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Michael Andre Franiatte

**An Equation of State Resolution  
for the Study of Fluids**  
*EoS Resolution*

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EoS Resolution

**Michael Franiatte**

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Before the past nobody had generalized a tool to understand the behavior of fluids. The synthesis presented here attempt to correlate all data on fluids with a simple program. Information about license, EULA and contract for using these following works can be found at <https://michaelfraniatte.wordpress.com>.

# **An Equation of State Resolution for the Study of Fluids**

Michael Franiatte\*

## **Abstract**

Fluids play an important role in many high-temperature geological and chemical processes. Consequently, understanding the behaviour of fluids at high temperature and high pressure in geological and industrial processes are of fundamental importance. The properties of fluids have been the object of numerous measurement and fitting studies but have never been represented and compared with simple parameters in an only equation of state (EOS). This has been done for the determination of pressure-volume-temperature-composition (*PVTX*) relations using different equations together simulating the measurements of fluids. An appropriate generalized method to resolve *PVTX* data of fluids combined with only four parameters describing a gas (molar mass and the three critical parameters), are in good agreement with the volumes observed by the studies made by the Scientifics in the past. The properties of fluids as well as the properties of the reactions occurring in the fluids were deduced from simple calculations and methods considering the studies of Scientifics whom were working on EOS. Such resolved equation of state is important to understand and correlate all the data on the fluids and the reactions acquired until this day and it's pretty innovating in chemical and petroleum industries.

**Keywords:** *fluids, PVTX properties, gas, critical parameters, reactions, equation of state*

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## 1. Introduction

Seward and Franck (1981) have studied the phase relations in the system  $\text{H}_2\text{-H}_2\text{O}$  covering the range of temperature between  $175^\circ\text{C}$  and  $440^\circ\text{C}$  and of pressure between 100 and 2500 bar. They have established the critical curves and the surface dividing the phase domains in term of *PVTX* data of this system.

The relations between the  $\text{H}_2$  dissolved concentrations and the  $\text{H}_2$  fugacities in the system  $\text{H}_2\text{-H}_2\text{O}$  were studied at elevated temperatures and pressure in the years of 1980 by Seward and Franck (1981) in term of volumetric properties of the system  $\text{H}_2\text{-H}_2\text{O}$  and by Kishima and Sakai (1984) in term of in situ  $\text{H}_2$  concentrations with the mineral buffer Hematite-Magnetite.

The EOS of  $\text{H}_2\text{-H}_2\text{O}$  was determined by Rimbach and Chatterjee (1987) whom have used mixture rules in order to calculate attraction and repulsion parameters of the system. The EOS is in agreement with the *PVTX* measurements of Seward and Franck (1982) but should be confirmed for the range of temperature (T) and pressure (P) around the experimental measures. Rimbach and Chatterjee (1987) have established a Redlich-Kwong type modified EOS (MRK equation) in order to calculate  $\text{H}_2$  and  $\text{H}_2\text{O}$  volumetric properties and the phase equilibrium in the system  $\text{H}_2\text{-H}_2\text{O}$  in the conditions of temperature and pressure of geologic interest (until  $1000^\circ\text{C}$  and 2000 bar).

## 2. Method

### 2.1. Redlich-Kwong type EOS

Fluids play an important role in the meteoric, diagenetic, hydrothermal, metamorphic and magmatic processes. By consequence it's necessary to calculate their thermodynamic properties in the temperatures and pressures encountering in the different geologic

environnements. These thermodynamic properties could be calculate from the EOS determining the fluid molar volume ( $V$ ) function of  $T$  and  $P$  expressed by

$$V = V(T, P) \quad (1)$$

The EOS most known was established by Van der Waals (1873). This EOS is written

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (2)$$

where  $R$  is the gas perfect constant,  $b$  is called repulsion parameter and  $a$  attraction parameter. Molar fractions of constituents deduced from there concentrations in mol number for one kilogram of solvent are introduced in the Redlich-Kwong EOS (Redlich and Kwong, 1949) modify by Soave (1972), in order to calculate the fugacity coefficients of volatile species in the fluid. The Soave-Redlich-Kwong EOS is written

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)} \quad (3)$$

where  $P$  is the total pressure (Pa),  $R$  is the gas constant (8.314472 J/mol/K),  $T$  is the absolute temperature (K), and  $V$  is the molar volume ( $\text{m}^3/\text{mol}$ ). The  $a(T)$  and  $b$  coefficients in Equation (3) are the attraction and repulsion parameters of the original van der Waals equation, given by

$$a_i(T) = a_i(T_c) \cdot \alpha_i(T) \quad (4)$$

and

$$b_i(T_c) = 0.08664 \frac{RT_c}{P_c} \quad (5)$$

where  $T_c$  and  $P_c$  are the critical temperature and pressure, characteristic of a pure constituent.

The  $a_i(T_c)$  term in Equation (4) is given by

$$a_i(T_c) = 0.42747 \frac{(R \cdot T_c)^2}{P_c} \quad (6)$$

where the division by 9 come from the better results enounced by Fowler and Guggenheim (1939) adapted for a mixture and not for a perfect gases without divide by 9. The temperature-dependent  $\alpha_i(T)$  term, equal to 1 at  $T_c$  and  $P_c$ , is evaluated from

$$\alpha_i(T) = \left[ 1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - \sqrt{T/T_c}) \right]^2 \quad (7)$$

where  $\omega$  is the acentric factor, characteristic of a given pure constituents. The expressions for the  $a(T)$  and  $b$  parameters for a fluid mixture are written

$$b = \sum_{i=1}^n x_i b_i(T_c) \quad (8)$$

and

$$a(T) = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{a_i(T) a_j(T)} \quad (9)$$

The molar volume is expressed in  $\text{m}^3/\text{mol}$  by

$$V = \frac{RT}{P} z \quad (10)$$

where  $z$  is the compressibility factor. The Newton-Raphson method is used to resolve  $z$  in the equation written

$$z^3 - (1 - B)z^2 + z(A - B - B^2) - AB = 0 \quad (11)$$

with

$$A = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{A_i A_j} \quad (12)$$

and

$$B = \sum_{i=1}^n x_i B_i \quad (13)$$

with

$$A_i = 0.42747 \frac{\alpha_i(T) P_r}{T_r^2} \quad (14)$$

and

$$B_i = 0.08664 \frac{P_r}{T_r} \quad (15)$$

where  $T_r = T / T_c$  and  $P_r = P / P_c$  are the reduced temperature and pressure, and  $\alpha_i(T)$  the temperature-dependent term in Equation (7). The fugacity coefficient of the  $i^{\text{th}}$  gas derived from the Redlich-Kwong EOS (Soave, 1972) is expressed by

$$\ln \varphi_i = \frac{B_i}{B} (z-1) - \ln(z-B) + \frac{A}{B} \left[ \frac{B_i}{B} - \frac{2}{a(T)} \sum_{j=1}^n x_j (1-k_{ij}) \sqrt{\alpha_i(T) \alpha_j(T)} \right] \ln \left( 1 + \frac{B}{z} \right) \quad (16)$$

The fugacity is written

$$f_i = \varphi_i \cdot x_i \cdot (P/100000) \quad (17)$$

where  $\varphi_i$  and  $x_i$  stand for the fugacity coefficient and mole fraction of the  $i^{\text{th}}$  gas in the gas mixture, respectively.

The method presented here is inspired from the theoretic study of Rimbach and Chatterjee (1987) because they obtained a good agreement in the reproduction of experimental volumes function of introduced quantities in the system, important for express the saturation pressure of a mixture multi-constituent for a given temperature. From molar fractions and quantities known of introduced constituents in a system, the method is based on the derivation of the EOS used by Rimbach and Chatterjee (1987) in order to determine constituent molar partial volumes of the system.

## 2.2. EOS Derivation

The Soave-Redlich-Kwong EOS derived is function of  $V$ ,  $a$  and  $b$  allowing to obtain the partial derived  $\partial V/\partial x$  to calculate the molar partial volumes ( $V_i$ ) of  $n$  constituents in a fluid according to the equations of Rimbach and Chatterjee (1987). In the study here, the  $n$  constituent's mixture is described by an improvement of the definition of the molar partial volume for the constituent  $i$  for a mol number of gas  $n^{g,l}$  expressed by

$$V_i^g = x_i \cdot \left( V - \frac{1}{6 \cdot n} \frac{\partial V}{\partial x_i} \right) \quad (18)$$

because the ancient definition expressed by

$$V_i^g = V + x_j \frac{\partial V}{\partial x_i} \quad (19)$$

can't be resolved for a large number of constituents. The total molar volume of a gas mixture is written

$$\frac{V^{tot}}{n^g} = \sum V_i^g \quad (20)$$

where  $V^{tot}$  correspond to the total volume occupied by the fluid.

The demonstration of the coefficient  $1/6n$  is as followed. The hypothesis presented here, named  $H_L$ , for a polynomial function  $L(x^m)$  is expressed by

$$L(x^m) = \sum_{m=0}^m \sigma_m \cdot x^m \quad (21)$$

and can be written

$$L(x^m) = \frac{x \cdot L'(x^m)}{m} + L(0) \quad (22)$$

define on the interval  $[0,1]$  and derivable on the interval  $]0,1[$ . Using the existing hypothesis  $H_F$  for the hypothesis  $H_L$  it exist a point  $x$  on the interval like it appear



$$L(1) - L(0) = L'(x^m) \quad (23)$$

being

$$L(x^m) - L'(x^m) \left( \frac{x}{m} \right) = L(0) \quad (24)$$

So we would have with the Equation (18)

$$L(x^m) - L'(x^m) \left( \frac{x}{m} \right) = V - \frac{1}{6 \cdot n} \frac{\partial V}{\partial x_i} \quad (25)$$

being

$$\left( \frac{x}{m} \right) = \frac{1}{6 \cdot n \cdot \partial x_i} \quad (26)$$

With  $m=3$ , because it correspond to the dimension of a molar volume, we would obtain

$$x \cdot \partial x_i = \frac{1}{2 \cdot n} \quad (27)$$

The end of the demonstration is to put  $x=0$ ,  $n=\infty$ , or  $x=1$ ,  $n=1$ , or  $x=0.5$ ,  $n=2$ , thus  $x$  is function of  $1/n$ , with  $\delta x=1$  for  $x=1$  and  $\delta x=0$  for  $x=0$ . So for  $1 < n < \infty$ , so we have

$$\frac{1}{n} > x \cdot \partial x_i > 0 \quad (28)$$

while imposing

$$x \cdot \partial x_i = \frac{1}{2 \cdot n} \quad (29)$$

like an average between 1 and the infinite for a large number of constituents  $n$  for the resolution of the partial molar volume, it's a good approximation well demonstrated here.

