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# **A new model to predict thermodynamic properties of molecules and free-radicals; new horizons for the modelling of liquid oxidation and supercritical combustion**

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## **Abstract**

Automatic kinetic mechanism generators used in detailed kinetic modeling of combustion processes can provide data for ideal gas phase only. To adapt this data to supercritical phases, diffusion and solvation corrections similar to those required for the liquid phase must be applied. In this study, a flexible framework for the calculation of the solvation correction is proposed, based on a cubic equation of state (tc-PR) combined with a quantum-based continuum solvation model (COSMO-RS) through an advanced mixing rule. The proposed model allows high throughput and accurate computations of solvation quantities of molecules in liquid and supercritical environments, and can be applied on free radicals, for the first time in the literature.

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## Introduction

Kinetic generators like EXGAS, RMG, MAMOX, NetGen, REACTION, and GENESYS provide a detailed and reliable representation of the complex free radical chain oxidation mechanism associated to combustion taking place in ideal gas phase [1–3]. However, in many applications of interest, the oxidation reactions occur in phases other than gas. For instance, one can mention the liquid phase oxidation that causes fuel aging [4,5]. This is a relevant subject for the energetic transition since aging is a major drawback for the usage of biofuels in aircraft [4–6]. There is also a growing interest of using supercritical fluids (SCF) as reaction medium for intensified combustion/oxidation systems. This new technology holds attractive potential in several applications, such as supercritical power-cycle systems, treatment of wastewater and sludge, hydrothermal spallation drilling, thermal recovery of heavy oil, etc [7–10].

Detailed kinetic models are essential tools for a better understanding of the aforementioned applications. For such cases, it is reasonable to assume that the elementary reactions of the mechanism are essentially the same as in gas-phase combustion, but with different reaction rates due to diffusion and solvation effects [11,12]. In this sense, the challenge is to find the best way to best introduce such physical phenomena into an existing gas-phase kinetic model. To that end, Jalan et al. [13] proposed an approach that relies on corrections applied to the gas-phase kinetic data, as shown in equation (1).

$$\frac{1}{k_{eff}} = \frac{1}{k_{diff}} + \frac{1}{k_{int}} \quad (1)$$

Where,  $k_{eff}$  is the effective reaction rate in liquid or supercritical phase,  $k_{diff}$  accounts for the diffusional rate based on the prediction of reactants diffusivity in the solvating phase, which can be obtained through correlations [14]. Finally,  $k_{int}$  is the intrinsic reaction rate that is obtained by incorporating solvent-solute interactions into the gas-phase kinetic constants ( $k_{gas}$ ), as follows:

$$k_{int} = k_{gas} \times \exp\left(-\frac{\Delta\Delta_{solv}G^\ddagger}{RT}\right)$$

This correction is based on the prediction of the solvation Gibbs energy of activation ( $\Delta\Delta_{solv}G^\ddagger$ ), i.e., the difference in the solvation Gibbs energy ( $\Delta_{solv}\bar{g}_i$ ) between the transition-state structure (TS) and the reactants (molecular species and free radicals) [13], as shown in equation (3).

$$\Delta\Delta_{solv}G^\ddagger = \Delta_{solv}\bar{g}_{liq}^{TS} - \sum_i \Delta_{solv}\bar{g}_{liq}^{reactant\ i}$$

The solvation Gibbs energy of a given specie "i" ( $\Delta_{solv}\bar{g}_i$ ) is defined as the change in the chemical potential when the molecule, devoid of kinetic energy, is transferred from a perfect gas phase into a solvent [15]. Different models can be used for the computation of such a solvation quantity [16], like

Abraham model [17], Transfer Learning [18], and continuum solvation models [19], but they are usually limited to pure liquid solvents only. To the best of our knowledge, only the use of an equation of state (EoS) can provide solvation Gibbs energy predictions in the supercritical region with the level of accuracy and computational cost required in detailed kinetic modeling.

