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Thermodynamics of Geothermal Fluids: a Benchmark Between Thermodynamic Models, from Henry's Approach to Advanced EoS (GECO Project)

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ABSTRACT

In the context of the Castelnuovo (Italy) non condensable gas reinjection project (EU Geothermal Gas Emission Control (GECO) project), relevant and rigorous tools to describe the thermodynamic behavior of fluids composed of water, salt (NaCl), CO_2 and other impurities such as H_2S, methane are needed. These tools will allow to represent and predict accurately the phase equilibrium and thermodynamic properties such as density, viscosity, compressibility, heat capacity and enthalpy, under the different conditions encountered in the process. Within this study, starting with a state of art, we propose a comparison between several thermodynamic models, different in nature and complexity, from Henry's approach to advanced Equation of State taking into account association (such as CPA, Cubic Plus Association EoS). To evaluate the thermodynamic models, not only experimental data from the laboratory can be used but also data generated by molecular simulations. These advanced methods of statistical thermodynamics make possible to obtain pseudo-experimental data even under tough conditions, difficult to reach in laboratories such as high temperature, high pressure, presence of toxic compounds.... The different thermodynamic approaches considered in this study will be compared and their advantage and drawback will be discussed. The aim of this work is to present a global assessment of thermodynamic approaches for different contexts of water – salt – CO_2 + impurities systems : the results of this study will be relevant and exploitable not only for the Castelnuovo context but also for many other geothermal contexts, including reservoir and surface conditions.

1. INTRODUCTION

Simulation of geothermal processes requires a good knowledge of the behavior of fluids as a function of temperature and pressure conditions. It is important to determine the state of the phases in equilibrium (liquid, vapor, liquid +vapour) as well as the volumetric properties of the phases such as density, viscosity, calorific capacity, thermal conductivity, surface tension. These data should be used to simulate the behavior of fluids on the surface as well as under reservoir conditions.

The fluids considered are composed of water, salt, carbon dioxide and other impurities such as methane, ethane, and other light hydrocarbons, hydrogen sulfide, hydrogen. Operating conditions correspond to wide temperature and pressure ranges. In the most extreme temperature situations, fluid modeling must be able to describe supercritical behaviors.

Accurately modeling the thermodynamic of such systems is a major challenge; we are dealing with compound presenting strong associative and polar interactions; the presence of salts (typically sodium chloride, but other mono or bivalent salts can be considered) further complicates the modeling of these fluids.

Equations of state (EoS) are widely used in industry. They are simple to use and accurately represent the relationships between temperature, pressure, and phase compositions for binary and multicomponent systems. In geothermal context, an EoS can be used in designing the surface plant facilities (heater, compressor, pumps,…) and also in well design. With an EoS it is possible to describe the whole phase envelope of a system and also provide the thermodynamic properties of phase such as volume, density, enthalpy and heat capacity. Furthermore, EoS are adequate for calculation of phase equilibrium and properties in the supercritical region.

Modeling carbon dioxide/water and hydrogen sulfide/water mixtures is challenging due to their polar nature and the resulting complexity of their phase behavior. Due to their importance and complexity, there is abundance of literature addressing these systems, in terms of modeling and measurements (Aasen *et al.* 2017, Springer *et al.* 2012, Takenouchi and Kennedy 1964, 1965). Plenty of approaches have been developed for cited systems, however, there are still lack of modeling solutions if brine systems are considered (Dubessy *et al.* 2005).

In this work, we will review different possible modeling approaches for such systems. We will first examine the restitution of phase equilibria before presenting methods for calculating volumetric properties.

2. MODELING OF PHASE EQUILIBRIUM

2.1 Salt effect

Geological systems are never made of pure water; dissolved salts are always present, for example, we find:

- monovalent salts: NaCl, $NaNO_3$, KCl, KNO_3 ;

- bivalent salts: $CaCl_2$, $MgCl_2$, $BaCl_2$, Na_2SO_4, $Mg(NO_3)_2$, $MgSO_4$;

- trivalent salts: $AlCl_3$, $Al_2(SO_4)_3$.

