

Solid-Liquid-Vapor Phases of Water and Water-Carbon Dioxide Mixtures Using a Simple Analytical Equation of State

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ABSTRACT

Recently we have proposed a unified analytical equation of state (EOS) for solid-liquid-vapor phases, and successfully applied the EOS for the solid-liquid-vapor states of pure substances, as well as binary mixtures. The present study is an extension of the earlier EOS work to water and its binary mixtures with carbon dioxide. It is found that the our proposed EOS can describe reasonably well the thermodynamic properties of water (having unordinary melting/freezing behaviors) around the triple point, although to set up the EOS parameters requires a special procedure different from the ordinary compounds like CO₂. A simplified version of EOS for water has also been developed by sacrificing accuracy in some of the water properties, in order to model water-containing mixtures. Using such a simplified EOS of water, we examine the feasibility of phase behavior prediction including the solid (clathrate hydrate) state for binary mixtures of water and CO₂. All important three-phase (triple-point) equilibrium lines (vapor-liquid-liquid, solid-liquid-liquid, solid-liquid-vapor equilibria) are fairly well predicted, using only the information of vapor-liquid equilibrium data and the quadruple points. Results are still tentative but are encouraging for further improvement. This is a completely new way to model the clathrate-forming system.

Key Words: carbon dioxide; clathrate; equation of state; ice; liquid; phase diagram; solid; vapor; water

1. INTRODUCTION

Solid, liquid and vapor phases are well-known states of matter. Thermodynamic properties of each state and phase equilibria among these states are major interests in applied thermodynamics, where equations of state (EOS) play an important role. Although the solid-liquid-vapor coexistence (triple point) was known for more than 130 years [1, 2], numerous EOS developed in the past have been devoted to fluid-only (liquid and vapor) states, and hardly any EOS for solid, liquid and vapor states in a unified way has been studied for long time. This may be in part due to the famous van der Waals EOS [3], which describes the continuity of liquid and gaseous states and the critical point of vapor-liquid coexistence discovered around the same time as the triple point discovery. The remarkable van der Waals EOS captured much attention, and many researches went further to improve the van der Waals EOS. The solid state seemed to be treated as less important in the field of chemical engineering, although the solid state was greatly studied in solid state physics and material sciences as an independent research field.

A commonly used method to include the solid state in the phase transition behavior of matter is to treat the solid state with a separate and/or different equation, adjusted at the triple point with thermodynamic relations, while fluid state properties are described by any well-developed fluid EOS [4-7]. This method is often sufficient for practical applications. However, it would be more convenient and philosophically more pleasing to describe the solid, liquid and vapor states in a single unified EOS. If such an EOS is a simple and analytically closed form, it is highly useful for practical applications. In this respect one of the pioneering efforts is by Wenzel and Schmidt [8]. They proposed an empirical EOS, which was a cubic fluid EOS plus an additional high-power attractive term, and demonstrated successful applications for real substances. One of the problems in their EOS is that the solid-liquid equilibrium has a critical point, although the critical point occurs at a very high pressure and a very low temperature and so there may be no practical problem. Another difficulty was a numerical convergence problem at low temperatures [9]. Later, Wenzel and his co-workers gave up their EOS [9] and went to another method to deal with the solid-liquid-vapor phases, where the solid state is regarded as clusters (reaction equilibrium equations of the cluster formation, or association model) and the fluid state is treated with a usual cubic EOS [10-12]. Salim and Trebble [13] proposed a method to include the solid state using two separate cubic EOS for the solid and the fluid states, and

EOS constants are determined so as to satisfy and match the equilibrium condition and properties at the triple point as well as the vapor pressure data. The method appears useful for practical applications, although the physical meaning and the justification are unclear. Apart from purely empirical and phenomenological EOS, Modarrress et al. [14, 15] recently applied a classical Lennard-Jones and Devonshire cell theory to develop a unified EOS for solid, liquid and vapor phases. Their improved version [15] is more physically reasonable, without giving negative triple point pressures [14], but the model seems to have still a critical point in solid-liquid equilibria against the known experimental fact. Furthermore, the EOS requires a numerical integration and the possibility for application to mixtures is quite uncertain.

Recently we have proposed a simple unified EOS for solid-liquid-vapor phases and successfully applied the EOS for pure substances such as argon, carbon dioxide, and methane, as well as binary mixtures of methane and carbon dioxide [16]. In addition, it has been demonstrated that the EOS can be applied for computer-simulated solid-fluid transition of hard spheres by eliminating the attractive term of the EOS. The present study is an extension of the earlier EOS work to water and its binary mixtures with carbon dioxide. Although water belongs to a simple class of triatomic molecules, the thermophysical properties are highly complex and unique, and also it is fundamentally important substance in our life. The proposed EOS cannot simply be applied for water as done for argon, carbon dioxide and methane. The existence of various crystal modifications is one complication and the density decrease of solid water (ice) w.r.t. liquid at the triple point is another, having a negative slope in the melting line, different from the characteristics of common substances, and the existence of a maximum in the saturated-liquid density around 4 °C [17, 18]. It is quite a challenge to model these unusual behaviors with a simple unified analytical EOS.

The purpose of the present study is to examine the feasibility of the application to water including the solid (ice-I) state within the framework of the present EOS model. We show the present model can reasonably describe the unique characteristics of water including solid state (Ice-I). However, the EOS form has to be different from that of the common compound like Ar or carbon dioxide. Thus it is inconvenient for modeling mixtures of water with other common substances. Another water EOS, which has a common form with Ar or carbon dioxide, is also developed for the mixture application,

although some of the volumetric properties of water must be abandoned. Then we try to apply the model for binary mixtures of water and carbon dioxide (CO₂), including the solid phase, to see whether such a simplified water EOS can be valid for the mixture phase calculations. Water-CO₂ mixtures are known to form clathrate hydrates [19] and there exist complex phase behaviors with various three-phase lines and quadruple points. The present approach is a new method, completely different from the traditional way to model clathrate containing systems.

First a brief description of our EOS is given in Section 2. Analyses and results of pure water and water-CO₂ mixtures are discussed Section 3, where first, water is treated as if it were an ordinary compound like Ar or CO₂, with the same type of EOS as the ordinary substances. This is a simplified version of EOS for water. Then a more realistic model for water is developed within the framework of the present EOS form. Next, the phase equilibrium behavior of binary water-CO₂ mixtures including the solid state (clathrates) is investigated, using the simplified version of water EOS. Discussions of the present work are given in Section 4, followed by concluding remarks in Section 5.

1. EQUATION OF STATE

The simplest form in the proposed general EOS [16] for solid-liquid-vapor states can be written as:

$$P = \frac{RT}{V-b} \left(\frac{V-d}{V-c} \right) - \frac{a}{V^2} = \frac{RT}{V-b} \left(1 + \frac{c-d}{V-c} \right) - \frac{a}{V^2}. \quad (1)$$

The parameters a , b , c are all positive, R is the universal gas constant, and the valid EOS region is $V > b$. It should be noted that b is equivalent (or interchangeable) with c , as clearly seen in Eq. (1). Here, for the sake of argument, we designate the smaller value as b , without loss of generality. For the proper (or ordinary) EOS type, the relation $b < d < c$ holds [16], although other relations are also physically reasonable and will be discussed later. Figure 1 illustrates the EOS behavior at the triple point condition. The equation of the second equal sign in Eq. (1) may provide some physical meanings for this empirical and phenomenological EOS. The term in the parenthesis $(c-d)/(V-c)$ can be regarded as a correction to the simple van der Waals repulsive (excluded volume) term and is negative when $c > V > b$, where the solid branch resides: see Fig. 1. The negative term

means an attractive correction, which reflects a physical meaning due to the statistical (“kinetic”) attraction in the high-density hard-sphere (purely repulsive) ensembles [20]. Thus, the present EOS has a good physical basis, although it is purely empirical and phenomenological.

In terms of dimensionless parameters, it becomes:

$$P_r = \frac{T_r}{Z_c(V_r - b_r)} \left(\frac{V_r - d_r}{V_r - c_r} \right) - \frac{a_r}{V_r^2 Z_c^2}, \quad (2)$$

where the reduced parameters are defined:

$$Z_c = \frac{P_c V_c}{RT_c}, \quad P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c} \quad (3)$$

$$b_r = \frac{b}{V_c}, \quad c_r = \frac{c}{V_c}, \quad d_r = \frac{d}{V_c} \quad (4)$$

$$a_r = \frac{P_c a}{(RT_c)^2}. \quad (5)$$

Then the compressibility factor, Z results:

$$Z = Z_c \frac{P_r V_r}{T_r} = \frac{V_r}{V_r - b_r} \left(\frac{V_r - d_r}{V_r - c_r} \right) - \frac{a_r}{V_r Z_c T_r}. \quad (6)$$

Depending upon a set of the EOS parameters, seven topologically different shapes of EOS arise. Figure 2 shows a summary chart from Ref.16 of the numerical and analytical analyses for the proper choice for b_r (or equivalently c_r) and Z_c parameters. Regions denoted as **A** in Fig. 2 are the proper parameter region, which corresponds to the EOS type in Fig. 1; *i.e.*, a physically stable solid-phase branch and VLE (vapor-liquid-equilibrium) critical point can exist. The parameter d_r is always between b_r and c_r in this case. In Regions **B** and **D**, the critical point occurs in the solid phase branch and for the latter no stable liquid-phase branch exists. Region **C** can have a critical point in the fluid phase branch but it is in a metastable state, and essentially no meaningful liquid phase can exist. Region **E** has a proper fluid EOS type, but does not have a physically meaningful solid-phase branch. In Region **F**, the parameter a_r is negative and physically incorrect. Finally, Region **G** cannot possess any kind of critical points.

