

"Energy Applications: Impact of Data and Models"

Energy Applications refers in this particular case to the wide application of equations of state upstream in the Production of Oil and Gas. The petroleum business is run on the basis of gas volumes at STP and oil volumes in stock tank barrels. The impact of data and models refers to the use of equations of state as representation of reservoir fluid to provide fluid properties as whatever conditions of pressure, temperature, composition and shear are involved in reservoir and production operations in the petroleum industry.

Equations which can relate the volumes at sales conditions to those in the reservoir have value in aiding a correct assessment risk in reservoir development. These same equations are used to forecast well performance test and reservoir evaluation, as well as developing process engineering that optimize the resource. These same equations are used in property generation for transient multiphase flow simulators to determine the operational envelope for deepwater production facilities. These tools are now used in live real time simulations models that aid field operations in making real time decisions on potential operational problems.

Similar fluid models constructed from data and equations of state have been used in enhanced oil recovery for many years especially where mass transfer effects are important in the reservoir process. An example of such can be found in miscible and immiscible gas recovery. These tools are also used in transportation and process simulation in LNG process design as well.

This talk describes the successes and short comings of such equations as presently used and the needs in this area for the future of the oil and gas business.

Equations of state classically relate the thermodynamic variables molar volume, pressure, and temperature. These equations have been effectively used for complex mixtures with relatively simple compositional mixture rules for a variety of applications during designing reservoir processes and facilities from the first discovery through the production of an asset to completion. The purpose of all EOS applications is the successful development of a model of a given process fluid which can effectively relate the properties of the fluids to changes in pressure, temperature, volume, and composition during a process of interest.

The strength of these equations is that they may now be used for evaluation of the quality of measured property studies performed to define reservoir fluids as well as a tool for simulation of properties consistent with a measured basis set for other conditions in the process. Typically in the past the quality measurements were restricted to material balance and "K" value correlations such as Hoffman, Crump, and Holcott¹. The contractor community also realizes this and typically "smoothes" the reported values so that it is difficult to assess errors in experimental data.

¹Hoffman, A.E., Crump, J.S., and Hocott, C.R., "Equilibrium Constants for a Gas Condensate System," Trans. AIME (1953) **198**, 1-10

Another example would be the series of separator tests used in the past to determine the optimum conditions for separator of gas and oil in a field development. The advent of cubic equations and application of these with personal computers allows ready optimization of conditions based on a single well done separator test.

In some situations, such as lean gas systems, where the determination of dew point is a key variable in reservoir simulation, many times the simulated dew point values may better estimated with a well determined composition and EOS compared with direct measurement.

