OLI Tips #19

Explaining true species versus apparent species

In the OLI electrolyte world, there are two methods of representing an aqueous solution. These are the true and apparent species views. Let's start with an example, consider the following input composition:

Temperature	25	^oC
Pressure	1	Atmosphere
H_2O	0.7	moles
$KHCO_3$	0.3	moles

The OLI electrolyte engine will evaluate its equilibrium equations to provide for the following solution composition:

```
pH                   7.99597
Species              Aqueous        Solid          Vapor
Total mol/hr         0.7916982      0.254294       2.86854E-04
------------------   mol/hr--------mol/hr--------mol/hr--------
H2O                  0.700565       0.0            8.26969E-06
CO2                  2.94920E-04    0.0            2.78584E-04
OHION                1.21606E-08    0.0            0.0
HCO3ION              0.0445589      0.0            0.0
HION                 1.05672E-10    0.0            0.0
KION                 0.0457059      0.0            0.0
CO3ION               5.73492E-04    0.0            0.0
KHCO3                0.0            0.254294       0.0
```

This is the "True" species, or rather the "Ionic", representation. As you can see the solution pH is 7.99597 and there are three phases present. Some of the input material is present as a solid phase, some present as a vapor phase the remainder is in the aqueous phase.

Some users prefer not to view this composition as true species instead preferring a molecular view. This is often preferable when the user has to translate the information to other computer programs which don't accept ions.

The following solution composition is a molecular view of the same stream:

pH	7.99597		
Species	Aqueous	Solid	Vapor
Total mol/hr	0.7911252	0.254294	2.86854E-04
------------------	mol/hr--------	mol/hr--------	mol/hr------
H2O	0.699992	0.0	8.26969E-06
CO2	0.0454273	0.0	2.78584E-04
KHCO3	0.0	0.254294	0.0
KOH	0.0457059	0.0	0.0

As you can see, the pH is identical to the true representation. You can also see that the solid $KHCO_3$ has the same value of 0.254294 moles/hour. The two vapor components also have the same values: H_2O = 8.26969E-06 mole/hour and CO_2 = 2.78584E-04 mole/hour. These value did not change in this view since they were already a molecular form.

The next question that arises is where did the KOH come from and where did the CO_2 come from in the Aqueous column.

The CO_2 is an easier question to answer. Let's consider all the equilibria equations that make up this calculation:

1: $CO_{2aq} + H_2O = H^+ + HCO_3^-$
2: $CO_{2VAP} = CO_{2AQ}$
3: $H_2O = H^+ + OH^-$
4: $H_2O_{VAP} = H_2O$
5: $HCO_3^- = H^+ + CO_2^{2-}$
6: $KHCO_{3PPT} = K^+ + HCO_3^-$
7: $KOH_{ppt} = K^+ + OH^-$

To have CO_2 in the vapor phase (CO_{2vap}) you must also have some CO_2 in the aqueous phase. Equation 2 shows this fact.

What about KOH? Where did it come from? There are a few rules in the OLI software that must be obeyed. First, besides the input components you entered, the program will automatically add a input component for every vapor and neutral aqueous species that is detected in the equation set. Thus we automatically add CO_2 as an input component.

A second rule is that for every solid that may possible appear we must also add an input component. In this model there are two possible solids, $KHCO_3$ and KOH. We already entered $KHCO_3$ so the program automatically adds KOH. Our actual input component list is:

Temperature	25	^oC
Pressure	1	Atmosphere
H_2O	0.7	moles
$KHCO_3$	0.3	moles
CO_2	0	moles
KOH	0	moles

The last two components have been grayed out to indicate that the program added them and not the user.

When converting the true (ionic) species into the molecular (apparent) species, the program must use the full list of input components. The rules that apply for this conversion are that any vapor, neutral aqueous or solid component must be mapped back to its corresponding input component. This leave us with the aqueous species of:

```
Species              Aqueous
------------------   mol/hr--------
OHION                1.21606E-08
HCO3ION              0.0445589
HION                 1.05672E-10
KION                 0.0457059
CO3ION               5.73492E-04
```

The program will now automatically convert these ions into the available molecular species. To fully account for the mass, the program may “Borrow” ions from some of the molecular species already converted. You can see from the above list that we have 0.0457059 moles of K^+ ion and only 0.0445589 moles of HCO_3^- ion. If we create 0.0445589 moles of $KHCO_3$ as an input component, we have .001147 moles of excess K^+. The other ions are insufficient to balance this species so we have to “Borrow” some ions from a neutral species. The largest concentration of neutral species in aqueous solutions is water. We borrowed .001147 moles of OH^- from water to make KOH. We, of course, change the amount of water to reflect this borrowing.