The coefficient 9 at the Equation (22) denominator according to Fowler and Guggenheim (1939) is caused by the modification of  $a(T)$  expression written

$$a = 3P_c \left( \frac{V^c}{m} \right)^2 = \frac{27(RT^c)^2}{64P^c} \quad (30)$$

and

$$b = \frac{\frac{V^c}{m}}{3} = \frac{RT^c}{8P^c} \quad (31)$$

becoming

$$a = \frac{P_c \left( \frac{V^c}{m} \right)^2}{3} = \frac{9(RT^c)^2}{192P^c} \quad (32)$$

and

$$b = \frac{\frac{V^c}{m}}{3} = \frac{RT^c}{8P^c} \quad (31)$$

The factor 3 between the definition of  $A$  and  $a(T)$  (or the volume and it's derived) where the hypothesis  $H_L$  allow to demonstrate the existence of the volume partial Equation (18) (where for  $V$ , it's  $A$  present, and for  $\partial V$  it's  $a(T)$  present) demonstrated by

$$L(x) = s \cdot L(x) + 1/s \cdot L'(x) \quad (33)$$

and

$$L(x) = x \cdot L'(x) + L(0) \quad (34)$$

with  $s=3$ , because both equations with the equation of the hypothesis  $H_L$  for  $m=1$  are compatible giving

$$L(x) = L(x) \quad (35)$$

and

$$x = -\frac{1}{6} \quad (36)$$

By resolving the Equation (33) for s=3 written

$$-\frac{1}{6 \cdot m} = \frac{1}{6 \cdot n \cdot \partial x_i} \quad (37)$$

and

$$-6 \cdot L(x) = L'(x) \quad (38)$$

with m=1

$$L(x) = \sigma \cdot x \quad (39)$$

and

$$L'(x) = \sigma \quad (40)$$

so we would have with the Equation (18) and Equation (36)

$$\partial x_i = -\frac{m}{n} \quad (41)$$

and the Equation (26) give

$$\frac{x}{m} = \frac{1}{6 \cdot n \cdot \partial x_i} \quad (42)$$

so we would have with the Equation (36) for m=1

$$n \cdot \partial x_i = -1 \quad (43)$$

with the Equation (26)

$$x = -\frac{1}{2} \quad (44)$$

and

$$\partial x_i = -\frac{1}{2} \quad (45)$$

and

$$n = 2 \quad (46)$$

corresponding to a molar volume equal to 0 having only one dimension, because when the constituents are in equimolar proportions, the results of calculations show the equality between molar partial volumes with Equation (45), because for  $m=3$ ,  $n=2$  and  $\partial x_i = 1/2$

$$x = \frac{1}{2} \quad (47)$$

### 2.3. EOS Derived

The derived function of  $V$ ,  $a$  and  $b$  of the Equation (3) is written

$$0 = -\frac{RT}{(V-b)^2}dV + \frac{RT}{(V-b)^2}db + \frac{a\alpha dV}{(V+b)V^2} + \frac{a\alpha dV}{V(V+b)^2} + \frac{a\alpha Vdb}{V^2(V+b)^2} - \frac{\alpha da}{V(V+b)} \quad (48)$$

$a$  and  $b$  are function of  $x_i$

$$0 = \left( -\frac{RT}{(V-b)^2} + \frac{a\alpha}{(V+b)V^2} + \frac{a\alpha}{V(V+b)^2} \right) dV + \left( \frac{RT}{(V-b)^2} + \frac{a\alpha}{V(V+b)^2} \right) \frac{\partial b}{\partial x_i} dx_i - \frac{a}{V(V+b)} \frac{\partial a}{\partial x_i} dx_i \quad (49)$$

written on the shape of

$$\frac{\partial V}{\partial x_i} = \frac{-(RTV^2(V+b)^2 + a\alpha(V-b)^2V) \frac{\partial b}{\partial x_i} + (V-b)V(V^2-b^2) \frac{\partial a}{\partial x_i}}{-RTV^2(V+b)^2 + a\alpha(V-b)^2(2V+b)} \quad (50)$$

with

$$\frac{\partial a}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \sum_{j=1}^n \sum_{j=1}^n x_i x_j (1-k_{ij}) \sqrt{a_i(T) a_j(T)} \right) \quad (51)$$

$$\frac{\partial b}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \sum_{j=1}^n x_i b_i(T_c) \right) \quad (52)$$

so by derivation

$$\frac{\partial a}{\partial x_i} = \sum_{j=1}^n x_j (1-k_{ij}) \sqrt{a_i(T) a_j(T)} \quad (53)$$

$$\frac{\partial b}{\partial x_i} = \sum_{i=1}^n b_i(T_c) \quad (54)$$

#### 2.4. Molar volumes determination in the gas and liquid phases

In order to calculate the molar volumes in the gas and liquid phase and in both phases the following equations are used.

At  $T$  and  $P$

$$x^l = \frac{n^g}{V^{tot}} \quad (55)$$

$$V^g = \frac{(1-x^l)V^{tot}}{n^g} \quad (56)$$

so

$$V^g = \frac{V^{tot}}{n^g} - M_{fluid} \quad (57)$$

$$V^l = M_{fluid} \quad (58)$$

with  $M_{fluid}$  the molar mass of the fluid corresponding to the sum of each constituent molar mass multiply by their molar fractions in the fluid.

Because  $x^l$  at  $T$  and  $P$  is incorporated in the molar volume calculation of the gas phase, the following relations are adopted

$$\frac{V^{tot}}{n^{g+l}_{tot}} = \frac{V^{tot}}{n^g + n^l} = \frac{V^{tot}}{\frac{(1-x^l)V^{tot}}{V^g} + \frac{x^l \cdot V^{tot}}{M_{fluid}}} = \frac{V^g + M_{fluid}}{2} \quad (59)$$

imply

$$n^l = \frac{V^{tot} - V^g - n^g}{V^l} \quad (60)$$

and

$$n^g = n^l \quad (61)$$

## 2.5. Molar fraction determination in the gas and liquid phases

In order to deduce the liquid molar fraction ( $x_i^l$ ) and the vapor fraction ( $x^v$ ) this study use the following relations

$$x^v + x^l = 1 \quad (62)$$

and

$$n^{l+v} = x^v n^{l+v} + x^l n^{l+v} \quad (63)$$

with

$$x^v = \frac{n^v}{n^{l+v}} \quad (64)$$

and

$$x^l = \frac{n^l}{n^{l+v}} \quad (65)$$

so

$$x_i^v = \frac{x_i^{l+v} - x_i^l(1 - x^v)}{x^v} \quad (66)$$

and

$$x_i^l = \frac{x_i^{l+v} - x_i^v x^v}{1 - x^v} \quad (67)$$

### 3. Analyze

The equilibrium constant ( $K_{eq}$ ) of a reaction is given by

$$K_{eq} = \frac{\prod (f_i^{\circ product})^{\alpha}}{\prod (f_i^{\circ reactants})^{\alpha}} \quad (68)$$

where  $f_i^{\circ products}$  and  $f_i^{\circ reactants}$  correspond respectively to the pure fugacities of products and reactants in a given reaction, and  $\alpha$  corresponds to the stoichiometric coefficient of the  $i$  constituent in the reaction. The reaction constant ( $K_r$ ) of a reaction is given by

$$K_r = \frac{\prod (f_i^{product})^{\alpha}}{\prod (f_i^{reactants})^{\alpha}} \quad (69)$$

where  $f_i^{products}$  and  $f_i^{reactants}$  correspond respectively to the mixture fugacities of products and reactants in a given reaction. When  $K_r = K_{eq}$ , the reaction is possible and reaction's one product can be purified with

$$f_i^{\circ product} = 1 \quad (70)$$

and

$$f_i^{product} = 1 \quad (71)$$

So it's possible to know the product activity ( $a_i^{product}$ ) using the formulation corresponding to

$$a_i^{product} = \frac{K_r}{K_{eq}} \quad (72)$$

The experiments on hydrothermal stability of adenine realized by Franiatte and al. (2008) can be discussed in regards of this analyze on the reactions and the method resolving the EOS of Soave (1972). The fugacities of gases obtained from the molar fraction considering mass balance and reactions explained in the paper of the authors and recalculate in this study must be in good agreement with the reality occurring on the reaction capacity of

a fluid, because *PVTX* data is in good agreement with the literature in regards of results, discussed in the next chapter. The Table 1 report the calculation on the experiment of the stability of adenine in an hydrothermal system at 300°C and 400 bar made by the authors. This imply that an equilibrium state was hinted in their experiments because the same fugacities of  $H_2$  were calculate in this study with the reactions of iron oxidation and water dissociation using the equilibrium constant of these reactions and the fugacities of the fluid. The Table 2 report the calculation on the experiment of the synthesis of acridine orange in a potential hydrothermal system at 250°C and 140 bars looking like the experiment of the authors whom report later the synthesis by an observation of an orange liquid after warmed 3 days and thin white sticks after one month. Both Tables reports the adenine and the acridine orange concentrations, the same as those observed by the authors. Despite of a little incertitude on the pressure and the water quantities but it's were calculate with accuracy using the method of resolving equation of state for the *PVTX* data and how the authors observed the remaining quantities in their experiments for the water quantities measurements.

## **4. Results**

### *4.1. Pure gases*

The values of molar masses and critical parameters of the ten gases studied are reported in the Table 3. The molar volumes of  $H_2$  gas determined by Presnall (1969) are compared in the Figure 1 and in the Table 4 with values calculated as part of this work from the resolution of Redlich-Kwong EOS (Redlich and Kwong, 1949) modified by Soave (1972) dependent of only four parameters describing a gas.

