Studio ScaleChem

Calculation comparison between ScaleChem Standard and Studio ScaleChem

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Studio ScaleChem is a new product from OLI Systems in 2012, developed by OLI in partnership with the Produced Water Group consortium and AQSim. Studio ScaleChem duplicates and expands the functionality of ScaleChem Standard within the OLI Analyzer line of products. This document is an explanation and comparison of the calculations found within both products. It was written to facilitate the migration for ScaleChem Standard to Studio ScaleChem, and to help explain some of the systemic differences between the two products

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1.0 Overview

In September 2012 OLI Systems, Inc. (Morris Plains, New Jersey) released a new version of the ScaleChem program. This new program is called the OLI Analyzer Studio: ScaleChem (" Studio-SC"). Studio-SC incorporates the best features of ScaleChem Standard ("SC") as well as the modern architecture of the OLI Analyzer Studio program. A concern of the SC client base is that the established calculations of ScaleChem Standard be maintained in the new program.

To that end, a conversion document is available (*PWG-12-Rel-002*) to explain how to perform those ScaleChem Standard calculations in Studio-SC. A companion document (this document, PWG-12-Rel-001) explains the calculation methods in ScaleChem Standard and how those methods changed in Studio-SC.

Perhaps the most significant change between ScaleChem Standard and Studio-SC is the inclusion of the Mixed-Solvent Electrolyte thermodynamic framework (MSE). MSE has been described in detailed elsewhere and the reader is guided to the OLI website (www.olisystems.com) for more information. The ScaleChem Standard program is limited to the traditional aqueous thermodynamic framework (AQ) which has a lower concentration limit than the MSE thermodynamic framework.

1.1 Scope of the document

The scope of this document is to explain how the current ScaleChem Standard program performs its calculations and then compare them to Studio-SC. In all cases, where we reference ScaleChem Standard we are referring to Version 4.1, and references to Studio-SC are to Version 9.0. We will not partake in a full discourse of thermodynamics in this document but rather explain at a higher level what the programs are calculating. We will highlight significant changes in the methodology that can lead to different numerical answers.

It is not the purpose of this document to illustrate the differences between the AQ and MSE thermodynamic frameworks. These two frameworks use similar but numerically different databanks and differences are to be expected.

1.2 Terminology

There are various terms used in this document that should have a clear definition as to be understood by the user.

AQ Framework

This is the traditional aqueous thermodynamic framework. It is the only thermodynamic framework used by ScaleChem Standard. It is characterized by:

- The Helgeson equation of state for equilibrium constant values
- Bromley-Zemaitis activity model
- Soave-Redlich-Kwong equation of state for vapor and non-aqueous phase liquid fugacity calculations

- Concentrations limited to a mole fraction of H_2O greater than 0.65
- The activity of the hydrogen ion (H^+) is considered as the basis for pH.

MSE Framework

This is the developing thermodynamic framework available in Studio-SC and Analyzers (all versions) but not in ScaleChem Standard (any version). It is characterized by:

- The Helgeson equation of state for equilibrium constant values
- The MSE activity model for aqueous and non-aqueous phase liquids
- Soave-Redlich-Kwong equation of state for fugacity calculations.
- Concentrations allowable up to mole fractions of 1.0 of the solute.
- The activity of the hydronium ion (H_3O^+) is considered for the basis of pH[1]

Initializer

This a subprogram of the solver used to set up the initial values for the non-linear equations used for electrolyte simulations.

Interface

This is the graphical user interface where the user interacts with the software. ScaleChem Standard and Studio-SC were both developed using Microsoft Visual C++. Little or no calculations are performed by the interface except as noted in this document.

Restart Vector

This is a list of all the solved variables for a particular equilibrium simulation. Usually the restart vector is used to initialize the non-linear equation variables in a survey to speed up the calculation without having to use the initializer subprogram.

Solver

The solver is the numerical calculation engine. This program, called by the interface, performs all equilibrium, activity and phase partitioning calculations. It also performs specific type calculations as required by the interface. The solver is essentially the same for all OLI products except for ScaleChem Standard which uses its own solver.

