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Phase Equilibria Analysis in the Presence of Solid Carbon Dioxide

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Carbon dioxide can be found in several gaseous streams, from which it has to be separated in order to meet commercial specifications or to comply with environmental regulations. Some examples are natural gas, which has to be sweetened to a pipeline-quality gas or to liquefied natural gas, and biogas, which has to be upgraded to biomethane or liquefied biomethane.

In recent years, an intense research has been carried out to develop novel technologies for the separation of CO_2 from these gaseous streams, considering the new challenges the world has to face. In this respect, the need for processing high-CO_2 content natural gases for meeting the increased demand for clean energy can be mentioned, which requires technologies other than the commercially available ones for a profitable exploitation of these low-quality reserves. A growing attention has been devoted to low-temperature/cryogenic technologies for this purpose, which requires reliable methods to correctly describe the thermodynamics of phase equilibria in the presence of solid CO_2 that plays a key role in the design of such processes. This work presents a thermodynamic method for the simultaneous stability analysis and multiphase equilibrium calculations of CO_2 mixtures with hydrocarbon and non-hydrocarbon components. The experimental data available in the literature for CO_2 frost points and solid-vapour equilibrium conditions have been used to validate the proposed method. The calculation results have been also compared with those obtained by using the RGibbs tool available in the Aspen Plus® process simulator, obtaining a good agreement between the two methods.

1. Introduction

Single-stage phase equilibrium calculations typically involve specification of a feed composition (global composition, z_i) and two additional variables, normally selected from temperature (T), pressure (P), vapour phase fraction (α_V), enthalpy, entropy, or a phase mole fraction. Such specifications, however, have to guarantee a unique solution. This is the case for specified T and P, where the solution corresponds to the global minimum in the Gibbs energy. A common problem in the calculation of phase equilibria is that the number of phases that are present at equilibrium is not known a-priori. Hence, two solution strategies have been applied. In the first one, a non-linear programming approach is used to minimize the Gibbs energy function with a large number of phases (Castillo and Grossmann, 1981; Lantagne et al., 1988). The second approach is to sequentially add a phase in the computations and test the stability of the solution (Michelsen, 1982).

Gupta (Gupta, 1990) developed a new stability criterion for multiphase reacting/non-reacting systems that allows the simultaneous calculation of phase stability and flash computations. The proposed solution provides a unified set of simultaneous equations that describes phase equilibrium, chemical equilibrium (if this applies) and the stability of the system. Gupta (1990) applied the model to compute the phase behaviour of systems involving vapour-liquid or vapour-liquid-liquid equilibria. Ballard and Sloan (Ballard and Sloan, 2004) have further investigated the model proposed by Gupta (1990) for the simultaneous calculation of stability and flash computations to predict equilibrium conditions with gas hydrates. More recently, Tang and co-workers (Tang et al., 2019) have extended this model to the solid-liquid-vapour-phase flash calculation of the CH_4-CO_2 mixture at a given P, T, and feed gas composition. In their study, the fugacity coefficients of fluid phases (i.e., vapour and liquid) are calculated using the GERG-2004 Equation of State (EoS), while the EoS that describes the thermodynamic behaviour of solid CO_2 is based on the Gibbs free energy method suggested by Jäger and Span (Jäger and Span, 2012). However, to our knowledge, this approach has not been applied to the simultaneous calculation of phase stability and multiphase equilibria of CO_2 mixtures with components other than methane. This is of interest for practical applications like low-temperature/cryogenic technologies (De Guido and Pellegrini, 2019a) for CO_2 removal from low-quality natural gas reserves (Pellegrini et al., 2015) or biogas (Qyyum et al., 2020), which are operated at T and P conditions where dry ice can form in multicomponent systems. This work contributes to this through the application of the method to the prediction of frost points and solid-vapour equilibrium (SVE) conditions of mixtures containing CO_2, methane and nitrogen, a contaminant that is present in both natural gas (De Guido et al., 2019b) and biogas.

2. Method

In this section, the theory behind the thermodynamic approach, which has been implemented in a Fortran code, is described.

