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Research paper

# Fast parametric relationships for the large-scale reservoir simulation of mixed CH<sub>4</sub>-CO<sub>2</sub> gas hydrate systems



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#### ABSTRACT

A recent Department of Energy field test on the Alaska North Slope has increased interest in the ability to simulate systems of mixed  $CO_2$ -CH<sub>4</sub> hydrates. However, the physically realistic simulation of mixed-hydrate simulation is not yet a fully solved problem. Limited quantitative laboratory data leads to the use of various *ab initio*, statistical mechanical, or other mathematic representations of mixed-hydrate phase behavior. Few of these methods are suitable for inclusion in reservoir simulations, particularly for systems with large number of grid elements, 3D systems, or systems with complex geometric configurations. In this work, we present a set of fast parametric relationships describing the thermodynamic properties and phase behavior of a mixed methane-carbon dioxide hydrate system. We use well-known, off-the-shelf hydrate physical properties packages to generate a sufficiently large dataset, select the most convenient and efficient mathematical forms, and fit the data to those forms to create a physical properties package suitable for inclusion in the TOUGH+ family of codes. The mapping of the phase and thermodynamic space reveals the complexity of the mixed-hydrate system and allows understanding of the thermodynamics at a level beyond what much of the existing laboratory data and literature currently offer.

#### 1. Introduction

#### 1.1. Sequestration of $CO_2$ in hydrate-bearing reservoirs

The Ignik Sikumi field test (Schoderbek et al., 2013), performed in 2012, attempted to test the process of  $CO_2$  sequestion in combination with natural gas production from methane hydrates. The objective was to establish whether such exchange-reaction sequestion is viable and determine how such a process can be implemented at the field scale. The field trial was performed by ConocoPhillips and the Japan Oil, Gas, and Metals National Co. (JOGMEC) on behalf of the Department of Energy. In anticipation of the test, several institutions have performed lab and theoretical investigations of the properties of mixed hydrates.

Previous research (Hester et al., 2011; Howard et al., 2011) had established the process by which injection of  $CO_2$  into methane hydrate-bearing sediments can 1) sequester  $CO_2$  as  $CO_2$ -hydrate, and 2) release free gaseous  $CH_4$  into the reservoir in such a way that it can be produced commercially. Such exchange of  $CO_2$  for  $CH_4$  would provide a nearly one-for-one process of exchanging previously emitted carbon for new, cleaner fossil-fuel resources. However, the ability to simulate such systems is currently limited. Previous work in the

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commercialization of methane hydrates has depended heavily on numerical simulation capabilities (Moridis et al., 2011), but currently mixed-hydrate systems are served by a limited number of simulation tools.

A key hint about the nature of the mixed CO<sub>2</sub>-CH<sub>4</sub> system comes from legacy cryonics literature. Donnelly and Katz (1954) generated a phase diagram for the mixed system with a noted focus on cryogenic properties, however, the higher-T end of their phase diagram, although low resolution and derived from a minimal number of data points, hints at a key insight into mixed systems. Instead of a critical point, such systems have a critical locus, whereby the critical point of the mixture varies with composition. For this system in particular, the critical locus appears to pass through the P-T region associated with hydrate formation, and in particular, the region in which a CO<sub>2</sub>-CH<sub>4</sub> exchange reaction will occur. This key insight warns that supercritical behaviors, for example, transitions from liquid to gas phases without a phase transition (assuming the correct path is taken in P-T space) may be considered, and that formation of a second liquid-CO<sub>2</sub> phase (appearing and disappearing as temperatures change between injection, re-equilibration, and production) may be a common occurrence during many injection-production strategies.

The existence of a CO<sub>2</sub>-CH<sub>4</sub> exchange reaction that occurs on daysto-weeks timescales has been confirmed in the lab (Hester et al., 2011; Howard et al., 2011), although quantitative measures of actual thermodynamic properties (i.e., P-T curves) were will beyond the scope of such work. The bulk of our knowledge comes from theoretical studies, that use ab initio, or statistical mechanical (statistical thermodynamic) methods-most notably a number of papers by Trout, Anderson, and Cao (Anderson, et al., 2005; Garapati et al., 2011), which develop a model using the methods proposed by van der Waals and Platteeuw (1959). A more accessible system for understanding pure and mixed hydrates was published with the seminal text on hydrates by Sloan and Koh (2008). CSMGem uses the Gibbs Free Energy minimization method (GEM) (Gupta, 1990; Ballard, 2002; Ballard and Sloan, 2004) to estimate a wide range of physical properties for complex hydrate systems over a wide range of conditions. Preliminary studies using both CSMGem and lab data have shown evidence of good agreement (Luzi et al., 2012).

White and collaborators at PNNL (White and Oostrom, 2006; White et al., 2011) created the first comprehensive mixed-hydrate simulator by incorporating  $CO_2$  injection processes in the STOMP family of simulation codes. This implementation used lookup tables derived from previously referenced theoretical work, but did not include some of the complex thermodynamics described in detail later in this paper. The goal of this continuing work is to implement additional necessary complexity within the framework of a generalpurpose reservoir simulator.

#### 1.2. Requirements for reservoir simulation

While previous reservoir simulation studies have used lookup tables derived from other data sources (notably TOUGH2-ECO2M, in Pruess, 2011), this approach is less desirable as reservoir simulation moves into more sophisticated terrain, representing larger systems (100,000 s to 1,000,000 s of gridblocks), three-dimensional geometries, and systems involving steep gradients and complex thermodynamics. A fully implicit reservoir simulator such as TOUGH+ may not only need to solve 10,000,000 equations at each timestep, but also engage in 2-10 N-Raphson iterations as well, with each iteration requiring a complete update of element-by-element and connection-by-connection properties. The slowness of interpolating values off a lookup table is likely to severely restrict the scope and size of such a simulation. If an extensive and detailed set of empirical data were available, there could be an acceptable tradeoff between speed and accuracy, but at the current time no such dataset exists for mixed CH<sub>4</sub>-CO<sub>2</sub> hydrates at the reservoir conditions of interest. Therefore, it is reasonable to use limited data, statistical mechanics, or ab initio-generated data to create efficient functional expressions for physical properties, since any inaccuracies allowed by the function form are proportional to the natural uncertainty of the underlying data (as long as this is acknowledged in the presentation of the results).

An additional issue is that of functional smoothness and continuity. Although it is simple to create visually smooth functions using any number of methods, the actual numerical smoothness of the function, and its derivatives, is absolutely crucial to the formulation of the numerical problem. For Jacobian-based numerical formulation, such as used by TOUGH+, the functions and their derivatives must be smooth and continuous. By careful selection of appropriate functional forms, these properties can be guaranteed.

This paper is the first in a series describing the formulation of the TOUGH+BinH code. A subsequent publication will describe how these physical properties relationships to the construction of a new TOUGH +"equation of state" module (i.e., the specific software package that describes phase transitions and computes evolving phase saturations and compositions for a given set of components and *PVTx* conditions) and the testing of the new simulator with 1-D and 2-D sample problems.

#### 2. Methods

#### 2.1. GSMGem

To provide a source for *P-T-x* data for the mixed CH<sub>4</sub>-CO<sub>2</sub> system, in the absence of a library of high-resolution data, we use CSMGem, the application published with the seminal text on hydrates by Sloan and Koh (2008). CSMGem uses the Gibbs Free Energy minimization method (GEM) (Gupta, 1990; Ballard, 2002) to compute the formation conditions for any phase, the phase present for a given T and P, hydrate formation T and P for a given feed composition. formation T and P for other fluid phases, as well as additional processes such as adiabatic flash or expansion through a turbine. Results for mixed hydrates of CH4 and various alkanes shows that CSMGem agrees well with laboratory-determined P-T phase boundary locations to within current experimental uncertainty (Ballard and Sloan, 2004; Luzi et al., 2012). As CSMGem is a proprietary code (although the methods have been published), we use the code interactively to generate the needed datasets-direct linking of CSMGem to TOUGH+HYDRATE was neither possible nor desirable due to the speed considerations discussed above.