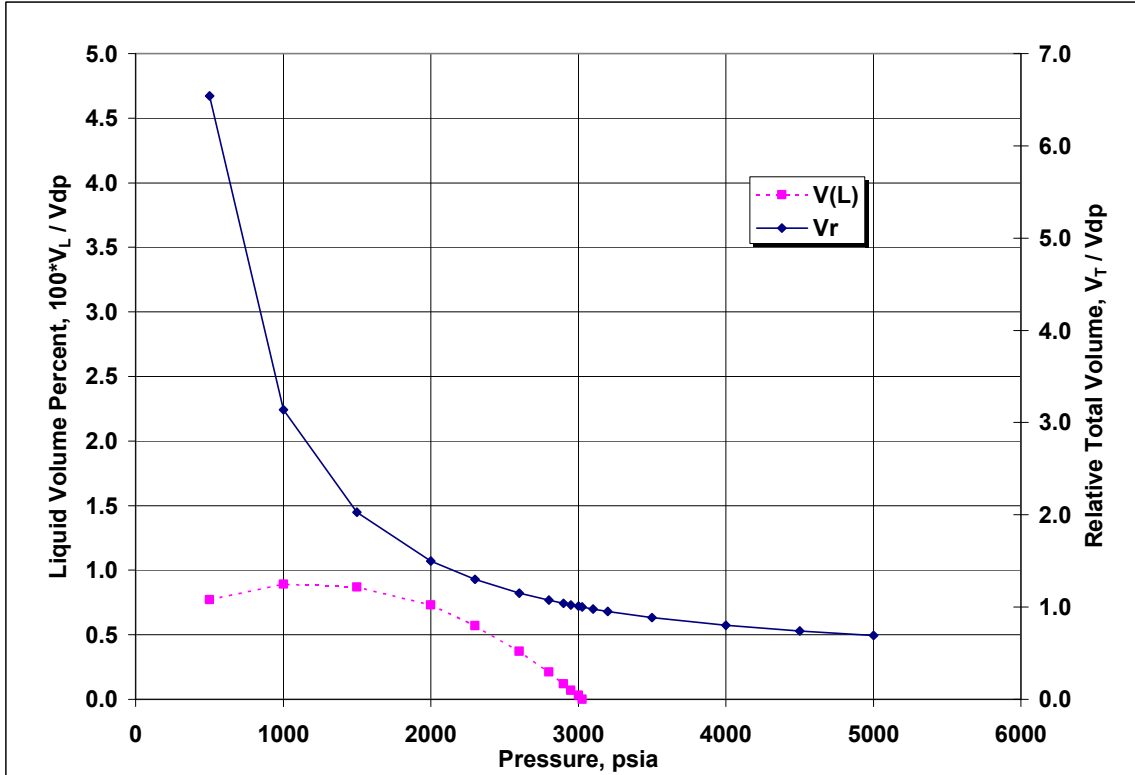


Figure 1 Simulation of Dew Point Pressure

There are however suggestions that the current cubic equations are insufficient for present and future reservoir assets.

There are fundamental problems that still exist with the temperature and pressure dependence of the predicted densities.

The temperature dependence continues to be a problem as equations of state are used in commercial applications involving flow lines and wellbores for example. In these situations the temperature may range from more than 300 °F in the reservoir to 40 °F in the subsea pipelines. The inability of the equations to predict the correct thermal expansion of fluid mixtures leads to problems in both the phase behavior as well as the simple density calculations. This also plays a role in the ability of the EOS to correctly represent interfacial tension and viscosity since calculations of both these variables requires reasonable density estimates. Figure 2 below shows the difficult with the

dependence in the fluid density as the $Z = PV_m/RT$ as a function of both temperature and pressure with either the traditional Soave Redlich Kwong² or the Peng Robinson³ equations of state.