1.3 Structure of the document

This document is structured to first discuss how ScaleChem Standard performs a calculation and then how Studio-SC performs a similar calculation. Finally a comparison of the two approaches will be discussed. In block outline form the structure will be:

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[1] Visit the OLI support website for a detailed description of calculating pH in the MSE framework:

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ScaleChem Standard Methodology

Studio-SC Methodology

Comparison/Differences between ScaleChem and Studio-SC

2.0 Analyses

2.1 Brines

2.1.1 Default phase behavior

ScaleChem Standard
Solid phases are prohibited from forming. If a solid is detected then a warning will appear. Any other phase is permitted to form.

Studio-SC
Solids are excluded from forming but not prohibited. A check box exists that lets user select one or more solids that are allowed to form. The other solids remain in solution.

Comparison/Differences
If a brine is reconciled using ScaleChem Standard and then the same brine is reconciled in Studio-SC the calculated pH may be different if solids are allowed to form. For example, if carbonate ions are present in solution, they may precipitate out in the Studio SC calculation. This will result in a lower pH being reported.

2.1.2 Electroneutrality
The solver uses a charge balance equation as part of the overall mass-balance equations. There are several options for making the sample electrically neutral. Here are the available methods:

ScaleChem Standard
ScaleChem Standard uses the interface to make the adjustments in electroneutrality.

Dominant Ion

This is the default method. The largest counter ion is added to balance charge.

Prorate Ion

The Prorate Ion method keeps the relative amounts of all deficient charged species the same and multiplies their value until the electroneutrality is achieved.

Na/Cl

Either sodium or chloride ion is added.

Make-up Ion

A single ion species chosen by the user will be added or removed.

User Choice

The user selects a cation/anion pair. Unlike the Make-up ion method, this method always adds material since both a cation and an anion are provided.

2.1.3 Density

The user has the option to either adjust the amount of water to match the input density (default), or to prorate the species concentration to match the input density.

Studio-SC

Studio-SC uses the ScaleChem Standard electroneutrality options. Studio SC uses the following approach for reconciling density.

Density

If the units are set to mg/L then the solver adjusts the amount of water (H_2O) to fix the solution (liquid phase) volume at 1.0 L. Solid, vapor, and oil phase volumes are ignored. The philosophy is that most water samples are measured in a laboratory and only contain a liquid water phase.

If the units are set to ppm (mass) then the amount of water is adjusted to make the water-phase solution exactly 1 kilogram.

Comparison/Differences

The major difference between ScaleChem Standard and Studio-SC is in the treatment of density. ScaleChem Standard used the measured density as the reliable value and adjusted the amount of water to match it. This way the user had an output value that matched the input value.

Normally the brine did not contain any other phases (unless the result of a saturation calculation) so the volume value was unimportant. If the brine had significant amounts of another phase – usually a solid – then that volume was also part of the density calculation.

Studio-SC takes the approach that the input volume assumed in the concentration unit is more reliable. The amount of water is adjusted accordingly. Since the sample should only contain the brine, the volumes of the co-phases are ignored.

2.1.4 pH and Alkalinity

ScaleChem Standard and Studio-SC use the same concept of pH and alkalinity. The alkalinity used is the total alkalinity with a titration end point pH (default pH = 4.5).

ScaleChem Standard

Reconciling pH and alkalinity is an iterative solver process. First the alkalinity is adjusted to the measured pH end point by adding or removing the inflow species CO_2. When the alkalinity end point is reached, the pH is then reconciled by adding or removing the inflow species HCl. Since adding/removing HCl affects total alkalinity a repetitive process is made to readjust the alkalinity. This, in turn, affects the pH which is then again reconciled. This process continues until there is no change in either the CO_2 or HCl inflow species.

Studio-SC

The methodology for reconciling pH and alkalinity is the same

Comparison/Differences

None.

2.1.5 CO₂ Fraction

The CO_2 fraction in gas calculation makes the assumption that brine is in contact with a production gas phase (usually at a gas-water separator). The brine pH can therefore be computed from the CO_2 partial pressure.

ScaleChem Standard

The mole fraction of CO_2 in the gas is entered by the user. The temperature and pressure at the contact point of the gas and water is also entered. The solver adds an amount of CH_4 to create a vapor phase. The solver then adjusts the amount of CO_2 inflow until the target mole fraction of CO_2 in the vapor is achieved. The equilibrium partitioning of CH_4, CO_2, and H_2O between the gas and water is computed. The results are saved to the brine. The gas phase results are also saved with the brine.