The EoS approach has already been benchmarked in our group for solvation of neutral solutes infinitely diluted in liquid solvents [20,21]. It was found that predictive versions of cubic EoS, such as UMR-PRU and PSRK, provide predictions with an average deviation of around 0.3-0.4 kcal/mol. However, these EoS relies on group contribution methods (GC), usually the Universal Functional Activity Coefficient model (UNIFAC), that do not comprise free radical groups. The lack of radical groups turns out to be a limiting factor for their application in the development of kinetic models. In order to circumvent this problem, one could think about adding radical groups in UNIFAC, but it would such a laborious (or even unfeasible) task, since the fitting procedure of UNIFAC binary interaction parameters between groups requires a large experimental database, which is not available for free radicals.

In this context, the present work proposes a more flexible framework for calculating solvation Gibbs energies with a cubic EoS, by combining the *translated-consistent* Peng-Robinson EoS (tc-PR) with a quantum-based continuum solvation model instead of UNIFAC: The *Conductor-like Screening Model for Real Solvents* (COSMO-RS). The use of COSMO-RS within the cubic EoS enables the treatment of a greater diversity of molecules (including free radicals), since only pure compound quantum-data is required. This data can be obtained either via *ab initio* calculations (which demands higher computational cost) or group contributions (which is a much faster but less accurate). In this work, the predictive power of the proposed EoS is tested for the calculation of solvation quantities in liquid fuels and supercritical solvents.

## Calculation of solvation quantities with a cubic equation of state (tc-PR/COSMO-RS)

For a given temperature ( $T$ ), pressure ( $P$ ) and composition ( $\mathbf{z}$ ), the solvation Gibbs energy ( $\Delta_{solv}\bar{g}_i$ ) can be calculated as follows:

$$\Delta_{solv}\bar{g}_i(T, P, \mathbf{z}) = RT \ln \left[ \frac{P \cdot V(T, P, \mathbf{z}) \cdot \varphi_i(T, P, \mathbf{z})}{RT} \right] \quad (4)$$

(3) This approach relies on the calculation of the fugacity coefficient of solute molecules ( $\varphi_i$ ), along with the estimation of the molar volume of the bulk phase ( $V$ ). Both of them can be straightforwardly estimated by a cubic EoS. By definition, other solvation quantities can be derived from  $\Delta_{solv}\bar{g}_i$ , such as the solvation entropy ( $\Delta_{solv}\bar{s}_i$ ), the solvation

enthalpy ( $\Delta_{solv}\bar{h}_i$ ), and the solvation heat capacity ( $\Delta_{solv}\bar{c}_{p,i}$ ).

In this study, a cubic EoS previously developed in our group was used: the tc-PR EoS (*translated-consistent* Peng-Robinson) [22]. The tc-PR is defined as follows:

$$P = \frac{RT}{(V + c_i - b_i)} - \frac{a_i(T)}{(V + c_i)(V + c_i + b_i) + b(V + c_i - b_i)} \quad (5)$$

For molecules whose critical temperature ( $T_{c,i}$ ), critical pressure ( $P_{c,i}$ ) and acentric factor ( $\omega_i$ ) are known, the attractive parameter ( $a_i$ ) and co-volume ( $b_i$ ) are calculated by the following equations:

$$a_i(T) = 0.45724 \frac{(RT_{c,i})^2}{P_{c,i}} \alpha(T_R)$$

$$b_i = 0.0778 \frac{RT_{c,i}}{P_{c,i}}$$

In this EoS, the consistent Twu91  $\alpha$ -function is considered [23]. tc-PR also has a volume translation parameter ( $c_i$ ) to improve the accuracy of the molar volume representation in liquid phase [24].