2.1 Thermodynamic model

For a system with N_c components and π possible phases, if all π phases are present at equilibrium, the following must be true, Eq(1).

$$\frac{\hat{f}_{ir}}{\hat{f}_{ik}} = \frac{x_{ir}\hat{\phi}_{ir}P}{x_{ik}\hat{\phi}_{ik}P} = 1 \qquad \text{for i=1, …, } N_c \text{ and for k = 1,…, } \pi \tag{1}$$

In Eq(1), the subscript r refers to a reference phase, $\hat{f}_{ik}$ to the fugacity of component i in phase k, x_{ik} to the mole fraction of component i in phase k, and $\hat{\phi}_{ik}$ to the fugacity coefficient of component i in phase k. Eq(1) can be rewritten making use of the equilibrium constant for component i:

$$K_{ik} = \frac{x_{ik}}{x_{ir}} = \frac{\hat{\phi}_{ir}}{\hat{\phi}_{ik}} \qquad \text{for i=1, …, } N_c \text{ and for k = 1,…, } \pi \tag{2}$$

As reported by Ballard (Ballard, 2002), it is necessary to seek for an equation that reduces to Eq(2) for phases that are present at equilibrium, but not for phases that are not present. Eq(3) can be used for this purpose.

$$\frac{\hat{f}_{ir}}{\hat{f}_{ik}} \begin{cases} = 1 & if\ \ phase\ k\ is\ present \\ < 1 & if\ \ phase\ k\ is\ not\ present \end{cases} \qquad \text{for i=1, …, } N_c \text{ and for k = 1,…, } \pi \tag{3}$$

By multiplying the mole fraction ratio in Eq(2) by the fugacity ratio in Eq(3), Eq(4) is obtained:

$$K_{ik} = \frac{x_{ik}}{x_{ir}} \exp\left[-\ln \frac{\hat{f}_{ik}}{\hat{f}_{ir}} \right] \qquad \text{for i=1, …, } N_c \text{ and for k = 1,…, } \pi \tag{4}$$

Gupta (1990) showed that the natural log of the ratio of fugacities in Eq(4) is equal for all components in a given phase k, and referred to this value as the stability of phase k, θ_k. Hence, rearranging Eq(4):

$$\frac{x_{ik}}{x_{ir}} = K_{ik} e^{\theta_k} \qquad \text{for i=1, …, } N_c \text{ and for k = 1,…, } \pi \tag{5}$$

Eq(5) is valid for all phases regardless of that phase's presence in the system. Gupta (1990) showed that defining the mole fraction ratio in this manner is equivalent to minimizing the Gibbs energy of the system conditional to:

$$S_k = \frac{\alpha_k \theta_k}{\alpha_k + \theta_k} = 0 \qquad \text{for k = 1,…, } \pi \tag{6}$$

With reference to Eq(6), it can be noticed that:

- if $\alpha_k > 0$, then phase k is present and $\theta_k = 0$;
- if $\alpha_k = 0$, then phase k is not present and $\theta_k \neq 0$.

By including Eq(5) into the combined overall and components' material balances and considering the difference between the stoichiometric equation for each phase and the one for the reference phase, it is possible to derive the objective function in Eq(7).

$$E_k = \sum_{i=1}^{Nc} \frac{z_i (K_{ik} e^{\theta_k} - 1)}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} = 0 \qquad \text{for k = 1,…, π} \qquad (7)$$

Therefore, the proposed method is based on the solution of the following system of (2π-1) equations in the (2π-1) unknowns, namely α_k (k = 1, …, π) and θ_k (k = 1, …, π and k ≠ r).

$$\begin{cases} S_k = \dfrac{\alpha_k \theta_k}{\alpha_k + \theta_k} = 0 & \text{for } k \ = 1,\ldots,(\pi - 1) \\ E_k = \displaystyle\sum_{i=1}^{Nc} \frac{z_i (K_{ik} e^{\theta_k} - 1)}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} = 0 & \text{for } k \ = 1,\ldots,(\pi - 1) \\ \alpha_r = 1 - \displaystyle\sum_{\substack{k=1 \\ k \neq r}}^{\pi} \alpha_k \end{cases} \qquad (8)$$

The above system (Eq(8)) is solved at a given set of K-values and composition. At the beginning, this requires to have initial estimates for molar phase fractions, α_k, for stability variables, θ_k, for K-values, K_{ik}, and for composition of phases, x_{ik}. The algorithm is started assuming that all phases are present with an equal amount of each, and, therefore, the stability variables are all zero (Ballard, 2002), and that K-values are composition-independent. Once the above system is solved, using the Newton-Raphson method, it is possible to calculate the mole fractions of each component in each phase using Eq(9) and the K-values removing the assumption according to which they were assumed composition-independent. Their expressions are reported in Table 1, depending on which phase is taken as the reference one. The fugacity coefficients in the vapour and liquid phases have been calculated with the Peng-Robinson Equation of State and the solid vapour pressure (P_{subl}) of CO_2 is calculated according to the 6-parameter correlation proposed by Jensen et al. (2015).

