Development of ternary mixtures' equilibrium calculation program with high performance using PC-SAFT equation of state

서울시립대학교
UNIVERSITY OF SEOUL

Seongbin Lee, Kyuran Kim, Yeonjoo Kang, Seji Yoon, Jaeeon Chang[*]
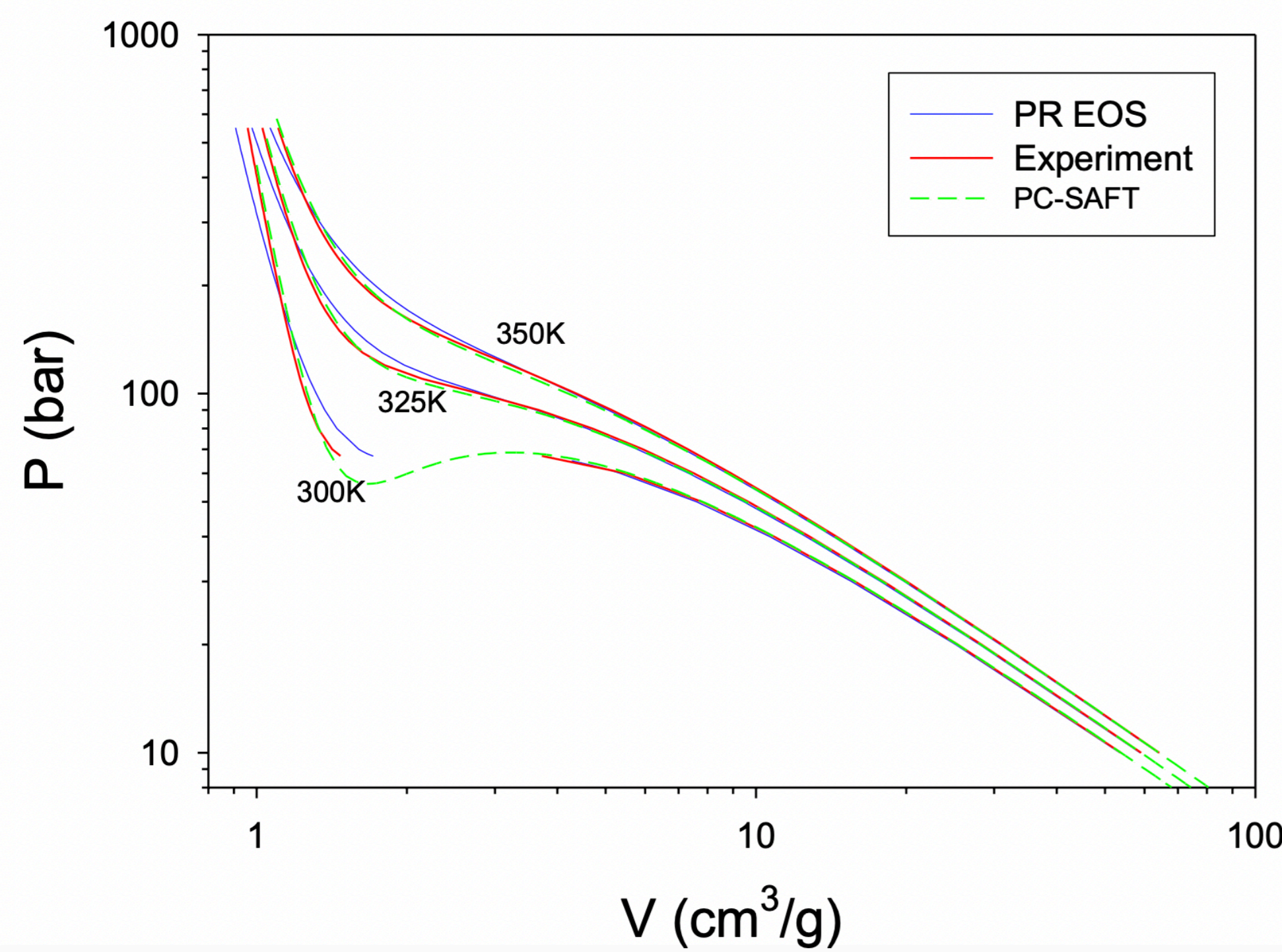
Introduction

Fig 1. PV diagram of carbon dioxide.