The molar specific volumes of  $H_2O$  reported in Figures 2 (a) and (b) can be used both to compare the experimental values of Kennedy (1950) with the values of steam tables (Grigull, 1984) and with the values obtained in this study. Densities of  $CO_2$  are presented and



compared with the experimental values reported by Kennedy (1954) in the Figure 3. The molar volumes of  $H_2$ ,  $SO_2$  and  $H_2S$  obtained in this study are presented and compared with the values reported by Shi and Saxena (1992) in the Figures 4 and 5. The comparisons of the molar volumes of  $CH_4$ ,  $CO_2$ ,  $N_2$ ,  $H_2$ ,  $Cl_2$ ,  $O_2$  and  $CO$  between the values obtained in this study and the values reported by Duan et al. (1992) are shown in the Tables 5 and 6. These comparisons show the good agreement with the authors for all gases excepted for  $H_2S$ .

#### 4.2. Mixture gases

The molar volumes of the system  $H_2O$ - $CO_2$  obtained in this study are presented and compared with the values reported by Shi and Saxena (1992) and the envelop of experimental values reported by Plyasunov and Zakirov (1991) in the Figure 6 and the Figure 7 respectively for each author. The molar volumes of the system  $H_2O$ - $H_2$  are reported in Figure 8 and compared with envelop of experimental values reported by Seward and Franck (1981) but for this Figure, the comparison isn't in good agreement with the authors. The data of Takenouchi and Kennedy (1964) on the composition of  $CO_2$  in  $H_2O$  under and beneath their system is compared with an interpretation resulting of this study. In the calculation of the composition, the consideration take place when all the  $CO_2$  gas and liquid is in the less dense phase for the composition of the gas and none appear in the liquid while the vapor fraction ( $X^V$ ) is the sum of the less dense phases and is used to calculate the composition of the liquid with the Equation (67) (Table 7).

### 5. Conclusion

The developing EOS resolution, unlike other EOS developed by Shi and Saxena (1992) or Duan et al. (1992), need only four parameters ( $M$ ,  $P_c$ ,  $T_c$  and  $\omega$ ) to be accurate to describe  $PVTX$  and the fugacities of a pure gas and mixture gases. This study demonstrate that

a liquid have always a density of 1 g/cm<sup>3</sup> and a fluid with both liquid and gas phase have a possible maximum density of 2 g/cm<sup>3</sup>. The equation of state resolution presented here can predict *PVTX* properties and fugacities of gases and systems which aren't limited to eight gases like the program realized for these fittings. This is practical for the study of chemical synthesis and analysis and somehow for the study of fluid inclusions.

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## Listing of Tables

Table 1: Thermodynamic interpretation of the experiments realized by Franiatte and al. (2008) on the adenine stability at 300°C and 400 bar.

Table 2: Thermodynamic interpretation of the experiments realized during the works of Franiatte and al. (2008) on the acridine orange synthesis at 250°C and 140 bars.

Table 3: Molar masses, critical parameters and acentric factors for the ten gases studied here.

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Table 5: Molar volumes of CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub> and CO function of T and P. The calculated molar volume values in this study ( $V^* = M/x^l$ ) are closer to the molar volumes (V) reported by Duan and al. (1992).

Table 6: Molar volumes of CH<sub>4</sub> function of T and P. The calculated molar volume values in this study ( $V^* = M/x^l$ ) are closer to the molar volumes (V) reported by Duan and al. (1992).

Table 7: Experimental data of Takenouchi and Kennedy (1964) compared to this study on the fraction of CO<sub>2</sub> in H<sub>2</sub>O+CO<sub>2</sub> in the gas phase  $X_{i,gas} = n_i / (n_j(1-x^l) + n_i)$  expressed in percents. The vapor fraction  $X^v = 1 - n_j(x^l)$  with  $V_i^g < V_i^l$  and  $V_j^g > V_j^l$  allow to deduce fraction of CO<sub>2</sub> in the liquid phase  $X_{i,liq} = 0$ .

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Table 1: Thermodynamic interpretation of the experiments realized by Franiatte and al. (2008) on the adenine stability at 300°C and 400 bar.

	Starting mass (g)	M (g/mol)	Mol number
Fe	2.0000	55.0000	0.0364
H <sub>2</sub> O	10.0000	18.0158	0.5551
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ,2H <sub>2</sub> O	0.2660	126.0660	0.0021
NH <sub>4</sub> Cl/NaNO <sub>2</sub>	0.1998	53.5900	0.0037
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	0.0013	134.6950	0.00001
	Mol number	Intermediary mass	Mass and mol of transformed water
3Fe + 4 H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 4 H <sub>2</sub>	0.0507	0.2048	1.8300
H <sub>2</sub> O = H <sub>2</sub> + 0.5 O <sub>2</sub>	0.5666	10.2086	0.1016
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ,2H <sub>2</sub> O = H <sub>2</sub> + 2 CO <sub>2</sub> + 2 H <sub>2</sub> O	0.0043	0.1879	mass and mol of producted H <sub>2</sub>
NaNO <sub>2</sub> + NH <sub>4</sub> Cl = N <sub>2</sub> + NaCl + 2 H <sub>2</sub> O	0.0038	0.1052	0.2048
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 10 H <sub>2</sub> O = 5 CO <sub>2</sub> + 2.5 N <sub>2</sub> + 12.5 H <sub>2</sub>	0.0000	0.0013	0.1016
	Final mass (g)	Massic fraction/H <sub>2</sub> O	X <sub>i</sub>
H <sub>2</sub>	0.2048	0.9761	0.1767
H <sub>2</sub> O	8.3786	1.0000	0.8088
CO <sub>2</sub>	0.1879	0.9781	0.0074
N <sub>2</sub>	0.1052	0.9876	0.0065
O <sub>2</sub>			0.0005
	P <sub>i</sub>	φ <sub>i</sub>	f <sub>i</sub>
H <sub>2</sub>	70.6645	6.4639	456.7660
H <sub>2</sub> O	323.5351	0.2705	87.5215
CO <sub>2</sub>	2.9705	2.2757	6.7600
N <sub>2</sub>	2.6116	7.3329	19.1506
O <sub>2</sub>	0.2183	4.6005	1.0041
	φ <sub>i</sub> <sup>°</sup>	f <sub>i</sub> <sup>°</sup>	a <sub>i</sub>
H <sub>2</sub>	1.1554	462.1436	0.9884
H <sub>2</sub> O	0.2213	88.5223	0.9887
CO <sub>2</sub>	1.0049	401.9508	0.0168
N <sub>2</sub>	1.2192	487.6827	0.0393
O <sub>2</sub>	1.1409	456.3403	0.0022
	Equilibrium constant	Reaction constant	f <sub>i</sub>
3Fe + 4 H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 4 H <sub>2</sub> (H <sub>2</sub> )	2.8709	2.8703	456.9187
H <sub>2</sub> + 0.5 O <sub>2</sub> = H <sub>2</sub> O (H <sub>2</sub> )	-2.0474	-0.7236	456.6454
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 6.25 O <sub>2</sub> = 5 CO <sub>2</sub> + 2.5 N <sub>2</sub> + 2.5 H <sub>2</sub> O (C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> )	7.9883	12.1994	6.1505×10 <sup>-5</sup>
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 10 H <sub>2</sub> O = 5 CO <sub>2</sub> + 2.5 N <sub>2</sub> + 12.5 H <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> )	33.58039	21.18021	2.5129×10 <sup>12</sup>



Table 2: Thermodynamic interpretation of the experiments realized during the works of Franiatte and al. (2008) on the acridine orange synthesis at 250°C and 140 bars.

	Starting mass (g)	M (g/mol)	Mol number
Fe	2.0000	55.0000	0.0364
H <sub>2</sub> O	10.0000	18.0158	0.5551
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ,2H <sub>2</sub> O	0.2660	126.0660	0.0021
NH <sub>4</sub> Cl/NaNO <sub>2</sub>	0.1998	53.5900	0.0037
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	0.0000	134.6950	0.0000
	Mol number	Intermediary mass	Mass and mol of transformed water
3Fe + 4 H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 4 H <sub>2</sub>	0.0506	0.1606	1.4350
H <sub>2</sub> O = H <sub>2</sub> + 0.5 O <sub>2</sub>	0.5667	10.2104	0.0797
C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ,2H <sub>2</sub> O = H <sub>2</sub> + 2 CO <sub>2</sub> + 2 H <sub>2</sub> O	0.0042	0.1857	mass and mol of producted H <sub>2</sub>
NaNO <sub>2</sub> + NH <sub>4</sub> Cl = N <sub>2</sub> + NaCl + 2 H <sub>2</sub> O	0.0037	0.1045	0.1606
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> + 10 H <sub>2</sub> O = 5 CO <sub>2</sub> + 2.5 N <sub>2</sub> + 12.5 H <sub>2</sub>	0.0000	0.0000	0.0797
	Final mass (g)	Massic fraction/H <sub>2</sub> O	X <sub>i</sub>
H <sub>2</sub>	0.1606	0.9820	0.1378
H <sub>2</sub> O	8.7754	1.0000	0.8425
CO <sub>2</sub>	0.1857	0.9793	0.0073
N <sub>2</sub>	0.1045	0.9882	0.0064
O <sub>2</sub>			0.0060
	P <sub>i</sub>	φ <sub>i</sub>	f <sub>i</sub>
H <sub>2</sub>	19.2868	29.0147	559.6001
H <sub>2</sub> O	117.9434	0.3239	38.1970
CO <sub>2</sub>	1.0218	6.1792	6.3141
N <sub>2</sub>	0.9029	32.4364	29.2882
O <sub>2</sub>	0.8451	17.1127	14.4617
	φ <sub>i</sub> <sup>o</sup>	f <sub>i</sub> <sup>o</sup>	a <sub>i</sub>
H <sub>2</sub>	1.0554	147.7499	3.7875
H <sub>2</sub> O	0.2738	38.3324	0.9965
CO <sub>2</sub>	0.9565	133.9039	0.0472
N <sub>2</sub>	1.0715	150.0148	0.1952
O <sub>2</sub>	1.0415	145.8122	0.0992
	Equilibrium constant	Reaction constant	f <sub>i</sub>
3Fe + 4 H <sub>2</sub> O = Fe <sub>3</sub> O <sub>4</sub> + 4 H <sub>2</sub> (H <sub>2</sub> )	2.3438	4.6634	147.2278
H <sub>2</sub> + 0.5 O <sub>2</sub> = H <sub>2</sub> O (H <sub>2</sub> )	-1.6679	-1.1676	10.0929
C <sub>13</sub> H <sub>9</sub> N + 26 H <sub>2</sub> O = 13 CO <sub>2</sub> + 0.5 N <sub>2</sub> + 30.5 H <sub>2</sub> (C <sub>13</sub> H <sub>9</sub> N)	53.7342	53.8149	8.3051×10 <sup>-1</sup>
C <sub>13</sub> H <sub>9</sub> N + 15.25 O <sub>2</sub> = 13 CO <sub>2</sub> + 0.5 N <sub>2</sub> + 4.5 H <sub>2</sub> O (C <sub>13</sub> H <sub>9</sub> N)	2.86457	0.56315	2.0018×10 <sup>2</sup>

Table 3: Molar masses, critical parameters and acentric factors for the ten gases studied here.