A normal EOS shape occurs with the parameters in Region **A**, as shown in Fig. 1, and ordinary molecules like Ar, CO₂, and methane were well modeled with this type of EOS [16]. However, as seen in Fig. 1, one can easily tell that this type of EOS will not work for water; that is due to the unique volumetric property of liquid water and ice. At the triple point, the liquid density must be larger than solid (ice) density in the case of water, but the liquid density (volume) is always smaller (larger) in the EOS type A of Fig. 1. This suggests we have to use different types of EOS in order to model water properly including the volumetric properties. Fortunately, EOS types of Region **C** and **E** may serve for the present purpose. The EOS in Region **C** has only stable solid and vapor branches, which is physically correct in the case below the triple point. The EOS in Region **E** has only stable liquid and vapor branches and is good for vapor-liquid states, which possess a vapor liquid critical point. Both types of EOS are illustrated in Fig. 3. The combination of the two type EOS can be used for the unique properties of water around the triple point as well as the extended region.

In our previous work [16], we treated the EOS parameters a and b (or equivalently c) as being temperature dependent. The proposed forms are:

$$a_r(T_r) = a_0 + a_1 T_r \exp(-a_2 T_r^n), \quad (7)$$

where a_0 , a_1 , a_2 and n are all positive. $a_r(0 \text{ or } \infty) = a_0$, $da_r/dT_r = a_1$ at $T_r = 0$ K, and the maximum occurs at $T_r = (na_2)^{-1/n}$, and

$$b_r(T_r) = b_0 + b_1 \exp(-b_2 T_r^m), \quad (8)$$

where $b_0 > 0$, $b_2 > 0$, $m > 0$, and $b_r(0) = b_0 + b_1 > 0$. Another important constraint is that the relative order among the parameters b_r , c_r , and d_r must satisfy the correct topological shape for each proper type of EOS for all temperatures.

2. ANALYSES AND RESULTS

The results of CO₂ phase diagrams in Ref.16 are repeated here in Fig. 4 for the readers' convenience, since CO₂ will be used in this study for the mixture analysis. For the EOS constants of CO₂, refer to Ref.16. A pure water system will be analyzed with two different approaches as discussed in the next subsection. After the analyses of pure water, the phase behaviors of binary water-CO₂ mixtures are investigated. In the present study as

well as our previous works, our purpose is not to develop highly accurate equations, which can be used for precise engineering applications, but to demonstrate the feasibility of the present solid-liquid-vapor EOS. The numerical accuracy for representing thermodynamic properties of actual substances is not our major concern, and physically reasonable property estimations are sufficient. Therefore, we use a minimum amount of experimental data to set up the EOS parameters, and do not seek for an optimum set of the parameters using any statistical fitting methods.

2.1. WATER

Ice has seven different crystal modifications [18]. Common ice around the triple point is called Ice-I, which we will only consider in the present study. First we analyze solid-liquid-vapor EOS of pure water with the same type of EOS as used for CO₂ (here we call it Type A EOS, or EOS-A). The detailed method for the determination of such EOS constants is given in Ref. 16. Basically, only the information of the vapor-liquid critical point and the triple point is used to set up the EOS parameters. However, as mentioned earlier, water has unique melting properties, and the type A EOS cannot model the volume expansion at ice formation. Therefore, the use of the type A EOS means that we have to sacrifice the accuracy and behavior of the volumetric properties of ice. However, the advantage is not only simple and convenient when we try to model the phase behaviors of water-CO₂ mixtures, but also such an EOS will be sufficient for modeling the phase equilibria of mixtures. The inaccurate volumetric properties of ice may not cause a serious problem for the phase behavior calculations like TPx (temperature-pressure-composition) diagrams; the error of the ice volume (or density) would be about 10 – 20 %. It is well known that the TPx diagram of vapor-liquid equilibria can be accurately calculated using a simple cubic EOS, whose liquid density estimation is very poor (with errors as much as 20 % or more). The volumetric properties are generally not sensitive to the phase equilibrium calculation with EOS. The parameters of the type A EOS for water are listed in the first row of Tables I and II, and will be used in Section 3.2, although they are by no means optimized. It is curious to see how badly or well this EOS behaves in the T - P and P - D projection diagrams. They are shown in Fig. 5, compared with some experimental data. The solid and liquid density around the triple point have errors of about 10 %, while the T -

P relation seems fair but it certainly needs some EOS parameter optimizations to get a better presentation.

Next, we try to model pure water more realistically, including the unique volumetric properties. This is done using type **C** and **E** EOS, as mentioned Section 2. Here again, the basic information to set up EOS parameters is the vapor-liquid critical point and the triple point conditions, and therefore the method for the parameter determination is essentially the same as that used in the type **A** EOS. The major difference is that we have to determine two sets of EOS parameters for both type of EOS (**C** and **E**) in a thermodynamically consistent way at the triple point. Above the triple point temperature, the EOS **E** is used for the solid state, and the EOS **C** is used for both liquid and vapor states.

The procedure is briefly described below. First we set up the parameters for the type **E** EOS. The critical compressibility factor Z_C and b_r at the vapor-liquid critical point are chosen rather arbitrarily from the region **E** in Fig. 2: e.g., $Z_C = 0.340$, and $b_r = 0.1352$. Then using the critical conditions, other parameters a_r , c_r and d_r can be determined at the critical point [16]. The parameters a_r and b_r at the triple point temperature are determined so as to reproduce the observed liquid density (or volume) well, using only the vapor-liquid equilibrium condition at the triple point. Then, while having these parameters at the two different temperatures, the T -dependence parameters (for a_r and b_r) in Eqs. (7) and (8) can be determined in the same way as type **A** EOS used in Ref. 16. Concerning the type **C** EOS, the same critical compressibility factor Z_C as the type **E** EOS is adopted. It should be, however, mentioned that the critical point in the type **C** EOS occurs in a metastable fluid state and it is merely a “formal” critical point for the EOS parameter determination. This does not cause any problem, since the EOS **E** will be actually used for the fluid state above the triple point temperature, and the EOS **C** will be used only for the solid state. The parameters a_r , b_r , c_r and d_r at both critical and triple point temperatures can be determined by combining the critical and triple point conditions, so as to reproduce the observed solid density (or volume) well. The T -dependent parameters in Eqs. (7) and (8) are obtained in the same way as the type **E** (or **A**) EOS. Several trial-and-error analyses were required to set up all parameters in a

thermodynamically consistent way at the triple point by repeating the whole processes above.

Although the EOS parameters thus obtained are by no means optimum sets, they are listed in the second and third rows of Tables I and II. Some thermodynamic properties at the triple point are calculated with these constants and shown in Table III, compared with the reported values [5, 17, 18]. The overall agreement seems quite reasonable. The unique melting properties of ice-I are well predicted: the volume shrinkage at melting and the negative slope of the melting line. In addition, it should be mentioned that the occurrence of the maximum saturated-liquid density around 4 °C is well predicted with the present EOS. Temperature-pressure and density-pressure phase diagrams calculated by the present EOS are compared with observed data in Fig. 6. They also seem quite reasonable while having the correct Ice-I melting behavior and greatly improved in the density property with respect to the previous simple EOS: compare Fig. 5.

2.2. WATER-CARBON DIOXIDE MIXTURES

Now that we have the EOS for both pure compounds, mixtures can be modeled with proper mixing rules for EOS parameters in a usual way. In this study the mixing rules for the volumetric parameters (b , c and d) in Eq. (1) are the same as used in the previous work for binary methane-CO₂ mixtures [16], but a modification of the attractive parameter a is made. It is known in a vapor-liquid equilibrium study [21] that a simple quadratic mixing for the a parameter does not work well in the case of water-CO₂ mixtures, and also our independent analyses reached the same conclusion. Thus, we use the “van Laar type” of mixing rule, which is often successfully applied for highly non-ideal systems [22, 23], and some justifications such mixing rules are discussed in Ref. 22. In terms of N -component mixtures, it can be written as:

$$a = \sum_{i,j=1}^N \sqrt{a_i a_j} (1 - K_{ij}) x_i x_j, \quad (9)$$

$$K_{ij} \equiv \frac{k_{ij} k_{ji} (x_i + x_j)}{k_{ji} x_i + k_{ij} x_j}, \quad \text{and } K_{ii} = 0. \quad (10)$$

When $k_{ij} = k_{ji}$ (symmetric), then it becomes the usual quadratic mixing in the mole fraction with $K_{ij} = k_{ij}$. Here, the binary interaction parameter k_{ij} can be a function of temperature if needed.

Before predicting the thermodynamic property of binary mixtures, two interaction parameters k_{12} and k_{21} must be set up properly. First, we estimate these parameters only using a limited amount of vapor-liquid equilibrium (VLE) data [24] among many other reported data [25], and then predict the solid-liquid-vapor phase characteristics of the present binary system. Based on recent CO₂ solubility data in liquid water [24], the following interaction parameters were estimated for the system CO₂(1)/Water(2), although they are by no means optimum.

$$k_{12} = -0.8478 + 2.428 \times 10^{-3} T \quad (T \text{ in Kelvin}) \quad (11)$$

$$k_{21} = -0.06 \quad (12)$$

The CO₂ solubility calculated with these parameters are compared with the literature data [24] in Fig. 7; the overall average deviation between the calculated and observed values is about 3 % in pressure.

Now the interesting and challenging question is whether the above mixture EOS based on the VLE data can describe the solid-liquid-vapor phase behaviors of binary CO₂-water mixtures. Here, the solid state in this binary system means clathrates of CO₂ hydrates. The clathrate containing system is generally analyzed using the van der Waals and Platteeuw type model [19, 26-31], where the solid (clathrate) state is treated with a clathrate model developed originally by van der Waals and Platteeuw [28], while the liquid and gaseous states are modeled with usual cubic type fluid EOS. The clathrate model has a good physical meaning with an assumption that the clathrate is made of ice cages (“host lattice”) and “guest” molecules trapped inside the cage. The thermodynamic properties of clathrates are derived from a statistical-mechanical theory using proper geometrical structures and interaction potentials between the host lattice and guest gas. There exist various modifications and improvements of the original clathrate model, and generally they provide good correlation for observed phase behaviors of the clathrate-liquid-vapor system, including pure ice.