Knowing the thermodynamic characteristics of the mixture is an essential element of designing chemical process.
Until recently, various equation of state(eos) have been developed. Especially statistical associating fluid theory(SAFT) eos based on thermodynamic perturbation theory(TPT) predicts well of real organic compound's thermal properties. There have been developed many versions of SAFT including perturbed-chain SAFT(PC-SAFT), soft-SAFT, SAFT-VR, SAFT-VR Mie etc. Among them, PC-SAFT eos is highly accurate and has good generality.

We developed ternary mixtures' equilibrium calculation program which shows ternary diagram. We tried to increase the convenience of equilibrium calculating process for users(working in processes) and further expand the base for thermodynamic property research, also. To make high performance program we developed the equilibrium calculation process with go language designed at Google.

Users can do the calculating work on the website "https://saftgo.app". Also, we are providing REST API, so users can build their own equilibrium calculation app.

Theory

• PC-SAFT EOS

Hard sphere fluid (A^{hs}) Chain formation (A^{hc}) Dispersion formation (A^{disp}) Polar complex (A^{polar}) Association complex (A^{assoc})
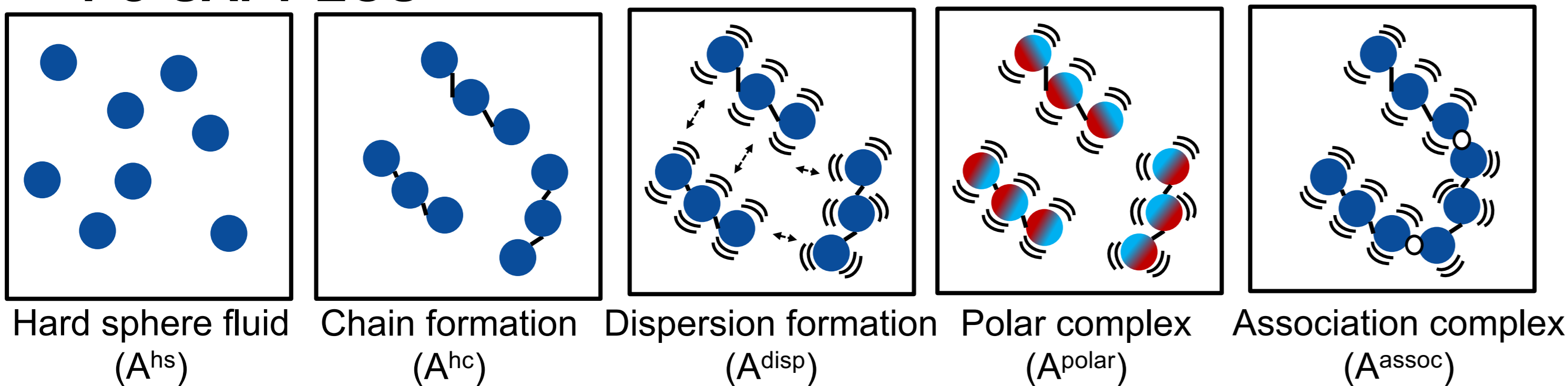
Fig 2. Formations of the chain molecules

$$Z = 1 + Z^{hc} + Z^{disp} + Z^{polar} + Z^{assoc} \qquad (1)$$

$$= 1 + \rho\frac{\partial \tilde{A}^{hc}}{\partial \rho} + \rho\frac{\partial \tilde{A}^{disp}}{\partial \rho} + \rho\frac{\partial \tilde{A}^{polar}}{\partial \rho} + \rho\frac{\partial \tilde{A}^{assoc}}{\partial \rho} \qquad (2)$$

The compressibility factor can be expressed as a term containing the Helmholtz energy of the system and is determined by the sum of various interactions. The meaning of 'hc', 'disp', 'polar' and 'assoc' are hard chain, dispersion, polar and association, respectively.

