

# Studies on Hydrogen-Pinch Analysis and Application of COSMO-SAC to Electrolytes

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## **Abstract**

This thesis describes the results of two process system engineering studies: (1) hydrogen pinch analysis; and (2) application of COSMO-SAC (conductor-like screening model – segment activity coefficient) to electrolytes. Part (1) presents an automated spreadsheet method that can quickly help minimize fresh hydrogen consumption and maximize hydrogen recovery and reuse in petroleum refineries and petrochemical complexes. Part (1) has appeared as a featured article on engineering practice in the *Chemical Engineering Magazine*, volume 115, pp. 56-61, June 2008. We present an automated spreadsheet on our research group website ([www.design.che.vt.edu](http://www.design.che.vt.edu)) and describe procedures for using the spreadsheet in this thesis. Part (2) discusses the application of the conductor-like screening model – segment activity coefficient (COSMO-SAC), a liquid-phase activity-coefficient model, to electrolytes. We offer detailed procedure for obtaining sigma profiles for electrolytes. A sigma profile is a molecular-specific probability distribution of the surface-charge density, which enables the application of solvation-thermodynamic models to predict vapor-liquid and solid-liquid equilibria, and other properties. We propose to add an additional term to the exchange energy to account for ion-ion attractive and repulsive forces. We also look at the resulting exchange energy behavior. Although accurate numerical results are not achieved, we are able to produce results that match literature data by adding an adjustment factor.

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## **PART 1: Studies on Hydrogen-Pinch Analysis**

### **1 Introduction**

In petroleum refineries and petrochemical complexes, there are many hydrogen consumers, such as hydrotreaters, hydrocrackers, isomerization units, and lubricant plants. There are also hydrogen producers, such as hydrogen plants and naphtha reformers. Through a systematic analysis of hydrogen sources and demands (sinks), hydrogen-pinch analysis<sup>1-8</sup> attempts to minimize the flow rate of fresh hydrogen makeup and off-gas discharge, as well as maximize the flow rate of hydrogen recovery and reuse, possibly through off-gas purification techniques.

#### **1.1 Mass Balance**

The first step in the hydrogen-pinch analysis is to perform a mass balance on hydrogen sources and demands in the hydrogen network. Hydrogen sources include fresh (or makeup) hydrogen and recycle hydrogen streams, outlet streams from hydrogen producers (for example, steam reformers), product and residue streams from hydrogen purifiers (for example, membrane separation, pressure swing adsorption (PSA), or cryogenic distillation), off-gas streams from high-pressure or low-pressure separators, and off gasses from hydrogen-consuming units (for example, hydrotreaters and hydrocrackers).

Hydrogen demands consist of inlet streams to hydrogen-consuming units, any exported stream (including streams sent to fuel), and feed streams to hydrogen purifiers. For each stream, we specify the flow rate, pressure and hydrogen purity. We must use standard volumetric flow rate or molar flow rate.

#### **1.2 Various Approaches**

Simply, hydrogen pinch is the purity at which the hydrogen network has neither hydrogen surplus nor deficit. The pinch shows the bottleneck for how much hydrogen we can recover and reuse. The current approach to hydrogen-pinch analysis<sup>1,2,6,7</sup> does not consider hydrogen pressure, but the analysis does provide a *theoretical* minimum fresh hydrogen requirement and gives significant insights to hydrogen savings and off-gas purification in petroleum refineries. Changes to the real network necessary to achieve this minimum might be as easy as opening and closing some valves, or as daunting as adding a multistage compressor to connect low-pressure sources to high-pressure demands. An intermediate change could be adding cascades between

the purge of one unit and the makeup of another<sup>3</sup>. To account for stream pressure in refinery hydrogen management, we can apply mathematical optimization techniques<sup>4,5,8</sup>.

Early approaches to hydrogen-pinch analysis<sup>1,2</sup> are graphical and iterative in nature, and require an initial assumption of the fresh hydrogen flow rate. The analysis involves plotting the purity versus flow rate for all hydrogen sources and demands, known as the hydrogen source-demand plot or the hydrogen composite curves. The area enclosed between the source and demand composites yields the hydrogen surplus diagram. To identify the hydrogen pinch, we need to repeat the graphical procedure several times with different fresh hydrogen flow rates until there is neither hydrogen surplus nor deficit.

A recent method for hydrogen-pinch analysis is the graphical method by Zhao et al.<sup>7</sup>. This method involves graphically moving the source and demand composite curves according to some guidelines, and eliminates the need for a hydrogen surplus diagram. All of these iterative methods suffer from the inaccuracy in reading and representing data typically associated with a graphical technique, and have not been tested with a multiple-pinch network where there are additional complications in developing the hydrogen surplus diagram.

Recently, Foo and Manan<sup>6</sup> proposed a gas-cascade analysis (GCA) technique for hydrogen-pinch analysis. Unfortunately, their technique has some limitations. First, the GCA technique does not allow the user to represent multiple source and demand streams having the same purity as separate streams with individual flow rates. Instead, it lumps together all streams with the same purity as a single stream. As a result, the user is unable to see the individual flow rates. This prevents the user from understanding the effects of changing the flow rate of an individual stream, making it difficult to do a sensitivity analysis. Second, it is important to label each stream with a name, which the GCA technique does not do. Specifying the stream names helps the user identify the hydrogen sources and demands that have significant effects on the hydrogen pinch. Third, to identify the pinch, the GCA technique still requires an initial assumption of a fresh hydrogen flow rate and goes through two iterations.

Part (1) of this thesis presents an automated pinch spreadsheet based in Excel that enables the user to quickly and accurately identify the hydrogen purity at the pinch point and the minimum flow rates of hydrogen utilities without an iterative graphical construction. The spreadsheet represents all streams with the same hydrogen purity separately as individual streams, can handle multiple-pinch problems easily, and is efficient in studying the quantitative

effects of varying flow rates of hydrogen utilities and adding off-gas purification techniques. Our hydrogen-pinch spreadsheet is an extension of our recent work on water-system optimization<sup>9</sup>.

### 1.3 Hydrogen-Consumer Model

Figure 1 shows a typical hydrogen-consuming process, and Figure 2 shows a standard hydrogen-consumer model to represent this typical process. Note that the off-gas stream from the separator is a hydrogen source. Its flow rate is the sum of the flow rates of recycle and purge streams. The inlet gas to the reactor is a hydrogen demand (sink). Its flow rate is the sum of the flowrates of the makeup and recycle streams.

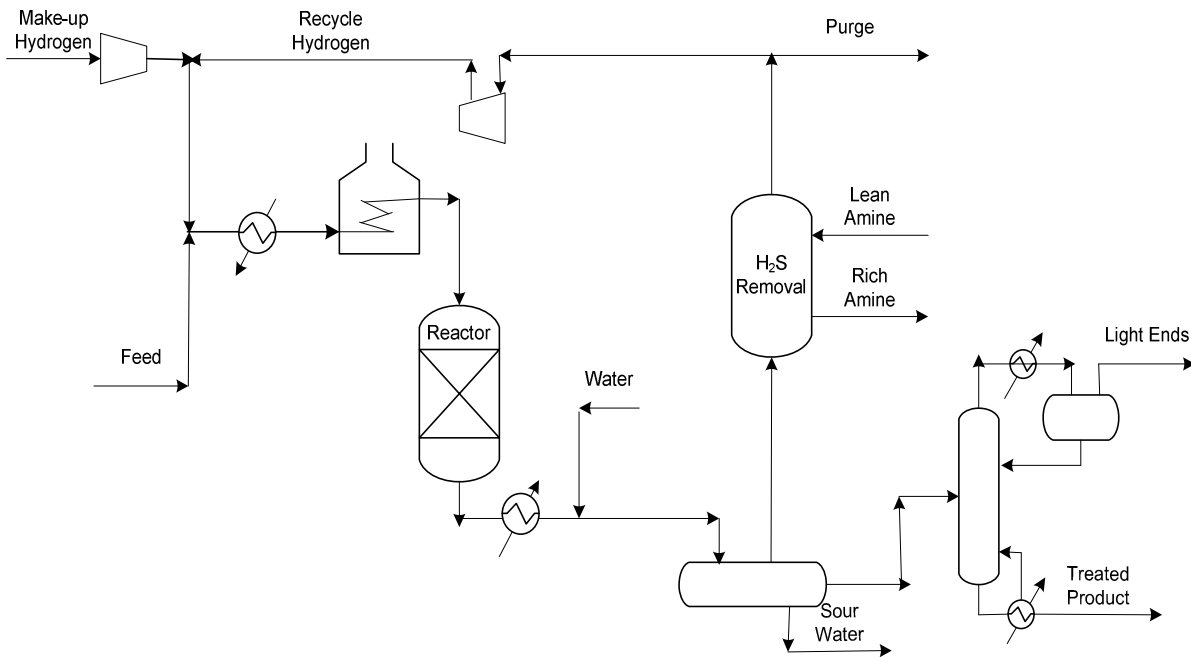
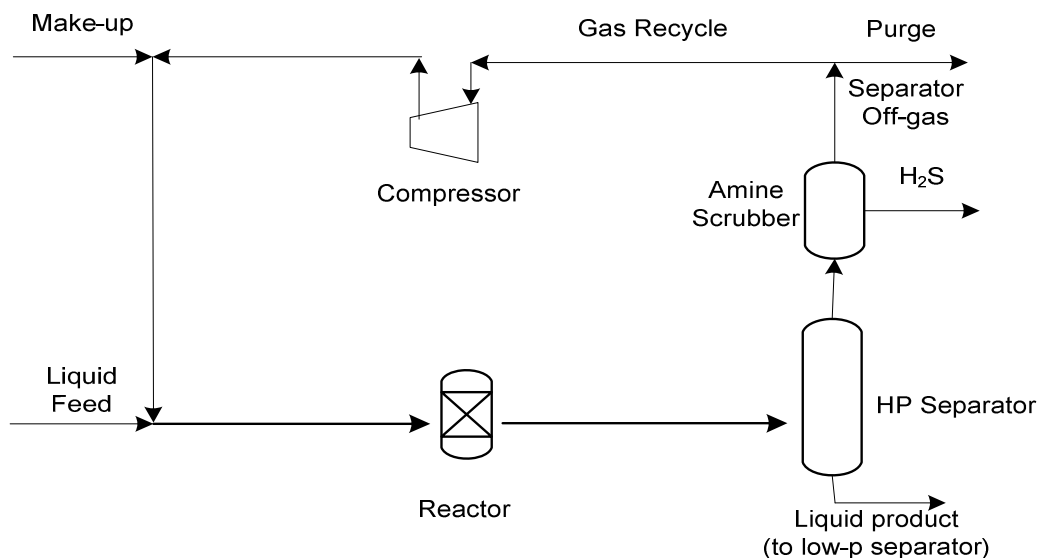


Figure 1: A typical hydrogen-consuming process<sup>10</sup>.



**Figure 2: A standard hydrogen consumer model.**

## 2 Hydrogen-Pinch Spreadsheet

The reader may freely download our automated hydrogen-pinch spreadsheet from our website ([www.design.che.vt.edu](http://www.design.che.vt.edu)). The user must click “Enable Macros” when opening the spreadsheet. We demonstrate its principles and applications by using Example 1 in Figure 3.

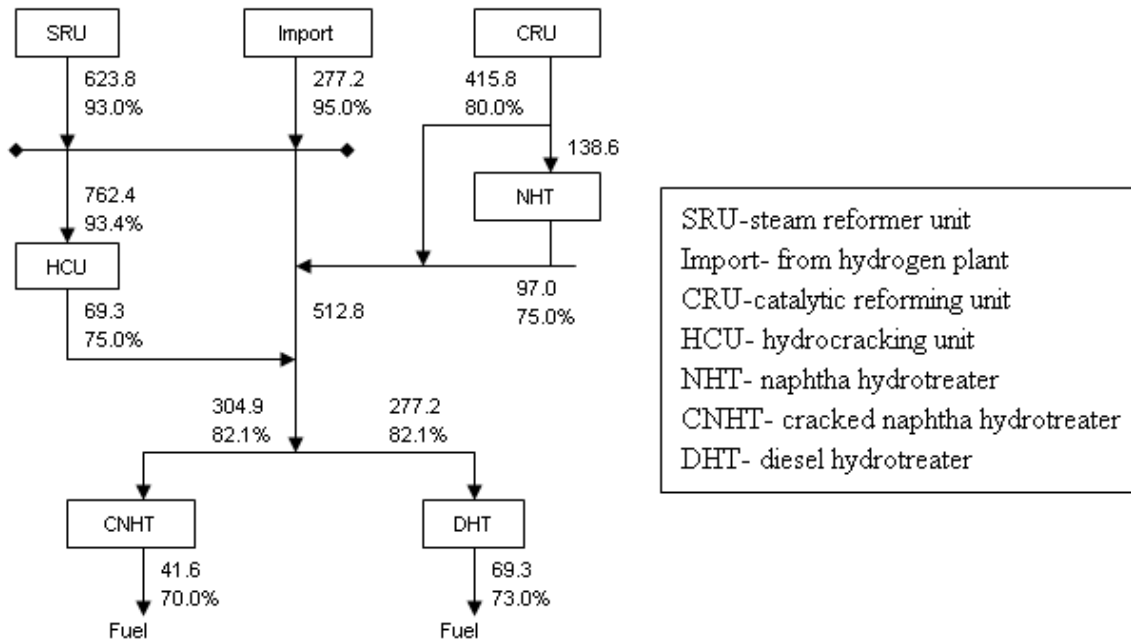
### 2.1 Example 1

As a first example we apply the preceding definitions of hydrogen source and demand to the hydrogen network of Example 1 in Figure 3<sup>1,6</sup>, to develop the table of stream data in Table 1 and Table 2. This example has seven hydrogen sources, including fresh hydrogen (import), outlets from two hydrogen producers (steam-reforming unit SRU and catalytic reforming unit CRU), and off gasses from four hydrogen-consuming units with each representing the sum of recycle and purge streams. The data for the fresh hydrogen (import) and outlets from two hydrogen producers (steam-reforming unit SRU and catalytic reforming unit CRU) are in Table 1. The four off-gas streams are HCUout from the hydrocracking unit, NHTout from the naphtha hydrotreater, CNHTout from the cracked naphtha hydrotreater, and DHTout from the diesel hydrotreater, as listed as sources in Table 2. There are also four hydrogen demands, including the inlets to four hydrogen-consuming units with each representing the sum of the makeup and

recycle hydrogen streams. We denote these four inlet streams as HCUin, NHTin, CNHTin and DHTin as sinks in Table 2.

**Table 1: Source data for Example 1.**

Source Data				
Source	Maximum (mol/s)	Minimum (mol/s)	Current (mol/s)	H <sub>2</sub> Purity (mol% H <sub>2</sub> )
SRU	623.8	0	623.8	93.00
SRU	415.8	415.8	415.8	80.00
Import	346.5	0	277.2	95.00



**Figure 3: Flow diagram and stream data for Example 1.**

**Table 2: Stream data for Example 1.**

<b>Stream Data</b>					
<b>Variable</b>	<b>Units</b>	<b>HCU</b>	<b>NHT</b>	<b>CNHT</b>	<b>DHT</b>
<b>Makeup</b>					
Flow rate	mol/s	762.4	138.6	304.9	277.2
Purity	mol% H <sub>2</sub>	93.36	80.00	82.14	82.14
<b>Purge</b>					
Flow rate	mol/s	69.3	97	41.6	69.3
Purity	mol% H <sub>2</sub>	75.00	75.00	70.00	73.00
<b>Recycle</b>					
Flow rate	mol/s	1732.6	41.6	415.8	277.2
<b>Sink = Demand = Makeup + Recycle</b>					
		<b>HCUin</b>	<b>NHTin</b>	<b>CNHTin</b>	<b>DHTin</b>
Flow rate	mol/s	2495	180.2	720.7	554.4
Purity	mol% H <sub>2</sub>	80.61	78.85	75.14	77.57
<b>Source = Recycle + Purge</b>					
		<b>HCUout</b>	<b>NHTout</b>	<b>CNHTout</b>	<b>DHTout</b>
Flow rate	mol/s	1801.9	138.6	457.4	346.5
Purity	mol% H <sub>2</sub>	75.00	75.00	70.00	73.00

**2.1.1. Step 1: Enter stream data**

Figure 4 shows the initial hydrogen-pinch spreadsheet for Example 1. This example has four hydrogen sinks (demands) and seven hydrogen sources. Enter 4 for the number of sinks and 7 for the number of sources, in cells B1 and B2, respectively. Choose the unit for the hydrogen flow rate (mol/s) from the pull-down menu in cell D2. The flow-rate units currently available in cell D2 include Nm<sup>3</sup>/h, scf/h and mol/s. If the desired unit is not available, add the new unit to column U. Then, click the “Initialize” button to delete the existing data and generate 4 rows for entering the sink data in cells B7 to E10, and 7 rows for entering source data in cells B17 to E23. The user must enter the initial flow rate and hydrogen purity in decreasing hydrogen purity. The spreadsheet will automatically generate the hydrogen purity in column F and the cumulative flow rate in column G.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	No. of Demands	4	Please select the unit for H2 flowrates				Initialize			Analyze		Set Units			
2	No. of Sources	7	Unit	mol/s										Format:	
3	1	2	3	4	5	6	7							6	
4		DEMAND	H2	Flow rate	H2	H2	Cumulative		Flow	Demand	Source	Maximum	H2	Cumulative	
5		Stream	demand		percentage	purity	flow rate		interval	purity	purity	purity	surplus	H2 surplus	
6		Name	(inlet)	mol/s	r%	(vol frac.)	mol/s		mol/s	(vol frac.)	(vol frac.)	(vol frac.)	mol/s	(Nm <sup>3</sup> /h)	
7	1	HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.95	0.95	-----	0	
8	2	NHTin	d2	180.2	78.85	0.7885	2675.2		277.2	0.8061	0.95	0.95	39.88908	39.88908	
9	3	DHTin	d3	554.4	77.57	0.7757	3229.6		277.2	0.8061	0.93	0.93	-----	39.88908	
10	4	CNHTin	d4	720.7	75.14	0.7514	3950.3		901	0.8061	0.93	0.93	77.28882	117.1779	
11									901	0.8061	0.8	0.8061	-----	117.1779	
12									1316.8	0.8061	0.8	0.8061	-2.53638	114.64152	
13									1316.8	0.8061	0.75	0.8061	-----	114.64152	
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		2495	0.8061	0.75	0.8061	-66.09702	48.5445	
15		Stream	Source		percentage	purity	flow rate		2495	0.7885	0.75	0.7885	-----	48.5445	
16		Name	(inlet)	mol/s	r%	(vol frac.)	mol/s		2675.2	0.7885	0.75	0.7885	-6.9377	41.6068	
17	1	Import	s1	277.2	95	0.95	277.2		2675.2	0.7757	0.75	0.7757	-----	41.6068	
18	2	SRU	s2	623.8	93	0.93	901		3118.7	0.7757	0.75	0.7757	-11.39795	30.20885	
19	3	CRU	s3	415.8	80	0.8	1316.8		3118.7	0.7757	0.75	0.7757	-----	30.20885	
20	4	HCUout	s4	1801.9	75	0.75	3118.7		3229.6	0.7757	0.75	0.7757	-2.85013	27.35872	
21	5	NHTout	s5	138.6	75	0.75	3257.3		3229.6	0.7514	0.75	0.7514	-----	27.35872	
22	6	DHTout	s6	346.5	73	0.73	3603.8		3257.3	0.7514	0.75	0.7514	-0.03878	27.31994	
23	7	CNHTout	s7	457.4	70	0.7	4061.2		3257.3	0.7514	0.73	0.7514	-----	27.31994	
24									3603.8	0.7514	0.73	0.7514	-7.4151	19.90484	
25									3603.8	0.7514	0.7	0.7514	-----	19.90484	
26									3950.3	0.7514	0.7	0.7514	-17.8101	2.09474	
27									3950.3	0	0.7	0.7	-----	2.09474	
28									4061.2	0	0.7	0.7	77.63	79.72474	
29									4061.2	0	0	0	-----	79.72474	
30															
31															
32															

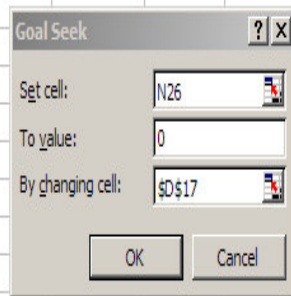


Figure 4: The initial spreadsheet for Example 1.

### 2.1.2. Step 2: Analyze the stream data

Clicking the “Analyze” button will generate the flow-interval data in column I. Starting with zero and arranging the cumulative flow rates of column G in an increasing order gives the boundary values of the flow interval in column I. Columns J to N contain values associated with each flow interval. Specifically, columns J and K list the hydrogen purity of the demand and source sides of each flow interval. Column L is simply the value of the higher purity between

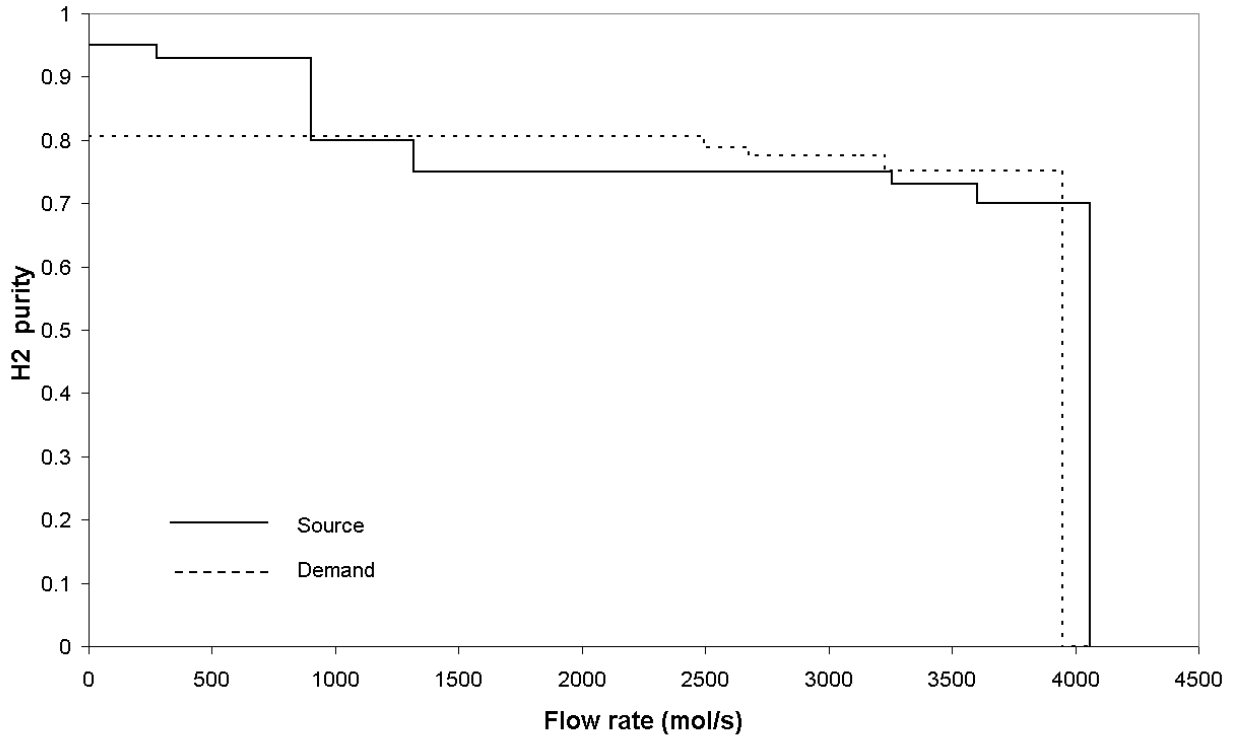
columns J and K. Column M gives the hydrogen surplus for each flow interval. We find this column by multiplying: (a) the difference in boundary values of hydrogen flow rates for a particular flow interval in Column I, by (b) the difference between the source purity in Column K and the demand purity in column J.

Lastly, we add together the hydrogen surplus in each flow interval in column M from the lowest to the highest flow rate to give the cumulative hydrogen surplus in column N. The term “Format” in cell N2 refers to the number of decimal points for displaying the cumulative hydrogen surplus in column N. For example, to display the data in column N with four decimal points, instead of the current six decimal points, we can change the number in cell N3 from 6 to 4.

### **2.1.3. Step 3: Display the hydrogen source-demand plot and surplus diagram**

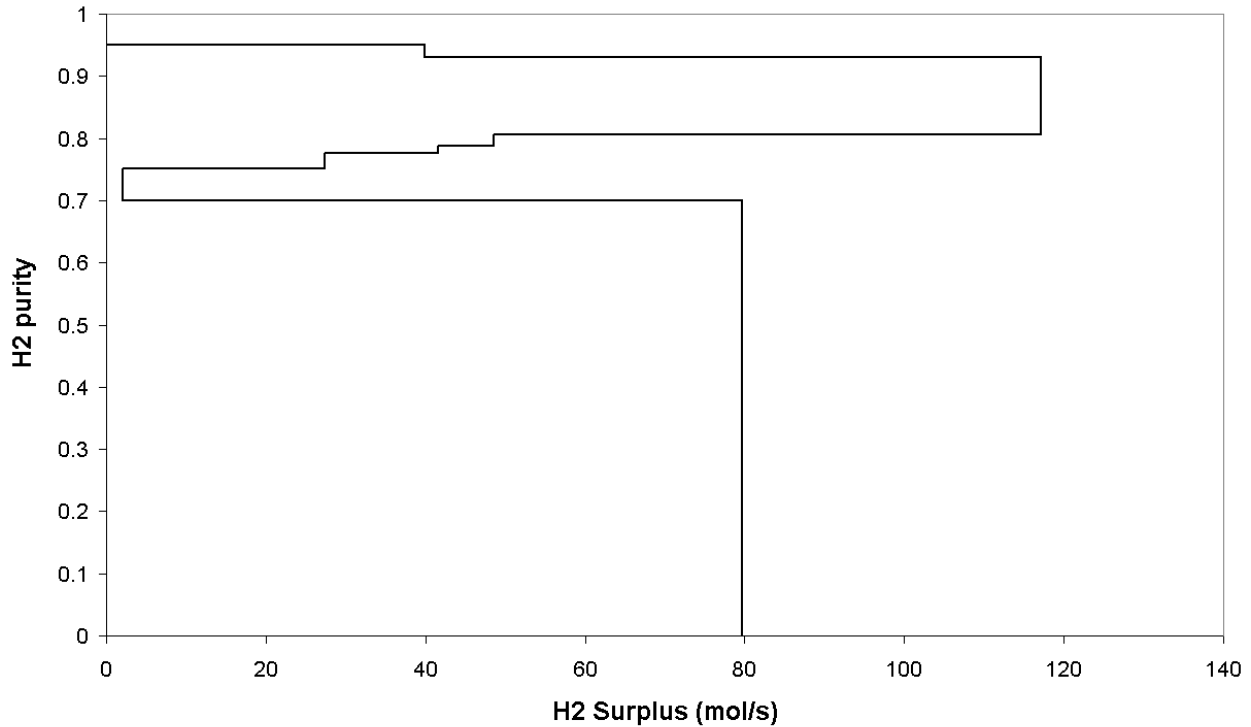
Refer to the initial spreadsheet in Figure 4. The spreadsheet automatically generates a hydrogen supply-demand plot (also called the hydrogen-composite curves) under the worksheet “SourceDemand”, as shown in Figure 5. This is a graph of the hydrogen purity (column F) versus the cumulative flow rate (column G), with separate lines for source and demand. In the graph, there is hydrogen surplus in areas where the source line (source-composite curve) is above or to the right of the demand line (demand-composite curve), and hydrogen deficit in areas where the source line is below or to the left of the demand line.





**Figure 5: The initial hydrogen source-demand plot (or hydrogen-composite curves) for Example 1.**

The spreadsheet also generates a hydrogen-surplus diagram under the worksheet “H2Surplus”, as shown in Figure 6. This is a graph of the hydrogen source purity (column K) versus the cumulative hydrogen surplus flow rate (column N). This diagram tells us if we can afford to decrease the flow rates of hydrogen utilities, including fresh hydrogen from import and hydrogen produced by reformers.



◀ ▶ ▢ \Data \SourceDemand \H2Surplus/

**Figure 6: The initial hydrogen-surplus diagram for Example 1.**

There is a surplus of hydrogen in the network, as column N in the spreadsheet of Figure 4 contains all positive values. We also see this in the hydrogen-surplus diagram in Figure 6, since the surplus line does not touch the y-axis. On the diagram, we can see which part of the curve is closest to the y-axis. We use this section of the diagram to optimize on our spreadsheet. By placing the cursor over the vertical line closest to the y-axis in the diagram, we can obtain the value (in this case, 2.09474 mol/s) that corresponds to the same number displayed in cell N26 in the spreadsheet.

#### **2.1.4. Step 4: Identify the hydrogen pinch**

This is performed by reducing the cumulative hydrogen surplus to zero by varying the flow rate of hydrogen utilities. The hydrogen pinch is the purity at which there is zero surplus and zero deficit. The surplus line will touch, but not cross, the y-axis at any point. The pinch location shows the bottleneck indicating how much hydrogen we can save. By using the spreadsheet and the “Goal Seek” function under Excel tools, we can easily determine the “target” flow rate of hydrogen at the pinch.

To illustrate, we first highlight the minimum cumulative hydrogen surplus flow rate of 2.09474 mol/s in cell N26 and we want to reduce this surplus to zero. We apply the “Goal Seek” function under Excel tools. By setting our highlighted cell N26 equal to zero through changing our “import” flow rate in cell D17, the “Goal Seek” function tells us that we can reduce the import hydrogen flow rate from the initial value of 277.2 mol/s to the optimized value of 268.82 mol/s (referred as Case 1 in Table 3). See the initial spreadsheet in Figure 4 and the pinched spreadsheet in Figure 7. The resulting hydrogen pinch has a demand purity of 0.7514 volume fraction (see cell J26) and a source purity of 0.7 mole fraction (see cell K26). Above this purity, Figure 7 shows that with a minimum hydrogen import of 268.82 mol/s, the available hydrogen sources can meet all the demands of hydrogen consumers, and the network has a hydrogen off-gas at a purity of 0.7 volume fraction (cell K28) and a flow rate of 71.764728 mol/h (cell N28).

Applying the same approach with the help of the “Goal Seek” function, we find that: (a) with a hydrogen stream produced from the steam reformer, SRU, at a source purity of 0.93 volume fraction and a flow rate of 614.69243 mol/s, the network has zero hydrogen surplus and an off-gas at a source purity of 0.7 volume fraction and a flow rate of 71.257405 mol/h (referred to as Case 2 in Table 3) ; (b) with a hydrogen stream produced from the catalytic reformer, CRU, at a source purity of 0.8 volume fraction and a flow rate of 394.8526 mol/s, the network has zero hydrogen surplus and an off-gas at a purity of 0.7 volume fraction and a flow rate of 62.96682 mol/s. Table 3 is an economic comparison of Cases 1 and 2 showing that Case 2 costs \$274,176/yr more than Case 1. The spreadsheet is very easy and efficient in doing this economic evaluation.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	No. of Demands	4	Please select the unit for H2 flowrates				Initialize			Analyze		Set Units			
2	No. of Sources	7	Unit	mol/s										Format:	
3		1	2	3	4	5	6	7						6	
4		DEMAND	H2	Flow rate	H2	H2	Cumulative		Flow	Demand	Source	Maximum	H2	Cumulative	
5		Stream	demand		percentage	purity	flow rate		interval	purity	purity	purity	surplus	H2 surplus	
6		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		mol/s	(vol frac.)	(vol frac.)	(vol frac.)	mol/s	(Nm3/h)	
7		1 HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.95	0.95	-----	0	
8		2 NHTin	d2	180.2	78.85	0.7885	2675.2		268.82104	0.8061	0.95	0.95	38.68335	38.683348	
9		3 DHTin	d3	554.4	77.57	0.7757	3229.6		268.82104	0.8061	0.93	0.93	-----	38.683348	
10		4 CNHTin	d4	720.7	75.14	0.7514	3950.3		892.62104	0.8061	0.93	0.93	77.28882	115.972168	
11									892.62104	0.8061	0.8	0.8061	-----	115.972168	
12									1308.421	0.8061	0.8	0.8061	-2.53638	113.435788	
13									1308.421	0.8061	0.75	0.8061	-----	113.435788	
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		2495	0.8061	0.75	0.8061	-66.56708	46.868708	
15		Stream	Source		percentage	purity	flow rate		2495	0.7885	0.75	0.7885	-----	46.868708	
16		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		2675.2	0.7885	0.75	0.7885	-6.9377	39.931008	
17		1 Import	s1	268.82104	95	0.95	268.82104		2675.2	0.7757	0.75	0.7757	-----	39.931008	
18		2 SRU	s2	623.8	93	0.93	892.62104		3110.321	0.7757	0.75	0.7757	-11.18261	28.748397	
19		3 CRU	s3	415.8	80	0.8	1308.42104		3110.321	0.7757	0.75	0.7757	-----	28.748397	
20		4 HCUout	s4	1801.9	75	0.75	3110.32104		3229.6	0.7757	0.75	0.7757	-3.065469	25.682928	
21		5 NHTout	s5	138.6	75	0.75	3248.92104		3229.6	0.7514	0.75	0.7514	-----	25.682928	
22		6 DHTout	s6	346.5	73	0.73	3595.42104		3248.921	0.7514	0.75	0.7514	-0.027049	25.655879	
23		7 CNHTout	s7	457.4	70	0.7	4052.82104		3248.921	0.7514	0.73	0.7514	-----	25.655879	
24									3595.421	0.7514	0.73	0.7514	-7.4151	18.240779	
25									3595.421	0.7514	0.7	0.7514	-----	18.240779	
26									3950.3	0.7514	0.7	0.7514	-18.24078	0	
27									3950.3	0	0.7	0.7	-----	0	
28									4052.821	0	0.7	0.7	71.76473	71.764728	
29									4052.821	0	0	0	-----	71.764728	
30															
31															
32															

Figure 7: Pinched spreadsheet for Example 1.

Table 3: An economic comparison of two options for Example 1.

	Case 1: Minimize hydrogen import	Case 2: Minimize H2 from SRU	Hydrogen Cost Difference (\$/yr): Case 2 - Case 1
Import (\$0.002/mol)	268.8 mol/s	277.2 mol/s	$(277.2 - 268.8) \text{ mol/s} \times \$0.002/\text{mol} \times 3600 \text{ s/hr} \times 8000 \text{ hr/yr} = \$484,840/\text{yr}$
From SRU (\$0.0008/mol)	623.8 mol/s	614.7 mol/s	$(614.7 - 623.8) \text{ mol/s} \times \$0.0008/\text{mol} \times 3600 \text{ s/hr} \times 8000 \text{ hr/yr} = -\$209,664/\text{yr}$
From CRU	415.8 mol/s	415.8 mol/s	No Change
Total	1308.5 mol/s	1307.7 mol/s	Net Increase: Case 2 - Case 1 \$274,176/yr

As mentioned before, the gas-cascade analysis technique proposed by Foo and Manan<sup>6</sup> does not allow for multiple streams at the same purity to be represented separately as individual

streams. All streams that have the same purity are lumped together, and thus, we are unable to see the effect of changing the flow rate of an individual stream. In Example 1, we see that the HCUout stream and the NHTout stream both have the same purity. If we wanted to change the flow rate of just one of these streams using the technique in reference 6, we would have to change the combined value, not the individual values.