Gas	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega^a$
H <sub>2</sub>	2.0158	33.20	13.00	-0.2150
H <sub>2</sub> O	18.0158	647.30	221.20	0.3440
CO <sub>2</sub>	44.0496	304.20	73.80	0.2250
CH <sub>4</sub>	16.0486	190.60	46.00	0.0080
N <sub>2</sub>	28.0134	126.20	33.90	0.0400
SO <sub>2</sub>	64.1508	430.64	78.84	0.2557
H <sub>2</sub> S	34.0814	373.20	89.40	0.1000
Cl <sub>2</sub>	70.9000	416.90	79.77	0.0000
O <sub>2</sub>	32.0852	154.60	50.50	0.0210
CO	28.0102	132.90	35.00	0.0490

<sup>a</sup> without dimension

Table 4: Comparison of molar volumes of H<sub>2</sub> measured [404.5] by Presnall (1969) and the calculate values in this study [402.4] from the resolution of Redlich-Kwong EOS modified by Soave (1972). The values between brackets correspond to the errors expressed in percents.

Pression (bar)	Température (°C)				
	200°C	300°C	400°C	500°C	600°C
101	404.5	486.1	567.4	649.0	-
	<i>402.4</i>	<i>485.2</i>	<i>567.7</i>	<i>650.1</i>	<i>732.3</i>
	(0.51)	(0.19)	(0.05)	(0.16)	-
152	274.6	329.5	-	-	-
	<i>273.1</i>	<i>328.5</i>	<i>383.6</i>	<i>438.6</i>	<i>493.5</i>
	(0.53)	(0.31)	-	-	-
203	210.4	251.4	291.1	331.8	372.6
	<i>208.6</i>	<i>250.2</i>	<i>291.6</i>	<i>332.9</i>	<i>374.1</i>
	(0.88)	(0.49)	(0.17)	(0.33)	(0.41)
304	145.4	172.7	199.3	226.2	253.3
	<i>144.1</i>	<i>171.9</i>	<i>199.6</i>	<i>227.2</i>	<i>254.8</i>
	(0.92)	(0.45)	(0.16)	(0.45)	(0.58)
405	113.3	133.4	153.2	174.0	193.6
	<i>111.9</i>	<i>132.8</i>	<i>153.7</i>	<i>174.4</i>	<i>195.1</i>
	(1.24)	(0.42)	(0.30)	(0.23)	(0.77)
507	93.9	109.9	125.6	142.2	158.3
	<i>92.6</i>	<i>109.4</i>	<i>126.1</i>	<i>142.7</i>	<i>159.3</i>
	(1.35)	(0.44)	(0.41)	(0.37)	(0.63)
608	80.9	94.3	107.5	121.1	134.7
	<i>79.8</i>	<i>93.8</i>	<i>107.8</i>	<i>121.6</i>	<i>135.4</i>
	(1.33)	(0.49)	(0.24)	(0.43)	(0.55)
709	71.5	83.1	94.4	106.0	117.4
	<i>70.7</i>	<i>82.7</i>	<i>94.7</i>	<i>106.6</i>	<i>118.4</i>
	(1.12)	(0.46)	(0.28)	(0.53)	(0.86)
811	64.6	74.7	84.7	94.8	104.8
	<i>63.9</i>	<i>74.4</i>	<i>84.8</i>	<i>95.3</i>	<i>105.6</i>
	(1.13)	(0.42)	(0.17)	(0.49)	(0.80)
912	59.2	68.1	76.9	85.8	94.7
	<i>58.6</i>	<i>67.9</i>	<i>77.2</i>	<i>86.5</i>	<i>95.7</i>
	(0.98)	(0.26)	(0.42)	(0.79)	(1.07)
1013	54.7	62.9	70.7	78.7	86.6
	<i>54.3</i>	<i>62.8</i>	<i>71.1</i>	<i>79.5</i>	<i>87.8</i>
	(0.69)	(0.24)	(0.60)	(0.97)	(1.36)
1115	51.2	58.5	65.6	72.9	80.1
	<i>50.9</i>	<i>58.5</i>	<i>66.1</i>	<i>73.7</i>	<i>81.3</i>
	(0.52)	(0.10)	(0.82)	(1.13)	(1.47)
1216	48.2	54.9	61.4	68.1	74.7
	<i>48.0</i>	<i>55.0</i>	<i>62.0</i>	<i>68.9</i>	<i>75.9</i>
	(0.32)	(0.20)	(0.96)	(1.23)	(1.57)
1317	45.6	51.9	57.9	64.0	70.0
	<i>45.6</i>	<i>52.0</i>	<i>58.5</i>	<i>64.9</i>	<i>71.3</i>
	(0.12)	(0.33)	(1.05)	(1.40)	(1.85)
1419	43.5	49.2	54.8	60.5	66.1
	<i>43.5</i>	<i>49.5</i>	<i>55.5</i>	<i>61.4</i>	<i>67.4</i>
	(0.04)	(0.56)	(1.26)	(1.54)	(1.92)
1520	41.6	46.9	52.1	57.4	62.6
	<i>41.7</i>	<i>47.3</i>	<i>52.9</i>	<i>58.4</i>	<i>64.0</i>
	(0.35)	(0.74)	(1.51)	(1.79)	(2.19)
1621	39.9	44.9	49.8	54.7	59.6
	<i>40.1</i>	<i>45.4</i>	<i>50.6</i>	<i>55.8</i>	<i>61.0</i>
	(0.66)	(1.14)	(1.67)	(1.98)	(2.40)
1723	38.4	43.1	47.7	52.3	56.9
	<i>38.7</i>	<i>43.7</i>	<i>48.6</i>	<i>53.5</i>	<i>58.4</i>
	(0.87)	(1.28)	(1.95)	(2.19)	(2.69)
1824	37.0	41.4	45.7	50.1	54.4
	<i>37.5</i>	<i>42.2</i>	<i>46.8</i>	<i>51.4</i>	<i>56.1</i>
	(1.38)	(1.72)	(2.33)	(2.65)	(3.13)

Table 5: Molar volumes of CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub> and CO function of T and P. The calculated molar volume values in this study ( $V^* = M/x^1$ ) are closer to the molar volumes (V) reported by Duan and al. (1992).

P (bar)	T (°C)	$V^*$ (cm <sup>3</sup> /mol)	V (cm <sup>3</sup> /mol)	P (bar)	T (°C)	$V^*$ (cm <sup>3</sup> /mol)	V (cm <sup>3</sup> /mol)
CO <sub>2</sub>				CH <sub>4</sub>			
25.0	800.00	3594.0520	3587.93	16.4	0.1	1330.4	1333.46
100.0	100.00	250.7958	238.45	41.8	350.1	1250.5	1253.88
100.0	800.00	917.2769	911.47	2026.5	50.4	35.8	40.20
500.0	100.00	56.2962	55.13	8612.6	50.4	28.4	29.01
500.0	800.00	203.5707	199.33	2026.5	400.4	51.2	55.29
1000.0	100.00	43.0439	45.46	8106.0	400.4	32.2	33.76
1000.0	800.00	114.4235	112.22	8612.6	400.4	31.8	33.16
2000.0	100.00	35.7606	39.11	18935.0	940.9	30.9	30.26
2000.0	300.00	46.5327	48.51	23436.0	315.9	27.6	24.72
4000.0	375.00	38.1752	41.25	H <sub>2</sub>			
8000.0	200.00	29.85202	31.93	5000.0	100.0	20.5	19.98
8000.0	399.90	32.18632	34.49	6000.0	100.0	19.5	18.64
8000.0	700.00	35.49961	37.97	7000.0	100.0	18.8	17.62
9208.2	1022.35	36.90336	39.72	5000.0	150.0	21.3	20.99
19911.3	916.55	30.33205	30.34	6000.0	150.0	20.2	19.53
28315.3	1672.05	30.82903	30.87	7000.0	150.0	19.4	18.43
21678.3	500.65	28.33784	27.51	Cl <sub>2</sub>			
N <sub>2</sub>				10.0	277.0	4488.2	4504.52
52.9	0.0	423.4	424.20	100.0	277.0	370.9	384.81
299.6	100.0	117.6	120.20	250.0	277.0	121.4	117.02
1444.0	100.0	42.1	47.54	100.0	627.0	735.3	736.58
2602.6	100.0	33.6	38.54	250.0	627.0	292.8	290.59
1594.5	-25.0	33.2	38.95	O <sub>2</sub>			
5107.7	-25.0	26.3	29.09	5066.0	200.0	25.2	28.91
7988.8	-25.0	25.0	26.29	7092.0	200.0	23.2	26.10
1000.0	1526.9	170.7	180.73	5066.0	300.0	26.9	30.76
5000.0	1526.9	52.0	58.51	9119.0	300.0	23.0	25.41
3000.0	0.2	29.3	33.81	5066.0	400.0	28.6	32.61
20000.0	0.2	23.7	21.64	10132.0	400.0	23.3	25.68
3000.0	24.3	30.0	34.55	1801.0	121.2	33.6	38.60
22000.0	24.3	23.7	21.26	6027.6	1022.8	35.8	40.27
3000.0	47.7	30.7	35.26	4049.2	134.0	25.5	29.62
22000.0	47.7	23.8	21.33	17037.2	920.7	23.7	25.74
3000.0	-25.7	28.6	33.01	CO			
5000.0	-25.7	26.3	29.22	2000.0	35.0	34.3	40.15
10000.0	-25.7	24.5	25.01	5000.0	35.0	27.9	31.11
15000.0	-25.7	23.9	22.90	10000.0	35.0	25.6	26.20
3000.0	0.2	29.3	33.81	2000.0	100.0	37.2	43.00
5000.0	0.2	26.8	29.74	5000.0	100.0	29.0	32.38
10000.0	0.2	24.7	25.27	10000.0	100.0	26.1	26.86
15000.0	0.2	24.0	23.06	2000.0	200.0	41.8	47.43
20000.0	0.2	23.7	21.64	5000.0	200.0	30.7	34.37
3000.0	24.3	30.0	34.55	10000.0	200.0	27.0	27.97
5000.0	24.3	27.2	30.21	2500.0	300.0	41.7	47.11
10000.0	24.3	24.9	25.51	5000.0	300.0	32.4	36.39
15000.0	24.3	24.2	23.21	10000.0	300.0	27.8	29.17
20000.0	24.3	23.8	21.72				
22000.0	24.3	23.7	21.26				
3000.0	47.7	30.7	35.26				
5000.0	47.7	27.6	30.66				
10000.0	47.7	25.1	25.74				
15000.0	47.7	24.3	23.35				
20000.0	47.7	23.9	21.81				
22000.0	47.7	23.8	21.33				

Table 6: Molar volumes of CH<sub>4</sub> function of T and P. The calculated molar volume values in this study ( $V^* = M/\bar{x}$ ) are closer to the molar volumes (V) reported by Duan and al. (1992).