• Ternary VLE Diagram
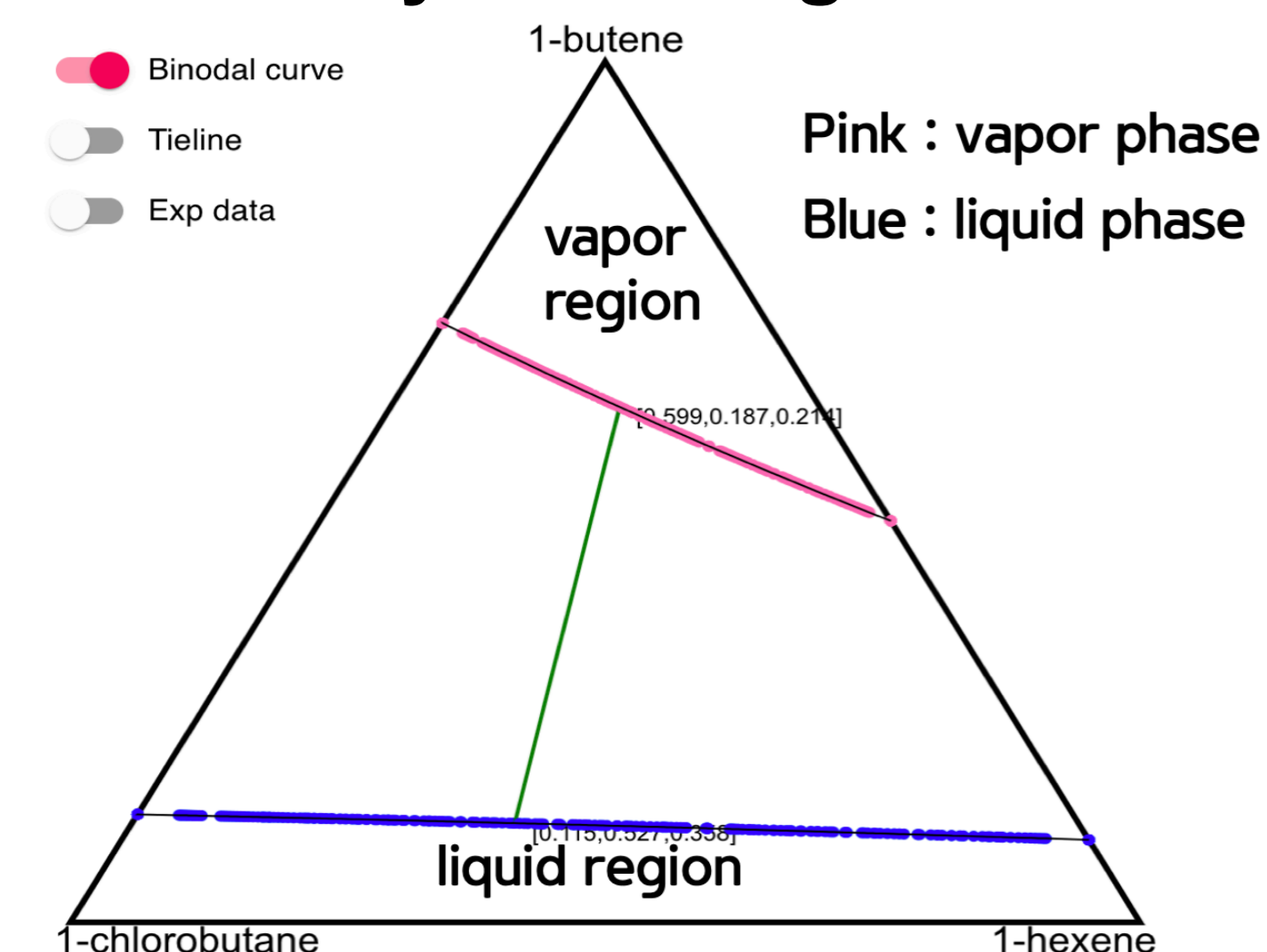

Pink : vapor phase
Blue : liquid phase

Fig 3. Ternary VLE Diagram of 1-butene, 1-chlorobutane, 1-hexene at 1 atm, 320 K

"Flash Calculation"

$$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \qquad (3)$$

Solve (3) to find V with newton method.

$$\therefore x_i = \frac{z_i}{1+V(K_i-1)} \qquad y_i = K_i x_i \qquad (4)$$

This is the result calculated by flash method when P and T are fixed. (P: 1atm, T: 320K)
The VLE diagram can be obtained on the principle that the fugacity of vapor and liquid is the same at equilibrium.

