

Chemistry

# The Development and Application of EOS-based VT Phase Behavior Calculation Algorithms in Petroleum Industry

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The use of equation of state (EOS)-based phase behavior calculations is widespread in the petroleum industry, including the calculation of oil and gas reserves, production forecasting, and optimization of enhanced oil recovery (EOR) plans, surface separator design, and pipe flow calculation. The most commonly used method for providing phase behavior information is PT phase-equilibrium-calculation algorithms, which have been extensively studied for decades. However, simulation and engineering design of these processes using VT phase-equilibrium-calculation algorithms is sometimes more convenient than using conventional PT algorithms and has distinct advantages. The VT algorithm has been continuously improved over the last decade to ensure calculation accuracy, robustness, and efficiency, and it has been gradually applied in the petroleum industry. This article provides an overview of research findings in the field of EOS-based VT phase behavior calculation algorithms and their applications in oil and gas engineering. The Helmholtz-free-energy minimization approach, the Gibbs-free-energy minimization approach, and the nested approach based on the PT algorithm are three typical VT algorithm approaches discussed. The petroleum industry's main applications of phase equilibrium calculation using the VT algorithm are described. Furthermore, some existing problems are identified, and several prospects for the application of the VT algorithm in the petroleum engineering field are presented. A critical review of the current state of the VT algorithm process, we believe, will fill the gap by shedding light on the process's flaws and limitations, future development areas, and new research topics.

**Keywords:** Phase Behavior Calculation; Phase Equilibrium Calculation; VT Algorithm; Petroleum Industry

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## Introduction

**T**HE applicability of phase behavior in petroleum engineering is vast. In the upstream petroleum business, multiple-phase equilibrium, including two-phase and three-phase equilibrium, is regularly encountered. For instance, when CO<sub>2</sub> injection is used to boost oil recovery in low-temperature reservoirs, gas/liquid/liquid three-phase equilibria can occur in the porous-media flow (1) or pipe flow (2). A new type of three-phase equilibria (i.e., gas/oil/water three-phase equilibria) can occur in the reservoir during the steam-injection process for heavy-oil recovery (3, 4). The reservoir engineer uses PVT (pressure/volume/temperature) relations to determine oil and gas reserves, production projections, and the effectiveness of enhanced oil recovery (EOR) methods, while the production engineers employ phase behavior data to construct surface separators and calculate pipe flow. The data on phase behavior can be derived from experiments (5-7), correlations (7-10), or equation of state (EOS) calculations (11-13). EOS-based compositional reservoir simulators were introduced as a result of the advancement of computer technology, and their application began in the late 1970s and early 1980s (14, 15).

Engineers and researchers typically rely on the PT phase-equilibrium-calculation techniques, which have been recognized as readily applicable in reservoir simulators, to perform multiphase equilibrium computations for a particular fluid mixture. In these algorithms, pressure, temperature, and feed composition are specified as inputs, and the goal is to calculate the number of equilibrium phases as well as their fractions, compositions, and volumes. On the basis of Michelsen's two seminal studies (16, 17), PT algorithms have been intensively explored for decades. This algorithm minimizes Gibbs free energy in relation to molecular numbers. Simultaneously, a sequential calculation framework consisting of stability tests and flash calculations is now widely used worldwide for computing multiphase equilibrium (18, 19). Numerous algorithms have been devised for stability tests and flash calculations, including the successive substitution (SS) approach (20, 21), Newton's method (22, 23), and trust-region method (24, 25), as well as numerous combinations of these algorithms (26).

The PT specification is merely one of the specifications for multiple equilibrium calculations, despite the fact that algorithms using PT specifications have been extensively developed (27, 28). For the purpose of computing phase equilibrium using EOS, Michelsen (28) developed a formal framework for articulating six specifications, such as pressure, enthalpy, and volume specifications. One of them is to take volume, temperature, and feed composition as known information and determine the pressure, the number of equilibrating phases, and their attributes. This is a significant alternative approach to solving the multiphase equilibrium problem. These VT phase-equilibrium calculation techniques, often known as VT algorithms, have a wide range of real-world and theoretical uses. Storage tank design in the chemical and petroleum industries can be done using VT algorithms. The design of the separation process can be guided by isochores and liquid-dropout curves (29). Additionally, VT algorithms that are derived from a VT formulation are easily connected to compositional reservoir or wellbore flow simula-

tors (30). In several recent studies, VT equilibrium calculation algorithms have been improved by accounting for the capillary pressure inside unusual rock nanopores (31-33). These studies demonstrate how the capillary pressure can be taken into account while doing phase equilibrium calculations in VT space. Additionally, using VT algorithms to direct phase-behavior studies in a fixed-volume PVT cell (34, 35). Additionally, VT algorithms have the potential to be used in the computation of thermodynamic equilibrium that incorporates gravity (38), the estimation of geological trapping pressures (36, 37), and other theoretical areas (39-41).

In recent years, VT algorithm research has become increasingly popular because it can be used in many different ways in the petroleum industry. The best way to solve the VT-phase equilibrium problem is to rewrite it as a problem of minimizing the Helmholtz free energy and then use optimization routines to solve the problem of minimizing the Helmholtz free energy. Mikyska and Firoozabadi (42) came up with new thermodynamic functions and used them to come up with a new VT algorithm. Later, a similar algorithm was used to figure out three-phase equilibrium (43, 44) and two-phase equilibrium (43, 44), with capillary pressure considered (45). Nichita (46) came up with a new unconstrained Helmholtz-free-energy minimization method for VT-phase equilibrium calculations that is more accurate. Because the Helmholtz-free-energy minimization method is hard to understand, Cismondi et al. (47) made a simpler VT algorithm that works well for both vapor-liquid and liquid-liquid equilibrium. Their VT algorithm is like the standard PT algorithm framework that Michelsen (17, 18) came up with. The only difference is that it solves the phase molar volumes by solving a pressure-equality equation when the pressure is guessed. A nested approach is another way to solve the VT phase equilibrium problem. Michelsen was the first person to come up with a general plan for a solution (28). Lu et al. (48) used a nested method to make a multiphase VT algorithm based on this framework. Using the trust-region method, the multiphase PT algorithm is built into the inner loop. For the outer loop, a good equation-solving algorithm (Brent's method) is used to find the pressure that corresponds to a given volume and temperature.

Compared to other types of algorithms, the EOS-based phase behavior calculation using the VT algorithm has distinct benefits and consequently has wide applicability in the petroleum business. The VT method has been regularly enhanced over the past decade to assure computation accuracy, robustness, and efficiency. Due to the short duration of this field's development, there are still many uncertainties and unanswered questions, such as how to combine the VT algorithm with a reservoir simulator or apply it to practical engineering calculations in the future. Despite the significant efforts and contributions made by scholars in this field, the limited time period of its development has left it with a limited range of applications.

This study aims to provide an overview of the contributions of researchers in the field of phase behavior calculation algorithms based on the equation of state (EOS) for specified volume/temperature/composition systems and their application in oil and gas engineering due to the lack of a systematic report

on the development and application of VT algorithms. In addition, based on a review of prior studies, this paper offers some projections for the future development of the VT algorithm in the petroleum business. In the Methodology and Algorithm section, we describe the methodology and numerical implementation of VT-based phase split calculations, which include three distinct approaches: the Helmholtz-free-energy minimization approach, the Gibbs-free-energy minimization approach, and the nested approach based on the PT algorithm. In the section titled “Applications of VT Algorithm in the Petroleum Industry,” we show how VT algorithms are used to solve technical challenges during oil and gas development for a variety of applications. In the final section of Summary and Prospect, the existing challenges are explored along with the potential applications of the VT algorithm in the field of petroleum engineering.

