From ideal gas to liquids and supercritical solvents: expanding the applicability of detailed kinetic models through a ML-based equation of state

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Highlights
- Predictive equation of state based on machine learning for detailed kinetic models.
- Versatile: applicable to closed-shell molecules and free radicals.
- Covers liquid and supercritical phases.
- Solvent mixtures can also be treated.

1. Introduction

Detailed kinetic models are valuable assets for unraveling the dynamics of complex reacting systems governed by radical-chain mechanisms. They provide a comprehensive overview of the various reaction pathways involved, helping in the identification of the key reaction steps that can be used in reactor design. Automatic kinetic generators are pivotal tools in the development of such models. These generators rely on ideal gas approximations to compute the required thermo-kinetic properties, employing group additivity methods along with predefined rate rules and reaction templates. However, in certain applications, these mechanisms take place within other phases than gas. For instance, the liquid-phase oxidation processes to produce phenol and KA oil, important precursors in the polymer sector. Similarly, new intensified combustion technologies use supercritical fluids as a reaction medium, like in the Allam cycle. Nonetheless, developing a detailed kinetic model for such scenarios is quite a challenge due to the extensive demand for solvent-dependent thermodynamic and kinetic data, which is virtually absent in complex mixtures and nonexistent for the free radicals at the heart of chain mechanisms. In this context, our current study proposes a predictive equation of state designed to correct the ideal gas thermochemistry data derived from automatic kinetic generators, allowing for precise predictions within the domains of liquids and supercritical fluids.

2. Methods

The mentioned corrections refer to thermodynamic quantities that are directly added to the ideal gas thermochemistry [1]. These quantities, known as solvation energies, account for solute/solvent interaction effects. Estimating these energies can be achieved straightforwardly through an equation of state (EoS), which basically describes the relationship between pressure, molar volume, and temperature (PVT) of pure substances and mixtures. In this work, a translated Peng-Robinson model (PR EoS) was considered [2], whose formulation for a pure compound "i" is given below.

$$P = \frac{RT}{(V + c_i - b_i)} - \frac{a_i(T)}{(V + c_i)(V + c_i + b_i) + b(V + c_i - b_i)} \tag{1}$$

The attractive parameter (a_i), the untranslated co-volume (b_i), and the volume translation constant (c_i), are traditionally determined using known critical temperature ($T_{c,i}$), critical pressure ($P_{c,i}$) and acentric factor (ω_i) values. To address cases lacking this data, we implemented a machine learning approach utilizing RDKit-derived molecular descriptors. The proposed approach offers swift estimation of the PR EoS parameters across diverse chemical families.

In mixture, the formulation of the PR EoS is the same, except for the fact that the pure compound parameters become mixture parameters. This conversion is achieved through mixing rules, which combine the parameters of individual components to determine the mixture parameters based on the composition of the system and the residual activity coefficients of each compound in mixture. In this study, we adopted the COSMO-RS activity coefficient model (short for Conductor-like Screening

Model for Real Solvents), which offers a distinct advantage: it solely relies on the screening charge distribution (known as σ-profile) of pure compounds to compute residual activity coefficients in mixtures [3]. Similarly, the σ-profiles were determined using a ML model trained on a dataset comprising σ-profiles obtained through Density Functional Theory calculations (DFT).

3. Results and discussion

The prediction of the pure compound parameters using the ML model is in good agreement with the reference data, since the average deviations obtained were less than 5%. Upon establishing a model for the pure compound parameters, we extended our analysis to compute solvation free energies for a diverse range of solutes infinitely diluted in various solvents spanning liquids to supercritical fluids. Our findings exhibited a good agreement with experimental data, revealing average deviations of less than 0.4 kcal/mol on a database of around 70,000 experimental points [4]. This outcome underscores the efficacy of our methodology in accurately predicting solvation behaviors across diverse solvent environments. The proposed model autonomously captures the temperature dependence of solvation free energies in liquid phase, as evidenced in the examples of Figure 1a. In the realm of supercritical solvents, where solvation energies become pressure-dependent, the model adeptly accounts for this effect, as shown in Figure 1b.
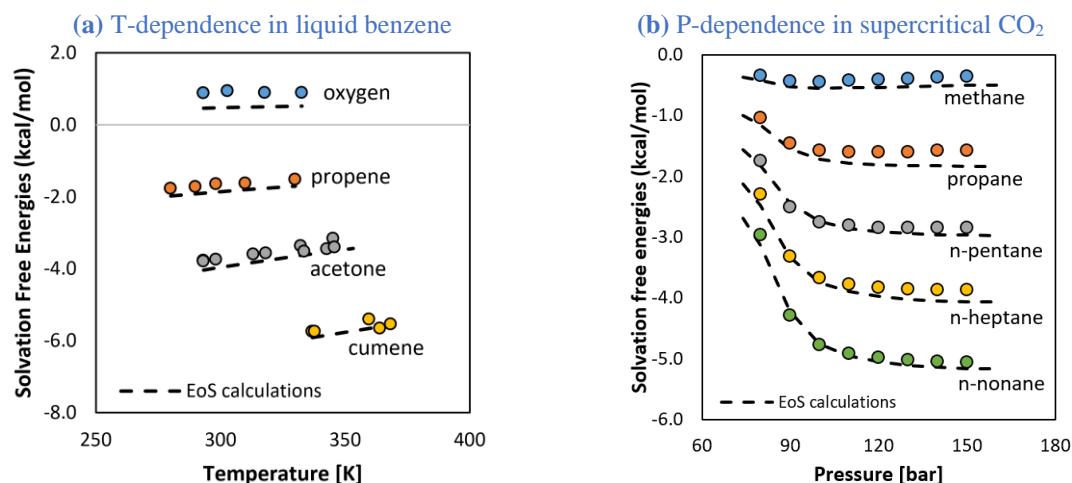

(a) T-dependence in liquid benzene   **(b)** P-dependence in supercritical CO_2

Figure 1. Comparative solvation free energy predictions: (a) Liquid benzene with experimental validation against Compsol database; (b) Supercritical CO_2 benchmarked against GERGE-08 model for hydrocarbons.

4. Conclusions

The proposed equation of state demonstrates remarkable accuracy and versatility in predicting solvation data for any molecule across various solvent phases, including both liquid and supercritical states. It can be used whether in pure solvents or within mixtures. By leveraging machine learning models to derive pure component data and activity coefficients with COSMO-RS, the need for experimental data and fitted binary interaction parameters (BIPs), commonly present in other equations of state, is eliminated. We believe that this advancement could serve as a catalyst for the creation of flexible kinetic generation frameworks, offering a promising pathway for future research and developments in kinetic modeling.

References

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Keywords