Two limitations are imposed upon the physical properties investigation. First, we look at sI hydrates only. Allowing for sII or other hydrate structures may extend the usefulness of the relationships to a wider range of systems, but the additional complexity is currently intractable, and in general, hydrates of interest for production are likely to be largely or entirely methane. We also limit our investigation to systems with excess water, again to focus the investigation on systems most likely to be encountered in a reservoir engineering context.

### 2.2. Choice of functional forms: novel and complex vs. established and simple

Our initial attempts at producing fast parametric relationships for the  $CH_4$ - $CO_2$  system used the technique of multiquadrics (MQ) (Hardy, 1990; Kansa, 1990). In this method, a linear combination of functions is used to represent "topographic" data—for example, the *P*-*T*-*x* surface marking a phase boundary in a multicomponent, multiphase system. While this method is extremely powerful and results in simple, easy-toimplement, fast parametric functions, the resulting surfaces fail in terms of the second criteria of Section 1.2. This system, when represented by a MQ expansion fit, would often include slight "waviness" in the interpolation between (*P*, *T*, *x*) points (Seim and Reagan, 2009). While these did not compromise the quality of fit (within the known uncertainty of the fit data), the first and second derivatives of these variations would be likely to induce large, non-physical effects when used in the simulation framework.

Also considered were simple fits to low- and high-order polynomials. Once again, the smoothness of the derivatives must be considered, even if one can assume that the polynomials converge. For data with simple dependencies (i.e., roughly linear or parabolic due to known factors like inherent physics), this might be sufficient, but much of the thermodynamic data considered here contains various complexities of functional form, such as inflection points, varying curvature, or points of strong curvature or near-discontinuity (i.e., a triple or quadruple point). One subspecies of polynomial that would prove easy to implement would be a power-law formulations or sums of power laws, i.e.  $f(x) = f_0 + ax^k$ , or  $f(x, y) = f_0 + ax^k + by^m$ , to represent data with varying curvatures.

When polynomials fail the smoothness test, a last resort is to use splines (Press et al., 1992; Stewart, 1998) to force smoothness of interpolation and smoothness of derivatives. While not as fast as polynomials, tables of data can be pre-processed into arrays of data points, and the first, second, and third derivatives at those points. Efficient Fortran routines exist to quickly interpolate such expressions with O(N), without the overhead of a full lookup table for all data.

A last set of functions considered are specialized functions—again chosen based on the form of the data—that are known to be (ideally, defined to be) smooth, have smooth derivatives, and that are easily calculated using fast, efficient intrinsic Fortran 95/2003 functions. We have explored the use of incomplete beta functions (von Seggern, 1993) as a means of representing complex curves. However, the data contained in this study, while occasionally exhibiting multiple inflection points and complex types of curvature, is still typically representable by complex *combinations* of otherwise simple functions. Since many of the function vary according to two or more parameters, combinations of simple forms are often easier to fit and implement than elaborate and complex functional forms.

It should be noted that the choice of form for a given physical property parameterization is essentially determined *ad hoc*, that is, they are selected by hand, and chosen for convenience, speed, and by identifying functional forms that most closely resemble the data as generated by CSMGem. We are not attempting limit ourselves to deriving expressions from first principles, rather, to engineer a practical toolkit that can provide estimates of system properties and fit into the TOUGH+ simulator framework.

#### 2.3. Curve fitting

The bulk of the work in fitting the tables of CSMGem data to various functional forms is performed within the data analysis environment of Igor Pro (Wavemetrics, 2013). Igor Pro takes data in spreadsheet format, organized in a columnar form described as "waves," and allows a wide range of operations to be performed on the data, including for the purposes of this work, curve fitting and 2D plotting. All of the curve fits presented here were performed using version 6.x of Igor Pro.

In performing these operations, we used a fit metric best described as "keep it simple-for the programmer." As this is not a statistical study to gauge whether laboratory data fits a model, but rather an engineering project to create workable relationships, our goal in each fit was to 1) choose the simplest functional form that can represent the data within the parametric range of interest, 2) insure that the curves intersect the data at each sampled point, 3) insist that the function vary smoothly under all circumstances, even if this results in introduction of approximations, and 4) create expressions that can quickly and easily be translated into Fortran or other scientific programming languages, preferably using standard (open source or nonproprietary, readily available) libraries. The smoothness criterion, as mentioned earlier, is essentially non-negotiable for application in the TOUGH+ framework. Thus, we used the internal Igor Pro metrics, including the chisquared test, to evaluate the relative usefulness of each functional form and the goodness of each individual fit, but the final selection of a particular set of fit parameters was driven primarily by the three points listed above. If additional field or laboratory data becomes available, these fits can be re-evaluated, perhaps with an eye to better matching real-world data. For now, the relationships provide a clean interpolation of CSMGem data in a concise, fast, and easy-to-implement package. Raw data used in the fitting process is available through the online appendix and resources provided by this journal.

## 3. Fast parametric functions for key components of the phase diagram

For all expressions, we use the TOUGH+ unit conventions, where P has units of Pa, T has units of °C, x (liquid) and Y (gas) are mole fractions. Parametric relationships generated from data reported in other units include the unit conversion to Pa or °C in the final expression, to preserve the identity of the original data.

We separate the properties relationships into two categories—those that require a more complex spline interpolation of data (typically due to the complexity of the shape of the physical properties envelope and/ or the necessity of matching data exactly at sampled points), and those that can be simply fit to some combination of polynomials and power-law forms.

#### 3.1. Cubic splines, or simple functions of cubic splines

These critical relationships generate quantities that define the fundamental shape of the phase envelope, and accuracy is critical. Therefore, we define the critical locus and phase surfaces by fitting either the data itself (if possible) or the parameters of a series of power-law fits to the data, to a cubic spline.

It is not within the scope of this paper to derive the cubic spline, and many good practical references exist to help the user understand the process and program appropriate spline coefficient generators and interpolators (Press et al., 1992; Stewart, 1998). However, we need to define an efficient notation for the purposes of describing the functional forms in Section 3.1. In the following toolkit, we define a cubic spline S(x) as a piecewise function that interpolates a set of (x,y) points, satisfying the conditions:

- 1)  $S(x) = S_i(x)$ , on the interval  $[x_i, x_{i+1}]$  for i=0, 1, ..., n-1;
- 2)  $S(x_i) = y_i$  for i=0, 1, ..., n; and
- S, S', and S" are continuous on [x<sub>0</sub>, x<sub>n</sub>], i.e. S is smooth. This gives us n simple cubic polynomial pieces written as:

$$S(x) = S_{y}(i) + S_{b}(i)(x - S_{x}(i)) + S_{c}(i)(x - S_{x}(i))^{2} + S_{d}(i)(x - S_{x}(i))^{3}$$
for  $i = 0, 1, ..., n - 1$  (1)

where  $S_y$ ,  $S_b$ ,  $S_c$ , and  $S_d$  represent 4 *n* unknown coefficients and  $S_x$  is the vectors of "knots"—i.e. selected values of *x*. These coefficients are precalculated as part of the curve-fitting exercise, and then interpolation of the actual value of S(x) can be accomplished quickly and cheaply by finding *i* and evaluating the corresponding sub-polynomial.