P (bar)	T (°C)	$V^*$	V	P (bar)	T (°C)	$V^*$	V
50.5	-14.6	363.3	364.96	2697.1	1607.6	83.5	-
60.6	20.4	360.5	360.65	3156.2	1993.0	85.1	-
86.3	109.7	355.5	355.13	3810.8	2425.0	83.9	-
131.1	284.0	362.1	361.96	313.4	19.4	70.3	71.01
193.3	517.6	359.2	359.48	455.6	73.6	69.0	71.12
281.9	855.5	356.9	357.79	611.5	136.5	68.5	71.39
407.4	1339.3	354.6	-	821.7	218.9	67.5	70.97
587.2	2041.5	352.8	-	1050.2	317.6	67.4	71.26
60.4	-62.1	166.3	-	1335.9	441.6	67.2	71.26
85.1	-21.4	181.3	182.03	1656.5	577.2	66.6	70.89
118.5	31.0	182.2	180.62	2053.5	742.8	65.9	70.35
158.2	92.0	180.5	179.42	2750.8	1059.5	65.7	70.43
209.5	175.8	180.8	180.54	3723.1	1500.1	65.1	-
266.7	270.2	180.5	180.88	4464.1	1855.5	65.1	-
342.2	390.3	178.2	179.09	5412.0	2300.0	64.8	-
429.4	538.4	178.0	179.33	6419.2	2817.2	65.1	-
535.9	724.4	178.1	179.86	251.1	-31.1	59.8	60.08
667.6	950.0	177.1	179.37	307.3	-15.6	59.2	60.33
833.2	1230.9	175.5	178.44	490.3	33.9	57.7	60.38
1035.6	1566.9	173.2	-	661.7	87.2	57.8	61.19
1261.3	1976.9	173.5	-	885.4	153.0	57.2	61.14
1551.8	2487.9	172.6	-	1166.3	228.5	56.0	60.27
1894.6	3103.8	172.1	-	1432.6	320.5	56.5	60.89
131.9	-8.6	120.9	120.06	1734.7	429.0	57.0	61.44
183.2	39.8	122.2	121.00	2161.8	554.9	56.1	60.68
261.6	109.6	120.1	119.91	2639.2	700.2	55.5	60.17
344.9	190.9	120.4	121.21	3122.5	867.7	55.6	60.33
437.1	282.9	120.5	121.93	3719.0	1073.0	55.5	60.39
565.7	404.0	118.8	120.75	4427.9	1332.6	55.7	-
715.8	549.2	117.6	120.03	5341.2	1640.5	55.3	-
880.5	728.4	118.5	121.24	6258.3	2005.6	55.7	-
1096.4	938.5	116.8	120.03	7353.6	2445.3	56.0	-
1367.6	1195.2	114.7	-	8753.9	2950.8	55.7	-
1692.0	1523.3	113.8	-	373.5	-39.8	48.4	50.37
2073.6	1902.0	112.6	-	594.3	2.9	47.8	51.28
2503.6	2387.2	113.3	-	908.0	49.4	45.8	50.06
3071.1	2961.5	112.0	-	1148.2	110.4	46.8	51.31
135.0	-33.0	90.4	90.75	1516.2	177.2	46.1	50.67
198.6	-192.4	29.5	91.83	1890.0	257.6	46.1	50.71
266.4	50.4	92.5	92.50	2383.9	359.3	45.9	50.42
372.2	111.4	90.2	91.33	2927.2	479.4	45.9	50.36
494.9	185.0	89.0	90.97	3651.6	621.7	45.4	49.78
806.7	380.6	87.7	90.67	4340.2	799.0	45.8	50.25
1011.1	508.4	86.8	90.11	5178.8	995.5	45.8	50.27
1245.4	663.9	86.5	90.12	6220.9	1251.2	45.9	50.44
1495.3	843.5	86.9	90.79	8668.1	1920.4	46.5	-
1838.1	1057.5	85.5	89.74	10059.7	2353.3	47.1	-
2233.1	1304.5	84.3	-	11928.8	2857.8	47.1	-
739.0	-29.2	40.7	44.48	9082.9	1037.3	37.5	40.61
971.4	1.0	40.4	44.70	10282.8	1243.6	37.8	40.97
1271.6	56.2	41.2	45.76	11901.1	1521.4	38.1	-
1622.2	106.5	40.9	45.55	13573.5	1831.3	38.4	-
2080.2	171.4	40.6	45.13	15513.5	2175.1	38.6	-
2422.1	234.4	40.9	45.37	2060.1	-52.4	31.7	34.68
2821.1	306.0	41.1	45.46	2482.4	-22.4	31.8	35.22
3131.0	350.6	40.9	45.16	2992.7	14.5	31.9	35.40
3305.3	391.2	41.2	45.44	3458.5	50.4	32.0	35.42
4002.6	496.3	40.9	44.95	4017.3	96.8	32.2	35.39
4390.0	589.8	41.4	45.48	4651.6	152.0	32.3	35.31
5232.5	737.0	41.3	45.33	5444.8	214.0	32.4	35.03
5833.9	855.1	41.5	45.45	6256.3	291.5	32.6	34.99
6546.7	992.6	41.5	45.52	6977.8	379.6	33.0	35.23
7508.3	1201.4	41.8	-	8118.6	470.7	32.9	34.88
8592.9	1427.5	42.0	-	9224.6	588.8	33.2	34.97
9906.1	1730.6	42.3	-	10372.2	735.0	33.5	35.32
11507.9	2056.0	42.3	-	11863.6	903.5	33.7	35.48
13101.0	2495.6	43.0	-	13543.8	1089.5	33.9	35.60
15227.7	2956.6	43.0	-	15302.5	1309.3	34.1	35.90
968.4	-52.2	36.2	39.70	17317.8	1596.0	34.5	-
1149.8	-30.1	36.4	40.46	20099.1	1934.9	34.7	-
1537.9	2.1	35.9	40.26	22438.8	2619.6	36.2	-
1889.4	36.9	35.8	40.23	5077.9	-42.7	28.7	29.92
2320.4	86.3	36.0	40.28	5549.5	-24.3	28.7	30.09
2791.0	139.6	36.0	40.16	6096.7	-1.9	28.8	30.16
3249.1	208.3	36.5	40.46	6583.8	29.1	28.9	30.36
3606.4	-259.8	25.7	40.06	7111.6	53.3	29.0	30.29
3866.9	280.0	36.5	40.19	7705.3	84.3	29.1	30.23
4447.0	363.3	36.7	40.30	8278.6	120.1	29.2	30.21
5216.9	452.4	36.6	39.98	9207.3	169.5	29.3	30.03
5641.1	515.3	36.8	40.07	9742.8	207.2	29.4	30.02
6002.3	575.4	37.0	40.25	10655.1	260.5	29.5	29.88
6434.3	643.2	37.1	40.37	11623.5	321.5	29.6	29.79
6985.3	705.1	37.0	40.14	12582.3	392.2	29.8	29.80
7397.9	780.7	37.2	40.40	13754.1	472.6	30.0	-
8138.7	854.3	37.0	39.99	16291.4	654.7	30.2	-
8638.4	949.2	37.2	40.31	20041.0	920.7	30.5	-

Table 7: Experimental data of Takenouchi and Kennedy (1964) compared to this study on the fraction of  $\text{CO}_2$  in  $\text{H}_2\text{O}+\text{CO}_2$  in the gas phase  $X_{i,\text{gas}} = n_i/(n_j(1-x^j) + n_i)$  expressed in percents. The vapor fraction  $X^v = 1 - n_j(x^j)$  with  $V_i^g < V_i^l$  and  $V_i^g > V_i^l$  allow to deduce fraction of  $\text{CO}_2$  in the liquid phase  $X_{i,\text{liq}} = 0$ .

