

The performance of state of the art industrial thermodynamic models for the correlation and prediction of acid gas solubility in water.

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Abstract

Currently available industrial thermodynamic models are quite effective at matching the data that was available at the time of their creation. Unfortunately the analysis techniques available at the time did not include a large liquid-liquid equilibrium dataset and as a result the thermodynamic models tend to be less reliable in the highly compressed and sub-cooled state. This work will compare the predictions of a widely used thermodynamic model to new water solubility in acid gases data obtained by Alberta Sulphur Research. The results will be discussed as will a path forward to most effectively make use of this new data to update thermodynamic models applied to fluid phase calculations.

Introduction

The proper design and safe operation of acid gas reinjection plants is based on the availability of reliable models for the calculation of phase equilibrium of fluids containing large amounts of water, carbon dioxide and hydrogen sulphide. The ability to calculate phase boundaries, especially dew temperatures and dew pressures is fundamental for the proper design of compression and cooling systems. These needs are well illustrated in the literature. For example Sitter and coworkers (2006) showed a detailed analysis of an acid gas reinjection process at the Wembley sour gas plant near Grande Prairie, Alberta where hydrogen sulphide and carbon dioxide are compressed and re-injected for permanent disposal. The fluids are composed of mostly sour gases, water and small amounts of hydrocarbons coming from an alkanolamine regeneration unit, with a hydrogen sulphide to carbon dioxide ratio varying from 40:60 to 85:15. The fluid must be compressed from near atmospheric conditions to pressures ranging from 10,000 to 20,000 kPag for disposal in the well.

Accurate dew point predictions are important to decide the amount of cooling that can be safely applied in the compressor inter-cooling stages, and these predictions must be combined with accurate predictions for enthalpies and entropies for proper modeling of compression equipment. Sitter et al. (2006) used the Advanced Peng-Robinson for Natural Gas model developed by Virtual Materials Group where the thermodynamic model was used in conjunction with the process simulator VMGSim and integrated with the Delta V control system thus providing an integrated tool for the operation and better understanding of the plant operation.

Thermodynamic Modeling

The basic problem related to water content modeling can be traced to two major problems. The accurate calculation of water fugacity and mixing rules flexible enough to model the non-idealities arising from the mixing of acid gases, water and natural gas. This is usually represented using the equality of fugacities, Equation 1.

$$f_i^v = f_i^l \quad 1$$

Equation 1 is the usual starting point for modeling and it simply states that at equilibrium the fugacity of a component is the same in the vapour and liquid phases. Our task is to find a reasonable model for the fugacity of the vapour and liquid phases that is able to capture the molecular interactions between different types of molecules. In the case of acid gases not only vapour-liquid equilibrium is important but also at high pressures and relatively low temperatures liquid-liquid behaviour is also observed.

Our preferred method for modeling this type of phenomena is to use an equation of state and modify its different parameters in order to ensure accurate representation of thermodynamic properties. Activity coefficient models could potentially be used, but they do not provide continuity across the critical point and therefore are not natural models for use in the simulation of gas processing plants. A reliable equation of state for modeling natural gas processes was proposed by Peng and Robinson (1976). This equation has been applied successfully to model many hydrocarbon based systems, and when properly parameterized it can also simply and reliably model polar systems. The basic equation of state is shown in Equation 2.

$$P = \frac{RT}{v-b} - \frac{a_c \alpha(T)}{v(v+b) + b(v-b)} \quad 2$$

The key feature of any well designed equation of state is its ability to accurately represent the vapour pressure of pure components (Satyro, 2009). This can be accomplished simply and reliably by treating the attractive term as an empirical function of temperature. This empirical dependency on temperature has well defined boundary condition at the critical point where it must equal one. At sub-critical temperatures Soave (1972) and Peng and Robinson (1976) found out that this empirical correction has a simple form and moreover it can be correlated with the acentric factor for simple substances, thus providing a simple and compact modeling platform as shown in Equation 3.

$$\sqrt{\alpha_i} = 1 + f_{w,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \quad 3$$