## Methodology and Algorithm

### Helmholtz-free-energy Minimization Approach

#### Volume Function and Volume Function Coefficient Framework

In contrast to isothermal-isobaric (PT) equilibrium calculations, which use the minimization of Gibbs free energy, isothermal-isochoric (VT) equilibrium calculations use the minimization of Helmholtz free energy. Mikyka and Firoozabadi (42) first came up with two new ideas — the volume function  $F$  and the volume function coefficient  $\Phi_i$  — to make the calculation simpler.

A mixture of  $c$  components with molecular weights  $n_1, n_2, \dots, n_c$  in a fixed volume  $V$  at a given temperature  $T$  reaches equilibrium when its total Helmholtz energy is minimal. The general expression for a bulk phase’s Helmholtz free energy is given by,

$$A = -PV + \sum_{i=1}^c n_i \mu_i \quad (1)$$

where  $P=P(V,T,n_1,\dots,n_c)$  denotes the pressure given by an equation of state, and  $\mu=\mu(V,T,n_1,\dots,n_c)$  implies the chemical potential of the  $i$ -th component in the mixture.

The change in chemical potential with volume at constant temperature and moles for ideal gas mixtures can be expressed as,

$$\begin{aligned} \mu_i(V_2, T, n_1, n_2, \dots, n_c) \\ = \mu_i(V_1, T, n_1, n_2, \dots, n_c) - RT \ln \frac{V_2}{V_1} \end{aligned} \quad (2)$$

Mikyka and Firoozabadi introduced the volume function of the  $i$ -th component  $F_i=F_i(V,T,n_1,\dots,n_c)$  to have a similar form of ex-

pression for the chemical potential of a component in a real mixture as in the ideal case (42). The following diagram depicts the change in chemical potential for real mixtures.

$$\begin{aligned} \mu_i(V_2, T, n_1, n_2, \dots, n_c) \\ = \mu_i(V_1, T, n_1, n_2, \dots, n_c) \\ - RT \ln \frac{F_i(V_2, T, n_1, n_2, \dots, n_c)}{F_i(V_1, T, n_1, n_2, \dots, n_c)} \end{aligned} \quad (3)$$

and

$$\lim_{V \rightarrow +\infty} \frac{F_i(V, T, n_1, n_2, \dots, n_c)}{V} = 1 \quad (4)$$

Additionally, they connected the dimensionless volume function coefficient  $\Phi_i$  (42) with the ideal fluid volume via,

$$\Phi_i(V, T, n_1, n_2, \dots, n_c) = \frac{F_i(V, T, n_1, n_2, \dots, n_c)}{V} \quad (5)$$

and

$$\lim_{V \rightarrow +\infty} \Phi_i(V, T, n_1, n_2, \dots, n_c) = 1 \quad (6)$$

The volume function  $F_i$  and volume function coefficient  $\Phi_i$  serves comparable roles to fugacity and fugacity coefficients, which are commonly employed in the PT algorithm, for a given temperature and moles mixture. The following equation can be used to evaluate the volume function coefficient  $\Phi_i$  analytically using an equation of state:

$$\begin{aligned} \ln \Phi_i(V, T, n_1, n_2, \dots, n_c) \\ = \int_V^{+\infty} \left[ \frac{1}{V} \right. \\ \left. - \frac{1}{RT} \frac{\partial P}{\partial n_i}(V, T, n_1, n_2, \dots, n_c) \right] dV \end{aligned} \quad (7)$$

where  $R$  denotes the constant of all gases. The degree of nonideality of a component in the mixture can be determined by the volume function coefficient.

Mikyka and Firoozabadi (42) proposed the successive substitution iteration method (SSI) to handle the two-phase split problem for specified volume, temperature, and composition in

2011. This was based on the volume function and volume function coefficient framework. For the computation of the phase-split properties, the fixed-point outer iteration and Newton's method in the inner iteration were combined. The Peng-Robinson equation has been used to obtain the volume-based formulation of two-phase equilibrium in terms of the volume function coefficients. It was tested on a number of examples of multicomponent mixes of varying complexity to demonstrate the effectiveness and precision of this method. The test findings show that the VT algorithm method, in contrast to the traditional PT methodology, can determine in a singular way the equilibrium state of a pure substance in a two-phase condition. According to the simulation results, the VT-flash method based on fixed-point iteration requires roughly the same number of iterations to achieve the same precision as the PT-flash method does under identical physical circumstances. Although the SSI method for VT-flash generally performs well, there are a few problems that need to be fixed. First, the SSI technique needs too much iteration to converge in some situations. Second, due to the convergence issue that may arise when we solve a 5-degree polynomial in the outer loop, the robustness of this technique cannot be guaranteed near the dewpoint at low temperatures (43, 45).

Jindrova and Mikyska (43) created a new technique for the computation of two-phase equilibria with constant volume, temperature, and moles in 2013 to address these problems. The approach used the Newton-Raphson method with line-search to minimize the total Helmholtz free energy  $A$  of the mixture. Every iteration of the modified Cholesky decomposition of the Hessian matrix results in a reduction of Helmholtz free energy. The robustness of this technique was demonstrated using six instances in this article. The algorithm was evaluated on hydrocarbon mixtures defined by the CPA equation of state and the Peng-Robinson equation of state, as well as on the  $H_2O-CO_2$  mixture. The findings demonstrate that the new algorithm is quick in comparison to the SSI approach created before (42), and no convergence issues have been seen in their cases.

Jindrova and Mikyska successfully applied the same approach in 2015 to multi-phase equilibrium calculations at constant volume, temperature, and moles (44). The suggested approach was based on repeated constant-volume stability testing (49) and constant-volume phase-split computation until a stable-phase state was discovered because the number of phases was not always known a priori. Several examples of two-, three-, and even four-phase equilibrium calculations of multicomponent mixtures under various conditions, including hydrocarbon mixtures described by the Peng-Robinson equation of state and water-containing mixtures described by the Cubic-Plus-Association equation of state, are used to demonstrate how well the algorithm performs. They discovered several instances of binary or multicomponent mixtures behaving in the same way in three- or even four-phase regions, demonstrating non-trivial mixtures for which volume was not a single function of pressure, temperature, and moles or was incredibly sensitive to small pressure changes. Additionally, they stated that the VT-specification was a well-conditioned formulation in this case that offered the PT-flash better robustness in a compositional simulator.

The SSI framework (42) was expanded to two-phase equi-

librium computations in 2019 by Lu et al. (45) taking capillary pressure into account (**Figure 1**). To increase efficiency, the vapor-phase fraction was solved using the interior point method in the inner loop by minimizing the objective function, and the vapor phase's volume fraction was updated in the outer loop by solving the pressure equilibrium equation while also taking the capillary pressure between the two phases into account. They also proposed a method based on the sub-interval bisection method to identify the proper root of the volume fraction in the outer loop, and an improved scheme of updating  $K_i$  values was adopted to resolve the convergence problem that is encountered when conducting two-phase VT under low temperature and high overall molar density conditions. These methods were proposed to ensure robustness.