Given that the critical properties and acentric factors of free radicals are unknown, the parameters of the cubic EoS cannot be estimated by the equations above. Because of this, a first-order group contribution method (GCM) was developed in this work to enable the estimation of  $a_i$  and  $b_i$  parameters, without  $T_{c,i}$ ,  $P_{c,i}$  and  $\omega_i$ . The aim is to estimate them based on the values of  $a_i$  and  $b_i$  obtained for their parent molecule (H-atom added to the radical site), whose  $T_{c,i}$ ,  $P_{c,i}$  and  $\omega_i$  are known. The estimation of  $b_i$  and  $a_i$  of the free radical is done by equations (8) and (9), respectively.

$$\frac{\left(\frac{b_i}{X}\right)_{\text{predicted}}^{\text{to be}}}{\left(\frac{b_i}{X_H}\right)_{\text{known}}} = \frac{V_{X\cdot}^{\text{cavity}}}{V_{X_H}^{\text{cavity}}}$$

$$\frac{\left(\frac{a_i(T)}{b_i RT}\right)_{\text{predicted}}^{\text{to be}}}{\left(\frac{a_i(T)}{b_i RT}\right)_{\text{known}}} = \frac{E_{X\cdot}^{\text{dispersion}}}{E_{X_H}^{\text{dispersion}}}$$

Where,  $V_{X\cdot}^{\text{cavity}}$  and  $V_{X_H}^{\text{cavity}}$  are the molecular volumes of the free radical ( $X\cdot$ ) and its parent molecule (XH), respectively. Further,  $E_{X\cdot}^{\text{dispersion}}$  and  $E_{X_H}^{\text{dispersion}}$  are estimations of the dispersion energy of the molecules at the COSMO-RS reference state, in which the molecules are embedded by a perfect conductor. Both cavity volume and dispersion energies are estimated by the group contribution approaches developed in this study, which was fitted from quantum calculation results.

Finally, the extension of tc-PR EoS to mixtures was done using an advanced mixing rule, which

ouples the EoS with an activity coefficient model [25]. As a result, it is possible to estimate the cubic EoS parameters,  $a(z)$  and  $b(z)$ , of a mixture with a given molar composition  $z$ , as denoted by equations (10) and (11).

$$b(z) = \sum_{i=1}^{NC} \sum_{j=1}^{NC} z_i z_j b_{ij} \quad (10)$$

$$\text{with } b_{ij} = \left( \frac{b_i^s + b_j^s}{2} \right)^{1/s}$$

$$\frac{a(T, z)}{b(z)RT} = \sum_{i=1}^{NC} z_i \left[ \frac{a_i(T)}{b_i RT} + \frac{\ln \gamma_i^{res}(T, z)}{\Lambda_{EoS}} \right] \quad (11)$$

As mentioned before, a quantum-based activity coefficient model, called COSMO-RS [26], was chosen to calculate the activity coefficients ( $\ln \gamma_{i,S}^{res}$ ).

- (6) This model allows the calculation of thermodynamic properties without the need for binary interaction parameters regressed from experimental data. This is a powerful feature since it enables the treatment of unconventional mixture, such as those involving free radicals. The pure compound data required corresponds to the probability distribution of the polarization charge density ( $\sigma$ ) over the surface of molecular cavities, which is obtained either by DFT (Density Functional Theory) calculations or estimated from group contribution (GC).

In the COSMO-RS framework, the calculations of activity coefficients are done by equation (12).

$$p_s(\sigma) = \sum_i z_i p_i(\sigma)$$

$$\ln(\Gamma_s(\sigma)) = - \ln \left\{ \int p_s(\sigma') \Gamma_s(\sigma') \exp \left[ - \frac{e(\sigma, \sigma')}{RT} \right] d\sigma' \right\} \quad (12)$$

$$\ln(\Gamma_i(\sigma)) = - \ln \left\{ \int p_i(\sigma') \Gamma_i(\sigma') \exp \left[ - \frac{e(\sigma, \sigma')}{RT} \right] d\sigma' \right\}$$

$$\ln \gamma_{i,S}^{res} = \int p_i(\sigma) [\Gamma_s(\sigma) - \Gamma_i(\sigma)] d\sigma$$

- (8) Where,  $p_s(\sigma)$  is the  $\sigma$ -profile of the mixture,  $\Gamma_s(\sigma)$  is the activity coefficient of a segment with density charge equals to  $\sigma$  in the mixture and,  $\Gamma_i(\sigma)$  is the activity coefficient of the same segment in pure "i". Moreover,  $e(\sigma, \sigma')$  stands for the contact energy (9) between two segments with charge density equals to  $\sigma$  and  $\sigma'$ . The interaction energy takes into account electrostatic effects, as well as hydrogen bonding [26].