The parameter $f_{w,i}$ is expressed as a function of the acentric factor of component i and this generalization works remarkably well for non-polar and slightly polar compounds. It is also common practice to use Equation 3 beyond the critical temperature and into the superheated region although the empirical basis of the correlation is limited to the pure component vapour pressure line. There are many enhancements to the basic model proposed by Peng and Robinson in the open literature. The model as

originally published was very good but limited in scope due to the use of a universal function to calculate the behaviour of polar components and an intrinsic inaccuracy related to liquid densities computations inherent to any two parameter equation of state. The latter limitation can be easily and systematically removed by the use of volume translation (Peneloux and Rauzi, 1982) and will not be discussed further in this paper. The first limitation can be removed by accepting that Equation 3 is empirical and additional accuracy can be gained by treating it as a fitting factor designed to match vapour pressures as suggested by Equation 4:

$$\sqrt{\alpha_i(T)} = 1 + A_i(1 - \sqrt{T_{r,i}}) + B_i(1 - \sqrt{T_{r,i}})^2 + \dots \quad 4$$

The empirical constants A_i , B_i and so on are determined by reducing the error between the actual and calculated vapour pressures of a pure component using Equation 1. This can be done quite simply using non-iterative methods such as the one proposed by Soave (1986) and a simple linear regression procedure. Care must be exercised when extrapolating beyond the critical point into the pure component superheated region and the method proposed by Mathias (1982) works quite well. Many other alternative functions to 4 have been proposed in the literature (Sandler book) and will not be discussed here. The use of this simple procedure is illustrated in Figure 1, where we compare the vapour pressure of water from the APRNG model against the values from the steam Tables (Lemmon et al, 2007). The average error in water vapour pressure is 1.06% from 280 to 640 K.

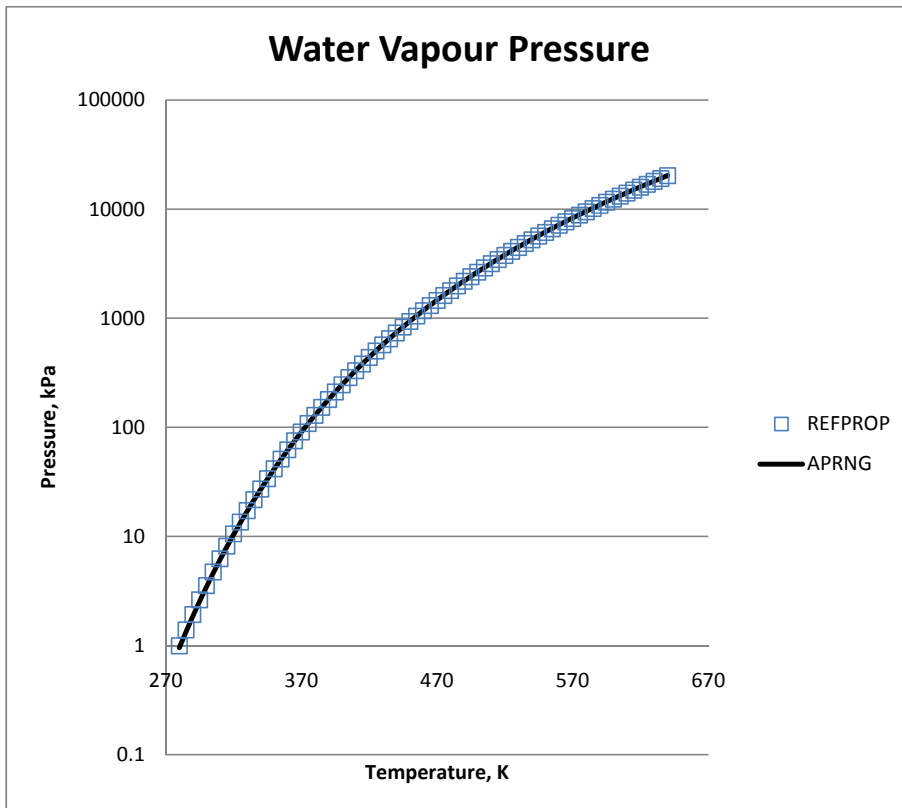


Figure 1 Water vapour pressure predicted using a cubic equation of state against values from the Steam Tables. The average error is 1.06%.

Using standard thermodynamic relationships and ideal gas heat capacity data derived physical properties can be quickly obtained for the calculation of enthalpies, entropies and heat capacities. The advantage of introducing empirical information into key model parameters is illustrated in Figure 2 (Satyro, 2009) where a significant increase in the quality of liquid heat capacity can be seen when Equation 3 is replaced by Equation 4.