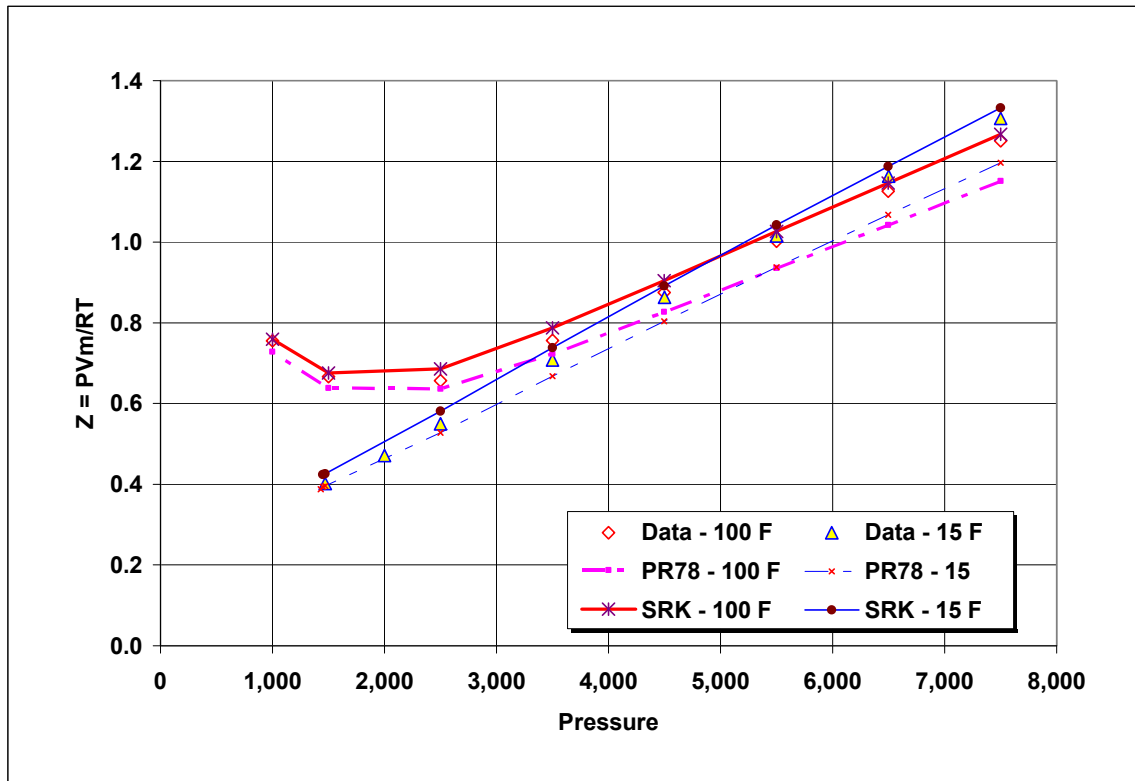


Figure 2: Variation of Z values with Pressure and Temperature

The temperature dependence in the cubic equation of state aside from the explicit temperature dependence from RT is from the $a(T)$ term which depends on reduced temperature, T/T_c and Pitzer's acentric factor $\omega = -\log(P_v^*/P_c) - 1$ where P_v is the vapor pressure at a reduce temperature $T/T_c = 0.7$. The temperature dependence of the pair potential is then given by

$$a(T) = (1 + \kappa \cdot (1 - T_r^{1/2})), \text{ where } \kappa = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2$$

The current correlations provide a variety of interesting and amazing results for acentric factors including some that show the acentric factor going to zero for large molecules while others give values as high as 2 to 3 for the same molecular weights. Our experience is that a maximum value of 1.2 to 1.3 is most likely and correlates well with the temperature dependence of the bubble point pressure for crude oil systems.

²Soave, G., "Equilibrium Constants From a Modified Redlich-Kwong Equation of State," Chem. Eng. Sci., (1972) **27**, No. 6, 1197-1203.

³Peng, D.Y., and Robinson, D.B., "A New Two-Constant Equation of State," *I. & E. C. Fundamentals* (1976) **15**, No. 1, 59-64.