The presence of these salts in solution, in the form of ions, will lead to a reduction in the solubilization of gases such as acid gases (H_2S and CO_2) and hydrocarbons. This well-known phenomenon is called ‘the salt effect’ and can be considered a physical absorption in the sense that it does not involve any reaction mechanism. The presence of hydrogen sulfide and carbon dioxide also pose the problem of chemical reactions in the aqueous phase. Indeed, depending on the pH of the solution, these acid gases can also be found in ionic forms HS^- and S^{2-} for hydrogen sulfide and CO_3^{2-} and HCO_3^- for carbon dioxide. For example, the carbonate ion can combine with calcium ions and precipitate forming limestone. In this case, physical absorption is combined with absorption due to the presence of chemical reactions and the solubility of carbon dioxide can then be increased. We can therefore conclude that the introduction of ions into the water system +hydrogen sulfide +carbon dioxide complicates the problem in two ways:

- the number of possible salts and their combinations increases exponentially;

- the presence of chemical reactions (acid-base reactions and formation of solid phases).

All in all, each system has its own reactions and is therefore quite specific. Given the complexity and the disparity of this subject, in this study, we are not going to deal with the reaction aspect. Here we will focus on purely physical systems. This restriction leads us to consider a smaller number of salts: their dissociation must be full, and the resulting ions must be "spectator" ions, i.e. they must not participate in any chemical reaction except their dissociation. From a practical point of view, the most studied brines are those containing sodium chloride and this salt is generally used as a model system. It should also be noted that salt analysis is generally not fully available and that an equivalent NaCl concentration is used in most cases (Markham and Kobe (1941)). Finally, the last limitation of the present work concerns the presence of solid phases. As it is not possible to dissolve infinite quantities of salts in water, all salts have a solubility limit. In this study, we only consider systems being below these solubility limits so that we do not deal with equilibria in the presence of solid phases.

2.2 Phase equilibrium diagrams

A water-acid gas (CO_2 or H_2S) and water and light hydrocarbon binary system exhibit a type III behavior according to Scott and Van Konynenburg's (1970) classification. Figure 1 shows. the vapor pressure curves of water and acid gas (i.e. hydrogen sulfide or carbon dioxide) are presented along with the locations of critical points in a pressure-temperature diagram.

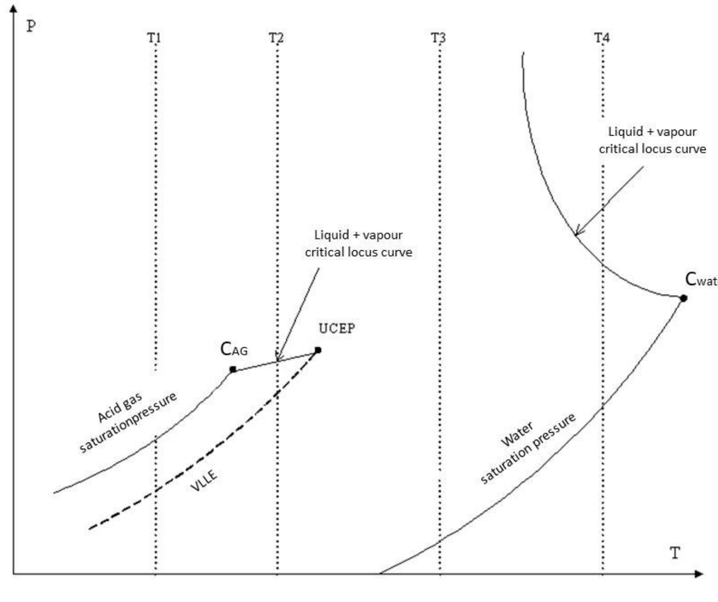

Figure 1: Critical point locus of water + acid gas (CO_2 or H_2S)

H_2O - H_2S or H_2O - CO_2 systems present liquid-liquid - liquid-vapor (VLLE) equilibrium situations (dotted line in Figure 1). This curve P = f(T) stops at the UCEP point (Upper Critical End Point). Above the UCEP temperature, it is no longer possible to find a three-phase equilibrium. Carroll and Mather (1989) founded the UCEP point for hydrogen sulfide at 106.2 °C and 93.9 bar and Kuenen and Robson (1899) measured the UCEP point for carbon dioxide at 31.05 °C and 73.34 bar. Each one of these two UCEP points is barely different from the critical point of pure acid gases. The water - sour gas binary diagrams have two branches of liquid-vapor critical points: one begins at the sour gas critical point and the other at the water critical point.