Studio-SC

The same calculation is run in Studio SC. However, only the amounts of CH_4 and CO_2 that are dissolved into the brine are saved to the brine. Any material in the vapor phase is discarded.

Comparison/Differences

To force a vapor phase, especially at elevated pressures, the solver uses an excess of non-condensable material such as CH_4. When the specified CO_2 fraction was met, there were several variables that could be saved to the brine.

$$CO_2(total) = CO_2(brine) + CO_2(vapor)^2$$

$$CH_4(total) = CH_4(brine) + CH_4(vapor)$$

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[2] CO_2 represents the sum of all carbonate ions in the phase such as CO_2, CO_3^{2-}, HCO_3^{1-}, etc.

What ScaleChem Standard saved to the brine was CO_2(total) and CH_4(total); the total values. When this brine was then used in a scaling calculation an unexpected vapor phase would sometimes appear due to the excess amount.

Studio-SC, by comparison saves CO_2(brine) and CH_4(brine) to the brine phase.

2.1.6 Equilibrium Calculation

The equilibrium calculation performs an isothermal calculation of the brine at the measured temperature, pressure, and dissolved species concentrations. This is the same isothermal calculation that is used in all OLI products. There is no difference between ScaleChem Standard and Studio-SC.

2.1.7 Total Dissolved Solids

The interface takes the brine species amounts (not the solid or vapor phases) returned by the solver and subtracts the amount of water. This is the mass of the solutes which is then divided by the brine volume (also returned by the solver).

The assumption is that there are no volatile species in the brine that will evaporate during a real TDS measurement. There is no difference between ScaleChem 4.1 and Studio-SC 9.0.

2.2 Gases

2.2.1 Normalized inflows

ScaleChem Standard
The user enters a gas composition. If the hydrocarbon content is not known, then the remainder of the gas is normalized using CH_4. For example if the H_2S composition is 2 mole % and the hydrocarbon is unknown then normalizing will add 98 mole % of CH_4.

OLI Studio-SC
OLI Studio-SC has the same functionality for normalization but also allows all the gas components entered to be prorated to 100 mole %.

2.2.2 Dew Point: Saturated Water Content

Frequently the gas composition is on a "Dry" basis. That means the water content was not measured. A dry gas strips (evaporates) water from brine in a scale calculation and can produce erroneous results. This Dew Point calculation avoids this problem by "saturating" the gas with water to simulate the real gas composition.

ScaleChem Standard
The mole fraction (or mole %) of H_2O is adjusted by the solver to create a saturated gas at a specified temperature and pressure. The target endpoint is when of 10^{-8} moles of excess liquid H_2O forms. The solution now has two

phases – a small amount of liquid and a vapor phase. It is possible that some solids can accumulate in the liquid phase. The calculation result can be saved as a new gas.

Studio-SC

The mole fraction (or mole %) of H_2O is adjusted by the solver to create a saturated gas at a specified temperature and pressure. The target endpoint is for the activity of H_2O in the gas and the water phase to be equal. The solution now has two phases – a small amount of liquid and a vapor phase. It is possible that some solids can accumulate in the liquid phase. The result can be saved as a new gas.

Comparison/Differences

To force a liquid phase the solver adds an excess amount of H_2O. When the specified condition was met, there were several variables that could be saved with the gas:

H_2O (Total) = H_2O(Liquid) + H_2O(vapor)

ScaleChem 4.1 saved the H_2O (Total) value. When this gas was used in a subsequent scaling calculation an unexpected liquid phase sometimes appeared. To eliminate this problem, Studio-SC saves H_2O(vapor) only.

2.2.3 Dew Point Temperature

ScaleChem Standard

The solver adjusts the temperature until a water phase forms. The target water amount is 10^{-8} moles.

Studio-SC

There is no corresponding calculation in Studio-SC, since this calculation can be performed as a dew point temperature survey in Studio Analyzer: Stream.

2.2.4 Dew Point Pressure

ScaleChem Standard

The solver adjusts the pressure until a water phase forms. The target water amount is 10^{-8} moles.

Studio-SC

There is no corresponding calculation in Studio-SC, since this calculation can be performed as a dew point pressure survey in Studio Analyzer: Stream.