Although a gas hydrate is often called as a clathrate “compound”, it can be regarded as a “solid solution” of the guest molecule in the (metastable) host lattice [28]. It

is certainly not the same as a stoichiometric (true) compound formation such as $\text{NH}_3 \bullet \text{H}_2\text{O}$ and $2\text{NH}_3 \bullet \text{H}_2\text{O}$ in ammonia-water binary mixtures, or $\text{HCl} \bullet \text{H}_2\text{O}$, $\text{HCl} \bullet 2\text{H}_2\text{O}$ and $\text{HCl} \bullet 3\text{H}_2\text{O}$ [28]. This point is important for the present EOS application, since if it is a true compound, a separate EOS unique for that compound is required in order to model the mixture system; then, the binary system becomes a ternary system. Therefore, when the clathrate hydrate is regarded as a solid solution, the present new approach to model the water- CO_2 system with the unified solid-liquid-vapor EOS may be justified. Our purpose is to see whether the present simple unified EOS can predict the phase behaviors of solid (clathrate)-liquid-vapor states.

Using the binary interaction parameters Eqs. (11) and (12) based on the VLE data only, three-phase equilibria lines for liquid-liquid-vapor (L_1L_2V) and solid(hydrate)-liquid(CO_2 rich)-vapor (HL_2V) are well predicted within an error of about 10 % in pressure. However, a quadruple point (Q_1) for the HL_1L_2V phase occurred around $T = 264$ K, which is far below the observed point of about 283 K [32]. The calculated HL_2V lines above 264 K turned out to be metastable states with respect to the L_1L_2V three-phase equilibria. Then it was found that in order to bring the Q_1 point to a much higher temperature, the binary interaction parameters in the solid (hydrate) state have to be much “stronger” than those in the liquid and vapor phases. Therefore, in order to make the Q_1 point more realistic, we estimated the binary interaction parameters for the hydrate phase at the Q_1 point in thermodynamically consistent way: $k_{12} = -0.420$ and $k_{21} = -0.06$. With these interaction parameters for the hydrate state and Eqs. (11) and (12) for the vapor and liquid states, the Q_1 point was calculated to be: $T = 283.3$ K and $P = 4.713$ MPa with CO_2 in $L_1 = 3.14$ mol %, CO_2 in $L_2 = 98.67$ mol %, CO_2 in H (hydrate) = 8.49 mol %, and CO_2 in vapor = 99.91 mol %. The corresponding Gibbs-free energy plot is shown in Fig. 8 at the quadruple point (Q_1) condition. This binary system showed highly complex behaviors, and phase equilibrium calculations were not straightforward without knowing the global phase transition characteristics in advance. In order to understand various phase interactions before performing the numerical calculations, we have used extensively the Gibbs-free energy plots, where the common-tangent method helps us to understand the existence or non-existence of stable and/or metastable equilibria at least qualitatively, without solving tedious nonlinearly coupled equations of equilibria.

Now, we have a thermodynamically consistent behavior around the Q_1 point. The next task is to see whether we can predict the clathrate dissociation line, *id est*, solid(hydrate)-liquid(water rich)-vapor three-phase line (HL_1V), which starts from Q_1 and ends at another quadruple point (Q_2): HL_1V coexisting with pure ice at about 272 K [32]. From trial-and-error analyses of the Gibbs-free energy plot, it was found that the clathrate-state interaction parameter (k_{12}) has a temperature dependence in order to model the entire region of the HL_1V line. A proper value for k_{12} at 272 K was estimated simply from a necessary condition that requires the existence of a thermodynamically stable three-phase equilibrium of HL_1V at 272 K: $k_{12} = -0.354$ and $k_{21} = -0.06$. The Gibbs-energy plot at the Q_2 point condition is shown in Fig. 9. It is clearly seen from Fig. 9 that the pure ice-I cannot coexist with the hydrate in the HL_1V three phase equilibrium and that a slightly modified ice-I' is needed in order to have a proper quadruple point. A proper EOS for the ice-I' was easily made by modifying only the b parameter of ice-I (water) EOS; the b parameter of the water EOS was reduced by a factor of 0.97364. This factor was found so as to satisfy the quadruple point (Q_2) of the ice-hydrate-liquid(water-rich)-vapor (IHL_1V) equilibrium. It may sound strange and inconsistent to have the two types of ice (ice-I and ice-I') in the analysis. However, this has a good physical meaning. If the ice in hydrates were the same pure ice (with the same structure), there is equilibrium between ice and hydrate. The "guest" molecule (here CO_2) can go into both the hydrate ice and the pure ice and then there is no distinction between the pure ice and hydrate. Therefore, the pure ice coexisting with hydrates must have a structure different from the ice forming hydrates and the molar volume of the former ice (ice-I') would be smaller than that of the latter ice (ice-I) in order to prevent the intrusion of "guest" molecules. In fact, the molar volume of the ice-I' was calculated to be about 1.1 % smaller at the Q_2 point than the ice-I in the present EOS model for the ice-I and ice-I'.

Concerning the temperature dependence of the binary interaction parameters for clathrate (solid) phases, it was estimated from the two values in k_{12} at Q_1 and Q_2 points mentioned above:

$$k_{12} = 1.222 - 5.794 \times 10^{-3} T \quad (T \text{ in Kelvin}) \quad (13)$$

$$k_{21} = -0.06 \quad (14)$$

Then, using Eqs. (11) and (12) for the liquid and vapor phases, Eqs. (13) and (14) for the clathrate (solid) phases, and the ice-I', all three-phase (triple-point) lines were constructed by solving the necessary phase equilibrium equations. The results are shown in Fig. 10, compared with some selected experimental data [32-37]. The vapor-liquid critical point (C. P.), two quadruple points (Q_1 and Q_2), and various three phase lines (liquid-liquid-vapor, solid-liquid-vapor, solid-liquid-liquid, including pure ice-I') are reasonably well predicted. It should be remarked that the present method and calculations are thermodynamically completely consistent without any approximations and that no fittings to the observed three-phase data were made except for the use of information of the two quadruple points.

3. DISCUSSIONS

We have demonstrated that highly unusual and unique thermodynamic properties of water can be modeled within the framework of the present solid-liquid-vapor EOS, although the two sets of EOS types are needed. It may be said that the predicted properties are in fair agreement with the observed data, particularly for the unique ice-I melting behavior, by considering the fact that the present EOS model has been based on only the information of the critical point and triple point. Using more experimental data, the accuracy in the property calculation will be further improved. However, such an effort is not our concern, since a highly accurate water fluid EOS and the method to combine the solid phase have already been developed in the literature [5, 17, 18]. The present purpose is to show merely the feasibility of our proposed simple unified EOS. It will, however, be more sensible and useful to improve the accuracy of the simplified version of water EOS, since it can be used for water-containing mixtures as discussed below.

Although the solid-liquid-vapor states of water have been modeled fairly well, the type of EOS is different from that of ordinary compounds such as CO_2 . It is inconvenient when we try to model mixture properties containing water. In order to model a binary system of water- CO_2 mixtures, a simplified water EOS has been developed, by treating water as if it were an ordinary compound. The volumetric properties of the condensed state by this EOS result in errors of about 10 % around the triple point. However, the phase transition behavior in the temperature-pressure-composition (TPx) projection is generally insensitive to the volumetric property, since the volume (or density) acts merely as an

intermediate variable. A good example here is that the VLE phase behavior in terms of the temperature-pressure-composition of mixtures can be modeled very well with a general simple “cubic” EOS, although the liquid density of such an EOS has an error of 10-20 % [21]. Furthermore, common solution (or activity) models such as Wilson, NRTL, regular-solution models, *etc.*[4] do not use the volumetric variable explicitly at all in the phase equilibrium calculation and yet describe the phase behavior very well. Therefore, the present simplified water EOS will be sufficient for modeling the TPx phase-transition behavior of water-containing mixtures, and in fact it was successfully applied in this study on water-CO₂ mixtures.

A binary system of water-CO₂ mixtures is known to form clathrates (gas hydrates) [19], and also an important binary system for practical applications [38, 39]. There is a standard method to analyze the clathrate-forming mixtures. It is based on the original work by van der Waals and Platteeuw [28], and numerous reports on clathrates in the past 50 years are all based on this model with various improvements in the numerical accuracy [19, 26-31]. A brief description of this model has already been given in Section 3.2: for details refer to Refs. 19, 26, and 28. The present method using a unified EOS is a completely new approach to model the clathrate-containing system, and is much simpler to use and thermodynamically consistent without any approximations. All important three-phase (triple-point) lines are reasonably well predicted using only the information of the quadruple points, although the numerical accuracy needs to be improved. In the present analysis, the solid (clathrate) state of the mixture requires the binary interaction parameters different from those in the fluid state, in contrast with the previous work on CO₂-methane binary mixtures [16]. This indicates that the clathrate state is not a simple solid solution and may be called as “pseudo-compounds”, although it can be regarded as a solid solution [28]. In fact, clathrate hydrates are known to have unique crystal structures (body-centered-cubic lattice of Structure I or diamond-cubic lattice of Structure II) [19, 28]. Therefore, the use of the different binary interaction parameters for the solid (clathrate) state in the present mixture would be more natural and justified.

The traditional (standard) method often provides good numerical correlation. However, the model parameters are usually determined by fitting the experimental data of the three-phase (clathrate dissociation) line, which is difficult to predict in *a priori* [28]. The numerical accuracy in the present method will be improved by setting up better EOS

parameters using more experimental data. Particularly, the vapor-pressure curve of water needs to be improved, as clearly seen in Fig 5, and the CO₂ EOS may need further refinement as well. The purpose of the present study is to see the feasibility of the new EOS method to model the clathrate-forming system. Now that this new approach seems working reasonably well, further numerical improvement is quite promising.

4. CONCLUSIONS

It has been found that the proposed solid-liquid-vapor EOS can be applied for water, which has unique and unusual thermodynamic properties, although the EOS type has to be different from that of ordinary compounds. In order to model water-containing mixtures, a simplified water EOS, which is compatible with ordinary compounds, has been developed by sacrificing the accuracy in the volumetric properties of the condensed phase by about 10 %.

Using the simplified EOS of water, a clathrate-forming system of water-carbon dioxide binary mixtures has been examined. All important three-phase (triple-point) lines are reasonably well predicted. The present method to model the clathrate-forming system is a completely new approach, and the result is still tentative but encouraging for future development.

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Table I. EOS Constants for Water in Eq. (2).