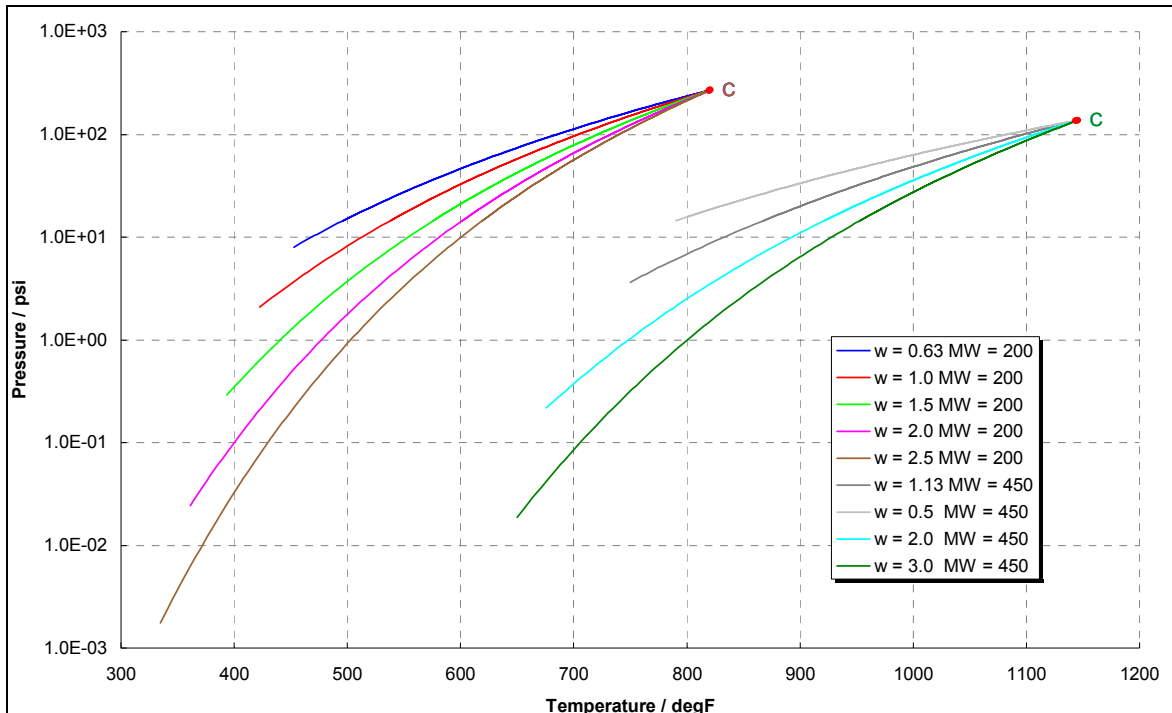


Figure 3 Variation of Vapor Pressure with Acentric Factor.

The following vapor pressure curves were made for pseudo components of differing molecular weights and showing the variation due to acentric factor variation. The values of 2 or 3 show unreasonable vapor pressures for hydrocarbons of effectively below 0.1 psi for any reasonable reservoir temperature ($T_{res(max)} < 400$ °F)

There are also problems with the pressure dependence as well. The typical equations of state are cubic in volume. This implies that the compressibility can be at most a linear function of pressure. The problem to be illustrated as reservoir simulators must relate fluid properties in the single phase region above saturation by correcting bubble point data with compression terms. The newer reservoir fluids have high pressure reservoirs (~20,000 psia) while also having bubble point pressures of less than 3,000 psi thus requiring accurate compression calculations over long ranges of pressure.

An example of this is shown in the figure below where the ability to forecast the reservoir volumes with typical simple compressibility where the compression can vary only linearly with pressure fall short of matching the reservoir fluid data. The volumes are expressed as relative volume to the bubble point condition in the particular experiment.

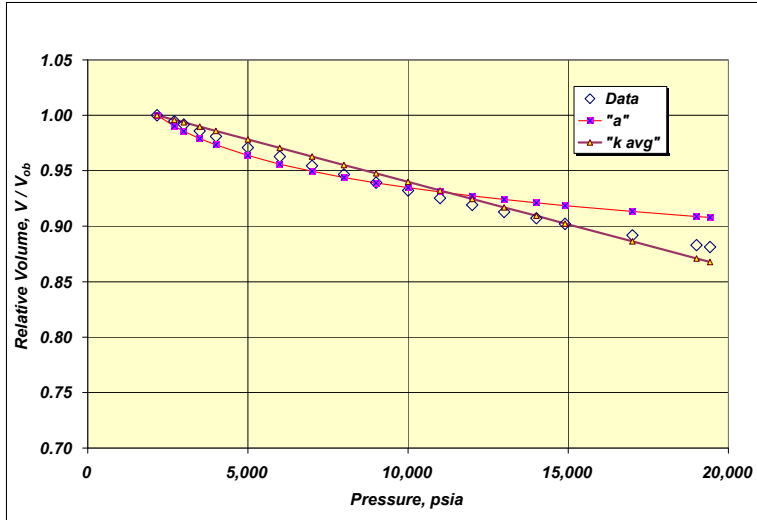


Figure 4: Compression corrections for Reservoir Simulation

Figure 4 shows two attempts at applying simple constant compressibility correction to estimate formation volume from the bubble point volume. The problem is not resolved having the compressibility as simple function of pressure.