#### 3.1.1. CH<sub>4</sub>-CO<sub>2</sub> hydrate phase diagram

The curves describing hydration pressure,  $P_{H}$ , as a function of composition are critical in defining the mixed CH<sub>4</sub>-CO<sub>2</sub> hydrate system, and are described in this section. A series of functions—quadruple-point temperature, critical locus, hydration curves, and VLE curves all form the basis of a workable mixed-hydrate phase diagram. The raw data for the diagram is archived online (through the journal website), and here we present the relationships with the final fitted parameters in place. To ensure accuracy, the parameters were generated by Igor Pro, output in columnar form, and converted via scripts into the formatted equations (and also, into the Fortran code as implemented in TOUGH +BinH), to minimize the chance of transcription errors.

3.1.1.1. Lower quadruple-point temperature. Unlike most hydrate systems, dissolved  $CO_2$  is one of a few species that significantly shifts the freezing point of water, and thus the quadruple point. Therefore composition variations in the  $CO_2$ -CH<sub>4</sub> system result in a locus of quadruple points. The lower quadruple points,  $(P_Q, T_Q)$ , serve as a point of discontinuity within the hydration curve, as the functional form of  $P_{H}(x_{CO2})$  must necessarily change at the transition between (low-*P*) aqueous-gaseous  $CO_2$ -gaseous CH<sub>4</sub> and the (higher-*P*) region of aqueous-liquid  $CO_2$ -gaseous CH<sub>4</sub> coexistence. This transition temperature, which will next be used as a parameter in the generation of the two-part hydration curve, can be represented by a straightforward polynomial:

 $T_{\mathcal{Q}}(x_{CO_2}) = 22.69841897231281 - 8.249662428066445x - 54.09319113815833x^2$ 

+  $278.7551606261848x^3 - 649.8072154486597x^4$ +  $690.4968291527629x^5 - 270.0932037615136x^6$ 

(2)

*3.1.1.2. Lower hydration curve.* The chosen functional form for the hydration curves is illustrated in Fig. 1. The two sections of the curve,



**Fig. 1.** Illustration of the upper and lower hydration curves (red lines) intersecting at a quadruple point ( $P_Q, T_Q$ ) (blue circle) overlaid upon the set of raw  $P_H(x_{CO2}, T)$  data generated by CSMGem (Xs). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the first below the quadruple-point temperature  $(P^{l_{ower}})$  and the second above the quadruple-point temperature  $(P^{upper})$ , are each represented by power-law expressions in T with parameters that vary as functions of  $x_{CO2}$ . Each set of  $P_H$  vs. T data (above and below the quadruple point) is calculated at a series of constant  $x_{CO2}$  values and fit to a power law of the form:

$$P_H(x_{CO_2}) = y + a(T^b) + c(T^d)$$
(3)

Then, each set of coefficients a, b, c, d are fit to curves as a function of  $x_{CO2}$ .

For  $P_H^{lower}(x_{CO2})$ , simple polynomials are sufficient to create smooth curves that intersect the calculated values of the coefficients *a*, *b*, *c*, *d*:

 $La(x_{CO_2}) = 0.1716335619153852 + 1.681663528706526x$ 

 $Lb(x_{CO_2}) = 1.347893452088037 - 3.905631910894871x$ 

 $Ld(x_{CO_2}) = 2.584503496503497 - 3.360602175602169x$ 

+ 20.88881178467625
$$x^2$$
 - 67.19629249913626 $x^3$   
+ 109.903147832899 $x^4$  - 83.88480603423835 $x^5$   
23.98809793649099 $x^6$ 

$$Lc(x_{CO_2}) = 7.415168696092792 \times 10^{-5} + 1.338473767020314 \times 10^{-4}x$$
  
- 7.737972315137834 × 10<sup>-5</sup>x<sup>2</sup>

$$+ 3.248310023310009x^2 1.241064491064483x^3$$
(7)

Once the coefficients are found, the lower hydration curve, up to the quadruple-point temperature, may be calculated as:

$$P_{H}^{lower}(x_{CO_{2}}) = Ly + La(T^{Lb}) + Lc(T^{Ld}) \quad \text{where} \quad 0.0 < x < T_{Q}$$
(8)

3.1.1.3. Upper hydration curve. For  $P_H^{upper}(x_{CO2})$ , simple polynomials are insufficient to create smooth curves that intersect and smoothly interpolate the computed values of the power-law coefficients *a*, *b*, *c*, *d*. Therefore, we use a combined method. The curve itself is still represented by a power law form, with constant exponents but with the pre-exponential coefficients fit to cubic splines as a function of, as defined in Section 3.1. The 11 knots, corresponding to a set of power-law parameters at  $x_{CO2} = \{0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0\}$  and corresponding values and derivatives, are listed in Appendix A for convenience. Using the interpolation method described in Section 3.1 to compute the interval *i* from the vector of knots  $S_x^U$  and *x*,

$$i(x, S_x^U) \to i \tag{9}$$

the upper hydrate pressure curve parameters are then calculated as:

$$Uy(x_{CO_2}) = S_y^{Uy} + S_b^{Uy}(i)(x - S_x^U(i)) + S_c^{Uy}(i)(x - S_x^U(i))^2 + S_d^{Uy}(i)(x - S_x^U(i))^3$$
(10)

$$Ua(x_{CO_2}) = S_y^{Ua} + S_b^{Ua}(i)(x - S_x^U(i)) + S_c^{Ua}(i)(x - S_x^U(i))^2 + S_d^{Ua}(i)(x - S_x^U(i))^3$$
(11)

$$Ub(x_{CO_2}) = S_y^{Ub} + S_b^{Ub}(i)(x - S_x^U(i)) + S_c^{Ub}(i)(x - S_x^U(i))^2 + S_d^{Ub}(i)(x - S_x^U(i))^3$$
(12)

allowing us to compute the upper hydration pressure curve:

$$P_{H}^{upper}(x_{CO_2}) = Uy + Ua(T^{1.5}) + Ub(T^{2.0}) \text{ where } T_Q < x < 1.0$$
(13)

The two hydration-pressure curves meet at the quadruple point  $(P_Q, T_Q)$  (Fig. 1), but for all but the lowest values of  $x_{CO2}$ , the curves do not smoothly and continuously transition across the connection point. To preserve smoothness in the coupling of the upper and lower curves while allowing minimal inaccuracy, we construct a pair of smoothing functions around  $T_Q$  using error functions:

$$MS(x_{CO_2}) = 1.0 + 1000.0 \cdot erfc(100.0 - 100.0x)$$
(14)

(4)

(5)



**Fig. 2.** Demonstration of the interpolation ability of the combined spline-power law representation of  $P_H$ . CSMGem data points are shown as blue symbols for  $x_{CO2}$  =0.7 and 0.8, while  $P_H(x_{CO2})$  as represented by the smooth parametric relationship is show in red for in 0.01 intervals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$UM(x_{CO_2}) = 0.5erf(MS \cdot (T - T_Q)) - 0.5$$
(15)

$$LM(x_{CO_2}) = 0.5erfc(MS \cdot (T - T_Q))$$
(16)

Therefore, the hydration pressure at any composition, smoothed, can be represented by:

$$P_H(x_{CO_2}) = LM \cdot P_H^{lower} + UM \cdot P_H^{upper}$$
(17)

A sample of the interpolating ability of this expression is illustrated in Fig. 2. The complete set of merged and smoothed curves, with quadruple points, is shown in Fig. 3 at 0.1 concentration intervals, along with the location of the sI hydrate-stable zone, the approximate location of the liquid and gaseous  $CO_2$  regions outside the hydration zone (roughly below and above  $P_Q$ ), and how the hydration boundary and quadruple point varies with CO<sub>2</sub> concentration.