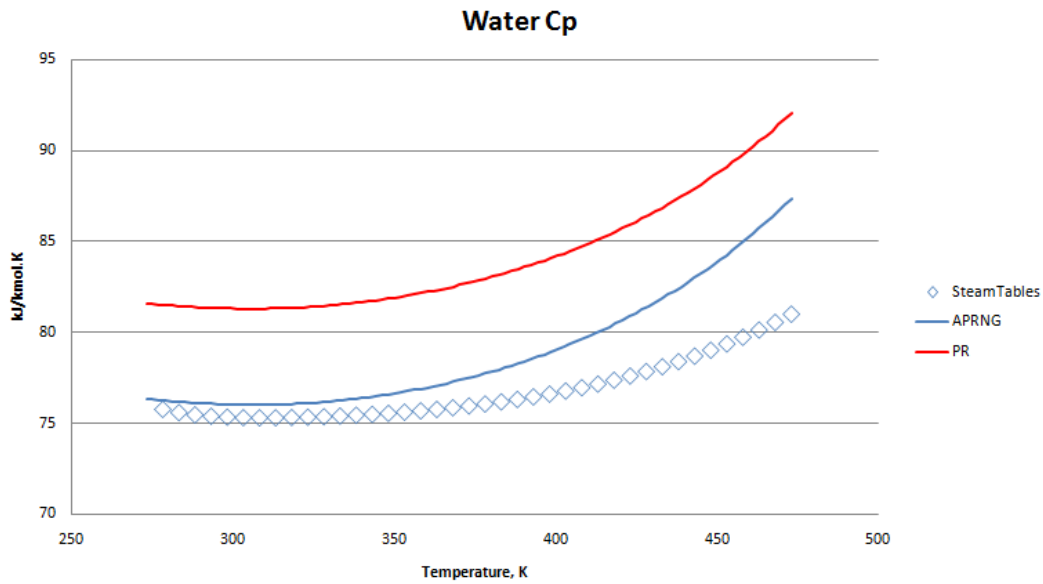


Figure 2 Liquid heat capacity of water calculated using original and modified versions of Peng-Robinson equation of state (Satyro, 2009)

The enthalpy and entropy calculations for carbon dioxide and hydrogen sulphide, shown in Figures 3 and 4 exemplify the model reliability for material, energy and entropy balances that are necessary to calculate compression horsepower requirements and cooling duties.

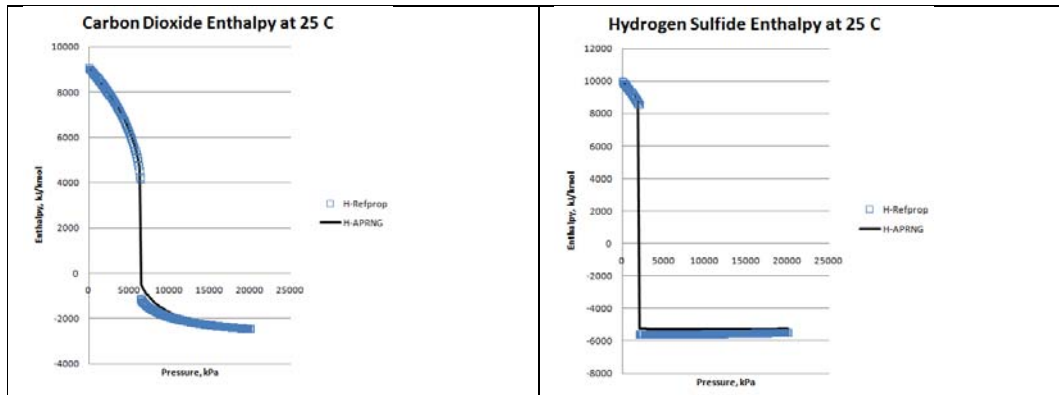


Figure 3. Enthalpy of Carbon Dioxide and Hydrogen Sulfide from atmospheric to 20,000 kPa from APRNG compared to values from REFPROP (Lemmon et al, 2007)