## Reference datasets

In order to benchmark the tc-PR/COSMO-RS EoS, two databases have been developed, one for liquid solvents and one for supercritical solvents.

For the liquid phase database, fuel and biofuel molecules such as hydrocarbons, alcohols and esters were chosen as solvents. Regarding non-radical molecules, the reference data for solvation energies were extracted from the *CompSol* database [27], comprising a large variety of temperature conditions (90-650 K). For free-radicals, since real experimental data are not available, a pseudo-experimental database

was created using the commercial software *COSMOTerm*. Different types of free radicals were considered, such as primary, secondary, tertiary, benzyl, phenyl, vinyl, acetylenic, alkoxy, peroxy, and carbonyl. In this case, the temperature range considered was between 298 and 398 K.

Experimental data for the solvation of solutes in supercritical solvents is very scarce in the literature. Because of this, we decided to generate pseudo-experimental data from a very accurate model: the GERG-08 EoS [28]. This EoS was specifically developed to predict thermodynamic quantities of one- or multi-component systems containing molecular compounds present in natural gas. Due to its robust theoretical formulation and flexibility resulting from the presence of numerous adjustable parameters, the GERG-08 EoS can estimate thermodynamic properties with an experimental precision within its range of application in terms of pressure (<350 bar) and temperature (60 to 700 K). In this work, the pseudo-experimental database built with GERG-08 EoS contains solvation data for the first 10 linear alkanes infinitely diluted in supercritical carbon dioxide, for pressures between 80 and 160 bar, and temperatures between 313 and 613 K.

### Computational details

The proposed EoS (tc-PR/COSMO-RS) uses, only pure compound data as input: critical temperature ( $T_{c,i}$ ), critical pressure ( $P_{c,i}$ ), acentric factor ( $\omega_i$ ) and charge density distribution ( $\sigma$ -profile). Experimental values of  $T_{c,i}$ ,  $P_{c,i}$ , and  $\omega_i$  were extracted from the DIPPR database, whereas  $\sigma$ -profiles were obtained from DFT calculations performed in TURBOMOLE v.14 for the BP-TZVPD-FINE level of theory. The solvation Gibbs energy calculations with tc-PR/COSMO-RS were carried out with an in-house MATLAB routine.

### Results and discussion

#### Prediction of solvation energies in liquid fuels

Starting with the results in liquid phase, Figure 1 presents a parity plot between the reference data and the predictions by the proposed equation of state, involving molecules (Figure 1.a) and free radicals (Figure 1.b) as solutes.