### 3 Multiple-Pinch Network

As a second Example (Table 4), represents a case with multiple pinches in the hydrogen network<sup>6</sup>.

**Table 4: Stream data for Example 2.**

<b>Demand</b>	<b>Flow rate (mol/s)</b>	<b>H<sub>2</sub> Purity (mol%)</b>
1	120	99.9
2	27.8	98.6
3	80	97.5
4	60	97.5
5	100	97
6	150	90
<b>Source</b>	<b>Flow rate (mol/s)</b>	<b>H<sub>2</sub> Purity (mol%)</b>
1	80	98.3
2	75	85
3	28.55	96
4	80	95
5	120	90
6	40	98.3
7	80	97.5
Fresh H <sub>2</sub>	150	99.9

Using our spreadsheet, we enter the flow rate and purity data accordingly and analyze the system. Starting at a fresh hydrogen flow rate of 150 mol/s, there is excess hydrogen of 105.1772 mol/s (cell N35) in the network (see Figure 8). To identify the hydrogen pinch, we need to carefully review the cumulative hydrogen surplus numbers in column N. Cells N1 to N23 show a continuing positive number for the cumulative hydrogen surplus, cells N24 to 26 depict a continuing declining number for the cumulative hydrogen excess because of the hydrogen deficits in cells M24 and M26, and cells N27 to N35 indicate a continuing positive number for the cumulative hydrogen surplus.

Following the same procedure demonstrated in Example 1, we use the “Goal Seek” function in Excel tools to reduce the cumulative hydrogen surplus of 1.2147 mol/s in cell N26 to zero by changing the flow rate of fresh hydrogen (cell D19). This results in a fresh hydrogen flow rate of 125.2102 mol/s (See Figure 9). However, when the “Goal Seek” function changes the fresh hydrogen flow rate in cell D19 from 150 to 125.2102 mol/s, it shifts the order of the flow-interval numbers in column I, particularly in cells I10 to I13. This requires the user to re-order the flow-interval numbers in column I. We can easily do this by clicking the “Analyze” button after making a change to the data. Figure 10 shows the pinched spreadsheet for Example 2. It shows a minimum fresh hydrogen flow rate of 125.2102 mol/s (cell D19), a minimum off-gas flow rate of 80.41220 mol/s (cell N35), a hydrogen pinch at a source purity of 0.95 volume fraction (cell K26) where the cumulative hydrogen surplus is essentially zero (0.000001 mol/s at cell N26), and a near-pinch at a source purity of 0.983 volume fraction where the cumulative hydrogen surplus is practically zero (-0.000036 mol/s at cell N12). We see both pinches clearly in the red circled areas in the hydrogen surplus diagram of Figure 11.

Recent reports<sup>6,8</sup> have not presented any effective means to quickly handle the complications of the shift in flow-interval ordering during the development of hydrogen surplus diagram when changing the flow rates of hydrogen utilities, as we demonstrate in Figure 9 and Figure 10.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	No. of Demands	6	Please select the unit for H2 flowrates				Initialize		Analyze		Set Units				
2	No. of Sources	8	Unit	mol/s										Format:	
3	1	2	3	4	5	6	7							6	
4		DEMAND	H2 demand (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		Flow interval mol/s	Demand purity (vol frac.)	Source purity (vol frac.)	Maximum purity (vol frac.)	H2 surplus mol/s	Cumulative H2 surplus (Nm <sup>3</sup> /h)	
5		Stream Name													
6															
7	1	demand1	demand	120	99.9	0.999	120		0	0.999	0.999	0.999	0	0	
8	2	demand2	d2	27.8	98.6	0.986	147.8		120	0.999	0.999	0.999	0	0	
9	3	demand3	d3	80	97.5	0.975	227.8		120	0.986	0.999	0.999	0	0	
10	4	demand4	d4	60	97.5	0.975	287.8		147.8	0.986	0.999	0.999	0.3614	0.3614	
11	5	demand5	d5	100	97	0.97	387.8		147.8	0.975	0.999	0.999	0	0.3614	
12	6	demand6	d6	150	90	0.9	537.8		150	0.975	0.999	0.999	0.0528	0.4142	
13									150	0.975	0.983	0.983	0	0.4142	
14									227.8	0.975	0.983	0.983	0.6224	1.0366	
15									227.8	0.975	0.983	0.983	0	1.0366	
16		SOURCE	H2 Source (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		230	0.975	0.983	0.983	0.0176	1.0542	
17		Stream Name							230	0.975	0.983	0.983	0	1.0542	
18									270	0.975	0.983	0.983	0.32	1.3742	
19	1	freshH2	H2	150	99.9	0.999	150		270	0.975	0.975	0.975	0	1.3742	
20	2	source6	s6	80	98.3	0.983	230		287.8	0.975	0.975	0.975	0	1.3742	
21	3	source1	s1	40	98.3	0.983	270		287.8	0.97	0.975	0.975	0	1.3742	
22	4	source7	s7	80	97.5	0.975	350		350	0.97	0.975	0.975	0.311	1.6852	
23	5	source3	s3	28.55	96	0.96	378.55		350	0.97	0.96	0.97	0	1.6852	
24	6	source4	s4	80	95	0.95	458.55		378.55	0.97	0.96	0.97	-0.2855	1.3997	
25	7	source5	s5	120	90	0.9	578.55		378.55	0.97	0.95	0.97	0	1.3997	
26	8	source2	s2	75	85	0.85	653.55		387.8	0.97	0.95	0.97	-0.185	1.2147	
27									387.8	0.9	0.95	0.95	0	1.2147	
28									458.55	0.9	0.95	0.95	3.5375	4.7522	
29									458.55	0.9	0.9	0.9	0	4.7522	
30									537.8	0.9	0.9	0.9	0	4.7522	
31									537.8	0	0.9	0.9	0	4.7522	
32									578.55	0	0.9	0.9	36.675	41.4272	
33									578.55	0	0.85	0.85	0	41.4272	
34									653.55	0	0.85	0.85	63.75	105.1772	
35									653.55	0	0	0	0	105.1772	
36															

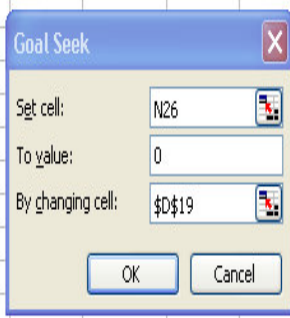


Figure 8: Initial spreadsheet for Example 2.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N		
1	No. of Demands	6	Please select the unit for H2 flowrates				Initialize		Analyze		Set Units					
2	No. of Sources	8	Unit	mol/s									Format:			
3	1	2	3	4	5	6	7									6
4		DEMAND	H2 demand (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		Flow interval mol/s	Demand purity (vol frac.)	Source purity (vol frac.)	Maximum purity (vol frac.)	H2 surplus mol/s	Cumulative H2 surplus (Nm <sup>3</sup> /h)		
5		Stream Name														
7	1	demand1	demand	120	99.9	0.999	120		0	0.999	0.999	0.999	0	0		
8	2	demand2	d2	27.8	98.6	0.986	147.8		120	0.999	0.999	0.999	0	0		
9	3	demand3	d3	80	97.5	0.975	227.8		120	0.986	0.999	0.999	0	0		
10	4	demand4	d4	60	97.5	0.975	287.8		147.8	0.986	0.999	0.999	0.3614	0.3614		
11	5	demand5	d5	100	97	0.97	387.8		147.8	0.975	0.999	0.999	0	0.3614		
12	6	demand6	d6	150	90	0.9	537.8		125.2102	0.975	0.999	0.999	-0.54216	-0.180755		
13									125.2102	0.975	0.983	0.983	0	-0.180755		
14									227.8	0.975	0.983	0.983	0.82072	0.639963		
15									227.8	0.975	0.983	0.983	0	0.639963		
16		SOURCE	H2 Source (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		205.2102	0.975	0.983	0.983	-0.18072	0.459245		
17		Stream Name							205.2102	0.975	0.983	0.983	0	0.459245		
18									245.2102	0.975	0.983	0.983	0.32	0.779245		
19	1	freshH2	H2	125.2102	99.9	0.999	125.210204		245.2102	0.975	0.975	0.975	0	0.779245		
20	2	source6	s6	80	98.3	0.983	205.210204		287.8	0.975	0.975	0.975	0	0.779245		
21	3	source1	s1	40	98.3	0.983	245.210204		287.8	0.97	0.975	0.975	0	0.779245		
22	4	source7	s7	80	97.5	0.975	325.210204		325.2102	0.97	0.975	0.975	0.18705	0.966296		
23	5	source3	s3	28.55	96	0.96	353.760204		325.2102	0.97	0.96	0.97	0	0.966296		
24	6	source4	s4	80	95	0.95	433.760204		353.7602	0.97	0.96	0.97	-0.2855	0.680796		
25	7	source5	s5	120	90	0.9	553.760204		353.7602	0.97	0.95	0.97	0	0.680796		
26	8	source2	s2	75	85	0.85	628.760204		387.8	0.97	0.95	0.97	-0.6808	0		
27									387.8	0.9	0.95	0.95	0	0		
28									433.7602	0.9	0.95	0.95	2.29801	2.29801		
29									433.7602	0.9	0.9	0.9	0	2.29801		
30									537.8	0.9	0.9	0.9	0	2.29801		
31									537.8	0	0.9	0.9	0	2.29801		
32									553.7602	0	0.9	0.9	14.3642	16.662194		
33									553.7602	0	0.85	0.85	0	16.662194		
34									628.7602	0	0.85	0.85	63.75	80.412194		
35									628.7602	0	0	0	0	80.412194		
36																
37																

Goal Seek Status

Goal Seeking with Cell N26  
found a solution.

Target value: 0  
Current value: 0

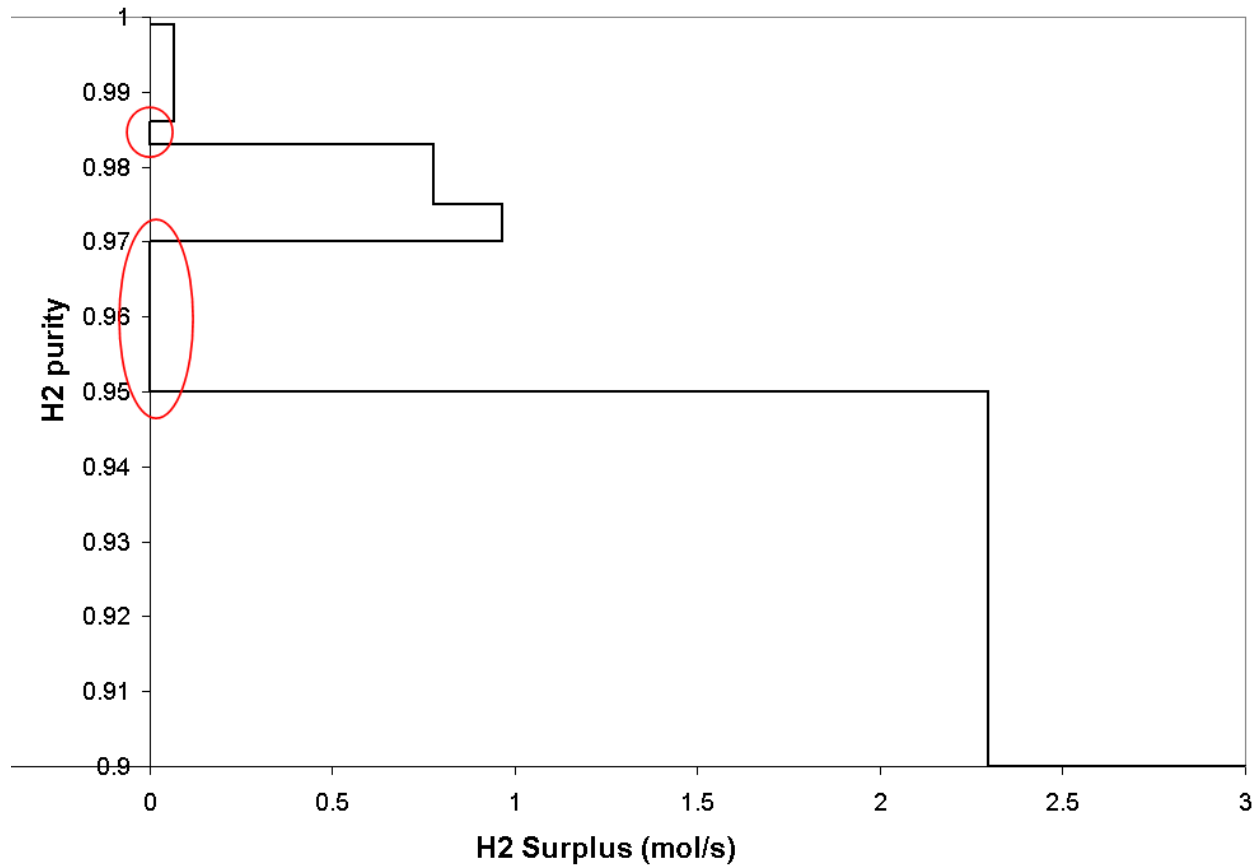
OK Cancel Step Pause

**Figure 9: Initial results for a multiple-pinch network, Example 2, before re-ordering the flow-interval numbers in column I.**



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	No. of Demands	6	Please select the unit for H2 flowrates												
2	No. of Sources	8	Unit	mol/s			Initialize		Analyze		Set Units			Format:	
3	1	2	3	4	5	6	7							6	
4		DEMAND	H2 demand (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		Flow interval mol/s	Demand purity (vol frac.)	Source purity (vol frac.)	Maximum purity (vol frac.)	H2 surplus mol/s	Cumulative H2 surplus (Nm3/h)	
5		Stream Name													
6															
7	1	demand1	demand	120	99.9	0.999	120		0	0.999	0.999	0.999	-----	0	
8	2	demand2	d2	27.8	98.6	0.986	147.8		120	0.999	0.999	0.999	0	0	
9	3	demand3	d3	80	97.5	0.975	227.8		120	0.986	0.999	0.999	-----	0	
10	4	demand4	d4	60	97.5	0.975	287.8		125.2102	0.986	0.999	0.999	0.06773	0.067733	
11	5	demand5	d5	100	97	0.97	387.8		125.2102	0.986	0.983	0.986	-----	0.067733	
12	6	demand6	d6	150	90	0.9	537.8		147.8	0.986	0.983	0.986	-0.06777	-0.000036	
13									147.8	0.975	0.983	0.983	-----	-0.000036	
14									205.2102	0.975	0.983	0.983	0.45928	0.459246	
15									205.2102	0.975	0.983	0.983	-----	0.459246	
16		SOURCE	H2 Source (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		227.8	0.975	0.983	0.983	0.18072	0.639964	
17		Stream Name							227.8	0.975	0.983	0.983	-----	0.639964	
18									245.2102	0.975	0.983	0.983	0.13928	0.779246	
19	1	freshH2	H2	125.2102	99.9	0.999	125.210204		245.2102	0.975	0.975	0.975	-----	0.779246	
20	2	source6	s6	80	98.3	0.983	205.210204		287.8	0.975	0.975	0.975	0	0.779246	
21	3	source1	s1	40	98.3	0.983	245.210204		287.8	0.97	0.975	0.975	-----	0.779246	
22	4	source7	s7	80	97.5	0.975	325.210204		325.2102	0.97	0.975	0.975	0.18705	0.966297	
23	5	source3	s3	28.55	96	0.96	353.760204		325.2102	0.97	0.96	0.97	-----	0.966297	
24	6	source4	s4	80	95	0.95	433.760204		353.7602	0.97	0.96	0.97	-0.2855	0.680797	
25	7	source5	s5	120	90	0.9	553.760204		353.7602	0.97	0.95	0.97	-----	0.680797	
26	8	source2	s2	75	85	0.85	628.760204		387.8	0.97	0.95	0.97	-0.6808	0.000001	
27									387.8	0.9	0.95	0.95	-----	0.000001	
28									433.7602	0.9	0.95	0.95	2.29801	2.298011	
29									433.7602	0.9	0.9	0.9	-----	2.298011	
30									537.8	0.9	0.9	0.9	0	2.298011	
31									537.8	0	0.9	0.9	-----	2.298011	
32									553.7602	0	0.9	0.9	14.3642	16.662195	
33									553.7602	0	0.85	0.85	-----	16.662195	
34									628.7602	0	0.85	0.85	63.75	80.412195	
35									628.7602	0	0	0	-----	80.412195	

Figure 10: Pinched spreadsheet for Example 2 after re-ordering the flow-interval numbers in column I of Figure 8.

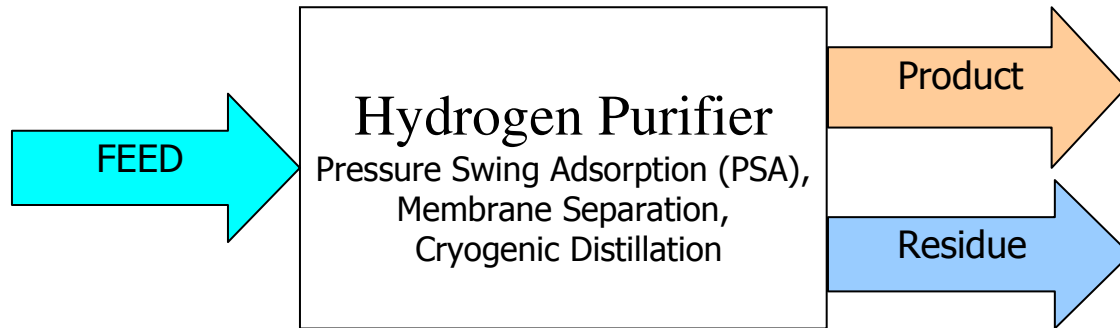


**Figure 11: Hydrogen-surplus diagram for the multiple-pinch network, Example 2.**

## 4 Purifier Placement

We now apply the spreadsheet to Example 1 to analyze different options for purifying an off-gas stream to increase its hydrogen purity. Hydrogen-pinch analysis does not tell us which stream to purify or what type of purifier to use. However, the spreadsheet can quickly determine if a purifier provides any potential savings, and if given multiple purifier options, which option gives the most savings. It is a bad practice to place the purifier below the pinch concentration, take hydrogen from a region of surplus, purify it and put it back in the same region; this is equivalent to buying a purifier to make purer hydrogen as an off-gas stream for burning. Instead, we should always place the purifier across the pinch concentration because it moves hydrogen from a region of surplus to a region of bottleneck in order to minimize the use of fresh hydrogen utility<sup>5</sup>. If the feed flow rate to the purifier is large enough, it can cause a shift of the pinch

location and the purifier could end up being above the pinch, not across. Figure 12 illustrates a typical hydrogen-purification process.



**Figure 12: A typical hydrogen-purification process.**

#### **4.1 Membrane Purification**

The first purifier option is a gas membrane that has a feed flow rate of 102.52 mol/s at a purity of 0.7 volume fraction with a purified product of 69.567 mol/s at a purity of 0.98 volume fraction, and a residue stream of 32.935 mol/s at a purity of 0.1089 volume fraction<sup>6</sup>. If we add these streams into Example 1, we find that there is a large surplus of hydrogen. See Figure 13 for the spreadsheet and Figure 14 for the new surplus diagram. After using the “Goal Seek” function in Excel tools, we find that the minimum flow rate of hydrogen import (cell D19) drops from 268.281 (Figure 13) to 197.06 mol/s (Figure 15), and the flow rate of the off-gas stream (cell N35) is decreased from 71.251932 (Figure 13) to 3.588583 mol/s (Figure 15).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	No. of Demands	5	Please select the unit for H2 flowrates			Initialize			Analyze		Set Units			
2	No. of Sources	9	Unit	mol/s										Format:
3	1	2	3	4	5	6	7							6
4		DEMAND	H2	Flow rate	H2	H2	Cumulative		Flow	Demand	Source	Maximum	H2	Cumulative
5		Stream	demand		percentage	purity	flow rate		interval	purity	purity	purity	surplus	H2 surplus
6		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		mol/s	(vol frac.)	(vol frac.)	(vol frac.)	mol/s	(Nm3/h)
7	1	HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.98	0.98	-----	0
8	2	NHTin	d2	180.2	78.85	0.7885	2675.2		69.567	0.8061	0.98	0.98	12.0977	12.097701
9	3	DHTin	d3	554.4	77.57	0.7757	3229.6		69.567	0.8061	0.95	0.95	-----	12.097701
10	4	CNHTin	d4	720.7	75.14	0.7514	3950.3		337.848	0.8061	0.95	0.95	38.60564	50.703337
11	5	Membrane Feed	d5	102.52	70	0.7	4052.82		337.848	0.8061	0.93	0.93	-----	50.703337
12									961.648	0.8061	0.93	0.93	77.28882	127.992157
13									961.648	0.8061	0.8	0.8061	-----	127.992157
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		1377.448	0.8061	0.8	0.8061	-2.53638	125.455777
15		SOURCE	H2	Flow rate	H2	H2	Cumulative		1377.448	0.8061	0.75	0.8061	-----	125.455777
16		Stream	Source		percentage	purity	flow rate		2495	0.8061	0.75	0.8061	-62.69467	62.76111
17		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		2495	0.7885	0.75	0.7885	-----	62.76111
18	1	Membrane Product	s1	69.567	98	0.98	69.567		2675.2	0.7885	0.75	0.7885	-6.9377	55.82341
19	2	Import	s2	268.281	95	0.95	337.848		2675.2	0.7757	0.75	0.7757	-----	55.82341
20	3	SRU	s3	623.8	93	0.93	961.648		3179.348	0.7757	0.75	0.7757	-12.9566	42.866806
21	4	CRU	s4	415.8	80	0.8	1377.448		3179.348	0.7757	0.75	0.7757	-----	42.866806
22	5	HCUout	s5	1801.9	75	0.75	3179.348		3229.6	0.7757	0.75	0.7757	-1.291476	41.57533
23	6	NHTout	s6	138.6	75	0.75	3317.948		3229.6	0.7514	0.75	0.7514	-----	41.57533
24	7	DHTout	s7	346.5	73	0.73	3664.448		3317.948	0.7514	0.75	0.7514	-0.123687	41.451643
25	8	CNHTout	s8	457.4	70	0.7	4121.848		3317.948	0.7514	0.73	0.7514	-----	41.451643
26	9	Membrane Residue	s9	32.953	10.89	0.1089	4154.801		3664.448	0.7514	0.73	0.7514	-7.4151	34.036543
27									3664.448	0.7514	0.7	0.7514	-----	34.036543
28									3950.3	0.7514	0.7	0.7514	-14.69279	19.34375
29									3950.3	0.7	0.7	0.7	-----	19.34375
30									4052.82	0.7	0.7	0.7	0	19.34375
31									4052.82	0	0.7	0.7	-----	19.34375
32									4121.848	0	0.7	0.7	48.3196	67.66335
33									4121.848	0	0.1089	0.1089	-----	67.66335
34									4154.801	0	0.1089	0.1089	3.588582	71.251932
35									4154.801	0	0	0	-----	71.251932

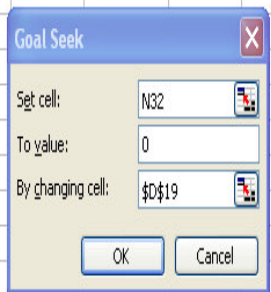
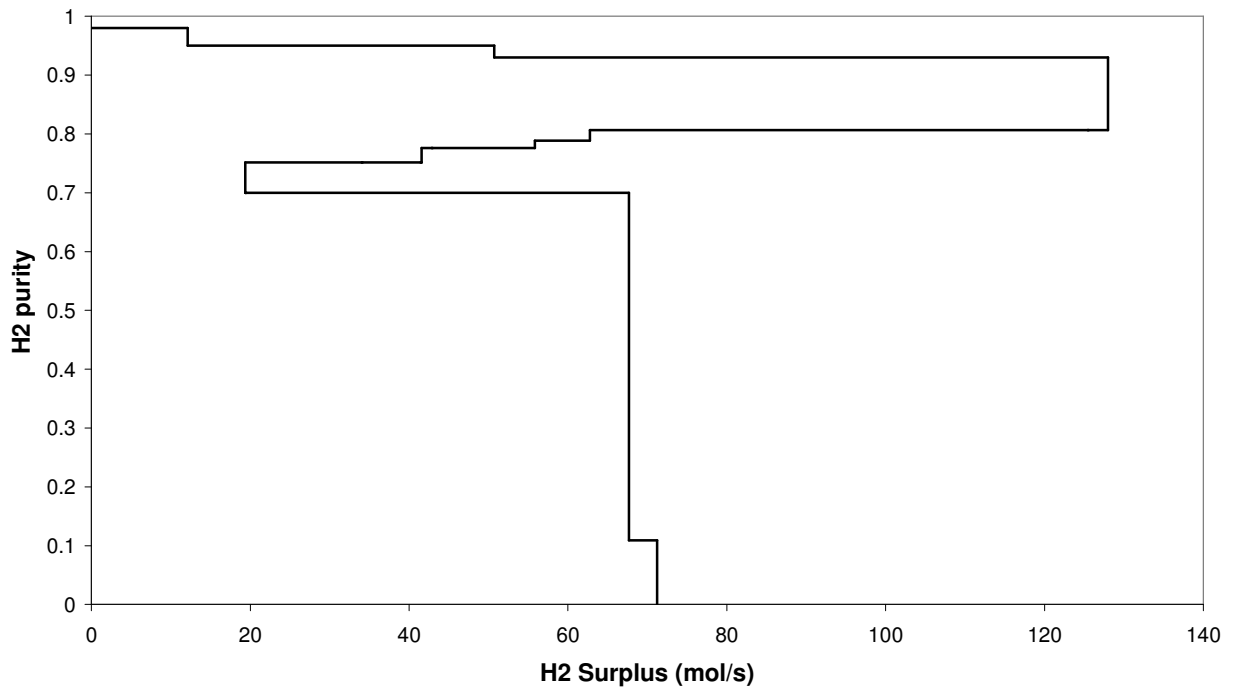


Figure 13: Gas membrane purifier added to Example 1 - initial spreadsheet.



**Figure 14: Hydrogen-surplus diagram for the gas-membrane purifier added to Example 1.**

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	No. of Demands	5	Please select the unit for H2 flowrates			Initialize			Analyze		Set Units			
2	No. of Sources	9	Unit	mol/s		Initialize			Analyze		Set Units			Format:
3	1	2	3	4	5	6	7							6
4		DEMAND	H2 demand (inlet)	Flow rate mol/s	H2 percentage v%	H2 purity (vol frac.)	Cumulative flow rate mol/s		Flow interval mol/s	Demand purity (vol frac.)	Source purity (vol frac.)	Maximum purity (vol frac.)	H2 surplus mol/s	Cumulative H2 surplus (Nm <sup>3</sup> /h)
5		Stream Name												
6														
7	1	HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.98	0.98	-----	0
8	2	NHTin	d2	180.2	78.85	0.7885	2675.2		69.567	0.8061	0.98	0.98	12.0977	12.097701
9	3	DHTin	d3	554.4	77.57	0.7757	3229.6		69.567	0.8061	0.95	0.95	-----	12.097701
10	4	CNHTin	d4	720.7	75.14	0.7514	3950.3		266.62342	0.8061	0.95	0.95	28.35642	40.45412
11	5	Membrane Feed	d5	102.52	70	0.7	4052.82		266.62342	0.8061	0.93	0.93	-----	40.45412
12									890.42342	0.8061	0.93	0.93	77.28882	117.74294
13									890.42342	0.8061	0.8	0.8061	-----	117.74294
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		1306.2234	0.8061	0.8	0.8061	-2.53638	115.20656
15		SOURCE	H2	Flow rate	H2	H2	Cumulative		1306.2234	0.8061	0.75	0.8061	-----	115.20656
16		Stream Name	Source (inlet)		percentage v%	purity (vol frac.)	flow rate mol/s		2495	0.8061	0.75	0.8061	-66.69037	48.516194
17									2495	0.7885	0.75	0.7885	-----	48.516194
18	1	Membrane Product	s1	69.567	98	0.98	69.567		2675.2	0.7885	0.75	0.7885	-6.9377	41.578494
19	2	Import	s2	197.05642	95	0.95	266.6234232		2675.2	0.7757	0.75	0.7757	-----	41.578494
20	3	SRU	s3	623.8	93	0.93	890.4234232		3108.1234	0.7757	0.75	0.7757	-11.12613	30.452362
21	4	CRU	s4	415.8	80	0.8	1306.223423		3108.1234	0.7757	0.75	0.7757	-----	30.452362
22	5	HCUout	s5	1801.9	75	0.75	3108.123423		3229.6	0.7757	0.75	0.7757	-3.121948	27.330414
23	6	NHTout	s6	138.6	75	0.75	3246.723423		3229.6	0.7514	0.75	0.7514	-----	27.330414
24	7	DHTout	s7	346.5	73	0.73	3593.223423		3246.7234	0.7514	0.75	0.7514	-0.023973	27.306441
25	8	CNHTout	s8	457.4	70	0.7	4050.623423		3246.7234	0.7514	0.73	0.7514	-----	27.306441
26	9	Membrane Residue	s9	32.953	10.89	0.1089	4083.576423		3593.2234	0.7514	0.73	0.7514	-7.4151	19.891341
27									3593.2234	0.7514	0.7	0.7514	-----	19.891341
28									3950.3	0.7514	0.7	0.7514	-18.35374	1.537605
29									3950.3	0.7	0.7	0.7	-----	1.537605
30									4052.82	0.7	0.7	0.7	0	1.537605
31									4052.82	0	0.7	0.7	-----	1.537605
32									4050.6234	0	0.7	0.7	-1.537604	0.000001
33									4050.6234	0	0.1089	0.1089	-----	0.000001
34									4083.5764	0	0.1089	0.1089	3.588582	3.588583
35									4083.5764	0	0	0	-----	3.588583

**Goal Seek Status** ✖

Goal Seeking with Cell N32  
found a solution.

Target value: 0  
Current value: 0.000001

Figure 15: Pinched data for the gas-membrane purifier added to Example 1.

## ***4.2 Pressure Swing Adsorption***

The second purifier option is a PSA purifier that has an entering flow rate of 102.52 mol/s at a purity of 0.7 volume fraction with a purified product of 64.65 mol/s at a purity of 0.999 volume fraction and a residue stream of 37.87 mol/s at a purity of 0.1895 volume fraction<sup>6</sup>. Adding these streams to Example 1 leads to a large surplus of hydrogen. See Figure 16 for the initial spreadsheet and Figure 17 for the new surplus diagram.

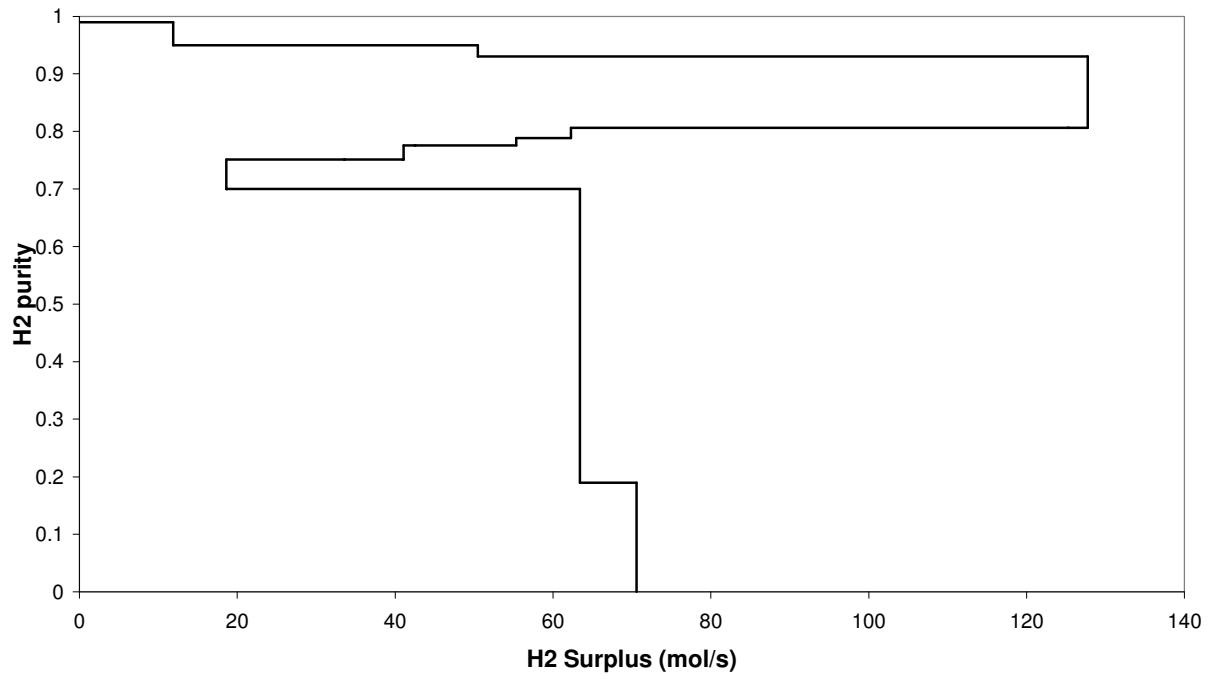
After using the “Goal Seek” function in Excel tools, we find that the minimum flow rate of hydrogen import (Cell D10) drops from 268.281 (Figure 16) to 201.4482 mol/s (Figure 18), and the flow rate of the off-gas stream (Cell N35) is decreased from 70.60 (Figure 16) to 7.176 mol/s (Figure 18).