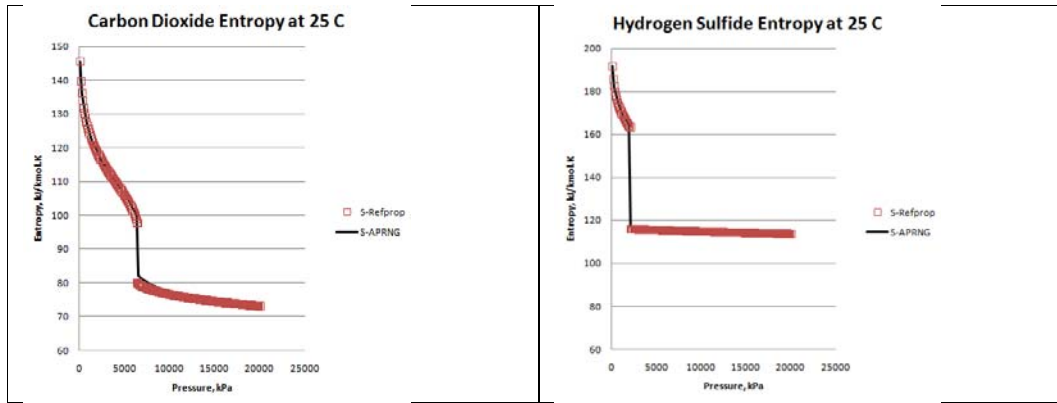


Figure 4. Entropy of Carbon Dioxide and Hydrogen Sulfide from atmospheric to 20,000 kPa from APRNG compared to values from REFPROP (Lemmon et al, 2007)

The remaining issue related to thermodynamic modeling is the definition of the mixing rules necessary for the calculation of the equation of state “a” and “b” terms. There are many mixing rules for equations of state in the literature. For modeling acid gas mixtures we found it valuable to keep the modeling very simple as originally suggested by Peng and Robinson (1980) where the interaction parameter for the “a” term is dependent on the nature of the phase. For non-aqueous phases the “a” term is calculated using the common formulation suggested in the literature (Soave, 1972, Peng and Robinson, 1976) slightly extended to use temperature dependency, Equations 5 and 6,

$$a = \sum \sum (1 - k_{ij}) \sqrt{a_i a_j} x_i x_j \quad 5$$

$$k_{ij} = k_{ij}^0 + \frac{k_{ij}^1}{T} + k_{ij}^2 \ln T \quad 6$$

The terms k_{ij}^0 , k_{ij}^1 and k_{ij}^2 are determined based on experimental vapour-liquid equilibrium data. Many times the parameters k_{ij}^1 and k_{ij}^2 can be assumed to be zero but not always, particularly when modeling wide boiling point mixtures.

This simple mixing rule is effective for hydrocarbon/hydrocarbon and acid gas/hydrocarbon mixtures as shown in Figure 5. This mixing rule is also useful for the calculation of water/hydrocarbon or hydrocarbon/water solubility, but not simultaneous water/hydrocarbon mutual solubility. It is common practice to model water solubilities in hydrocarbons and estimate the solubility of hydrocarbon in water. This is usually unreliable and a more complex mixing rule is required.

Peng and Robinson’s suggestion is to utilize two interaction parameters, one for the non-aqueous phase and another for the aqueous phase, which may be composition as well as temperature dependent, as shown in Equation 7.

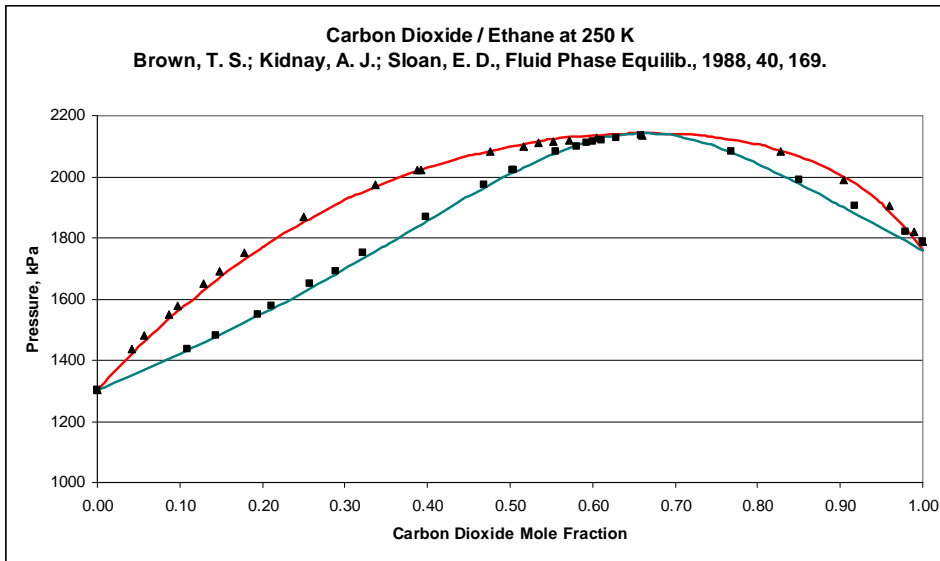


Figure 5. Carbon Dioxide and Ethane thermodynamic equilibrium calculated using APRNG at 250K