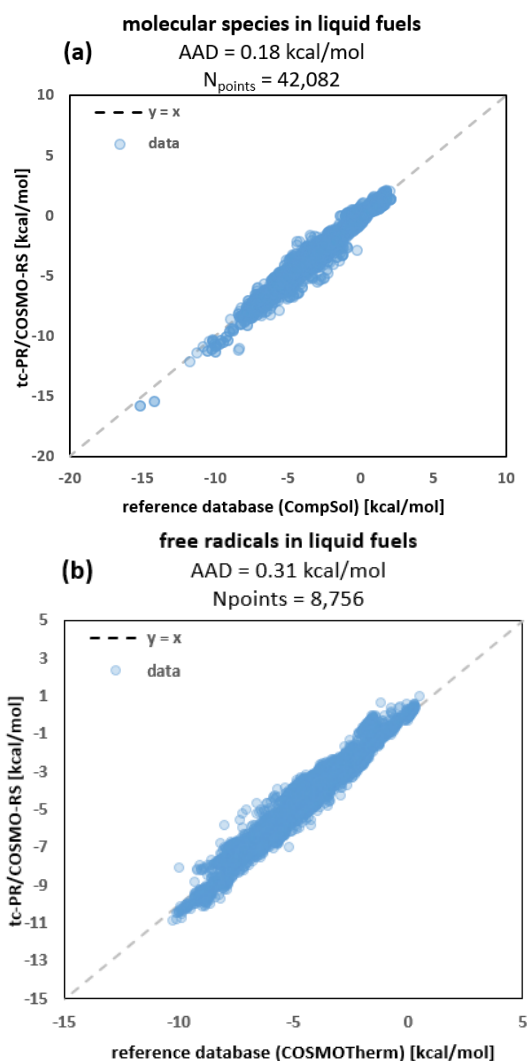


Figure 1 – Parity plot between the reference data and tc-PR/COSMO-RS predictions for the solvation Gibbs energy ( $\Delta_{solv}\bar{g}_i$ ) of solutes in a set of liquid fuels (hydrocarbons, alcohols, esters, etc...).

Figure 1.a shows that a good agreement between experimental and calculated data was obtained for the solvation of non-radical molecules, since the average deviation (AAD) was around 0.2 kcal/mol. The same was observed for the solvation of free radical species, which had an average absolute deviation close to 0.3 kcal/mol.

It was found that alkyl radicals (primary, secondary, tertiary, vinylic, acetylenic, benzyl, and phenyl) have a solvation energy very close to that obtained for their parent molecules. However, the same is not observed for carbonyl, alkoxy and peroxy radicals, especially in polar and associating solvents. To illustrate this, let us evaluate the solvation of 1-propanol and its primary alkyl radical as well as its alkoxy radical in ethanol, which corresponds to a polar and associating solvent. Figure 2 shows the solvation results for those three solutes.

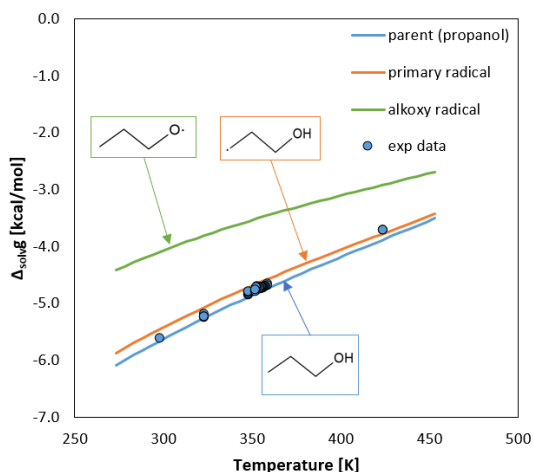


Figure 2 – Solvation Gibbs energy of *n*-propanol (blue line) and its primary (orange line) and alkoxy (green line) radicals in ethanol calculated with *tc*-PR/COSMO-RS.

As it can be seen, no major changes were observed for the primary radical. Nonetheless, the removal of a H-atom from the hydroxyl group considerably changes the solvation behavior of the radical compared to the parent molecule, because its hydrogen donor site is lost. Given that hydrogen bonds tend to stabilize the liquid phase, the value of the solvation Gibbs energy of the alkoxy radical is higher than its parent molecule because of the reduced hydrogen bonding network. Same conclusions can be drawn for peroxy and carbonyl radicals.

#### Prediction of solvation energies in supercritical $\text{CO}_2$

Regarding the application of the *tc*-PR/COSMO-RS EoS in the supercritical domain, very reliable results were obtained for mixtures in which supercritical carbon dioxide is the solvent. The average absolute deviation obtained in such a case was only 0.11 kcal/mol (see **Erreur ! Source du renvoi introuvable.**).

It was found that, for supercritical solvents,  $\Delta_{\text{solvg}}$  becomes pressure dependent. To illustrate such a dependence, Figure 4 shows the results obtained for the solvation of some *n*-alkanes in supercritical  $\text{CO}_2$ . It can be observed that there is a significant pressure dependence for  $\Delta_{\text{solvg}}$ , especially for pressure conditions close to the critical point of  $\text{CO}_2$  (around 74 bar). This is an interesting feature for this type of fluid, because reaction rates and selectivities can be controlled by the pressure, in addition to the temperature.

