuses on the proposed thermodynamic approach, the results of which have been validated on the basis of those obtained using the RGibbs tool available in the Aspen Plus[®] (AspenTech, 2016b) process simulator. To our knowledge, it is the only calculation block available in Aspen Plus[®] that is able to solve a system involving phase equilibria also in the presence of a solid phase (Schach et al., 2011). It uses Gibbs free energy minimization techniques with phase splitting, instead of methods based on the equality of fugacities of each component in each phase. The system is considered at equilibrium when the distribution of the components corresponds to the minimum of the Gibbs free energy (subject to atom balance constraints). According to the literature from Aspen Technology, this method can be used for any number of phases and components and always yields stable solutions. However, since the RGibbs tool cannot handle phase equilibria between solid and fluid phases of a component directly (e.g., CO₂-dry ice equilibria), it is necessary to identify the solid component as a different one.

2.1 Expressions for the fugacity of a solid pure component for SVE calculations

As reported by Riva et al. (Riva et al., 2014) different expressions are used in the literature for the calculation of solid fugacity in solid-liquid and solid-vapour equilibria (respectively denoted by SLE and SVE), assuming in both cases that the solid phase consists of the pure freezing component.

Focusing on SVE conditions for pure CO₂, Soave (Soave, 1979) obtained such conditions by equating the fugacities of the pure component in the two phases (Eq. (1)), and relating the one in the solid phase to that in the liquid state, at the same temperature, T , and pressure, P (Prausnitz et al., 1999), Eq. (2). The Soave-Redlich-Kwong (SRK) EoS (Soave, 1972) was used to calculate the fugacities in the liquid and vapour phases, whereas the terms $(\Delta h_{fus}/R/T_{fus})$ and $(\Delta C_p/R)$ were determined to best fit the experimental vapour pressures of the solid.

$$f_{CO_2}^S(T, P) = f_{CO_2}^V(T, P) \quad (1)$$

$$\ln \frac{f_{CO_2}^S(T, P)}{f_{CO_2}^L(T, P)} = -\frac{\Delta h_{fus}}{RT_{fus}} \left[\frac{T_{fus}}{T} - 1 \right] + \frac{\Delta C_p}{R} \left(\frac{T_{fus}}{T} - 1 - \ln \left(\frac{T_{fus}}{T} \right) \right) \quad (2)$$

The same expression (Eq. (2)) for the solid fugacity has been also used for performing SLVE calculations considering both binary and multicomponent mixtures containing CO₂ (De Guido et al., 2014).

As far as SVE conditions for mixtures containing CO₂ are concerned, Eggeman and Chafin (Eggeman and Chafin, 2003; Eggeman and Chafin, 2005) considered the possibility that solid CO₂ is formed by desublimation from a vapour mixture when its content exceeds its solubility limit. In this case, they selected an EoS approach (using the Peng-Robinson EoS (Peng and Robinson, 1976), with binary interaction parameters defaulted to the values used for VLE calculations) to derive the equilibrium relation, Eq. (3), subject to the fact that the temperature has to be lower than the CO₂ triple point temperature for the solid to be stable if formed. The same approach was also later used by Zarenezhad and Eggeman (ZareNezhad and Eggeman, 2006) to model SVE occurring in a NGLs plant demethanizer column. In addition to that, also Riva and Stringari (Riva et al., 2014), who however focused on SLVE models for cryogenic biogas upgrading, have written the equality of fugacities of CO₂ in the solid (pure CO₂) and vapour mixture in the form of Eq. (3) when they considered SVE.

$$P_{subl,CO_2}(T) \phi_{CO_2}^V(T, P_{subl,CO_2}(T)) \exp \left[\frac{v_{CO_2}^S}{RT} (P - P_{subl,CO_2}(T)) \right] = P \hat{\phi}_{CO_2}^V(T, P, \mathbf{x}^V) x_{CO_2}^V \quad (3)$$

In Eq. (3):

- $\phi_{CO_2}^V(T, P_{subl,CO_2}(T))$ is the fugacity coefficient of pure CO₂ in the vapor phase evaluated at its sublimation pressure and equilibrium temperature;
- $\hat{\phi}_{CO_2}^V(T, P, \mathbf{x}^V)$ is the fugacity coefficient of CO₂ in the vapor mixture evaluated at the equilibrium temperature, pressure and composition;
- $v_{CO_2}^S$ is the solid molar volume of CO₂;
- the exponential term on the left-hand side is the well-known Poynting factor.