2.3 Oils

2.3.1 Specific Gravity

ScaleChem Standard

The specific gravity of the oil can be entered. This value is used to convert volumetric flow into molar flow for the solver.

Studio-SC

There is no entry for specific gravity for Studio-SC. The volume of the oil is calculated from the ideal volumes stored in the databank.

2.3.2 Hydrocarbon Characterization

Both ScaleChem Standard and Studio-SC use the same methods for characterizing hydrocarbons. Studio-SC however has additional methods for the MSE thermodynamic framework which ScaleChem Standard does not have.

The characterization process includes the following general steps. The first step is to convert properties such as a boiling point or distillation curve into a set of pseudocomponents by performing a set of systematic cuts on the curve. Thereafter an average boiling point and density of each cut is estimated. Via standard correlations, molecular weight and critical properties of each cut are estimated. If any of the properties TB (boiling point), SG (specific gravity) or MW (molecular weight) are overwritten, then checks are made to ensure the component has realistic properties. These checks are detailed in the appendix. The final step is taking these thermodynamic properties and estimating OLI parameters such as Gibbs free energy of formation.

2.3.3 Characterization Methods

API

Both API-5 and API-8 characterization methods are supported.

Cavett

Cavett, R.H. 1962. Physical Data for Distillation Calculations – Vapor-Liquid Equilibria, 27th Mid-Year Meeting of the API Division of Refining, 42[III], 351-357

Lee-Kesler

Lee, B.I. and Kesler, M.G., 1975, A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States, AIChE J 21, 510-527

Kesler, M.G., and Lee, B.I., 1976, Improve Prediction of Enthalpy of Fractions, Hydrocarbon Processing 53 (3), 153-158

Assay Types

The purpose of entering assay data is to convert the data into a True Boiling Point Curve. From this boiling point curve pseudocomponents are created, which are then converted into OLI thermodynamic properties. There are four assay data methods supported in ScaleChem and Studio-SC:

- ASTM D86
- ASTM D1160
- ASTM D2887
- TBP Curve

In the case of ASTM data input, standard API techniques are applied to convert this data into an equivalent TBP curve.

Conversion to OLI properties

A discussion of how this is performed in the software is provided in Appendix 1.

2.3.4 Reconciliations

ScaleChem Standard

ScaleChem Standard performs a pressure or temperature survey depending on the user's choice. The calculation then plots the fraction of the vapor present in the calculation. The user will also specify a range for the survey.

Studio-SC

The calculations for Studio-SC are the same as for ScaleChem Standard.

2.3.5 Water (H_2O) Saturation

Frequently the oil composition is on a "Dry" basis. That means the H_2O content was not measured. A dry oil strips water from a brine in subsequent scaling calculations and can produce erroneous results. This calculation eliminates the problem by "Saturating" the oil with water to simulate the real oil composition.

ScaleChem Standard

The solver adjusts the amount of H_2O inflow until a liquid water phase of 10^{-8} moles is created. The solution now has two phases –an organic phase and a small amount of water. It is possible that some solids can accumulate in the non-organic phase. The results are saved as a new oil.

Studio-SC

The solver adjusts the amount of H_2O inflow such that the activity of H_2O in the water and organic phase are equal. The solution now has two phases – a small

amount of liquid and an organic liquid phase. It is possible that some solids can accumulate in the non-liquid phase. Only the amount of H_2O present in the oil after the adjustment is saved as the solution. The result can be saved as a new oil.

Comparison/Differences

To force a liquid phase the solver would use an excess amount of water. When specified condition was met, there were several variables that could be saved to the oil:

H_2O(Total) = H_2O(Liquid) + H_2O(vapor) + H_2O(oil)

ScaleChem Standard saved H_2O (Total). When this oil was used in a subsequent scaling calculation an unexpected liquid water or vapor phase would sometimes form. Studio-SC eliminates this problem by saving H_2O(oil) only.

3.0 Calculations

3.1 Global Solver Routine

All calculations in ScaleChem Standard and Studio SC are isothermal (and isobaric). These calculations use the standard equilibrium solver. A small electroneutrality adjustment is calculated for the brines. An alkalinity calculation can be included for each scaling calculation point.