### **The Unconstrained Minimization of the Helmholtz Free Energy Framework**

For performing reliable phase equilibrium calculations at a constant temperature, volume, and number of moles, Nichita (46) created a brand-new unconstrained Helmholtz-free-energy minimization technique in 2018. Nichita viewed volume as a variable dependent on molecular numbers at a specific iteration level and addressed this reliance with a nonlinear volume-balance equation. By examining the block structure of the Hessian matrix, formal connections were made between the suggested technique and the volume-based VT flash and the PT flash (by analyzing the way the partial derivatives in the Hessian matrix are calculated). Similar to the PT flash, the calculation framework combines successive substitution with the Newton method, using mole numbers or natural logarithms of equilibrium constants as independent variables. Additionally, a number of samples of various combinations under various circumstances were examined to confirm the effectiveness and resilience of the algorithm.

### **The Minimization Approach for Gibbs Free Energy**

Although setting up the VT algorithm code using the Helmholtz-free-energy minimization method is not a simple operation, it is the most natural way to solve the VT phase equilibrium problem. In 2018, Cismondi et al. (47) created a more straightforward yet effective VT algorithm for both vapor/liquid and liquid/liquid equilibria due to the complexity of the Helmholtz-free-energy minimization method. The only difference between their VT algorithm and the traditional PT algorithm framework proposed by Michelsen (16, 17) is that their algorithm determines the phase molar volumes under a guessed pressure by solving a pressure-equality equation under a volume distribution restriction, as shown below,

$$F = P^V(v^V) - P^L(v^L) = 0 \quad (8)$$

where  $P^V$  and  $P^L$  stand for, respectively, the pressures of the liquid-like phase and the vapor-like phase. The volume of the liquid-like phase,  $v^L$ , can be used to indicate the volume of the vapor-like phase,  $v^V$ ,

$$v^V = \frac{v - (1 - \beta)v^L}{\beta}$$

with

$$\left(\frac{\partial v^V}{\partial v^L}\right) = -\frac{1 - \beta}{\beta} < 0$$

(9)

where  $v$  is the entire volume provided and represents the phase fraction of the vapor phase.

Cismondi et al. (49) came to the conclusion that the phase equilibrium problem with VT specification might be regarded as a Gibbs-free-energy minimization problem with PT specification under a specified pressure-equality constraint. The flowchart is depicted in **Figure 2**. Due to the modification of the original two-phase PT technique to a VT approach, however, its resilience cannot be guaranteed when three-phase equilibria are encountered. This is the reason why the VT method developed by Cismondi et al. (47) has trouble estimating the isochores within the three-phase region.

### The Nested Approach Based on the PT Algorithm

An alternative technique would be to use a standard PT algorithm to solve the VT phase equilibrium problem. Such an approach was created in 1991 by Agarwal et al. (50) to carry out isentropic equilibrium calculations with an incorporated PT algorithm. The PT algorithm is constructed in the inner loop of the algorithm by Agarwal et al. (50), and the temperature is solved in the outer loop to fulfill the energy balance equation. In 1999, Michelsen (28) proposed a general solution framework that incorporates a Newton technique and a nested approach to handle phase equilibrium issues with various specifications. The Newton method uses a single loop to solve every unknown. In the layered technique, the inner loop calculates a PT equilibrium while the outer loop solves the unknown variables. The nested approach's unknown variables can be resolved using either a root-finding method or a second-order maximization method, according to Michelsen (28). However, Michelsen (28) did not provide any additional details on how to numerically implement the nested approach's root-finding mechanism.

In 2021, Lu et al. (28) used the nested approach to develop a simpler and more robust phase-split algorithm for multiphase equilibrium computations at temperature and volume specifications, following the instruction of Michelsen. The multiphase PT algorithm (**Figure 3**) is embedded without further modification in the inner loop, while an effective equation-solving algorithm (i.e., Brent's method) is applied to the outer loop to solve for the pressure corresponding to a given volume and temperature specification. The combined use of the trust-region-method-based PT algorithm and Brent's method ensures the robustness of the newly developed VT algorithm (**Figure 4**). In previous studies as well as the current one, these two algorithms were shown to be very robust. As examples, several fluid mixtures are calculated to show that the new VT

algorithm can always converge to the correct phase equilibrium, including one-phase equilibrium, vapor/liquid or liquid/liquid two-phase equilibrium, and vapor/liquid/liquid three-phase equilibrium. In the meantime, the new algorithm has proven to be relatively efficient. For two-phase and three-phase equilibrium, fewer than ten PT algorithm calls are required to converge the VT algorithm calculations.

### The Application of VT Algorithms in the Petroleum Industry

In the petroleum industry, phase behavior computation has a variety of applications in reservoir engineering, production engineering, oil-gas storage and transportation engineering, and petroleum refining engineering, among others. It can be used to offer fundamental information about a mixture or fluid, such as volumetric behavior and phase composition, as well as density, isothermal compressibility, and component distribution within each phase. For a combination with a known composition, it is possible to determine the phase equilibrium, including saturation conditions, over a broad temperature and pressure range. Flow calculations require transport characteristics as well. Despite the fact that the PT algorithm is the most popular way for obtaining such information, the VT algorithm has its own distinct benefits and a wide range of practical and theoretical applications.

VT algorithms can be used to guide the design of storage tanks and separation processes (29), coupled to compositional reservoir and wellbore-flow simulators (30), and used to calculate the reservoir fluid properties inside unconventional rock nanopores (31-33) and direct phase-behavior experiments in fixed-volume PVT cells (34, 35). We will provide an overview of these applications.

### Design of a Storage Tank and Separation Process

Cismondi et al. (47) have shown that isochores and liquid-dropout curves can be used to guide the design of storage tanks and separation processes. Case examples were offered to highlight the applications. The fourteen-component natural gas mixture is one of the cases. As illustrated in **Figure 5**, the phase envelopes and isochores for this system were plotted on pressure-temperature graphs (47). In practical terms, it was demonstrated that the isochores can provide information such as how the pressure would change or behave throughout the heating or temperature increase of a vessel with a constant volume and a specific amount of the specified fluid. **Figures 6** and **7** depict, respectively, the phase fractions and  $C^{5+}$  concentrations in both phases along the isochores. These diagrams can assist in the search for conditions suitable for isolating the heavier condensable fractions of natural gas. A higher loading of storage or separation tanks, which implies a lower specific volume, will yield bigger fractions of the condensed phase during cooling, resulting in a lower proportion of heavier fractions in those condensed phases. Consequently, the optimal design is contingent upon the fluid's composition and the process's parameters. Calculations based on the VT method can provide valuable data for the design of separation processes that attempt to tune the composition before transport to prevent condensation.

