

Calculating Fugacities in OLI Studio

If you are working at high pressures where only a water (aqueous) and hydrocarbon (second liquid) phase are present, you can still calculate fugacities using values generated in the OLI software.

Fugacity can be computed indirectly when the gas phase is absent.

The fugacity is computed automatically by OLI Studio software when a gas (vapor) phase is present. When a gas is absent, usually due to high pressures, the fugacity can be computed indirectly using thermodynamic values generated by the software.

Using H₂S as an example, the software constructs the elements that contribute to the following Gibbs Energy equation.

$$G_{H_2S,vap} = G_{H_2S,vap}^0 + RT \ln f_{H_2S} = G_{H_2S,vap}^0 + RT \ln(\varphi_{H_2S} y_{H_2S} P_T) \quad (1)$$

- $G_{H_2S,vap}^0$ - Standard State Gibbs Energy, which is a function of temperature only.
- φ_{H_2S} - Fugacity coefficient
- y_{H_2S} - Vapor phase mole fraction
- P_T - Total Pressure

Similar equations exist for the water (AQ) phase and hydrocarbon (ORG) phase¹.

We will use H₂S as an example

$$G_{H_2S,Aq} = G_{H_2S,Aq}^0 + RT \ln a_{H_2S,Aq} = G_{H_2S,Aq}^0 + RT \ln(\gamma_{H_2S,Aq} X_{H_2S,Aq}) \quad (2)$$

$$G_{H_2S,org} = G_{H_2S,org}^0 + RT \ln a_{H_2S,org} = G_{H_2S,org}^0 + RT \ln(\gamma_{H_2S,org} X_{H_2S,org}) \quad (3)$$

At equilibrium, the following is true:

In equilibrium the value of G_{H_2S} is computed for each phase that exists ...

- The values of G_{H_2S} for each phase that exists is known (computed)
- The values of $G_{H_2S}^0$ is known, even if the phase does not exist

¹ The standard states for the aqueous and organic phases are different from the gas phase. The aqueous-phase standard-state is the state of a species at infinite dilution in water at the hypothetical concentration of 1 m. As such, it depends on both T and P. The organic phase standard-state differs depending on the model. In the OLI AQ model, it is the same as for the gas phase and in the OLI MSE model it is the same as for the aqueous phase.

- When the phases are in equilibrium, the following relationship is true:

$$G_{H_2S,vap} = G_{H_2S,Aq} = G_{H_2S,Org} \quad (4)$$

Thus, elements in equations (1) to (3) can be rearranged to solve for fugacities or activities of a missing, or unmeasured phase. For example, there is no gas-phase at 150C and 1000 bar. Therefore, the fugacity can be computed from the aqueous H₂S concentration by combining equation (4) and (1):

....and the value of G_{H_2S} in each phase is equal

$$G_{H_2S,Aq} = G_{H_2S,vap}^0 + RT \ln(\phi_{H_2S} Y_{H_2S} P_T) = G_{H_2S,vap}^0 + RT \ln \frac{f_{H_2S}}{f_{H_2S}^0} \quad (5)$$

The Standard state $G_{H_2S,vap}^0$ value is based on a reference pressure of 1 bar, or; $f_{H_2S}^0 = 1bar$. The equation is rearranged to:

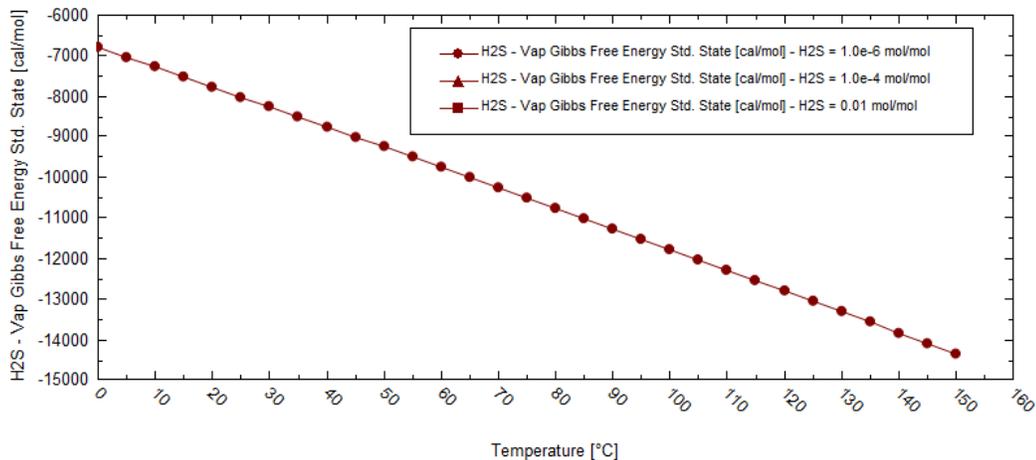
$$f_{H_2S}(bar) = e^{\frac{G_{H_2S,Aq} - G_{H_2S,vap}^0}{RT}} \quad (6)$$

A similar fugacity relationship can be made when the H₂S concentration in the oil phase is known.

$$f_{H_2S}(bar) = e^{\frac{G_{H_2S,org} - G_{H_2S,vap}^0}{RT}} \quad (7)$$

Standard State Gibbs Energy of the vapor-phase H₂S ($G_{H_2S,vap}^0$)

By definition, the value of $G_{H_2S,vap}^0$ is independent of composition.