To visualize the influence of composition on phase diagrams behavior, we have plotted in figures 2a to 2d four particular isotherms (T1 to T4 temperatures specified in Figure 1 by vertical dotted lines). These figures describe the behavior of the system as a function of hydrogen sulfide content; (similar diagrams are observed when carbon dioxide is considered). At temperature T1, in most cases, the three-phase curve separates the binary domain "aqueous liquid-vapor" from a binary domain "aqueous liquid - acid liquid" (Figure 2a). However, for high H_2S contents, it is possible that all the water solubilizes in the liquid acid and vapor phases at high pressure and there is no "aqueous liquid-vapor" range. The three-phase curve then separates the binary domain "aqueous liquid-vapor" at low pressure from the domain "acid-vapor liquid". At temperature T2, the behavior of the system is similar to the one described for temperature T1 except for mixtures rich in H_2S at high pressure: T2 being higher than the critical temperature of H_2S (see Figure 1) the increase in pressure of a mixture rich in H_2S leads to the formation of a supercritical phase with the presence of a critical point. The location of these critical points starts at the UCEP point and ends at the H_2S critical point. At temperature T3, there is no longer any three-phase equilibrium or critical point (Figure 2c). Finally, at higher temperatures (Figure 2d), a new critical point appears whose location starts at the critical point of pure water (see Figure 1).

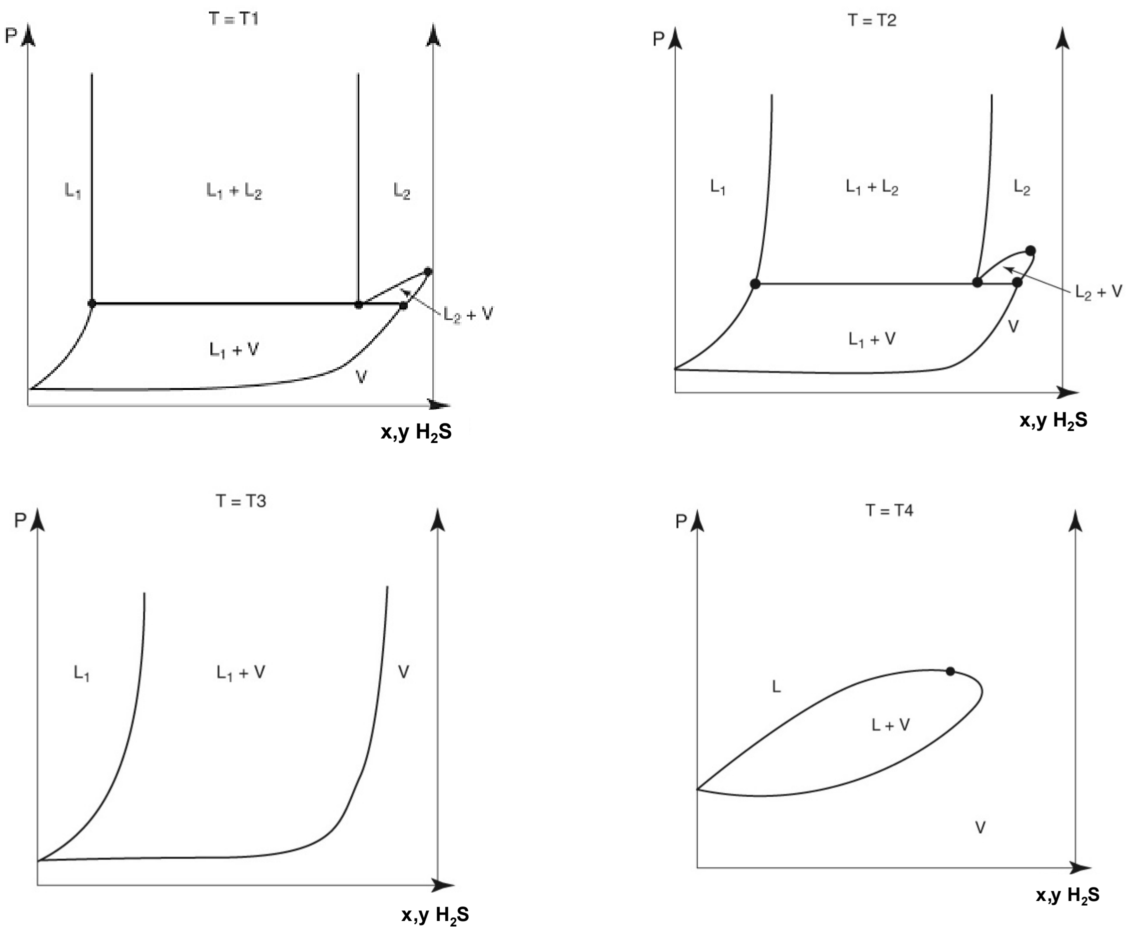

Figure 2a to 2d: H_2S - H_2O phase diagrams in the Pressure - Composition plane (x and y being respectively the molar fractions of H_2S in the liquid phase and in the gas phase). The indications L1, L2, V correspond respectively to the aqueous phase, the liquid H_2S phase, and the vapor phase. Temperatures refer to Figure 1. The same kind of phase diagram is obtained with CO_2