The gas-membrane purifier gives us a lower target hydrogen import flow rate than the PSA purifier. This shows that even if a purifier has a higher purity output than another purifier, it is not necessarily the best option.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	No. of Demands	5	Please select the unit for H2 flowrates				Initialize			Analyze		Set Units			
2	No. of Sources	9	Unit	mol/s										Format:	
3	1	2	3	4	5	6	7							6	
4		DEMAND	H2	Flow rate	H2	H2	Cumulative		Flow	Demand	Source	Maximum	H2	Cumulative	
5		Stream	demand		percentage	purity	flow rate		interval	purity	purity	purity	surplus	H2 surplus	
6		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		mol/s	(vol frac.)	(vol frac.)	(vol frac.)	mol/s	(Nm <sup>3</sup> /h)	
7	1	HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.99	0.99	-----	0	
8	2	NHTin	d2	180.2	78.85	0.7885	2675.2		64.65	0.8061	0.99	0.99	11.88914	11.889135	
9	3	DHTin	d3	554.4	77.57	0.7757	3229.6		64.65	0.8061	0.95	0.95	-----	11.889135	
10	4	CNHTin	d4	720.7	75.14	0.7514	3950.3		332.86	0.8061	0.95	0.95	38.59542	50.484554	
11	5	PSA Feed	d5	102.52	70	0.7	4052.82		332.86	0.8061	0.93	0.93	-----	50.484554	
12									956.66	0.8061	0.93	0.93	77.28882	127.773374	
13									956.66	0.8061	0.8	0.8061	-----	127.773374	
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		1372.46	0.8061	0.8	0.8061	-2.53638	125.236994	
15		SOURCE	H2	Flow rate	H2	H2	Cumulative		1372.46	0.8061	0.75	0.8061	-----	125.236994	
16		Stream	Source		percentage	purity	flow rate		2495	0.8061	0.75	0.8061	-62.97449	62.2625	
17		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		2495	0.7885	0.75	0.7885	-----	62.2625	
18	1	PSA Product	s1	64.65	99	0.99	64.65		2675.2	0.7885	0.75	0.7885	-6.9377	55.3248	
19	2	Import	s2	268.21	95	0.95	332.86		2675.2	0.7757	0.75	0.7757	-----	55.3248	
20	3	SRU	s3	623.8	93	0.93	956.66		3174.36	0.7757	0.75	0.7757	-12.82841	42.496388	
21	4	CRU	s4	415.8	80	0.8	1372.46		3174.36	0.7757	0.75	0.7757	-----	42.496388	
22	5	HCUout	s5	1801.9	75	0.75	3174.36		3229.6	0.7757	0.75	0.7757	-1.419668	41.07672	
23	6	NHTout	s6	138.6	75	0.75	3312.96		3229.6	0.7514	0.75	0.7514	-----	41.07672	
24	7	DHTout	s7	346.5	73	0.73	3659.46		3312.96	0.7514	0.75	0.7514	-0.116704	40.960016	
25	8	CNHTout	s8	457.4	70	0.7	4116.86		3312.96	0.7514	0.73	0.7514	-----	40.960016	
26	9	PSA Residue	s9	37.87	18.95	0.1895	4154.73		3659.46	0.7514	0.73	0.7514	-7.4151	33.544916	
27									3659.46	0.7514	0.7	0.7514	-----	33.544916	
28									3950.3	0.7514	0.7	0.7514	-14.94918	18.59574	
29									3950.3	0.7	0.7	0.7	-----	18.59574	
30									4052.82	0.7	0.7	0.7	0	18.59574	
31									4052.82	0	0.7	0.7	-----	18.59574	
32									4116.86	0	0.7	0.7	44.828	63.42374	
33									4116.86	0	0.1895	0.1895	-----	63.42374	
34									4154.73	0	0.1895	0.1895	7.176365	70.600105	
35									4154.73	0	0	0	-----	70.600105	

Figure 16: PSA purifier added to Example 1 - initial spreadsheet.





**Figure 17: Hydrogen-surplus diagram for the PSA purifier added to Example 1.**

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	No. of Demands	5	Please select the unit for H2 flowrates			Initialize			Analyze		Set Units			
2	No. of Sources	9	Unit	mol/s										Format:
3	1	2	3	4	5	6	7							6
4		DEMAND	H2	Flow rate	H2	H2	Cumulative		Flow	Demand	Source	Maximum	H2	Cumulative
5		Stream	demand		percentage	purity	flow rate		interval	purity	purity	purity	surplus	H2 surplus
6		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		mol/s	(vol frac.)	(vol frac.)	(vol frac.)	mol/s	(Nm <sup>3</sup> /h)
7	1	HCUin	d1	2495	80.61	0.8061	2495		0	0.8061	0.99	0.99	.....	0
8	2	NHTin	d2	180.2	78.85	0.7885	2675.2		64.65	0.8061	0.99	0.99	11.88914	11.889135
9	3	DHTin	d3	554.4	77.57	0.7757	3229.6		64.65	0.8061	0.95	0.95	.....	11.889135
10	4	CNHTin	d4	720.7	75.14	0.7514	3950.3		266.09817	0.8061	0.95	0.95	28.98839	40.877526
11	5	PSA Feed	d5	102.52	70	0.7	4052.82		266.09817	0.8061	0.93	0.93	.....	40.877526
12									889.89817	0.8061	0.93	0.93	77.28882	118.166346
13									889.89817	0.8061	0.8	0.8061	.....	118.166346
14		SOURCE	H2	Flow rate	H2	H2	Cumulative		1305.6982	0.8061	0.8	0.8061	-2.53638	115.629966
15		SOURCE	H2	Flow rate	H2	H2	Cumulative		1305.6982	0.8061	0.75	0.8061	.....	115.629966
16		Stream	Source		percentage	purity	flow rate		2495	0.8061	0.75	0.8061	-66.71983	48.910133
17		Name	(inlet)	mol/s	v%	(vol frac.)	mol/s		2495	0.7885	0.75	0.7885	.....	48.910133
18	1	PSA Product	s1	64.65	99	0.99	64.65		2675.2	0.7885	0.75	0.7885	-6.9377	41.972433
19	2	Import	s2	201.44817	95	0.95	266.0981684		2675.2	0.7757	0.75	0.7757	.....	41.972433
20	3	SRU	s3	623.8	93	0.93	889.8981684		3107.5982	0.7757	0.75	0.7757	-11.11263	30.8598
21	4	CRU	s4	415.8	80	0.8	1305.698168		3107.5982	0.7757	0.75	0.7757	.....	30.8598
22	5	HCUout	s5	1801.9	75	0.75	3107.598168		3229.6	0.7757	0.75	0.7757	-3.135447	27.724353
23	6	NHTout	s6	138.6	75	0.75	3246.198168		3229.6	0.7514	0.75	0.7514	.....	27.724353
24	7	DHTout	s7	346.5	73	0.73	3592.698168		3246.1982	0.7514	0.75	0.7514	-0.023237	27.701116
25	8	CNHTout	s8	457.4	70	0.7	4050.098168		3246.1982	0.7514	0.73	0.7514	.....	27.701116
26	9	PSA Residue	s9	37.87	18.95	0.1895	4087.968168		3592.6982	0.7514	0.73	0.7514	-7.4151	20.286016
27									3592.6982	0.7514	0.7	0.7514	.....	20.286016
28									3950.3	0.7514	0.7	0.7514	-18.38073	1.905282
29									3950.3	0.7	0.7	0.7	.....	1.905282
30									4052.82	0.7	0.7	0.7	0	1.905282
31									4052.82	0	0.7	0.7	.....	1.905282
32									4050.0982	0	0.7	0.7	-1.905282	0
33									4050.0982	0	0.1895	0.1895	.....	0
34									4087.9682	0	0.1895	0.1895	7.176365	7.176365
35									4087.9682	0	0	0	.....	7.176365
36														

Figure 18: Pinched data for the PSA purifier added to Example 1.

## 5 Validation of Results with Professional Software

In order to show that the results from the automated spreadsheet are valid, we are able to compare them to results we obtain from a software program called “RefOpt”, which stands for Refinery Optimization. This software package is developed by the University of Manchester in the United Kingdom<sup>11</sup>. We use Example 1 to show that our results are the same as the results

from RefOpt. This program refers to the units that produce high-purity hydrogen as “producer units”, and the units that consume hydrogen as “consumer units”. We enter the data for the inlet stream (sinks) and off gas stream (sources) for these units in the consumer units.

First, we open a new RefOpt file. Then we select EDIT – PRODUCER UNIT and click “insert” to add the H2 Import, SRU and CRU. We enter the corresponding data for each unit as shown in Figure 19 to Figure 21.

The image shows a software dialog box titled "Producer Data" with a close button (X) in the top right corner. Below the title bar, the word "Edit" is displayed. The main area contains the following fields:

- Producer Number: 1 of 3
- Name: Import
- Specification section (bordered box):
  - Current flowrate: 277.2 [t/hr]
  - Purity: 0.95 [Mass frac.]
  - Pressure: 1.01325 [Bar]
  - Minimum flowrate: 0 [t/hr] (checked)
  - Maximum flowrate: 346.5 [t/hr] (checked)
  - Production cost: 2 [GBP/t]

At the bottom of the dialog, there are six buttons: OK, Cancel, Insert, Delete, Table, and Help.

**Figure 19: Producer unit – H2 import.**

Producer Data

Edit

Producer Number 2 of 3 Name SRU

Specification

Current flowrate	623.8	[t/hr]
Purity	0.93	[Mass frac.]
Pressure	1.01325	[Bar]
Minimum flowrate	0	<input checked="" type="checkbox"/> [t/hr]
Maximum flowrate	623.8	<input checked="" type="checkbox"/> [t/hr]
Production cost	0.8	[GBP/t]

OK Cancel Insert Delete Table Help

**Figure 20: Producer unit – SRU.**

Producer Data

Edit

Producer Number 3 of 3 Name CRU

Specification

Current flowrate	415.8	[t/hr]
Purity	0.8	[Mass frac.]
Pressure	1.01325	[Bar]
Minimum flowrate	415.8	<input checked="" type="checkbox"/> [t/hr]
Maximum flowrate	415.8	<input checked="" type="checkbox"/> [t/hr]
Production cost	0	[GBP/t]

OK Cancel Insert Delete Table Help

**Figure 21: Producer unit – CRU.**

Then we select EDIT –CONSUMER UNIT and click “insert” to add each of the four units. For each unit we enter the corresponding inlet and outlet data as shown in Figure 22 to Figure 25.

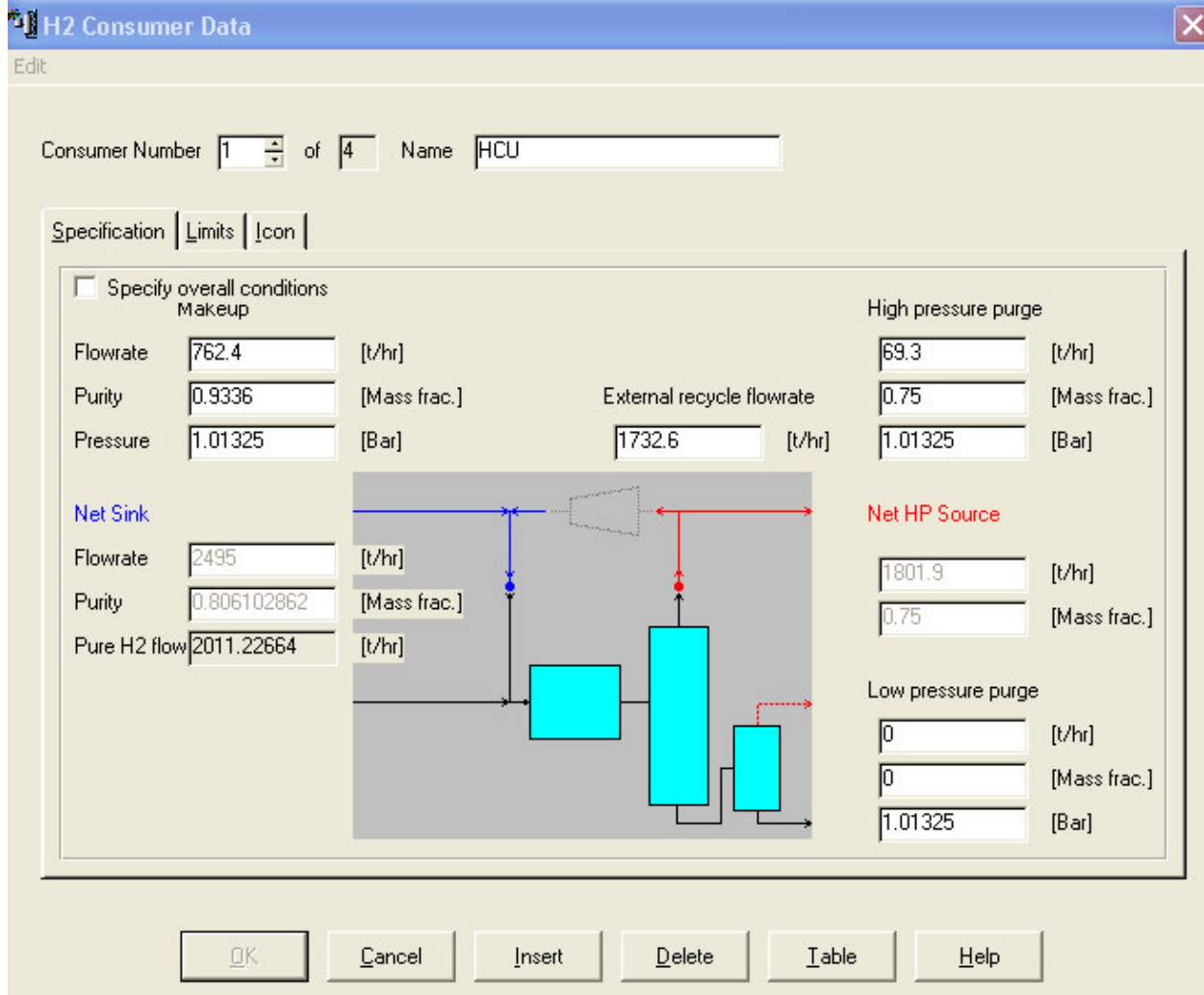


Figure 22: Consumer unit – HCU.

H2 Consumer Data X

Edit

Consumer Number  of  Name

Specification | Limits | Icon

Specify overall conditions

Makeup

Flowrate	<input type="text" value="138.6"/>	[t/hr]	High pressure purge	<input type="text" value="97"/>	[t/hr]
Purity	<input type="text" value="0.8"/>	[Mass frac.]	External recycle flowrate	<input type="text" value="0.75"/>	[Mass frac.]
Pressure	<input type="text" value="1.01325"/>	[Bar]		<input type="text" value="41.6"/>	[t/hr]
				<input type="text" value="1.01325"/>	[Bar]

Net Sink

Flowrate	<input type="text" value="180.2"/>	[t/hr]	Net HP Source	<input type="text" value="138.6"/>	[t/hr]
Purity	<input type="text" value="0.78845727"/>	[Mass frac.]		<input type="text" value="0.75"/>	[Mass frac.]
Pure H2 flow	<input type="text" value="142.08"/>	[t/hr]	Low pressure purge	<input type="text" value="0"/>	[t/hr]
				<input type="text" value="0"/>	[Mass frac.]
				<input type="text" value="1.01325"/>	[Bar]

OK Cancel Insert Delete Table Help

**Figure 23: Consumer unit – NHT.**

**H2 Consumer Data** [X]

Edit

Consumer Number  of  Name

Specification | Limits | Icon

Specify overall conditions  
Makeup

Flowrate	<input type="text" value="304.9"/>	[t/hr]	High pressure purge	<input type="text" value="41.6"/>	[t/hr]
Purity	<input type="text" value="0.8214"/>	[Mass frac.]	External recycle flowrate	<input type="text" value="0.7"/>	[Mass frac.]
Pressure	<input type="text" value="1.01325"/>	[Bar]		<input type="text" value="415.8"/>	[t/hr]
				<input type="text" value="1.01325"/>	[Bar]

**Net Sink**

Flowrate	<input type="text" value="720.7"/>	[t/hr]			
Purity	<input type="text" value="0.751359595"/>	[Mass frac.]			
Pure H2 flow	<input type="text" value="541.50486"/>	[t/hr]			

**Net HP Source**

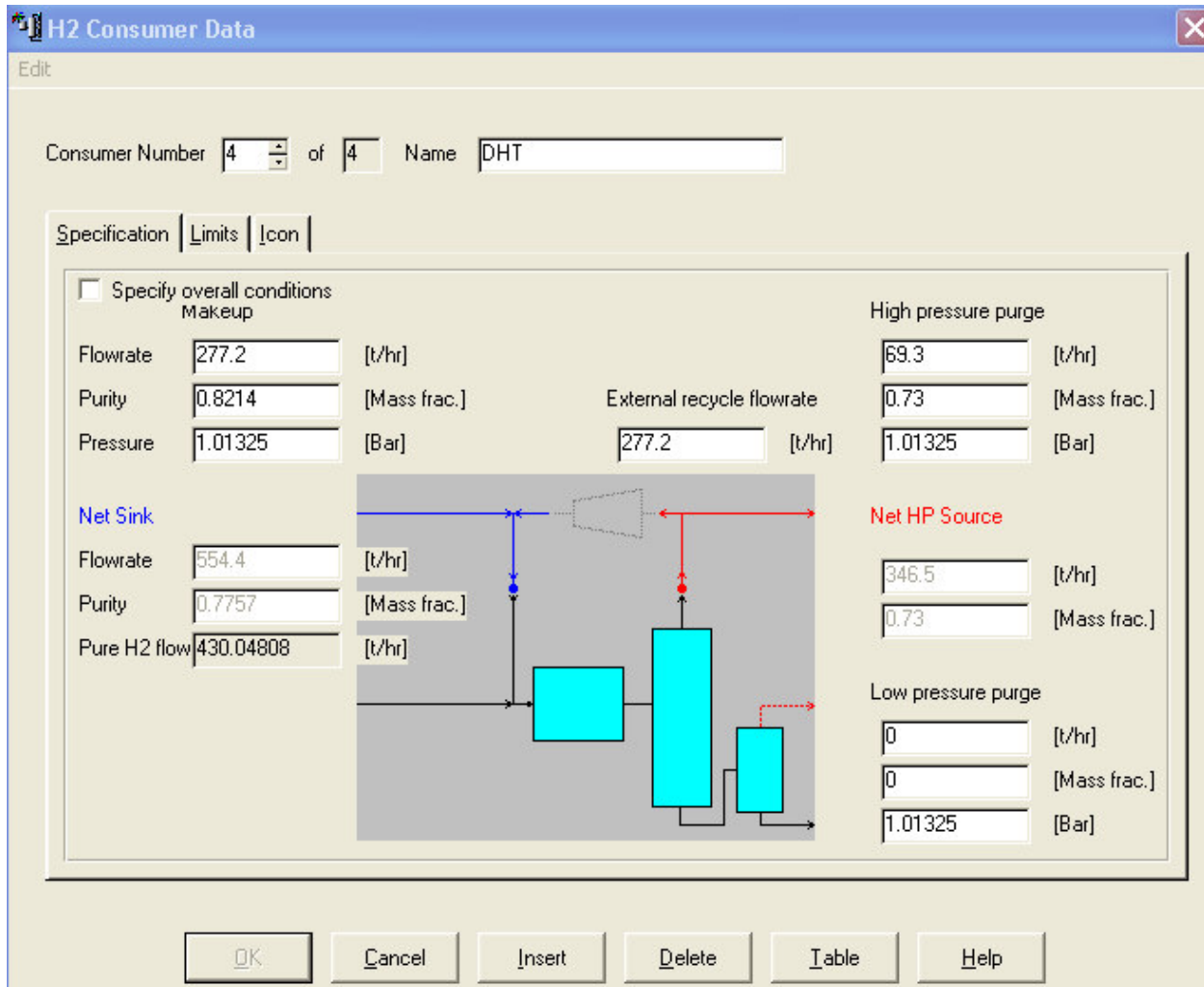
	<input type="text" value="457.4"/>	[t/hr]			
	<input type="text" value="0.7"/>	[Mass frac.]			

**Low pressure purge**

	<input type="text" value="0"/>	[t/hr]			
	<input type="text" value="0"/>	[Mass frac.]			
	<input type="text" value="1.01325"/>	[Bar]			

OK Cancel Insert Delete Table Help

**Figure 24: Consumer unit – CNHT.**



**Figure 25: Consumer unit – DHT.**

After entering all of the stream data, we can compare the RefOpt hydrogen-composite curve (also referred to as the source-demand plot in Figure 5), to our Excel spreadsheet hydrogen-composite curve. In RefOpt, we can generate this curve by selecting “HYDROGEN NETWORK – COMPOSITE CURVES”. We have changed the axes in Figure 5 to match the axes from the RefOpt software plot in order to show the similarity. See Figure 26 for our Excel spreadsheet hydrogen-composite curve and Figure 27 for the RefOpt hydrogen-composite curve.



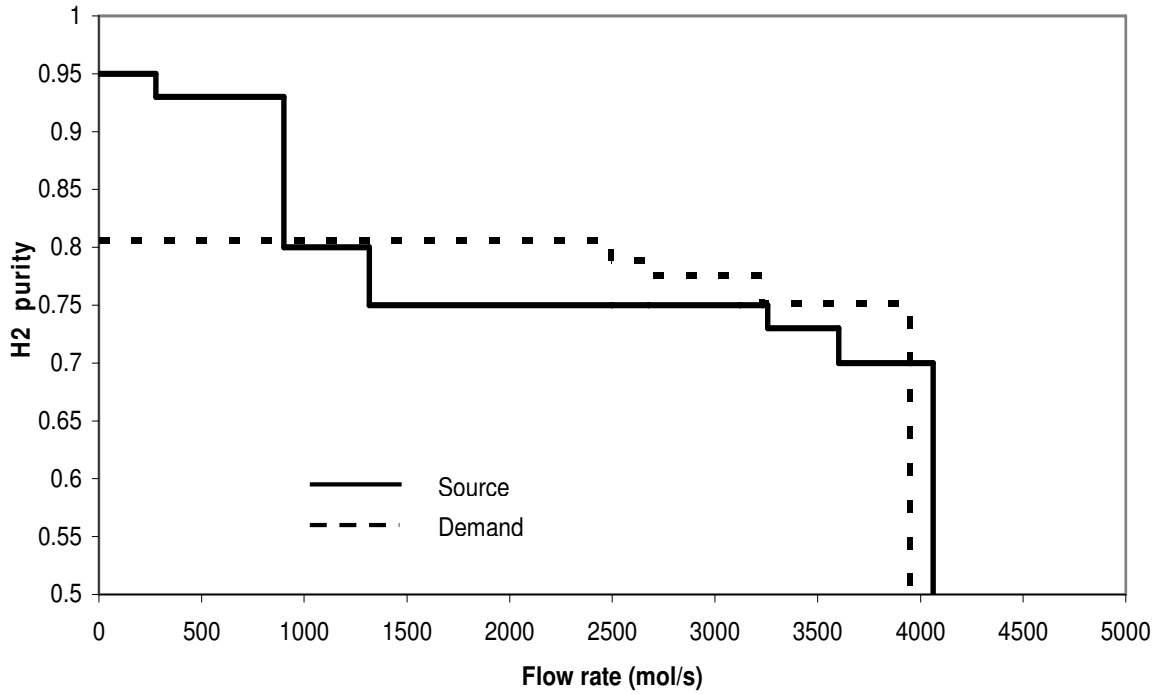


Figure 26: The initial hydrogen-composite curves for Example 1 with changed axes.

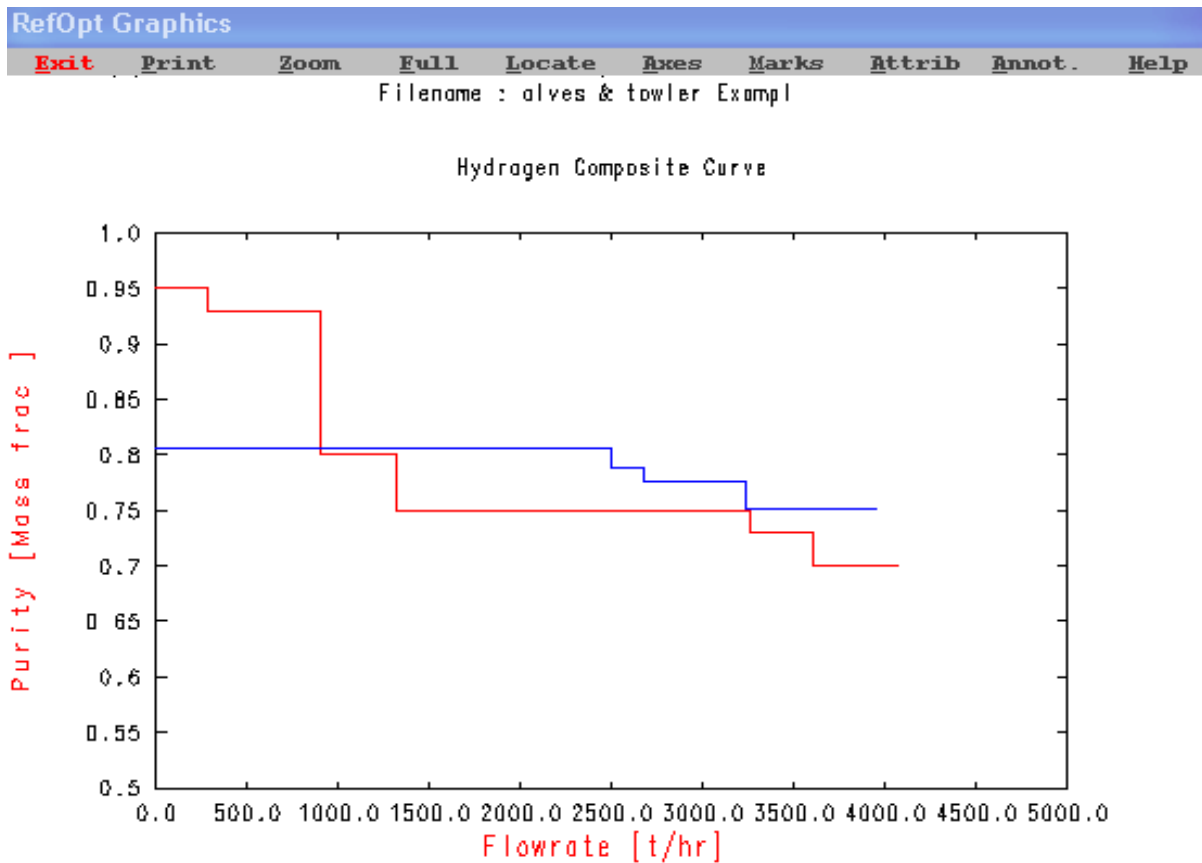
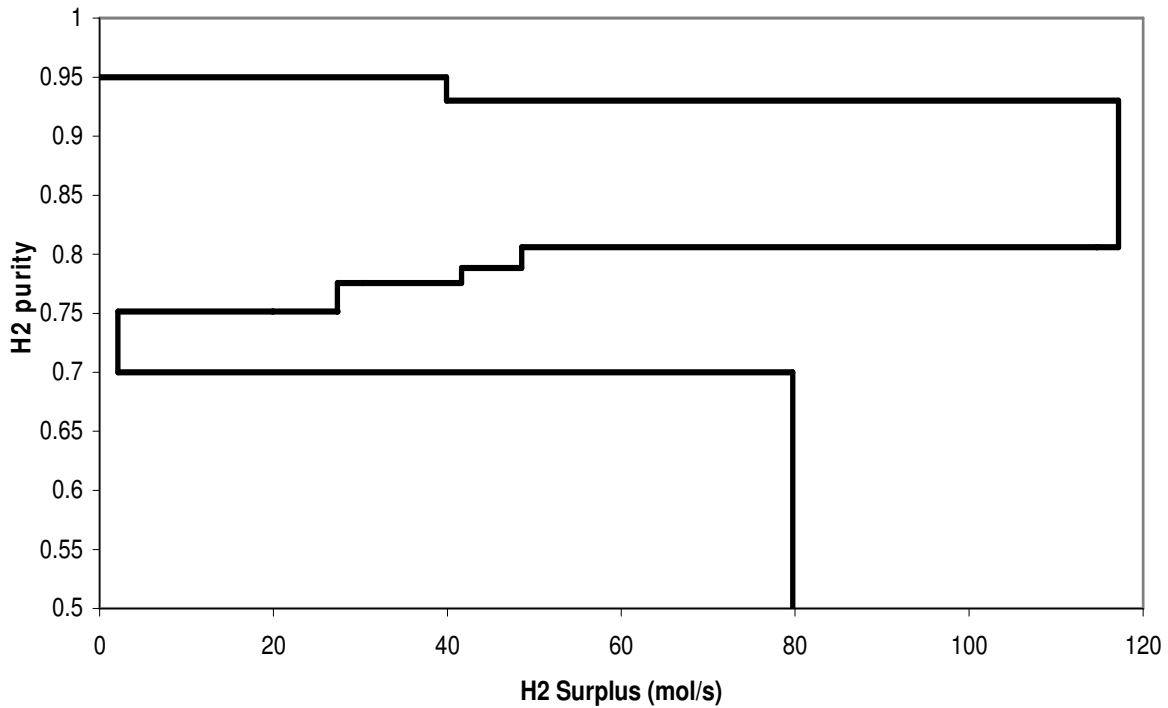
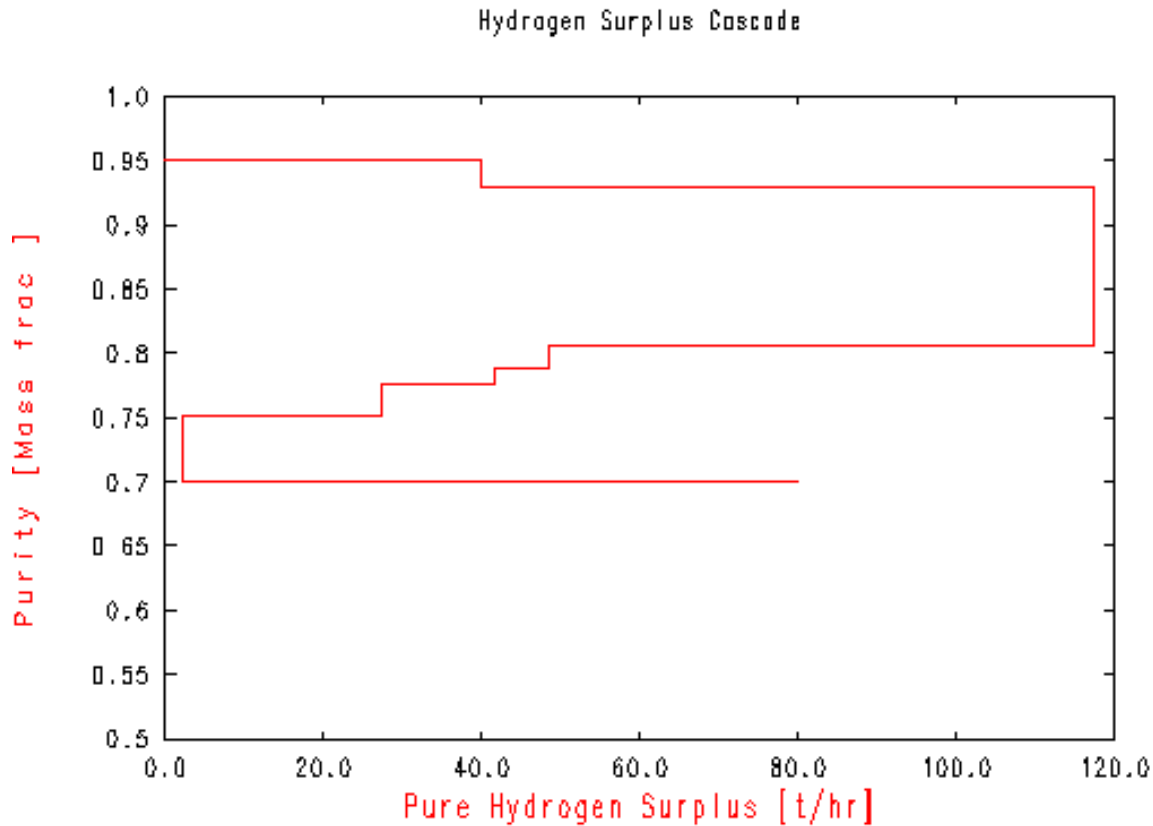


Figure 27: RefOpt hydrogen-composite curve for Example 1.

We can also compare the RefOpt hydrogen-surplus diagram with our hydrogen-surplus diagram (originally in Figure 6). We can generate the hydrogen-surplus diagram in RefOpt by selecting HYDROGEN NETWORK- HYDROGEN SURPLUS CASCADE. We have changed the axes in Figure 6 to match the axes in the RefOpt hydrogen-surplus diagram to show the similarity. See Figure 28 for our excel spreadsheet hydrogen-surplus diagram and Figure 29 for the RefOpt hydrogen-surplus diagram.



**Figure 28: The initial hydrogen-surplus diagram for Example 1 with changed axes.**



**Figure 29: RefOpt hydrogen-surplus diagram.**

Another way to verify the actual numbers used in the hydrogen-surplus diagrams is to compare the cumulative hydrogen surplus flow rate of column N from Figure 4 to the “hydrogen surplus cascade report” in RefOpt. We can generate this report by selecting HYDROGEN NETWORK-CASCADE REPORT. See Figure 30 for a larger view of column N from Figure 4 and see Figure 31 for the RefOpt output. We can see there is a slight difference in the hundredths place for these numbers due to the fact that RefOpt uses more decimal places when calculating its hydrogen purity (called demand purity in our spreadsheet).

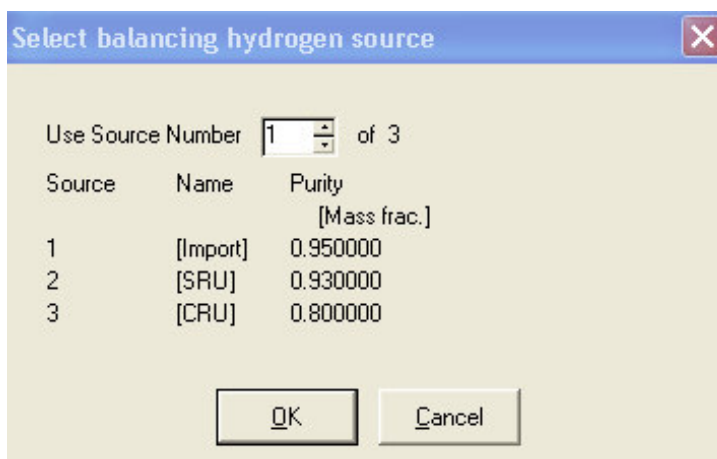
Flow interval mol/s	Demand purity (vol frac.)	Source purity (vol frac.)	Maximum purity (vol frac.)	H2 surplus mol/s	Cumulative H2 surplus (Nm <sup>3</sup> /h)
0	0.8061	0.95	0.95	-----	0
277.2	0.8061	0.95	0.95	39.88908	39.88908
277.2	0.8061	0.93	0.93	-----	39.88908
901	0.8061	0.93	0.93	77.28882	117.1779
901	0.8061	0.8	0.8061	-----	117.1779
1316.8	0.8061	0.8	0.8061	-2.53638	114.64152
1316.8	0.8061	0.75	0.8061	-----	114.64152
2495	0.8061	0.75	0.8061	-66.09702	48.5445
2495	0.7885	0.75	0.7885	-----	48.5445
2675.2	0.7885	0.75	0.7885	-6.9377	41.6068
2675.2	0.7757	0.75	0.7757	-----	41.6068
3118.7	0.7757	0.75	0.7757	-11.39795	30.20885
3118.7	0.7757	0.75	0.7757	-----	30.20885
3229.6	0.7757	0.75	0.7757	-2.85013	27.35872
3229.6	0.7514	0.75	0.7514	-----	27.35872
3257.3	0.7514	0.75	0.7514	-0.03878	27.31994
3257.3	0.7514	0.73	0.7514	-----	27.31994
3603.8	0.7514	0.73	0.7514	-7.4151	19.90484
3603.8	0.7514	0.7	0.7514	-----	19.90484
3950.3	0.7514	0.7	0.7514	-17.8101	2.09474
3950.3	0	0.7	0.7	-----	2.09474
4061.2	0	0.7	0.7	77.63	79.72474
4061.2	0	0	0	-----	79.72474

Figure 30: Part of the initial spreadsheet for Example 1 - cumulative surplus column.