$$x_{ik} = \frac{z_i K_{ik} e^{\theta_k}}{1 + \sum_{\substack{j=1 \\ j \neq r}}^{\pi} \alpha_j (K_{ij} e^{\theta_j} - 1)} \qquad \text{for i=1, …, } N_c \qquad (9)$$

Table 1: Expressions for K_{ik} depending on which phase is taken as the reference (r) phase

K_{ik}	r = V	r = L	r = S
K_{iV}	$= \dfrac{x_{iV}}{x_{iV}} = 1$	$= \dfrac{x_{iV}}{x_{iL}} = \dfrac{\hat{\phi}_i^L (T, P, \mathbf{x}_L)}{\hat{\phi}_i^V (T, P, \mathbf{x}_V)}$	$\begin{cases} = \dfrac{x_i^V}{x_i^S} \rightarrow \infty & \text{for i} \neq \text{CO}_2 \\ = \dfrac{x_i^V}{x_i^S} = \dfrac{P_i^{subl}(T)}{P \cdot \hat{\phi}_i^V (T, P, \mathbf{x}_V)} & \text{for i} = \text{CO}_2 \end{cases}$
K_{iL}	$= \dfrac{x_{iL}}{x_{iV}} = \dfrac{\hat{\phi}_i^V (T, P, \mathbf{x}_V)}{\hat{\phi}_i^L (T, P, \mathbf{x}_L)}$	$= \dfrac{x_{iL}}{x_{iL}} = 1$	$\begin{cases} = \dfrac{x_i^L}{x_i^S} \rightarrow \infty & \text{for i} \neq \text{CO}_2 \\ = \dfrac{x_i^L}{x_i^S} = \dfrac{P_i^{subl}(T)}{P \cdot \hat{\phi}_i^L (T, P, \mathbf{x}_L)} & \text{for i} = \text{CO}_2 \end{cases}$
K_{iS}	$\begin{cases} = 0 & \text{for i} \neq \text{CO}_2 \\ = \dfrac{x_{iS}}{x_{iV}} = \dfrac{P \cdot \hat{\phi}_i^V (T, P, \mathbf{x}_V)}{P_{subl,i}(T)} & \text{for i} = \text{CO}_2 \end{cases}$	$\begin{cases} = 0 & \text{for i} \neq \text{CO}_2 \\ = \dfrac{x_{iS}}{x_{iL}} = \dfrac{P \cdot \hat{\phi}_i^L (T, P, \mathbf{x}_L)}{P_{subl,i}(T)} & \text{for i} = \text{CO}_2 \end{cases}$	$= \dfrac{x_i^S}{x_i^S} = 1$

2.2 Application of the thermodynamic model to the prediction of frost points and SVE conditions

In this work, the calculation of CO_2 frost points and SVE conditions has been carried out, respectively, for the CO_2-CH_4 mixture and for the CO_2-CH_4-N_2 mixture. Calculations have been also performed using the RGibbs tool available in Aspen Plus$^{®}$ V9.0 (AspenTech, 2016) that, to our knowledge, is the only unit operation able to deal with phase equilibria also in the presence of a solid phase if properly set-up for this type of phase equilibrium calculations (Pellegrini et al., 2020). As for the calculation of CO_2 frost points for the binary mixture, the same P and global composition as the experimental ones (Pikaar, 1959; Agrawal and Laverman, 1995; Le and Trebble, 2007; Zhang et al., 2011) have been specified and the temperature has been varied so that the highest value for which the CO_2 solidification ratio (defined as the ratio between the solid molar phase fraction and the CO_2 mole fraction in the feed stream) is less than or equal to 0.001 has been taken as the T of frost point. Such calculated temperature (T_{calc}) is compared with the one reported in the literature (T_{exp}). As for the calculation of SVE conditions for the ternary mixture, the experimental data (Xiong et al., 2015) are given in terms of T, P, mole fraction of N_2 in the ternary mixture (i.e., 3 mol % or 5 mol %) and composition of the vapour phase at equilibrium. In this case, the global composition, which is required as input data in addition to P and T, has been assigned considering the given mole fraction of N_2 and a mole fraction of CO_2 greater than the one in the vapour phase at equilibrium. The performances of the two methods have been assessed by comparing the calculated and the experimental CO_2 mole fraction in the vapour phase.