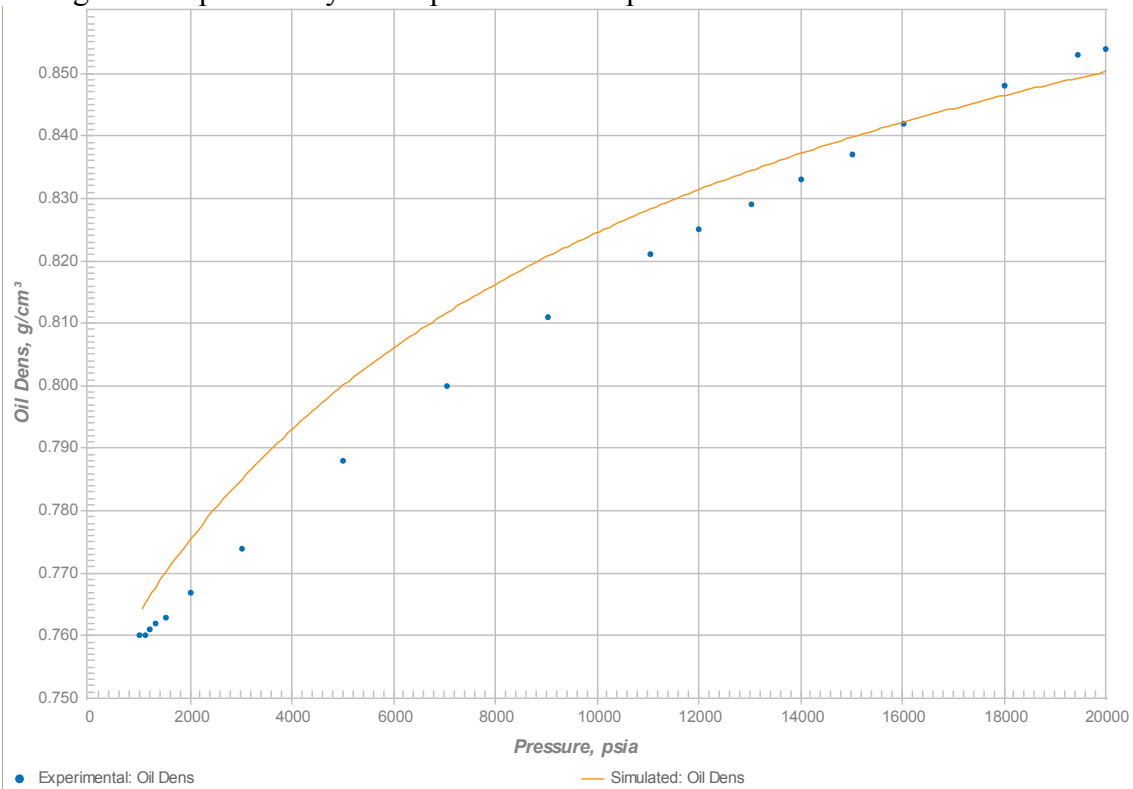


Figure 5: Typical fit of experimental density with equation of state.

Figure 5 shows a cubic equation of state SRK with volume shift density predictions compared to the experimental data. The incorrect dependence of density on pressure is shown as the curvature from the equation of state relative to the experimental data.

Figure 6 and 7 compare data from the NIST Chemistry Web Book and P.W. Bridgman's "The Physics of High Pressure" against the prominent equation of state tools.