2.2 Proposed method

This section outlines the procedure that has been developed to perform SVE calculations for a flue gas mixture. Since the number and type of phases present at equilibrium are not known a-priori, the choice of studying SVE conditions for the system of interest has to be considered as an assumption and should be checked using methods that allow the computation of simultaneous phase and – when they apply - chemical equilibria (Castillo and Grossmann, 1981; Gupta et al., 1991; Lantagne et al., 1988). The considered flue gas mixture consists of 14.0 mol% CO₂, 83.0 mol% N₂ and 3.0 mol% O₂ (Baxter et al., 2009), which is typical of a flue gas from coal-fired power plants.

The problem is considered as a two-phase flash problem (illustrated in Figure 1) with assigned pressure and recovery of CO₂ in the solid phase, which is assumed to be composed of pure CO₂.

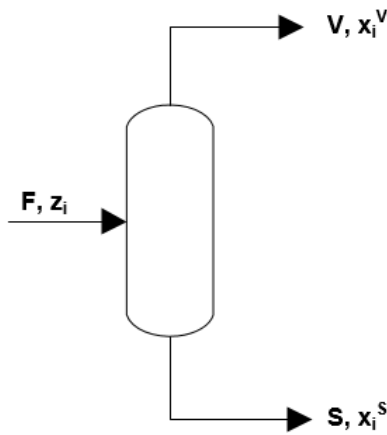


Figure 1. Two-phase flash with an inlet stream of molar flow rate F with composition \underline{z} and the vapour and solid outlet phases (of molar flow rates, respectively, V and S) with compositions \underline{x}^V and \underline{x}^S , respectively.

The aim of the work is to plot the equilibrium temperature curve as a function of pressure for each recovery level (0 %, 90 %, 95 % and 99 %), defined according to Eq. (4), where S and F denote the molar flow rates of the solid phase and of the feed stream, respectively, and $x_{CO_2}^S$ and z_{CO_2} refer to the molar fraction of CO₂ in the solid phase and in the feed stream, respectively. The values considered for the recovery of CO₂ in the solid phase have been chosen for comparison with the results presented by Baxter and coworkers (Baxter et al., 2009), even if it is not clearly stated which thermodynamic approach has been adopted to obtain them.

$$REC = \frac{S \cdot x_{CO_2}^S}{F \cdot z_{CO_2}} = \frac{S}{F \cdot z_{CO_2}} \quad (4)$$

From Eq. (4), it is evident that:

$$S = F \cdot z_{CO_2} \cdot REC \quad (5)$$

By combining the overall material balance (Eq. (6), where V denote the molar flow rate of the vapour phase) and the components' material balances (Eq. (7), which holds for each i -th component different from CO₂ (namely, N₂ and O₂), and Eq. (8) that holds for CO₂), it is possible to get the composition of the vapor phase at equilibrium for each case study (i.e., for each pair of pressure and CO₂ recovery), assuming a unitary value for the feed flow rate, F .

$$V = F - S \quad (6)$$

$$Vx_i^V = Fz_i \quad (7)$$

$$Vx_{CO_2}^V = (1 - REC) \cdot Fz_{CO_2} \quad (8)$$

2.2.1. Ideal case study

If the system under investigation is assumed to have an ideal behaviour (ideal case), the SVE problem can be solved using the Rachford-Rice equation (Eq. (9), where NC refers to the total number of components in the system), which is a function of the equilibrium temperature, T .

$$f(T) = \sum_{j=1}^{NC} \frac{z_j (k_j - 1)}{(k_j - k_r) \frac{Vx_r^V}{Fz_r} + k_r} = 0 \quad (9)$$

In Eq. (9), the subscript r refers to CO₂ (namely, the reference component for which the recovery in the solid phase is known) and the equilibrium constants are expressed according to Eqs. (10)-(11).