ScaleChem Standard

A programming routine in the solver called the Initializer sets up the first calculation point. The initializer makes an initial guess on the final composition and properties, which helps solve the non-linear equilibrium equations.[3] Subsequent points are initialized by using the solution for the previous point. In the OLI parlance this reusing of the variables is said to use the "Restart Vector".

Studio-SC

Calculations in Studio-SC are also isothermal (and isobaric) calculations and the alkalinity at each point can be calculated (though not implemented as of V9.0.0)

The same Initializer programming routine is used for the initial guess to solve the non-linear equilibrium equations When the AQ framework is being used, subsequent points are initialized using the solution for the previous point. In the OLI parlance this reusing of the variables is said to use the "Restart Vector". This setting can be changed via the calculation options.

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[3] See the OLI guide to thermodynamics for a brief overview about how the equations are set up and solved.

When the MSE framework is used, subsequent points are initialized by the initializer. The restart vector is not used. This setting can be changed via the calculation options.

Comparison/Differences

During the development of MSE-based modeling it was found that the restart vector occasionally produced inconsistent results. The problem has yet to be fully resolved but by forcing MSE-based calculations to use the initializer there is a better chance obtaining a realistic solution. This work is in progress.

3.2 Scaling Scenarios

ScaleChem Standard

The calculation approach in ScaleChem 4.1 is described in the Global Solver Routine above.

Studio-SC

The calculation approach in Studio SC is described in the Global Solver Routine above.

Comparison/Differences

The differences between the two products are described in the Global Solver Routine above.

3.3 Saturator Study

ScaleChem Standard

The saturation calculation is similar to the precipitation point calculation in the OLI Analyzers. Inflow species is adjusted to match a target value of 10^{-6} moles of the solid phase. This saturation calculation occurs for each point in the study. The saturated brine, gas or oil is optionally saved for the last point in the study.

The solver calculation approach in ScaleChem Standard is described in the Global Solver Routine above.

Studio-SC

The saturation calculation is similar to the precipitation point calculation in the OLI Analyzers. Inflow species is adjusted to match a target value of 10^{-6} moles of the solid phase. The Studio-SC saturator calculation is performed for a single point.

The solver calculation approach in Studio SC is described in the Global Solver Routine above.

Comparison/Differences

Comments about the restart vector for MSE found in the Scaling Scenario discussion apply to the saturator calculations as well.

It was found that most saturator applications were single temperature-pressure point calculations. In previous versions of ScaleChem Standard it was thought that a converged answer may need the restart vector approach so multiple points were allowed to approach the answer from less severe conditions. In later versions of ScaleChem Standard this was not necessary.

Studio-SC eliminated the ability to use multiple points (surveys) for the Saturator Calculation.

3.4 Mixer

The concept of a mixer calculation (which is not to be confused with a MIX calculation in the Analyzers) was to take two brines with an optional gas or oil and mix then isothermally in various ratios.

ScaleChem Standard

The mixing waters calculation takes two brines with a combined flow rate. An optional gas or oil can be added, each with a specified flow rate. One temperature and pressure value is entered. The brines can be mixed in the following ways:

- Ratio – The multiplier of the first brine is fixed between 0 and 1. The multiplier of the second brine is set to a value 1 minus the first value. For example if the multiplier of the first brine is set to 0.7 the second brine multiplier is set to 1.0 – 0.7 = 0.3
- Percent – this is similar to ratio except that the sum value is 100 and not 1. For example if the ratio of the first brine is set to 70% the second brine ratio is set to 100% – 70% = 30%
- Flow – this takes total brine flow as specified by the user and subtracts out the setting for the first brine. For example if the total flow is 1200 bbl/day and the first brine is set to 300 bbl then the second brine is 1200 bbl/day – 300 bbl/day = 900 bbl/day

The last point of the mixing waters calculation can be optionally saved as a new brine, gas and/or oil.

The initializer, solver, and Restart Vector method described in the Global Solver Routine are also used in this calculation.

Studio-SC

Studio-SC uses the same mixing approach as ScaleChem.

The initializer, solver, and Restart Vector (AQ framework only) method described in the Global Solver Routine are used in this calculation.

Comparison/Differences

There are no significant differences between the mixing approaches of the two programs.

3.5 Facilities

Facilities calculations are often thought of as a mini-process-flowsheet.