#### 3.1.2. Critical locus

Using the definition of cubic spline interpolation in Section 3.1, we process CSMGem data to produce the vectors of 12 knots, values, and derivatives for  $x_{CO2}$  ranging from 0.6 to 1.0, since for lower values of  $x_{CO2}$ , the vapor-liquid equilibrium zone (VLE) is entirely within the gas hydrate stability zone (GHSZ) where we expect a solid CH<sub>4</sub>-CO<sub>2</sub> hydrate phase. As in the previous implementations of cubic splines, we use the interpolation method described in Section 3.1 to compute the interval *i* from the vector of knots  $S_x$  and x,



**Fig. 3.** Set of spline-power law curves for the upper and low  $P_{H}$  curve fits, showing the approximate location of liquid and gaseous CO<sub>2</sub> zones (above and below the quadruple point), the sI hydrate zone, and variation with  $x_{CO2}$ .



**Fig. 4**.  $T_{sat}$  vs.  $P_{sat}$  for a range of  $x_{CO2}$  from 0.7 to 1.0. CSMGem data are gray points, red lines are the parametric functions derived from the data, and the critical locus is in blue. The hydration curves for  $x_{CO2} = 1.0$  and  $x_{CO2} = 0.0$  are also indicated to show the varying transition line between the GHSZ and the multiphase CH<sub>4</sub>-CO<sub>2</sub>-aqueous regions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$i(x, S_x) \to i$$
 (18)

and the mixture critical pressure may thus be calculated by:

$$P_{crit,mix}(x_{CO_2,mix}) = S_y + S_b(i)(x - S_x(i)) + S_c(i)(x - S_x(i))^2 + S_d(i)(x - S_x(i))^3$$
(19)

where  $1.0 > x_{CO2,mix} > 0.60$ .

For the complementary expression for  $T_{crit}$ , the calculated values of critical temperature vs. composition may be represented by a simple polynomial:

$$T_{crit,mix}(x_{CO_2,mix}) = -117.1902467431329 + 1066.521547692588x^{1.1} - 918.3081766017568x^{1.2}$$
(20)

where  $1.0 > x_{CO2,mix} > 0.60$ . The critical locus is highlighted in blue in Fig. 4. Note that for  $x_{CO2,mix} < 0.60$ , the critical point of the mixture is within the sI hydrate region if hydrate can form (no water limitation), and  $T_{crit} < 0$  °C.

#### 3.1.3. VLE Saturation curves

Once we have the critical pressure (and critical temperature, see Section 3.2.1), we can begin to describe the 3-D VLE envelope of the binary system. Using CSMGem, we calculate the lower and upper  $P_{sat}$  vs.  $T_{sat}$  curves as a function of  $P_{crit}$ . As the curvature of the  $P_{sat}$  vs.  $T_{sat}$  data on either side of the critical point is such that a given T may map to two P values (and  $P_{sat}$  is at a maximum at  $T_c$ ), it is more convenient to fit the data as  $T_{sat}$  vs. P.

For each of several 2-D slices of the 3-D phase space (slicing across values of  $x_{CO2}$ ), we fit the curves of  $T_{sat}$  vs. *P* to a power law form:

$$T_{sat,lower}(P, P_{crit}(x_{CO_2}), x_{CO_2}) = y_0^L(x_{CO_2}) + A^L(x_{CO_2}) \times \left(\frac{P_{crit} - P}{10^6}\right)^{1/2} + B^L(x_{CO_2}) \times \left(\frac{P}{10^6}\right)^{C^L(x_{CO_2})}$$
(21)

$$T_{sat,upper}(P, P_{crit}(x_{CO_2}), x_{CO_2}) = y_0^U(x_{CO_2}) + A^U(x_{CO_2}) \times \left(\frac{P_{crit} - P}{10^6}\right)^{1/2} + B^U(x_{CO_2}) \times \left(\frac{P}{10^6}\right)^{C^U(x_{CO_2})}$$
(22)

Determining parameters  $y_0$ , A, B, C at each  $x_{CO2}$  such that  $P_{crit}$  matches for each pair of curves. The dependence of these parameters on  $x_{CO2}$  does not lend itself to simple polynomial forms, and therefore to exhibit both smoothness and accuracy at the sampled point, we again interpolate with cubic splines. Choosing eight knots for  $x_{CO2}$  (outside of the GHSZ), we create vectors of values and derivatives to define the cubic splines for each of the parameters (See Appendix A) such that:

$$y_0^L(x_{CO_2}) = S_y^{y_0} + S_b^{y_0}(i)(x - S_x(i)) + S_c^{y_0}(i)(x - S_x(i))^2 + S_d^{y_0}(i)(x - S_x(i))^3$$
(23)

$$A^{L}(x_{CO_{2}}) = S_{y}^{A} + S_{b}^{A}(i)(x - S_{x}(i)) + S_{c}^{A}(i)(x - S_{x}(i))^{2} + S_{d}^{A}(i)(x - S_{x}(i))^{3}$$
(24)

$$B^{L}(x_{CO_{2}}) = S_{y}^{B} + S_{b}^{B}(i)(x - S_{x}(i)) + S_{c}^{B}(i)(x - S_{x}(i))^{2} + S_{d}^{B}(i)(x - S_{x}(i))^{3}$$
(25)

$$C^{L}(x_{CO_{2}}) = S_{y}^{C} + S_{b}^{C}(i)(x - S_{x}(i)) + S_{c}^{C}(i)(x - S_{x}(i))^{2} + S_{d}^{C}(i)(x - S_{x}(i))^{3}$$
(26)

and:

$$y_0^U(x_{CO_2}) = S_y^{y_0} + S_b^{y_0}(i)(x - S_x(i)) + S_c^{y_0}(i)(x - S_x(i))^2 + S_d^{y_0}(i)(x - S_x(i))^3$$
(27)

 $A^{U}(x_{CO_{2}}) = S_{y}^{A} + S_{b}^{A}(i)(x - S_{x}(i)) + S_{c}^{A}(i)(x - S_{x}(i))^{2} + S_{d}^{A}(i)(x - S_{x}(i))^{3}$ (28)

$$B^{U}(x_{CO_{2}}) = S_{y}^{B} + S_{b}^{B}(i)(x - S_{x}(i)) + S_{c}^{B}(i)(x - S_{x}(i))^{2} + S_{d}^{B}(i)(x - S_{x}(i))^{3}$$
(29)
$$C^{U}(x, y) = S_{c}^{C} + S_{c}^{C}(i)(x - S_{x}(i)) + S_{c}^{C}(i)(x - S_{x}(i))^{2} + S_{d}^{C}(i)(x - S_{x}(i))^{3}$$

$$C^{U}(x_{CO_{2}}) = S_{y}^{C} + S_{b}^{C}(i)(x - S_{x}(i)) + S_{c}^{C}(i)(x - S_{x}(i))^{2} + S_{d}^{C}(i)(x - S_{x}(i))^{3}$$
(30)

The resulting family of curves defines the phase envelope outside the hydrate stability zone, interpolating the CSMGem data such that the boundaries of the volume can be defined for any (P,T,x) condition. Fig. 4 shows several slices of the phase envelope for  $x_{CO2} = 0.7, 0.8$ , 0.85, 0.9, 0.95, and 1.0. Note that the curves are smooth, intersect the critical point (a requirement of the spline fits), and coalesce into a single line for pure CO<sub>2</sub>. However, a few thermodynamic difficulties (in terms of both modeling and production management in real systems) become apparent. The phase diagram extends over a range of pressures and temperatures that encompass the likely range of operating pressures and temperatures within a permafrost-associated hydrate system subjected to the injection of CO<sub>2</sub> at significant rates. This phase diagram indicates that, as temperature and pressure evolve, regions of the reservoir may exist in aqueous-gas, aqueous-liquid CO2-gas, aqueous-supercritical fluid, hydrate-gas, hydrate-aqueous, hydrateliquid CO<sub>2</sub>, hydrate-liquid CO<sub>2</sub>-aqueous states. Note that we are seeing slices of a 3-D phase space where many properties are coupled, such that the VLE curves describing the instantaneous state of the system necessarily changes in concert with concentration changes-while concentrations change as hydrate forms or dissociates, phases evolve and disappear, and P-T changes alter chemical equilibria between phases. This highlights the complexity of the system, and serves as a warning when implementing complex thermodynamics in a simulator context.