$$k_r = \frac{x_{CO_2}^V}{x_{CO_2}^S} = \frac{P_{subl,CO_2}(T)}{P} \quad (10)$$

$$k_j = \frac{x_j^V}{x_j^S} \quad j = 1, \dots, NC \quad (11)$$

The sublimation pressure, $P_{subl,CO_2}(T)$, in Eq. (10) and in Eq. (3), has been calculated with Eq. (12), using the expression proposed by Jensen et al. (Jensen et al., 2015), where $P_{subl,CO_2}(T)$ is in Pa and T in K.

$$P_{CO_2}^{subl}(T) = \exp\left(57.52 - \frac{3992.84}{T} - 4.9003 \cdot \ln(T) + 2.415 \cdot 10^{-15} T^6 + \frac{8125.6}{T^2}\right) \quad (12)$$

Since the solid phase is assumed to consist of pure CO₂, the molar fraction of the other species in the solid phase is equal to zero. So, taking the limit for $k_j \rightarrow \infty$ for $j \neq \text{CO}_2$, of the Rachford-Rice equation (Eq. (9)), Eq. (13) is obtained.

$$f(T) = \frac{z_{\text{CO}_2}(k_{\text{CO}_2} - 1)}{k_{\text{CO}_2}} + \frac{z_{\text{N}_2}}{\frac{Vx_{\text{CO}_2}^r}{Fz_{\text{CO}_2}}} + \frac{z_{\text{O}_2}}{\frac{Vx_{\text{CO}_2}^r}{Fz_{\text{CO}_2}}} = 0 \quad (13)$$

Solving Eq. (13), it is possible to obtain the equilibrium temperature for each pair of pressure and recovery values.

2.2.2. Real case study

If the system under investigation is assumed to have a real behavior (real case), following the classical approach based on the equality of the chemical potential of each component in the two phases, Eq. (3) must be true for CO₂. In order to compute the fugacity coefficients, the PR EoS (Peng and Robinson, 1976) has been used. Therefore, given the recovery of CO₂ in the solid phase and the pressure of the system, Eq. (3) is a function of the equilibrium temperature only.

It is important to point out that the following assumptions have been made when solving the SVE problem for the flue gas case study under investigation in this work: i) the value of the solid molar volume, has been assumed constant and equal to 0.0282 m³/kmol (Pellegrini et al., 2020); ii) a constant value of the binary interaction parameters, k_{ijs} , has been considered and taken from the Aspen Hysys[®] V9.0 (AspenTech, 2016a) process simulator.

3. Results

In this section, the results obtained with the proposed approach and with the RGibbs tool are presented and discussed, first focusing on the validation of the expression (Eq. (12)) used for the calculation of the CO₂ sublimation pressure as a function of temperature.

3.1 Correlation for CO₂ sublimation pressure

Before solving the SVE problem described above, the reliability of the correlation used for the CO₂ sublimation pressure (Eq. (12)) has been tested. For comparison purposes, the correlation (Eq. (14)) proposed by Span and Wagner (Span and Wagner, 1996) has been also taken into account. In Eq. (14), $T_t = 216.592$ [K] (triple point temperature of CO₂), $P_t = 0.51795$ [MPa] (triple point pressure of CO₂), $a_1 = -14.740846$, $a_2 = 2.4327015$, and $a_3 = -5.3061778$.

$$\ln \left(\frac{P_{\text{CO}_2}^{\text{subl}}}{P_t} \right) = \frac{T_t}{T} \left\{ a_1 \left(1 - \frac{T}{T_t} \right) + a_2 \left(1 - \frac{T}{T_t} \right)^{1.9} + a_3 \left(1 - \frac{T}{T_t} \right)^{2.9} \right\} \quad (14)$$

The results obtained using Eqs. (12) and (14) are illustrated in the parity plots in Figure 2.