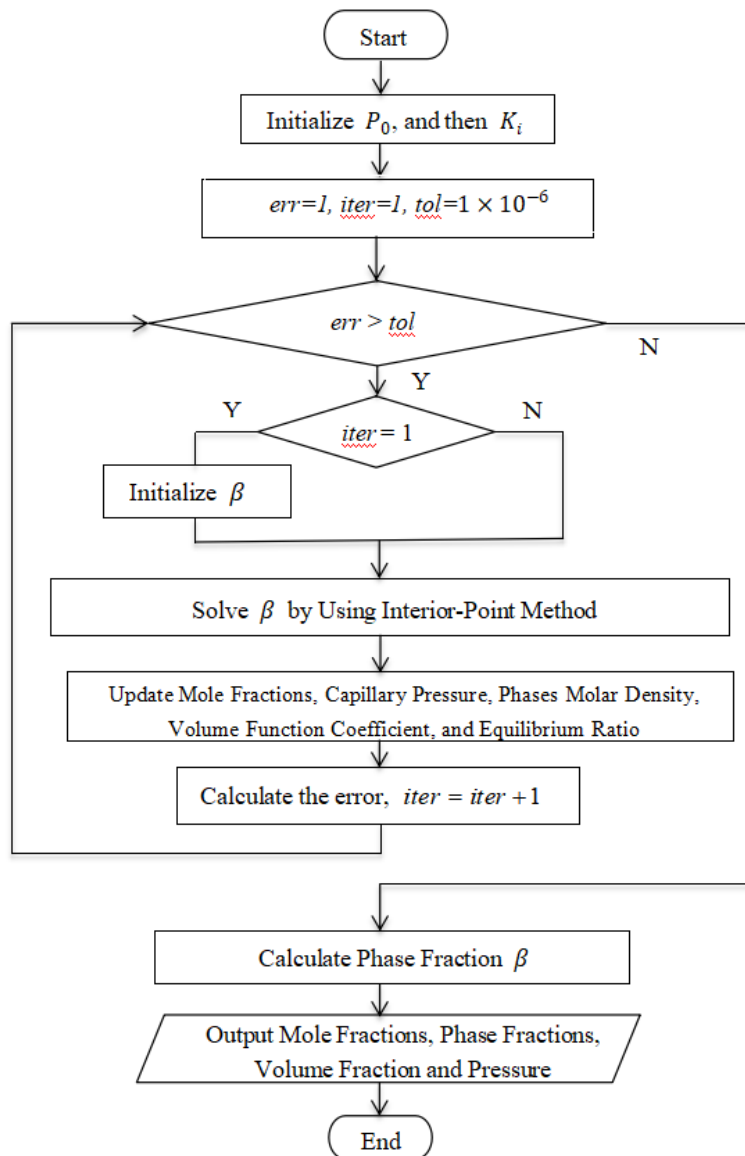


Figure 1. Flow Chart of the Two-Phase VT-Flash Algorithm with the Effect of Capillary Pressure (44).

### Coupling into Compositional Reservoir/Wellbore-Flow Simulators

Compositional reservoir and wellbore flow simulators that are developed from a VT formulation can be simply connected to the VT algorithms. Instead of using a PT-based formulation, Polivka and Mikyska (30) have created a novel VT-based formulation of the compositional model for the reservoir simulation. Instead of constant temperature and pressure, this model calculates the phase equilibrium at constant temperature and volume. The compositional data is shown using VT-Flash techniques. Since the equation of state does not need to be inverted and there are no root selection issues, Polivka and Mikyska (30) showed that the VT-based formulation is not only more robust than the conventional PT-based formulation but also offers a

convenient and natural manner to compute the pressure. Testing has been done on eight examples of binary and multicomponent mixtures that fit the Peng-Robinson equation of state. As an illustration, **Figure 8** (30) depicts a reservoir simulation of a CO<sub>2</sub> injection process in the bottom left corner of a horizontal reservoir that was initially filled with oil. They provided examples to show how, in contrast to conventional methods, their approximation of the component flux between elements does not rely on phase identification and pairing between elements. Therefore, since CO<sub>2</sub> is frequently injected into the reservoir in the supercritical state, VT-based formulations are effective for solving carbon sequestration-related challenges. To contrast with the decoupled (sequential) IMPEC techniques, Polivka and Mikyska also noted that the VT-based method is totally coupled,

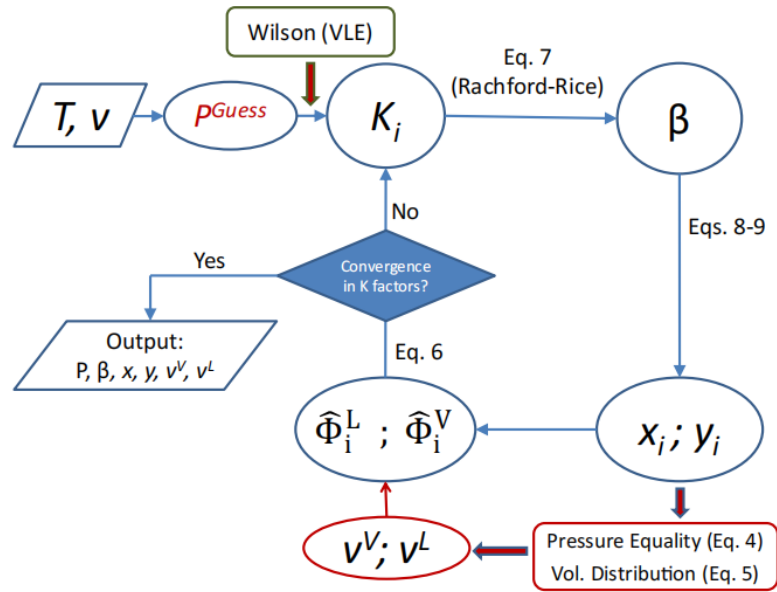


Figure 2. Schematic Representation of the Successive Substitution Strategy Proposed and Implemented in This Work for Solving the T-v Flash Problem (47).