Fig. 5 shows the complete phase diagram including  $P_{H}$ , the critical locus, and the VLE envelopes for pressures up to 12 MPa. An assessment of this diagram will be performed in Section 3.3.

#### 3.2. Other properties

The following additional properties of the binary system can be represented by polynomials, power-law functions, or power-law functions with parameters fit to polynomial forms. In each case, these derived properties were harvested from the CSMGem program, fit to convenient expressions through the methods described earlier, and the results are presented here. These expressions are valid only through the investigated range of conditions: P < 12 MPa (although the data extends to 80 MPa) and T < 32 °C, and the expressions may diverge in unphysical ways outside the stated range. Original data may be

examined through the online resources. However, outside these ranges (particular high-*T*), the thermodynamic and phase behavior will be increasing easier to predict using conventional methods. Note that only novel properties, primarily CO<sub>2</sub>-related, are described here. Pure methane and methane hydrate properties are described in the HYDRATE equation-of-state package of the TOUGH+ family of codes (Moridis et al., 2008).

#### 3.2.1. Densities

For density of the  $CO_2$  liquid phase, we first fit the data to create pressure-dependent parameters using simple polynomials:

$$A(P_{liq}) = -6.4988736236065927 + 2.9951749158531462 \times 10^{-7}P$$
  
- 6.3881898510082682 × 10<sup>-15</sup>P<sup>2</sup> (31)

$$\begin{split} B(P_{liq}) &= 1.0893731993111961 + 9.5254531177322741 \times 10^{-9}P \\ &- 7.3920675456387732 \times 10^{-16}P^2 + 1.2140982621920791 \\ &\times 10^{-23}P^3 \end{split}$$

(32)

$$y_0(P_{liq}) = 898.79334855854381 + 9.5687460221041598 \times 10^{-6}P$$
  
- 2.2868869121504460 × 10<sup>-13</sup>P<sup>2</sup> + 2.7601866131215190  
× 10<sup>-21</sup>P<sup>3</sup>

(33)

which are then used to shape a power-law form for density:

$$\rho_{CO_{2},liq}(P_{liq}, T_{liq}) = y_0(P_{liq}) + A(P_{liq}) \times T^{B(r_{liq})}$$
(34)

#### 3.2.2. Methane phase equilibria

Gas-phase mole fraction vs. liquid phase mole fraction is also calculated via CSMGem and fits to a simple power-law form:

$$Y_{CH_4}(x_{CH_4}) = 1.11106721025438x^{1.3695}$$
(35)

#### 3.2.3. Heat capacities

Heat capacities of liquid  $CO_2$  are most conveniently fit to a powerlaw form in *T*, with pressure dependent parameters described via



Fig. 5. Phase diagram for the CO<sub>2</sub>-CH<sub>4</sub> hydrate system. Hydration pressure curves are in red, VLE phase envelopes in blue, the critical locus in green, and the approximate *P*-*T* space for the Ignik Sikumi reservoir is marked in orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

simple polynomials:

$$A(P_{liq}) = 2.1670238871063212 - 3.6214160370115135 \times 10^{-7}P + 2.5712819297978501 \times 10^{-14}P^2 - 8.2207649831525329 \times 10^{-22}P^3 + 9.6828167007265819 \times 10^{-30}P^4$$
(36)

$$B(P_{liq}) = 1.4689866130279257 - 1.7060827005377455 \times 10^{-8}P + 1.9224893097696102 \times 10^{-16}P^2$$
(37)

$$y_0(P_{liq}) = 115.90286947473265 - 2.3407325547425592 \times 10^{-6}P + 4.0314371148066704 \times 10^{-14}P^2$$
(38)

$$Cp_{CO_2, liq}(P_{liq}, T_{liq}) = y_0(P_{liq}) + B(P_{liq}) \times T^{B(P_{liq})}$$
(39)

#### 3.2.4. Thermal conductivities

The thermal conductivity of liquid CO2 may similarly be represented, with temperature dependent parameters controlled a powerlaw expression in *P*:

$$A(T_{liq}) = -7.8579044050122865 \times 10^{-3} + 5.5394710718504299 \times 10^{-3}T$$
  
- 6.2929748865142208 × 10<sup>-4</sup>T<sup>2</sup> + 1.9060028896215096 × 10<sup>-5</sup>T<sup>3</sup>  
(40)

$$B(T_{liq}) = 0.74520450096844948 + 3.1526443778506458 \times 10^{-3}T$$
  
- 2.5164621737342511 × 10<sup>-3</sup>T<sup>2</sup> + 9.7444027088786222  
× 10<sup>-5</sup>T<sup>3</sup> - 1.3337735750482373 × 10<sup>-6</sup>T<sup>4</sup>

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$$y_0(T_{liq}) = 0. \ 11853632077933009 - 7.6586100389543889 \times 10^{-3}T + 6.8576404138889703 \times 10^{-4}T^2 - 2.2434324176145396 \times 10^{-5}T^3 (42)$$

$$\kappa_{CO_2,liq}(P_{liq}, T_{liq}) = y_0(T_{liq}) + A(T_{liq}) \times \left(\frac{P}{10^5} - 35.0\right)^{B(T_{liq})}$$
(43)

3.2.5. Enthalpies

Enthalpies of liquid CO<sub>2</sub> may be described in the same fashion:

$$A(T_{liq}) = 6.8922373855486381 - 7.4944873020148099T$$
  
-0.42407562184666392T<sup>2</sup> + 3.1434245395365421 × 10<sup>-2</sup>T<sup>3</sup>  
- 1.1110460840569548 × 10<sup>-3</sup>T<sup>4</sup>  
+ 1.5063125985170777 × 10<sup>-5</sup>T<sup>5</sup>  
(44)

$$B(T_{liq}) = -7.0753126628472024 \times 10^{-2} + 8.5007373669959731$$

$$\times 10^{-3}T - 3.7250751496378199 \times 10^{-3}T^{2}$$

$$+ 1.9770700452401366 \times 10^{-4}T^{3}$$

$$- 4.2502200308654369 \times 10^{-6}T^{4}$$
(45)

$$\begin{split} y_0(T_{liq}) &= 0.\ 11853632077933009 - 7.6586100389543889 \times 10^{-3}T \\ &+ 6.8576404138889703 \times 10^{-4}T^2 - 2.2434324176145396 \\ &\times 10^{-2}T^3 \end{split}$$

$$H_{CO_2,liq}(P_{liq}, T_{liq}) = y_0(T_{liq}) + A(T_{liq}) \times \left(\frac{P}{10^5} - 30.0\right)^{B(T_{liq})}$$
(47)