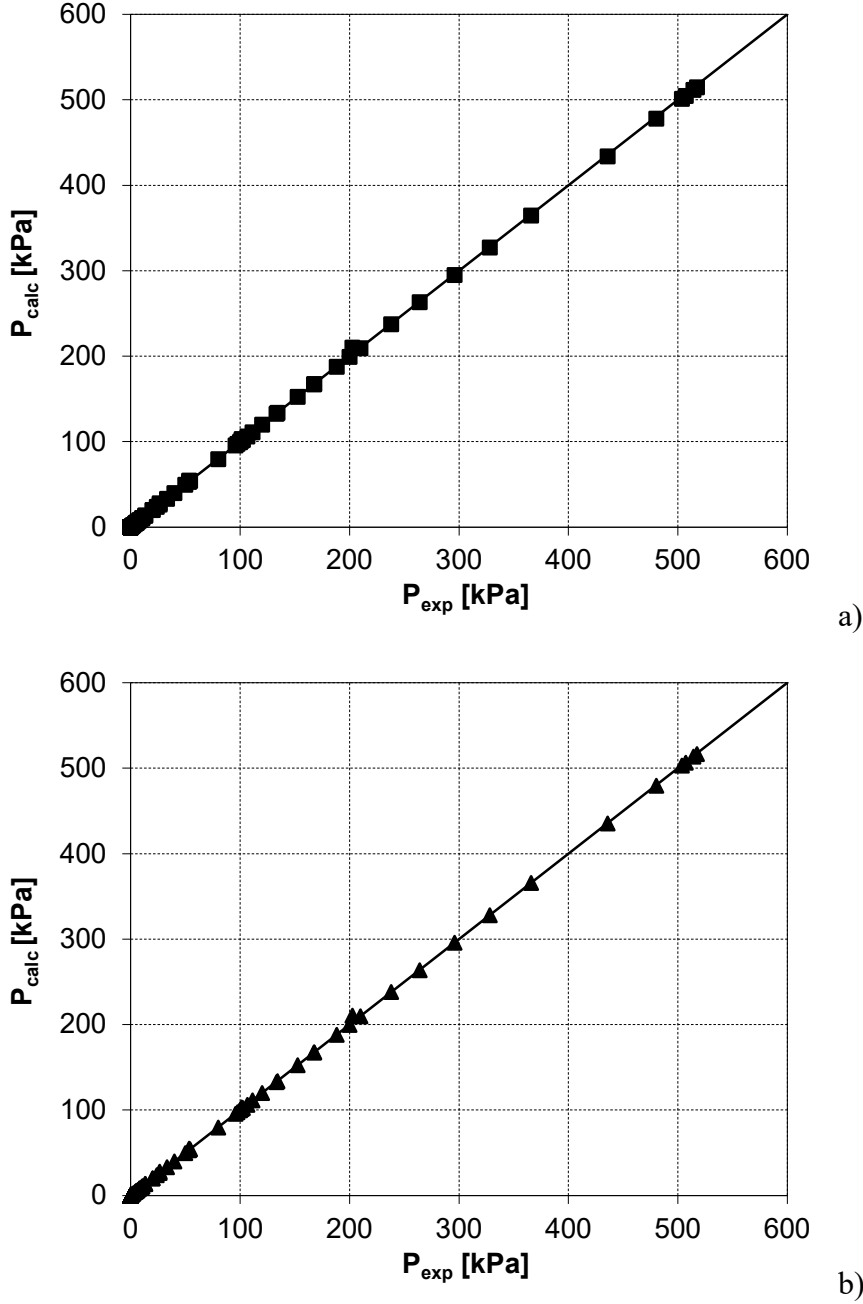


Figure 2. Parity plot for CO₂ sublimation pressure. Experimental data have been taken from the literature (Bryson III et al., 1974; Fernández-Fassnacht and Del Río, 1984; Giaque and Egan, 1937; Kaye and Laby, 1973; Stull, 1947; Thermodynamics Research Center, 1980) and cover the temperature range 69.7-216.6 K. Calculated values have been obtained using: a) Eq. (12) (Jensen et al., 2015); b) Eq. (14) (Span and Wagner, 1996).

As shown in Figure 2, both Eqs. (12) and (14) perform well in predicting CO₂ sublimation pressures. To quantify their performances the deviations for the j -th point have been computed according to Eqs. (15)-(17), where N_{pt} stands for the number of points. Results are summarized in Table 1 and suggest that the correlation proposed by Jensen et al. (Jensen et al., 2015), which has been used in the expression of the fugacity of pure CO₂ in the solid phase (Eq. (3)), performs better than the one proposed by Span and Wagner (Span and Wagner, 1996).

$$err_j = \frac{P_{calc,j} - P_{exp,j}}{P_{exp,j}} \quad (15)$$

$$AAD\% = \frac{100}{N_{pt}} \sum_{j=1}^{N_{pt}} |err_j| \quad (16)$$

$$Bias\% = \frac{100}{N_{pt}} \sum_{j=1}^{N_{pt}} err_j \quad (17)$$

Table 1. Summary of the statistical errors (AAD% and Bias%) in calculating sublimation pressures at fixed temperatures considering the overall temperature range (69.69-216.56 K), the low-temperature (low-T) range (69.69-102.5 K) and the high-temperature (high-T) range (194.23-216.56 K).