	Pure Hydrogen Surplus Purity [Mass frac.]	Pure Hydrogen Surplus [t/hr]
1	0.950000	0.00000
2	0.950000	39.8883
3	0.930000	39.8883
4	0.930000	117.175
5	0.806103	117.175
6	0.806103	114.638
7	0.806103	114.638
8	0.806103	48.5374
9	0.788457	48.5374
10	0.788457	41.6074
11	0.775700	41.6074
12	0.775700	27.3593
13	0.751360	27.3593
14	0.751360	27.3216
15	0.751360	27.3216
16	0.751360	19.9205
17	0.751360	19.9205
18	0.751360	2.12442
19	0.700000	2.12442
20	0.700000	79.7544

**Figure 31: RefOpt hydrogen-surplus cascade.**

Now that we know that all of the input data to RefOpt are the same as the data we are using, we can use RefOpt to optimize the system based on one of the fresh hydrogen streams. To do this, we select HYDROGEN NETWORK - BAL. COMPOSITES CURVES. Then, we select the Import (Source #1) to balance the system. This means that RefOpt will vary the flow rate of the Import to optimize the system. See Figure 32 for the RefOpt screen.



**Figure 32: RefOpt screen to pick “Import” (Source #1) as flow rate to vary.**

By using the same approach we use above to get the original composite curve (source-demand plot) from RefOpt, we can now also obtain the optimized composite curve based on varying the Import flow rate. Figure 33 shows pinched hydrogen composite curve. We can compare it to our excel spreadsheet pinched hydrogen-composite curve shown in Figure 34. Figure 33 shows that the target (or pinched) flow rate for the Import stream has decreased to 268.702 mol/s. We can compare this to the result we obtain from our excel spreadsheet in Figure 7 in column D row 17, which is 268.821mols/s. In Figure 35, we have enlarged Figure 7 and highlighted the pinched (or target) Import flow.

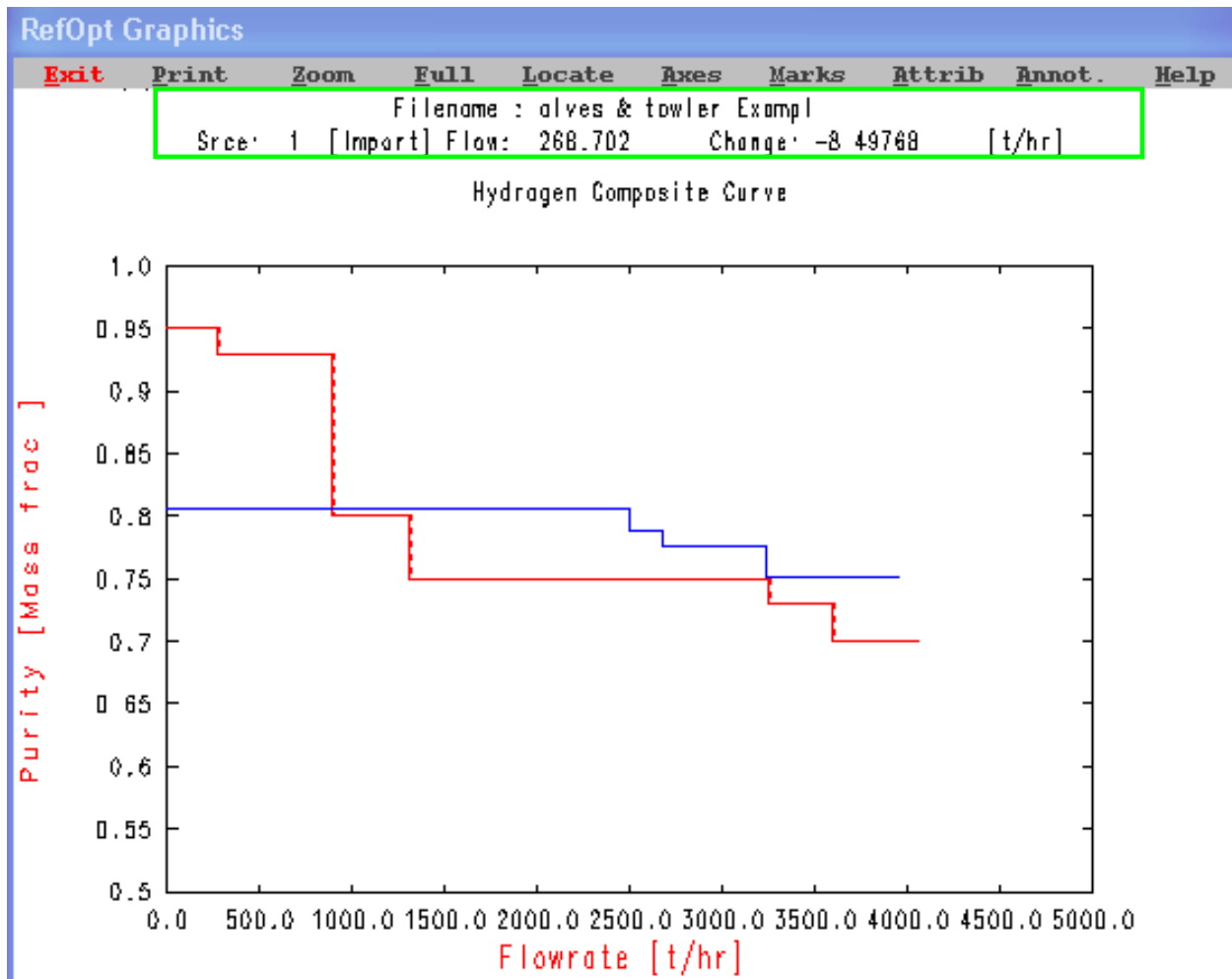


Figure 33: RefOpt optimized hydrogen-composite curve.

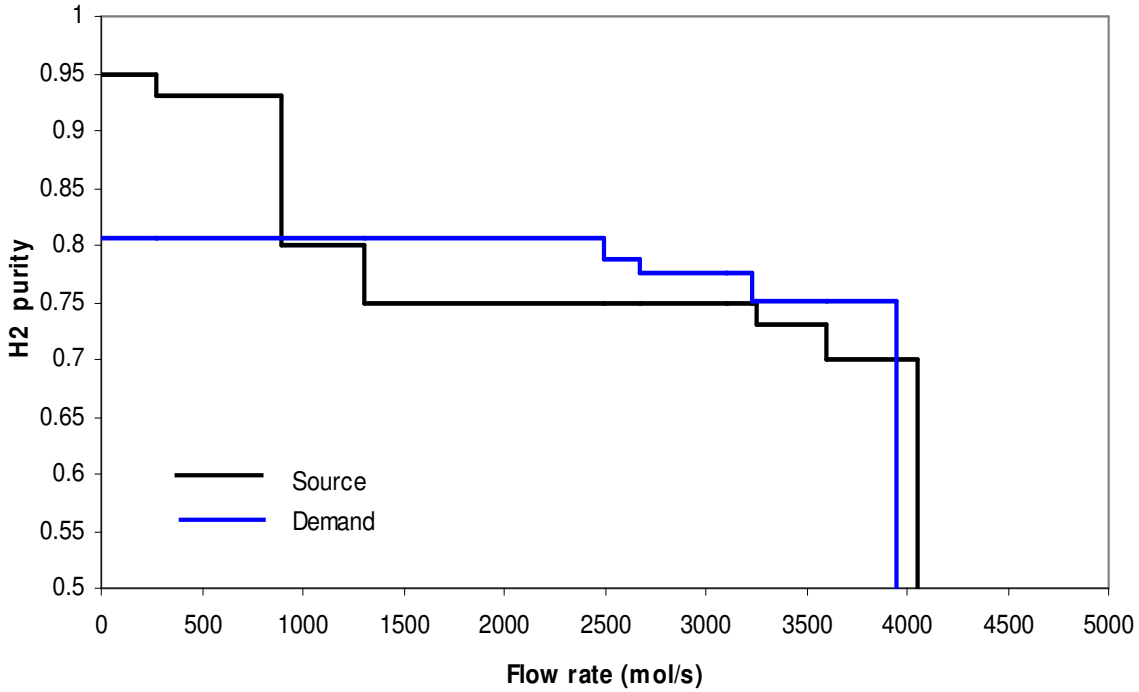


Figure 34: Example 1 Excel spreadsheet pinched composite curve.

SOURCE	H2	Flow rate	H2	H2	Cumulative							
Stream	Source		percentage	purity	flow rate							
Name	(inlet)	mol/s	v%	(vol frac.)	mol/s							
						2495	0.8061	0.75	0.8061	-66.56708	46.868708	
						2495	0.7885	0.75	0.7885	-----	46.868708	
						2675.2	0.7885	0.75	0.7885	-6.9377	39.931008	
1	Import	<b>268.821</b>	95	0.95	268.82104	2675.2	0.7757	0.75	0.7757	-----	39.931008	
2	SRU	623.8	93	0.93	892.62104	3110.321	0.7757	0.75	0.7757	-11.18261	28.748397	
3	CRU	415.8	80	0.8	1308.42104	3110.321	0.7757	0.75	0.7757	-----	28.748397	
4	HCUout	1801.9	75	0.75	3110.32104	3229.6	0.7757	0.75	0.7757	-3.065469	25.682928	
5	NHTout	138.6	75	0.75	3248.92104	3229.6	0.7514	0.75	0.7514	-----	25.682928	
6	DHTout	346.5	73	0.73	3595.42104	3248.921	0.7514	0.75	0.7514	-0.027049	25.655879	
7	CNHTout	457.4	70	0.7	4052.82104	3248.921	0.7514	0.73	0.7514	-----	25.655879	
						3595.421	0.7514	0.73	0.7514	-7.4151	18.240779	
						3595.421	0.7514	0.7	0.7514	-----	18.240779	
						3950.3	0.7514	0.7	0.7514	-18.24078	0	
						3950.3	0	0.7	0.7	-----	0	
						4052.821	0	0.7	0.7	71.76473	71.764728	
						4052.821	0	0	0	-----	71.764728	

Figure 35: Example 1 pinched spreadsheet enlarged and target flow rate highlighted.

We can also compare the RefOpt pinched surplus diagram to our excel spreadsheet pinched surplus diagram. In RefOpt, we select HYDROGEN NETWORK – BAL. HYDORGEN SURPLUS CASCADE. Then, we select Import (Source #1) to balance. This



produces Figure 36. Figure 37 shows that our excel spreadsheet pinched hydrogen surplus diagram matches the RefOpt diagram.

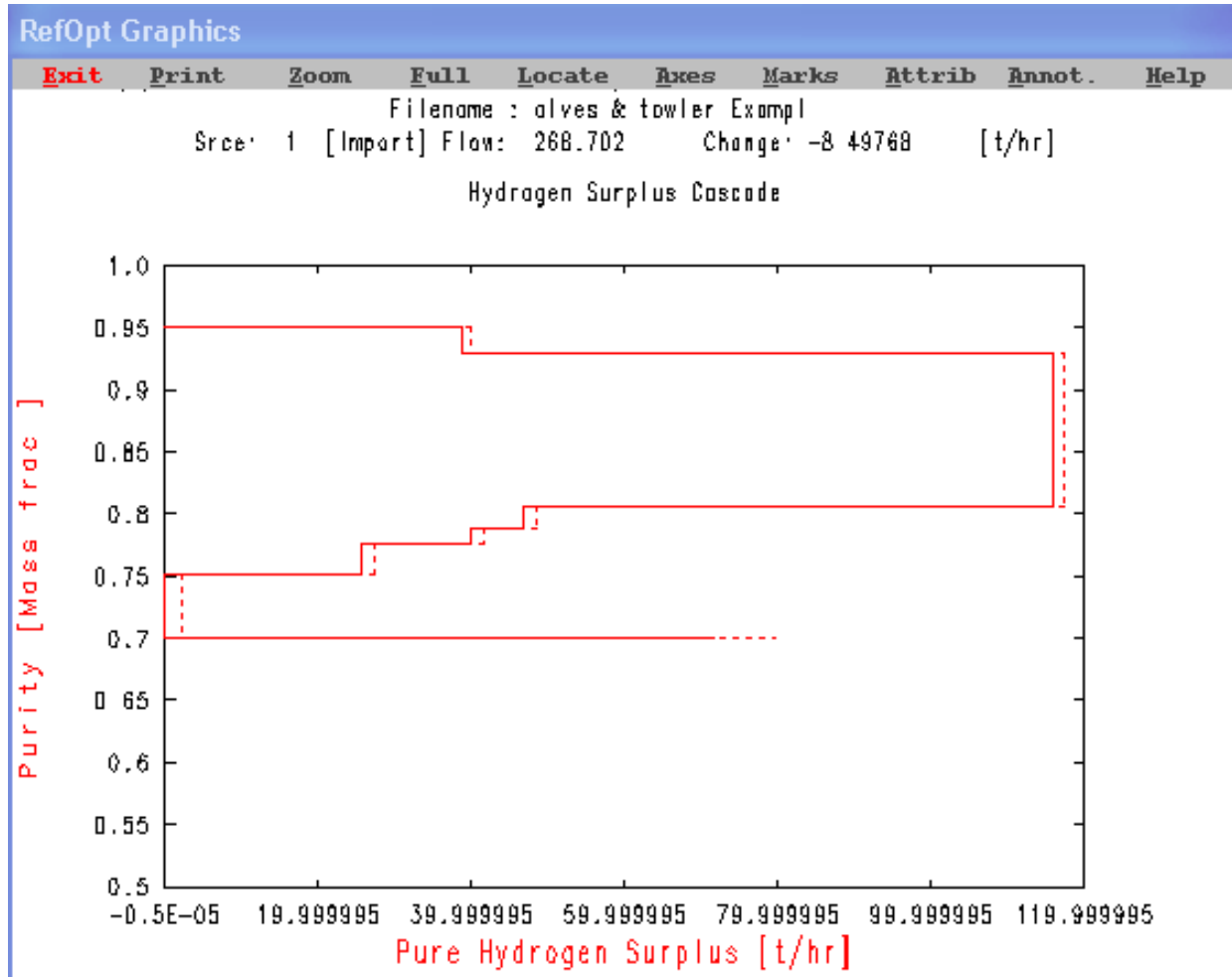
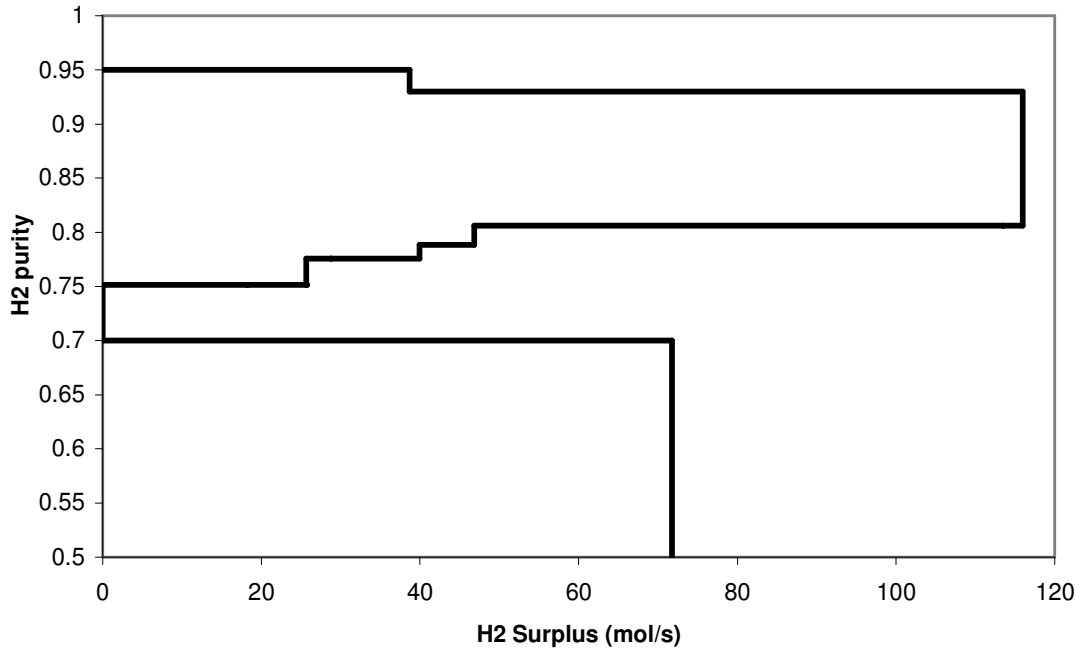


Figure 36: RefOpt pinched hydrogen-surplus diagram.



**Figure 37: Excel spreadsheet pinched hydrogen-surplus diagram for Example 1.**

By comparing the RefOpt initial hydrogen-composite curve, initial surplus diagram, and the hydrogen-surplus cascade report to our initial spreadsheet, we can see that our spreadsheet is making the correct initial calculations. Once we pinch the system, we can see again by comparing the pinched hydrogen-composite curves and pinched surplus diagram from RefOpt to our spreadsheet results that they are the same. We also compare the pinched hydrogen flow rate for our import stream to the target flow rate calculated by RefOpt, which we find to only differ by 0.1 mol/s. We provide a free copy of our spreadsheet on our website [www.design.che.vt.edu](http://www.design.che.vt.edu), whereas the RefOpt software is costly.

## 6 Resources

All of the examples present above are available on our website: [www.design.che.vt.edu](http://www.design.che.vt.edu) and can be freely downloaded. A blank starting spreadsheet is also available for downloading on the website for those that want to try it with their own systems.

## 7 Conclusions

The automated pinch spreadsheet tells users easily and quickly if there is excess hydrogen in a network and approximately how much hydrogen we could save if we were to make a few changes. This method is robust and can handle not only general pinch problems, but also multiple-pinch situations along with purifier placement. The method does not lump together hydrogen streams with the same purity, and it labels each stream individually. This enables users to easily see the effects of changing the flow rate of an individual stream. The next step would be to account for pressure and to do cost comparisons through mathematical optimization.

## 8 References

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<http://www.ceas.manchester.ac.uk/research/centres/centreforprocessintegration/software/packages/refopt/>

## PART 2: Application of COSMO-SAC to Electrolytes

### 9 Introduction

#### 9.1 *Motivation and significance of this research*

Engineers are often willing to sacrifice accuracy in return for saving both time and money when using predictive thermodynamic models, which could significantly enhance the success of developing and manufacturing a new drug. Predictive thermodynamic models allow researchers to perform phase-equilibrium calculations and to account for liquid-phase nonidealities resulting from molecular interactions. UNIFAC, a group-contribution method and the NRTL activity-coefficient model are two of the models researchers use frequently. These methods require binary interaction parameters regressed from experimental data, and therefore have little or no applicability to compounds with new functional groups (in the case of UNIFAC) or new compounds (in the case of NRTL) without substantial experimentation.

An alternative approach to the group-contribution methods is to use solvation-thermodynamics methods to characterize molecular interactions and account for liquid-phase nonideality. The theory of these methods is based on computational quantum mechanics, which allows researchers to predict physical properties without experimental data.

Two *a priori* models are the Conductor-like Screening Model–Realistic Solvation, (COSMO-RS)<sup>12,13,14,16</sup> and Conductor-like Screening Model–Segment Activity Coefficient (COSMO-SAC),<sup>17,18</sup> which predict intermolecular interactions based only on molecular structure and a few adjustable parameters. COSMO-RS is the first extension of a dielectric continuum – solvation model to liquid – phase thermodynamics, and COSMO-SAC is a variation of COSMO-RS. These models predict liquid-phase activity coefficients, which we then use for phase-equilibrium calculations.

The COSMO solvation-thermodynamic methods use sigma profiles, which are a molecular-specific distribution of the surface-charge density. This sigma profile is similar to the parameter databases input UNIFAC requires; however the UNIFAC binary interaction parameters are specific to each functional group, whereas the sigma profiles are molecular-specific. By performing quantum-mechanical calculations, we generate sigma profiles from the

molecular structure. The generation of the sigma profiles is the most time-consuming step when using COSMO-based methods, at 90% of the computational effort.

Modeling solute solubilities within electrolytic solvents is an important area of research because solvent selection in drug manufacturing requires solubilities data. The groundwork for applying COSMO-SAC to electrolytes and the motivation for this work come from the graduate work of Richard J. Oldland<sup>23</sup> and P. Eric Mullins<sup>25</sup>.

## **9.2 Thesis Part 2 overview**

In part 2 of the thesis, we present the application of COSMO-SAC to electrolytes. We give background theory on other electrolyte models that researchers currently use, along with all the background theory for the COSMO-SAC model itself. We present details on how to generate molecular-specific sigma profile for electrolytes from a single structure by performing quantum-mechanical calculations, along with some example results. Lastly, we present changes to the current COSMO-SAC model to cover electrolytes. We present the FORTRAN programs for the sigma-averaging algorithm for electrolytes and the COSMO-SAC model for electrolytes. We compare our predictions of activity coefficients with literature results.

# **10 Background Theory**

In this Section, we give a brief overview of the current electrolyte models that are in use. We discuss why we will not be using any of them to add onto the existing COSMO-SAC model used by Mullins et al<sup>24,25</sup>. We also summarize the COSMO-SAC model that we will use as a basis.

## **10.1 Current Electrolyte Theory**

There are three main models that are currently used to account for ion-ion interactions. They include the extended Debye-Hückel<sup>44</sup> (EDH), the Pitzer-Debye-Hückel<sup>37</sup> (PDH), and the mean spherical approximation<sup>38</sup> (MSA). These models can be used in conjunction with the NRTL (non-random two-liquid) models. The NRTL models are powerful for solvent mixtures and are widely used in industry<sup>38</sup>. There are three combinations we discuss: e-NRTL<sup>36</sup>, e-NRTL-SAC<sup>37</sup>, and MSA-NRTL<sup>38</sup>.

The ion-ion interaction contribution changes with salt concentration. At low salt concentrations, long-range electrostatic forces begin to become significant<sup>40</sup>. As the concentration increases, there is a progressive screening of ion-ion interactions and short-range forces become increasingly more important<sup>40</sup>. At high salt concentrations, short-range interactions dominate due to screening of charges in concentrated solutions<sup>39</sup>. Short range forces include volume-exclusion interactions and electrostatic forces of shorter range than ion-ion Coulombic forces<sup>38</sup>, for example ion-dipole forces.

The extended Debye-Hückel (EDH)<sup>44</sup> model is satisfactory for dilute solutions of ionic strength up to 0.1 molal. This concentration range is not sufficient. It is best for 1-1 electrolytes such as NaOH with Na<sup>+</sup> and OH<sup>-</sup> ions, which leaves out many other types of electrolytes that we must consider in the pharmaceutical industry. Part of the EDH model deals with the long range interaction effects and the other makes a correction for short range effects.

The Pitzer-Debye-Hückel (PDH) model covers the long-range ion-ion interaction contribution. The PDH model needs the Born-term correction, which is used to correct for the change of the infinite-dilution reference state from the mixed solvent composition to the aqueous solution<sup>37</sup>. The Born term accounts for solvation effects<sup>38</sup>. The PDH model is used in the e-NRTL<sup>36</sup> model and the e-NRTL-SAC<sup>37</sup> model. The Born term represents the energy necessary to transfer an ion from infinite dilution in mixed solvent to the reference state of an infinitely diluted aqueous solution<sup>38</sup>.

The mean spherical approximation<sup>39</sup> (MSA) model describes long-range electrostatic interactions. It is good for moderate or intermediate salt concentration ranges, but stops working at concentrations of 1mol/L because at this concentration two ions statistically are separated by less than one solvent molecule and the solvent-averaged model basis becomes questionable. The only fitted parameter is the mean ionic size (diameter) and thus the results are very sensitive to ionic diameters<sup>43</sup>. The MSA model is used in MSA-NRTL<sup>38</sup> model, which does not need the Born term because the mixture of pure solvents and the infinite dilution of ions in the solvent mixture is the reference state<sup>38</sup>.

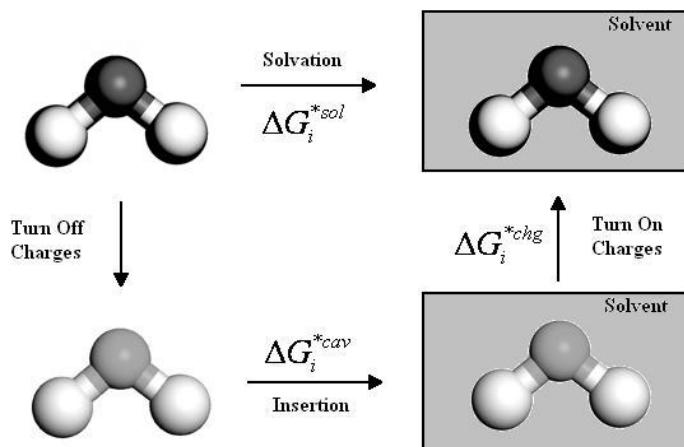
The e-NRTL<sup>36</sup> and e-NRTL-SAC<sup>37</sup> model both use the NRTL expression to cover the local (short-range) interactions. The long-range ion-ion interactions are covered by the PDH model along with the Born term for non-aqueous or mixed solvents. The MSA-NRTL<sup>38</sup> model

uses the NRTL model to covers all short-range interactions and the MSA model to cover only the long-range interactions (in place of PDH model).

We initially looked to these methods as examples of what type of correction term might need to be added to the current COSMO-SAC model that Mullins et al<sup>24,25</sup> use. However, there are a few problems or shortcomings with these methods. First of all, with some of them, as discussed above, there are concentration ranges that are not covered. Second, these models might need fitted parameters, which would mean the model is not as predictive as we are hoping for. We also notice that we might have all the information we need to extend the COSMO-SAC model to electrolytes in the sigma profile of the electrolyte. We discuss this aspect more in Section 12.1.

## 10.2 Overview of COSMO-SAC model

COSMO-based thermodynamic models use the “solvent-accessible surface” of the solute molecule<sup>13,15</sup>. These models create a cavity for the molecule within the solvent having a dielectric constant  $\epsilon$ , and then place the molecule in the cavity. Figure 38 illustrates the ideal solvation process that COSMO-based methods use.



**Figure 38: Conceptual diagram of ideal solvation process with a COSMO-based model.**

In Figure 38,  $\Delta G_i^{*sol}$  is the solvation free energy,  $\Delta G_i^{*cav}$  is the cavity-formation free energy, and  $\Delta G_i^{*chg}$  is the charging free energy. The solvation free energy is the sum of the cavity-formation free energy and the charging free energy in equation (1).



$$\Delta G_i^{*sol} = \Delta G_i^{*cav} + \Delta G_i^{*chg} \quad (1)$$

The solvation free energy is the change in Gibbs free energy associated with moving a molecule  $i$  from a fixed position in an ideal gas to a fixed position in a solution  $S$ . The cavity-formation free energy represents the change in Gibbs free energy required to form a cavity within a solution  $S$  of the exact size of the molecule  $i$ . The charging free energy is the Gibbs free energy required to remove the residual screening charges from the surface of the molecular cavity.

We use the definition from Lin and Sandler<sup>18</sup> for the activity coefficient,  $\gamma_{i/S}$ , where  $i$  is the molecule in a solution  $S$ . The activity coefficient is the difference in the charging Gibbs free energy for a pure species and for a pure species within solution, and is represented in the first term in equation (2). The Staverman-Guggenheim combinatorial term,  $\ln \gamma_{i/S}^{SG}$ , accounts for molecular size and shape effects. Lin and Sandler<sup>19,20</sup> suggest that this term improves the calculation of the cavity-formation free energy. The definition for Staverman-Guggenheim combinatorial term is in equation (3) below.

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*chg} - \Delta G_{i/i}^{*chg}}{RT} + \ln \gamma_{i/S}^{SG} \quad (2)$$

$$\ln \gamma_{i/S}^{SG} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (3)$$

In equation (3),  $\theta_i = x_i q_i / \sum_j x_j q_j$ ,  $\phi_i = x_i r_i / \sum_j x_j r_j$ , and  $l_i = (z/2)(r_i - q_i) - (r_i - 1)$ , where  $x_i$  is the mole fraction of component  $i$ , and  $z$  is the coordination number. The normalized volume,  $r_i = V_i / r$  and the normalized surface area,  $q_i = A_i / q$ , where  $A_i$  is the cavity surface area,  $V_i$  is the cavity volume, and  $r$  and  $q$  are COSMO-SAC model parameters. We assign values for these COSMO-SAC parameters and others in Table 6.

Lin and Sandler<sup>18</sup> define the charging Gibbs free energy as the sum of two terms because Klamt<sup>12</sup> treats the solvent as perfect conductor. These two terms are (1) the ideal solvation energy,  $\Delta G^{IS}$  and (2) the restoring free energy,  $\Delta G^{*res}$ . Since the ideal solvation energy for a solute in a solvent  $S$  or a pure liquid  $i$  are equivalent the two terms cancel, and the equation for the activity coefficient simplifies to equation (4).<sup>17,18</sup>

$$\ln \gamma_{i/S} = \frac{\Delta G_{i/S}^{*res} - \Delta G_{i/i}^{*res}}{RT} + \ln \gamma_{i/S}^{SG} \quad (4)$$

The restoring free energy is the sum of the products of the sigma profile and the natural log of the segment activity coefficients over all surface segments<sup>18</sup>, as equation (5) below shows.

$$\frac{\Delta G_{i/s}^{*res}}{RT} = \sum_{\sigma_m} \left[ n_i(\sigma_m) \frac{\Delta G_{\sigma_m/s}^{*res}}{RT} \right] = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln \Gamma_s(\sigma_m) \quad (5)$$

Here  $n_i(\sigma_m)$  is the number of segments with a surface-charge density  $\sigma_m$ ;  $n_i$  is the total number of surface segments around the molecular cavity;  $p_i(\sigma_m)$ , the sigma profile for a molecule  $i$ , is the probability of finding a segment with a surface-charge density  $\sigma_m$ ;  $\Gamma_s(\sigma_m)$  is the activity coefficient for a segment  $m$  of charge density,  $\sigma_m$ . We calculate the segment activity coefficient, which is derived rigorously using statistical mechanics<sup>18</sup>, for the segment in a solution  $\Gamma_s(\sigma_m)$  and in a pure liquid  $\Gamma_i(\sigma_m)$  using equation (6).

$$\begin{aligned} \ln \Gamma_s(\sigma_m) &= -\ln \left\{ \sum_{\sigma_n} p_s(\sigma_n) \Gamma_s(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \\ \ln \Gamma_i(\sigma_m) &= -\ln \left\{ \sum_{\sigma_n} p_i(\sigma_n) \Gamma_i(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \end{aligned} \quad (6)$$

In equation (6),  $\Delta W(\sigma_m, \sigma_n)$  is called the exchange energy, and is defined as the energy required to obtain one  $(\sigma_m, \sigma_n)$  pair from a neutral pair<sup>17</sup>. Currently, it has contributions from electrostatic interactions or misfit energy in the first term of equation (7), hydrogen-bonding interactions ( $E_{hb}$ ) in the second term of equation (7), and non-electrostatic interactions ( $E_{ne}$ ) of the segment pairs.<sup>16,17</sup> Non-electrostatic interactions are short-range interactions (dispersive or van der Waals forces). They are not specific to the interacting molecules.<sup>17</sup> They are assumed to be proportional to the contact surface area between molecules, and thus the non-electrostatic energy contribution is assumed constant.<sup>17</sup> Therefore it drops out of equation (7).

$$\begin{aligned} \Delta W(\sigma_m, \sigma_n) &= \left( \frac{\alpha'}{2} \right) (\sigma_m + \sigma_n)^2 + c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} + \sigma_{hb}] \\ &[\equiv] \text{ kcal} \cdot \text{mol}^{-1} \end{aligned} \quad (7)$$

In equation (7),  $\sigma_m$  is the segment charge density of segment  $m$ ,  $\alpha'$ , is the misfit energy constant,  $c_{hb}$  is the hydrogen bonding constant,  $\sigma_{hb}$  is the hydrogen bonding sigma cutoff value (0.0084 e/Å<sup>2</sup>), and  $\sigma_{acc}$  and  $\sigma_{don}$  are the larger and smaller values of  $\sigma_m$  and  $\sigma_n$ . When segment pairs form due to hydrogen bonding, there is an additional attractive energy gained

because of the electron penetration between the hydrogen bond donor and acceptor<sup>17</sup>. A hydrogen bond donor ( $\sigma_{don}$ ) is a segment with a charge density smaller than the cutoff value  $-\sigma_{hb}$ , and a hydrogen bond acceptor ( $\sigma_{acc}$ ) is a segment with a charge density greater than  $\sigma_{hb}$ . The hydrogen bonding energy contribution is zero unless  $\sigma_{acc}$  is greater than the cut off value  $\sigma_{hb}$  and  $\sigma_{don}$  is less than  $-\sigma_{hb}$ . In the  $\max[0, \sigma_{acc} - \sigma_{hb}]$  part of term 2, we use the minus sign in conjunction with the maximum function to make sure that the value of  $\sigma_{acc}$  is great than  $\sigma_{hb}$  (0.0084) in order for this term to be non-zero. In the  $\min[0, \sigma_{don} + \sigma_{hb}]$  part of term 2, we use the plus sign in conjunction with the minimum function to make sure that  $\sigma_{don}$  is less than  $-\sigma_{hb}$  (-0.0084) in order for this term to be non-zero.

In Table 5, we have created examples to show some of the possible combinations for the  $\sigma_m$  and  $\sigma_n$  values. In examples 1 through 3, all of the  $\sigma_m$  and  $\sigma_n$  values are neither greater than  $\sigma_{hb}$ , nor are they less than  $-\sigma_{hb}$ . Both the max and min terms are zero, and thus, there is no hydrogen bonding contribution. In examples 4 through 7, either the  $\sigma_m$  value or  $\sigma_n$  value is either greater than  $\sigma_{hb}$ , or is less than  $-\sigma_{hb}$ , but the other corresponding value is not. In these cases, either the max or the min term is non-zero, but both are not non-zero, and thus, there is no hydrogen bonding contribution. In examples 8 and 9,  $\sigma_m$  and  $\sigma_n$  are both greater than  $\sigma_{hb}$ , or both less than  $-\sigma_{hb}$ , which also does not meet the criteria, and thus, there is no hydrogen bonding contribution. Examples 10 and 11 are the only cases where either  $\sigma_m$  or  $\sigma_n$  is greater than  $\sigma_{hb}$ , and the other is less than  $-\sigma_{hb}$ . We can see that both the max and min terms are non-zero, thus, this is the only time we have a contribution to the hydrogen bonding energy.