In order to construct and evaluate a thermodynamic approach, experimental data from the laboratory are commonly used. However, the experimental exploration of high pressure and high temperatures regions and measurement on systems containing toxic or corrosive components like acid gases can be a major issue. In such cases, an effective alternative option is to use molecular simulation techniques to generate pseudo-experimental data even under these tough conditions. Molecular simulation is a widespread technique based on statistical thermodynamics which consists of performing a detailed simulation of microscopic systems and of calculating appropriate averages in order to derive macroscopic fluid properties. The extrapolation capacity of molecular simulation makes it the safer way to predict equilibria and thermophysical properties (Ungerer *et al*. (2005), Lachet *et al.* (2012), Creton *et al.* (2018)). As an example, such approach has been employed for H_2S or H_2 absorption in brines (Fauve et al.,2017; Lopez-Lazaro et al., 2019).

2.3 Modelling of water and acid gases and light hydrocarbons systems

To model phase equilibria of water or brine and acid gases, different models could be employed. Two major approaches can be distinguished: heterogeneous approaches (i.e. one different model per each phase) and homogeneous approaches (same model for all phases).

A category of a heterogeneous approaches interesting for the systems studied in this work couple an activity model for aqueous phase with a state equation for the vapour phase. An example of this approach is the coupling of the Pitzer model (activity model) for the liquid phase and a cubic state equation such as Peng and Robinson (PR) or Soave Redlich Kwong (SRK) for the vapour phase. The modelling of phase equilibrium is then written as:

$$H.x_i.\gamma_i^*.\Im = P.y_i.\varphi_i$$

H is the Henry's constant of solute in aqueous phase, x is the molar fraction in liquid phase, $\gamma^*$the activity of solute in aqueous phase, $\Im$ is the Poynting factor (effect of pressure), P is the pressure, y is the molar fraction in vapor phase and φ the fugacity coefficient in vapour phase. Use an activity model as Pitzer model for the description of the aqueous phase allows us to describe the water and the brine systems. This kind of approach is well adapted for the systems of interest for a moderate range pressure (lower than 150 bar). Another example of useful heterogeneous approach has been developed by Søreide and Whitson (1992). This model combines two equations of state: one for each of the two phases. For such a kind of approach, the phase equilibrium is then written as:

$$P.x_i.\varphi_i^L = P.x_i.\varphi_i^V$$

In this equation, φ^L is the fugacity coefficient in liquid phase and φ^V is the fugacity coefficient in the vapor phase. The main advantage of such approach resides in its capability to accurately reproduce experimental data in low and medium pressure regions, but, in spite of this, it is unable to cover situations under high temperature - high pressure conditions that imperatively require a continuity of description between aqueous and vapor phase.

The EoS give the fugacity of each component in each phase and will be coupled with a flash algorithm in order to obtain the composition of each phase in equilibrium. EoS give also different thermophysical properties such as molar volume, density, heat capacity, enthalpy, etc…The basic expression for these calculations can be found in classical handbooks of thermodynamics (de Hemptinne *et al*. 2013; Kontogerogis and Folas 2010)

Among the homogeneous models, classical state equations (PR or SRK) complemented with complex mixing laws (excess enthalpy mixing laws) or advanced state equations such as the Cubic Plus Association (CPA) model which includes a specific term for associative interactions had to be mentioned. The phase equilibrium is expressed by the same relationship and the fugacity of each compound are obtained using the same equation of state for both phases. It should be noted that these approaches make it possible to accurately reproduce water and light gas systems but that they are not able to reproduce the brine and gas systems without significative modifications.

In the next section, we give concrete examples of the application of these two different approaches.

2.3.1 Example of the heterogeneous approach: the Søreide and Whitson model

The Søreide and Whitson model (1992) modifies the cubic state equation of Peng and Robinson to take into account the presence of water and salt. The equation form remains that of Peng and Robinson:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2}$$

It connects the pressure P, to the temperature T and the molar volume v and uses a covolume term b and an attractive term a(T). The first modification made by Søreide and Whitson concerns a specific attraction term of water/brine which is considered as a function of the molality of the solution. For the other components, the reduced attraction term of the basic equation of Peng and Robinson is conserved. According to Søreide and Whitson, the modification of the water's attraction term makes possible to predict the vapor pressure with an uncertainty of 0.2% between 15 and 325 °C. For a mixture of several components, it is assumed that the classical mixture rules of the Peng and Robinson equation are used. These mixing rules take into account binary parameters which are adjusted on experimental data. The second modification of Søreide and Whitson affects these binary parameters; they result to be different and specific for each considered phase.