	T range	Sublimation pressure calculated by Eq. (12)	Sublimation pressure calculated by Eq. (14)
AAD%	overall	15.76	26.85
	low-T	31.28	54.29
	high-T	1.20	1.11
Bias%	overall T	-14.5	-26.1
	low-T	-30.27	-54.29
	high-T	0.21	0.33

3.2 SVE calculations

Figure 3 and Figure 4 show the equilibrium temperatures calculated according to the approach previously described in Section 2 for the ideal and real case studies, respectively. The assumption of an ideal behaviour (Figure 3) leads to results that are in agreement with those presented in the literature (Baxter et al., 2009) up to about 1.5 MPa. For higher pressures, this assumption does not hold anymore and Eq. (13) is no more adequate to describe the physics of the problem. Indeed, for pressures higher than about 1.5 MPa the curves in Figure 3 begin to deviate from those in Figure 4, which have been obtained assuming a real behaviour for the considered ternary flue gas mixture.

In Figure 4, two frost point curves (corresponding to a null value of the recovery of CO₂ in the solid phase) are plotted: the solid purple line has been obtained using the proposed approach, whereas the dotted and dashed purple line has been reproduced using the “CO₂ Freeze Out” tool available in Aspen Hysys[®] (AspenTech, 2016a). Such a tool is used to calculate the incipient solid formation point for mixtures containing CO₂ by means of an EoS-based approach. The model can be used for predicting the initial solid formation point (temperature) in equilibrium with either a vapour or liquid phase that exists at the stream conditions. The fugacity of the resultant pure CO₂ solid is obtained

from the known enthalpy of fusion, triple point temperature and heat capacity difference between liquid and solid, therefore by means of an approach that makes use of an expression of the type reported in Eq. (2). The fugacity of the corresponding fluid phase (in equilibrium with the solid) is calculated from the EoS (CO₂ solid prediction is restricted to the PR EoS and SRK EoS). Despite the different expression used for the fugacity of CO₂ in the solid phase, the two frost point curves in Figure 4 show a good agreement with each other. As for the symbols shown in this figure, they give the values of each curve in correspondence of the values of pressure where the proposed approach registers a maximum (filled symbols and coloured numbers), and in correspondence of the values of pressure where a maximum is registered by other literature works (Baxter et al., 2009) (empty symbols and black numbers). This shows that the proposed method is about 2 K more conservative in correspondence of the value of pressure where the maximum is reported in the literature.

