

# MSE-SRK: Mixed Solvent Electrolyte + Soave-Redlich-Kwong

A thermodynamic model for HPHT upstream oil and gas

The MSE-SRK thermodynamic framework was developed to accurately simulate mixtures containing H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, hydrocarbons, and various salts that typically exist in high temperature/high pressure upstream oil and gas production environments.

This framework calculates the phase equilibria of upstream oil and gas multiphase systems by combining thermodynamic formulations that are suitable for each of the phases. For the aqueous phase, MSE-SRK combines an equation of state for standard-state properties of individual species, an excess Gibbs energy model to account for solution non-ideality in the aqueous electrolyte phase, and the Soave-Redlich-Kwong equation of state (SRK EOS) to calculate the properties of both the gas phase and the second (usually organic-rich) liquid phase, assuming the second liquid phase to be non-ionic. Calculating the phase equilibria of the gas and second liquid phase using the same equation of state allows the MSE-SRK framework to more easily reproduce the critical behavior of nonelectrolyte systems.

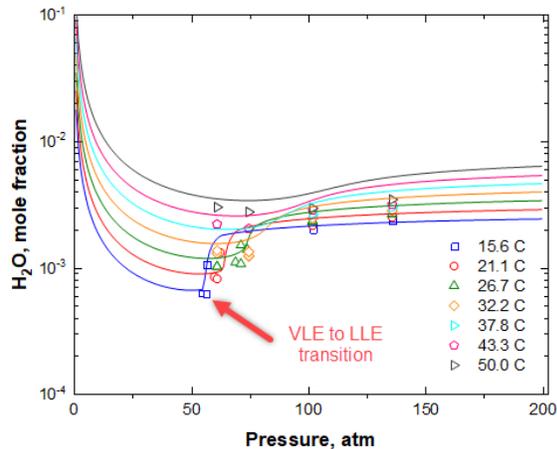


Figure 1. Water solubility in a mixture of 5% CH<sub>4</sub> and 95% CO<sub>2</sub> at various temperatures. The MSE-SRK model is able to predict the behavior of fluid mixtures as they transition from subcritical to supercritical regions

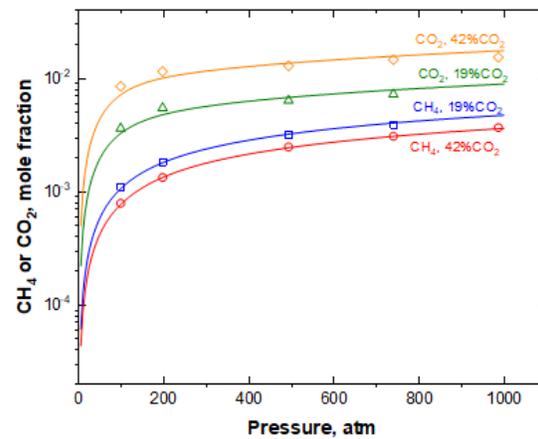


Figure 2. Calculated and experimental solubilities of CH<sub>4</sub> and CO<sub>2</sub> in H<sub>2</sub>O in a ternary system at 71 °C. Under all conditions, the CH<sub>4</sub> and CO<sub>2</sub> mixtures are above the critical temperature of the mixture. The MSE-SRK model predicts the effect of both temperature and pressure on the solubility of gases in the aqueous phase.

Advantages of the MSE-SRK model include:

- ✓ Reproducing the behavior of fluid mixtures as they transition from subcritical to supercritical conditions (see Figure 1).
- ✓ Reproducing phase equilibria in near-critical and super-critical regions.
- ✓ Predicting the effects of salts on the solubility of acid gases in aqueous solutions
- ✓ Accurately predicting non-ideality effects when temperature and pressure are at supercritical or near-critical conditions.
- ✓ Reliably predicting production fluid properties such as pH, which is of great importance for evaluating the corrosion resistance of metallic materials.

## MSE-SRK Thermodynamic Framework

In the MSE-SRK model, the electrolyte-containing (usually aqueous) liquid phase is represented by a combination of the Helgeson-Kirkham-Flowers-Tanger equation of state (HKFT-EOS) for standard-state properties and the MSE activity coefficient model for solution nonideality. Accordingly, the chemical potential of a species *i* in a liquid electrolyte phase is calculated as:

$$\mu_i^L = \mu_i^{L,0,x}(T, P) + RT \ln x_i \gamma_i^{x,*}(T, P, x) \quad (1)$$

where  $\mu_i^{L,0,x}(T, P)$  is the standard-state chemical potential from the HKF theory,  $x_i$  is the mole fraction, and  $x_i \gamma_i^{x,*}(T, P, x)$  is the activity coefficient from the MSE theory of Wang et al. [1], which accounts for long-range electrostatic, specific ionic, and short-range intermolecular interactions.