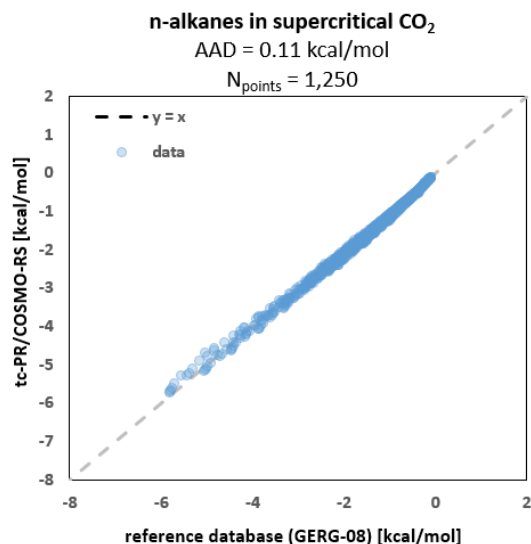


Figure 3 – Parity plot between reference data and *tc*-PR/COSMO-RS predictions for the solvation Gibbs energy ( $\Delta_{\text{solvg}}$ ) of *n*-alkanes in supercritical carbon dioxide. Range of pressure: 80 to 160 bar. Range of temperature: 313 to 613 K.

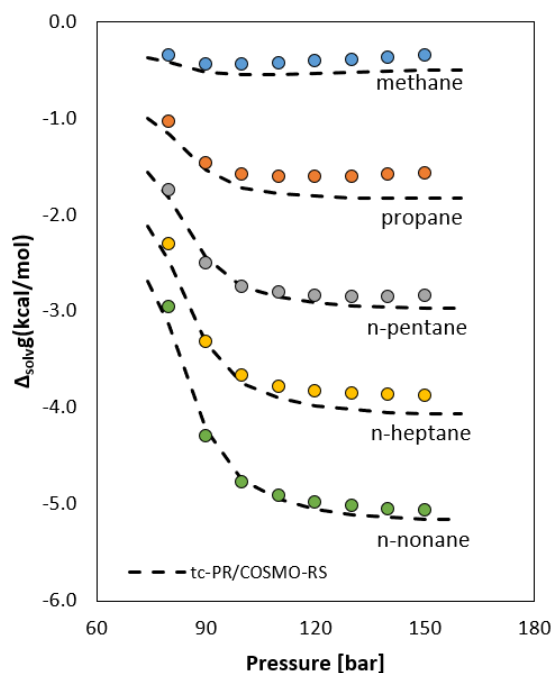


Figure 4 – Solvation Gibbs energy of *n*-alkanes in supercritical  $\text{CO}_2$  at 313.15 K. The dots are the reference data generated with the GERG-08 EoS.

Figure 4 also shows that, unlike most of the available methods, with an equation of state it is possible to capture the effect of pressure on  $\Delta_{\text{solvg}}$ . In fact, other approaches usually assume incompressible condensed phase and, hence, neglect the pressure dependence, which is not the case with an EoS. Models based on such an assumption are limited to be applied in liquid phase calculations only, far from the critical region.

Note that following the proverb “he who can do more can do less”, EoS properties tend to ideal-gas

properties in conditions where the ideal-gas law applies, i.e., at low pressure and / or at very high temperature. This is illustrated in Figure 5 that plots the molar enthalpy and heat capacity of n-alkanes infinitely diluted in CO<sub>2</sub> at 100 bar against temperature. As expected, it can be observed that these properties tend asymptotically to ideal-gas properties at high temperatures.