Figures 3 and 4 give the phase diagram of the water + CO_2 system. They show a good agreement between the experimental data and the defined model. The quality of the restitution comes from the binary interaction parameters.

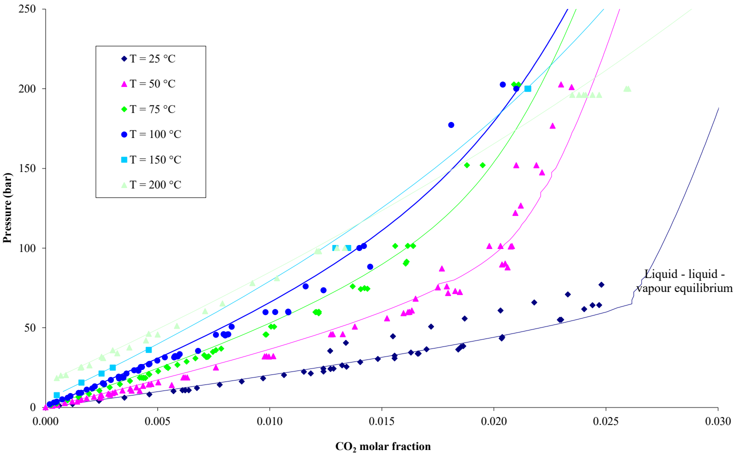

Figure 3: CO_2 - H_2O phase diagrams in the pressure - composition plane (aqueous phase). Symbols are experimental data and lines represent Søreide and Whitson model.

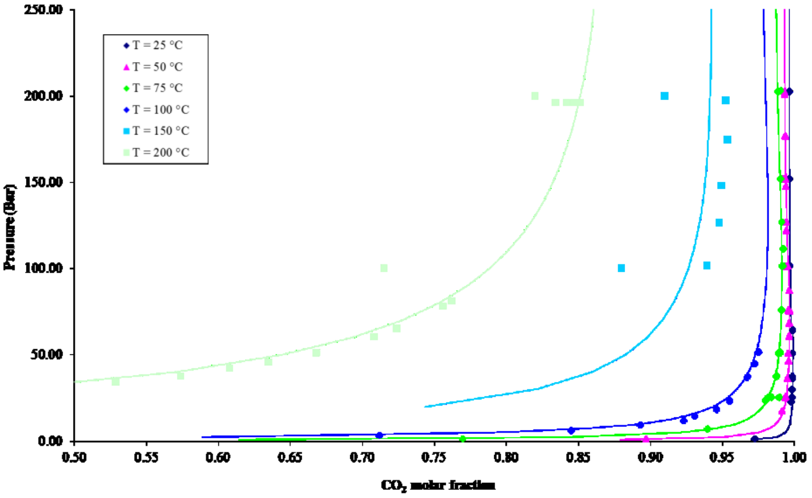

Figure 4: CO_2 - H_2O phase diagrams in the pressure - composition plane (vapor phase). Symbols are experimental data and lines represent Søreide and Whitson model.

<u>2.3.2 Example of the homogeneous approach: Peng and Robinson with Gibbs free energy mixing rules model</u>

As mentioned earlier, a classical state equation cannot be used to represent complex situations such as water + acid gases. If we assume to employ the same description for all phases some new enhancement had to be introduced. For this purpose, more complex mixing laws such as the forms proposed by Huron - Vidal must be considered:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{G^E}{\Lambda}$$

Where a and b are respectively the attractive term and the covolume; x_i is the molar fraction. G^E is the Gibbs free energy of the system which is adjusted on experimental data and Λ is a empirical parameter specific of the equation of state. This kind of equation is able to produce complex phase diagram such as described in figure 5.