P (bars)	This study			Exp. study			P (bars)	This study			Exp. study		
	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>		X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>	X <sub>i,liq</sub>	X <sub>i,gas</sub>	X <sup>v</sup>
			350°C, 10.5%							250°C, 28.8%			
200	0.00	11.99	0.88	1.50	9.00	1.20	100	0.00	30.55	0.94	1.20	41.00	0.69
250	0.00	13.80	0.76	4.00	16.20	0.53	200	0.00	45.15	0.64	2.70	63.60	0.43
300	0.00	15.76	0.67	6.40	16.60	0.40	300	0.00	49.79	0.58	4.20	68.00	0.39
325	0.00	16.37	0.64	10.50	10.50	-	400	0.00	52.98	0.54	5.50	67.60	0.38
			325°C, 18%				500	0.00	55.62	0.52	6.40	66.00	0.38
150	0.00	19.56	0.92	1.00	10.60	1.77	600	0.00	57.93	0.50	7.40	63.60	0.38
200	0.00	20.77	0.87	2.60	24.60	0.70	700	0.00	60.03	0.48	8.40	61.30	0.39
250	0.00	23.68	0.76	4.30	32.10	0.49	800	0.00	61.97	0.46	9.40	59.30	0.39
300	0.00	26.48	0.68	6.10	34.20	0.42	900	0.00	63.79	0.45	10.40	58.00	0.39
350	0.00	28.27	0.64	8.20	33.40	0.39	1000	0.00	65.51	0.44	11.50	56.70	0.38
400	0.00	29.67	0.61	11.20	28.60	0.39	1100	0.00	67.16	0.43	12.50	55.50	0.38
435	0.00	30.51	0.59	18.00	18.00	-	1200	0.00	68.73	0.42	13.20	54.80	0.38
			300°C, 23.6%				1300	0.00	73.28	0.31	13.60	54.20	0.37
100	0.00	24.80	0.95	0.40	8.00	3.05	1400	0.00	71.72	0.40	14.00	54.00	0.37
150	0.00	25.82	0.91	1.60	29.00	0.80	1500	0.00	73.15	0.39	14.40	54.00	0.36
200	0.00	27.86	0.85	2.90	39.00	0.57				200°C, 28.8%			
250	0.00	32.44	0.73	4.10	43.40	0.50	100	0.00	55.72	0.52	1.30	71.50	0.39
300	0.00	35.44	0.67	5.40	45.40	0.46	200	0.00	59.00	0.49	2.60	82.00	0.33
350	0.00	37.48	0.63	6.80	45.60	0.43	300	0.00	61.73	0.47	3.40	82.50	0.32
400	0.00	39.12	0.60	8.40	44.80	0.42	400	0.00	64.14	0.45	4.10	81.60	0.32
450	0.00	40.54	0.58	10.40	42.20	0.42	500	0.00	66.33	0.43	4.70	80.00	0.32
500	0.00	41.80	0.56	12.70	38.00	0.43	600	0.00	68.36	0.42	5.20	78.00	0.32
550	0.00	42.96	0.55	17.00	32.00	0.44	700	0.00	70.27	0.41	5.60	76.00	0.33
575	0.00	43.51	0.54	23.60	23.60	-	800	0.00	72.08	0.40	5.80	74.50	0.33
			275°C, 27%				900	0.00	75.71	0.32	6.10	73.20	0.34
100	0.00	28.47	0.95	1.00	25.60	1.06	1000	0.00	75.47	0.38	6.30	72.00	0.34
150	0.00	29.92	0.90	1.90	42.60	0.62	1100	0.00	77.07	0.37	6.50	71.60	0.34
200	0.00	35.53	0.76	2.80	50.00	0.51	1200	0.00	78.62	0.37	6.70	70.60	0.35
250	0.00	40.45	0.67	3.80	54.00	0.46	1300	0.00	80.12	0.36	6.90	70.00	0.35
300	0.00	43.00	0.63	4.90	55.80	0.43	1400	0.00	81.58	0.35	7.00	69.40	0.35
400	0.00	46.58	0.58	7.20	55.80	0.41	1500	0.00	83.01	0.35	7.20	69.00	0.35
500	0.00	49.34	0.55	9.60	53.00	0.40				150°C, 28.8%			
600	0.00	51.69	0.52	12.00	49.60	0.40	100	0.00	70.88	0.41	1.35	88.00	0.32
700	0.00	53.79	0.50	14.40	46.00	0.40	200	0.00	73.20	0.39	2.15	91.00	0.30
800	0.00	55.72	0.48	17.50	42.00	0.39	300	0.00	75.36	0.38	2.60	90.00	0.30
885	0.00	57.25	0.47	27.00	27.00	-	400	0.00	77.39	0.37	2.90	88.20	0.30
			270°C, 28.8%				500	0.00	76.96	0.34	3.20	86.20	0.31
200	0.00	37.50	0.77	2.70	53.00	0.52	600	0.00	81.15	0.35	3.45	84.00	0.31
250	0.00	42.62	0.68	3.60	57.00	0.47	700	0.00	82.92	0.35	3.70	82.40	0.32
300	0.00	45.30	0.64	4.60	59.00	0.44	800	0.00	84.62	0.34	3.90	80.80	0.32
400	0.00	49.05	0.59	6.70	59.00	0.42	900	0.00	86.26	0.33	4.05	79.40	0.33
500	0.00	51.92	0.55	8.70	57.00	0.42	1000	0.00	87.86	0.33	4.20	78.00	0.33
600	0.00	54.36	0.53	10.60	54.60	0.41	1100	0.00	90.92	0.32	4.40	77.00	0.34
700	0.00	56.53	0.51	12.50	52.00	0.41	1200	0.00	92.39	0.31	4.50	76.40	0.34
800	0.00	58.52	0.49	14.50	49.60	0.41	1300	0.00	93.83	0.31	4.60	75.80	0.34
900	0.00	60.38	0.48	16.60	46.20	0.41	1400	0.00	95.24	0.30	4.70	75.40	0.34
1000	0.00	62.12	0.46	19.00	42.40	0.42	1500	0.00	70.88	0.41	4.80	75.20	0.34
1100	0.00	63.78	0.45	21.50	38.20	0.44				110°C, 28.8%			
1200	0.00	65.36	0.44	25.00	34.00	0.42	100	0.00	84.13	0.34	1.40	95.60	0.29
1230	0.00	65.82	0.44	28.80	28.80	-	200	0.00	86.14	0.33	2.10	95.80	0.28
			260°C, 28.8%				300	0.00	77.72	0.35	2.40	94.80	0.29
200	0.00	41.77	0.69	2.70	57.20	0.48	400	0.00	89.92	0.32	2.60	93.20	0.29
250	0.00	45.23	0.64	3.50	62.00	0.43	500	0.00	91.70	0.31	2.80	91.40	0.29
300	0.00	47.53	0.61	4.40	64.00	0.41	600	0.00	93.43	0.31	3.00	89.30	0.30
400	0.00	50.98	0.56	5.90	64.20	0.39	700	0.00	95.10	0.30	3.15	87.20	0.31
500	0.00	53.73	0.54	7.30	62.40	0.39	800	0.00	96.73	0.30	3.30	85.40	0.31
600	0.00	56.10	0.51	8.70	60.40	0.39	900	0.00	98.31	0.29	3.45	84.00	0.31
700	0.00	58.24	0.49	10.00	58.00	0.39	1000	0.00	99.86	0.29	3.60	83.00	0.32
800	0.00	60.21	0.48	11.30	56.00	0.39	1100	0.00	101.37	0.28	3.70	82.20	0.32
900	0.00	62.04	0.46	12.50	54.80	0.39	1200	0.00	102.85	0.28	3.75	81.60	0.32
1000	0.00	63.78	0.45	13.50	53.60	0.38	1300	0.00	104.30	0.28	3.85	81.00	0.32
1100	0.00	65.43	0.44	14.50	52.40	0.38	1400	0.00	105.72	0.27	3.90	80.40	0.33
1200	0.00	67.01	0.43	15.50	51.00	0.37	1500	0.00	107.11	0.27	4.00	80.00	-0.05
1300	0.00	68.53	0.42	16.00	50.40	0.37							
1400	0.00	70.00	0.41	16.50	50.20	0.36							
1500	0.00	71.42	0.40	17.50	50.00	0.35							

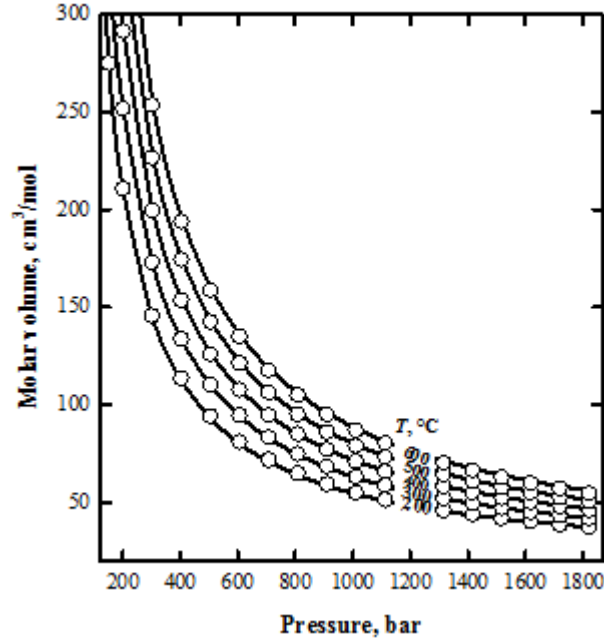


Figure 1: The pressure-volume-temperature relations for  $H_2$  gas. The symbols correspond to the values measured by Presnall (1969). The curves were calculated in this study from the Redlich-Kwong EOS modified by Soave (1972) and improved as part of this work.

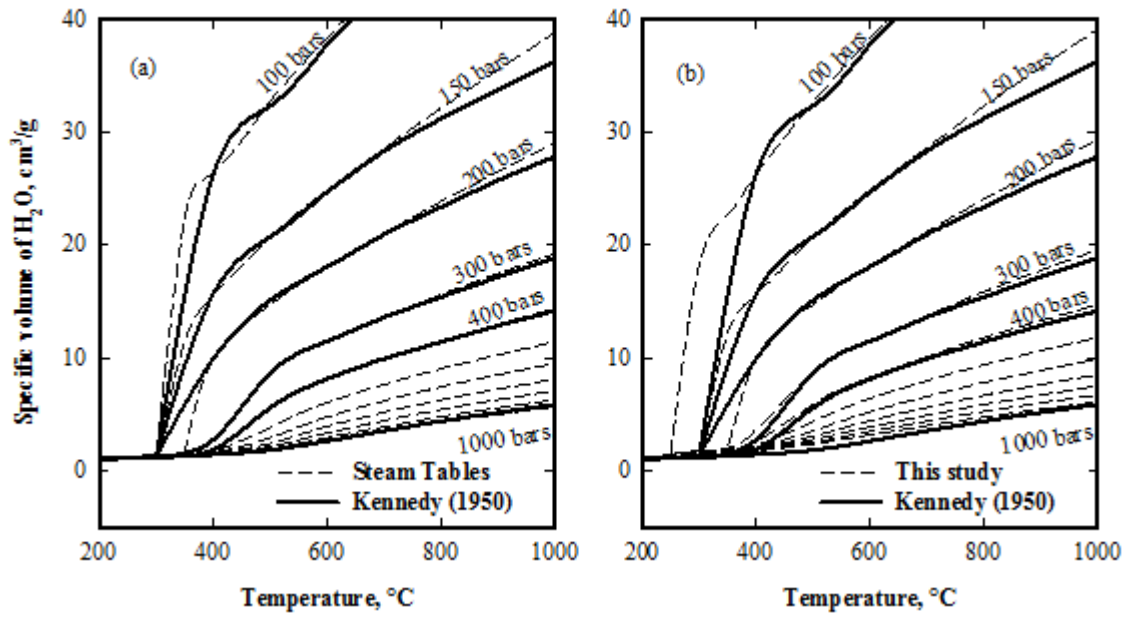


Figure 2: Specific volumes of  $H_2O$  reproduced with the steam table of Grigull (1984) for (a) and reproduced with this study for (b) (dashed lines), compared with the experimental specific volumes of Kennedy (1950) drawn for some pressures (dark lines).