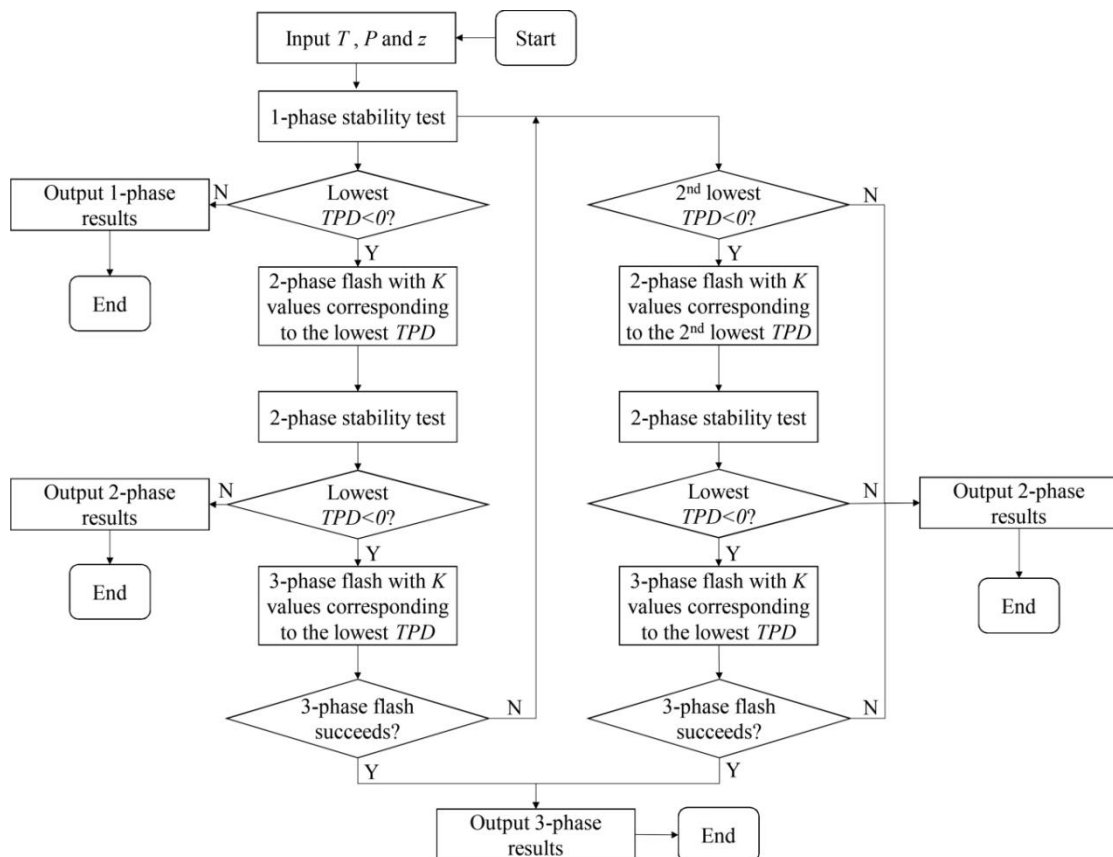


Figure 3. A Flow Chart of the Multiphase PT Equilibrium Calculation Algorithm Proposed by Pan et al. (48, 26).

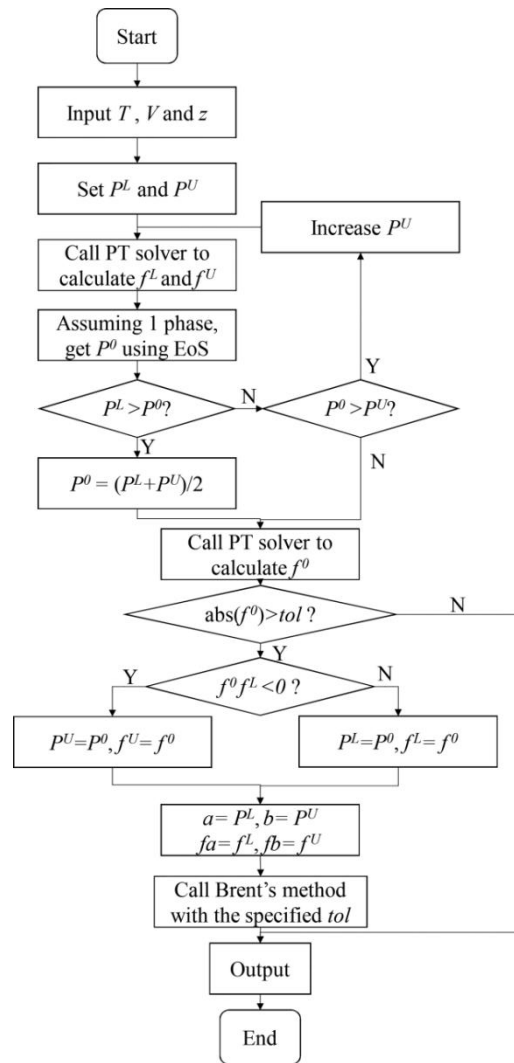


Figure 4. A Flow Chart of the Developed Multiphase VT Algorithm (48) Based on the Multiphase PT Algorithm Proposed by Pan et al. (26).

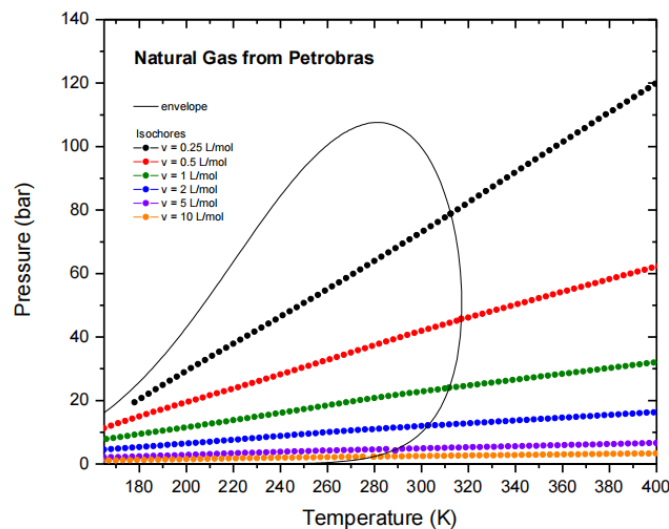
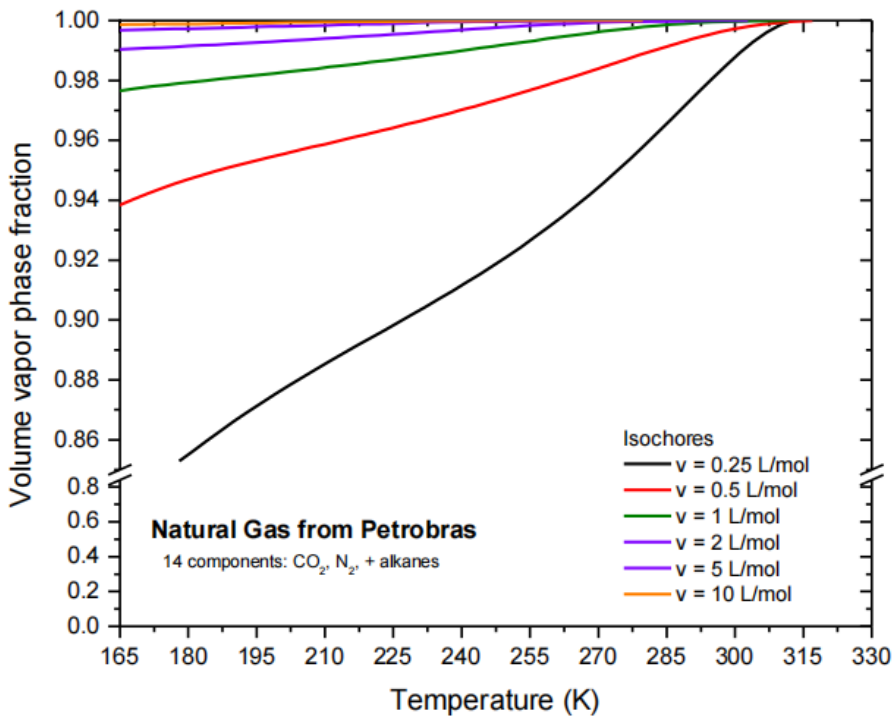
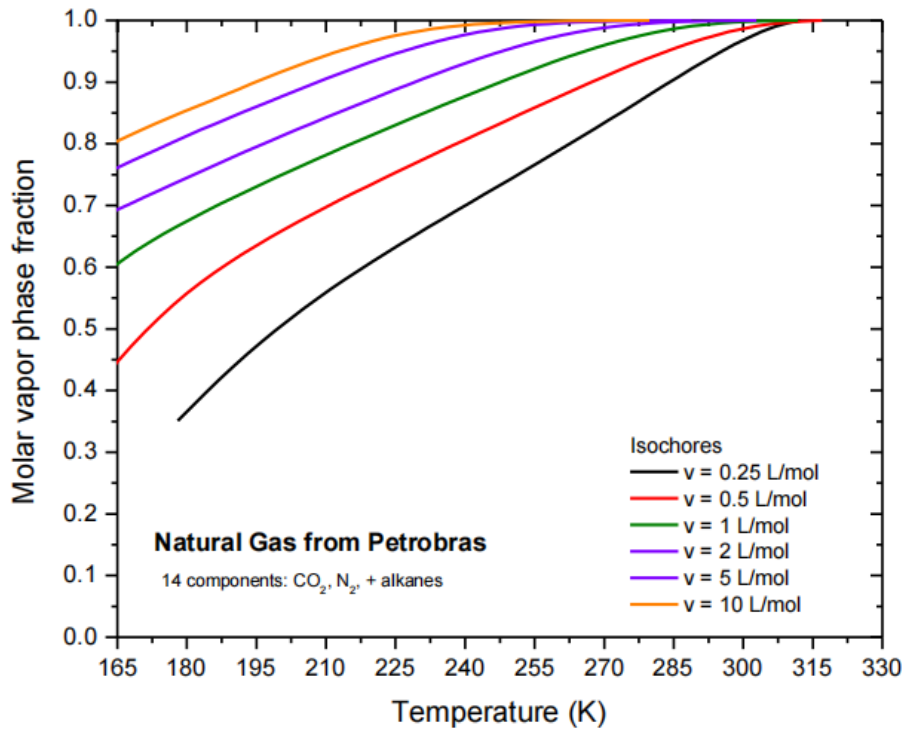