EOS Type	c_r	d_r	Z_c
A	0.337577	0.329306	0.37503
C	0.646949	0.654560	0.34000
E	0.117355	-0.588605	0.34000

Table II. EOS Constants for Water a_r and b_r in Eq. (2), using Eqs. (7) and (8).

EOS Type	a_0	a_1	a_2	n	b_0	$b_1 (\times 10^{-2})$	b_2	m
A	0.28617	152.935	7.02781	0.4092	0.32816	-0.30309	5.61866	6.00
C	0.22577	249.170	7.08807	0.3150	0.38081	5.84853	5.61866	6.00
E	0.52116	36.5736	6.00423	0.5050	0.00533	44.9134	1.24081	0.75

Table III. Some Thermodynamic Properties of Water (Ice-I [Ice], Liquid [Liq], and Vapor [Vap] at the Triple Point^{a)}.

Properties	Calculated Values	Literature Values
$\Delta V(\text{Liq} - \text{Ice}) / V(\text{Ice})$ [%]	- 8.2	- 8.3
$\Delta S(\text{Vap} - \text{Ice}) / R$	21.7	22.5
$\Delta S(\text{Liq} - \text{Ice}) / R$	7.5	2.7
$\Delta S(\text{Vap} - \text{Liq}) / R$	14.1	19.8
$C_V(\text{Ice}) / R$	7.8	3.0
$C_V(\text{Liq}) / R$	10.6	9.1
$C_V(\text{Vap}) / R$	3.0	3.1
Speed of Sound (Ice) [m/s]	4.3×10^3	3.2×10^3
Speed of Sound (Liq) [m/s]	2.1×10^3	1.4×10^3
Speed of Sound(Vap) [m/s]	3.3×10^2	4.1×10^2
$\beta(\text{Ice})$ [1/K]	6.2×10^{-4}	1.6×10^{-4}
$\beta(\text{Liq})$ [1/K]	$- 3.0 \times 10^{-5}$	$- 6.8 \times 10^{-5}$
$\beta(\text{Vap})$ [1/K]	3.7×10^{-3}	3.7×10^{-3}
$\kappa(\text{Ice})$ [1/MPa]	9.1×10^{-5}	10.4×10^{-5}
$\kappa(\text{Liq})$ [1/MPa]	2.2×10^{-4}	5.2×10^{-4}
$\kappa(\text{Vap})$ [1/MPa]	1.6×10^2	1.6×10^2

^{a)} ΔV is volume change, $\Delta S / R$ is dimensionless entropy change (R: the universal gas constant), C_V / R is dimensionless isochoric heat capacity, β is thermal expansion coefficient, and κ is isothermal bulk compressibility. Calculated values are based on the present EOS model, and literature values are taken from Refs. 5, 17, and 18.

FFIGURE CAPTIONS

Figure 1. Schematic isothermal PV diagram of EOS-A type (region **A** in Fig. 2) at the solid-liquid-vapor triple point. The hatched areas are the Maxwell's equal area construction, and the solid circles are the equilibrium points for the solid, liquid, and vapor phases.

Figure 2. Classification chart of various topological shapes in Eq. (1). The area denoted **A** is the proper EOS parameter region for ordinary compounds. Other regions such as **B**, **C**, and **E** are also physically acceptable [16]: see text for the description of the topological EOS shapes.

Figure 3. Schematic isothermal PV diagrams of EOS-C type (region **C** in Fig. 2) and EOS-E type (region **E** in Fig.2). The hatched areas are the Maxwell's equal area construction for solid-vapor equilibrium (EOS-C) and liquid-vapor equilibrium (EOS-E).

Figure 4. Phase diagrams of carbon dioxide. (a) temperature-pressure projection. (b) pressure-density projection. Lines: calculated with the present EOS. Symbols: selected experimental data: for details refer to Ref. 16.

Figure 5. Phase diagrams of water with EOS-A type. (a) temperature-pressure projection. (b) pressure-density projection. Solid lines: calculated with the present EOS-A. Symbols and dotted lines: selected experimental data [17, 18].

Figure 6. Phase diagrams of water with EOS-C and E types. (a) temperature-pressure projection. (b) pressure-density projection. Solid lines: calculated with the present EOS-C and EOS-E. Symbols and dotted lines: selected experimental data [17, 18].

Figure 7. Carbon dioxide solubility in water between 1 °C (274.15 K) and 15 °C (288.15 K). Lines: calculated with the present EOS model. Symbols: observed values in Ref. 24.

Figure 8. Dimensionless Gibbs-free energy plot of water-carbon dioxide binary mixtures at a quadruple point (Q_1) condition: $T = 283.3$ K and $P = 4.713$ MPa. The reference point is the solid state of each pure compound at the same T and P . The dotted line is the common tangent line for the thermodynamically stable phase equilibrium.

Figure 9. Dimensionless Gibbs-free energy plot of water-carbon dioxide binary mixtures at a quadruple point (Q_2) condition: $T = 271.9$ K and $P = 1.042$ MPa. The reference point is the solid state of each pure compound at the same T and P . The dotted line is the

common tangent line for the thermodynamically stable phase equilibrium. A pure ice coexisting with a clathrate hydrate is denoted as Ice-I'.

Figure 10. Phase diagram of triple-point (three-phase) equilibria of water-carbon dioxide binary mixtures in the temperature-pressure projection. Solid lines: calculated by the present model. Symbols: selected experimental data; o: Ref. 33, ●: Ref. 32, □: Ref. 36, ►: Ref. 34. H: solid (clathrate hydrate). L1: carbon-dioxide rich liquid. L2: water rich liquid. V: vapor. I': pure ice coexisting with hydrates. Q₁ and Q₂: upper and lower quadruple points. C.P.: vapor-liquid critical point.

Figure 1.

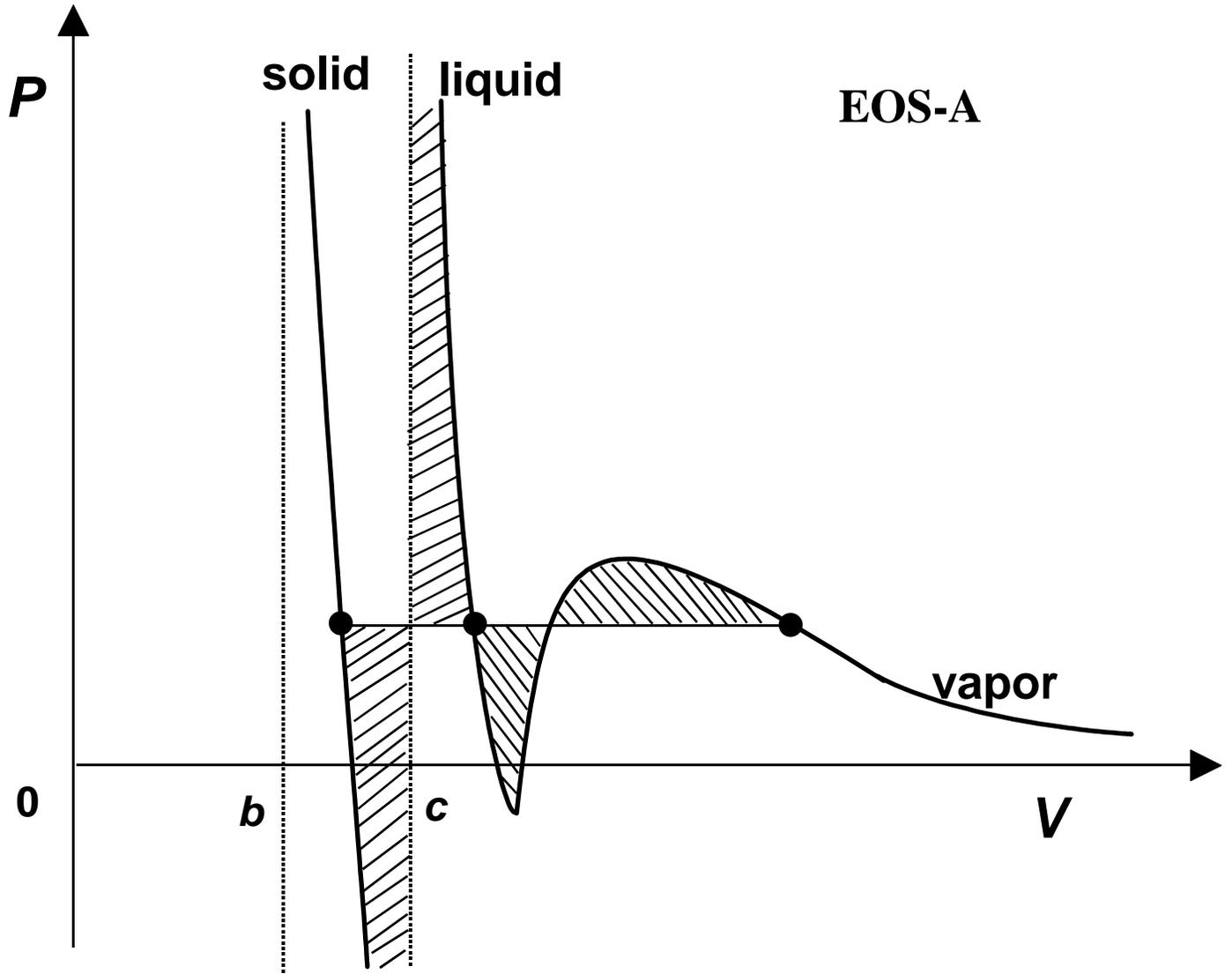


Figure 2.