7

$$k_{ij} = k_{ij}(T, \vec{z})$$

The function suggested by Equation 7 is empirical in nature and can be tailored to represent not only hydrocarbon/water liquid-liquid equilibrium but also carbon dioxide and hydrogen sulphide liquid-liquid equilibrium with water, effect of brine in solution, etc. It is readily recognized that the formulation suggested by Equations 5, 6 and 7 is not entirely consistent from a thermodynamic point of view and other alternative formulations are available, for example by combining an activity coefficient with an equation of state (Huron and Vidal, 1979). Nevertheless, for natural gas processing modeling this formulation works remarkably well and provides a simple, flexible and reliable modeling platform.

The “b” term is modeled without the use of interaction parameters as shown in Equation 8.

$$b = \sum x_i b_i \tag{8}$$

Although temperature dependency on the “b” term can increase the accuracy of the equation of state (Trebble, 1986) its use is not recommended due to the possibility of unphysical property prediction at high pressures (Salim and Trebble, 1991; Satyro and Trebble, 1996).

The usefulness of this approach is shown in Figure 6 where the mutual solubility of carbon dioxide in water as a function of pressure is shown at 167 F.

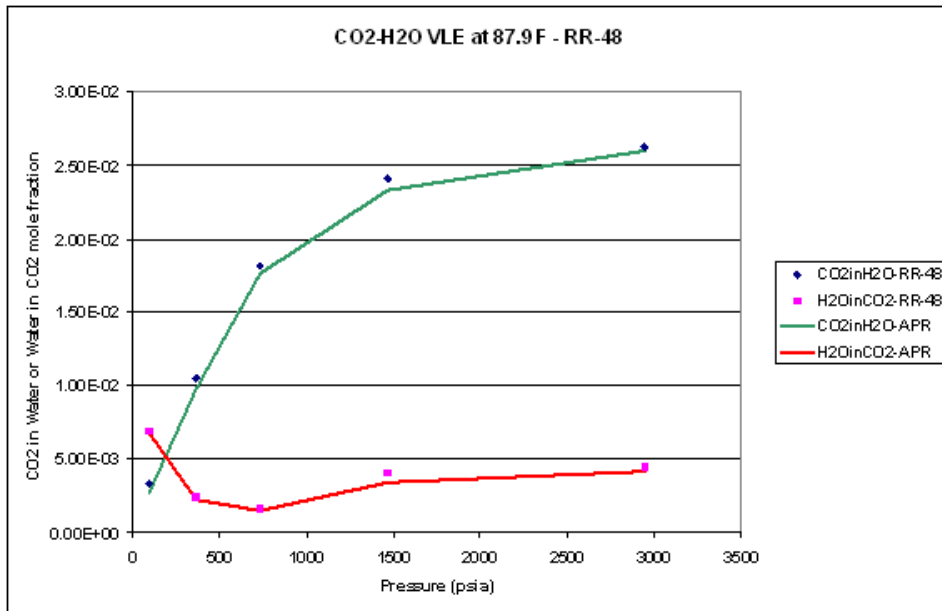


Figure 6 Mutual solubility of Carbon Dioxide and Water from 100 to 3000 psia at 87.9 F using the mixing rules suggested by Equations 5 to 8 combined with the modified Peng-Robinson equation of state.

Water Content

The thermodynamic model can now be tested against experimental water content data. In this case, 311 water content points were graciously provided by ASRL (Marriott, 2009). The data collection covers extensive pressure, temperature and composition ranges and permits an objective assessment of the quality of the thermodynamic model for acid gas processing purposes. The experimental matrix was taken from Marriott's work and is reproduced as Table 1. Using the experimental conditions provided by Marriott the thermodynamic model was then used to calculate the water content for each reported experimental data point. It is important to note that the results were obtained without any special fits, the interaction parameters between water and acid gases were determined based on vapour-liquid and liquid-liquid equilibrium data. The results are summarized in Figure 7.