ScaleChem Standard

The Facilities calculation takes brines, gases and oils – each with a specified flow rate – and mixes them at a specified temperature and pressure. This mix is referred to as a "Node". The resultant brine, solid, gas and oil phases may be used in a subsequent calculation or a new node. Any brine, gas or oil is automatically transferred to a downstream node. The user has the option to prevent any solids from being transferred downstream (also known as "Dropped Solids").

The solver routine is slightly different from the other calculations. The Solver makes an initial guess for each point to set up the non-linear equations used to solve the equilibrium. This process is completed by a portion of the solver called the initializer. **There is no restart vector** for these calculations since each node may be very different from the upstream node.

Studio-SC

The Facilities calculation takes brines, gases and oils – each with a specified flow rate – and mixes them at a specified temperature and pressure. This mix is referred to as a "Node". The resultant brine, solid, gas and oil phases is automatically transferred to a downstream node unless the user has optionally selected to separate the gas or oil or drop solids.

The solver approach is similar to ScaleChem Standard in that the initializer and solver routines are used. The restart vector is not used.

Comparison/Differences

The facilities calculation in Studio-SC is more graphical than in ScaleChem. The user can see immediately if they have separated phases. This interface however does not change the way that mass is transferred from one node to the next.

3.6 Contour Plot

ScaleChem Standard

This calculation does not exist in any version of ScaleChem.

Studio-SC

Contour plots are obtained from a set of isothermal (and isobaric) calculations. These calculations use the standard equilibrium solver. The contour plot is built on the Analyzers ability to perform dual surveys.

The contour plot calculation takes brines, gases and oils – each with a specified flow rate – and mixes them at a specified range of temperatures and pressures.

The initializer, solver, and Restart Vector method described in the Global Solver Routine is used here.

Only the scaling tendencies (pre-scaling and actual scaling) are stored for display.

## 3.7 Reservoir to Surface

ScaleChem Standard

This calculation does not exist in any version of ScaleChem.

Studio-SC

The Reservoir-to-Surface calculation is designed to answer the question "What is the reservoir fluid composition based on what is measured at the surface?" As many ScaleChem clients know, sampling techniques are very important to obtain an accurate fluid representation. Loss of carbon dioxide on the way to the laboratory is a common (and unobserved) error when measuring brine concentrations.

The user enters an initial gas, oil, and brine compositions. They also enter the conditions where these phases are separated at the surface (e.g. high or low pressure separator). Lastly they enter the formation mineralogy. From this input data, the software back-calculates a reservoir fluid. We call this the "Whole Fluid."

The schematic below is symbolic of what this calculation simulates.
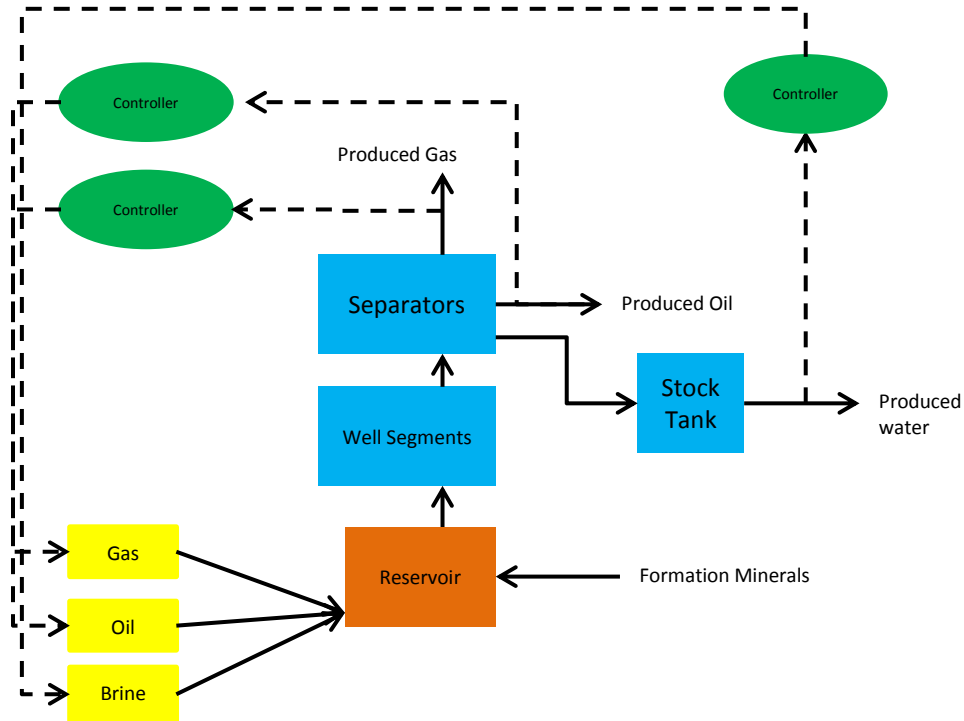
The user enters the temperature and pressure for all blocks: reservoir, well segments, separators and stock tank. The stock-tank flow rates and sample compositions are entered for produced gas, oil and brine. The controllers, internal to the calculation, attempt to adjust the flow rates of the produced gas, oil and water by adjusting the flows of their corresponding objects in the reservoir. The H_2S and CO_2 composition in the gas (and oil) are adjusted by altering the gas composition into the reservoir. The brine composition is adjusted by saturating the brine with known minerals from the formation minerals.