**Table 5: Possible combinations for  $\sigma_m$  and  $\sigma_n$  to show hydrogen bonding contribution.**

Example	$\sigma_m$	$\sigma_n$	$\sigma_{acc}$	$\sigma_{don}$	$\max[0, \sigma_{acc} - \sigma_{hb}]$	$\min[0, \sigma_{don} + \sigma_{hb}]$	Hydrogen bond contribution?
1	-0.004	0.005	$\sigma_n$	$\sigma_m$	$\max[0, 0.005 - 0.0084]$ = $\max[0, -0.0034]$ 0	$\min[0, -0.004 + 0.0084]$ = $\min[0, 0.0044]$ 0	no
2	0.004	0.005	$\sigma_n$	$\sigma_m$	$\max[0, 0.005 - 0.0084]$ = $\max[0, -0.0034]$ 0	$\min[0, 0.004 + 0.0084]$ = $\min[0, 0.0124]$ 0	no
3	-0.004	-0.005	$\sigma_m$	$\sigma_n$	$\max[0, -0.004 - 0.0084]$ = $\max[0, -0.0124]$ 0	$\min[0, -0.005 + 0.0084]$ = $\min[0, 0.0034]$ 0	no
4	0.01	-0.005	$\sigma_m$	$\sigma_n$	$\max[0, 0.01 - 0.0084]$ = $\max[0, 0.0016]$ 0.0016	$\min[0, -0.005 + 0.0084]$ = $\min[0, 0.0034]$ 0	no
5	0.01	0.005	$\sigma_m$	$\sigma_n$	$\max[0, 0.01 - 0.0084]$ = $\max[0, 0.0016]$ 0.0016	$\min[0, 0.005 + 0.0084]$ = $\min[0, 0.0134]$ 0	no
6	-0.01	-0.005	$\sigma_n$	$\sigma_m$	$\max[0, -0.005 - 0.0084]$ = $\max[0, -0.0134]$ 0	$\min[0, -0.01 + 0.0084]$ = $\min[0, -0.0016]$ -0.0016	no
7	-0.01	0.005	$\sigma_n$	$\sigma_m$	$\max[0, 0.005 - 0.0084]$ = $\max[0, -0.0034]$ 0	$\min[0, -0.01 + 0.0084]$ = $\min[0, -0.0016]$ -0.0016	no
8	0.01	0.009	$\sigma_m$	$\sigma_n$	$\max[0, 0.01 - 0.0084]$ = $\max[0, 0.0016]$ 0.0016	$\min[0, 0.009 + 0.0084]$ = $\min[0, 0.0174]$ 0	no
9	-0.01	-0.009	$\sigma_n$	$\sigma_m$	$\max[0, -0.009 - 0.0084]$ = $\max[0, -0.0174]$ 0	$\min[0, -0.01 + 0.0084]$ = $\min[0, -0.0016]$ -0.0016	no
10	0.01	-0.009	$\sigma_m$	$\sigma_n$	$\max[0, 0.01 - 0.0084]$ = $\max[0, 0.0016]$ 0.0016	$\min[0, -0.009 + 0.0084]$ = $\min[0, -0.0006]$ -0.0006	yes
11	-0.009	0.01	$\sigma_n$	$\sigma_m$	$\max[0, 0.01 - 0.0084]$ = $\max[0, 0.0016]$ 0.0016	$\min[0, -0.009 + 0.0084]$ = $\min[0, -0.0006]$ -0.0006	yes

The definition for the exchange energy in equation (7) does not include a term for the contribution due to ion-ion interactions. We will discuss this in more detail in Section 12.1. The electrostatic contribution (misfit energy) is a correction for induced surface charges. These charges screen any polarization effects by placing the molecule in an ideal conductor, instead of

next to another molecular cavity. Klamt and co-workers<sup>13,16</sup> fit  $\alpha'$ ,  $c_{hb}$ , and  $\sigma_{hb}$  to experimental data. All three of these constants are COSMO-SAC model parameters. We assign values for these COSMO-SAC parameters and others in Table 6. In equation (7),  $\alpha'$  is the product of the polarizability factor  $f_{pol}$  and constant  $\alpha$ . Klamt suggests setting  $f_{pol}$  to a constant 0.64, although normally it is a function of the dielectric constant of the medium, as equation (8) shows.

$$f_{pol} = \frac{\epsilon - 1}{\epsilon + 1/2} = 0.64 \quad (8)$$

$$\alpha = \frac{0.3a_{eff}^{3/2}}{\epsilon_0} \quad [\equiv] \quad \text{kcal} \cdot \text{\AA}^4 \cdot \text{mol}^{-1} \cdot \text{e}^{-2} \quad (9)$$

$$\alpha' = f_{pol}\alpha \quad [\equiv] \quad \text{kcal} \cdot \text{\AA}^4 \cdot \text{mol}^{-1} \cdot \text{e}^{-2} \quad (10)$$

In equation (9),  $a_{eff}$  is the effective surface segment surface area, which is a COSMO-SAC model parameter and its value is assigned in Table 6. The permittivity of free space is  $\epsilon_0$  and its value is 2.395E-04.

By combining equations (2) through (10), Lin and Sandler<sup>18</sup> arrive at equation (11) below for the activity coefficient of a species  $i$  in a mixture  $s$  as a function of the pure component and mixture segment activity coefficient.

$$\ln \gamma_{i/s} = n_i \sum_{\sigma_m} p_i(\sigma_m) [\ln \Gamma_s(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma_{i/s}^{SG} \quad (11)$$

Since we use a different definition of our sigma profiles for pure components as explained in more detail in Section 11.1, we must modify both equations (6) and (11) slightly. We substitute the area-weighted sigma profile  $p'_i(\sigma)$  in place of the standard sigma profile  $p_i(\sigma)$ , which is similar to the equation used by Klamt.<sup>16</sup> In equation (12), all of the terms have the same definitions as in equation (6), and equation (13) incorporates the area-weighted sigma profile change.

$$\ln \Gamma_i(\sigma_m) = -\ln \left\{ \sum_i \frac{p'_i(\sigma_n)}{A_i} \Gamma_i(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \quad (12)$$

$$\ln \gamma_{i/s} = \frac{1}{a_{eff}} \sum_{\sigma_m} p'_i(\sigma_m) [\ln(\Gamma_s(\sigma_m)) - \ln(\Gamma_i(\sigma_m))] + \ln \gamma_{i/s}^{SG} \quad (13)$$

We refer to equation (13) as the COSMO-SAC model from this point forward and the COSMO-SAC parameters are defined below in Table 6.

**Table 6: Parameter Values Used in the COSMO-SAC model.**<sup>13,18</sup>

Symbol	Units	Value	Description
$r_{av}$	Å	0.81764	sigma averaging radius
$a_{av}$	Å <sup>2</sup>	2.100265	sigma averaging area
$a_{eff}$	Å <sup>2</sup>	7.5	effective surface segment surface area
$c_{hb}$	Å <sup>4</sup> *kcal/(e <sup>2</sup> *mol)	85580.0	hydrogen-bonding constant
$\sigma_{hb}$	e/Å <sup>2</sup>	0.0084	sigma cutoff for hydrogen-bonding
$\alpha'$	Å <sup>4</sup> *kcal/(e <sup>2</sup> *mol)	16466.72	misfit energy constant
$z$	dimensionless	10	coordination number
$q$	Å <sup>2</sup>	79.53	standard area parameter
$r$	Å <sup>3</sup>	66.69	standard volume parameter

## 11 Sigma Profiles for Electrolytes

### 11.1 Theory

A sigma profile is a molecular-specific probability distribution of the surface-charge density of a molecule or a mixture. As shown in Figure 38 in Section 10.2, COSMO-based models, in our case COSMO-SAC, first “turn off” any charges on the molecule and then create a cavity in the solvent, which is assumed to be a perfect conductor<sup>12</sup>. Then, the charges on the surface of the molecule are “turned on” and they draw the exact opposite charge from the solvent to the surface. This essentially cancels or screens the electric field, which allows the molecule to move around in the solvent without changing the overall energy of the system. We can calculate these charges on the surface of the molecule from Poisson’s equation and the zero total potential boundary condition.

$$\Phi_{tot} = \Phi_i + \Phi(q^*) = \Phi_i + Aq^* = 0 \quad (14)$$

In equation (14),  $\Phi_{tot}$  is the total potential on the cavity surface,  $\Phi_i$  is the potential due to the charge distribution of the solute molecule  $i$ ,  $\Phi(q^*)$  is the potential as a function of the ideal screening charge  $q^*$ . We can see from equation (14) that  $\Phi(q^*)$  is equal to the product of the ideal screening charge  $q^*$  and Coulomb Interaction Matrix  $A$ , which describes potential interactions between surface-charges and is a function of the cavity geometry<sup>16</sup>. The surface-

charge distribution for the cavity is well-approximated by a scaling of the surface-charge density,  $\sigma^*$ , in a conductor.

From the COSMO calculation output obtained in the energy calculation in Accelrys' Materials Studio<sup>27, 28, 29, 30</sup>, which is discussed in detail in Section 11.2, we average the segment surface-charge densities,  $\sigma^*$ , according to equation (15) to obtain a new surface-charge density.

$$\sigma = q_{avg} / a_{eff} \quad (15)$$

In equation (15),  $q_{avg}$  is the average screening charge for a given segment and  $a_{eff}$  is the effective area of a standard surface segment. This effective area represents the contact area between different segments, which is thus a theoretical bonding site. Klamt<sup>12</sup> defines the sigma profile  $p_i(\sigma)$  for a molecule  $i$  as the probability of finding a segment with a surface-charge density  $\sigma$  using equations (16) to (18).

$$p_i(\sigma) = n_i(\sigma) / n_i = A_i(\sigma) / A_i \quad (16)$$

$$n_i = \sum_{\sigma} n_i(\sigma) = A_i / a_{eff} \quad (17)$$

$$A_i = \sum_{\sigma} A_i(\sigma) [\equiv] \text{\AA}^2 \quad (18)$$

Here,  $n_i$  is the total number of surface segments around the molecular cavity,  $n_i(\sigma)$  is the number of segments with a surface-charge density  $\sigma$ ,  $A_i$  is the surface area of the molecular cavity, and  $A_i(\sigma)$  is the total surface area of all of the segments with a particular charge density  $\sigma$ . As defined by Lin and Sandler<sup>18</sup>,  $A_i(\sigma)$  and  $n_i(\sigma)$  are proportional by  $a_{eff}$ ,  $A_i(\sigma) = a_{eff} n_i(\sigma)$ .

As we briefly discussed above, we use area-weighted sigma profiles  $p_i'(\sigma)$  in place of the standard sigma profile  $p_i(\sigma)$ , for all charged and non-charged molecules as equation (19) shows.

$$p_i'(\sigma) = p_i(\sigma) A_i = A_i(\sigma) [\equiv] \text{\AA}^2 \quad (19)$$

In order to calculate a sigma profile for a mixture, we must also use a weighted average of the pure-component sigma profiles. Theoretically, a mixture sigma profile  $p_S(\sigma)$  in equation (20) is not limited to a specific number of components.

$$p_S(\sigma) = \frac{\sum_i x_i n_i p_i(\sigma)}{\sum_i x_i n_i} = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i} = \frac{\sum_i x_i p_i'(\sigma)}{\sum_i x_i A_i} \quad (20)$$

To calculate the new surface charge densities  $\sigma$ , we use an averaging algorithm for the segment surface-charge densities  $\sigma^*$  from Lin and Sandler<sup>18</sup>.

$$\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{eff}^2}\right)}{\sum_n \frac{r_n^2 r_{eff}^2}{r_n^2 + r_{eff}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{eff}^2}\right)} [\equiv] \text{e}/\text{\AA}^2 \quad (21)$$

In equation (21),  $\sigma_m$  is the average surface-charge density on segment  $m$ , the summation is over  $n$  segments which we get from the COSMO output, and  $r_n$  is the radius of the actual surface segment, which we assume has circular geometry. The effective radius,  $r_{eff} = \sqrt{a_{eff}/\pi}$ , is an adjustable parameter, and  $d_{mn}$  is the distance between the two segments  $m$  and  $n$ <sup>13,18</sup>. The paired segments  $m$  and  $n$  have segment charge densities  $\sigma_m$  and  $\sigma_n$ , respectively.

Since we use an average radius<sup>14</sup>,  $r_{av} = 0.81764 \text{ \AA}$ , instead of the effective radius  $r_{eff}$ , we must modify the sigma-averaging algorithm in equation (21). If we use the definition above for the effective radius, we can calculate the average segment surface area to be  $a_{av} = \pi r_{av}^2 = 2.100265 \text{ \AA}^2$ . Equation (22) shows the implementation of this change. We use equation (22) to calculate the average surface-charge density  $\sigma_m$ .

$$\sigma_m = \frac{\sum_n \sigma_n^* \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{av}^2}\right)}{\sum_n \frac{r_n^2 r_{av}^2}{r_n^2 + r_{av}^2} \exp\left(-\frac{d_{mn}^2}{r_n^2 + r_{av}^2}\right)} [\equiv] \text{e}/\text{\AA}^2 \quad (22)$$

We use a different value for  $r_{av}$  than Lin and Sandler<sup>18</sup> and Klamt and co-workers<sup>12,13</sup> use, however, our averaging algorithm is the same. Our  $r_{av}$  equals  $0.81764 \text{ \AA}$ , however, Klamt and co-workers report that “the best value for the averaging radius  $r_{av}$  turns out to be  $0.5 \text{ \AA}$ .”

The sigma-profile generation procedure makes two assumptions. The first assumption, which can save a great deal of computational time for large molecules, is that the optimized geometry from the DMol3 calculation in the vapor phase is identical to the optimal geometry in the condensed phase. Different geometries in a condensed phase than in an ideal gas can be due to solvent polarity, molecule size, and solvent-solute interactions. The second assumption requires that the molecule is in the lowest energy conformation once optimized. Several low-energy structural conformations may exist because of the freedom in choosing dihedral angles, and each conformation results in a different sigma profile.



We use equation (22) when generating all sigma profiles for electrolytes. Since electrolytes have larger positive and more negative overall charges, we must expand our x-axis (screen charge density) in order to include the data that we need. In order to do this, we change part of the sigma averaging FORTRAN code (see Appendix A). The main changes are in the following lines of codes:

```
(Lines 165 to 169)
!SETTING CHGDEN MATRIX
DO J=1,201
    SP(J)=0.D0
    CHGDEN(J) = -0.10D0+0.001D0*DBLE(J-1)
END DO
```

and

```
(Lines 178 to 180)
DO J=1,201
    WRITE(FILEOUT(F),*) CHGDEN(J),SP(J)
END DO
```

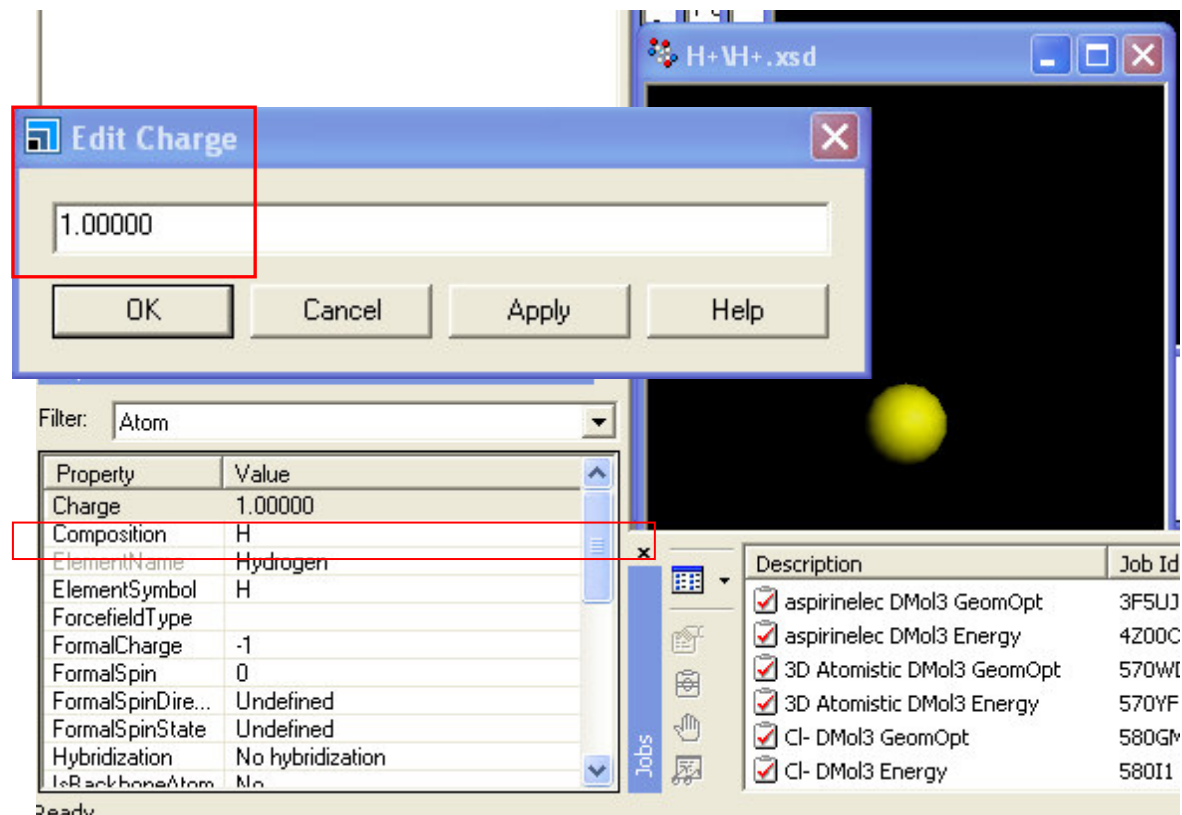
Thus, each sigma profile contains 200 segments, ranging from  $-0.1 \text{ e}/\text{\AA}^2$  to  $0.1 \text{ e}/\text{\AA}^2$  with a step size of  $0.001 \text{ e}/\text{\AA}^2$ . See Appendix A: FORTRAN Code for the full new version of the FORTRAN sigma averaging code.

## 11.2 Procedure

Our procedure for calculating the sigma profiles of electrolyte molecules includes three main steps. There is an optional pre-geometry-optimization step which can be included. We will outline the main steps and how they differ from the procedure for calculating the sigma profile of a non-charged molecule. References 24 and 25 give more information on the pre-geometry-optimization step and on the sigma profile procedure for non-charged molecules.

The first step is to calculate the optimum low-energy geometry of an individual molecule in the ideal gas phase based on the Hamiltonian energy using density-functional theory (DFT)<sup>31</sup>. We do this by using the DMol geometry calculation in Accelrys' Materials Studio<sup>27, 28, 29, 30</sup>. After we draw the molecule correctly and use the "clean" tool, we are almost ready to optimize the molecular geometry. We must first define the charge on the atoms. As an example, we have

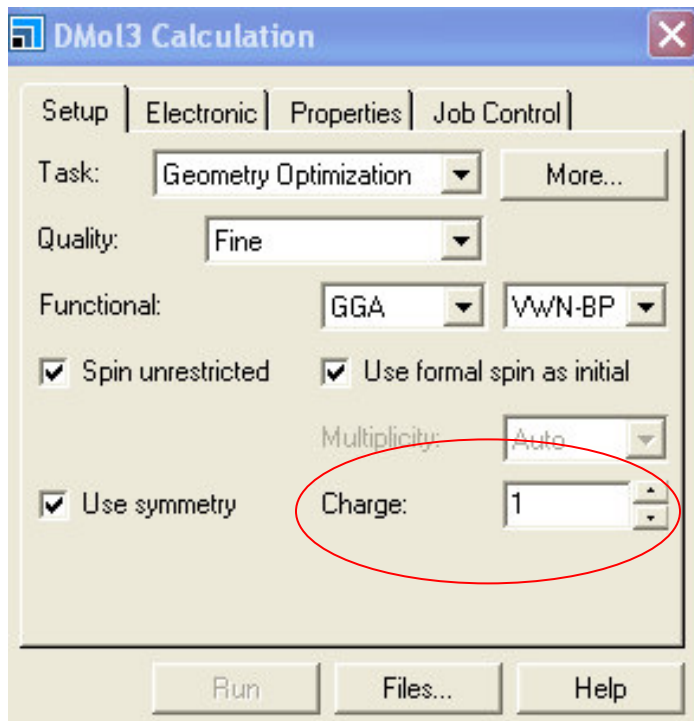
the H<sup>+</sup> molecule. In Figure 39 below, we show that in the properties box for the atom, the charge is equal to positive one. To change this, we double-click on the word “charge” and it brings up the “Edit charge” box where we can change the value of the charge on the atom.



**Figure 39: Editing the initial charge on the molecule in Materials Studio.**

Now we are ready to run the “Geometry Optimization” task in a DMol module to obtain the optimum low-energy geometry in the ideal gas phase. We use the DNP v4.0.0 basis set, which is recommended by Accelrys’ Materials Studio for COSMO applications<sup>21</sup>. We use the GGA/VWN-BP functional setting, which stands for generalized gradient approximation and the Becke-Perdew version of the Volsko-Wilk-Nusair functional<sup>31, 32, 33, 34</sup>. We optimize the geometry under “fine” tolerances. We also want to make sure that we adjust the overall charge on the molecule in the DMol calculation box. The “Spin unrestricted” box must also be checked for any electrolyte. Figure 40 shows an example of how the DMol geometry calculations should be set up for H<sup>+</sup>, our example electrolyte. We do keep in mind that the geometry-optimization

task is not necessary, although the calculation will run, for a single atom since there are no bond angles to optimize.



**Figure 40: Geometry Optimization DMol calculation box for electrolyte  $H^+$ .**

As we do for all uncharged molecules, we must add in the text “Basis\_Version v4.0.0” to our input file for electrolytes. We can also see that the input file correctly reflects the charge we have set in the previous steps. Figure 41 below shows what the input file looks like for our example of  $H^+$ .

```

H+H+ DMol3 GeomOptH+.input

# Task parameters
Calculate                optimize
Opt_energy_convergence  1.0000e-005
Opt_gradient_convergence 2.0000e-003 A
Opt_displacement_convergence 5.0000e-003 A
Opt_iterations           50
Opt_max_displacement    0.3000 A
Symmetry                 on

Basis_Version            v4.0.0

# Electronic parameters
spin_polarization       unrestricted
Charge                   1
Basis                    dnp
Pseudopotential         none
Functional               vwn-bp
Aux_density              octupole
Integration_grid         fine
Occupation               fermi
Cutoff_Global            3.1000 angstrom
scf_density_convergence  1.0000e-006
scf_charge_mixing        0.2000
scf_spin_mixing          0.5000
scf_iterations           50
scf_diis                  6 pulay

# Print options
Print                    eigval_last_it

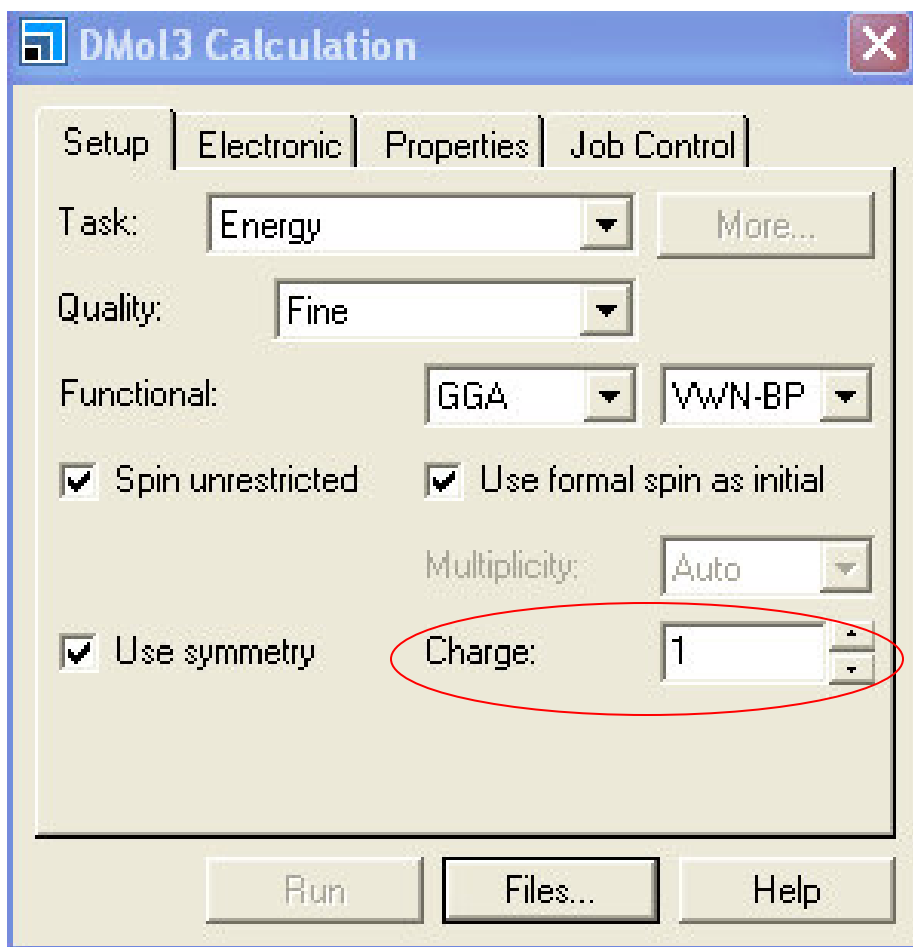
# Calculated properties

```

**Figure 41: DMol geometry calculation input file for H<sup>+</sup> reflecting the adjusted charge for an electrolyte.**

The second step is to calculate the surface screening charges and position of each segment on the surface of the geometrically optimized molecule in the condensed phase using both DFT and COSMO calculations. We assume that the low-energy optimal geometry does not change from the ideal gas phase to the condensed phase. This step is completed by performing an “Energy Calculation” in the DMol module, along with the addition of several keywords to turn on the built-in COSMO program in Materials Studio.

For the “energy calculation”, we use the same settings and tolerances as we do for the geometry calculation. Again, we make sure that we adjust the overall charge on the molecule in the DMol calculation box and check the “Spin unrestricted” box. Figure 42 shows how to set up the DMol energy calculations for the H<sup>+</sup> electrolyte.



**Figure 42: DMol Energy Calculation box for electrolyte  $H^+$ .**

Just as we add “Basis\_Version v4.0.0” to our input file for the geometry-optimization step, we must also add this line of code plus other COSMO keywords. For a full description of the keywords, see Table 7. We also see that the input file correctly reflects the charge we have set in the previous steps. Figure 43 shows what the input file for the energy calculation step looks like for our example of  $H^+$ . It reflects the added COSMO keywords and the overall charge on the molecule.

```
H+H+ DMol3 GeomOptH+ DMol3 GeomOptH+ DMol...
# Task parameters
Calculate          energy
Symmetry          on

Basis_Version     v4.0.0

# Environment Keywords
Cosmo             on
Cosmo_Grid_size   1082
Cosmo_Segments    92
Cosmo_Solvent_Radius 1.300000
Cosmo_A-Matrix_Cutoff 7.000000
Cosmo_Radius_Incr 0.000000
Cosmo_A-Constant  1.882190
Cosmo_B-Constant  0.010140
Cosmo_RadCorr_Incr 0.150000
Cosmo_Atomic_Radii
  1      1.300000
  6      2.000000
  7      1.830000
  8      1.720000
  9      1.720000
 15      2.120000
 16      2.160000
 17      2.050000
 35      2.160000
 53      2.320000

# Electronic parameters
Spin_polarization unrestricted
Charge            1
Basis             dnp
Pseudopotential  none
Functional        vwn-bp
Aux_density       octupole
Integration_grid  fine
Occupation        fermi
Cutoff_Global     3.1000 angstrom
```

**Figure 43: DMol energy calculation input file for H+ reflecting the added COSMO keywords and the adjusted charge for and electrolyte.**

**Table 7: COSMO keywords<sup>25</sup> used in calculating surface segment charges in DMol3<sup>a</sup>**

Keyword name	Default Value	Description
Cosmo	on	Turns on COSMO solvation procedure
Cosmo_Grid_Size	1082	Tells DMol3 how many basic grid points per atom to consider
Cosmo_Segments	92	Specifies the maximum number of segments on each atomic surface
Cosmo_Solvent_Radius	1.300000	Solvent probe radius
Cosmo_A-Matrix_Cutoff	7.000000	Determines the accuracy of the electrostatic interactions on the COSMO surface
Cosmo_Radius_Incr	0.000000	Specifies the increment to the atomic radii used in the construction of the COSMO cavity
Cosmo_RadCorr_Incr	0.150000	Used to construct the outer cavity for the outlying charge correction
Cosmo_A-Constraint	1.882190	Used to approximate the non-electrostatic contribution to the solvation energy within the COSMO model
Cosmo_B-Constraint	0.010140	Used to approximate the non-electrostatic contribution to the solvation energy within the COSMO model

<sup>a</sup> Detailed parameter descriptions are available in the Accelrys MS software documentation.<sup>22</sup>

The final step is to average the surface screening charges using equation (22) to generate the sigma profile using the FORTRAN program found in Appendix A: FORTRAN Code and discussed in Section 11.1.

### 11.3 Results

We run molecules in materials studio and created their sigma profiles using the modified sigma averaging FORTRAN program, as discussed above. We present results for water, sulfuric acid, nitric acid, phosphoric acid, and Aspirin below. Because of the correct trends (discussed more below) that are present with each set of molecules, we know that our results are valid.

We consider the following “water family” molecules: H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>, OH<sup>-</sup>, and H<sup>+</sup>. Figure 44 shows the sigma profiles for all these molecules. It shows that the molecules having a positive charge (for example the H<sup>+</sup> or the H<sub>3</sub>O<sup>+</sup> molecule) need a negative screening charge density. Molecules with negative charges (for example the OH<sup>-</sup> molecule) need positive screening charge. The water molecule having no overall charge needs some negative and some

positive screening charge density. We also see that the  $H^+$  molecule peak falls at a more negative screening charge density and has a higher peak than the  $H_3O^+$  molecule, which is expected.

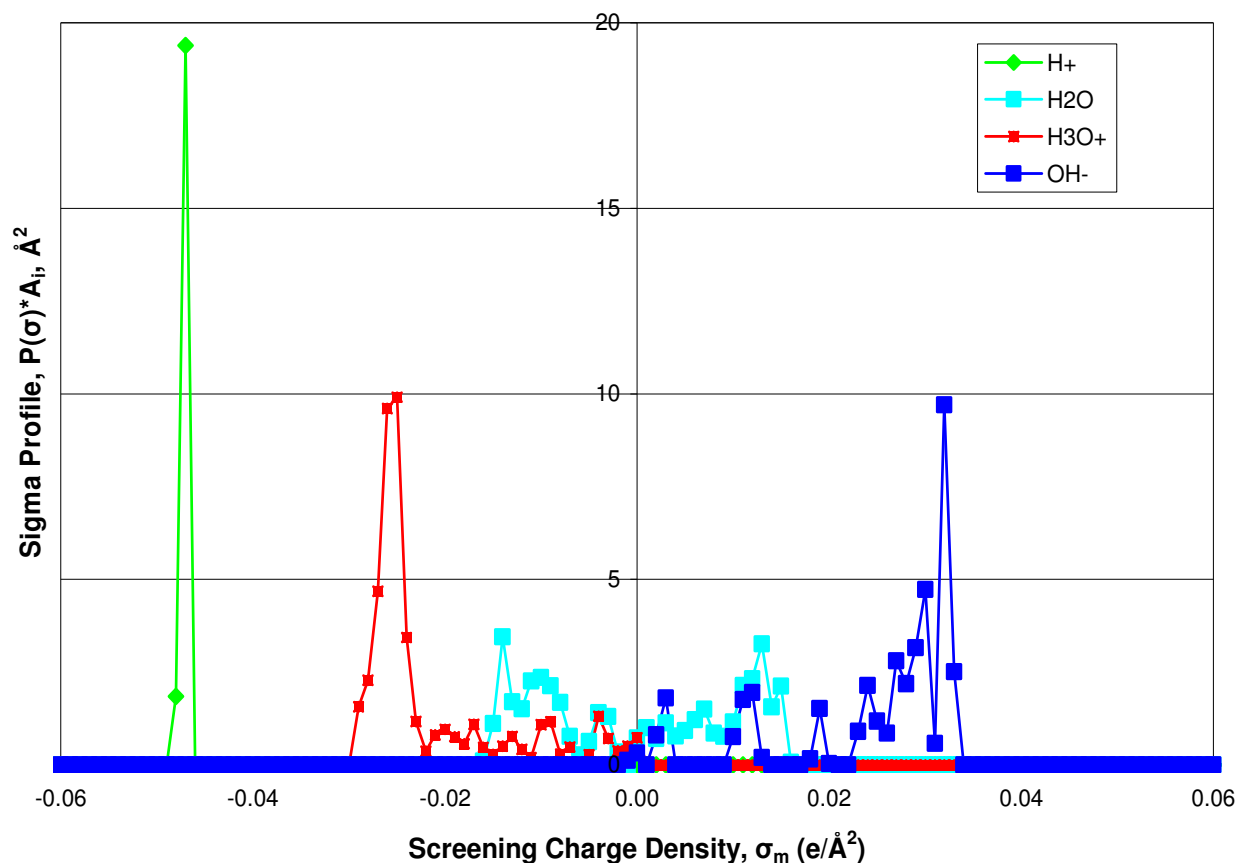
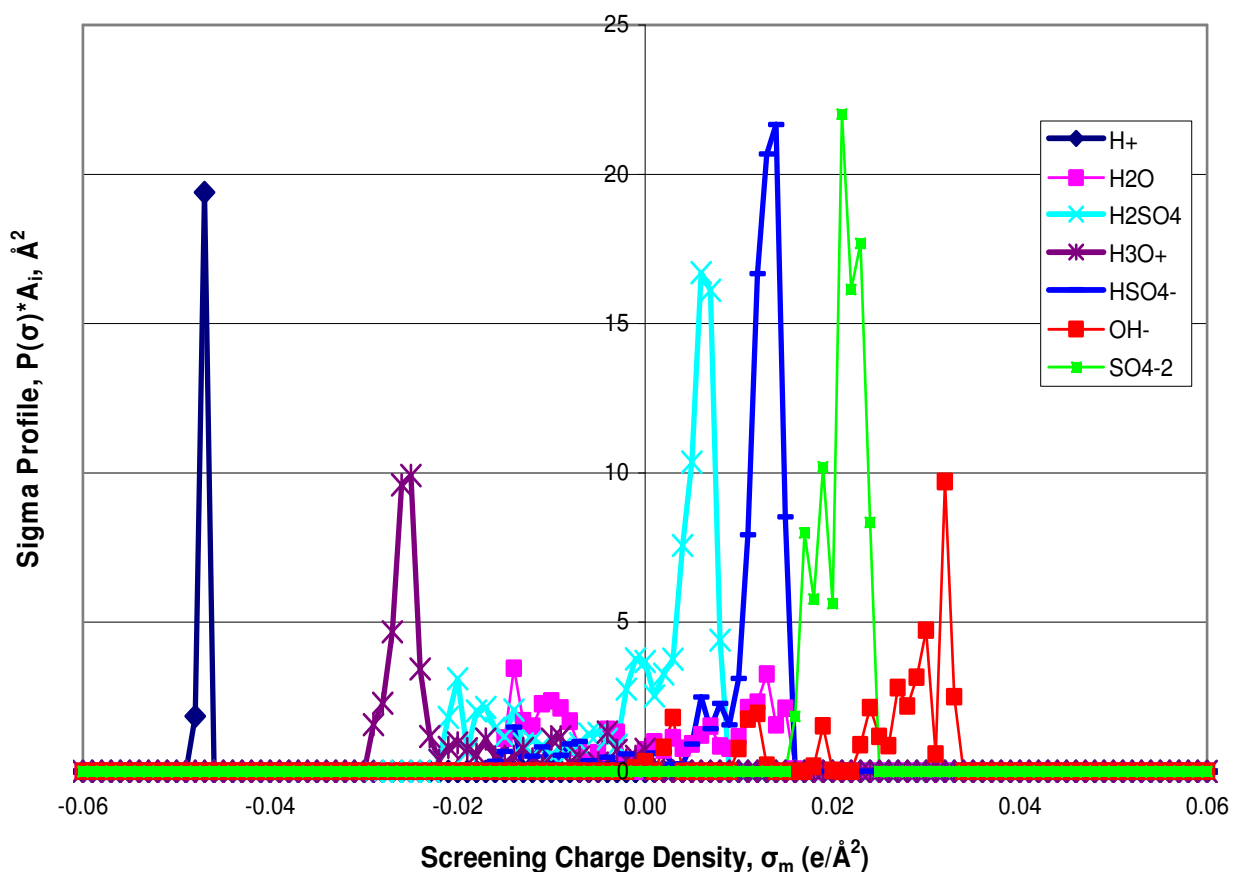


Figure 44: Sigma profiles for all water family molecules.