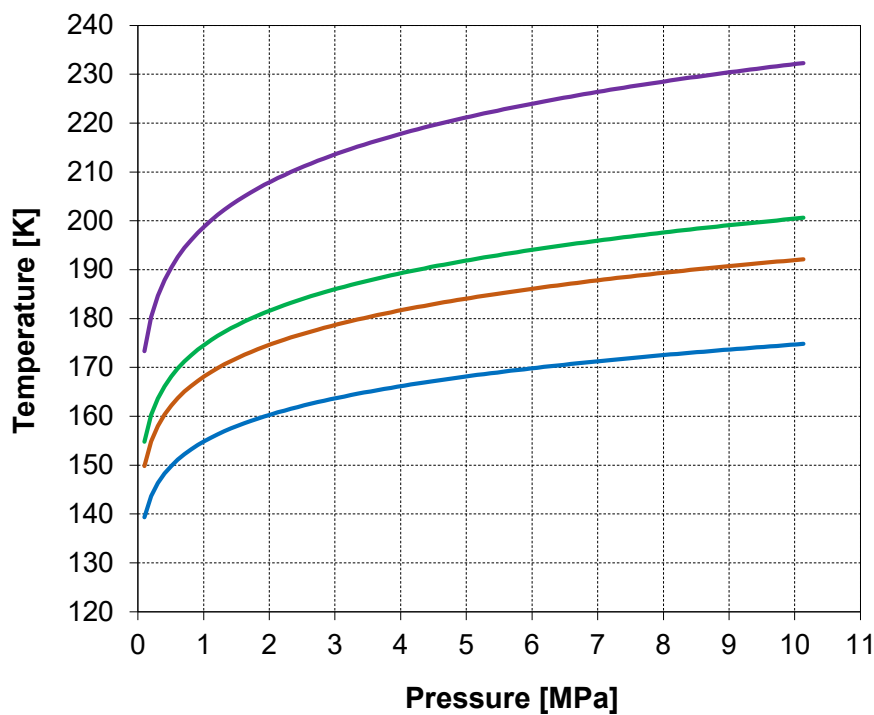


Figure 3. SVE temperatures as a function of pressure (ideal case study) at assigned recovery of CO₂ in the solid phase: 0 % or frost point (purple line); 90 % (green line); 95 % (brown line); 99 % (blue line).

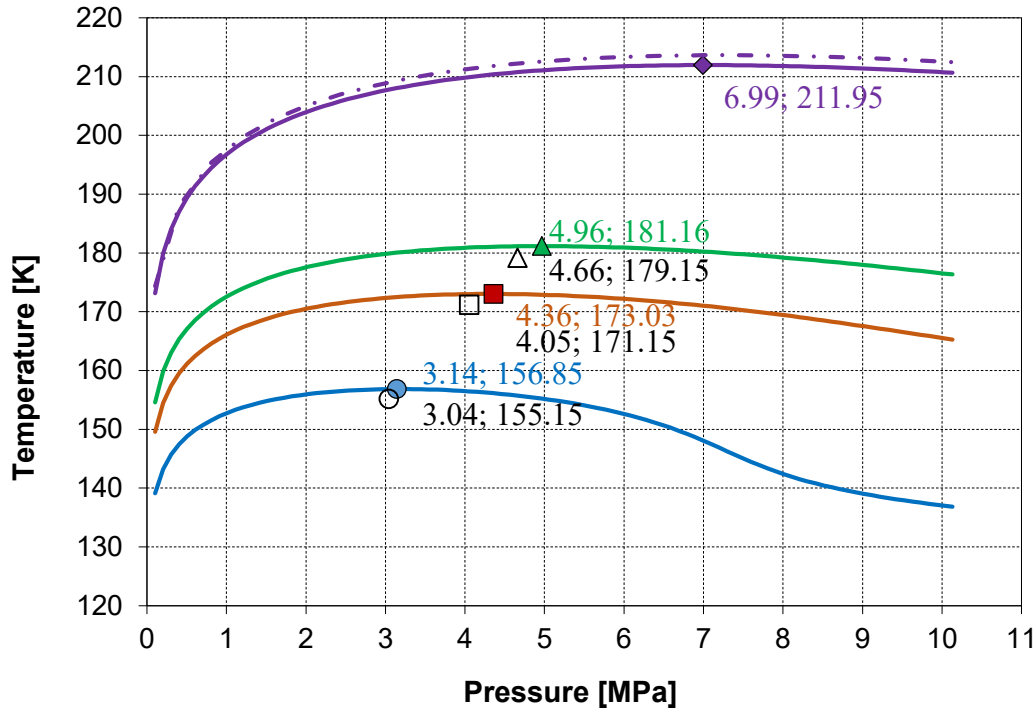


Figure 4. SVE temperatures as a function of pressure (real case study) at assigned recovery of CO₂ in the solid phase: 0 % or frost point (purple solid line; the purple dotted and dashed line has been obtained using the “CO₂ Freeze Out” tool available in the Aspen Hysys[®] process simulator); 90 % (green line); 95 % (brown line); 99 % (blue line). Filled symbols refer to the P, T pairs where the calculation performed by means of the proposed approach registers the maximum temperature; empty symbols refer to the P, T pairs at the pressure where the maximum temperature is registered as reported in the literature (Baxter et al., 2009).