Therefore, $G_{H_2S,vap}^0$ can be computed using temperature only; without needing the gas phase composition, or existence. These values can there be used directly in the above equations, regardless of the phases present.

Example: Low temperature, Vapor-Water phases present

Consider the low temperature and pressure state first. The screenshots below are the output of a flash calculation at 25C, 1 atm, and 0.01% H₂S vapor (0.0001 atm PP). The Gibbs Energy for the water (aq) and gas (vap) phase, $G_{H_2S,vap} = G_{H_2S,aq} = -13481.6 \frac{cal}{mol}$, are equal because the phases are in equilibrium. Also computed (automatically) is the standard state Gibbs energy of H₂S in the gas phase, $G_{H_2S,aq} = -8021.04 \frac{cal}{mol}$. Lastly, the gas phase, H₂S fugacity coefficient is calculated automatically, $\varphi_{H_2S} = 0.994$, because the gas phase is present.

Software calculations at ambient T & P, where the gas & water phases are present

Mixture Properties

Temp	25.0000	°C
Pres	1.00000	atm

Species Output (True Species)

	Aqueous	Vapor
	mol/mol	mol/mol
H2S	1.73217e-7	1.0e-4

Gibbs Free Energy of Formations

	Aqueous	Vapor
	cal/mol	cal/mol
H2S	-13481.6	-13481.6

Gibbs Free Energy of Formations - Standard State

	Aqueous	Vapor
	cal/mol	cal/mol
H2S	-4257.26	-8021.04

Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

Species	γ x-based	Species	Fugacity Coefficient
H2S - Aq	0.999801	H2S - Vap	0.993972

Software output shows the Gibbs Energy of each phase and the fugacity

Internal consistency therefore, requires equation (5) to be an equality:

$$G_{H_2S, aq} = G_{H_2S, vap}^0 + RT \ln(\varphi_{H_2S} Y_{H_2S} P_T)$$

$$-13481.6 \frac{cal}{mol} = -8021.04 \frac{cal}{mol} + 1.9872 * 298.15 \ln(0.994 * 0.0001 * 1) \frac{cal}{mol}$$

$$-13481.6 \frac{cal}{mol} (= -8021.04 - 5460.54) \frac{cal}{mol}$$

The fugacity is the $(\varphi_{H_2S} Y_{H_2S} P_T)$ term, and has a value of: $0.994 * 0.0001 * 1 = 9.94e^{-5}$, or 0.6% below the ideal partial pressure of $1e^{-4}$ bar. Thus, this example displays the internal consistency of these equations.

Example: High Temperature/Pressure case, oil phase only (no vapor)

When no gas phase is present, use thermodynamic relationships to calculate

The next example is a 50:50 CH₄:Decane mixture containing, $5e^{-5} \frac{mol}{mol}$ H₂S. The conditions are 150C and 1500 bar, where no gas phase exists, and thus no fugacity is shown. The software calculates the Gibbs energy of H₂S in the 2nd Liquid phase:

$$G_{H_2S, org} = -17843.5 \frac{cal}{mol}$$

Gibbs Free Energy of Formations

	Aqueous	Vapor	2nd Liquid
	cal/mol	cal/mol	cal/mol
C10H22			-10454.1
CH4			-13200.6
H2S			-17843.5

The standard state Gibbs energy for H₂S in the vapor is $G_{H_2S, vap} = -14369.3 \frac{cal}{mol}$.

Gibbs Free Energy of Formations - Standard State

	Aqueous	Vapor	2nd Liquid
	cal/mol	cal/mol	cal/mol
C10H22		-9807.67	
CH4		-17869.3	
H2S		-14369.3	

We can use equation (7) to compute the gas phase fugacity by entering the data from the above tables.

The Gibbs energy of the phase and the standard state Gibbs energy can be used to calculate fugacity

$$f_{H_2S} = e^{\frac{G_{H_2S,oil} - G_{H_2S,vap}^0}{RT}} = e^{\frac{-17843.5 \frac{cal}{mol} - (-14369.3 \frac{cal}{mol})}{1.987 * 423.15}} = 0.016$$

Since the reference fugacity is 1 bar, $f_{H_2S} = 0.016 \text{ bar}$. If this mixture were a hypothetical 100% vapor, then the partial pressure could be computed by setting the gas-phase mole fraction $y_{H_2S} = 5e^{-5} \frac{mol}{mol}$, and:

$$P_{H_2S} = 5e^{-5} \frac{mol}{mol} * 1500 \text{ bar} = 0.075 \text{ bar}.$$

The fugacity coefficient is then computed from equation (1):

$$\varphi_{H_2S} = \frac{f}{y_{H_2S} P_T} = \frac{0.016 \text{ bar}}{0.075 \text{ bar}} = 0.21$$

The OLI Studio will automate the fugacity calculation when there is no gas phase present beginning with release V9.2.3. For more information please contact Pat McKenzie, Business Development Director for OLI at pat.mckenzie@aqsim.com or 1-973-998-0240 x112