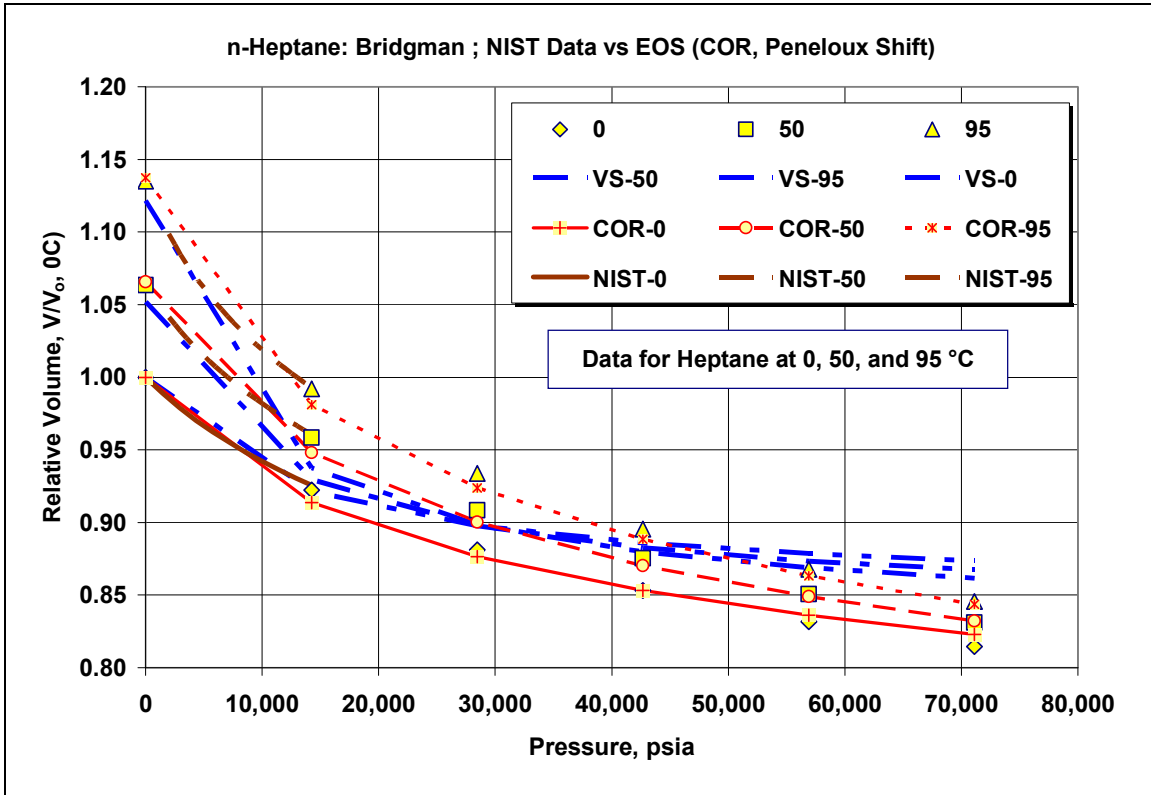


Figure 6 Relative Volume as a function of Pressure

COR is Chain of Rotators from M.C.H. Chien and M.R. Monroy, "Two New Density Correlations," SPE 15676 , SPE ATCE 1986. (Chien, M, C. H., Greenkorn, R. A., and Chao, K. C, "Chain-of-Rotators Equation Of State", AIChE J. (July 1983) 29, 560-571).

VS refers to volume shift parameters in the cubic equations of state.

Peneloux, A., Rauzy, E., and Freze, R., "A Consistent Correction for Redlich-Kwong-Soave Volumes," Fluid Phase Equilibria (1982)8,7-23. and for Peng Robinson equations of state, Jhaveri, B, S., "Three-Parameter Modification of the Peng-Robinson Equation of State to Improve Volumetric Predictions," SPE Paper 13118 presented at the 59th Annual Technical Conference and Exhibition of the SPE of AIChE in Houston, TX, September 16-19, 1984

Figure 7 compares one of the newer equations of state, PC-SAFT with P.W. Bridgman data for n-heptane and benzene.