Figure 5. The Phase Envelope Together with Six Different Isochores Calculated with VT Algorithm for A 14-Component Natural Gas Case (47).





**Figure 6. Calculated Molar and Volume vapor phase fractions along different isochors for a 14-component natural gas case (47).**

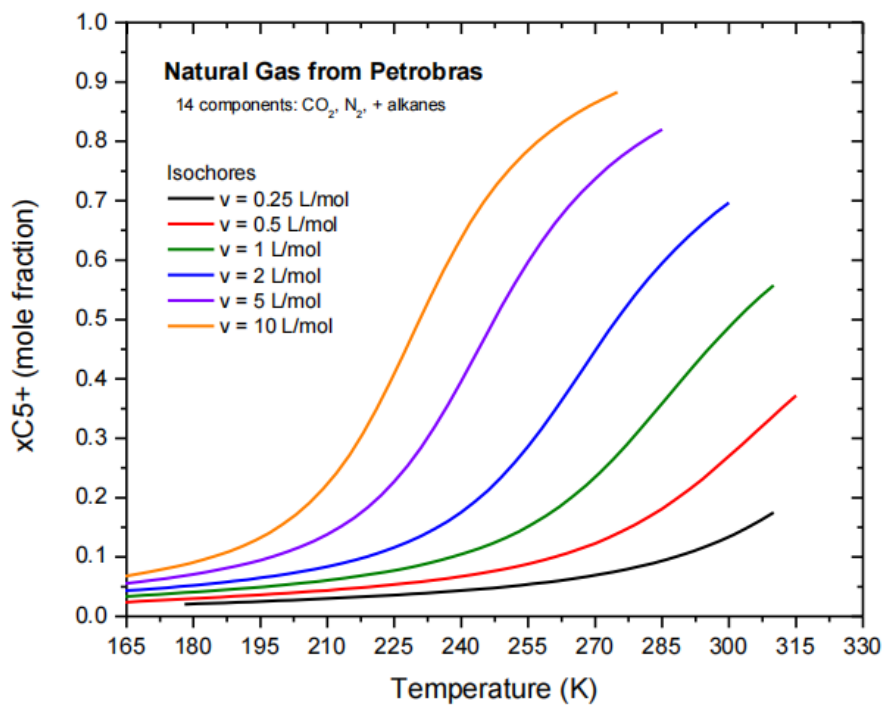
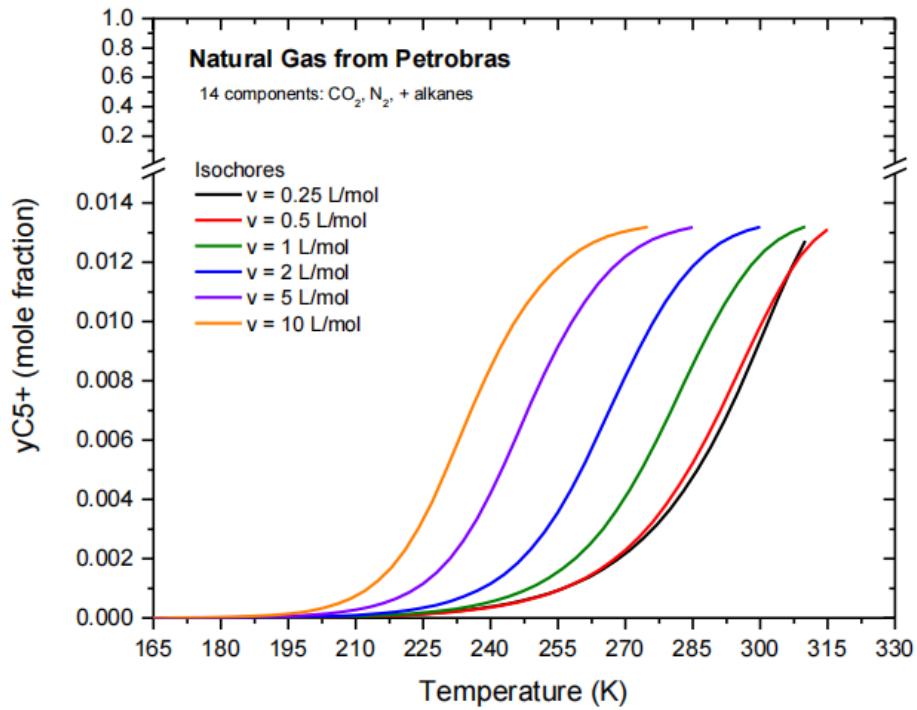
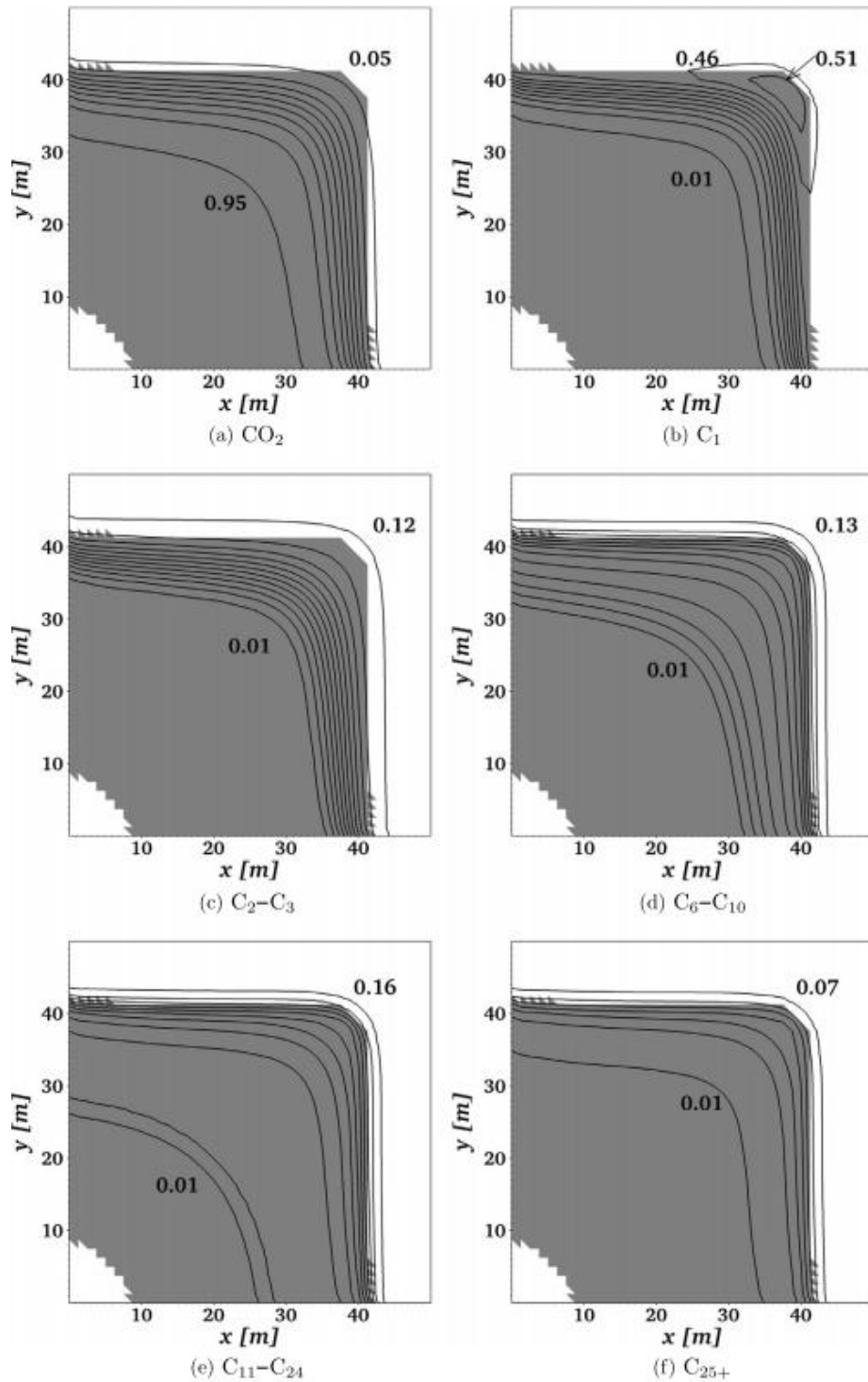
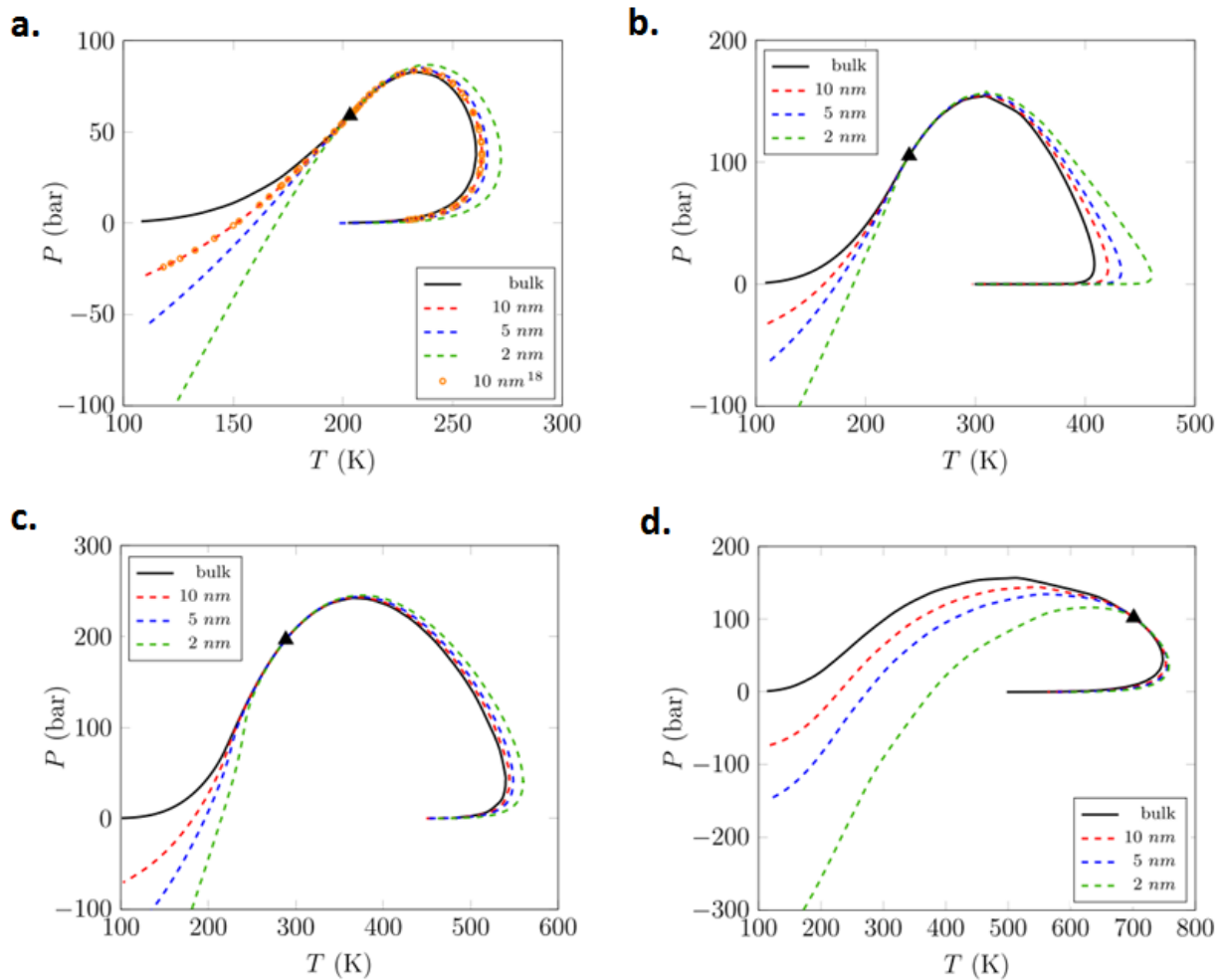


Figure 7. Calculated C<sup>5+</sup> Fractions in Vapor and Liquid Phases along the Isochores for A 14-Component Natural Gas Case (47).



**Figure 8. Isolines of the Overall Molar Fractions and the Two-Phase Region (Gray Color) at  $t = 1.36$  Years of a Case Study Drawn by VT-based Formulation Reservoir Simulation Model (30).**



**Figure 9. Phase Envelopes for (a) Natural Gas (System II), (b) Gas Condensate (System III), (c) Gas Condensate (System IV) and (d) Eagle-Ford Black Oil (System V) at Different Capillary Radii (31).**

fully implicit, and hence far more expensive. The effectiveness and reliability of VT-flash calculation are key factors in lowering CPU costs, which is a crucial problem that needs to be resolved in the future. Furthermore, in the compositional simulation, the extension of the ideas generated in the immiscible flow has historically been used to formulate capillarity. However, the currently existing theories of capillarity mainly rely on phase identification, even though the VT-based formulation appears to be very advantageous in this case compared to PT. As a result, better VT algorithms that take the confinement effect into account are required.