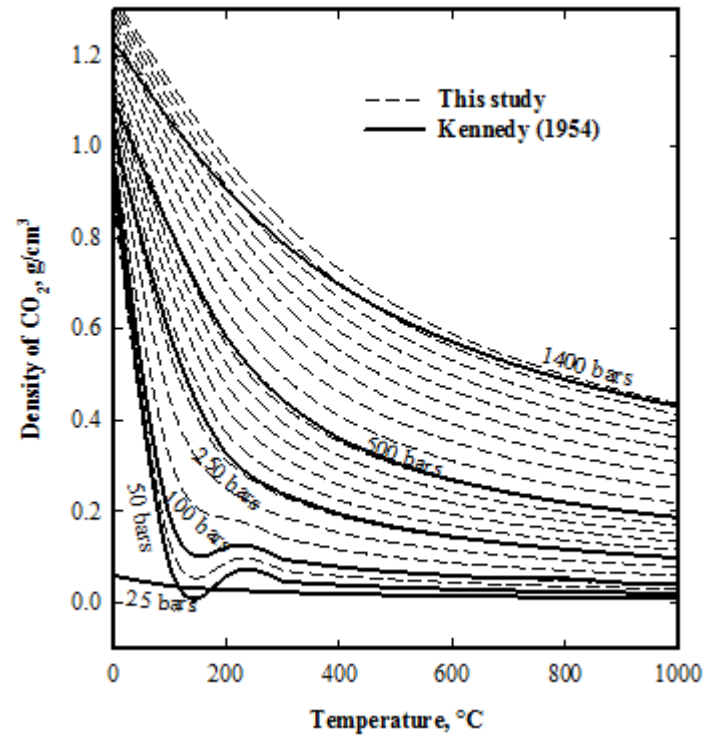


Figure 3: Density of CO<sub>2</sub> reproduced in this study. The dashed lines are the results of this study for CO<sub>2</sub>, and the dark lines are the results of the experimental study of Kennedy (1954) for the some pressures. The results are relatively closed (with  $V^{\text{fluid}} = M/x$ ).



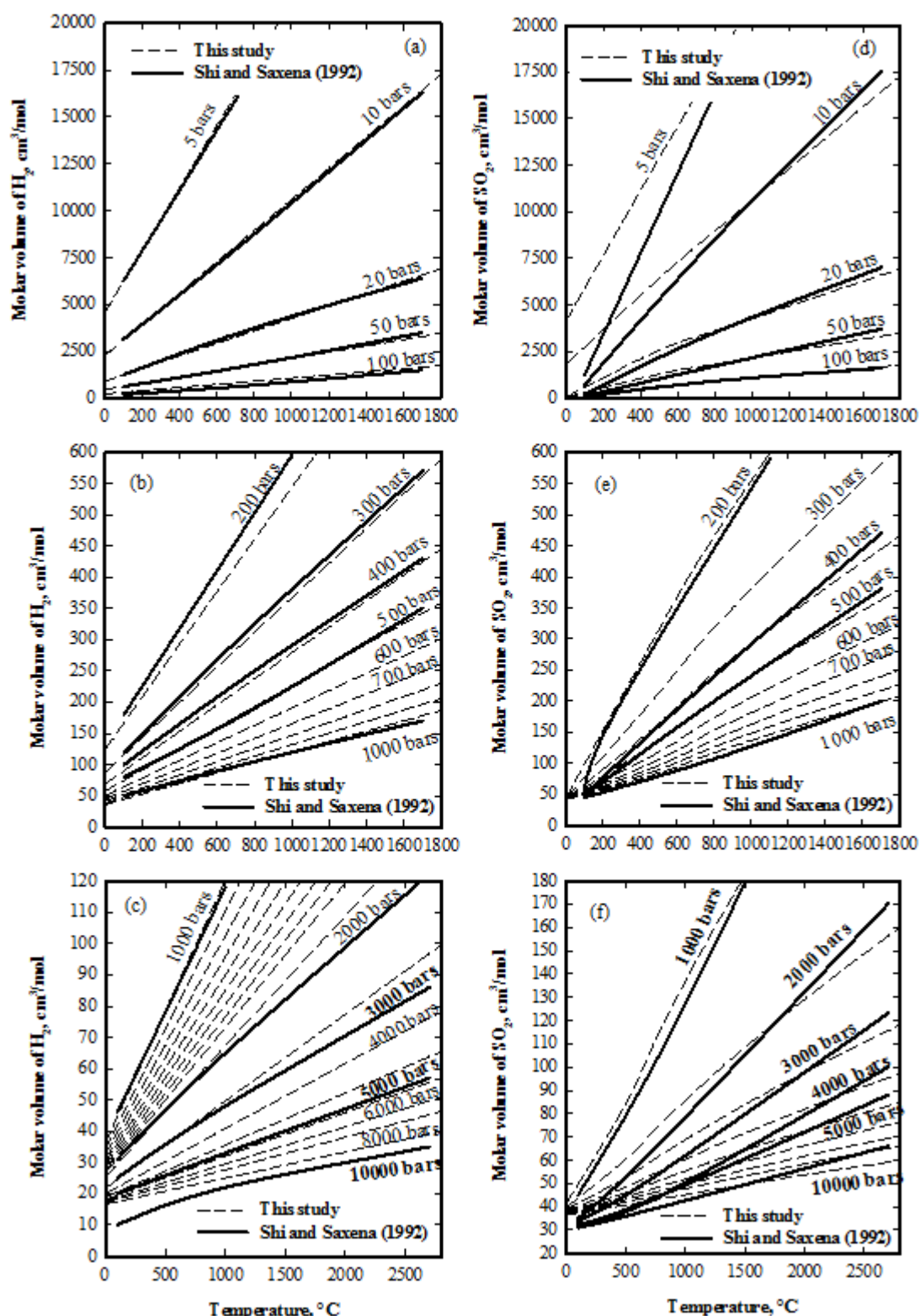


Figure 4: Molar volumes of H<sub>2</sub> for (a), (b) and (c) and SO<sub>2</sub> for (d), (e) and (f) function of T and P. The curves were drawn for pressures from 5 to 100 bars for (a, d) from 200 to 1000 bars for (b, e) and from 1000 to 10000 bars for (c, f). The values were calculated in this study (dashed lines) compared to the molar volumes reported by Shi and Saxena (1992) reproduced and drawn from their figures (dark lines). The results are relatively closed (with  $V^{\text{fluid}} = M/x^{\text{f}}$ ).

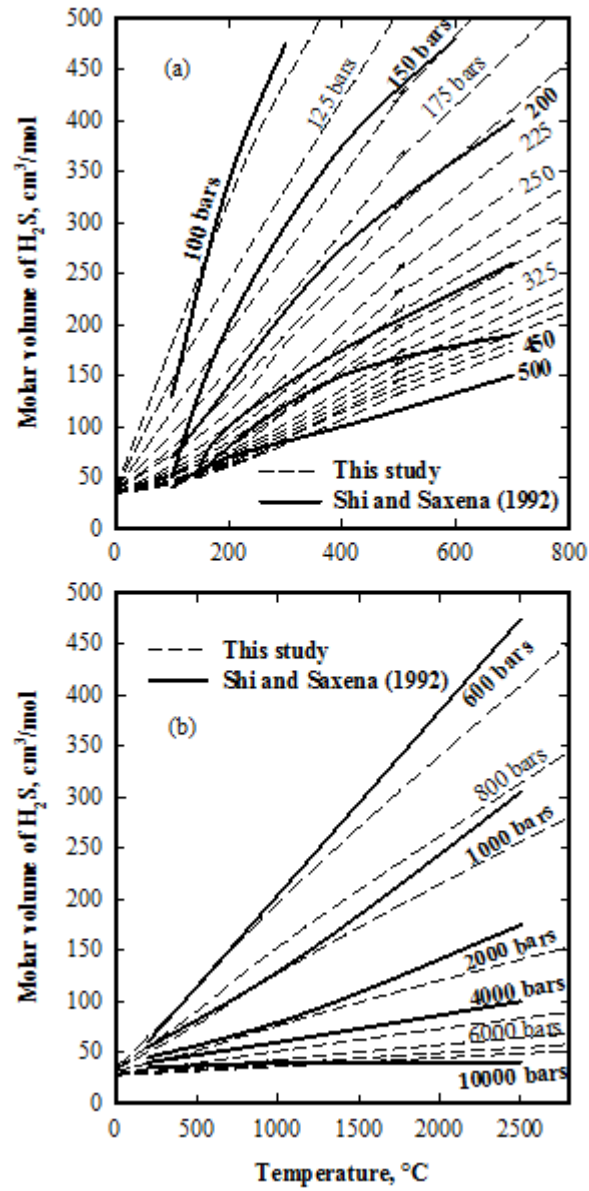


Figure 5: Molar volumes of  $H_2S$  function of  $T$  and  $P$ . The curves were drawn for pressures from 100 to 500 bars for (a) and from 600 to 10000 bars for (b). The values were calculated in this study (dashed lines) compared to the molar volumes reported by Shi and Saxena (1992) reproduced and drawn from their figures (dark lines). The results are relatively closed (with  $V^{fluid} = M / \rho$ ).