COMPILED EXPERIMENTAL WATER CONTENT FOR ACID GAS MIXTURES

Data Source	<i>n</i>	<i>T</i> (min) °C	<i>T</i> (max) °C	<i>p</i> (min) MPa	<i>p</i> (max) MPa	<i>x</i> _{H2S} (min) mol%	<i>x</i> _{H2S} (max) mol%
MAC ⁴	91	-1.3	98.5	0.77	37.9	1.2	85.9
Huang <i>et al.</i> ⁵	16	37.8	176.7	4.82	18.2	9.4	81.0
This work SA	42	30.0	90.0	2.00	10.0	20.0	80.0
This work EQ	62	24.6	60.8	1.21	7.85	9.3	89.6
This work VDP	10	9.0	23.0	4.65	10.5	48.1	50.0
This work IFP/ μ S	91	39.9	60.1	2.03	19.95	7.3	89.5
Summary	312	-1.3	176.7	0.77	37.9	1.2	89.6

260 raw experimental data were tabulated for the June 2007 ASRL Chalk Talks and 30 additional data are reported here (January 2008, Chalk Talks).

ASRL Experimental Techniques include:

- (1) Stirred Autoclave (low pressure, VLE), SA
- (2) Equilibrium Cell (low pressure, VLE), EQ
- (3) Visual dew point (high pressure, hydrate region, SLE), VDP
- (4) Isolated Floating Piston with Micro Sampler (high pressure, LLE), IFP/ μ S

4. M. A. Clark (1999) *Experimentally obtained saturated water content, phase behavior and density of acid gas mixtures*, PhD. Thesis, University of Calgary.

5. S. S.-S. Huang, A.D. Leu, H.-J. Ng and D. B. Robinson (1985) *Fluid Phase Equilibria* **19**, 21-32.

Table 1 Experimental Pressure, Temperature and Composition Ranges and keys for thermodynamic equilibrium data.