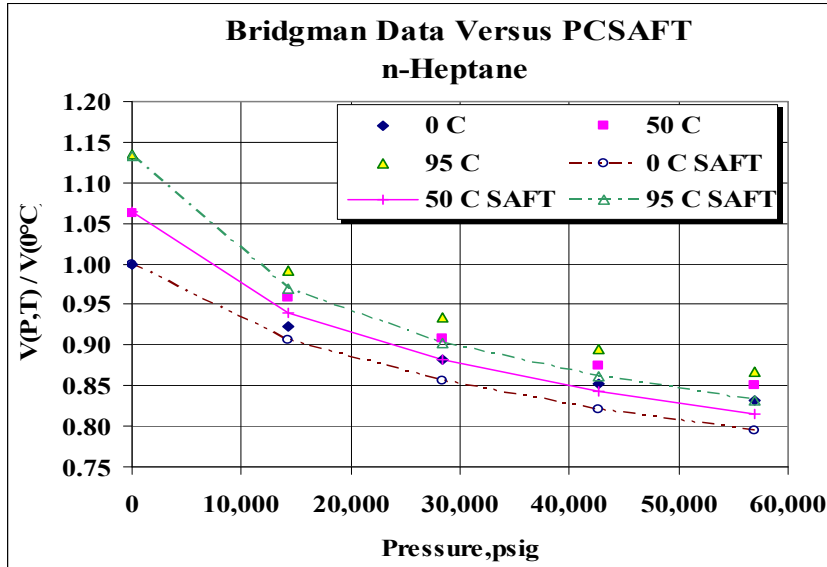


Figure 7 SAFT versus Bridgman Data for Heptane

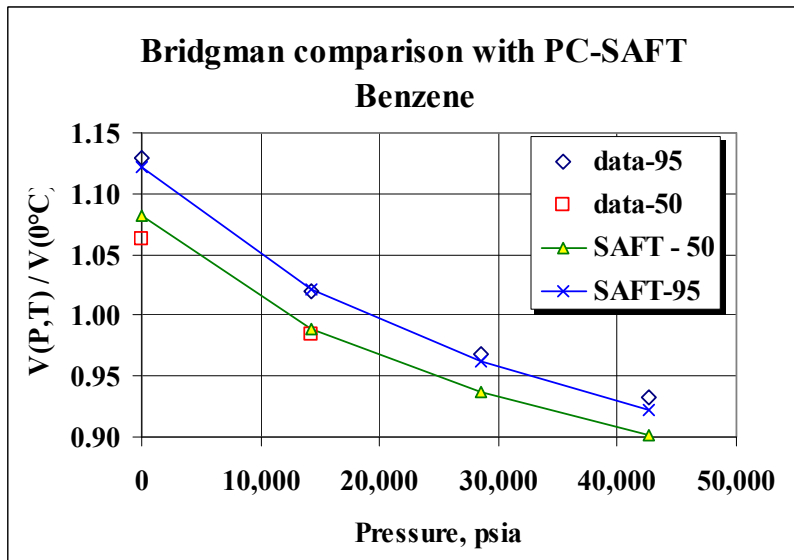


Figure 8: Comparison of PC-SAFT with P.W. Bridgman data for Benzene

While the heptane agreement is not as good as desired the benzene data agreement is good.

In conclusion the cubic equations of state are widely in simulations for petroleum exploration and production. These simple ready to used equations have been a nice balance between accuracy and simplicity. These equations will continue to serve the industry as new equations are developed for the frontier of developments where better pressure and temperature dependence are required.

Gross, J.; Sadowski, G., - Perturbed-Chain SAFT: "An Equation of State Based on a Perturbation Theory for Chain Molecules," Ind. Eng. Chem. Res. 2001, 40, 1244-1260.

W.G. Chapman, K.E. Gubbins, G. Jackson, and M. Radosz, "SAFT: Equation- of-State Solution Model for Associating Fluids," *Fluid Phase Equilibria*, **52**, 31-38 (1989).