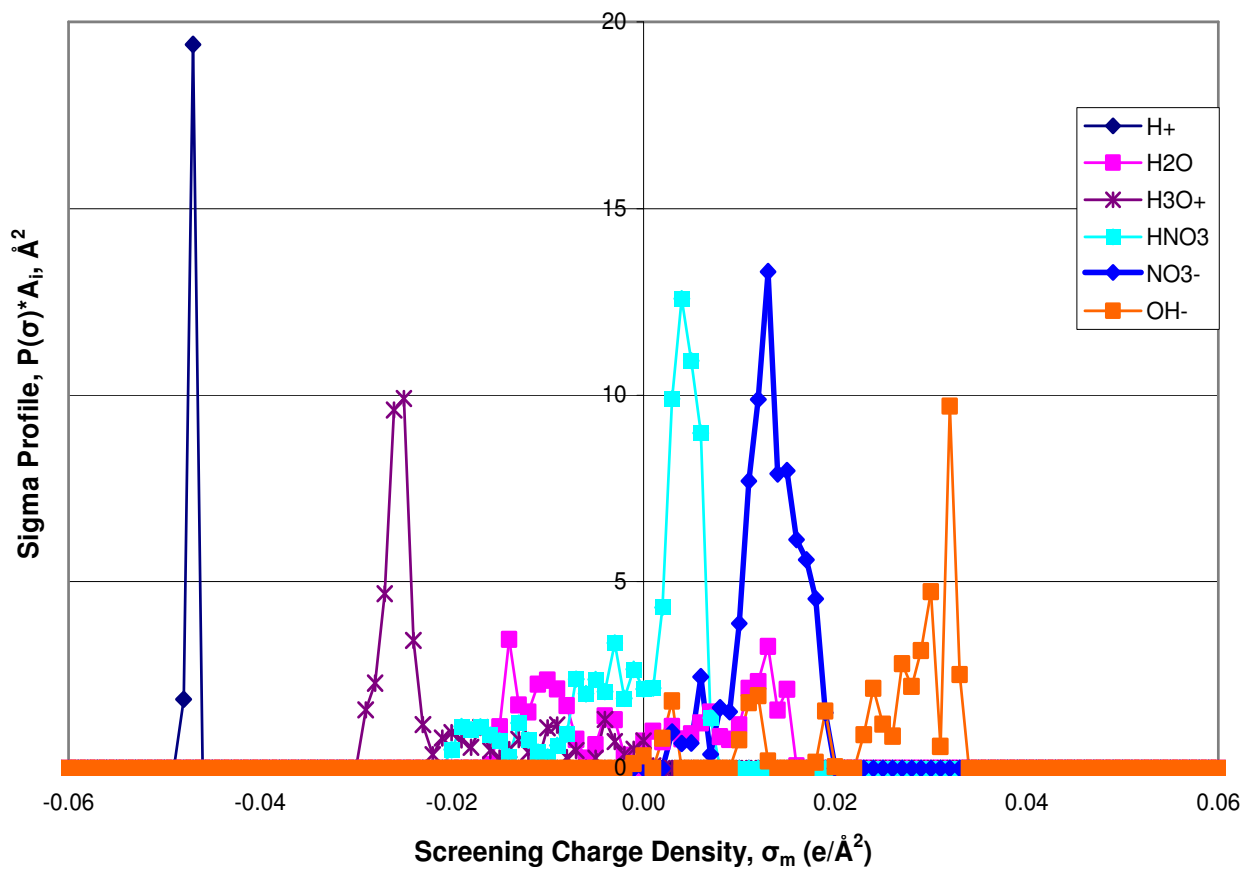


We run the following “sulfuric acid family” molecules:  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ . As the  $\text{H}_2\text{SO}_4$  molecule loses its hydrogen atoms, the molecule has a greater negative charge. This is reflected in Figure 45. Specifically, as the molecule gets more negative, the screening charge density becomes more positive. We also notice that as the molecule becomes more negative, the peak height gets higher. For comparison purposes, we keep the water family molecules in this figure.



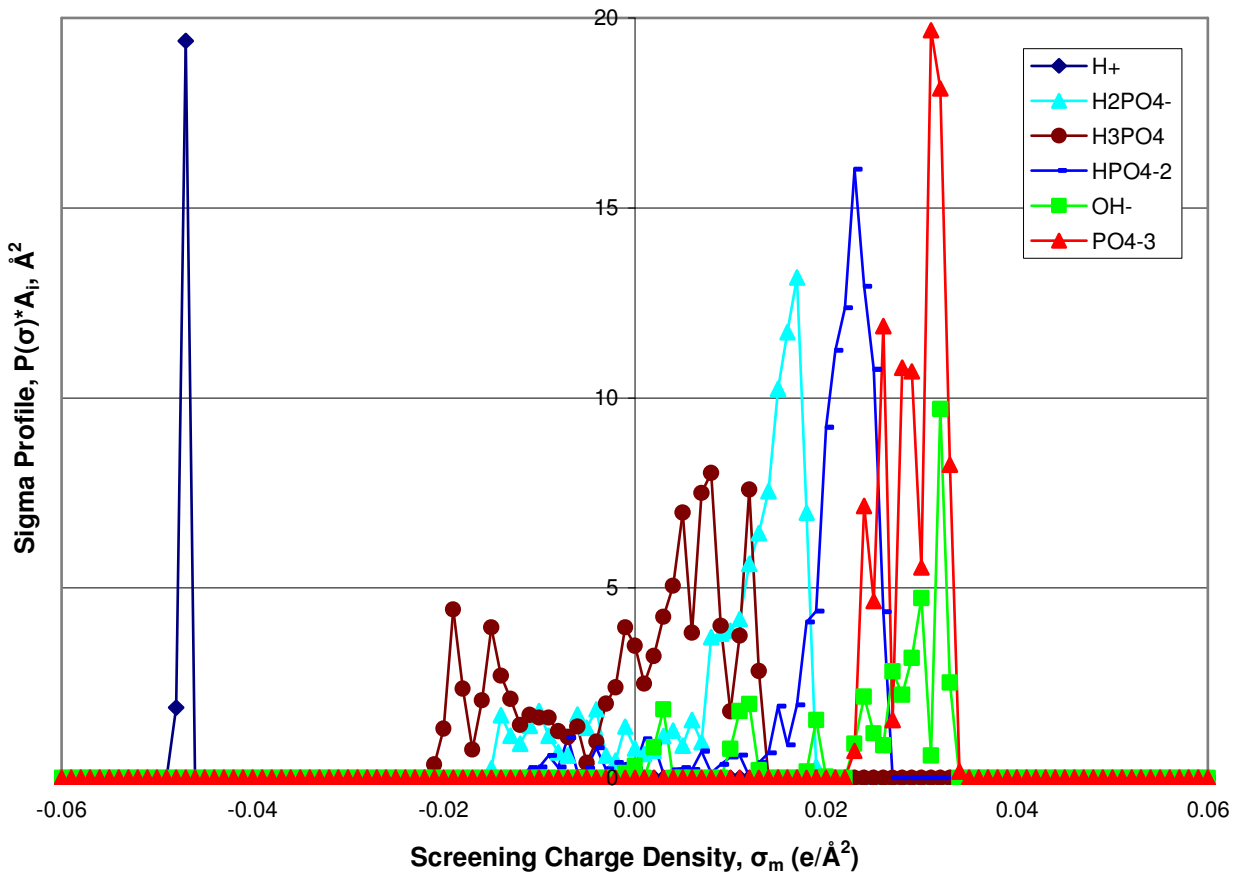
**Figure 45: Sigma profiles for all sulfuric acid family molecules.**

Figure 46 shows the sigma profiles for the “nitric acid family” molecules:  $\text{HNO}_3$ , and  $\text{NO}_3^-$ . Again, the neutral molecule has a more balanced sigma profile, whereas  $\text{NO}_3^-$  has a net positive sigma profile. For comparison purposes, we keep the water family molecules in this figure.



**Figure 46: Sigma profiles for all nitric acid family molecules.**

We run the following “phosphoric acid family” molecules:  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . Once again, we see that as the  $\text{H}_3\text{PO}_4$  molecule loses its hydrogen atoms, the molecule has a greater negative charge and this is reflected in the graph. In particular, as the molecule gets more negative, the screening charge density becomes more positive. We also notice that as the molecule becomes more negative, the peak height gets higher.



**Figure 47: Sigma profiles for all phosphoric acid family molecules.**

Figure 48 shows the sigma profiles for aspirin and the Aspirin electrolyte. We look at aspirin to show that the sigma profiles for large pharmaceutical electrolytes are also valid. We notice that the aspirin electrolyte sigma profile is distinctly shifted to a more positive screening charge density to make up for its more negative charge, when compared to the aspirin-c sigma profile. For comparison purposes, we keep the water family molecules in this figure.

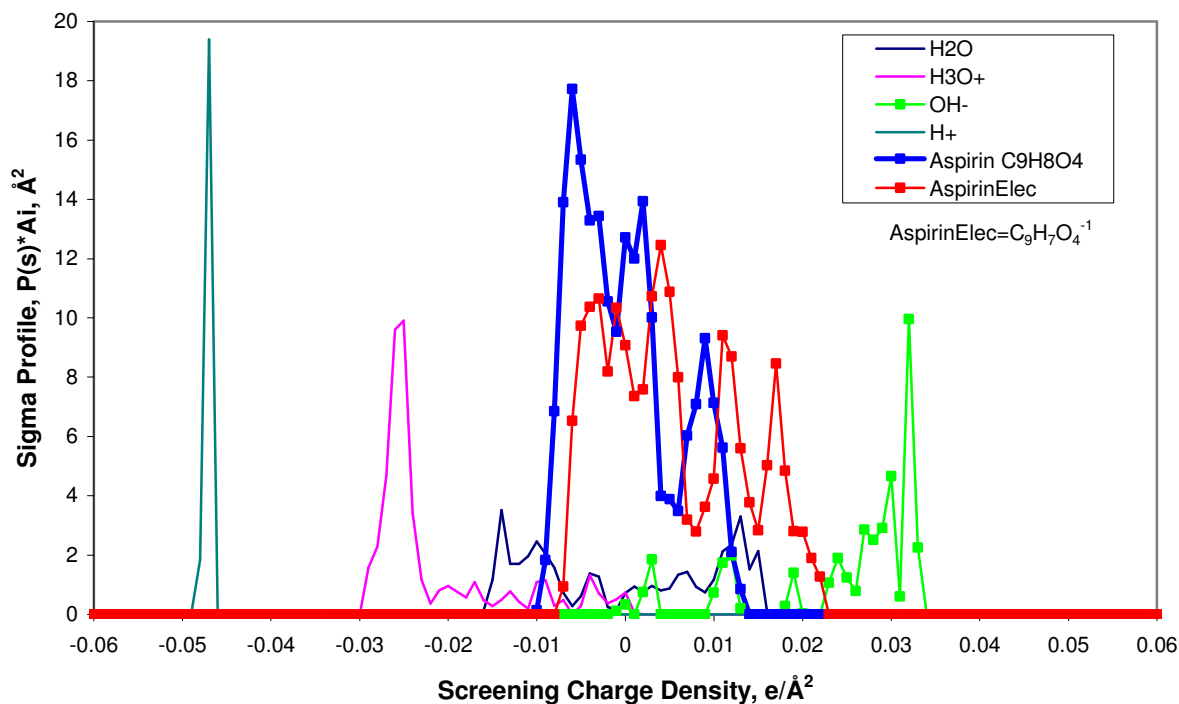


Figure 48: Sigma profiles for Aspirin molecules.

## 12 COSMO-SAC for Electrolytes

### 12.1 Theory

To start, we use the current exchange energy term found in equation (7) above in Section 10.2 and repeated below in equation (23). As stated above, the first term in the equation accounts for the electrostatic interaction or misfit energy, and the second term accounts for the hydrogen bonding contribution. This definition for the exchange energy uses the hydrogen bonding term for any two sigmas,  $\sigma$ , outside of the set sigma hydrogen bonding constant  $\sigma_{hb}$ .

However, what we want to consider is that at some point past  $\sigma_{hb}$ , which we will call  $\sigma_{ion}$ , the hydrogen bonding stops and ion-ion interactions begin to become significant.

$$\Delta W(\sigma_m, \sigma_n) = \left(\frac{\alpha'}{2}\right)(\sigma_m + \sigma_n)^2 + c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} + \sigma_{hb}] \quad (23)$$

[≡] kcal · mol<sup>-1</sup>

In equation (23),  $\sigma_m$  is the segment charge density of segment  $m$ ,  $\alpha'$ , is the misfit energy constant,  $c_{hb}$  is the hydrogen bonding constant,  $\sigma_{hb}$  is the hydrogen bonding sigma cutoff value (0.0084 e/Å<sup>2</sup>), and  $\sigma_{acc}$  and  $\sigma_{don}$  are the larger and smaller values of  $\sigma_m$  and  $\sigma_n$ . A hydrogen bond donor ( $\sigma_{don}$ ) is a segment with a charge density smaller than the cutoff value  $-\sigma_{hb}$ , and a hydrogen bond acceptor ( $\sigma_{acc}$ ) is a segment with a charge density greater than  $\sigma_{hb}$ . The hydrogen bonding energy contribution is zero unless  $\sigma_{acc}$  is greater than the cut off value  $\sigma_{hb}$  and  $\sigma_{don}$  is less than  $-\sigma_{hb}$ .

We propose, in equation (24), an exchange energy that has three contributions,  $E_{mf}$ ,  $E_{hb}$ , and  $E_{ion}$ , which represent the misfit energy, the hydrogen bonding energy, and the ion-ion interaction energy.

$$\Delta W(\sigma_m, \sigma_n) = E_{mf} + E_{hb} + E_{ion} \quad (24)$$

The misfit energy term remains unchanged from the original definition in equation (7) and is repeated in equation (25) below.

$$E_{mf} = \left(\frac{\alpha'}{2}\right)(\sigma_m + \sigma_n)^2 \quad (25)$$

Now we give more background on how this term evolves. The interaction energy is the energy between two molecules as a result of the contact with each other. If the two segments have equal and opposite charges, then the interaction energy is zero. This is called “ideal electrostatic contact”<sup>16</sup> and each molecule screens its partner just like a conductor would do. In most cases, however, the two charges are not going to be equal and opposite; in this case, the interaction energy is the energy which is required to remove the residual (extra) screening charge density from the contact area<sup>16</sup>. When the two molecules’ charges do not vanish (cancel each other), then there is what is called a misfit of the partners<sup>16</sup>. This is where the term of misfit energy

comes from. The energy of removal follows the elementary electrostatic theory<sup>16</sup>,  $E_{mf} = a_{eff} e_{misfit}$ , where  $e_{misfit}$  is the misfit energy density on the contact surface.

We explore two possible options for the hydrogen bonding energy and the ion-ion interaction energy. These are options 1 and 2 below.

For option 1, the hydrogen bonding contribution term remains the same as it is in equation (23); however, we must place a restriction that  $E_{hb}$  is equal to zero when the absolute value of both  $\sigma_{acc}$  and  $\sigma_{don}$  are greater than  $\sigma_{ion}$ . This accounts for the fact that we can have ion-ion interactions and not hydrogen bonding. We choose the  $E_{hb}$  term to be similar to the  $E_{hb}$  term proposed by Klamt to try to mirror the success.  $E_{hb}$  (in equation (23)) was chosen because its form qualitatively captures some of the physics of hydrogen bonding. It was made quantitative by fitting the parameters. This new hydrogen bonding energy for option 1 is in equation (26) below.

$$E_{hb} = \left\{ \begin{array}{l} 0 ; \text{ when } \text{abs}(\sigma_{acc}) > \sigma_{ion} \ \& \ \text{abs}(\sigma_{don}) > \sigma_{ion} \\ else \\ c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} + \sigma_{hb}] \end{array} \right\} \quad (26)$$

The third term in the exchange energy,  $E_{ion}$ , accounts for ion-ion interactions. We model this term after the hydrogen bonding term to see if we can duplicate the success of the original  $E_{hb}$  term in equation (23). The ion-ion interaction term is more complicated than the hydrogen bonding term. We account for both ion-ion attraction and ion-ion repulsion. We only have ion-ion attraction when one of the segments has a screening charge density less than negative  $\sigma_{ion}$  and the other segment has a screening charge density greater than positive  $\sigma_{ion}$ . This is the first term of  $E_{ion}$ , which always produces a negative value when it is not zero. This negative value reflects that this is an attractive force.

We also take into account that when either both segments are great than  $\sigma_{ion}$  or both segments are less than negative  $\sigma_{ion}$ , we have a repulsive force. These are terms two and three, respectively, of  $E_{ion}$ . These two terms always produce a positive value, which reflects the fact that they are repulsive forces. We give a form of  $E_{ion}$  that qualitatively captures ion-ion interactions and reasonable estimates of  $\sigma_{ion}$  and  $c_{ion}$  to see if a qualitative match with experiments is achieved. As we discuss more at the end of this section, the next step is to make it quantitative by fitting the parameters.

The proposed ion-ion interaction term for option 1 is below in equation (27).

$$\begin{aligned}
 E_{ion} = & c_{ion} \max [0, \sigma_{acc} - \sigma_{ion}] \min [0, \sigma_{don} + \sigma_{ion}] \\
 & + c_{ion} \max [0, \sigma_{acc} - \sigma_{ion}] \max [0, \sigma_{don} - \sigma_{ion}] \\
 & + c_{ion} \min [0, \sigma_{acc} + \sigma_{ion}] \min [0, \sigma_{don} + \sigma_{ion}]
 \end{aligned} \tag{27}$$

In equation (27), there are two new constants that we must assign values for:  $\sigma_{ion}$  and  $c_{ion}$ . We define  $\sigma_{ion}$  as the ion-ion interaction sigma cut off value, similar to  $\sigma_{hb}$ , the hydrogen bonding sigma cutoff value. We define  $c_{ion}$  as the ion-ion interaction constant, similar to  $c_{hb}$ , the hydrogen bonding constant. We know that that  $\sigma_{hb}$  must be less than  $\sigma_{ion}$ . As a first approximation, we use the sigma profiles for the compounds that we presented in Section 11.3. In particular, we look at the water sigma profile (Figure 44) and compare it to the  $H^+$  and  $OH^-$  profiles. We can see that the sigma profile for water extends from a screening charge density of  $-0.016 \text{ e}/\text{\AA}^2$  to  $-0.016 \text{ e}/\text{\AA}^2$ . Also, we look at the profiles for  $H_2SO_4$ ,  $HNO_3$ , and  $H_3PO_4$  and see that their ranges of screening charge densities are  $-0.022$  to  $0.008$ ,  $-0.020$  to  $0.007$ , and  $0.021$  to  $0.013$ , respectively. We see that the bulk of the sigma profile falls in this  $-0.016 \text{ e}/\text{\AA}^2$  to  $-0.016 \text{ e}/\text{\AA}^2$  range and that their counter part electrolyte compounds shift well past  $\sigma_{ion}$  and  $-\sigma_{ion}$ . Thus, we choose  $\sigma_{ion}$  equal to  $0.016 \text{ e}/\text{\AA}^2$ . For the new ion-ion interaction constant  $c_{ion}$ , we estimate that it is of the same order of magnitude as  $c_{hb}$ . Obviously, some sort of fitting of data for  $\sigma_{ion}$  and  $c_{ion}$ , would greatly increase our reasoning and hopefully results. This is discussed more in Section 12.2.

In Table 8, we have created examples to show some of the possible combinations for the  $\sigma_m$  and  $\sigma_n$  values and how they affect the first term of  $E_{ion}$ , which is the attractive term. In examples 1 through 3, all of the  $\sigma_m$  and  $\sigma_n$  values are neither greater than  $\sigma_{ion}$ , nor are they less than  $-\sigma_{ion}$ . Both the max and min terms are zero, and thus, there is no ion-ion attractive energy contribution. In examples 4 through 7, either the  $\sigma_m$  value or  $\sigma_n$  value is either greater than  $\sigma_{ion}$ , or is less than  $-\sigma_{ion}$ , but the other corresponding value is not. In these cases, either the max or the min term is non-zero, but both are not non-zero, and thus, there is no ion-ion attractive energy contribution. In examples 8 and 9,  $\sigma_m$  and  $\sigma_n$  are both greater than  $\sigma_{ion}$ , or both less than  $-\sigma_{ion}$ , which also does not meet the criteria for an attractive force, and thus, there is no ion-ion attractive energy contribution. These two particular cases are, however, are going to

contribute in the second and third terms of  $E_{ion}$  because they are repulsive. Examples 10 and 11 are the only cases where either  $\sigma_m$  or  $\sigma_n$  is greater than  $\sigma_{ion}$ , and the other is less than  $-\sigma_{ion}$ . We can see that both the max and min terms are non-zero, thus, this is the only time we have an attractive energy contribution to the ion-ion interaction energy.

**Table 8: Possible combinations for  $\sigma_m$  and  $\sigma_n$  to show the attractive energy contribution for the first term of  $E_{ion}$ .**

Example	$\sigma_m$	$\sigma_n$	$\sigma_{acc}$	$\sigma_{don}$	$\max[0, \sigma_{acc} - \sigma_{ion}] * \min[0, \sigma_{don} + \sigma_{ion}]$	$E_{ion}$ 1 <sup>st</sup> term only - <b>attractive</b> contribution?
1	-0.01	0.014	$\sigma_n$	$\sigma_m$	$\max[0, 0.014 - 0.016] * \min[0, -0.01 + 0.016]$ $\max[0, -0.002] * \min[0, 0.006]$ $= 0 * 0 = 0$	no
2	0.01	0.014	$\sigma_n$	$\sigma_m$	$\max[0, 0.014 - 0.016] * \min[0, 0.01 + 0.016]$ $\max[0, -0.002] * \min[0, 0.026]$ $= 0 * 0 = 0$	no
3	-0.01	-0.014	$\sigma_m$	$\sigma_n$	$\max[0, -0.01 - 0.016] * \min[0, -0.014 + 0.016]$ $\max[0, -0.026] * \min[0, 0.002]$ $= 0 * 0 = 0$	no
4	0.02	-0.01	$\sigma_m$	$\sigma_n$	$\max[0, 0.02 - 0.016] * \min[0, -0.01 + 0.016]$ $\max[0, 0.004] * \min[0, 0.006]$ $= 0.004 * 0 = 0$	no
5	0.02	0.01	$\sigma_m$	$\sigma_n$	$\max[0, 0.02 - 0.016] * \min[0, 0.01 + 0.016]$ $\max[0, 0.004] * \min[0, 0.036]$ $= 0.004 * 0 = 0$	no
6	-0.02	-0.01	$\sigma_n$	$\sigma_m$	$\max[0, -0.01 - 0.016] * \min[0, -0.02 + 0.016]$ $\max[0, -0.026] * \min[0, -0.004]$ $= 0 * -0.004 = 0$	no
7	-0.02	0.01	$\sigma_n$	$\sigma_m$	$\max[0, 0.01 - 0.016] * \min[0, -0.02 + 0.016]$ $\max[0, -0.006] * \min[0, -0.004]$ $= 0 * -0.004 = 0$	no
8	0.025	0.02	$\sigma_m$	$\sigma_n$	$\max[0, 0.025 - 0.016] * \min[0, 0.02 + 0.016]$ $\max[0, 0.009] * \min[0, 0.036]$ $= 0.009 * 0 = 0$	no - but this is a repulsive force-see next table
9	-0.025	-0.02	$\sigma_n$	$\sigma_m$	$\max[0, -0.02 - 0.016] * \min[0, -0.025 + 0.016]$ $\max[0, -0.036] * \min[0, -0.009]$ $= 0 * -0.009 = 0$	no - but this is a repulsive force-see next table
10	0.017	-0.018	$\sigma_m$	$\sigma_n$	$\max[0, 0.017 - 0.016] * \min[0, -0.018 + 0.016]$ $\max[0, 0.001] * \min[0, -0.002]$	yes



					$=0.001 * -0.002 = 2 \times 10^{-6}$	
					$\max[0, 0.02 - 0.016] * \min[0, -0.017 + 0.016]$	
<b>11</b>	-0.017	0.02	$\sigma_n$	$\sigma_m$	$\max[0, 0.004] * \min[0, -0.001]$ $=0.004 * -0.001 = 4 \times 10^{-6}$	yes

In Table 9, we have created examples to show some of the possible combinations for the  $\sigma_m$  and  $\sigma_n$  values and how they affect the second and third terms of  $E_{ion}$ , which is the repulsive term. In examples 1 through 3, all of the  $\sigma_m$  and  $\sigma_n$  values are neither greater than  $\sigma_{ion}$ , nor are they less than  $-\sigma_{ion}$ . Both the max and min terms are zero, and thus, there is no ion-ion repulsive energy contribution. In examples 4 through 7, either the  $\sigma_m$  value or  $\sigma_n$  value is either greater than  $\sigma_{ion}$ , or is less than  $-\sigma_{ion}$ , but the other corresponding value is not. In these cases, either the max or the min term is zero, or both are zero, and thus, there is no ion-ion repulsive energy contribution. In examples 8 and 9,  $\sigma_m$  and  $\sigma_n$  are both greater than  $\sigma_{ion}$ , or both less than  $-\sigma_{ion}$ , which meets the criteria for a repulsive force, and thus, this is the only time there is an ion-ion repulsive energy contribution. For examples 10 and 11 either  $\sigma_m$  or  $\sigma_n$  is greater than  $\sigma_{ion}$ , and the other is less than  $-\sigma_{ion}$ . We can see that either the max or min term is zero, thus, there is no ion-ion repulsive energy contribution.

**Table 9: Possible combinations for  $\sigma_m$  and  $\sigma_n$  to show the repulsive energy contribution for the second and third terms of  $E_{ion}$ .**

Example	$\sigma_m$	$\sigma_n$	$\sigma_{acc}$	$\sigma_{don}$	$E_{ion}$ 2 <sup>nd</sup> term - $\max[0, \sigma_{acc} - \sigma_{ion}] * \max[0, \sigma_{don} - \sigma_{ion}]$	$E_{ion}$ 3 <sup>rd</sup> term - $\min[0, \sigma_{acc} + \sigma_{ion}] * \min[0, \sigma_{don} + \sigma_{ion}]$	$E_{ion}$ repulsive contribution?
1	-0.01	0.014	$\sigma_n$	$\sigma_m$	$\max[0, 0.014 - 0.016] * \max[0, -0.01 - 0.016]$ $= \max[0, -0.002] * \max[0, -0.026]$ $= 0 * 0 = 0$	$\min[0, 0.014 + 0.016] * \min[0, -0.01 + 0.016]$ $= \min[0, 0.03] * \min[0, 0.006]$ $= 0 * 0 = 0$	no
2	0.01	0.014	$\sigma_n$	$\sigma_m$	$\max[0, 0.014 - 0.016] * \max[0, 0.01 - 0.016]$ $= \max[0, -0.002] * \max[0, -0.006]$ $= 0 * 0 = 0$	$\min[0, 0.014 + 0.016] * \min[0, 0.01 + 0.016]$ $= \min[0, 0.03] * \min[0, 0.026]$ $= 0 * 0 = 0$	no
3	-0.01	-0.014	$\sigma_m$	$\sigma_n$	$\max[0, -0.01 - 0.016] * \max[0, -0.014 - 0.016]$ $= \max[0, -0.026] * \max[0, -0.03]$ $= 0 * 0 = 0$	$\min[0, -0.01 + 0.016] * \min[0, -0.014 + 0.016]$ $= \min[0, 0.006] * \min[0, 0.002]$ $= 0 * 0 = 0$	no

4	0.02	-0.01	$\sigma_m$	$\sigma_n$	$\max[0, 0.02-0.016]^*$ $\max[0, -0.01-0.016]$ $=\max[0, 0.004]^*$ $\max[0, -0.026]$ $=0.004*0 = 0$	$\min[0, 0.02+0.016]^*$ $\min[0, -0.01+0.016]$ $=\min[0, 0.036]^*$ $\min[0, 0.006]$ $=0*0 = 0$	no
5	0.02	0.01	$\sigma_m$	$\sigma_n$	$\max[0, 0.02-0.016]^*$ $\max[0, 0.01-0.016]$ $=\max[0, 0.004]^*$ $\max[0, -0.006]$ $=0.004*0 = 0$	$\min[0, 0.02+0.016]^*$ $\min[0, 0.01+0.016]$ $=\min[0, 0.036]^*$ $\min[0, 0.036]$ $=0*0 = 0$	no
6	-0.02	-0.01	$\sigma_n$	$\sigma_m$	$\max[0, -0.01-0.016]^*$ $\max[0, -0.02-0.016]$ $=\max[0, -0.026]^*$ $\max[0, -0.036]$ $=0*0 = 0$	$\min[0, -0.01+0.016]^*$ $\min[0, -0.02+0.016]$ $=\min[0, 0.006]^*$ $\min[0, -0.004]$ $=0*-0.004 = 0$	no
7	-0.02	0.01	$\sigma_n$	$\sigma_m$	$\max[0, 0.01-0.016]^*$ $\max[0, -0.02-0.016]$ $=\max[0, -0.006]^*$ $\max[0, -0.036]$ $=0*0 = 0$	$\min[0, 0.01+0.016]^*$ $\min[0, -0.02+0.016]$ $=\min[0, 0.026]^*$ $\min[0, -0.004]$ $=0*-0.004 = 0$	no
8	0.025	0.02	$\sigma_m$	$\sigma_n$	$\max[0, 0.025-0.016]^*$ $\max[0, 0.02-0.016]$ $=\max[0, 0.009]^*$ $\max[0, 0.004]$ $=0.009*0.004 = 3.6 \times 10^{-5}$	$\min[0, 0.025+0.016]^*$ $\min[0, 0.02+0.016]$ $=\min[0, 0.041]^*$ $\min[0, 0.036]$ $=0*0 = 0$	yes-from 2 <sup>nd</sup> term
9	-0.025	-0.02	$\sigma_n$	$\sigma_m$	$\max[0, -0.02-0.016]^*$ $\max[0, -0.025-0.016]$ $=\max[0, -0.036]^*$ $\max[0, -0.041]$ $=0*0 = 0$	$\min[0, -0.02+0.016]^*$ $\min[0, -0.025+0.016]$ $=\min[0, -0.004]^*$ $\min[0, -0.009]$ $=-0.004*-0.009 = 3.6 \times 10^{-5}$	yes-from 3 <sup>rd</sup> term
10	0.017	-0.018	$\sigma_m$	$\sigma_n$	$\max[0, 0.017-0.016]^*$ $\max[0, -0.018-0.016]$ $=\max[0, 0.001]^*$ $\max[0, -0.034]$ $=0.001*0 = 0$	$\min[0, 0.017+0.016]^*$ $\min[0, -0.018+0.016]$ $=\min[0, 0.033]^*$ $\min[0, -0.002]$ $=0*-0.002 = 0$	no
11	-0.017	0.02	$\sigma_n$	$\sigma_m$	$\max[0, 0.02-0.016]^*$ $\max[0, -0.017-0.016]$ $=\max[0, 0.004]^*$ $\max[0, -0.033]$ $=0.004*0 = 0$	$\min[0, 0.02+0.016]^*$ $\min[0, -0.017+0.016]$ $=\min[0, 0.036]^*$ $\min[0, -0.001]$ $=0*-0.001 = 0$	no

In option 2, the hydrogen bonding contribution term remains the same as it is in equation (23); however we must place a restriction that  $E_{hb}$  is equal to zero when the absolute value of either  $\sigma_{acc}$  or  $\sigma_{don}$  is greater than  $\sigma_{ion}$ . This accounts for the fact that we then have ion-ion

interactions and not hydrogen bonding. This new hydrogen bonding energy for options 2 is expressed in equation (28) below.

$$E_{hb} = \left. \begin{cases} 0 ; \text{ when } \text{abs}(\sigma_{acc}) > \sigma_{ion} \\ 0 ; \text{ when } \text{abs}(\sigma_{don}) > \sigma_{ion} \\ else \\ c_{hb} \max[0, \sigma_{acc} - \sigma_{hb}] \min[0, \sigma_{don} + \sigma_{hb}] \end{cases} \right\} \quad (28)$$

The third term in the exchange energy,  $E_{ion}$ , accounts for ion-ion interactions. We account for both ion-ion attraction and ion-ion repulsion. We have ion-ion interactions when the absolute value of  $\sigma_{acc}$  is greater than  $\sigma_{ion}$ . This is the first term in  $E_{ion}$ , in equation (29) below. We also have ion-ion interactions when the absolute value of  $\sigma_{don}$  is greater than  $\sigma_{ion}$ . This is the second term in  $E_{ion}$  in equation (29) below. In these two terms, we can see that the design of the term automatically takes care of whether the interaction is attractive or repulsive. For example, if  $\sigma_{acc}$  is positive and  $\sigma_{don}$  is positive, then the term is positive, reflecting repulsion. Also if  $\sigma_{acc}$  is negative and  $\sigma_{don}$  is negative, then the term is positive, reflecting repulsion. If one of either  $\sigma_{acc}$  or  $\sigma_{don}$  is positive and the other one is negative, then the term is negative, reflecting attraction. The proposed ion-ion interaction term for option 2 is below in equation (29).

$$E_{ion} = \left. \begin{cases} c_{ion} \sigma_{acc} \sigma_{don} ; \text{ when } \text{abs}(\sigma_{acc}) > \sigma_{ion} \\ c_{ion} \sigma_{acc} \sigma_{don} ; \text{ when } \text{abs}(\sigma_{don}) > \sigma_{ion} \\ else \\ 0 \end{cases} \right\} \quad (29)$$

In equation (29), there are two new constants that we must assign values for:  $\sigma_{ion}$  and  $c_{ion}$ . We define  $\sigma_{ion}$  as the ion-ion interaction sigma cut off value, similar to  $\sigma_{hb}$ , the hydrogen bonding sigma cutoff value. We define  $c_{ion}$  as the ion-ion interaction constant, similar to  $c_{hb}$ , the hydrogen bonding constant. We know that that  $\sigma_{hb}$  must be less than  $\sigma_{ion}$ . We choose  $\sigma_{ion}$  equal to  $0.016 \text{ e}/\text{\AA}^2$  for the same reasoning given for equation (27). For the new ion-ion interaction constant  $c_{ion}$ , we estimate that it is of the same order of magnitude as  $c_{hb}$ . In this representation of  $E_{ion}$ , we account for ionic attractions and repulsions being stronger than hydrogen bonds in part by the surface charges being greater than the surface charges for hydrogen bonding. In equation (29), we multiply the full value of  $\sigma_{acc}$  and  $\sigma_{don}$  together, not  $(\sigma_{acc} - \sigma_{ion})$  times

$(\sigma_{don} + \sigma_{ion})$  as we do in equation (27). This is one reason why we estimate  $c_{ion}$  of the same order of magnitude as  $c_{hb}$ . For option 2, we are unable to get the FORTRAN to run correctly and give any activity coefficient results.

