Chemstations™

ELECTROLYTES IN CHEMCAD

Adding Electrolytes in a CHEMCAD Simulation

Overview

This document describes the procedure of adding an electrolyte reaction to a simulation in CHEMCAD, using sodium acetate as an example.

The data used on this document has been extracted from The *NBS Tables of Chemical Thermodynamics Properties* (1982). This public government document discusses how to adapt data from other sources to be consistent.

About the Components: Regular Components, Ion Species, and Molecular Species

The electrolyte models in CHEMCAD rely on the use of *ion species* and *molecular species* analog for component data. These species components have a very limited amount of physical property data. Only formula, molecular weight, and a few parameters for the electrolytes model are specified for a species.

An *ion species* component is a charged ion, such as 1009 Cl- or 1002 H+. A *molecular species* is a neutral component that represents the actual component in your list. The species 1017 HCl is the molecular species analog for 104 hydrochloric acid. It is important that the actual component be used (e.g., *Hydrochloric acid*) in simulations; the molecular species analog exists for CHEMCAD's use. This is discussed in the documentation of Erbank.sf.

About the Data

With electrolyte reactions, we are interested in the dissociation constant *K*, where:

$$K = \frac{[H^+][A^-]}{[HA]}$$

for the electrolyte dissociation of:

$$HA \leftrightarrow H^+ + A^- .$$

There are two ways to determine the value of *K* with CHEMCAD. If you have temperature-dependent data, it can be regressed into coefficients for the equation:

$$\ln(K) = A + B/T + C(\ln(T)) + DT + ET^2 .$$

This is not discussed in this document. If you have no data for the dissociation, CHEMCAD can *approximate* the dissociation from thermodynamic properties of the ions. The following information is required for this approximation: heat of formation, Gibbs of formation, molecular weight, and either entropy or heat capacity of the ion. Note that all properties are at standard-state conditions.

This data can be found in the Wagman reference listed below. The equations used to estimate dissociation from these parameters are found on pp. 33-35 of Zemaitis. *The approximation for K is not always representative of real-world behavior. Test the results of your model to verify that the equilibrium dissociations predicted by CHEMCAD are reasonable. This is an approximation method which may not give stable or accurate results.*

The Example

This tutorial details how to set up an electrolyte reaction for sodium acetate. Sodium acetate dissociates with the following reaction, which is not in the standard CHEMCAD database.

Sodium Acetate: $NaCH_3CO_2 \leftrightarrow Na^+ + CH_3CO_2^-$

Data for the regular sodium acetate component and ionic species Na^+ is available in the CHEMCAD database. Information on molecular species $NaCH_3CO_2$ and ionic species $CH_3CO_2^-$ is required to create the reaction model.

The following data was obtained from *Wagman*:

Substance	MW	ΔHf (kJ/mol)	ΔGf (kJ/mol)	S J / (mol K)	Cp J / (mol K)
$NaCH_3CO_2$	82.035	-726.13	-613.2	145.6	40.2
CH_3CO_2-	59.0452	-486.01	-369.31	86.6	-6.3

Setting Up the Regular Component for Your System

This step is not necessary for this particular example because sodium acetate is already in the CHEMCAD database.

For sodium acetate ($NaCH_3CO_2$):

1. Create a new component (Thermophysical > Database >New Component).
2. Specify data for the component. The formula and molecular weight must match those of the 'molecule' species.

Setting Up the Ion and Molecule Species for Your System

For sodium acetate ($NaCH_3CO_2$):

1. Thermophysical > Database > copy component 1206, NaCl.
2. Thermophysical > Database > View/Edit the new component.
3. Change the Synonym/Name to *NaCH3CO2*.
4. Change the Formula to *NaCH3CO2*.
5. In the Basic data section, enter the correct Molecular weight.
6. Now click the Electrolytes data button on the 'view/edit' toolbar.
7. Set the ion to aqueous and molecule.
8. Enter the correct molecular weight (this value is not updated from previous screen).
9. Enter the remaining information. Press [F6] to call the units converter, if the data is in different units.

For CH_3CO_2:

1. Thermophysical > Database > copy component 1009, Cl-.
2. Repeat the procedure described above, except this is aqueous and anion.
3. Click the Class button on the 'view/edit' toolbar
4. The field electrolytes and true species must both have check marks.