3.2.6. Viscosities

Viscosity of liquid CO2 may also use this form:

$$A(T_{liq}) = 194.47399566335787 - 276.23497588809352T$$

$$+ 100.73462527792871T^2 - 15.254550481820440T^3$$

+ 1.1088306087554245 $T^4$  - 3.8309820806714766 ×  $10^{-2}T^5$ 

+ 
$$5.0508243207209285 \times 10^{-4}T^{6}$$

(48)

$$B(T_{liq}) = 0.77947264848861364 + 8.7862026724561271 \times 10^{-3}T$$
  
- 3.7364594467981928 × 10<sup>-3</sup>T<sup>2</sup> + 1.8285005907721914  
× 10<sup>-4</sup>T<sup>3</sup> - 3.1838465124297668 × 10<sup>-6</sup>T<sup>4</sup> (49)

$$y_0(T_{liq}) = 903.59752929883086 + 284.91889111950320T$$

$$\begin{array}{l} - \ 110.50532839691671T^2 + \ 16.568405839893483T^3 \\ - \ 1.1971697407203625T^4 + \ 4.1156481746371522 \times 10^{-2}T^5 \\ - \ 5.4075637696365732 \times 10^{-4}T^6 \end{array}$$

(50)

$$\mu_{CO_2, liq}(P, T) = y_0(T_{liq}) + A(T_{liq}) \times \left(\frac{P}{10^5} - 40.0\right)^{B(T_{liq})}$$
(51)

#### 3.2.7. Implementation

The primary and secondary physical-properties expressions have been implemented as part of the BinH equation of state module for TOUGH+. TOUGH+BinH is currently a research code, and not part of the standard licensed suite of TOUGH+ codes found on the LBNL tech transfer website (http://esd.lbl.gov/research/projects/tough/ licensing/). However, we direct questions from interested researchers to the authors of this paper. Future plans include expanding the existing set of LBNL/Earth Science physical properties tools (http:// esdtools.lbl.gov/gaseos) to include the BinH properties modules. A description of the TOUGH+BinH code and its validation using both simple and complex mixed-hydrate problems will be presented in a forthcoming paper.

#### 3.3. The complete phase diagram

Fig. 5 shows the complete phase diagram including  $P_{H}$ , the critical locus, and the VLE envelopes for pressures up to 12 MPa. Note again that we are presenting multiple slices of 3-D phase envelopes on a single plot. To clarify this, Fig. 6 presents the same phase diagram in six panels, for single values of *x*<sub>CO2</sub>: 0.0, 0.6, 0.7, 0.8, 0.9, and 1.0, in order to illustrate the geometry of the individual 2D slices that comprise the 3D phase envelope that is represented in Fig. 5.

Thus, the hydration pressure curves, in red, and the upper and lower curves for saturation temperature/pressure are actually crosssections of 3-D surfaces, with the critical loci forming a critical curve that extends across the top of the volume generated by the VLE envelope. The upper and lower (in P) saturation curves also form enclosed volumes, with the critical locus as the upper/rightmost (high-T, high-P) seam of the volume. These surfaces and volumes are bounded in the third dimension  $(x_{CO2})$  by the pure-CH<sub>4</sub> and pure  $CO_2$  phase diagrams, x = 1.0 and x = 0.0. Also note the hydration curve (2-D slice) for x=0.4 (Fig. 5) which serves roughly as an upper-T limit of the hydration surface.

Several other regions of interest are identified in Figs. 5 and 6. First, to the lower right, below the phase envelopes and to the right of the hydration curve, is an aqueous-gas region. Second, above the phase envelopes, to the right of the hydration curves, is an aqueouscondensed fluid zone, with the fluid being supercritical to the right of the mixture critical point and subcritical to the left (above the critical pressure, the subcritical to supercritical transition is smooth and continuous). Note that a system that follows a P-T path that travels past the mixture critical point in T, moves upward through increased pressure, and then moves left due to a decrease in T could actually skirt

(46)



Fig. 6. Phase diagrams for the  $CO_2$ -CH<sub>4</sub> hydrate system, at selected single values of  $x_{CO2}$ . Hydration pressure curves are in red, VLE phase envelopes in blue, the critical locus (when relevant) in green, and the approximate *P*-*T* space for the Ignik Sikumi reservoir is marked in orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the gas-liquid phase transition zone and move from gas to liquid/fluid without a discrete phase transition. Note also that the critical locus places the location of such a potential transition within the reasonable range of hydrate reservoir conditions at  $CO_2$  concentrations of 70–80%.

Also highlighted, by an orange strip, is the approximately P-T range of the Ignik Sikumi field test. While it is clear that such a system is very stable with regard to CO<sub>2</sub>-bearing hydrates (and thus a good candidate for a sequestration test), it is also clear that any field test involving

injection of warm  $CO_2$ -bearing fluids certainly risks an excursion into the thermodynamically complex zones in the center of the phase diagram. The simulation of complex regimes with mixed hydrates, multiple fluid phases, and the possible entrance of the near-critical region is likely to be a challenging problem. The fast parametric relationships described here allow this problem to be understood, such that the investigation can identify complex regimes and thus comprehend the potential difficulties of simulating the process.

#### 4. Conclusions

The use of these expressions in a reservoir simulation will be described in subsequent publications. However, the mere exploration of the data space and the gathering, fitting, plotting, and attempts to understand the data reveal a system that is extremely complex, and these investigations have already extended understanding of the system beyond what has been described in the literature.

Key observations include:

- 1) The mixed-hydrate phase behavior is poorly constrained by data. therefore speed was chosen over fidelity. While incorporation of ab initio-style methods directly into simulator leads to the greatest flexibility, with the creation of detailed look-up tables close behind in this regard, such methods limit the extent of the simulated system due to the computational overhead for operations that may be performed thousands or millions of times within a simulation cycle. More recent work in methane hydrate simulation by this group, including (Reagan et al., 2015; Moridis et al., 2013; Reagan et al., 2010) has demonstrated the need to simulate large, complex, heterogeneous, geologically realistic, and often three-dimensional systems. Such simulations require highly efficient physical properties relationships. While these relationships are limited by the necessarily simplicity of the functional forms, it is important to recognize that the underlying dataset is itself derived from a model. Such model-derived properties have a maximum of the accuracy or realism (or at least a limit to the certainty), therefore it is clear that ad hoc fast parametric relationships are a fair, efficient, and sufficient means by which to represent the data. As additional field and laboratory data is gathered, these relationships can be updated and evaluated for accuracy and realism.
- 2) These physical properties relationships must be used carefully and results must be evaluated according to physical knowledge and likely system behavior. The most important product of this research is an understanding of the complexity of the  $CO_2$ -CH<sub>4</sub> hydrate system. It is not merely an interpolation of single-component phase diagrams—the second component results in additional degrees of freedom, new liquid phases, and the need to represent phase boundaries as surfaces and volumes.
- 3) A direct consequence of (2) is that the phase behavior will be actively coupled to changes in concentration in addition to changes