$$y_i \hat{\phi}_i^v P = x_i \hat{\phi}_i^l P \qquad (5)$$

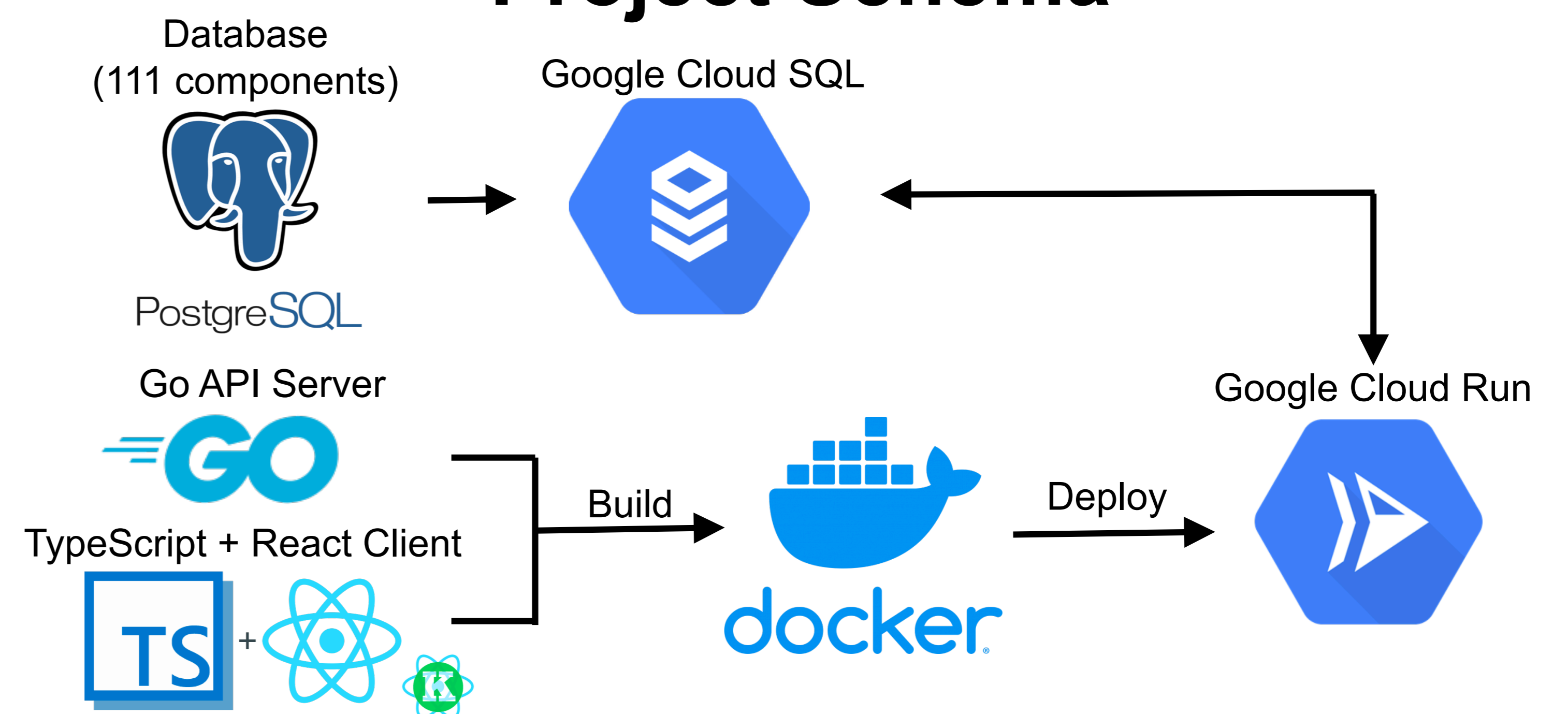To calculate fugacity coefficient ϕ, PC-SAFT eos is used.