3. Results and discussion

In this section, results are illustrated and discussed taking into account the average absolute deviation (AAD%) calculated according to Eq(10) in order to compare the performances of the two methods.

$$AAD\% = \frac{100}{No.points}\sum_{j=1}^{No.points}\frac{\left|variable_{calc,j} - variable_{exp,j}\right|}{variable_{exp,j}} \qquad (10)$$

In Eq(10), $variable_{calc,j}$ and $variable_{exp,j}$ respectively denote the calculated and experimental values for the variable of interest for the j-th point, which is the temperature in the case of frost point calculations and the CO_2 mole fraction in the vapor phase in the case of SVE calculations.

3.1 CO_2-CH_4 binary mixture

Figure 1 shows the results obtained when using the two methods for the calculation of CO_2 frost points of different CO_2-CH_4 mixtures, according to the literature sources. The results are summarized in Table 2 in terms of AAD%. The calculated values show a good agreement with the experimental ones and suggest both methods are conservative, in most cases (as shown in Figure 1b and in Figure 1d), in predicting the temperature at which CO_2 freezes out. Higher deviations (Table 2), though still acceptable, have been obtained considering the data of Le and Trebble (Le and Trebble, 2007). To better understand the reason for this, all the available experimental data have been reported on the same plot (not shown) for assessing the consistency of each data set with the other ones. It has been observed that at higher pressures and lower amounts of carbon dioxide in the initial mixture (ca. 1 mol %), where the largest disagreement exists, the data by Le and Trebble are close to the data by Pikaar (Pikaar, 1959) and are shifted to the right with respect to the data by Agrawal and Laverman (Agrawal and Laverman, 1995). On the contrary, at higher amounts of carbon dioxide (ca. 3 mol %) the experimental data by the different literature works are very close to each other. However, the experimental data provided by Le and Trebble (Le and Trebble, 2007) cover higher pressures (9 - 25 bar) than those by Pikaar (Pikaar, 1959) (2 - 18 bar), so it is not possible to safely state whether some of the data available in the literature are not reliable.

Table 2: AAD% (Eq(10)) for the CO_2 frost temperature calculated with the two methods considering the different literature sources for the experimental data

	Proposed method	RGibbs tool
Pikaar (1959)	0.354	0.633
Agrawal and Laverman (1995)	1.079	0.873
Le and Trebble (2007)	1.239	1.364
Zhang et al. (2011)	0.297	0.375