#### Appendix A. Vectors of cubic spline parameters

3.1.13  $P_h^{upper}(x_{CO2})$ 

 $S_{x} = \{ 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 \}$ 

```
S_{y}^{Uy} = \{ 44.540802205791, \}
                           47.194620682007, 47.418637801017, 47.238773097740,
         46.483681230367,
                           45.497887865020,
                                                45.020000607331, 44.252445392531,
         43.870589467427,
                           38.591601938069,
                                              20.484870944437 }
S_b^{Uy} = \{ 46.0809033265, 10.3719987559, \}
                                          -1.23383049348,
                                                            -4.11210430996,
                                                            -2.91722385012,
      -10.3664493863.
                        -6.64865512624,
                                           -6.94934879957
                        -103.451719795,
      -15.8640899970,
                                           -271.900586510 }
S_c^{Uy} = \{ -229.1925112262, \}
                            -127.8965344803,
                                               11.83824198625,
                                                                 -40.62098015098,
        -21.92247061287.
                            59 10041321388
                                             -62.10734994721,
                                                                 102.4285994417
        - 231.8972609110,
                            -643.9790370740,
                                               -1040.50963007
                                                                }
S_d^{Uy} = \{ 337.6532558195, 465.7825882220, -174.8640737908, 62.32836512704, \}
      270.0762794225, -404.0258772036, 548.4531646300, -1114.419534509,
```

- 1373.605920543, -1321.768643336, -1321.768643336 }

in *P* and *T*. For example, during hydrate formation, the hydration phase boundary *and* the composition of the formed hydrate is dependent on the concentration of  $CO_2$  and  $CH_4$  in the aqueous phase, but subsequent removal of  $CH_4$  and  $CO_2$  from the aqueous phase (not in 1:1 proportion) will move a simulated grid element into a difference slice of the phase diagram in the *x*-dimension as well as in *P*-*T* space. This creates a new question for reservoir simulators—whether each element retains a history of hydrate formation and dissociation along with the relation concentration changes, or whether some averaging assumption is used to create a hysteretic process of formation-dissociation in mixed systems. The practical numerical consequences of this have not fully been explored.

4) This understanding will be tested and validated by future analyses of the Ignik Sikumi test results. Although the 2012 field test went beyond the parameters originally proposed as this research began—particularly in the use of injected N<sub>2</sub> for flow assurance—the data gathered shows, in preliminary analysis, evidence that the exchange reactions occurred *in situ*, and the BinH physical properties package will be validated against the available data and extended in necessary. However, it is unlikely that the N<sub>2</sub> component can be added to the parameterized phase diagram, due to the order-of-magnitude increase in complexity beyond the 3D-phase diagram presented here. Future publications by this group and others will explore this area.

For now, we present this first simple, concise, easy-to-implement set of fast parametric relationships for mixed  $\rm CO_2-CH_4$  hydrate systems.

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- $$\begin{split} S_y^{Ua} = \{ & -2.144067539313, & -2.390018043677, & -2.561046481243, & -2.719739488264, \\ & -2.867329294068, & -3.026885481117, & -3.248306619803, & -3.545521805380, \\ & -4.040042256155, & -4.72099850490, & -6.167211750641 \ \} \end{split}$$
- $$\begin{split} S_b^{Ua} = \{ & -3.060754328082, & -1.962566819605, & -1.598346651396, & -1.535689912412, \\ & -1.447378083698, & -1.889177538412, & -2.425231534688, & -3.968986050716, \\ & -5.450893353028, & -9.491741522785, & -20.39722539038 \ \ \} \end{split}$$
- $$\begin{split} S_c^{Ua} = \{ & 7.055603448658, & 3.926271636118, & -0.2840699540319, & 0.9106373438693, \\ & -0.027519056720, & -4.390475490419, & -0.9700644723457, & -14.46748068793, \\ & -0.351592335176, & -40.05688936239, & -68.997949313614 \ \ \} \end{split}$$
- $$\begin{split} S_d{}^{Ua} = \{ & -10.43110604180, & -14.03447196716, & 3.982357659671, & -3.127188001966, \\ & -14.54318811233, & 11.40137006024, & -44.99138738530, & 47.05296117586, \\ & -132.3509900907, & -96.47019983740, & -96.47019983740 \ \} \end{split}$$
- $$\begin{split} S_y^{Ub} = \{ \begin{array}{ccc} 0.429010783418, & 0.476201872159, & 0.513666328255, & 0.550738619151, \\ 0.588199766283, & 0.630742709757, & 0.688620015725, & 0.769327916966, \\ 0.905326912506, & 1.13361139367, & 1.809597021278 \ \ \} \end{split}$$
- $$\begin{split} S_b{}^{Ub} = \{ \begin{array}{ccc} 0.554181967705, & 0.405197252854, & 0.364695365969, & 0.372123693015, \\ 0.382813002808, & 0.496747013926, & 0.642806424741, & 1.089583503368, \\ 1.500066465217, & 3.838654937081, & 10.27341704963 \ \ \} \end{split}$$
- $$\begin{split} S_c^{Ub} = \{ \begin{array}{cc} -0.978285260403, & -0.511561888112, & 0.106543019270, & -0.0322597488124, \\ & 0.139152846742, & 1.000187264431, & 0.460406843721, & 4.0073639425477, \\ & 0.097465675947, & 23.28841904269, & 41.05920208276 \ \ \} \end{split}$$
- $$\begin{split} S_d{}^{Ub} = \{ \begin{array}{ccc} 1.555744574300, & 2.060349691278, & -0.4626758936107, & 0.5713753185165, \\ & 2.870114725628, & -1.799268069031, & 11.82319032942, & -13.03299422200, \\ & 77.30317788915, & 59.23594346692, & 59.23594346692 \ \ \} \end{split}$$

3.1.2  $P_{crit,mix}(T)$ 

 $S_x = \{0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.875, 0.90, 0.925, 0.95, 0.975, 1.00\}$ 

$$\begin{split} S_y &= \{8.7967996597290, 8.7739000320435, 8.6856002807617, 8.5450000762939, \\ &8.3632001876831, 8.1492996215820, 8.0326995849609, 7.9107999801636, \\ &7.7842998504639, 7.6538000106812, 7.5198998451233, 7.3831000328064\} \end{split}$$

 $3.1.3 T_{sat}(P, P_{crit}, x_{CO2})$ 

3.1.3.1 T<sub>sat,lower</sub>(P, P<sub>crit</sub>, x<sub>CO2</sub>)

 $S_x = \{ 0.70, 0.80, 0.85, 0.90, 0.925, 0.95, 0.975, 1.00 \}$ 

For  $y_0^{L}(x_{CO2})$ :

- $S_{y}^{y0} = \{ -149.50999450684, -129.61700439453, -116.00000000000, -103.08000183105, -82.971801757812, -61.752799987793, -57.365299224854, -56.712398529053 \} \}$
- $S_b^{y0} = \{ -353.13337879513, 529.41936919226, 547.97287490418, 463.12943880822, \\ 432.56918228372, 286.22594265260, 88.107725553651, -33.808669818381 \} \}$