### Calculation of Reservoir Fluid Properties Inside Unconventional-Rock Nanopores

Gas injection strategies are needed to improve the recovery of gas and oil in unconventional reservoirs with lots of nanopores. The most effective use of gas injection requires a thorough comprehension of the in-situ phase behavior of reservoir fluid

and how it interacts with multi-component transport processes. Recent research has created algorithms for VT equilibrium calculation that account for the capillary pressure inside unconventional rock nanopores (31-33). These studies demonstrate how considering the capillary pressure can greatly benefit phase equilibrium calculations performed in VT space. The methods that use conventional formulations and algorithms based on the minimization of Gibbs free energy have been reported to have a number of convergence issues (51-54). Achour and Okuno (32, 33) carried out a few case studies to show that Helmholtz free energy can be used to solve the phase-split problem with capillary pressure more effectively than Gibbs free energy.

Along with Achour and Okuno (32, 33), Sandoval et al. (31) used the VT algorithm to study capillarity in porous media and made a contribution to the phase behavior calculation. They showed that the VT-flash may naturally avoid the negative pressures brought on by capillary pressure in the wetting phase, which is typically liquid. Additionally, the VT formulation can

get around the capillary pressure function's high level of implicitness for the pressure variable. They also confirmed that the interfacial tension models' simpler derivatives—which are better suited for situations with high capillary pressures or saturation-dependent capillary pressures that take pore size distribution into account—are produced when volume is used as an independent variable. For a number of cases, including gas, gas condensate, and black oil fluid, the VT method is utilized to generate the phase envelope (**Figure 9**) (31) and perform the isothermal flash calculation with capillary pressure. Extreme capillary pressure conditions are utilized to test the algorithms at capillary radii as small as 2 nm.

### Guidance on Phase-Behavior Experiments in a Fixed-Volume PVT Cell

As demonstrated by Fontalba et al. (34) and Kikani and Ratulowski (35), a three-phase VT method can be utilized to direct fixed-volume three-phase equilibrium observations. In such tests with a constant volume, the temperature is either increased or decreased. The resulting equilibrium pressure and phase volumes are then measured. Before conducting experiments involving three-phase equilibrium, it is required to develop a feed composition that may cause the formation of three-phase equilibrium in the fixed-volume PVT cell. During these experiments, preliminary VT calculations can be performed on a few potential feeds.

Moreover, VT algorithms may be applied to the estimation of geological trapping pressures (36, 37), thermodynamic equilibrium calculations taking gravity into account (38), and other theoretical aspects (39-41) that we will not describe in detail here.

### Conclusion and Perspective

In this article, we examine the contributions made by researchers in the field of EOS-based phase behavior computation algorithms for specified volume, temperature, and composition systems, as well as their applications in oil and gas engineering.

- i. The phase behavior calculations by the EOS-based VT algorithm are implemented using three common approaches: the Helmholtz-free-energy minimization approach, the Gibbs-free-energy minimization approach, and the nested approach based on the PT algorithm.
- ii. The Helmholtz-free-energy minimization approach is the most “natural” way to solve the phase-split problem for a system with a given volume, temperature, and composition. Existing methods can tackle multiphase split problems, such as two-phase, three-phase, and four-phase equilibrium calculations and two-phase equilibrium calculations with capillary pressure. However, algorithm formulation is a difficult task.
- iii. The Gibbs-free energy minimization approach has the advantage of being simple to implement. However, its robustness cannot be guaranteed for three-phase equilibrium, and it is difficult to determine the isochores within the three-phase region.
- iv. Because the nested approach based on the PT algorithm may be implemented by invoking the already-existing multiphase PT algorithm as needed, it is reliable, deriva-

tive-free, and simple to set up. On-site engineers can quickly configure a VT algorithm of this type to carry out VT computations. However, improving computing efficiency is a crucial problem.

- v. The petroleum industry is introduced, along with a number of the principal applications of phase equilibrium calculations based on the VT method. It can be used to direct phase-behavior experiments in a fixed-volume pressure/volume/temperature (PVT) cell, guide the design of storage tanks and separation processes, couple with compositional reservoir and wellbore-flow simulators, calculate the reservoir fluid properties inside unconventional rock nanopores, and more.

Although there has been significant progress in the development of VT algorithms in recent years and they have begun to be used in the petroleum industry, there are still many issues that impede their application, and more work should be done in the future.

- i. The most important characteristics for an algorithm when it comes to solving real-world engineering issues are robustness, accuracy, and efficiency, especially when it comes to reservoir simulations or wellbore simulations. It is necessary to create an algorithm that is more reliable, accurate, and effective.
- ii. The erroneous prediction of pressure by the equation of state for a system with defined volume, temperature, and moles is a further difficulty that hinders the integration of VT algorithms in a reservoir simulator or a wellbore simulator. Especially when the fluid is in a single liquid phase, the pressure prediction is quite sensitive to the change in volume, which can easily cause the reservoir/wellbore simulation to fail. To encourage the use of VT algorithms in reservoir and wellbore simulators, it is necessary to develop a methodology capable of resolving the problem of erroneous pressure calculation.
- iii. When calculating the parameters of reservoir fluid inside unusual rock nanopores, VT algorithms take capillarity pressure into account. However, due to the significant adsorption impact of oil and gas molecules on the wall in shale or tight reservoirs, taking into account capillary pressure alone cannot ensure the correctness of modeling findings. It is necessary to create a more precise VT-based approach because doing so will hasten the field's adoption of unconventional oil and gas exploitation.
- iv. Previous studies have found that there is a significant amount of shale oil present in the dissolved state in the organic matter in shale reservoirs, in addition to the vapor-liquid equilibrium dwelling in the nanopores (55). The main element in these organic materials is kerogen, which has a dissolving effect on hydrocarbons. Shale oil's phase behavior may be significantly impacted by the dissolution and liberation of hydrocarbons in kerogen, which will alter the composition of shale oil that is equilibrating with kerogen. The three-phase gas-oil-kerogen equilibrium in shale oil reservoirs can be modeled using the VT-based equilibrium calculation algorithm.
- v. One of the hottest study areas in the near future will be the application of VT algorithms in the area of CCUS (Carbon

Capture, Utilization, and Storage). In more recent oil discoveries, fields with high concentrations of acid gases like CO<sub>2</sub> and hydrogen sulfide are typical. An efficient method is to use hollow fiber membranes to absorb these acid gases underground in order to reduce production costs and environmental harm in such locations. The gas passes through the membrane and can either be stored or reinjected into the reservoir for EOR. Calculating the pressure and gas composition in the hollow fiber membrane, or performing a T-V flash calculation, is a problem

associated with this method.  
vi. Moreover, four-phase vapor-liquid-liquid-aqueous or vapor-liquid-aqueous-asphaltene equilibrium difficulties commonly develop in reservoirs containing water and asphaltene oil. At a given volume, temperature, and composition, it is worthwhile to construct a suite of robust and efficient four-phase vapor-liquid-aqueous-asphaltene equilibrium calculation methods. However, this task is significantly more complicated and demands more careful algorithm configuration design. ■

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