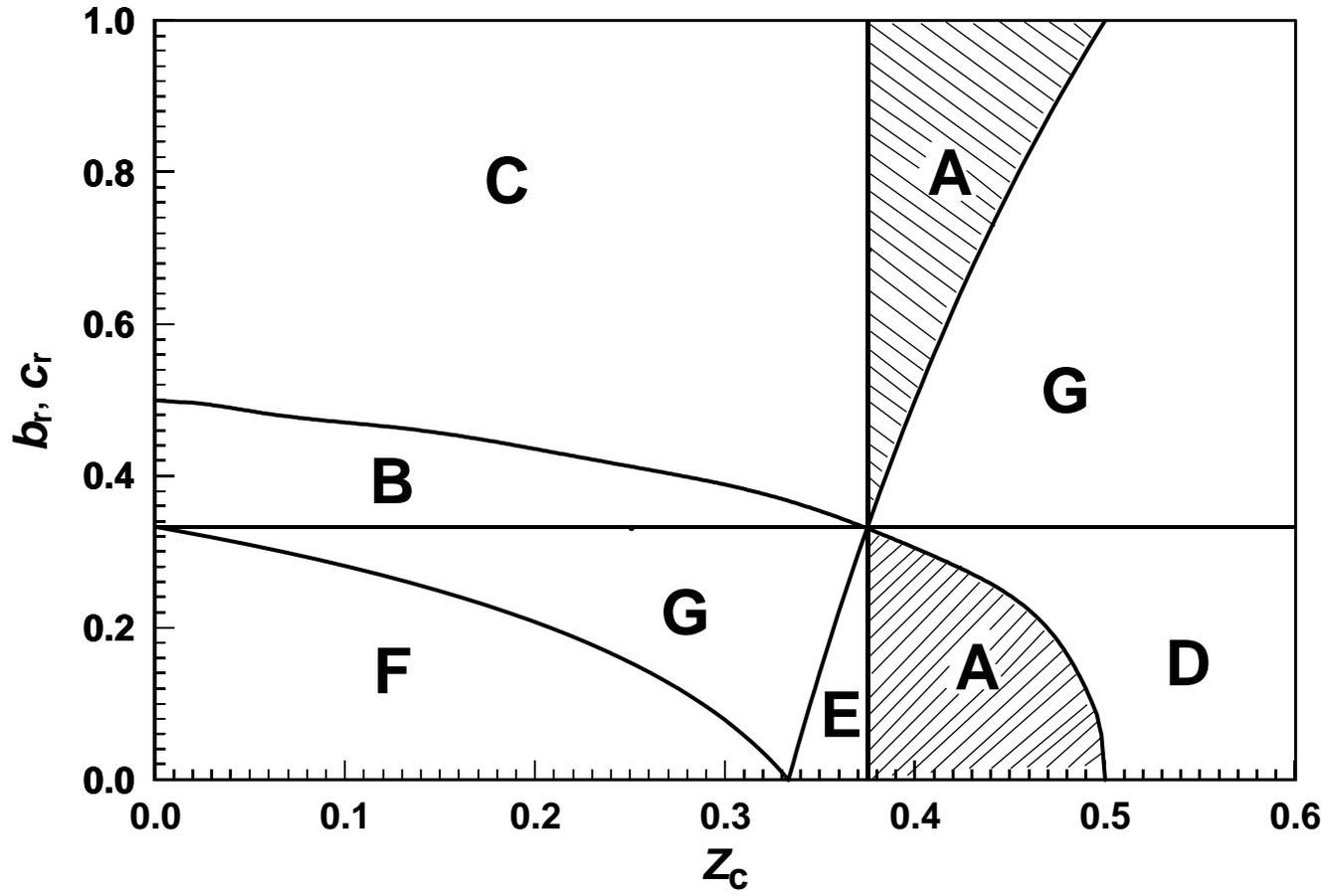
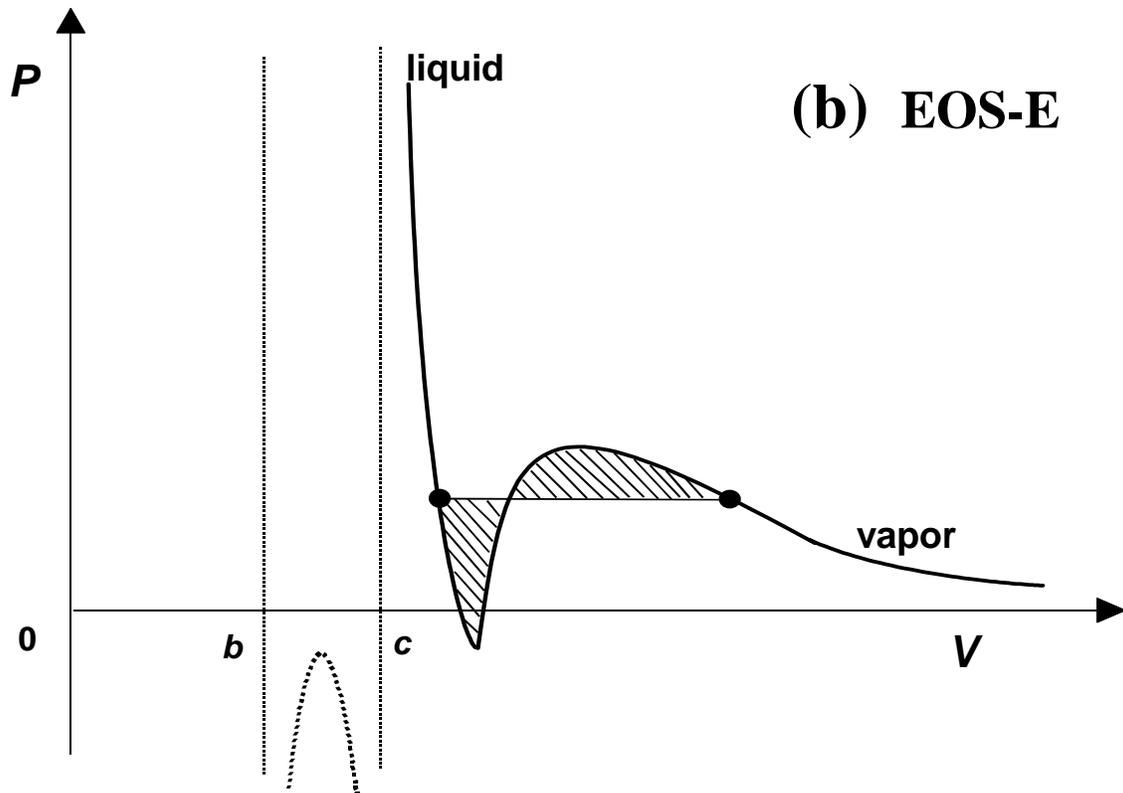
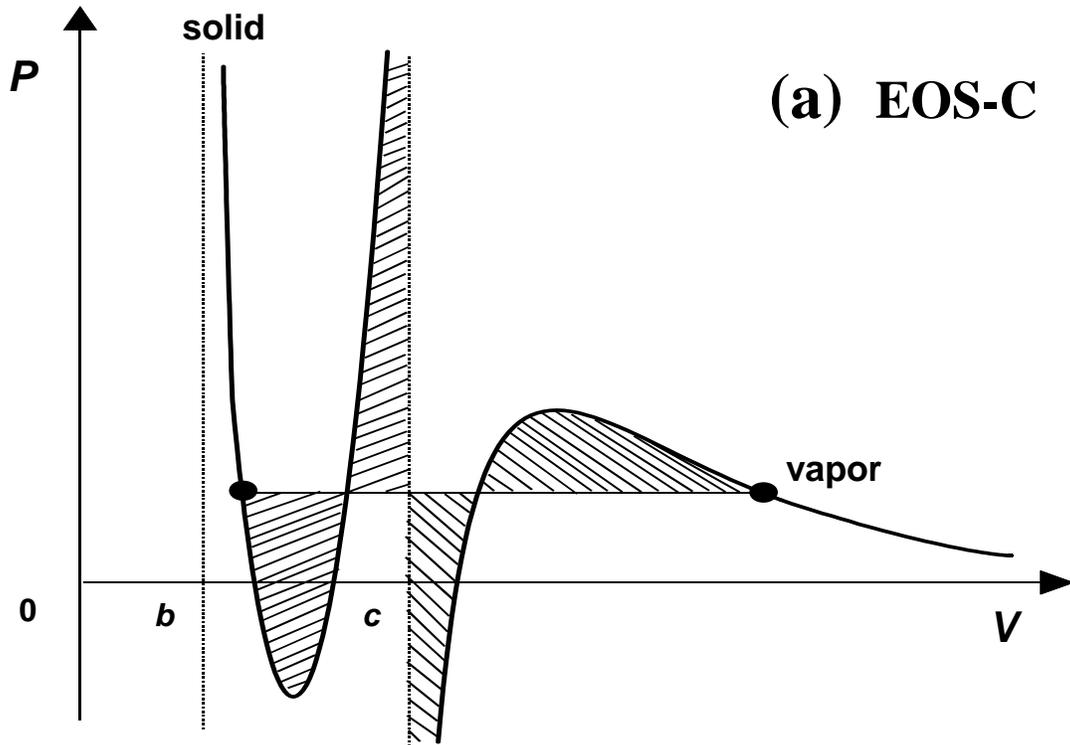