$S_c^{y0} = \{ 7736.3709176714, 1089.1565622025, -347.01633372566, -3046.7211101126, \}$
$2435.5159796226,  -5362.3807722450,  -2562.3479117131,  -2314.3079031682 \hspace{2mm} \}$
$S_d^{y0} = \{ -22157.381184896, -19148.971945709, -35996.063685160, 36548.247264902, -51985.978345784, 37333.771473758, 3307.2001139325, 3307.2001139325 \}$
For $A^L(x_{\text{CO2}})$ :
$ S_y^A = \{ \begin{array}{ccc} -13.363599777222, & -9.4989995956421, & -7.7455401420593, & -6.0714201927185, \\ & -2.8874299526215, & -1.2684899568558, & 0.050986301153898, & 2.000000000000 \} \\ \end{array} $
$ S^A_b = \{ \begin{array}{ccc} -13.559678649381, & 69.824308013394, & 68.228785420640, & 68.570078654879, \\ & 44.950159477069, & 39.805097588610, & 65.014978329767, & 92.353783915013 \end{array} \} $
$\begin{split} S_c^A = \{ \begin{array}{ccc} 732.33054732756, & 101.50931930019, & -165.33022301037, & 178.98195237993, \\ & -651.38033593613, & 548.47909816694, & 459.91613147936, & 633.63609193048 \  \} \end{split}$
$ S_d^A = \{ \begin{array}{ccc} -2102.7374267579, & -3557.8605641409, & 4590.8290052041, & -5535.7485887737, \\ & 7999.0628940205, & -1180.8395558345, & 2316.2661393484, & 2316.2661393484 \ \} $
For $B^L(x_{\text{CO2}})$ :
$S_y^B = \{ \begin{array}{cccc} 86.607398986816, & 67.680198669434, & 54.0000000000, & 42.069000244141, \\ & 29.501199722290, & 23.901399612427, & 22.854700088501, & 22.440200805664 \ \} \end{array} $
$ S^B_b = \{ \begin{array}{ccc} 451.40132523918, & -545.75555294100, & -532.03929166971, & -399.43109141533, \\ & -156.84284088587, & -63.253582944022, & -25.415776891991, & -10.427166299537 \end{array} \} $
$S^B_c = \{ \begin{array}{ccc} -9248.6310705885, & -722.93771121332, & 1271.5881620650, & 4032.7398481100, \\ 819.02516247926, & 1052.7599963577, & 460.75224572358, & 138.79217797456 \ \} \\ \end{array} \}$
$ S^B_d = \{ \begin{array}{cccc} 28418.977864584, & 26593.678310377, & 36815.355813934, & -21424.764570872, \\ 1558.2322258561, & -7893.4366751212, & -4292.8009033203, & -4292.8009033203 \\ \end{array} \} $
For $C^L(x_{\text{CO2}})$ :
$S_y^C = \{ \begin{array}{ccc} 0.26699998974800, & 0.35600000619888, & 0.42617699503899, & 0.50800001621246, \\ & 0.61945998668671, & 0.64627200365067, & 0.66000002622604, & 0.68117702007294 \ \} \\ \end{array} \}$
$S_b^C = \{ \begin{array}{ccc} -1.1055035337768, & 2.4841832463902, & 3.1546565516628, & 3.1371917485884, \\ 1.1926597152332, & 0.38848863677098, & 0.68992745003464, & 1.0404035337631 \ \} \\ \end{array}$
$ S_c^C = \{ \begin{array}{ccc} 23.968243146898, & 11.928624654771, & 14.890307556133, & -15.588899679108, \\ - 23.301740987996, & 7.2183194187524, & 4.8392331117939, & 9.1798102373433 \ \} $
$S_d^C = \{ -40.132061640424, 39.489105351485, -406.38942980320, -51.418942059258, 203.46706937833, -31.721150759446, 57.874361673991, 57.874361673991 \}$

3.1.3.2 T<sub>sat,upper</sub>(P, P<sub>crit</sub>, x<sub>CO2</sub>)

 $S_x = \{ 0.70, 0.80, 0.85, 0.90, 0.925, 0.95, 0.975, 1.00 \}$ 

For  $y_0^U(x_{\text{CO2}})$ :

$$\begin{split} S_y^{y0} &= \{ \begin{array}{c} -126.44499969482, \\ -97.731597900391, \\ -92.495498657227, \\ -87.336402893066, \\ -83.302803039551, \\ -81.411201477051, \\ -70.891700744629, \\ -56.712398529053 \\ \} \\ S_b^{y0} &= \{ \begin{array}{c} 494.27800768209, \\ 80.785357207229, \\ 214.81890243558, \\ 549.27130844107, \\ 551.95221755991 \\ \} \\ S_c^{y0} &= \{ \begin{array}{c} -2671.7796597474, \\ -870.76037263799, \\ -5975.8971740015, \\ 11337.238983136, \\ 2040.8572570838, \\ -1933.6208923303 \\ \} \\ S_d^{y0} &= \{ \begin{array}{c} 6003.3976236979, \\ 3294.3996206495, \\ 17742.388970241, \\ -110142.06786663, \\ 230841.81542850, \\ -123951.75634736, \\ -52993.041992188, \\ -52993.041992188 \\ \} \\ \\ \text{For } A^U(x_{\text{CO2}}): \\ S_y^A &= \{ \begin{array}{c} 7.9442000389099, \\ 5.9846801757812, \\ 2.2245700359344, \\ 1.5733000040054, \\ 2.0000000000000 \\ \} \\ \end{split}$$

$S_b^A = \{ -14.673955225174, -23.646837290899, -19.511123357277, -36.289483260095, -36.28948260095, -36.2894860095, -36.2894860095, -36.2894860095, -36.2894860095, -36.2894860095, -36.28948600000000000000000000000000000000000$
$-28.657673416565,  -24.331411895058,  -14.931486322846,  57.108952874309  \}$
$S_c^A = \{ \begin{array}{ccc} -57.908481526133, & -31.820339131112, & 114.53461780354, & -450.10181585989, \\ & 755.37420960110, & -582.32374874082, & 958.32077162927, & 1923.2967962569 \ \} \end{array}$
$ S^A_d = \{ \begin{array}{cccc} 86.960474650069, & 975.69971289767 & -3764.2428910895, & 16073.013672813, \\ & -17835.972777892, & 20541.926938268, & 12866.346995036, & 12866.346995036 \\ \end{array} \} $
For $B^U(x_{CO2})$ :
$S_y^B = \{ \begin{array}{cccc} 57.721000671387, & 41.733898162842, & 41.496398925781, & 41.117698669434, \\ & 41.099998474121, & 41.00000000000, & 34.741500854492, & 22.440200805664 \ \} \end{array} $
$S^B_b = \{ \begin{array}{ccc} -345.46418320498, & -27.396890606866, & 0.86627157128403, & -13.040165282762, \\ 25.202328934714, & -101.89299078812, & -380.65008013768, & -602.68259198146 \ \} \\ \end{array}$
$S^B_c = \{ \begin{array}{ccc} 2387.1218176048, & 793.55110837632, & -228.28786481331, & -49.840872267607, \\ & 1579.5406409666, & -6663.3534298802, & -4486.9301441021, & -4394.3703296489 \ \} \end{array} \}$
$ S^B_d = \{ \begin{array}{ccc} -5311.9023640950, & -6812.2598212642, & 1189.6466169714, & 21725.086843123, \\ -109905.25427796, & 29018.977143708, & 1234.1308593751, & 1234.1308593751 \ \} $
For $C^U(x_{CO2})$ :
$S_y^C = \{ \begin{array}{ccc} 0.37927299737930, & 0.46559700369835, & 0.47099998593330, & 0.47814500331879, \\ & 0.47349500656128, & 0.47875100374222, & 0.52399998903275, & 0.68117702007294 \ \} \\ \end{array} $
$\begin{split} S^C_b = \{ & 1.8144867943976, & 0.18114048965238, & 0.16837416272703, & -0.10175716333424, \\ & -0.12256468069718, & 0.66473593693475, & 3.5242188295341, & 9.5295107046150 \  \} \end{split}$
$S_c^C = \{ \begin{array}{c} -12.203938888762, \\ 8.4445234468908, \\ 23.047501258387, \\ 91.331814445588, \\ 148.87986055765 \end{array} \}$
$S_d^C = \{ \begin{array}{ccc} 26.914715766907, & 53.358145192487, & -87.673478410610, & 236.28463451066, \\ 194.70637081994, & 910.45750916269, & 767.30728149414, & 767.30728149414 \\ \end{array} \}$

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