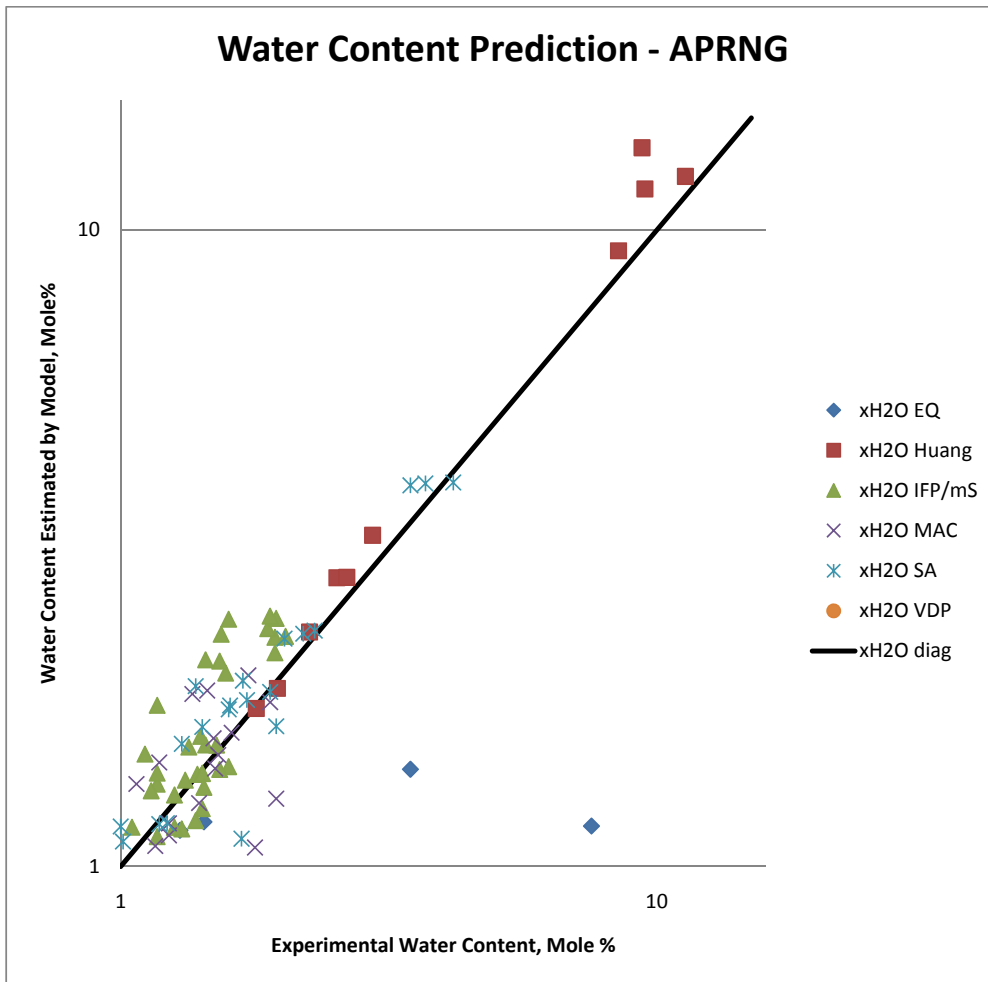


Figure 7. Water content dispersion plot using ASRL data and model shown in this paper.

It is interesting to observe that with the exception of two points measured using the equilibrium cell method (EQ) the dispersion is approximately random with an absolute average error of 26.1%, a bias of -4.01% and an absolute average deviation in water mole % in the non aqueous phase equal to 0.258%. A more useful way of looking at the results is to calculate the errors based on each of the individual datasets, as shown in Table 2.

Set	Average Absolute % Error	Average Deviation, mole %	Bias, %
MAC	22.4	0.147	-2.51
Huang	10.0	0.604	9.34
SA	23.4	0.204	13.3
EQ	41.2	0.405	-8.00
VDP	4.77	0.030	-4.37
IFP/ μ S	25.7	0.258	-13.0

Table 2. Errors and deviations in water content prediction for different datasets

An estimate of the error in the measurements will provide a measure of the actual quality of the thermodynamic model. The only dataset with readily accessible error estimates is that by Huang (Huang et al., 1985). Unfortunately the authors did not publish an error estimate but rather repeatability and the reported value is 0.2 mole% while the model average deviation in water concentration in mole% is 0.6%. According to the authors the water composition analysis was calibrated using carbon dioxide saturated with water. When we analyse this dataset more closely we note that the largest errors occur at higher temperatures, in the vicinity of 176.7 C. When we ignore the high temperature data points the average absolute error drops of 5.24% and the average deviation in water mole fraction is reduced to 0.11% placing the model roughly inside the repeatability range. Detailed results are shown in Table 3.

Taking into consideration all of the available data the average deviation in water mole % in the non-aqueous phase is equal to 0.26%, somewhat above the stated repeatability of Huang's data set. Unfortunately the estimated errors for the other datasets are not available, and repeatability should not be confused with the actual accuracy of the available data.

T/C	P/kPa	C1	CO2	H2S	Experiment	Model	% Bias	Absolute Deviation	Absolute % Error
37.8	4820	30.4	59.6	10	0.19	0.20	4.63	0.009	4.63
37.8	7600	30.4	59.8	9.8	0.17	0.17	-1.27	0.002	1.27
107.2	8360	29.7	60.4	9.9	2.25	2.34	3.80	0.086	3.80
107.2	7560	12.1	11.5	76.5	2.53	2.84	12.34	0.312	12.34
107.2	12270	10.9	11.8	77.3	2.64	2.85	7.81	0.206	7.81
37.8	12520	30.3	59.8	9.9	0.19	0.19	0.90	0.002	0.90
107.2	12930	29.9	60.3	9.8	1.96	1.90	-2.81	0.055	2.81
107.2	17170	29.9	60.2	9.9	1.79	1.77	-1.02	0.018	1.02
37.8	13000	9	10	81	0.93	1.01	8.56	0.080	8.56
37.8	16460	9	10.7	80.3	0.91	1.02	12.40	0.113	12.40
107.2	16920	12.5	12.2	75.4	2.95	3.31	12.34	0.364	12.34
							5.24	0.113	6.17

Table 3. Error summary for Huang et al data set (1985).

Given the limitations of how the estimated errors were reported, the best we can say is that the model estimates water contents within the experimental repeatability reported for this dataset.

Conclusions and Recommendations

A model for the calculation of water content of sour natural gases using a simple equation of state was presented. The model provides a reliable platform for modeling the thermodynamic equilibrium of

aqueous systems of interest for the natural gas industry while providing accurate physical properties important for the design of equipment. Taking into account all available data the absolute average error in the prediction of water content of sour gases is 26.1% with a error bias of 4.01% and an absolute average deviation in the water mole % in the non-aqueous phase equal to 0.26%.