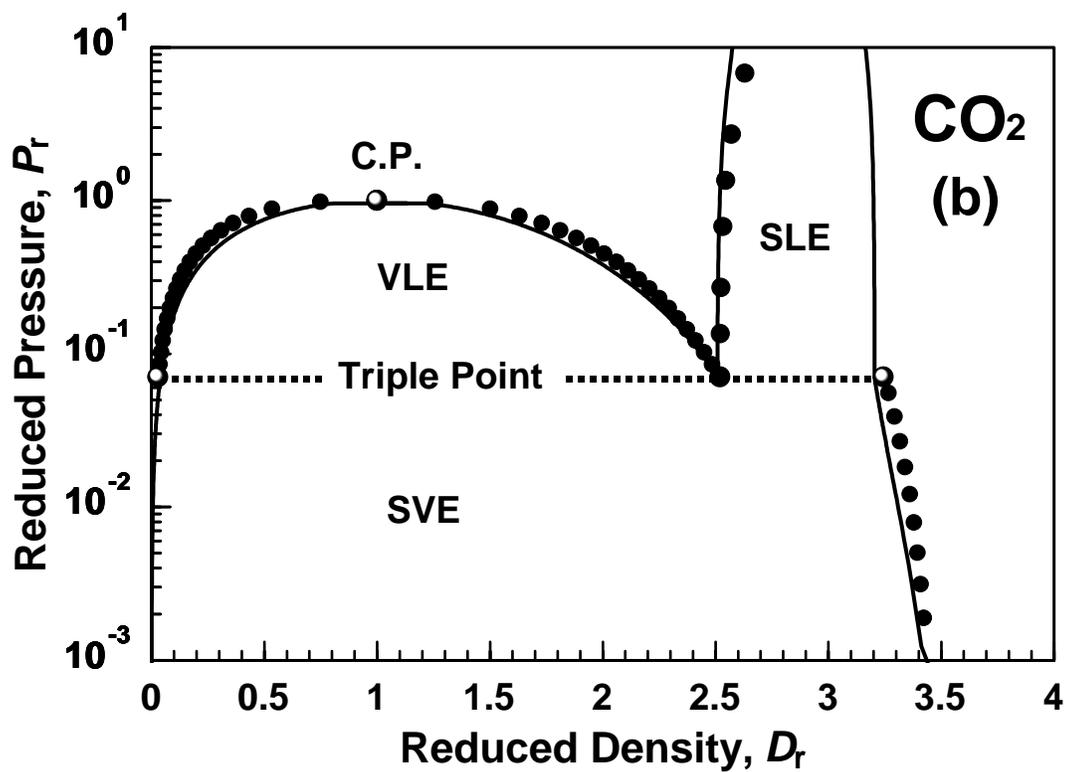
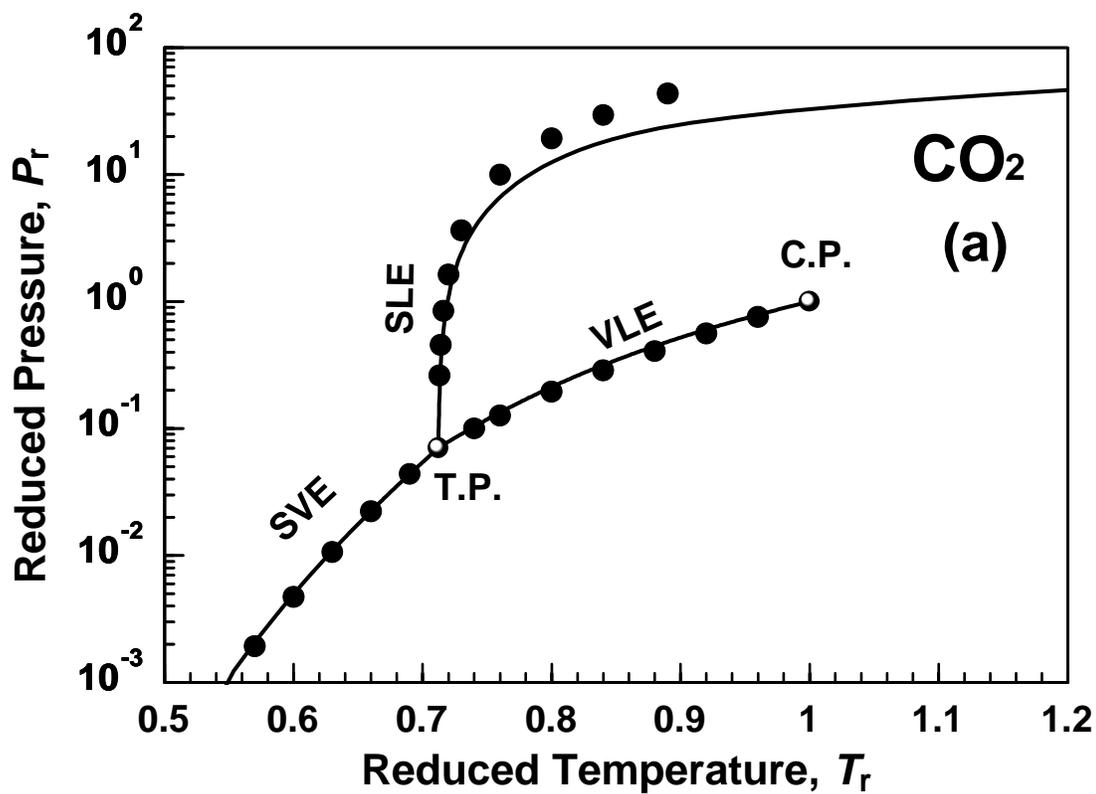
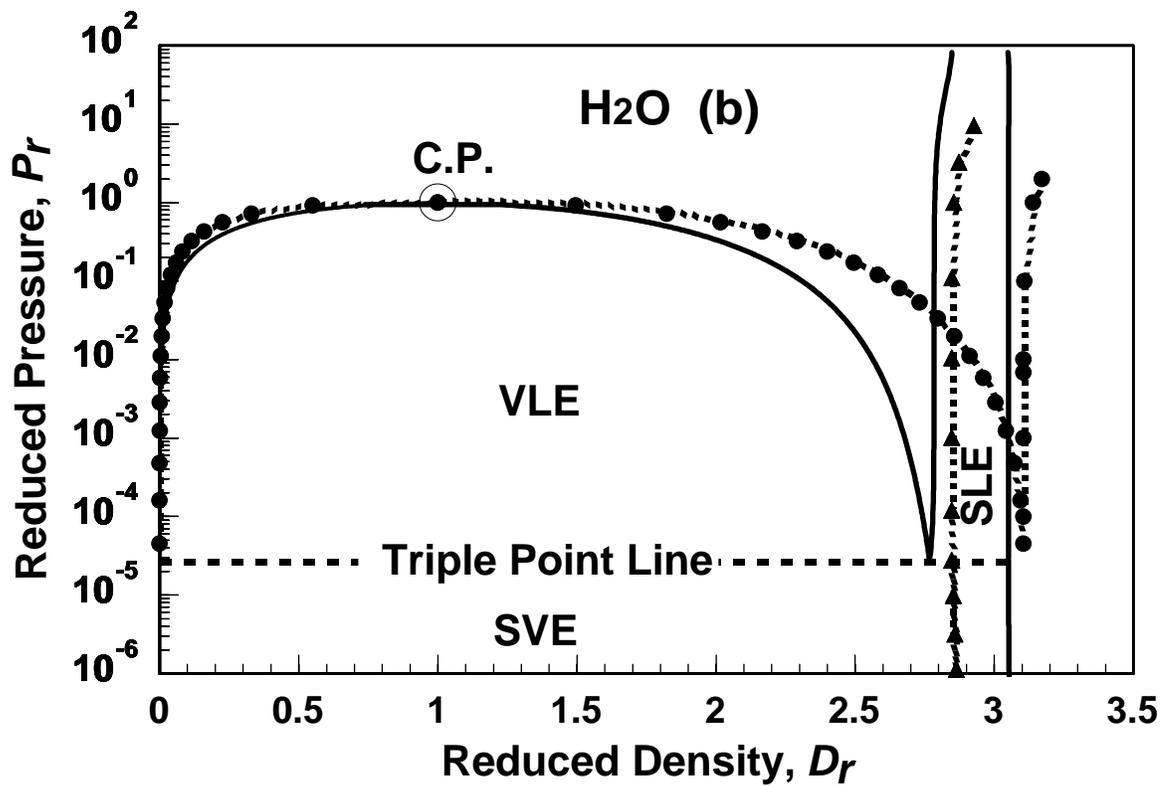