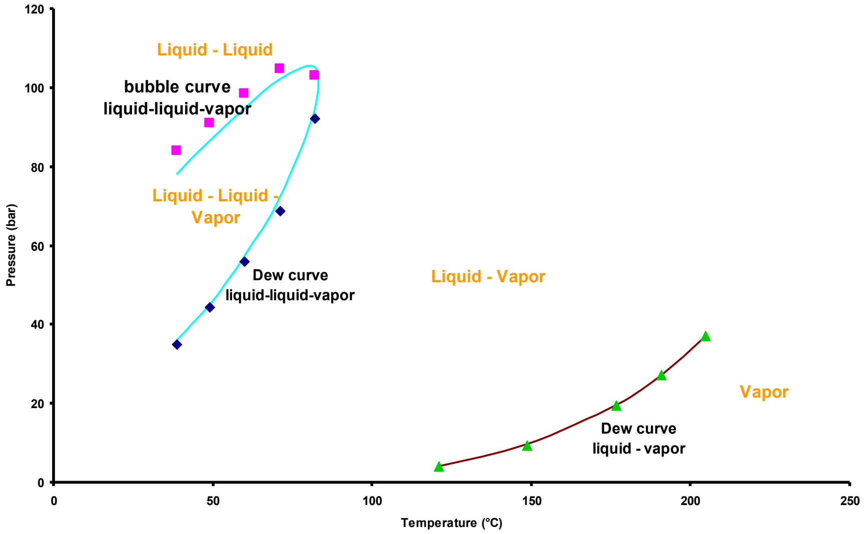

Figure 5 :Phase diagram of the quaternary system: water/hydrogen sulfide/ carbon dioxide/methane (50/40/5/5 molar fractions). Symbols are experimental data (Robison et al., 1982) and lines represent PR with Huron-Vidal mixing rule.

Such a model is generally built and shaped on binary systems. We firstly adjusted each sub-binary system on available experimental data, hence, we were able to predict the whole phase diagram of the quaternary system. Figure 5 shows the good agreement between the experimental data from Robinson et al. (1982) and the prediction of the system. The model is able to reproduce the behavior of the system according to different temperature and pressure conditions. These are not only the classic phase equilibrium, vapor and vapor-liquid situations but also the most complex liquid-liquid and liquid-liquid-vapor equilibrium. Such results can be also obtained with the CPA (Cubic Plus Association) equation of state. These models constructed on more physical basis allow to better reproduce the behavior of water – carbon dioxide - impurities systems although their extension to electrolytic systems (presence of salts) need the inclusion of specific terms which make these state equations even more complex to handle.

2.3.3 Performances of equilibrium models

To evaluate and compare the different approaches, we used two sets of data, detailed in Table 1.

Table 1: Temperature – Pressure conditions of the dataset for the $CO_2 + H_2O$ and $H_2S + H_2O$ systems

$CO_2 + H_2O$ system			
Temperature range	N data	Pressure range	N data
T < 300 K	195	P < 250 bar	667
300 K < T < 400 K	352	250 bar < P < 500 bar	158
400 K < T < 500 K	168	500 bar < P < 1000 bar	78
500 K < T < 600 K	235	P > 1000 bar	64
T > 600 K	17		
	967		**967**
$H_2S + H_2O$ system			
Temperature range	N data	Pressure range	N data
T < 300 K	91	250	116
300 K < T < 400 K	25		
	116		**116**

Obviously, there is more data concerning CO_2 than H_2S in the public literature, in addition the temperature and pressure range with H_2S is narrower. We focused on data to cover surface and shallow well conditions. In the case of deeper situations (e. g. supercritical geothermal energy), a more specific data set would be required. Table 2 gives the performance of these kind of models to describe the experimental data for water + CO_2 system and water + H_2S system.

Table 2: Performances of different models for equilibria (VLE) calculations (Δx/x) relate to the solubility of acid gases and (Δy/y) relate to the water content of the vapor phase

	Δx/x (%) of acid gas		Δy/y (%) of water	
	$CO_2 + H_2O$ system	$H_2S + H_2O$ system	$CO_2 + H_2O$ system	$H_2S + H_2O$ system
Set 1: Henry law with PR EoS	19.0	14.9	61.1	24.6
Set 2: Søreide and Whitson	13.8	8.4	21.8	16.2
Set 3: PR with complex mixing rules (Gibbs free energy)	23.2	8.8	22.8	18.6
Set 4: CPA EoS	15.0	9.4	56.0	25.2

We can see that all the approaches given similar deviations for the representation of water content in the vapour phase. This is because all these approaches degenerate into a classical cubic state equation (i.e. PR or SRK) when vapour phase is considered. For aqueous phase of the H_2S+ H_2O system, the results are very close except in the case of Henry Law approach which shows larger deviation at high temperature and high pressure. This is due to the fact that under these conditions the system deviate from ideality and assumptions underlying the Henry formalism are no more valid. For the CO_2+H_2O system, the deviations are globally larger compared to H_2S+ H_2O system: this is most likely due to the fact that the number of experimental data is much larger and the PT range is also broader. Inherent discrepancies between experimental data are also observed. Set 3 and Set 4 approaches show similar performances and the deviations in agreement with experimental ones. The CPA EoS results indicates a good restitution of the aqueous phase even if the deviation of the water content is larger; this is explained by a larger deviation on a specific region (low temperature) of the phase diagram which is widely represented in the experimental database. These results show that these kinds of approaches can achieve equivalent performance; the quality of the model being a function of the temperature and pressure ranges.