Project Schema

Fig 4. Project schema

Database (111 components) PostgreSQL
Google Cloud SQL
Go API Server GO
TypeScript + React Client TS
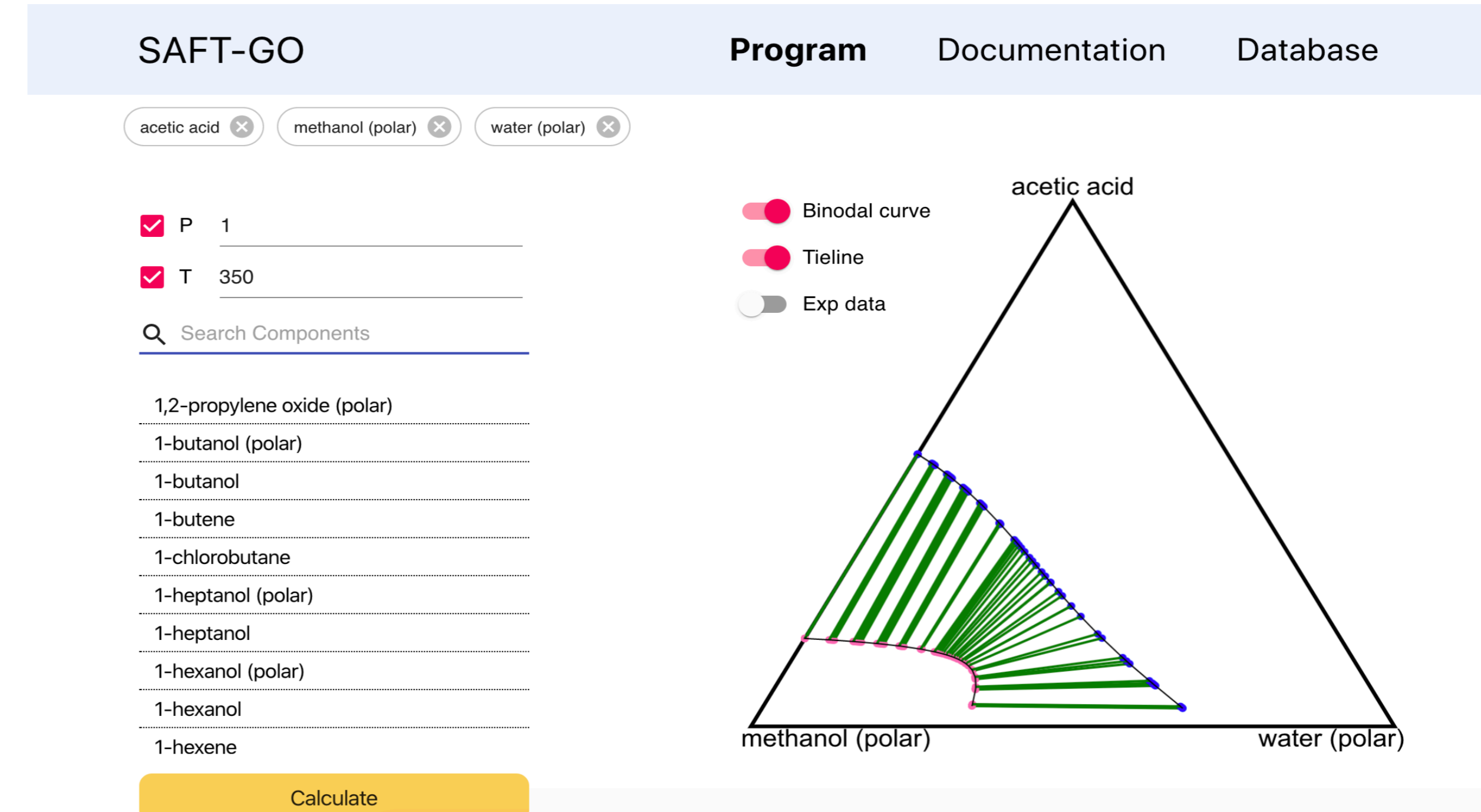Build docker Deploy
Google Cloud Run

Fig 5. Main screen of SAFT-GO client

Users can do many jobs on SAFT-GO.
• User can hover mouse cursor over the graph to read the composition.
• User can toggle to see binodal curve(with spinodal curve) and tie-line.
• Experimental data could be entered to compare with calculated values.
• User can request calculation with appropriate input data. (type : json, see **Documentation** tab)