We implemented the option 1 changes to the exchange energy in our new FORTRAN code. This code is in Appendix A: FORTRAN Code.

## 12.2 Results

In this results section we discuss the behavior of each of the exchange energy terms of option 1,  $E_{mf}$ ,  $E_{hb}$ , and  $E_{ion}$ , and a few of the numerical problems that we encounter. We also show results for the activity coefficients; however, accurate numerical results with the new exchange energy have yet to be obtained.

As an example, we use the system of HCl in water. Since HCl is a strong acid, we assume that it completely dissociates in water, and thus we only have three components: water,  $H^+$  and  $Cl^-$ . We show the mixture sigma profile along with the sigma profiles for water,  $H^+$  and  $Cl^-$  in Figure 49 below. The sigma profile for the mixture is shown on the same graph with the same x-axis; however, it is on a secondary y-axis (on the right). Recall that the mixture sigma profile is a weighted average of the pure-component sigma profiles and is calculated based on equation (20) repeated below.

$$p_s(\sigma) = \frac{\sum_i x_i n_i p_i(\sigma)}{\sum_i x_i n_i} = \frac{\sum_i x_i A_i p_i(\sigma)}{\sum_i x_i A_i} = \frac{\sum_i x_i p_i'(\sigma)}{\sum_i x_i A_i} \quad (20)$$

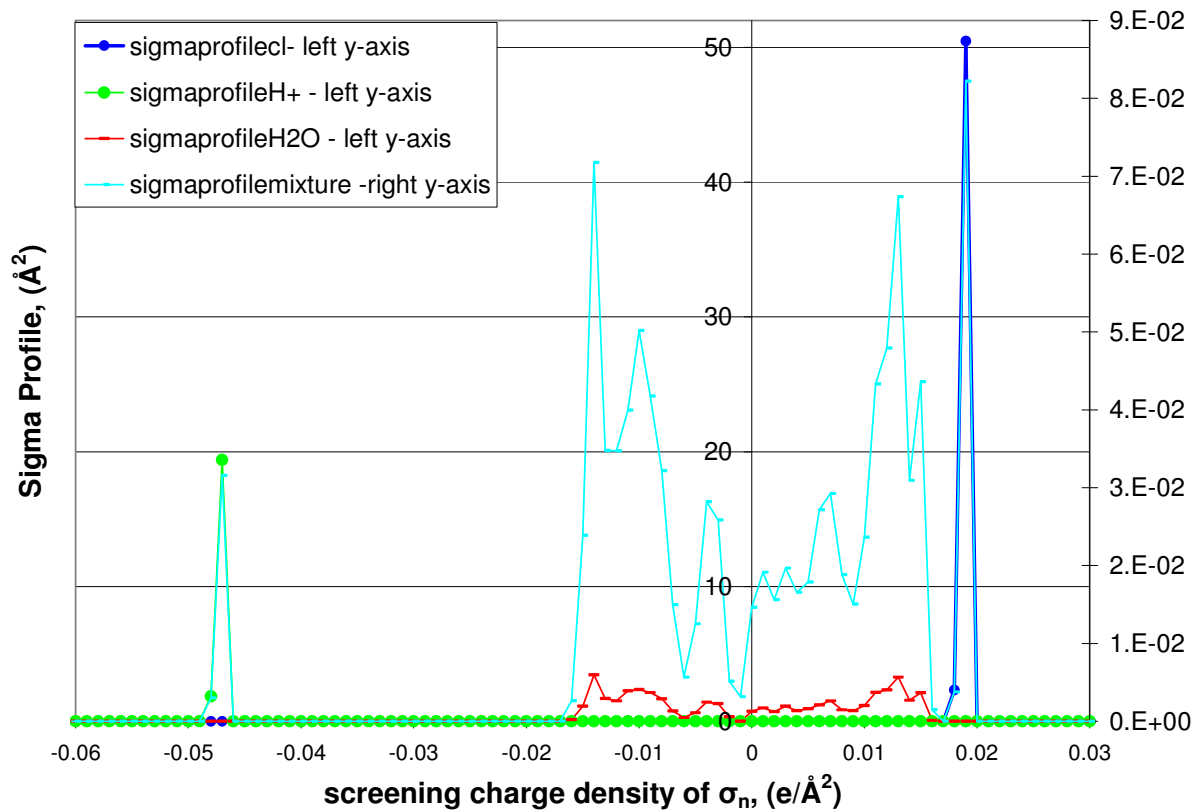
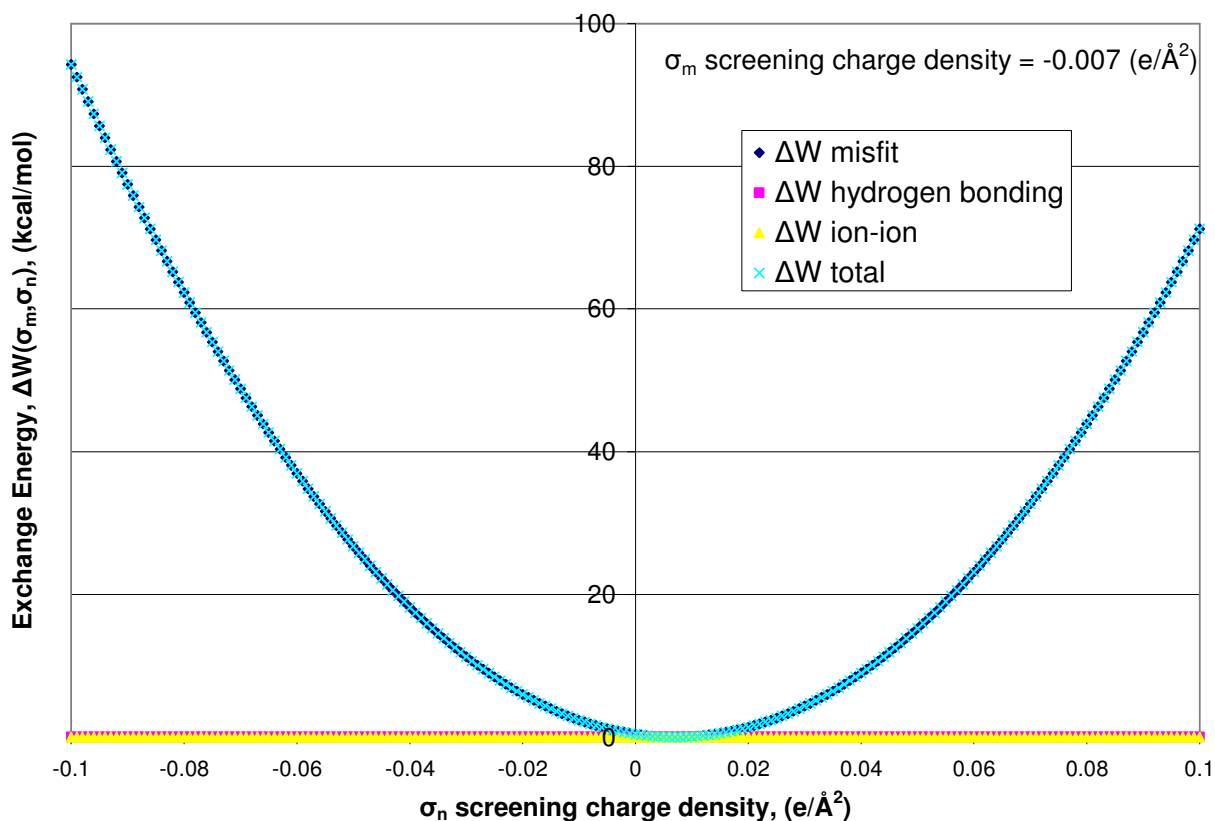


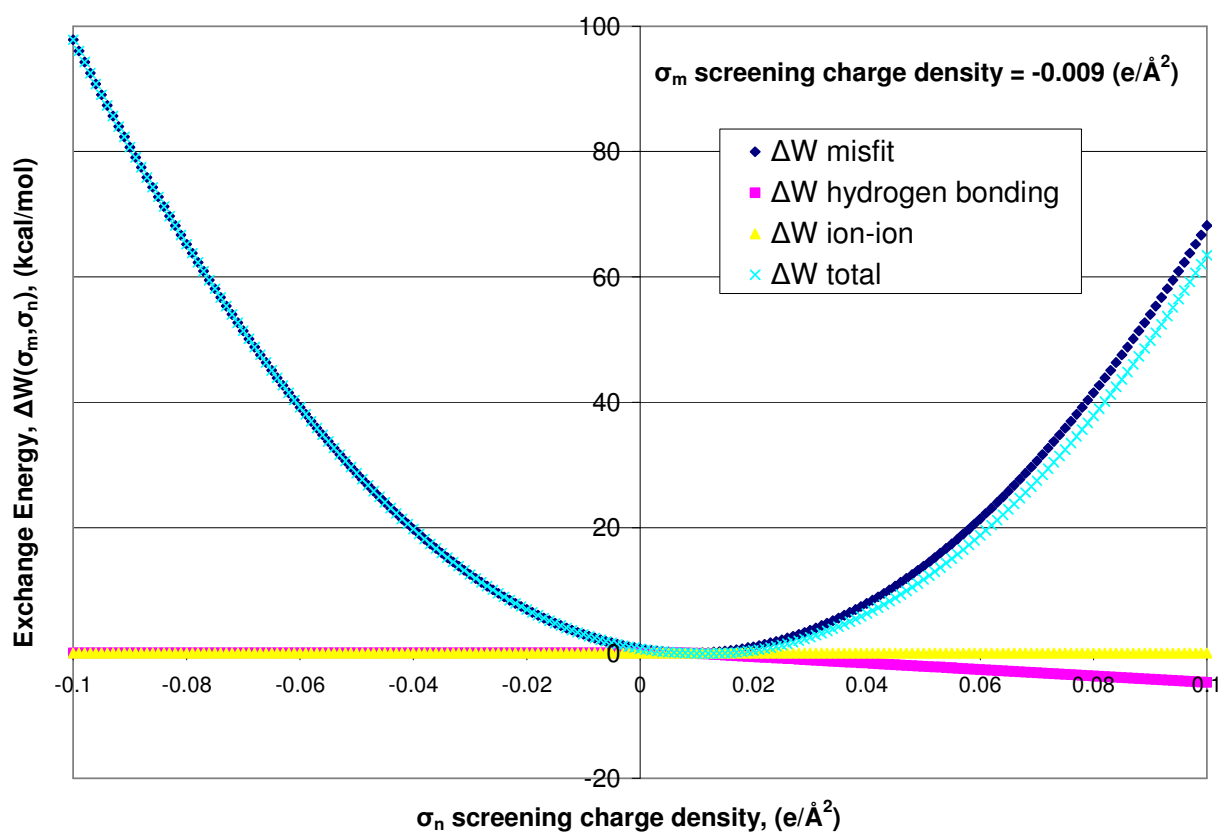
Figure 49: Mixture and pure species sigma profiles for  $\text{H}^+$  and  $\text{Cl}^-$  in water.

To show the contributions of the different parts of the exchange energy, we use the same system of  $H^+$  and  $Cl^-$  in water. First, we set the  $\sigma_m$  screening charge density to  $-0.007 (e/\text{\AA}^2)$  and let the  $\sigma_n$  screening charge density vary from  $-0.1(e/\text{\AA}^2)$  to  $0.1(e/\text{\AA}^2)$ . We choose  $-0.007 (e/\text{\AA}^2)$  because this density is less than both  $\sigma_{hb}$  and  $\sigma_{ion}$ , and thus, there should be no hydrogen bonding and no ion-ion interactions. In Figure 50, we see that this is indeed the case. We have misfit energy only represented by the navy blue line. We also notice that the misfit energy curve has the correct trend of increasing as  $\sigma_n$  moves away from  $\sigma_m$  in both directions. When the screening charge density of  $\sigma_n$  is equal to  $+0.007 (e/\text{\AA}^2)$ ,  $E_{mf}$  should be zero, which it is. Then, as we change the screening charge density of  $\sigma_n$  away from  $+0.007 (e/\text{\AA}^2)$ ,  $E_{mf}$  should increase in the positive direction, showing that the difference in the charges between the two segments is increasing, which Figure 50 also does.



**Figure 50: Exchange energy contributions for  $\sigma_m$ 's screening charge density equal to  $-0.007 (e/\text{\AA}^2)$ .**

Next, we set the  $\sigma_m$  screening charge density to  $-0.009 \text{ (e/\text{Å}^2)}$  and let the  $\sigma_n$  screening charge density vary from  $-0.1 \text{ (e/\text{Å}^2)}$  to  $0.1 \text{ (e/\text{Å}^2)}$ . We choose  $-0.009 \text{ (e/\text{Å}^2)}$  because this density is just greater than  $\sigma_{hb}$  but still less than  $\sigma_{ion}$ , and thus, there should be hydrogen bonding and no ion-ion interactions. In Figure 51, we see that the misfit energy has remained the same, but we see the addition of hydrogen bonding. Since hydrogen bonding is an attractive force, the exchange energy value for it is negative. By plotting the total exchange energy value, we see how each part of the exchange energy moves the total energy plot up and down.



**Figure 51: Exchange energy contributions for  $\sigma_m$ 's screening charge density equal to  $-0.009 \text{ (e/\text{Å}^2)}$ .**

Now, we set the  $\sigma_m$  screening charge density to  $-0.014 (e/\text{\AA}^2)$  and let the  $\sigma_n$  screening charge density vary from  $-0.1(e/\text{\AA}^2)$  to  $0.1(e/\text{\AA}^2)$ . We choose  $-0.014 (e/\text{\AA}^2)$  because this density is significantly more than  $\sigma_{hb}$  but just slightly less than  $\sigma_{ion}$ , and thus, there should be more hydrogen bonding effects than in Figure 51 but still no ion-ion interactions. In Figure 52, we see that the hydrogen bonding contribution is much greater and how it really pulls the total energy curve downward.

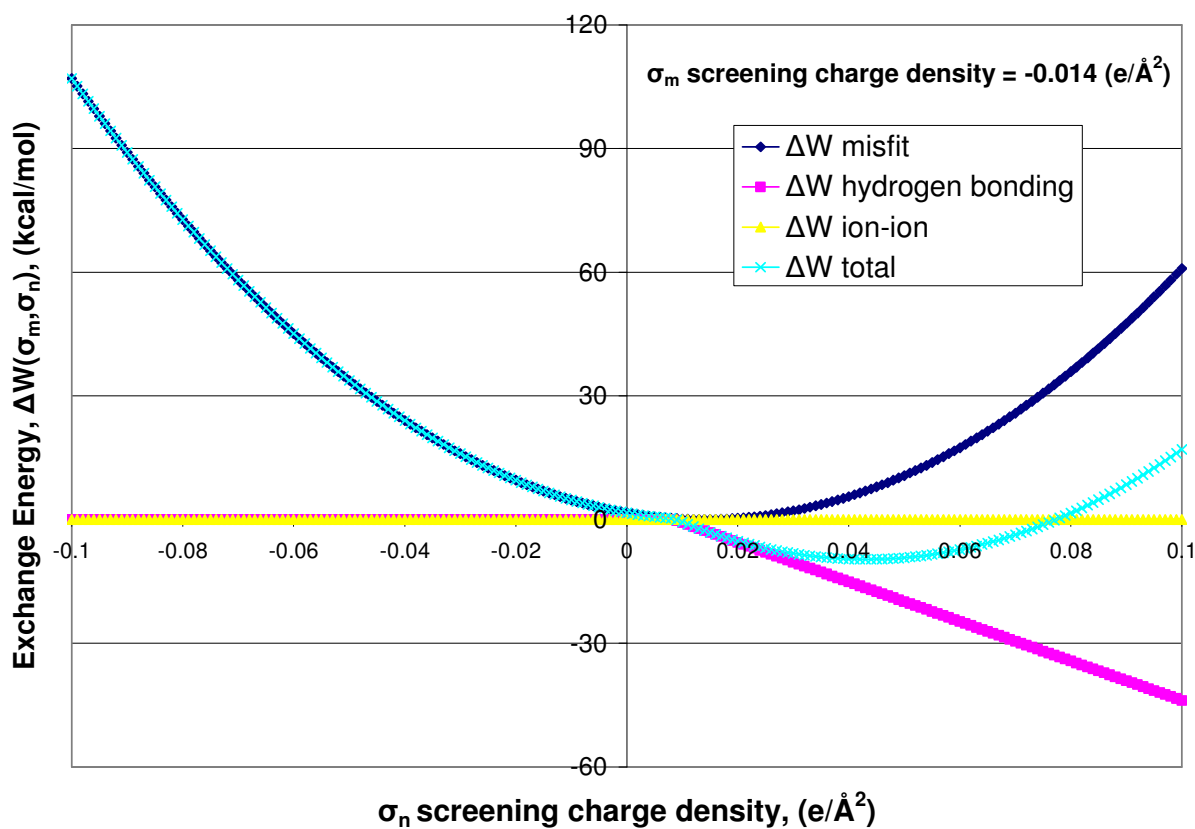


Figure 52: Exchange energy contributions for  $\sigma_m$ 's screening charge density equal to  $-0.014 (e/\text{\AA}^2)$ .



In Figure 53, we set the  $\sigma_m$  screening charge density to  $-0.018 (e/\text{\AA}^2)$  and we let the  $\sigma_n$  screening charge density vary from  $-0.1(e/\text{\AA}^2)$  to  $0.1(e/\text{\AA}^2)$ . We choose  $-0.018 (e/\text{\AA}^2)$  because this density is greater than both  $\sigma_{hb}$  and  $\sigma_{ion}$ , and thus, there should be some hydrogen bonding effects and also some ion-ion interactions. In Figure 53, we see that the hydrogen bonding contribution only appears when the screening charge density for  $\sigma_n$  is between  $\sigma_{hb}$  and  $\sigma_{ion}$ . We also see that once  $\sigma_n$  is greater than  $\sigma_{ion}$ , the ion-ion interaction begins to show up. We also notice that there is a discontinuity in the plot of the hydrogen bonding energy. We discuss the next step of how to fix this issue at the end of this section.

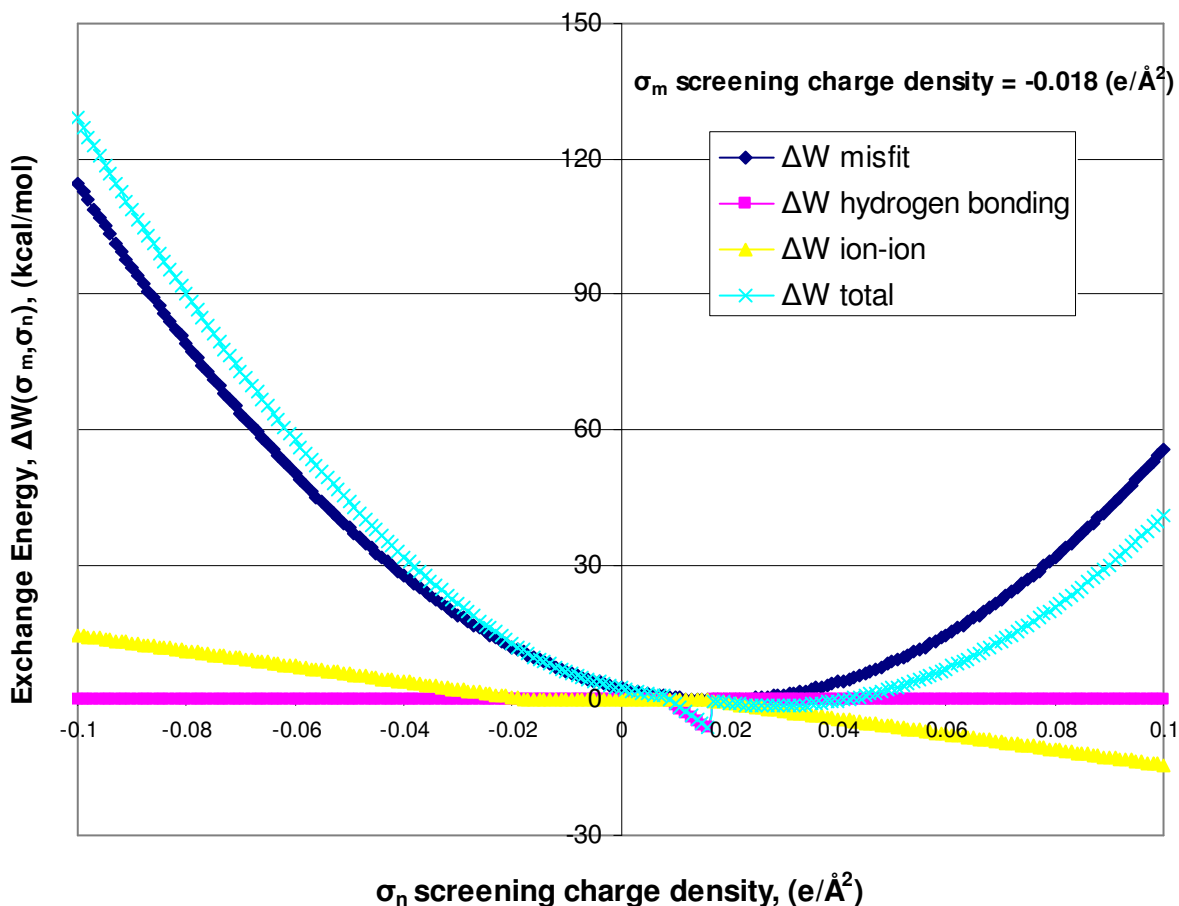


Figure 53: Exchange energy contributions for  $\sigma_m$ 's screening charge density equal to  $-0.018 (e/\text{\AA}^2)$ .

Lastly, we set the  $\sigma_m$  screening charge density to  $-0.1 (e/\text{\AA}^2)$  in Figure 54, and let the  $\sigma_n$  screening charge density vary from  $-0.1(e/\text{\AA}^2)$  to  $0.1(e/\text{\AA}^2)$ . We choose  $-0.1 (e/\text{\AA}^2)$  because this density shows the full interactions of both the hydrogen bonding and the ion-ion interactions. In Figure 54, we see that the misfit energy is at its maximum when  $\sigma_m = -0.1$  and  $\sigma_n = -0.1$  (the very left side of the graph) because they have equal but not opposite charges. The misfit energy is at its minimum when  $\sigma_m = -0.1$  and  $\sigma_n = 0.1$  (the very right side of the graph) because they have equal and opposite charges.

In Figure 54, we also plot the sigma profile of the mixture and of each individual pure species on top of the exchange energy graph. All of the sigma profiles use the secondary axis on the right and all of the exchange energies use the main axis in the center of the graph. This overlay helps us see what parts of the exchange energy graph are important. Only the parts where there are values for the sigma profiles end up having an effect on the system. If we look at the graphs when the screening charge density of  $\sigma_m$  are  $+0.1$ ,  $+0.018$ ,  $+0.014$ ,  $+0.009$ , and  $+0.007 (e/\text{\AA}^2)$  we obtain similar graphs, except that they would be mirror images reflected on the y-axis.

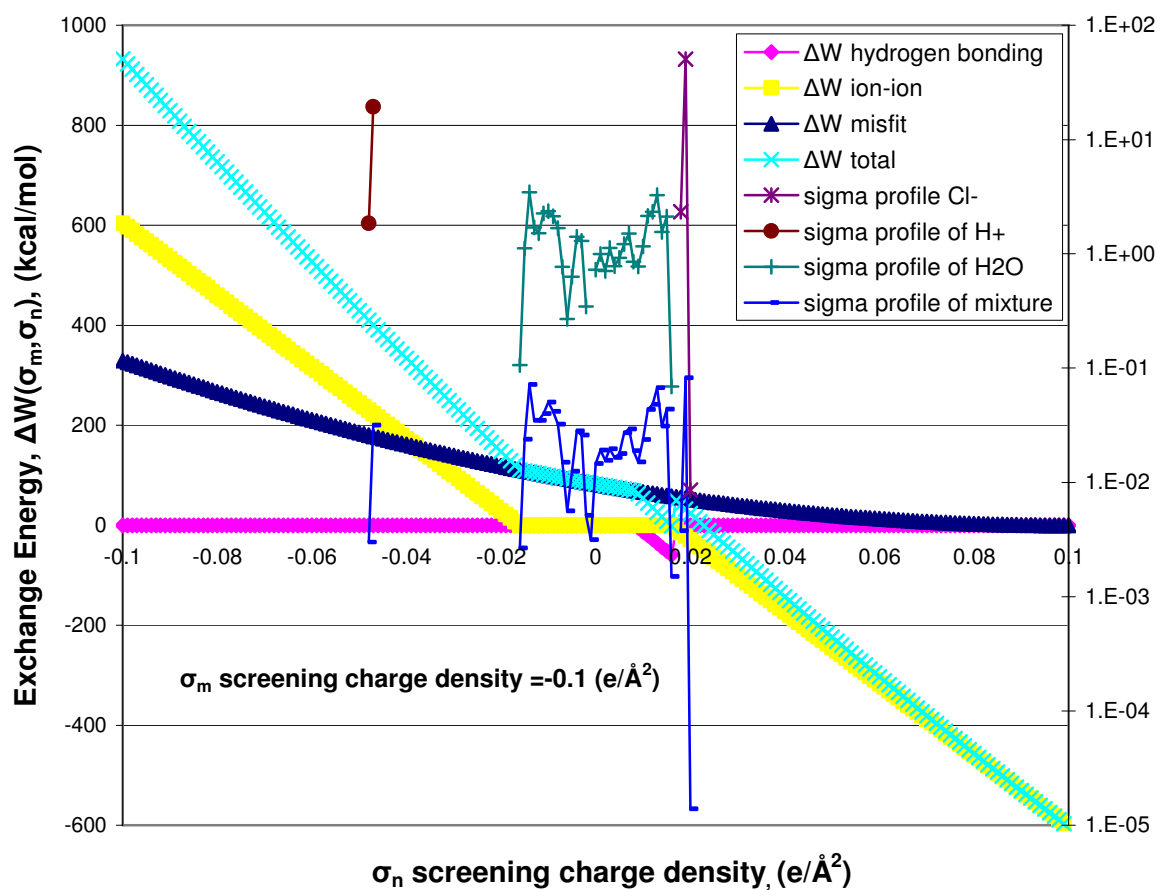


Figure 54: Exchange energy contributions for  $\sigma_m$ 's screening charge density equal to -0.1 ( $e/\text{\AA}^2$ ), with sigma profiles overlaid.

One problem we run into is that the values for the exchange energy are sometimes too negative. We also at times have very positive value for the exchange energy. The computer is able to handle the very large positive values of  $\Delta W(\sigma_m, \sigma_n)$  because, as we can see in equation (12) repeated below, when we take the exponent of the negative of  $\Delta W(\sigma_m, \sigma_n)$  at very large values, the computer eventually recognizes this value to be zero. It may calculate the exponent to be very small, for instance, values on the order of  $10^{-200}$ , and since these very small values are added into the summation they have no real effect on the system.

$$\ln \Gamma_i(\sigma_m) = -\ln \left\{ \sum_i \frac{P_i(\sigma_n)}{A_i} \Gamma_i(\sigma_n) \exp \left[ \frac{-\Delta W(\sigma_m, \sigma_n)}{RT} \right] \right\} \quad (12)$$

However, when the exchange energy has very negative values, we end up with the exponent of a very large number, which the computer cannot handle and we then get overflow errors. In order to try to get around this problem, we create a variable called “mostnegdw”, which stands for the most negative exchange energy value. We set up the program to find the most negative exchange energy for each screening charge density value of  $\sigma_m$ . This means we will have an array of 201 most negative exchange energies. We make sure that we only consider the exchange energies of interest. In equation (12), whether we are calculating the mixture segment gammas or the pure species segment gammas, we must multiply the exponential term by the respective sigma profile. Since the mixture sigma profile encompasses each pure species profiles, we only look at the exchange energy when the mixture profile values are non-zero. If the mixture sigma profile is zero at a particular screening charge density, then we know that the term that we are adding to the summation is zero. Thus, we set up the program to only add on to the summation when the profile is non-zero. This helps, because we do not ask the computer to calculate the exponential value when we know the term will be zero anyways.

Once we have our “mostnegdw” value, we subtract it from  $\Delta W(\sigma_m, \sigma_n)$ , whenever  $\Delta W(\sigma_m, \sigma_n)$  is used in a calculations. We are basically setting up “mostnegdw” to be the energy reference. So long as we subtract “mostnegdw” in both the computation of the mixture segment activity coefficient, and the pure species segment activity coefficients, this will remain valid. One way to see this is that we are taking the largest in magnitude negative energy,

“mostnegdw”, and multiplying all terms in equation (12) by it. Since we then take the difference of two of the log terms (see equation (13) repeated below), we effectively are doing nothing.

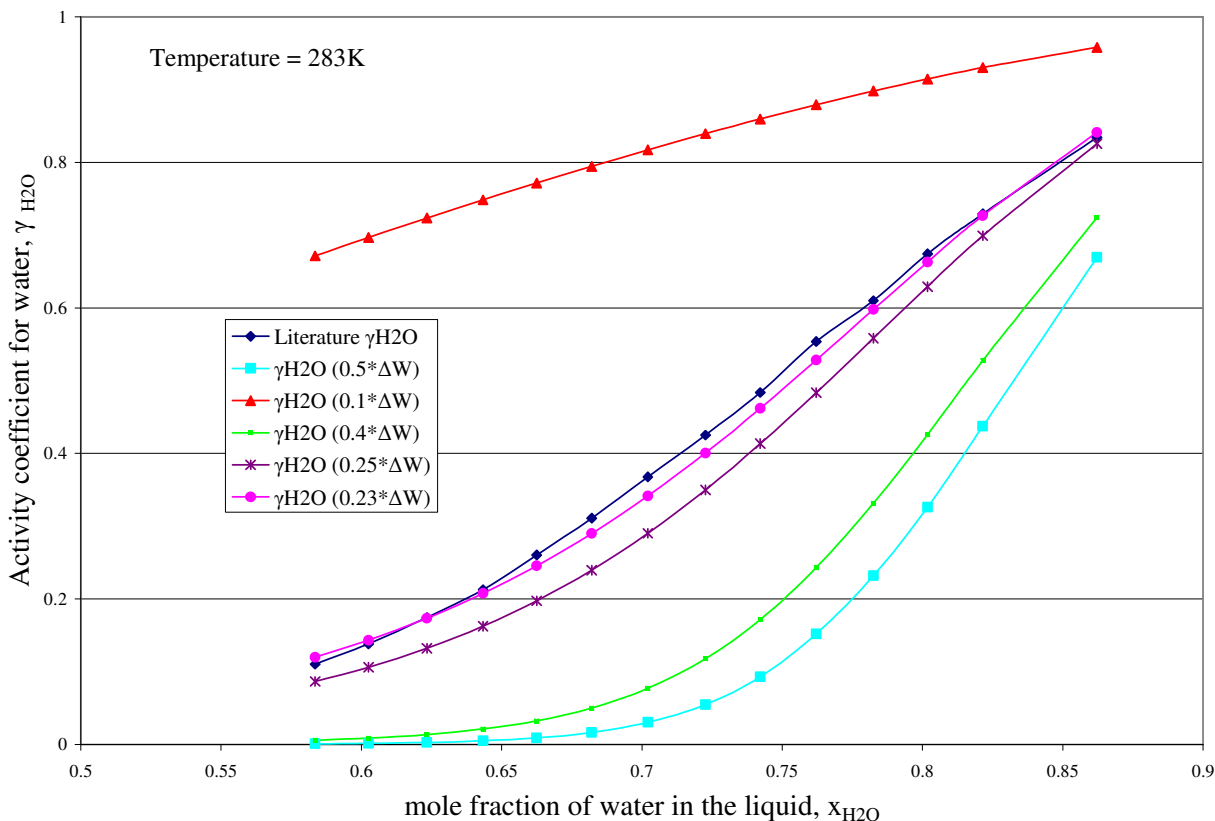
$$\ln \gamma_{i/s} = \frac{1}{a_{eff}} \sum_{\sigma_m} p'_i(\sigma_m) [\ln(\Gamma_s(\sigma_m)) - \ln(\Gamma_i(\sigma_m))] + \ln \gamma_{i/s}^{SG} \quad (13)$$

We also run into problems when our summation (the summation inside the braces in equation (12)) value is very small, or zero. Clearly, we cannot take the log of zero. Also, in some cases, the summation values are about  $10^{-300}$ , and when we go to take the log of that summation we get a value of -300. Then in order to calculate the segment gamma value,  $\Gamma_i(\sigma_m)$ , we must then take the exponent of the negative of our log value, in this case, the exponent of  $-(-300)$ . When the computer tries to calculate the exponent of 300, this number becomes too large for the computer to handle and we get overflow errors. One way to fix this is to rewrite  $\Gamma_i(\sigma_m)$ , and let  $\Gamma_i(\sigma_m)$  be equal to 1 divided by the summation value. This works as an intermediate fix, however, we still run into problems because the segment gamma,  $\Gamma_i(\sigma_m)$ , is then a very large number. This only delays the problem from being detected until later in the calculations using equation (13). We also still have problems if the summation is zero, because dividing any number by zero does not exist and the computer calculates “not a number” or “NAN”, which interferes with subsequent calculations.