3. MODELING OF PHASE PROPERTIES

3.1 Density

The density of vapor phase composed by acid gases or hydrocarbons is easily modeled using the classical cubic equation of state (PR or SRK). If liquid hydrocarbon or acid gases are considered, a volume translation had to be added. Some correlations able to describe the density of such systems have been reported in the literature (Peneloux et al., 1982, Ungerer and Batut, 1997).

For the aqueous/brine phase, a lot of empirical correlations have been published (Rowe and Chou, 1970; Batzle and Wang, 1992): in general, the density of solution is modeled as a function of temperature, pressure and salt content.

Considering the aqueous phase densities in the presence of sour gas, they can be expressed as:

$$\rho = \rho_{water}\left(1 + \frac{gas\ weight/water\ weight}{gas\ volume/water\ volume}\right)$$

The ratio between the mass of gas and one of water can be calculated by using the molality and molar mass of the gas. The ratio between gas and water volumes involves the molality, the molar mass of the gas and the partial molar volumes of the water and gas. At this stage, two strong assumptions had to be made:

- the partial molar volume of the water in solution is considered equal to the one of pure water under the same temperature and pressure conditions;

- the partial molar volume of the gas is considered equal to the molar volume at infinite dilution.

Then comes the following relationship:

$$\rho = \rho_{water}\left(1 + \frac{m_{gas}M_{gas}}{m_{gas}\rho_{water}v_{gas}^{\infty}}\right)$$

In this expression, m_{gas} is the molality of the gas in the aqueous phase, M_{gas} is the molar mass of the gas, ρ_{water} is the density of the water under the considered temperature and pressure conditions and v_{gas}^{∞} is the volume of the gas in the water at infinite dilution. The use of this expression requires knowledge of the value of the density of water, the solubility of a gas in water and the molar volume at infinite dilution. Ennis-King and Paterson (2003) presented a compilation of these infinitely diluted molar volumes for carbon dioxide in water. Figure 6 shows some of these data and the correlation proposed by these authors.

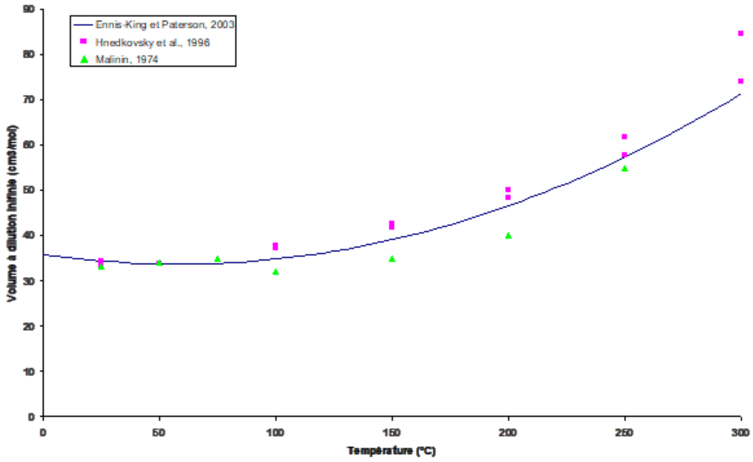

Figure 6: Molar volume of CO_2 at infinity dilution in the aqueous phase

Therefore, considering only a temperature dependency, the molar volume at infinite dilution can be correlated as follows:

$$v_{gas}^{\infty}(T) = 104.764 - 0.4285.T + 6.459.10^{-4}.T^2$$

With T in K and v_{gas}^{∞} is expressed in cm^3/mol. This relationship is to be used in the range 273 to 673 K and pressures up to 350 bar. It should be noted that the average experimental uncertainty over this volume is not negligible: ± 2 cm^3/mol.

The density model thus defined was compared to measurements concerning the water-carbon dioxide system (Teng et al., 1997). These measurements cover the range of 5 to 20 °C and 65 to 300 bar. Using the Rowe and Chou correlation for the density of pure water and the correlation for the infinitely diluted volume, we obtain an average relative deviation of 0.26% over the 24 experimental data.