Results & Assessment
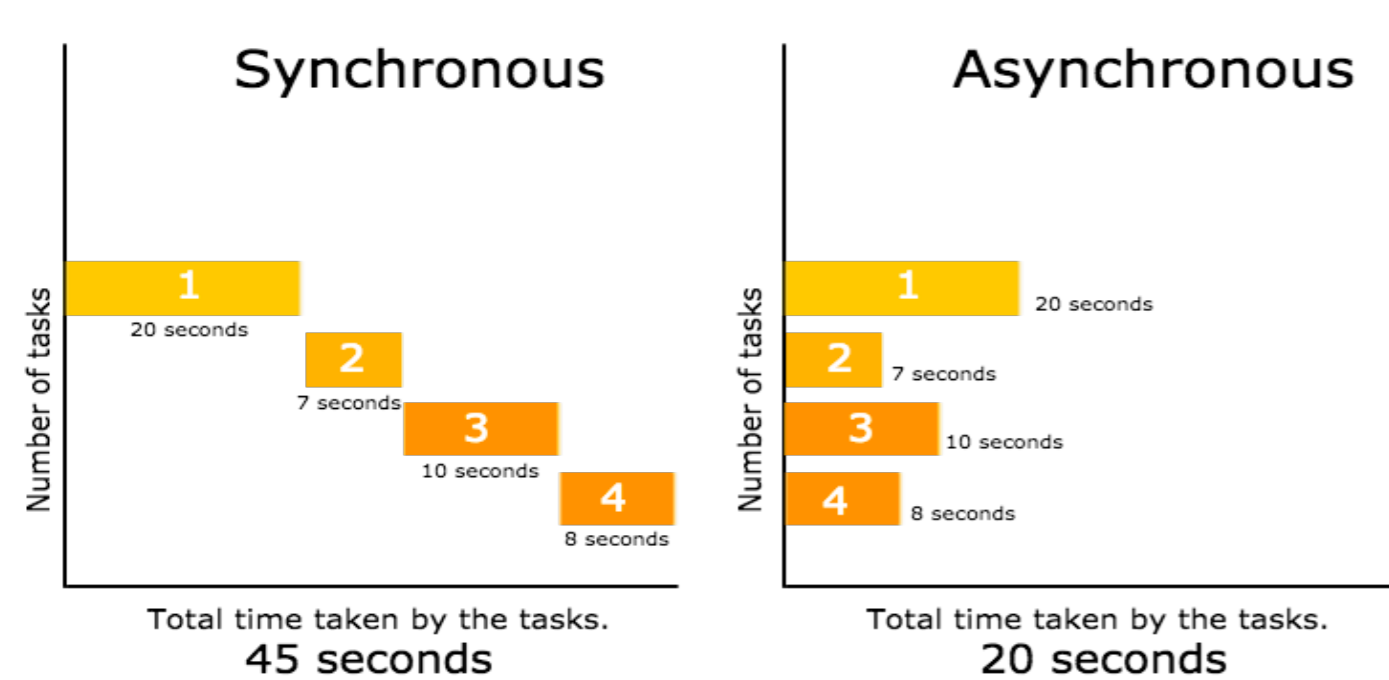
1. Calculation Speed

Fig 6. Difference of Synchronous and Asynchronous calculation

• The Go language, unlike Python, can do asynchronous computations effectively. This means that the calculations are done in nonsequential order, and it can do other calculations immediately in the area where the calculations are completed.
• This program could be 40 times faster than Python.(10 times faster in a single-phase calculation and 4 calculations simultaneously : depends on CPU).

2. Conveniences
• The SAFT-GO program can be used on any devices, such as a desktop computer or a mobile device, as long as you are connected to internet.
• If the user enters the wrong input or does not fill in the required information, the program prompts user to enter the required value.

3. Design
• We tried to create a user-friendly UI that makes it easy for people who first encounter the program.
• The tabs for the program were separated into three sections to simplify, and the 'Documentation' tab provides users with appropriate usage and information.
• The diagram obtained through the 'SAFT-GO' can be saved as an image.

4. Accuracy
The following method was used to calculate the error rate between the experimental and calculated values.

$$T\ err(\%) = \frac{|\ system's\ Temperature\ - experimental\ composition's\ BubbleT\ or\ DewT\ |}{system's\ Temperature} \times 100$$

As a result, SAFT-GO seems to predict well both on non-associable components and associable components.