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The organic (second liquid) phase is modeled using the Soave-Redlich-Kwong equation of state (SRK-EOS). The chemical potential in this phase is calculated as:

$$\mu_i^G = \mu_i^{G,0}(T) + RT \ln \frac{P y_i \phi_i(T, P, y)}{P^0} \quad (2)$$

where  $\mu_i^{G,0}(T)$  is the chemical potential of pure component  $i$  in the ideal gas state,  $y_i$  is the mole fraction,  $\phi_i(T, P, y)$  is the fugacity coefficient from the SRK-EOS,  $P$  is the total pressure, and  $P^0 = 1 \text{ atm}$ . The properties of the gas phase are also obtained from the SRK equation according to Equation (2).

The vapor-liquid and liquid-liquid equilibrium (VLE and LLE, respectively) conditions are defined by the equality of the chemical potentials in the coexisting phases, i.e.,

$$\mu_i^L = \mu_i^G \text{ for VLE} \quad (3)$$

$$\mu_i^{L1} = \mu_i^{L2} \text{ for LLE} \quad (4)$$

The distinction between VLE and LLE is unambiguous when the components are below the critical region. When supercritical components are present, a smooth transition between a VLE-like region at lower pressures and an LLE-like region at higher pressures occurs as seen in Figure 1. In the LLE-like region, an aqueous phase is in equilibrium with a dense phase dominated by  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and other hydrocarbons.

The chemical potentials are also used for calculating speciation equilibria within the aqueous phase and for predicting the solubility of scale-forming minerals and corrosion products. The MSE-SRK model's accuracy in representing both phase equilibria and speciation allows it to predict the aggressiveness of upstream oil and gas production fluids.

## Speciation and pH

For the evaluation of a material's performance in production environments, accurate prediction of pH is of great importance. In the MSE-SRK model, the calculated pH is a reflection of the equilibrium state of dissociation reactions of the acid gases that dissolve in solution ( $\text{pK}_a$ ). The pH depends on both the standard state properties of the aqueous phase and the activity coefficients of neutral and ionized species.

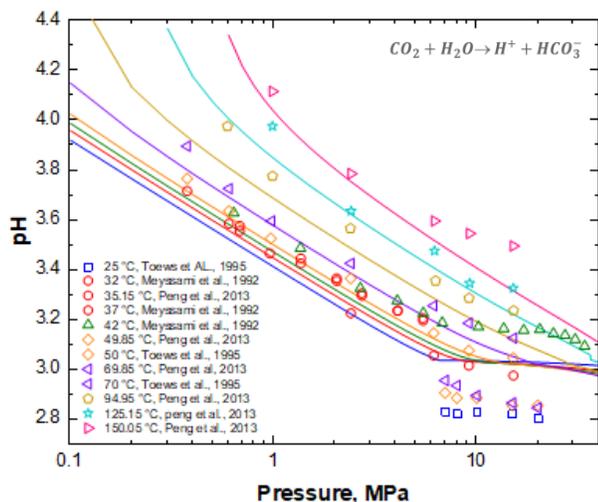


Figure 3. pH of  $\text{CO}_2$ -Saturated water systems as a function of pressure. The prediction of pH of the  $\text{CO}_2$  containing system is a manifestation of both **chemical equilibria** and **phase equilibria**.

The intrinsic equilibrium constants ( $\text{pK}_a$ ) are calculated using the HKFT-EOS. This equation accurately quantifies the standard-state thermodynamic properties as a function of both temperature and pressure. The non-ideality effects are calculated using the MSE activity coefficient model, see Equation 1.

Because of its ability to predict pH, activities and fugacities in complex ionic mixtures, and the effect of high pressure on multiphase equilibria, MSE-SRK can serve as a foundation for studying metal/environment interactions in upstream oil and gas environments.

## Validation materials

OLI has extensive Excel-based validation plots for solutions that MSE-SRK model parameters have been established. [Contact OLI](#) to learn more about how you can access our data validation capabilities.