Given the available error repeatability of Huang's data set for temperatures between 37.8 C and 107.2 C, pressures between 4820 kPa and 17170 kPa, Carbon Dioxide concentrations between 10 and 60.4 mole % and Hydrogen Sulfide concentrations between 10 and 80.3 mole percent we can say that the model provides results within the stated repeatability of water content although an actual error estimate for the the water content is not available.

The use of carbon dioxide and water and hydrogen sulphide and water data was sufficient for determining of the necessary interaction parameters and the available water content data was not used in the definition of the model parameters. If reliable error estimates for the available data can be obtained for appropriate statistical weighting of individual points the model parameters can be re-evaluated using the available data and a better error analysis can be provided.

Acknowledgements

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Nomenclature

- a Peng-Robinson attractive term
- b Peng-Robinson co-volume
- f Fugacity
- k Interaction parameter
- P Pressure
- R Gas constant
- T Absolute temperature
- v Molar volume
- z Mole fraction vector

Subscripts

- c At the critical point
- i Component index
- j Component index

r Reduced property

Superscripts

l Liquid

v Vapour

Greek Letters

α Peng-Robinson attractive term multiplier based on vapour pressure data

Bibliography

Huang, S.S-S.; Leu, A.-D.; Ng, H.-J. and Robinson, D.B.; "THE PHASE BEHAVIOR OF TWO MIXTURES OF METHANE, CARBON DIOXIDE, HYDROGEN SULFIDE, AND WATER"; Fluid Phase Equilibria, 19 (1985) 21-32

Lemmon, E.; Huber, M.L. and McLinden, M.O.; REFPROP Reference Fluid Thermodynamic and Transport Properties, NIST Standard Reference Database 23, Version 8.0 (2007)

Marriott, R.; Personal Communication, 2009

Mathias, P.M.; "Versatile Phase Equilibrium Equation of State", Ind. Eng. Chem. Process. Des. Dev., Vol. 22, No. 2, 385-391

Peneloux, A.; Rauzy, E. and Freze, R.; "A CONSISTENT CORRECTION FOR REDLICH-KWONG-SOAVE VOLUMES"; Fluid Phase Equilibria, 8, (1982), 7-23

Peng, D.-Y. and Robinson, D.B.; "A New Two-Constant Equation of State"; Ind. Eng. Chem., Fundam., Vol. 15, No. 1, 1976

Peng, D.-Y. and Robinson, D.B.; "Two and Three Phase Equilibrium Calculations for Coal Gasification and Related Processes"; *Thermodynamics of Aqueous Systems with Industrial Applications*, ACS Symposium Series 133 (1980)

Salim, P.H and Trebble, M.A.; "A modified Trebble-Bishnoi equation of state: thermodynamic consistency revisited"; Fluid Phase Equilibria, 65 (1991) 59-71

Sandler, S.I.; "Models for Thermodynamic and Phase Equilibria Calculations"; Marcel Dekker, Inc., 1993

Satyro, M.A.; "The Role of Thermodynamic Modeling Consistency in Process Simulation"; Keynote Lecture, 8th World Congress of Chemical Engineering, Palais des Congres, Montreal, August 23-27 2009

Satyro, M.A. and Trebble, M.A.; On the applicability of the Sandler-Wong mixing rules for the calculation of thermodynamic excess properties: V^E , H^E , S^E , C_p^E ; Fluid Phase Equilibria 115 (1996) 135-164

Sitter, J.R.; Hay, G. and Neumeister, L.; "Enhancing Operations"; Hydrocarbon Engineering, February 2006

Soave, G.; "Equilibrium constants from a modified Redkh-Kwong equation of state"; Chemical Engineering Science, 1972, Vol. 27, pp. 1197-1203.

Soave, G.; "DIRECT CALCULATION OF PURE-COMPOUND VAPOUR PRESSURES THROUGH CUBIC EQUATIONS OF STATE"; Fluid Phase Equilibria, 31 (1986) 203-207

Trebble, M.A.; "DEVELOPMENT OF A NEW FOUR-PARAMETER CUBIC EQUATION OF STATE"; Fluid Phase Equilibria, 35 (1987) 1-18