Figure 5 shows the results obtained using the RGibbs tool available in Aspen Plus[®] V9.0 (AspenTech, 2016b), together with those obtained by the proposed approach and with those presented in the literature (Baxter et al., 2009) (that have been taken from the available curves using the “Get Data” tool). As illustrated in Figure 5, the results obtained with RGibbs are very close to those obtained by the proposed approach, in particular for pressures lower than 5 MPa. The difference with respect to the approach used in the literature (Baxter et al., 2009) could be due to the different assumptions made to solve the equilibrium problem (which are, however, not clearly stated in the original paper). It is unlikely that the difference is due to the little amount (100 ppm) of impurities (HCl, NO and SO) contained in the dry flue gas considered by Baxter and co-workers (Baxter, 2011).

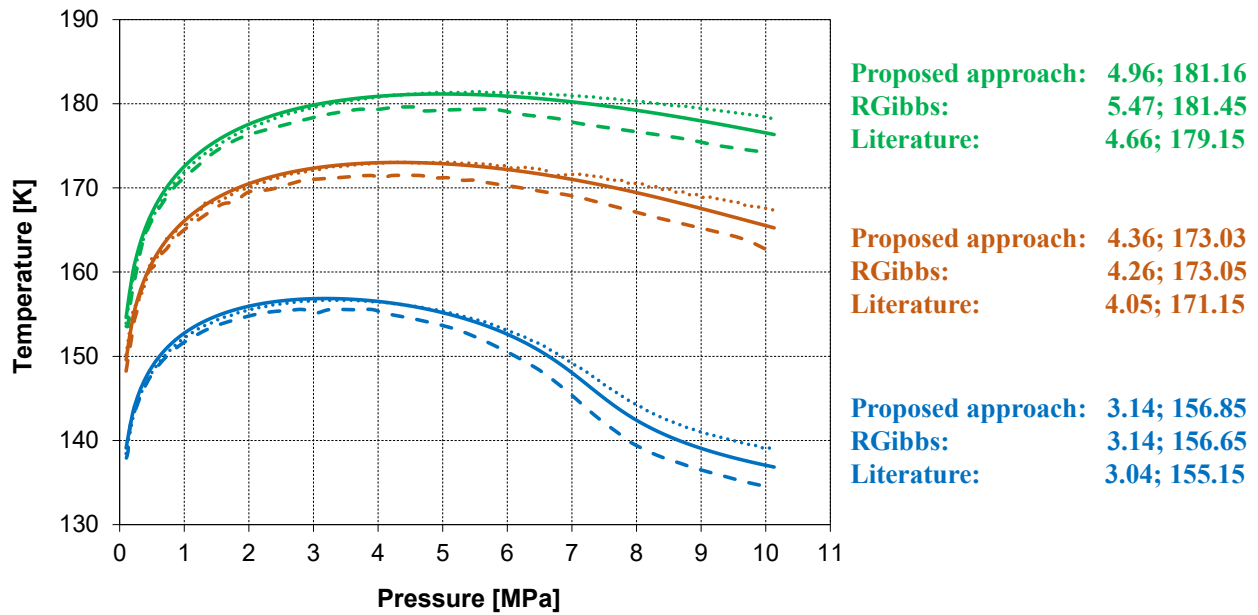


Figure 5. SVE temperatures as a function of pressure at assigned recovery of CO₂ in the solid phase for the real case study: results obtained by the proposed approach (solid line), by using the RGibbs tool of Aspen Plus[®] V9.0 (AspenTech, 2016b) (dotted line) and the ones presented in the literature (Baxter et al., 2009) (dashed line). The different colours refer to the different CO₂ recovery values: 90% (green); 95% (brown); 99% (blue). For each curve the values reported on the right correspond to the pressure (x coordinate, MPa) at which each calculation approach registers the maximum temperature (y coordinate, K).

The results shown in Figure 5, despite some differences among the different approaches, allow to state that, for achieving a higher recovery of CO₂ in the solid phase at a given pressure, it is necessary to operate the process at a lower temperature. Moreover, the maximum trend the curves in Figure 5 exhibit suggests that, if a certain CO₂ recovery is desired, the process can be operated at a higher temperature at increasing pressure and, viceversa, for pressures up to the maximum point. Beyond the maximum in Figure 5, higher pressures and lower temperatures are required to achieve the same CO₂ recovery in the solid phase, both of which would make the CO₂ separation process more energy-intensive. Therefore, for each curve in Figure 5, the portion up to the maximum is the one corresponding to the operating conditions of interest for the process, which aims at separating CO₂ from a flue gas mixture by desublimation.