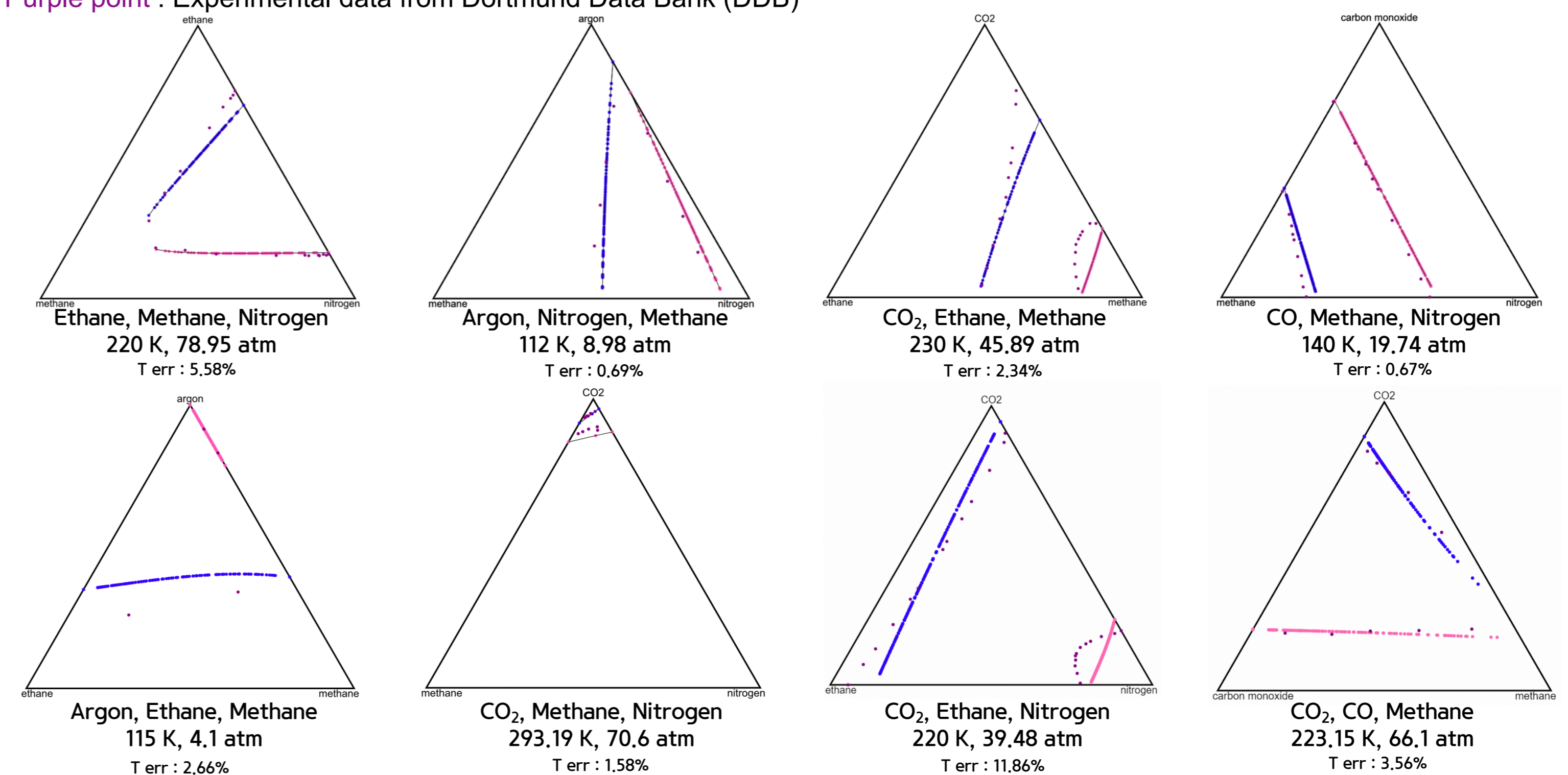Purple point : Experimental data from Dortmund Data Bank (DDB)