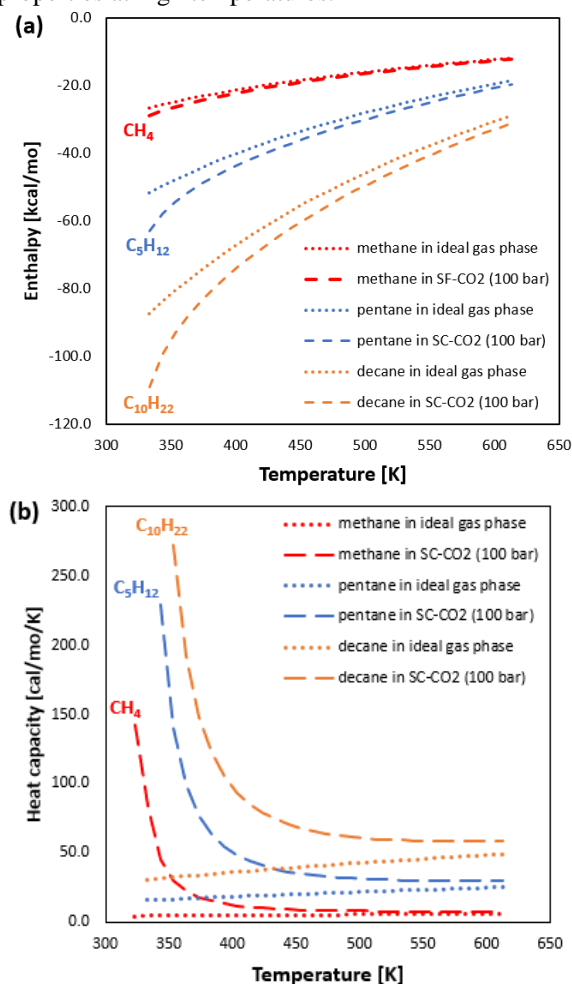


Figure 5 – Enthalpies and heat capacities as a function of temperature for 3 alkanes in ideal gas phase (dotted lines) and in supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) at 100 bar (dashed lines). Ideal gas enthalpies and heat capacities were calculated with NASA polynomials, whereas the enthalpies and heat capacities in supercritical CO<sub>2</sub> were calculated with tc-PR/COSMO-RS.

However, these results revealed important deviations from the ideal gas law at low and moderate temperatures. In particular, when approaching the critical temperature of CO<sub>2</sub>, at 303 K, these deviations increase very fast (it is recalled that the heat capacity of any compound at its critical point is infinite, thus explaining the divergence trend of the mixture heat capacity when approaching 303 K). This means that the solvation correction to the ideal gas-phase data should be applied to combustion and oxidation processes at low temperatures (< 600-700 K for the alkanes tested in this study, with chains containing a maximum of 10 carbons). For higher temperatures,

this correction would thus have a milder impact, since the enthalpies and heat capacities in supercritical CO<sub>2</sub> tend to their ideal gas limit.

There is also a significant correlation between the size of the solute and the temperature at which the thermodynamic properties in the supercritical phase approach those of the ideal gas phase. For instance, one observes that for fuels that are composed of hydrocarbons with carbon chains containing more than 10 carbons (as is the case with kerosene and diesel) the differences in thermodynamic properties between ideal gas and supercritical phase would still be significant even under temperature conditions up to 1000 K.

## Conclusions

In this study, a predictive equation of state was proposed to calculate solvation Gibbs energies, which can be used to correct gas phase thermo-kinetic to liquid and supercritical phases. The proposed model has the following advantages regarding the existing models:

- Can treat both radical and non-radical solutes
- Can treat pure solvents or blends
- Can treat liquids and supercritical fluids
- Mixture calculations depend on pure component information only
- An equation of state can perform other calculations than solvation energies, such as solubilities, phase equilibria, enthalpies and entropies for energy and exergy balances, etc.

It was found that the proposed equation of state (called tc-PR/COSMO-RS) can provide reliable predictions of solvation energies for all cases tested in liquid and supercritical phases.

We believe that this work can be a springboard for the development of flexible kinetic generation frameworks that can cover the entire region of the phase diagram, including various applications such as gas phase combustion, oxidations process taking place in liquid phase, as well as innovative combustion systems using supercritical fluids.

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