The product of this calculation is the whole fluid leaving the reservoir block.

The Reservoir-to-Surface object is available in version 9.0 of Studio-SC for the Produced Water Group members only, pending validation of this new calculation against field results.

Appendix 1 – Conversion to OLI properties from Assays to pseudocomponents

The starting point for the development of OLI parameters is to assume that the pseudocomponent is a sparingly soluble organic in water. We begin this process be developing an equilibrium constant for the vapor-liquid equilibrium.

$$K_{p_i} = \frac{55.51 * V_w * S_i}{V_{p_i}}$$

(1)

Where:

K_{pi}= equilibrium constant for species "i" (1/atm)

V_w = molar volume of water (m^3/mole)

S_i = solubility of species "i" in water (mole/m^3)

V_{Pi}= pure component vapor pressure (atm)

To utilize any other set of units, it becomes necessary to develop the appropriate conversion factors and to build them into the above equation. For example, it is often convenient to utilize V_w in cm^3/mole and S_i in wt% (g/100g solution).

The conversions are as follows:

V_w (m^3/mole) = 10^{-6} * V_w (cm^3/mole)

S_i (mole/m^3) = (10^4 * RHO$_w$ / MW$_i$) * S_i (gm/100 gm H$_2$O)

Note that for sparingly soluble substances in water, 100 g solution is, in the limit, the same as 100 g of H$_2$O.

Thus, the following formula should be used in conjunction with the following set of units:

K_{Pi} = 0.5551 * V_w * S * RHO$_w$ / (V_{Pi} * MW$_i$)

Entity	Units
K_{Pi}	atm

V_w	cm^3/gmole
S_i	g/100 gm H$_2$O
RHO$_w$	g H$_2$O/cm^3
V_{Pi}	atm
MW$_i$	g/gmole

A further simplification can be made by observing that V_w * RHO$_w$ in these units is exactly 18.015 and thus the equation can be written:

$$K_{p_i} = \frac{10 * S_i}{\left(V_{p_i} * MW_i\right)}$$

Thus, based upon this relationship, the equilibrium constant as a function of temperature, K(T), can be developed. If we now recognize that the VLE K is simply related to the difference in the free energy between the vapor and the aqueous molecular species, we can use available thermodynamics for the vapor phase to back out the free energy for the aqueous molecule.

Once we have the free energy of the aqueous molecule as a function of temperature, we can do a linear regression for the Helgeson equation of state coefficients. The reference state free energy for the aqueous molecule can be obtained directly from the knowledge of the VLE K at the reference state and the free energy of the vapor at this temperature.

The HREF for the aqueous molecule can be obtained from the van 't Hoff equation which relates the difference the reference state enthalpy for the vapor and aqueous molecule to the first derivative of the VLE K(T) with respect to temperature. Finally, the SREF for the aqueous molecule can be obtained from the third law of thermodynamics since both vapor and aqueous molecule free energy and enthalpy are known at that point.