This approach can be extended to brines in the following manner:

$$\rho = \rho_{brine}\left(1 + \frac{m_{gas}M_{gas}(1 - w_{salt})}{m_{gas}\rho_{brine}v_{gas}^{\infty}(1 - w_{salt})}\right)$$

With: ρ_{brine} the density of the brine free of acid gas, m_{gas} the gas molality (number of moles based on the water mass), w_{salt} the mass fraction of salt in the water + salt mixture and v_{gas}^{∞} the infinitely diluted molar volume in the brine. It had to be noticed that there are very few experimental data available for the infinitely diluted volume in brines. Malinin (1974) measured infinitely diluted volume for a 1 M sodium chloride solution and it had to be noticed that, given the uncertainties, the reported values are not very different from the ones measured for pure water. Therefore, we assumed using the correlation already presented. To assess the capabilities of this approach, we modeled the data of CO_2 densities in the waters of the Weyburn field reported in Li et al (2004) publication. In this work, the authors provide an analytical detail of the composition of water studied; we have therefore firstly transformed this information into an equivalent NaCl content in order to obtain the density of the water without carbon dioxide. We obtained a NaCl mass fraction of 9.25% while the analysis provides 8.75% of different salts. Then we compared our model to the CO_2 densities measurements reported by Li et al. (2004) and we obtained an average relative deviation of less than 0.17%. If a salt content of 8.75% is considered, the relative difference remains the same. These results are quite encouraging. However, as considered salt and CO_2 concentrations are relatively low, this is just a partial validation of our approach: only an extensive experimental data acquisition campaign will improve the prediction of water-salt-carbon dioxide systems.

3.2 Viscosity

To represent the viscosity of such systems, it is necessary to use different approaches depending on the nature of the phases.

Thus, for the aqueous phase, different correlative approaches have been proposed that allow aqueous brine solutions to be treated. One example is the model proposed by Kestin et al. (1981) which cover the temperature range up to 150 °C and a pressure range up to 350 bar. There are few experimental data to quantify the impact of CO_2, but it is generally accepted to be small except under extreme temperature and pressure conditions. McBride-Wright et al. (2015) give an overview of the modelling of this system using correlative approaches.

For non-aqueous phase modelling, fairly conventional approaches such as the Lohrenz Bray et Clark model (1964) or friction theory (*f*-theory) (2000) can be used. These models make it possible to reproduce the viscosities of pure acid gases with uncertainties in the order of 5%. In equilibrium with water, the deviations are a little bit increased and deviation about 10 % are observed.

4. CONCLUSIONS

In the present work, we propose a review and a comparison of thermodynamic approaches applied to geothermal context (reservoir and surface conditions). The systems considered are composed of water, salt (NaCl), carbon dioxide and other impurities such as hydrogen sulfide, methane. We compared the performances of different equations of state in reproducing phase equilibria (more or less complex) and volumetric properties, such as density and viscosity. At different extent, the examined approaches are able to correctly reproduce experimental data present in literature. Concerning phase equilibria, heterogeneous approaches only make it possible to reproduce low and medium pressure situations, homogeneous approaches must be used to simulate the behavior at higher temperatures and pressures. We observe larger deviation for CO_2+H_2O system compared to H_2S+H_2O system, this is most likely due to the fact that the number of experimental data is much larger and the PT range is also broader. We have also examined the restitution of two volumetric thermodynamic properties: the density and the viscosity. For these properties, phase-specific approaches are traditionally used; they allow properties to be restored with an uncertainty of around 10%.

Solubilities (equilibrium phase compositions) and densities are the two most important thermodynamic properties in the context of CCS (capture, transport and storage) and geothermal energy. Accurate predictions are needed for reservoir and surface conditions and can be calculated by an EoS. In other hand, accurate dew point predictions are also needed in transport of humid CO_2-rich mixtures, to avoid a sour water-rich liquid phase and subsequent corrosion of equipment. Accurate density and solubility predictions of the aqueous phase are important when CO_2 is pumped into aquifers for reinjection in the well ; furthermore, is also necessary to access the amount of impurities dissolved in brine in reservoir conditions to evaluate potential risk of dispersion.

On balance, the accuracy of thermodynamic models in reproducing and predicting equilibria and properties can be generally considered correct but can surely be further enhanced. To this end, new experimental data from laboratory or generated by molecular simulation will be necessary. In the foreseeable future, the comparison could be extended to other thermodynamic methods such as advanced EoS like CPA or SAFT family equation, more complex fluid containing other relevant impurities could be considered and other thermodynamic properties like calorific capacity, thermal conductivity, surface tension….

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