4. Conclusions

This work presents a thermodynamic approach for solid-vapour equilibrium calculations for flue gas mixtures. The motivation for this lies in the recent development of novel low-temperature/cryogenic technologies for the separation of CO₂ from gaseous streams, including flue gas. Such processes have received great attention to cope with the disadvantages of conventionally adopted technologies mainly based on absorption. Since some of these processes, in particular those based on CO₂

desublimation, are operated at conditions where CO₂ freezes out, it is important to have a tool capable of satisfactorily predicting phase equilibria in the presence of a solid phase, which is not always taken into account in phase equilibria calculations. This is important for a correct process design. In this work, a thermodynamic model is proposed for this purpose and the obtained results are validated on the basis of those reported in the literature and of those obtained with a calculation tool that is based on a different approach, i.e. Gibbs free energy minimization. The good agreement between the different methods suggests that the proposed approach can reliably be used to determine the operating conditions of low-temperature/cryogenic processes aimed at separating CO₂ out of flue gas. In particular, for achieving 99 % recovery of CO₂ in the solid phase, temperatures of about 140 K have to be reached at atmospheric pressure or higher temperatures (up to about 155 K) at increasing pressures up to about 3 MPa. Above this pressure value, due to the maximum trend exhibited by the temperature-pressure curve at fixed CO₂ recovery, the process should be operated at lower temperatures, which is disadvantageous since this makes it more energy-intensive.

Nomenclature

Acronyms

<i>CCCTM</i>	Cryogenic Carbon Capture TM
<i>CCC-ECL</i>	External Cooling Loop Cryogenic Carbon Capture
<i>CCS</i>	Carbon dioxide Capture and Storage
<i>CFZTM</i>	Controlled Freeze Zone TM
<i>CO₂CCU</i>	CO ₂ Capture and Compression Unit
<i>DCCDTM</i>	Dual Column Cryogenic Distillation TM
<i>EoS</i>	Equation of State
<i>GPP[®]</i>	Gastreatment Power Package
<i>IEA</i>	International Energy Agency
<i>IPCC</i>	Intergovernmental Panel on Climate Change
<i>LNG</i>	Liquefied Natural Gas
<i>NGLs</i>	Natural Gas Liquids
<i>PR EoS</i>	Peng-Robinson EoS
<i>REC</i>	Recovery of CO ₂ in the solid phase (Eq. (28))
<i>SLE</i>	Solid-Liquid Equilibria
<i>SLVE</i>	Solid-Liquid-Vapour Equilibria
<i>SRK EoS</i>	Soave-Redlich-Kwong EoS
<i>SVE</i>	Solid-Vapour Equilibria

VLE Vapour-Liquid Equilibria

Symbols

a_1, a_2, a_3	Parameters in Eq. (14)
f	Fugacity [MPa]
F	Molar flow rate of the feed stream [mol/h]
k	K -value
k_{ij}	EoS binary interaction parameter
NC	Number of components
N_{pt}	Number of points
P	Pressure [MPa]
P_{subl}	Sublimation pressure [MPa]
P_t	Triple point pressure [MPa]
R	Gas constant [J/mol/K]
S	Molar flow rate of the solid phase [mol/h]
T	Temperature [K]
T_{fus}	Fusion (melting) temperature [K]
T_t	Triple point temperature [K]
v	Molar volume [m ³ /mol]
V	Molar flow rate of the vapor phase [mol/h]
x	Component molar fraction
z	Component molar fraction in feed stream

Greek symbols

ΔC_p	Difference between the molar specific heat of liquid and solid pure component [J/mol/K]
Δh_{fus}	Molar enthalpy of fusion [J/mol]
ϕ	Fugacity coefficient

Subscripts

CO_2	Referred to CO ₂
i	Referred to the i -th component
j	Referred to the j -th component/point
r	Referred to the reference component

Superscripts

<i>L</i>	Referred to the liquid phase
<i>S</i>	Referred to the solid phase
<i>V</i>	Referred to the vapour phase
\wedge	Referred to mixture properties

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