Derivation of Equation (1)

The starting point in derivation of equation (1) is based upon the definition of equilibrium which is that the chemical potential, or Gibbs free energy of each species in the vapor phase and aqueous phase is equal. Specifically:

$G_i(VAP) = G_i(AQ)$

In each case, the Gibbs free energy can be expressed by the sum of a standard state contribution and an excess contribution:

$$G_{i'(vap)}+RTln(F_{i(vap)} * p_i)=G_{i'(aq)}+RTln(f_{i(aq)} * m_i)$$

where:

G_i = Gibbs free energy

G_i' = standard state Gibbs free energy

R = gas constant

T = absolute temperature

f_i = fugacity (activity) coefficient

VAP = vapor phase

AQ = aqueous phase

p_i = partial pressure

m_i = molality in the aqueous phase

Rearranging terms we get:

$$K_{p_i} = exp\left(\frac{('G_{i(aq)}\text{-}G_{i'(vap)})}{RT} \right) = \frac{f_{i(aq)} * m_i}{(f_{i(vap)} * p_i)}$$

(3)

We now make two assumptions upon which the rest of the derivation is based:

(1) The organic i is sparingly soluble in water.
(2) Water is sparingly soluble in the organic liquid.

Using assumption number 1, we can approximate m_i:

m$_i$ = 55.51 * x$_i$ (3)

Using assumption number 1 and the asymmetric convention for aqueous activity coefficients:

f$_i$(AQ) = 1.0   (4)

Using assumption number 1, we can approximate x$_i$:

x$_i$ = V$_w$ * S$_i$ (5)

Finally, using both assumptions:

 p$_i$ = Vp$_i$ (6)

p$_w$ = Vp$_w$

These equations can be best understood by considering the following process. We take a volume of liquid water and a volume of pure liquid organic at an equal pressure which assures that both species are in the liquid state. We next allow them to come to liquid -liquid equilibrium still as a pressure above that which allows vapor to form via equilibrium. We next lower the pressure to the bubble point. At this point all 3 phases are in equilibrium which implies that any two phases are in equilibrium. By assumption 2, above, we have an organic phase which is almost purely organic in equilibrium with a vapor. Clearly, in the limit as the organic approaches the pure substance, p$_i$ approaches Vp$_i$, the pure component vapor pressure. By assumption 1, above, we have an aqueous phase which is almost pure water in equilibrium with a vapor. Clearly, in the limit as the water approaches the pure substance, p$_w$ approaches Vp$_w$.

In addition, it follows that total Pressure = Pt = Vp$_i$ + Vp$_w$ and:

y$_i$ = Vp$_i$ / Pt

y$_w$ = Vp$_w$ / Pt

When approximations (3-6) are substituted in (2), we get:

$$K_{P_i} = \frac{55.51 * V_w * S_i}{V_{p_i} * f_{i(vap)}}$$

This is the same as equation (1) except for the presence of $f_i(VAP)$. Since $f_i(VAP)$ is a function of the four known quantities, T, Pt, y_i and y_w, we can calculate this quantity (which does not, in general, approach any particular limit) directly.

Appendix 2 – Rules used to calculate the third property given two (or three) of TB, SG, MW

TB/SG/MW entered:

- Calculate Watson K = $TB^{1/3}$ / SG
- If 9.5 ≤ K ≤ 12.5, use the given SG
- Else limit to 9.5 or 12.5 and use the SG calculated at this limit

TB/SG entered:

- Calculate Watson K = $TB^{1/3}$ / SG
- If 9.5 ≤ K ≤ 12.5, use the given SG
- Else limit to 9.5 or 12.5 and use the SG calculated at this limit
- MW calculated by API 5/8

TB/MW entered:

- If API8 and (TB < 90 F or TB > 1500 F) then set K=11, and calculate SG
- Else get SG limits (API8: 9.5 < K < 12.5) (API5: 0.228 < SG < 1.6)
- Iterate to find the SG that will give the MW entered
- If SG outside limits, limit SG, but leave TB/MW as entered

SG/MW entered:

- Set limits for SG (API8: 0.6 < SG < 1.25) (API5: 0.228 < SG < 1.6)
- Set limits for TB (API8: 9.5 < K < 12.5) (API5: 360R < TB < 2500R)
- If SG outside limits, set K=11, calculate TB
- Else using given SG, calculate MW at TB limits
- If given MW outside MW limits, set TB = limit and use MW at that limit
- Else iterate to find the TB that will give the MW entered