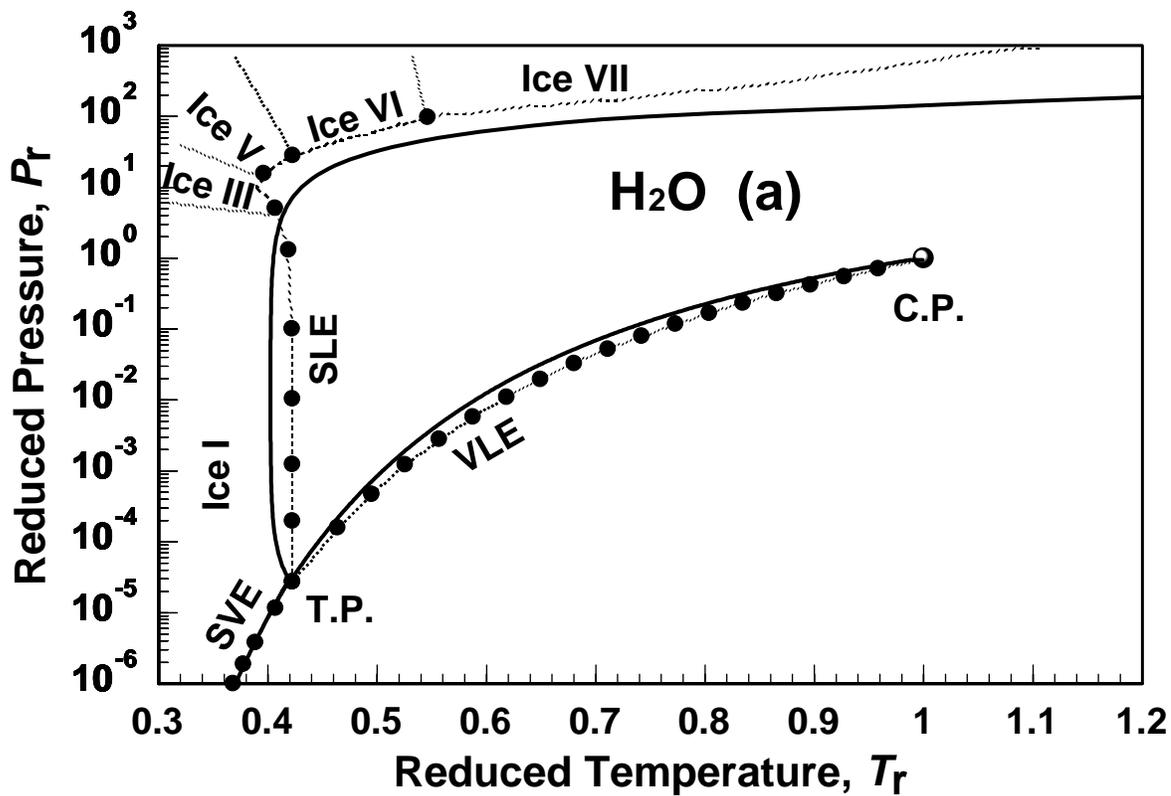
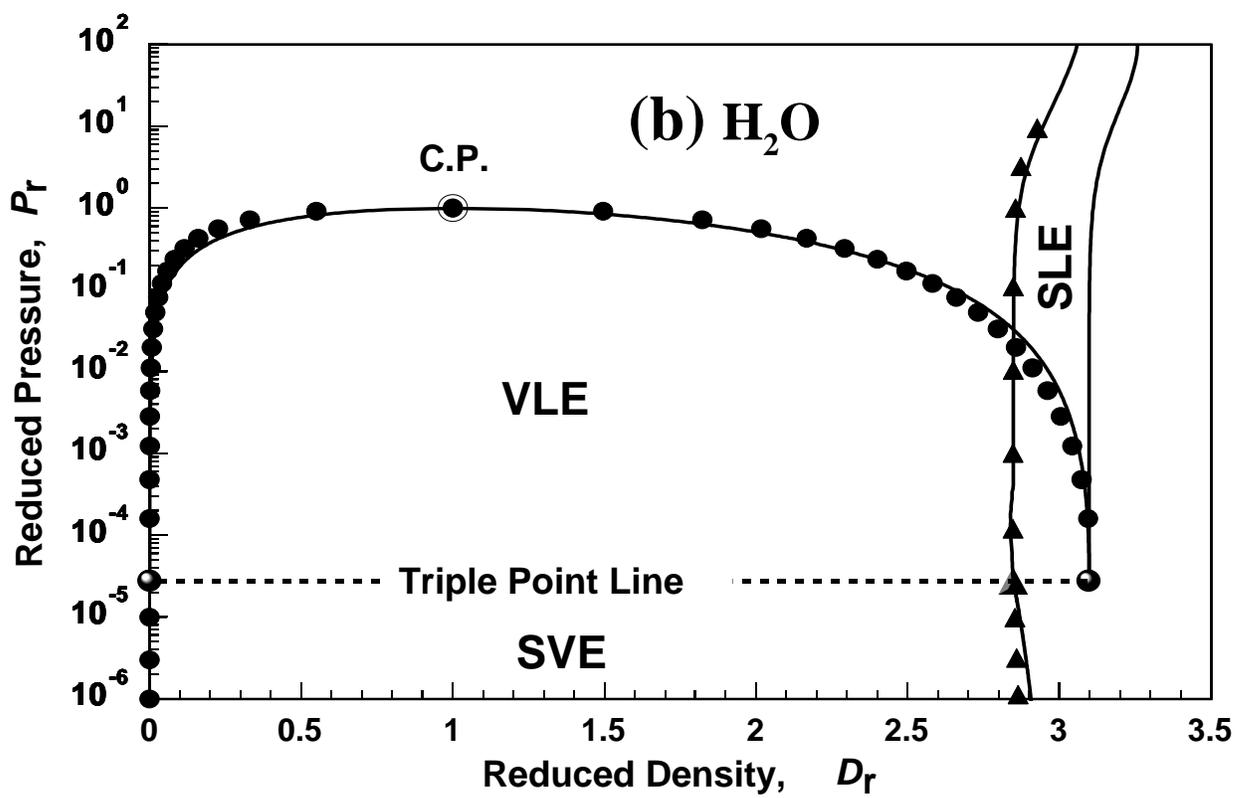
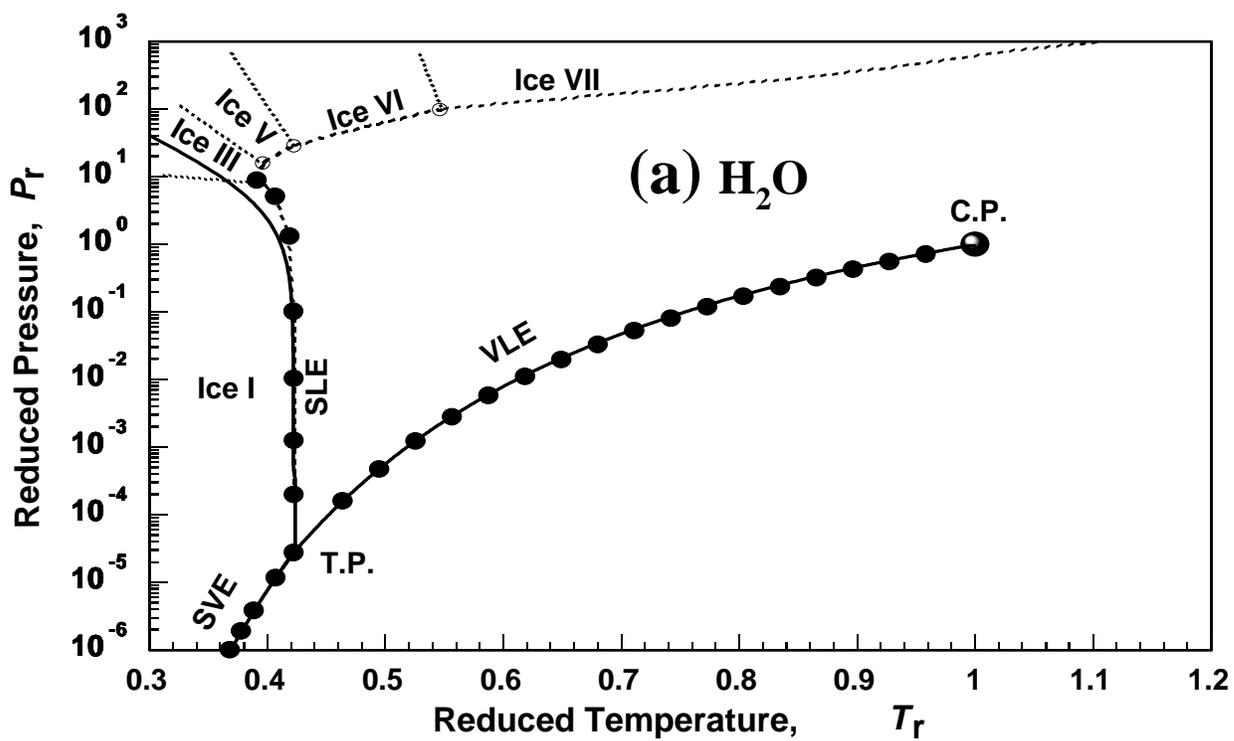