Using the New Electrolytes in a Simulation

1. Start a new simulation.
2. Put the following components in the list: 62 water and 1239 sodium acetate.
3. Now go to Thermophysical > Electrolytes.
4. Click OK on the message that warns you CHEMCAD is going to choose electrolytes.
5. In the Electrolyte Species Selection box, add 1198 Na+, and the components you created for NaCH3CO2 and CH3COO1, as shown on Figure 1.

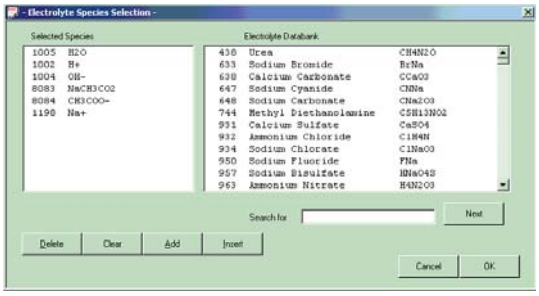

Figure 1: Electrolyte Species Selection Dialog

6. In the General Electrolyte dialog, add 1 to the 'n of reactions' and choose $NaCH_3CO_2$ as 'may form solid', as shown on figure 2. This selection allows CHEMCAD to consider this component as a possible salt/precipitate.

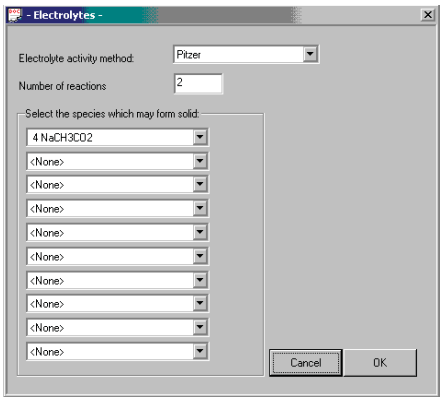

Figure 2: General Electrolyte Dialog

7. Fill out the blank Equilibrium Data dialog as shown on Figure 3.

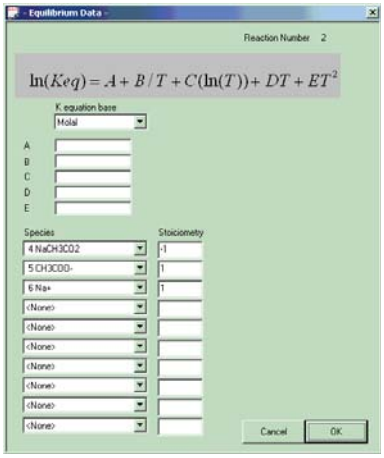

Figure 3: Equilibrium Data Dialog

8. Click **OK** to the Henry's constant and Pitzer screens, then click **Exit** on the electrolytes menu.

The electrolytes **apparent species** model is now being used by the simulation. The model is considering sodium acetate as a dissociating electrolyte. When you flash a stream the temperature and VLE will be adjusted for the heats of dissociation. This is a 'back of envelope calculation' approach.

Turning On the Electrolyte True Species Model

1. Go to Thermophysical > Electrolytes.
2. Press OK at the species selection screen.
3. Go to the General page and checkmark convert to true species.
4. Click **OK**.
5. Click **Exit** to close the electrolytes setup screens.

This simulation is now running in 'true species' electrolytes mode. When you clicked **Exit**, CHEMCAD copied the ions from the species list to the end of your component list. Stream dialogs show molecules and ions.

If you enter T, P, water, and sodium acetate flow rates for a stream, and then click **Flash**, CHEMCAD will calculate the dissociation. Note that they *may form solids*, instructs CHEMCAD that any sodium acetate which does not dissociate will form a solid or precipitate.

You will need to follow this procedure for every simulation in which you use the new electrolyte reactions unless you modify EMAP.SF and ERBANK.SF. If you modify the .SF files, save the modified files as .UF files and the reactions will be available in all CHEMCAD simulations you create.

References

1. Wagman, D.D.; Evans, W.H.; et al, *The NBS Tables of Chemical Thermodynamic Properties. Selected Values for inorganic and C1 and C2 organics substances in SI Units*; Volume 11, Supplement No. 2, 1982.

2. Zemaitis, Clark, et al., *Handbook of Aqueous Electrolyte Thermodynamics*, AICHE/DIPPR, 1986.