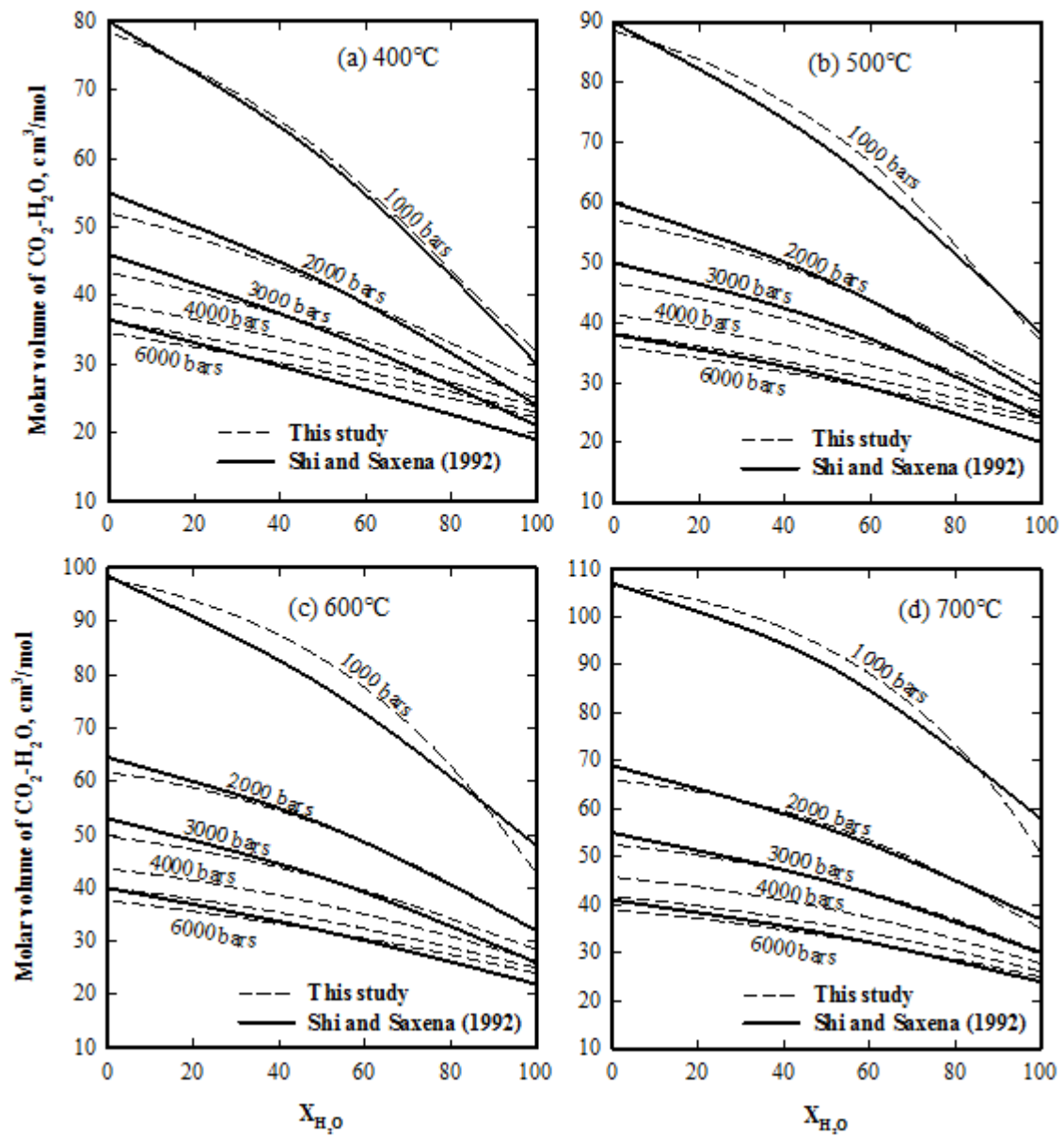


Figure 6: Molar volumes of  $\text{H}_2\text{O-CO}_2$  system at 400°C for (a), at 500°C for (b), at 600°C for (c) and at 700°C for (d), function of molar fraction of  $\text{H}_2\text{O}$  and P. The curves were drawn for pressures from 1000 to 6000 bars and calculated in this study (dashed lines). The values reported by Shi and Saxena (1992) were reproduced and drawn from their figures (dark lines). The results are relatively closed (with  $V^{\text{fluid}} = M/x^{\text{I}}$ ).

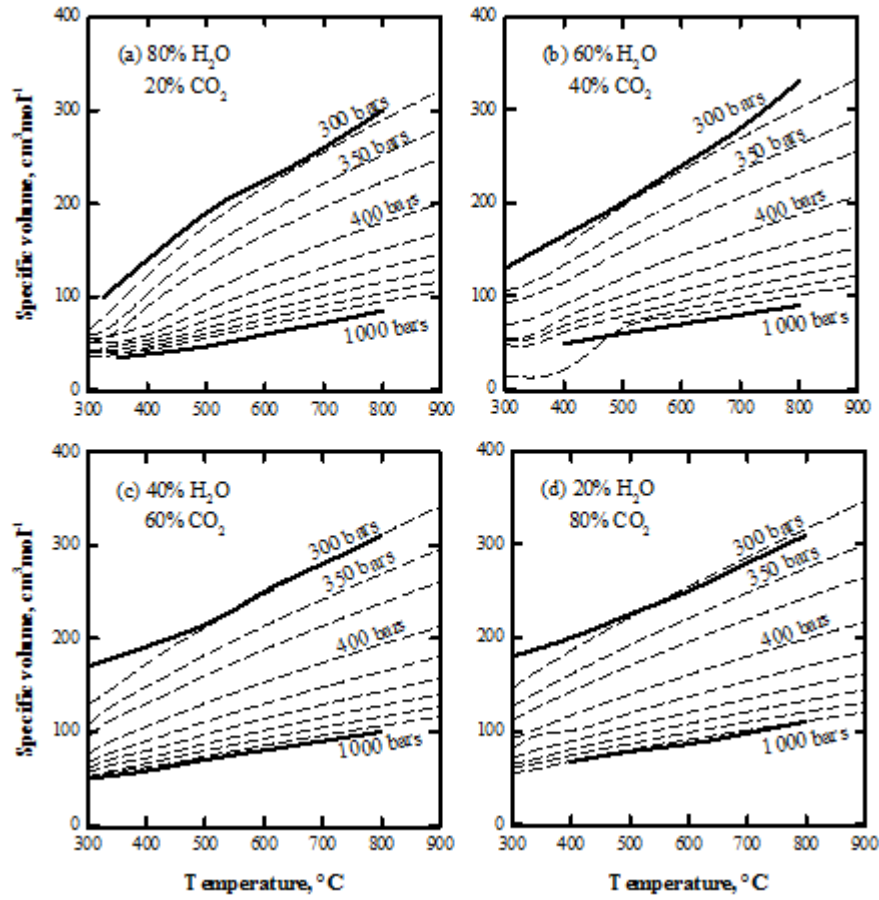


Figure 7: Specific volume of H<sub>2</sub>O-CO<sub>2</sub> system reproduced in this study. The dashed lines are the results of this study, and the dark lines are the results of the experimental study of Plyasunov and Zakirov (1991) for the extreme pressures. Both results are in good agreement (with  $V^{\text{fluid}} = M/x^{\text{f}}$ ).

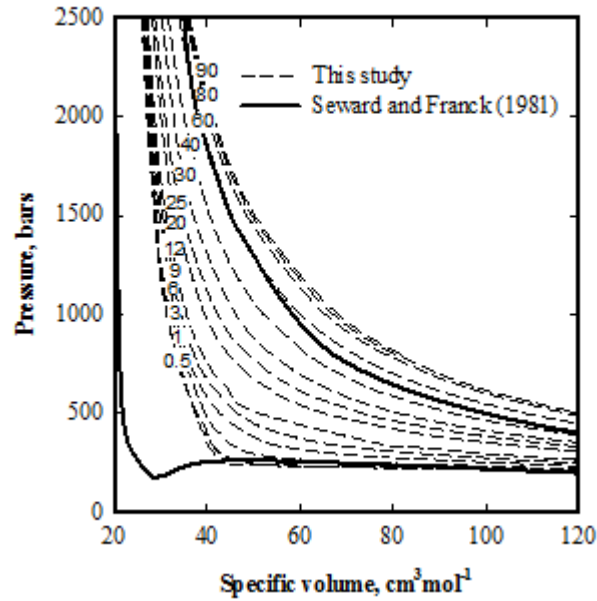


Figure 8: Specific volume of H<sub>2</sub>O-H<sub>2</sub>, with 0.5% to 100% of H<sub>2</sub>, reproduced in this study (dashed lines). The dark line corresponds to the values of Seward and Franck (1981) for 0.5% and 90% of H<sub>2</sub>. Both results aren't in good agreement (with  $V^{\text{fluid}} = M/x^{\text{f}}$ ).

## **6. Use and Agreement Contract**

**Owner:** Michael Andre Franiatte.

**Contact:** [michael.franiatte@gmail.com](mailto:michael.franiatte@gmail.com).

**Owning:** All works from scratch of the owner.

**Proof of Owning:** Works published, and writings/speakings all over.

**Requirements of Use:** Pay the owner, quote the owner, agreement of the owner.

**Availability of Works:** Only under the shapes of the owner built, only for personal use.

**Subjects of Claims:** Works published by the owner on Google Play and Google Books.

**Concerning Author Rights:** Equations and codes from scratch of the owner, softwares built from it, all things of people arising from it.

**End User License Agreement:** A commercial license is required to use in personal manner. Do not redistributing in any manner, including by computer media, a file server, an email attachment, etc. Do not embedding in or linking it to another programs, source codes and assistances including internal applications, scripts, batch files, etc. Do not use for any kind of technical support including on customer or retailer computer, hardware or software development, research, discovery, teachery, talk, speech, write, etc. Do not use for win money or for commercialisation of any products arising from my programs, source codes and assistances. Do not use and do not copy the way it run in other programs, source codes and assistances. Do not use without pay me, quote me and my agreement. Do not steal or copy or reproduce or modify or peer or share. Do not use in other manner than personal. It stand for my programs, source codes and assistances or programs, source codes and assistances stealing or copying or reproducing or modifying or peering or sharing my programs, source codes, and assistances. If you aren't agree you shall not use.

**Terms of License and Price:** The present contract acceptance is required to use works of the owner and built from it in all kind of manner. The price for each user shall be defined with the owner by contacting him and this for each subject of works the owner claims. Each user shall contact the owner for asking his agreement. It can be refused by the owner depending who asking and the price defined. People don't respecting the present contract shall not use the works of the owner.