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Application of thermodynamic models for high pressure processes

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ABSTRACT

Hydrogen has proven to be a non polluting energy vector. However great mass production and storage facilities at high pressure are required where one of the most promising ways is metal hydrides, particularly when their surface is modified by different methods using supercritical fluids. Therefore it is important to have thermodynamics models capable to determine these conditions and particularly at phase equilibrium.

The present work aims to examine and test different thermodynamic models for certain high pressure processes. This study is also an opportunity to show the importance of the choice of the most appropriate equation of state equation in association with the most suitable mixing rule, for the given operating conditions.

Finally this work can be seen as a basis for considering more deeply processes which use supercritical fluids, particularly supercritical extraction and hydrogen production in supercritical water-cooled nuclear reactor.

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Introduction

A great number of industrial processes particularly those involving separation techniques or those concerned with hydrogen production and its storage do operate at high pressure using even supercritical fluid (SCF) [1]. This technology makes use of the fact that if compressed up to their critical conditions, supercritical fluids behave as solvents with powerful properties such as interesting combinations of liquid like density and solvency, and gas like viscosity, diffusivity, compressibility.

For instance hydrogen which has proven to be a non polluting energy vector requires great mass production and storage facilities. In fact ways of hydrogen storage for subsequent use may involve different approaches, like high and low

pressures, chemical compounds that reversibly release H₂ upon heating, etc. However one of the most promising ways is metal hydrides, compared to pressure or liquefaction based alternatives [2]. Magnesium a low cost and abundant metal has shown a great capacity, particularly when its surface is modified by different methods using supercritical fluids. Also liquid organic hydrogen carriers such as the unsaturated heterocyclic aromatic compounds N-ethylcarbazole and dibenzyltoluene can store huge amounts of Hydrogen. They are hydrogenated or dehydrogenated again for storage or need of energy/hydrogen, respectively. Surely these operations do involve phase equilibria at high pressure.

The present work is mainly devoted to the modelling of the behaviour of chosen systems at high pressure particularly for the determination of the phase equilibria which is not always easy to measure experimentally.

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Table 1 – Cubic Equations of state.

Equation of state	u	w	b	A
RK	1	0	$\frac{0.08644RT_c}{P_c}$	$\frac{0.42748R^2T_c^{2.5}}{P_c T_c^{0.5}}$
RKS	1	0	$\frac{0.08644RT_c}{P_c}$	$\frac{0.42748R^2T_c^2}{P_c}(1+f_\omega(1-T_r^{0.5}))^2$ $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$
PR	2	-1	$\frac{0.0788RT_c}{P_c}$	$\frac{0.42748R^2T_c^2}{P_c}(1+f_\omega(1-T_r^{0.5}))^2$ $f_\omega = 0.37464 + 1.542274\omega - 0.2699\omega^2$

Thermodynamic models at high pressure

Vapour–liquid phase equilibrium at high pressure

The usual and convenient approach used for the modelling of vapour–liquid phase equilibria at high pressure is to express isofugacity the condition by means of a properly chosen equation of state [3]. Hence one can write:

$$f_i^L = f_i^V \quad (1)$$

where f_i^L and f_i^V are the fugacities of component i in the liquid and vapour phases, respectively.

For each phase, the fugacity coefficient ϕ_i is defined as:

$$\phi_i^L x_i = \phi_i^V y_i \quad (2)$$

ϕ_i^L and ϕ_i^V can be calculated, respectively, from the following expressions:

$$\ln \phi_i^V = \frac{1}{RT} \int_{V^V}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln \frac{PV^V}{n_T RT} \quad (3a)$$

$$\ln \phi_i^L = \frac{1}{RT} \int_{V^L}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln \frac{PV^L}{n_T RT} \quad (3b)$$

Where P , T and V are the pressure, temperature and volume, respectively, R is the universal gas constant, n_i and n_T are the number of moles of component i and the total number of moles, respectively.

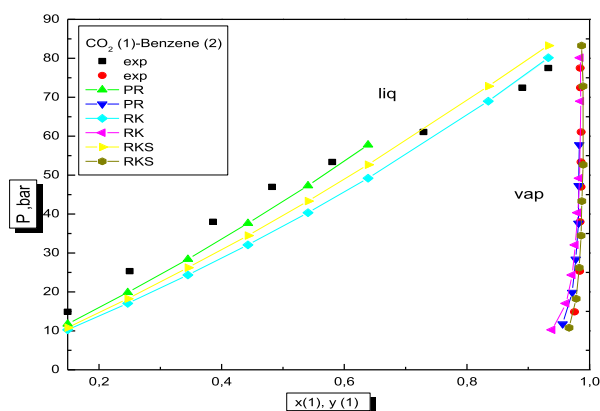


Fig. 1 – Vapour–liquid equilibria of CO₂ (1)–Benzene (2) – at 313.15 K.

Solid–liquid phase equilibrium at high pressure

For the case of the solubility of an organic solute in a supercritical fluid, the phase equilibrium condition is obtained from the fugacities equations concerning the stationary (solute) and mobile (supercritical) phases as follows:

$$P_i^s \exp \left(\int_{P_i^s}^P \frac{V_i^s}{RT} dP \right) = y_i^{sf} \phi_i^{sf} P \quad (4)$$

with P_i^s the pressure at saturation of solid at a given temperature, ϕ_i^{sf} the fugacity coefficient of supercritical fluid, V_i^s the molar volume of the solid at saturation, y_i^{sf} the solubility of solute in supercritical fluid, P , T and R as defined previously.

Cubic equations of state (EOS)

Equations of state (EOS)

The common two parameter cubic equations can be expressed in a general manner as follows:

$$P = \frac{RT}{V-b} + \frac{a}{u^2 + ubV + wb^2} \quad (5)$$

The three well known cubic equations of state are those due to Peng–Robinson (PR), Redlich–Kwong (RK) and Soave (RKS).

For these equations u and w are integer taking values as shown in Table 1 and the parameters a and b are the attractive

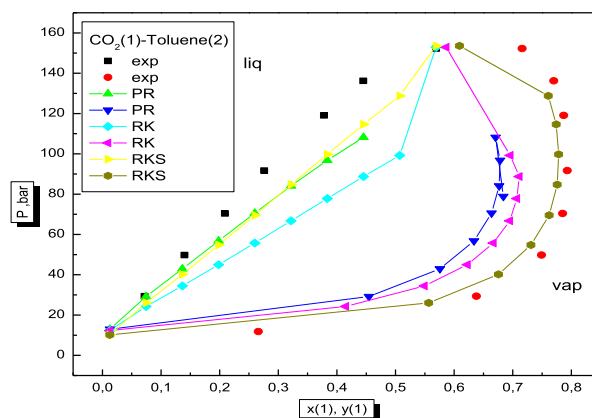


Fig. 2 – Vapour–liquid equilibria of CO₂ (1)–Toluene (2) at 477.15 K.

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