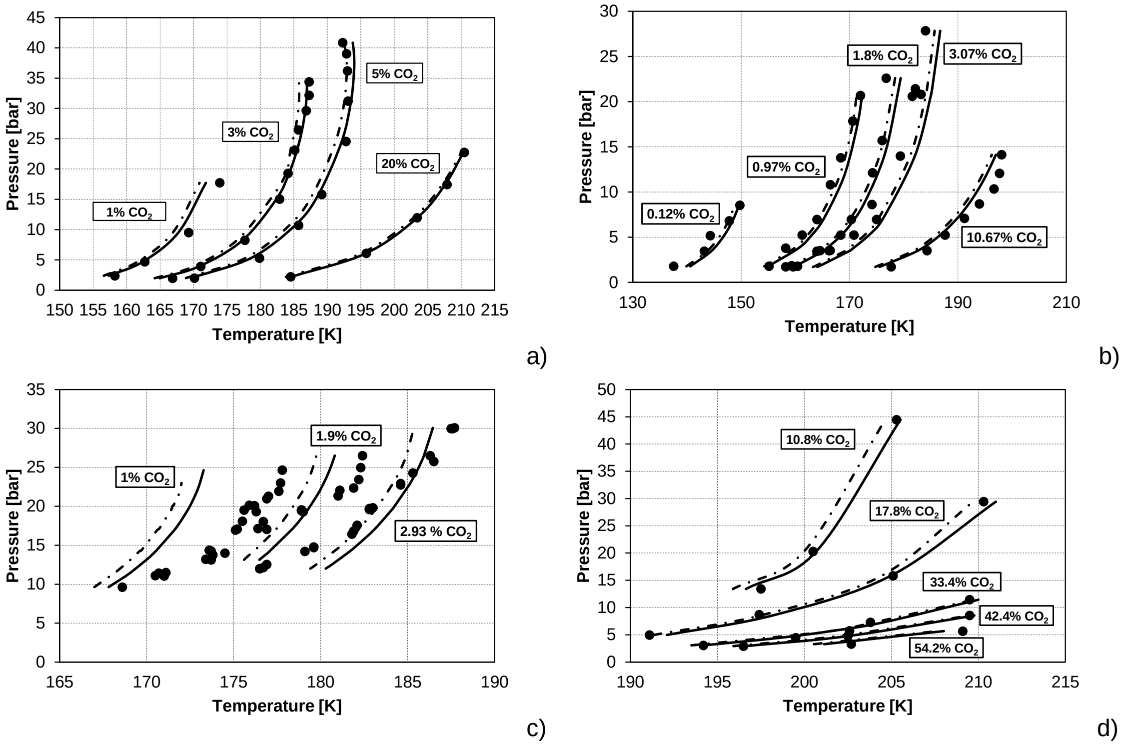

Figure 1: Comparison between the results obtained with the proposed approach (solid lines) and with the RGibbs tool (AspenTech, 2016; dashed and dotted lines), and the experimental frost point data for the CO_2- CH_4 system for different CO_2 contents (as specified in the labels) as reported by: a) Pikaar (1959); b) Agrawal and Laverman (1995); c) Le and Trebble (2007); d) Zhang et al. (2011)

3.2 CO_2-CH_4-N_2 ternary mixture

By comparing SVE data at two nitrogen contents (3 and 5 mol %), Xiong et al. (2015) investigated the effect of nitrogen on SVE conditions in the CO_2-CH_4-N_2 mixture. Figure 2 shows the results obtained with the two methods. Both of them exhibit a good agreement with the experimental data, to a higher extent for the proposed method (AAD% = 11.44 %) rather than for the RGibbs tool (AAD% = 15.17 %). In particular, the curves confirm the observations made on the basis of the experimental data (Xiong et al., 2015), namely that the nitrogen addition, at least up to 5 mol %, has little effect on CO_2 freezing conditions, even if with its increasing content the maximum pressure increases enabling the mixture to keep in the solid-vapour region at higher pressures.

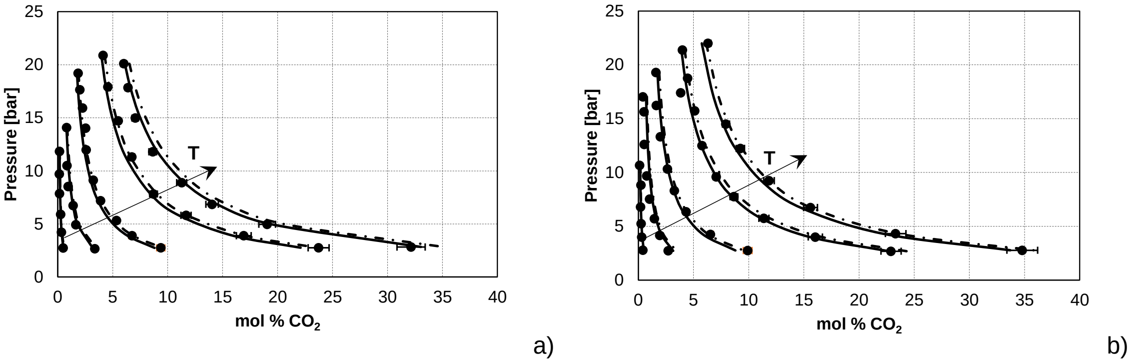

Figure 2: Comparison between the results obtained with the proposed approach (solid lines), with the RGibbs tool (AspenTech, 2016; dashed and dotted lines) and the experimental data by Xiong et al. (2015) at increasing temperatures (as indicated by the arrow) of 153.15 K, 168.15 K, 178.15 K, 188.15 K, 193.15 K for the: a) CO_2-CH_4-3 mol % N_2 mixture; b) CO_2-CH_4-5 mol % N_2 mixture

4. Conclusions

This work deals with a novel thermodynamic method for the simultaneous stability analysis and multiphase equilibrium calculations of CO_2 mixtures with hydrocarbons and non-hydrocarbon components, taking into account the solid phase in addition to fluid phases. The proposed method allows performing isothermal-isobaric flash computations in multiphase systems at given temperature, pressure and their global composition without knowing a-priori the number and the type of phases present at equilibrium. It has been shown that it is able to reliably predict frost point temperatures and the vapour phase composition at solid-vapour equilibrium conditions, respectively, for the CO_2-CH_4 and CO_2-CH_4-N_2 mixtures, with average absolute deviations lower than 1.3 % and 11.5 % in the two cases. The application of the proposed method is useful for the study and correct design of the recently developed CO_2 low-temperature/cryogenic removal processes.

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