Ethane, Methane, Nitrogen
220 K, 78.95 atm
T err : 5.58%

Argon, Nitrogen, Methane
112 K, 45.89 atm
T err : 0.69%

CO$_2$, Ethane, Methane
230 K, 8.98 atm
T err : 2.34%

CO, Methane, Nitrogen
140 K, 19.74 atm
T err : 0.67%

Argon, Ethane, Methane
115 K, 4.1 atm
T err : 2.66%

CO$_2$, Methane, Nitrogen
293.19 K, 70.6 atm
T err : 1.58%

CO$_2$, Ethane, Nitrogen
220 K, 39.48 atm
T err : 11.86%

CO$_2$, CO, Methane
223.15 K, 66.1 atm
T err : 3.56%

Fig 7. Ternary diagrams of non-associable components

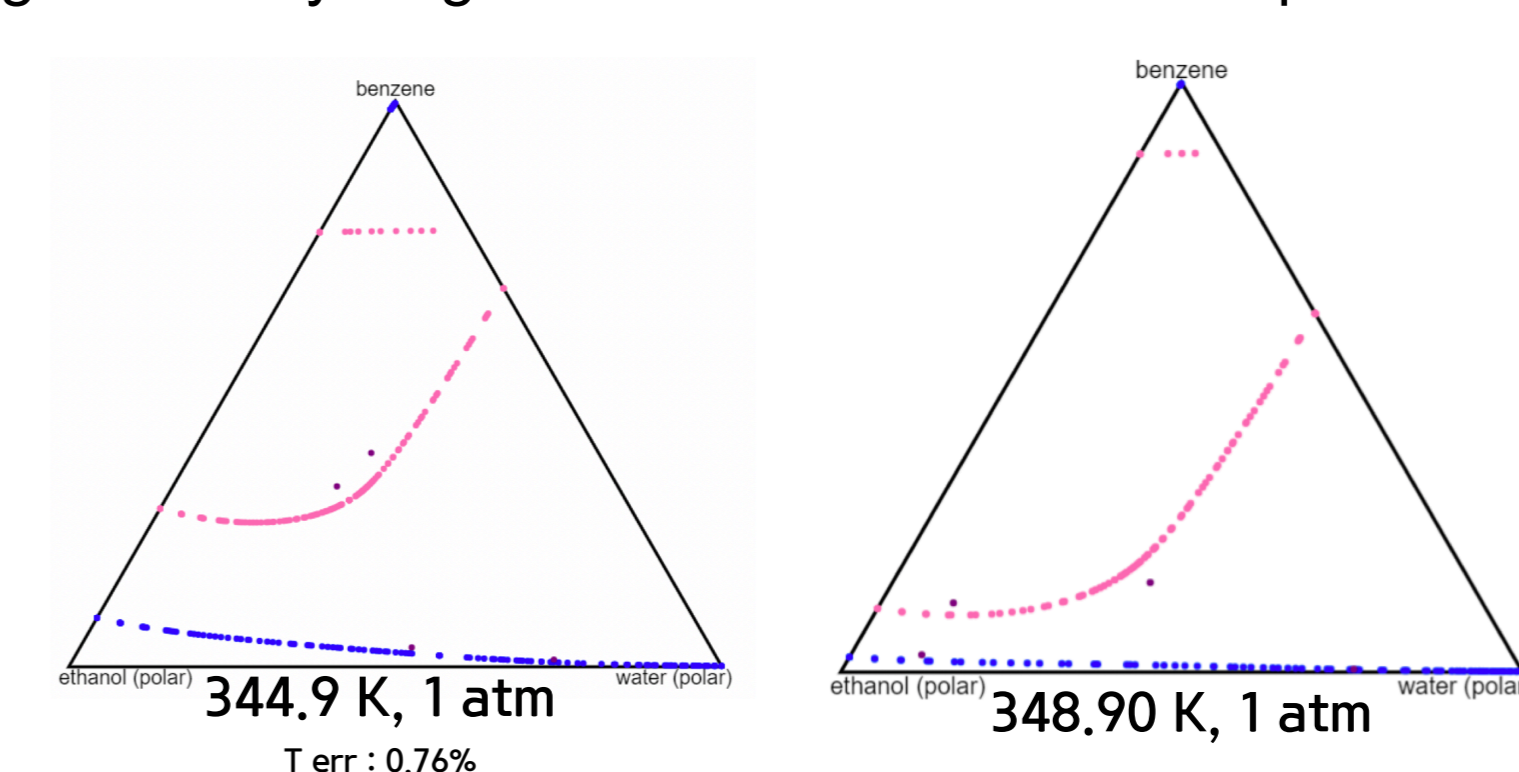344.9 K, 1 atm
T err : 0.76%

348.90 K, 1 atm
T err : 0.34%

Fig 8. Ternary diagrams of associable components(benzene, ethanol, water)