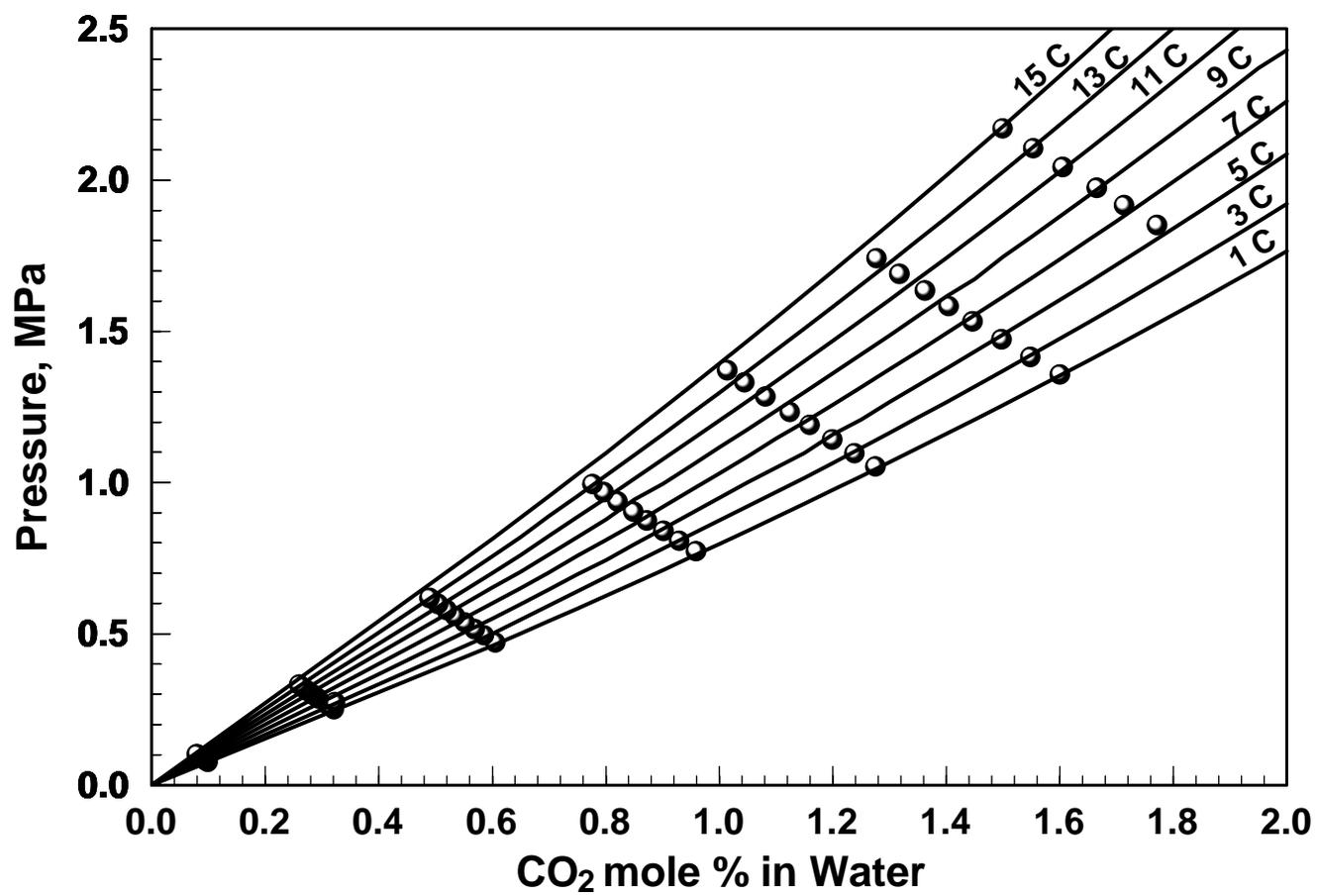
Fig.3











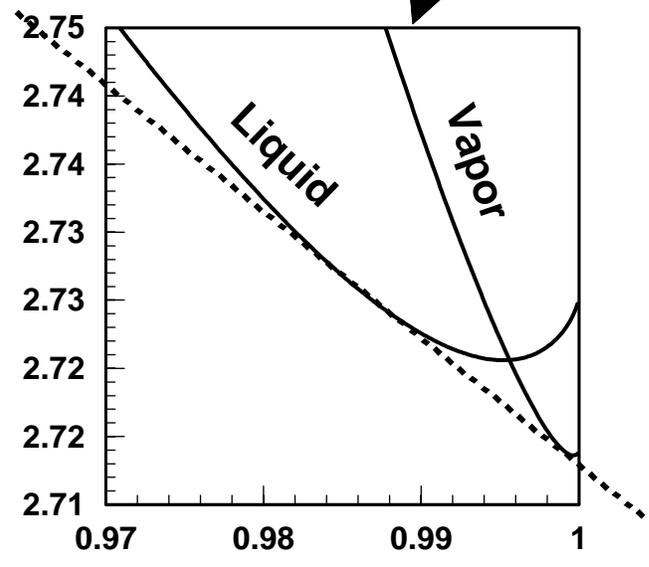
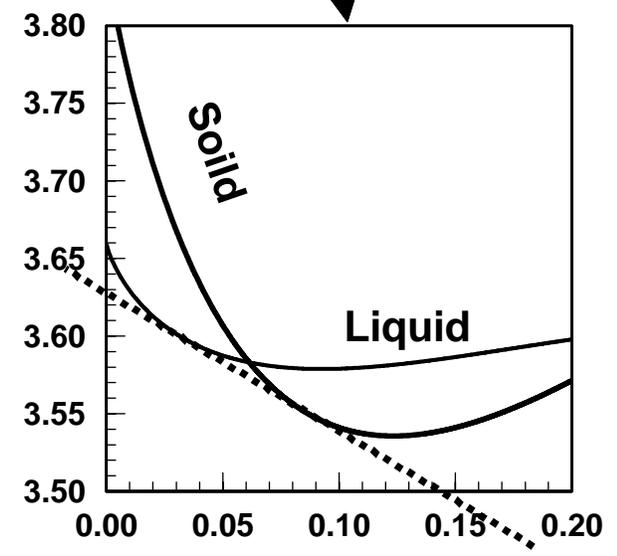
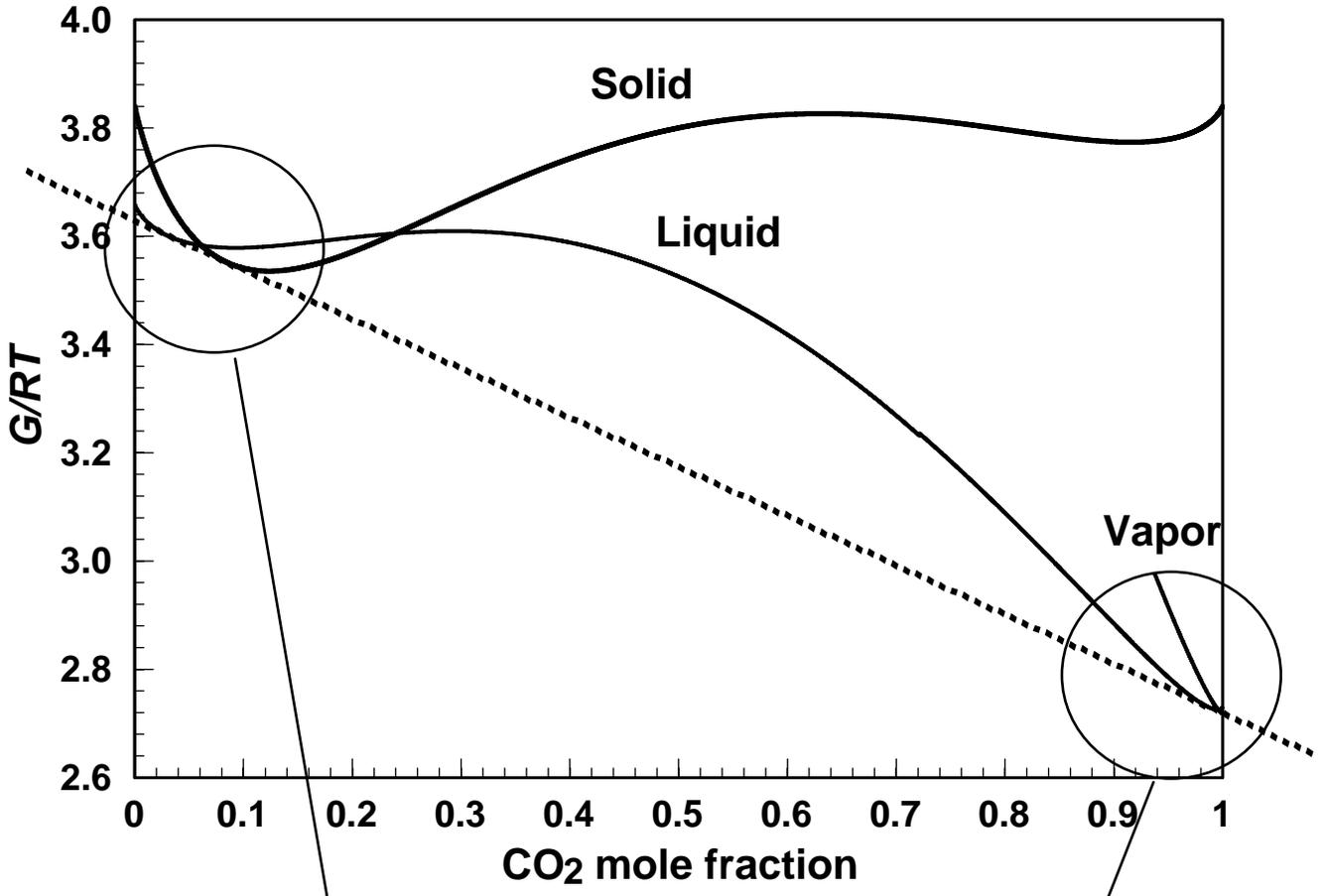


Fig. 9

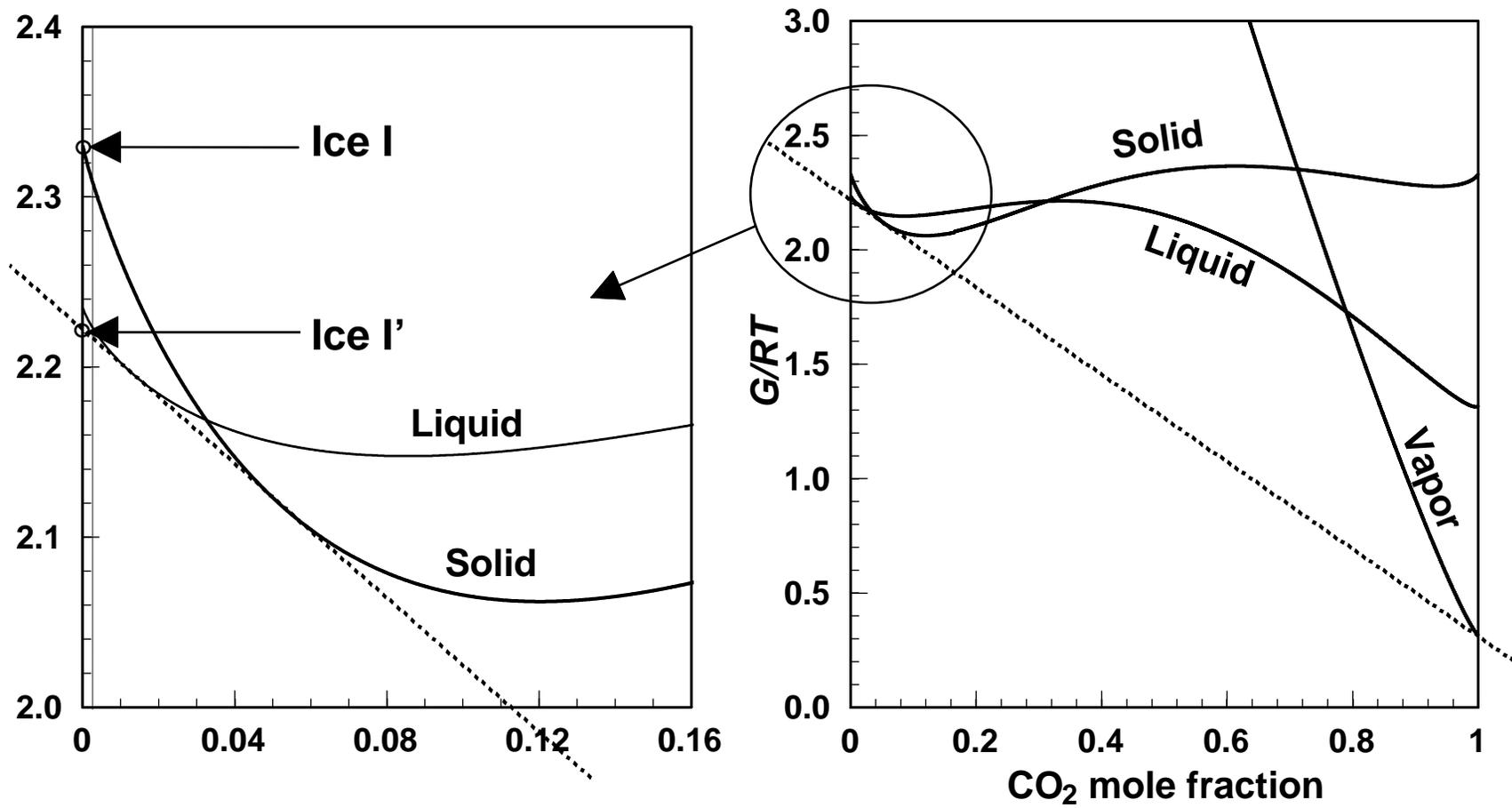


Fig. 10