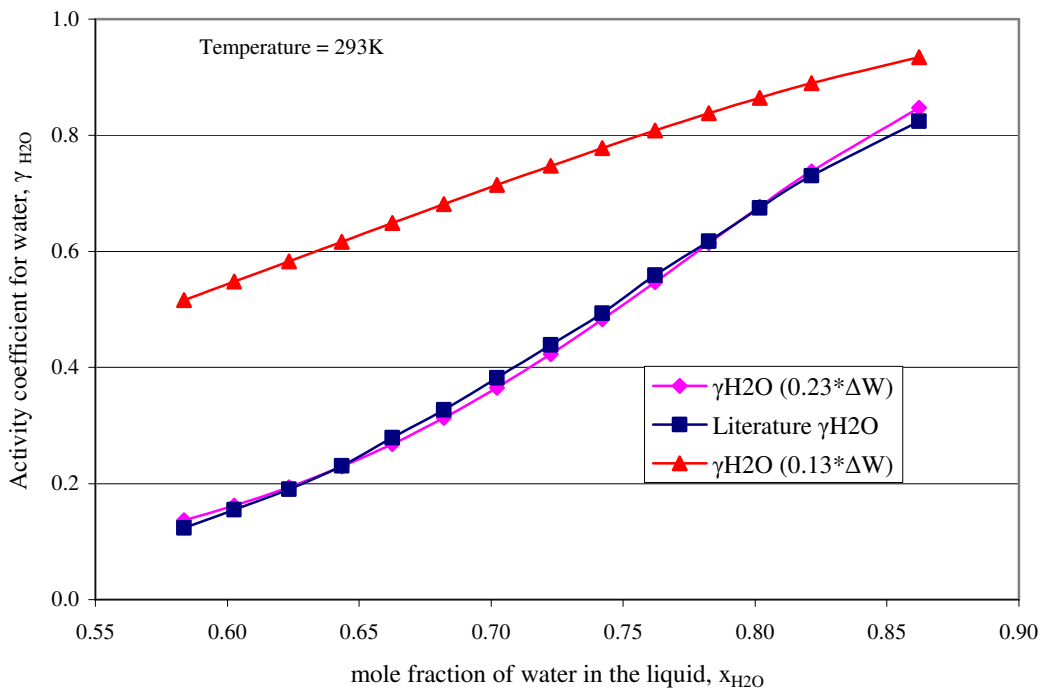
After adding in the changes described above, we still have some difficulty with the FORTRAN code for COSMO-SAC for electrolytes. In order to get the program to run all the way through to obtain the final results, the activity coefficient predictions, we use a constant multiplied by the exchange energy term. Since we were having problems with very large positive and very large negative values of the exchange energy, we decided to scale the exchange energy down to see if this allows us to obtain results. For our first system of water,  $H^+$  and  $Cl^-$ , we are able to obtain good fits to the literature data for varying temperatures by arbitrarily multiplying the exchange energy by a constant of 0.23.

In Figure 55, we show the literature experimental data along with various scaling constants for the exchange energy at a temperature of 283 Kelvin. We also run the same constant for temperatures of 293 Kelvin (Figure 56) and 303 Kelvin (Figure 57) and find that the 0.23 constant places our activity coefficient results in direct correlation with the literature data. This scaling is equivalent to increasing the temperature by a factor that is the inverse of the

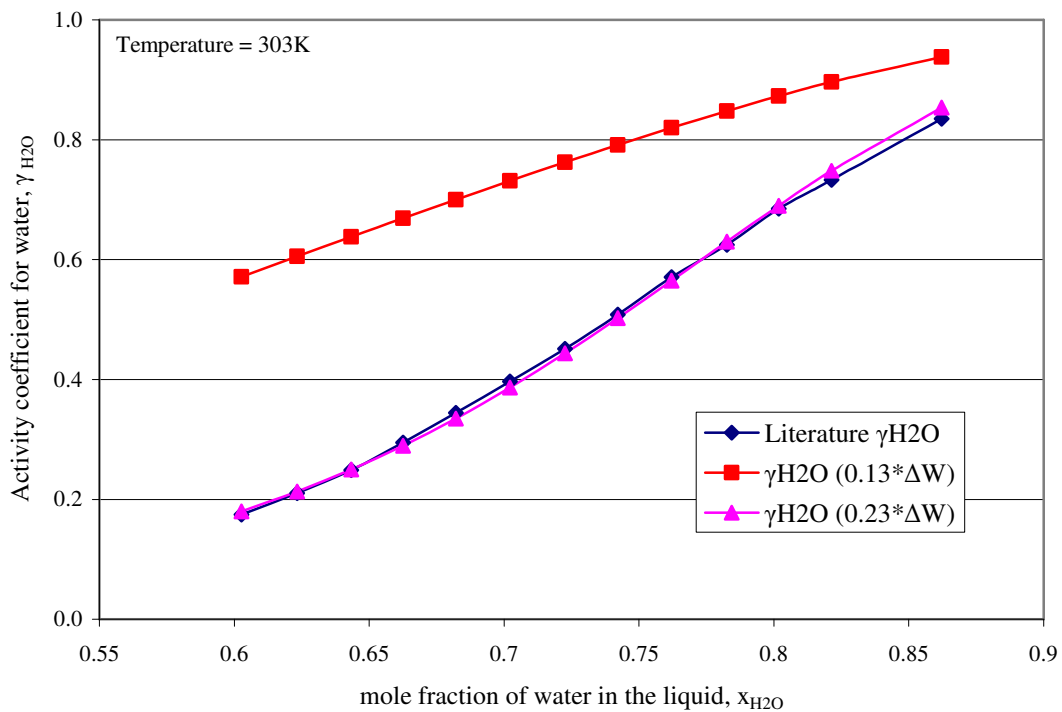
factor used to scale the energy. This scaling might be telling us that qualitatively the procedure of adding the  $E_{ion}$  correction to the exchange energy is able to capture the correct physics. A more detailed analysis is required to see if this  $E_{ion}$  correction is indeed capturing the correct physics.



**Figure 55: COSMO-SAC for electrolytes prediction for  $H^+$  and  $Cl^-$  in water at  $T=283$  K compared to literature data<sup>48</sup>.**

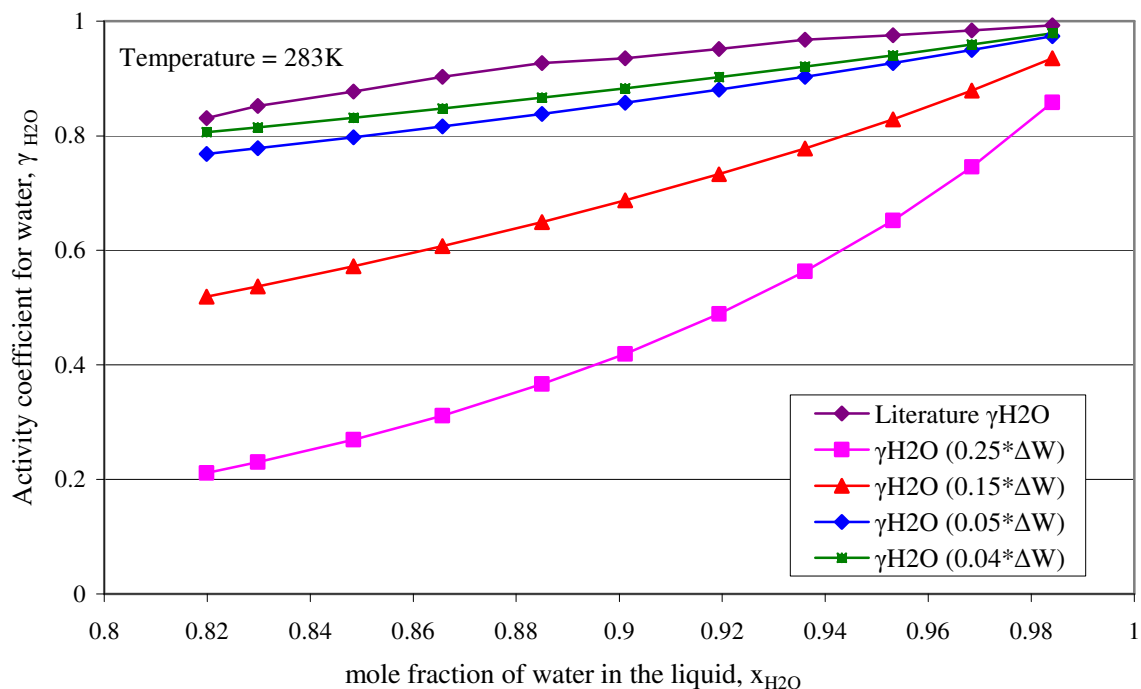


**Figure 56: COSMO-SAC for electrolytes prediction for  $H^+$  and  $Cl^-$  in water at  $T=293$  K compared to literature data<sup>48</sup>.**



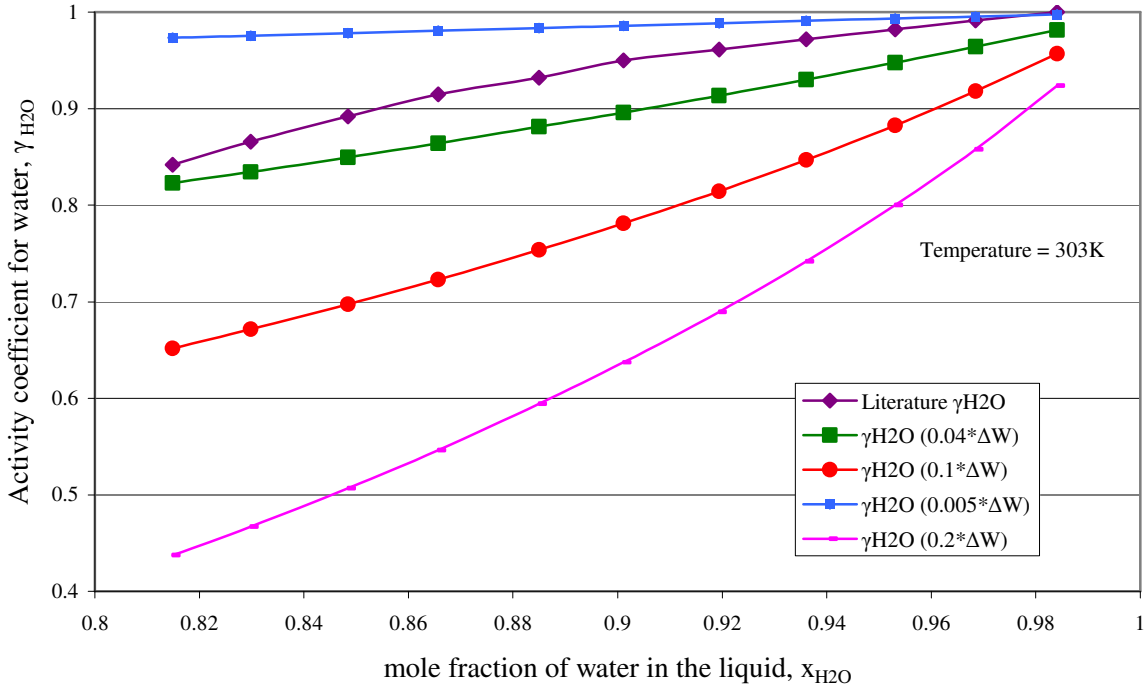
**Figure 57: COSMO-SAC for electrolytes prediction for  $H^+$  and  $Cl^-$  in water at  $T=303$  K compared to literature data<sup>48</sup>.**

In order to determine if the scaling constant of 0.23 that we use above is valid for other systems, we try  $\text{Na}^+$  and  $\text{Cl}^-$  in water. We find that the 0.23 scaling constant is not good for this system. We are able to find a constant that allows our results from the COSMO-SAC model for electrolytes to be very close to the literature results; however it is one order of magnitude smaller than the constant we use for  $\text{H}^+$  and  $\text{Cl}^-$  in water. We find that using 0.04 times the exchange energy works well for this system. Figure 58 shows this new system of electrolytes at a temperature of 283 Kelvin and Figure 59 shows it at a temperature of 303 Kelvin.



**Figure 58: COSMO-SAC for electrolytes prediction for  $\text{Na}^+$  and  $\text{Cl}^-$  in water at  $T=283\text{ K}$  compared to literature data<sup>48</sup>.**





**Figure 59: COSMO-SAC for electrolytes prediction for  $\text{Na}^+$  and  $\text{Cl}^-$  in water at  $T=303\text{ K}$  compared to literature data<sup>48</sup>**

The next step is to determine why our FORTRAN code for the COSMO-SAC model for electrolytes is unable to function at full exchange energy values. It is possible that there is a fundamental problem in the procedure and our new exchange energy term, especially where the new ion-ion term is concerned, or that there is a numerical problem within the code. Since we were able to use a scaling factor for the exchange energy and get good results, we think a good next step is to look at each term of the exchange energy and try to scale each term individually. This would give good insight into which part of the exchange energy term is having problems.

Also, we think that equation (13), repeated below, needs to be modified for electrolytes. Instead of having just component  $i$  (which could be either the cation or anion) in the mixture, it needs to consider both the cation and anion in the mixture. The cation cannot exist without the anion in the mixture and vice versa.

$$\ln \gamma_{i/s} = \frac{1}{a_{\text{eff}}} \sum_{\sigma_m} p'_i(\sigma_m) \left[ \ln(\Gamma_s(\sigma_m)) - \ln(\Gamma_i(\sigma_m)) \right] + \ln \gamma_{i/s}^{SG} \quad (13)$$

We might need to consider using the mean ionic activity coefficient for the molecule that dissociates into cation and anion. The mean ionic activity coefficient<sup>43</sup>,  $\gamma_{\pm}$ , is defined in equation (30).

$$\gamma_{\pm} = (\gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}})^{1/\nu} \quad (30)$$

Here,  $\nu_{+}$  is the number of cations and  $\nu_{-}$  is the number anions that result when the molecule dissociates. For HCl,  $\nu_{+}$  would be one and  $\nu_{-}$  would also be one. However, for H<sub>2</sub>SO<sub>4</sub>, if we assume complete dissociation, then  $\nu_{+}$  would be two and  $\nu_{-}$  would be one. Here,  $\gamma_{+}$  and  $\gamma_{-}$  are the activity coefficient of the cation and anion, respectively.

One way to further our theory with the ion-ion interaction term in the exchange energy is to determine  $c_{\text{ion}}$  and  $\sigma_{\text{ion}}$  based on fitting of data. We believe a good place to start is to fit data based on how Klant<sup>26</sup> optimized  $\sigma_{\text{hb}}$  and  $c_{\text{hb}}$ . Another option is to consider the possibility that  $\sigma_{\text{ion}}$  could change depending on the compounds in the system. This could be determined from the sigma profiles of each system. The misfit energy term could also need some changes. First, it is possible that we need to stop accounting for misfit energy once we get into the ion-ion interaction region. Also we may need to use a different value for  $\alpha'$ .

Figure 53 shows that the option 1  $E_{\text{hb}}$  and  $E_{\text{ion}}$  terms give a discontinuous energy. Correcting this could help with the accuracy of our results. This can be corrected by changing equation (26). Instead of turning  $E_{\text{hb}}$  off when the surface charges are larger in magnitude than  $\sigma_{\text{ion}}$ ,  $E_{\text{hb}}$  can be locked into its value that is acquires at that point. This would make the exchange energy continuous as a function of surface charge.

## 13 Resources

All of the examples present above can be found on our website: [www.design.che.vt.edu](http://www.design.che.vt.edu). The sigma averaging and COSMO-SAC for electrolytes FORTRAN code are available on the website for download. We also provide a revised step-by-step tutorial for using Materials Studio with electrolytes, according to the changes discussed above.

## 14 Conclusions

We generate molecular-specific sigma profiles for electrolytes successfully using Materials Studio. We propose a new term to the exchange energy for account for ion-ion interactions. Based on our results for our new exchange energy term, we believe that the term is a good starting point, however, the new constants that we present and the application of this term within the FORTRAN code need to be explored further to determine how well our COSMO-SAC model for electrolytes actually represents ion-ion interaction in electrolyte solutions.

## 15 Nomenclature

### English Symbols

$A$	Coulomb Interaction Energy matrix
$a_{av}$	Average segment surface area, $\text{Å}^2$
$a_{eff}$	Effective segment surface area, $\text{Å}^2$
$A_i$	Total molecular cavity surface area, $\text{Å}^2$
$A_i(\sigma_m)$	Area of segments with charge density $\sigma$ , $e/\text{Å}^2$
a.u.	Atomic unit, Bohr radius, $5.2918 \times 10^{-11} \text{Å}$
$c_{hb}$	Hydrogen bonding Constant, $\text{kcal } \text{Å}^4 \text{ mol}^{-1} e^{-2}$
$c_{ion}$	Ion-Ion Interaction Constant, $\text{kcal } \text{Å}^4 \text{ mol}^{-1} e^{-2}$
$d_{mn}$	Distance between surface segment $m$ and $n$ , $\text{Å}$
$e$	Elementary charge, $1.6022 \times 10^{-19}$ coulomb
$E_{hb}$	Hydrogen-bonding contribution of the Exchange Energy, $\text{kcal mol}^{-1}$
$E_{ion}$	Ion-ion interaction contribution of the Exchange Energy, $\text{kcal mol}^{-1}$
$E_{mf}$	Misfit energy contribution of the Exchange Energy, $\text{kcal mol}^{-1}$
$f_{pol}$	Polarizability factor, 0.64
$\Delta G$	Gibbs Free Energy Change, kcal/mol
$\Delta G^{IS}$	Gibbs Ideal Solvation Energy, kcal/mol
$\Delta G^{*cav}$	Cavity Formation Free Energy, kcal/mol
$\Delta G^{*chg}$	Charging Free Energy, kcal/mol
$\Delta G^{*res}$	Restoring Free Energy, kcal/mol
$\Delta G^{*sol}$	Solvation Free Energy, kcal/mol
$\Delta H$	Enthalpy Change, kJ/mol
$l_i$	SG combinatorial term parameter
$n_i$	Total number of segments on the surface of the molecular cavity
$n_i(\sigma)$	Number of segments with charge density $\sigma$
$p_i(\sigma)$	Sigma profile, probability of segment $i$ having a charge density $\sigma$
$p_i'(\sigma)$	Area-weighted Sigma Profile of component $i$ , $\text{Å}^2$
$p_S(\sigma)$	Sigma Profile of Mixture $S$
$q$	Standard area parameter, $79.53 \text{Å}^2$
$q^*$	Ideal screening charge, $e$
$q_{avg}$	Average screening charge, $e$
$q_i$	Normalized surface area parameter for SG combinatorial term
$r$	Standard volume parameter, $66.69 \text{Å}^2$
$r_{av}$	Average segment radius, $\text{Å}$
$r_{eff}$	Effective segment radius, $\text{Å}$
$r_i$	Normalized volume parameter for SG combinatorial term

$r_n$	Circular segment radius, $\text{\AA}$
$R$	Ideal Gas Constant, $0.001987 \text{ kcal mol}^{-1} \text{ K}^{-1}$ , $8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1}$
$\Delta S$	Entropy change, J/K
$T$	System Temperature, K
$V_i$	Molecular cavity volume, $\text{\AA}^3$
$\Delta W(\sigma_m, \sigma_n)$	Exchange Energy between segments $\sigma_m$ and $\sigma_n$ , $\text{kcal mol}^{-1}$
$x_{sol}$	Solute mole fraction, m.f.
$x_i$	Mole fraction of component $i$
$x_{j,I}$	Segment mole fraction of component $i$
$z$	Coordination Number

### Greek Symbols

$\alpha$	Model constant, $\text{\AA}^4 \text{ kcal } e^{-2} \text{ mol}^{-2}$
$\alpha'$	Misfit energy constant, $\text{\AA}^4 \text{ kcal } e^{-2} \text{ mol}^{-2}$
$\gamma_i$	Activity coefficient of solute $i$
$\gamma_{i/S}^{SG}$	Staverman-Guggenheim activity coefficient of solute $i$ in a solvent $S$
$\gamma_{sol}$	Solute activity coefficient
$\Gamma_i(\sigma_m)$	Segment activity coefficient of segment $\sigma_m$ in a pure liquid $i$
$\Gamma_s(\sigma_m)$	Segment activity coefficient of segment $\sigma_m$ in a solvent $S$
$\varepsilon$	Dielectric constant
$\varepsilon_o$	Permittivity of free space, $2.395\text{E-}04$
$\theta_i$	Composition-weighted volume fraction
$\sigma$	charge density, $e/\text{\AA}^2$
$\sigma^*$	surface segment charge density from COSMO calculation output
$\sigma_{acc}$	Hydrogen acceptor segment
$\sigma_{don}$	Hydrogen donor segment
$\sigma_{hb}$	Hydrogen-bonding cutoff value, $0.0084 e/\text{\AA}^2$
$\sigma_{ion}$	Ion-ion interaction cutoff value, $0.016 e/\text{\AA}^2$
$\sigma_m$	segment charge density of segment $m$
$\phi_i$	Composition-weighted surface area fraction
$\Phi_i$	Potential due to the charge distribution of the solute $i$
$\Phi(q^*)$	Potential as a function of the ideal screening charge $q^*$
$\Phi_{tot}$	Total potential on the cavity surface

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## **17 Appendices**

**A: FORTRAN Code**

**B: Sample Materials Studio output files and sample sigma profile for an Electrolyte**



## *Appendix A: FORTRAN Code*

A1: Electrolyte Sigma Profile .f90 Code

```
PROGRAM SIGMAPROFILEV3
```

```
!*****
```

```
!CREATED USING DIGITAL VISUAL FORTRAN 6.0 (2006)
```

```
!
```

```
! This program reads the modified COSMO output file (in text format) from Accelrys'  
! Materials Studio DMol3 and averages the surface segment charge densities per  
! Klamt (1995), Klamt et al (1998), Klamt et al (2000), Lin and Sandler (2002) to  
! establish the segment charges for the "sigma-profile". This program creates  
! a text file that MS Excel can read and plot.
```

```
!
```

```
! THIS PROGRAM WRITTEN BY:
```

```
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! BLACKSBURG, VA 24060
```

```
!
```

!  
 ! VALUES READ FROM THE DATA FILE:  
 ! ATOM = ATOM NUMBER IN MOLECULE  
 ! POSXAU = X-CORDINATE OF THE SEGMENT POSITION IN ATOMIC UNITS  
 ! POSYAU = Y-CORDINATE OF THE SEGMENT POSITION IN ATOMIC UNITS  
 ! POSZAU = Z-CORDINATE OF THE SEGMENT POSITION IN ATOMIC UNITS  
 ! POSXA = X-CORDINATE OF THE SEGMENT POSITION IN ANGSTROMS  
 ! POSYA = Y-CORDINATE OF THE SEGMENT POSITION IN ANGSTROMS  
 ! POSZA = Z-CORDINATE OF THE SEGMENT POSITION IN ANGSTROMS  
 ! A = SURFACE SEGMENT AREA; APPROXIMATED AS CIRCULAR (ANGSTROMS SQUARED)  
 ! CHG = CHARGE OF THE SURFACE SEGMENT (SIGMA, e)  
 ! SIGMA = RATIO OF SURFACE CHARGE TO AREA (SIGMA/A, e/A\*\*2)  
 ! POTENT = SURFACE POTENTIAL  
 !  
 ! FROM SEGMENT CHARGE AVERAGING:  
 ! REFF = RADIUS OF THE AREA THAT AFFECTS THE SURFACE SEGMENT CHARGE (ANGSTROMS)  
 ! DMN = DISTANCE BETWEEN CALCULATED SEGEMENT AND SEGEMENTS AFFECTING IT (ANGSTROMS)  
 ! RAD = RADIUS OF THE PARTICULAR SURFACE SEGMENT (ASSUMED CIRCULAR, ANGSTROMS SQUARED)  
 ! SIGMANEW = NEW AVERAGED SIGMA VALUE  
 ! SIGMASUM = SUMMATION OF EFFECTS FROM OTHER SURFACE SEGMENTS  
 ! NORMDIST = NORMALIZATION FACTOR  
 ! NORMSUM = SUMMATION OF ALL NORMALIZATION FACTORS  
 !  
 ! REQUIRED INPUT (ON PROMPT):  
 !       NAME OF FILE (INCLUDING LOCATION AND EXTENSION)  
 !       NAME OF CHEMICAL (THIS WILL APPEAR IN THE OUTPUT FILE)  
 !       NUMSEGMENT = THE NUMBER OF SURFACE SEGMENTS  
 !  
 ! THE OUTPUT FILE "CHEMICAL'SIGMA-PROFILE.TXT" IS THE SORTED SIGMA PROFILE  
 !  
 ! LITERATURE CITED:  
 ! Klamt, A. Conductor-like Screening Model for Real Solvents: A New Approach to the  
 ! Quantitative Calculation of Solvation Phenomena. J. Phys. Chem 1995, 99, 2224.

```

! Klamt, A.; Jonas, V.; Burger, T.; Lohrenz, J. Refinement and Parameterization of
!   COSMO-RS. J. Phys. Chem A 1998, 102, 5074.
! Klamt, A.; Eckert, F.; COSMO-RS: A Novel and Efficient Method for the a Priori
!   Prediction of Thermophysical Data of Liquids. Fluid Phase Equilibria 2000,
!   172, 43.
! Lin, S.T.; Sandler, S. A Priori Phase Equilibrium Prediction from a Segment
!   Contribution Solvation Model. Ind. Eng. Chem. Res, 2002, 41, 899
! Lin, S.T.; Quantum Mechanical Approaches to the Prediction of Phase Equilibria:
!   Solvation Thermodynamics and Group Contribution Methods, PhD. Dissertation,
!   University of Delaware, Newark, DE, 2000
!*****

```

```

IMPLICIT NONE

```

```

CHARACTER(128):: FILEINDEX, FILEOUTPUT
CHARACTER(16):: CHEMICAL
CHARACTER(1) :: RESPONSE
CHARACTER (256) :: FILENAME
INTEGER :: I, J, K, F, M, N, O, DUMBI, TMP, NUMSEGMENT
INTEGER, DIMENSION (:), ALLOCATABLE :: ATOM
INTEGER, DIMENSION (1500) :: FILEIN, FILEOUT
REAL*8 :: REFF, PI
REAL*8, DIMENSION (:), ALLOCATABLE :: POSXAU, POSYAU, POSZAU, POSXA, POSYA, POSZA, A
REAL*8, DIMENSION (:), ALLOCATABLE :: CHG, SIGMA, POTENT, SIGMANEW, SIGMASUM, RAD, NORMDIST
REAL*8, DIMENSION (:), ALLOCATABLE :: NORMSUM, DMN
REAL*8, DIMENSION(1:201) :: CHGDEN,SP

```

```

! ESTABLISH INPUT FILE UNIT NUMBERS

```

```

DO N = 1, 1500
  FILEIN(N) = N+20
END DO

```

```

! ESTABLISH OUTPUT FILE UNIT NUMBERS

```

```

DO O = 1, 1500

```

FILEOUT(O) = O+1521

END DO

!ESTABLISH CONSTANTS

PI = 3.14159265358979D0

REFF = 0.81764200000000D0

!REPETITION LOOP TO CALCULATE MULTIPLE P(S)

DO F = 1, 1500

!ESTABLISHING THE COSMO FILE TO READ

WRITE(\*,\*) "TYPE THE NAME OF THE FILE YOU WISH TO READ IN,"

WRITE(\*,\*) "INCLUDING LOCATION (MAX 256 CHARACTERS), AND HIT ENTER"

READ (\*,\*) FILENAME

!ESTABLISH THE CHEMICAL NAME

WRITE(\*,\*) "TYPE IN THE NAME OF THE CHEMICAL (MAX 16 CHARACTERS), AND HIT ENTER"

READ (\*,\*) CHEMICAL

!OPEN THE COSMO FILE WITH ALL SEGMENTS AND CORRESPONDING CHARGE DENSITIES

OPEN(UNIT=FILEIN(F), FILE = FILENAME, STATUS = "OLD", ACTION = "READ", POSITION = "REWIND")

!ESTABLISH THE NUMBER OF SURFACE SEGMENTS AND ALLOCATE THE ARRAYS

WRITE(\*,\*) "TYPE THE NUMBER OF SURFACE SEGMENTS, FROM THE COSMO OUTPUT, AND HIT ENTER"

READ (\*,\*) NUMSEGMENT

ALLOCATE(ATOM(NUMSEGMENT), POSXAU(NUMSEGMENT), POSYAU(NUMSEGMENT), &

POSZAU(NUMSEGMENT), POSXA(NUMSEGMENT), POSYA(NUMSEGMENT), &

POSZA(NUMSEGMENT), A(NUMSEGMENT), CHG(NUMSEGMENT), SIGMA(NUMSEGMENT), &

POTENT(NUMSEGMENT), SIGMANEW(NUMSEGMENT), SIGMASUM(NUMSEGMENT), &

RAD(NUMSEGMENT), NORMDIST(NUMSEGMENT), NORMSUM(NUMSEGMENT), DMN(NUMSEGMENT))

!READ THE COSMO FILE AND ESTABLISH THE DATA ARRAYS

```

DO I = 1, NUMSEGMENT
  READ(FILEIN(F),*) DUMBI,ATOM(I),POSXAU(I),POSYAU(I),POSZAU(I),CHG(I),A(I),SIGMA(I),POTENT(I)
    !CONVERT THE POSITIONS FROM ATOMIC UNITS TO ANGSTROMS AND ASSIGN NEW ARRAYS
    POSXA(I) = POSXAU(I) * 0.529177249D0
    POSYA(I) = POSYAU(I) * 0.529177249D0
    POSZA(I) = POSZAU(I) * 0.529177249D0
    RAD(I) = SQRT(A(I)/PI)
END DO

```

```

!CLOSE COSMO FILE
CLOSE(FILEIN(F))

```

```

!BEGIN AVERAGING SURFACE CHARGES

```

```

DO J=1, NUMSEGMENT
  SIGMANEW(J) = 0.D0
  NORMSUM(J)=0.D0

  DO K=1, NUMSEGMENT
    DMN(K) = SQRT((POSXA(K)-POSXA(J))**2+(POSYA(K)-POSYA(J))**2+ &
      (POSZA(K)-POSZA(J))**2)
    SIGMASUM(K)= SIGMA(K)*(RAD(K)**2*REFF**2)/(RAD(K)**2+REFF**2)* &
      DEXP(-(DMN(K)**2)/(RAD(K)**2+REFF**2))
    NORMDIST(K) =(RAD(K)**2*REFF**2)/(RAD(K)**2+REFF**2)* &
      DEXP(-(DMN(K)**2)/(RAD(K)**2+REFF**2))
    NORMSUM(J) = NORMSUM(J) + NORMDIST(K)
    SIGMANEW(J) = SIGMANEW(J) + SIGMASUM(K)
  END DO

  SIGMANEW(J) = SIGMANEW(J)/NORMSUM(J)
END DO

```

```
FILEOUTPUT = 'C:\CdriveAPRILPROFILES\//CHEMICAL//'.TXT
!CONTAINS AVERAGED SIGMA-PROFILE
OPEN (FILEOUT(F), FILE = FILEOUTPUT)
```

```
!SETTING CHGDEN MATRIX
```

```
DO J=1,201
    SP(J)=0.D0
    CHGDEN(J) = -0.10D0+0.001D0*DBLE(J-1)
END DO
```

```
!SIGMA PROFILE SORTING TAKEN FROM LIN DISSERTATION**
```

```
DO J=1,NUMSEGMENT
    TMP=INT((SIGMANEW(J)-CHGDEN(1))/0.001D0)
    SP(TMP+1)=SP(TMP+1)+A(J)*(CHGDEN(TMP+2)-SIGMANEW(J))/0.001D0
    SP(TMP+2)=SP(TMP+2)+A(J)*(SIGMANEW(J)-CHGDEN(TMP+1))/0.001D0
END DO
```

```
DO J=1,201
    WRITE(FILEOUT(F),*) CHGDEN(J),SP(J)
END DO
```

```
CLOSE(FILEOUT(F))
```

```
DEALLOCATE(ATOM, POSXAU, POSYAU, POSZAU, &
    POSXA, POSYA, POSZA, A, &
    CHG, SIGMA, POTENT, SIGMANEW, &
    SIGMASUM, RAD, NORMDIST, NORMSUM, &
    DMN)
```

```
!REPEAT SIGMA PROFILE CALCULATION FOR ANOTHER COMPOUND
WRITE (*,*) "DO YOU WISH TO CALCULATE ANOTHER SIGMA PROFILE (Y or N)"
READ (*,*) RESPONSE
```

```
IF (RESPONSE=="N") EXIT
```

```
END DO
```

```
END PROGRAM SIGMAPROFILEV3
```

A2: Electrolyte COSMO-SAC FORTRAN .f90 Code

Input: components, COSMO volumes, temperature, solute melting temperature(s), solute latent heat(s) of fusion, sigma profiles, and initial guess for mole fractions from input file

Output: solvent and solute mole fractions, activity coefficients

Notes:

(1) Easily modifiable to calculate solubility at multiple temperatures

(2) Iterative calculation scheme for segment activity coefficient and solute mole fraction

```
PROGRAM GAMMA1electrolyte
```

```
!*****
```

```
! This program uses the sigma profiles of two pure components to calculate  
! the liquid-phase activity coefficients in a solution. This is the first  
! step in predicting VLE for mixtures.
```

```
!  
! This program uses the COSMO-SAC model as published (Lin, S.T.,  
! S.I. Sandler, Ind. Eng. Chem. Res. 41, (2002), 899-913),  
! with modifications for elctorlytes
```

```
!  
! Program currently being revised for electrolytes by:  
! APRIL N. VANSANT  
! DEPARTMENT OF CHEMICAL ENGINEERING  
! VIRGINIA TECH  
! BLACKSBURG, VA 24060
```

```
!  
!  
! THIS PROGRAM WRITTEN BY:  
! RICHARD OLDLAND (roldland@vt.edu) MIKE ZWOLAK (zwolak@caltech.edu)
```

! DEPARTMENT OF CHEMICAL ENGINEERING PHYSICS DEPARTMENT  
! VIRGINIA TECH CALIFORNIA INSTITUTE OF TECHNOLOGY  
! BLACKSBURG, VA 24060 PASADENA, CA 91125  
!

! PHYSICAL CONSTANTS AND PARAMETERS:

! EO = PERMITTIVITY IN A VACUUM ( $\epsilon^2 \cdot \text{mol/Kcal} \cdot \text{Angstrom}$ )  
! AEFFPRIME = EFFECTIVE SURFACE AREA ( $\text{ANGSTROMS}^2$ ) --FROM LIN  
! RGAS = IDEAL GAS CONSTANT ( $\text{Kcal/mol} \cdot \text{K}$ )  
! VNORM = VOLUME NORMALIZATION CONSTANT ( $A^3$ ) --FROM LIN  
! ANORM = AREA NORMALIZATION CONSTANT ( $A^2$ ) --FROM LIN  
! COORD = THE COORDINATION NUMBER --FROM LIN  
! CHB = HYDROGEN BONDING COEFFICIENT ( $\text{Kcal/mole} \cdot \text{Angstroms}^4/\epsilon^2$ )  
! SIGMAHB = CUTOFF VALUE FOR HYDROGEN BONDING ( $\text{e}/\text{Angstrom}^2$ )  
! CION = IONIC BONDING INTERACTION CONSTANT ( $\text{Kcal/mole} \cdot \text{Angstroms}^4/\epsilon^2$ )  
! SIGMAION = ION-BONDING CUT OFF VALUE ( $\text{e}/\text{Angstrom}^2$ )  
! EPS = RELATIVE PERMITTIVITY --FROM LIN  
! ALPHAPRIME = A CONSTANT USED IN THE MISFIT ENERGY CALCULATION  
!

! INPUT PARAMETERS:

! SYSTEMP = THE SYSTEM TEMPERATURE (K)  
! COMP = NUMBER OF COMPONENTS IN THE SYSTEM --SET TO 2 FOR BINARY  
! SYSCOMP = NAMES OF COMPONENTS IN THE SYSTEM  
! VCSOMO = CAVITY VOLUME FROM COSMO OUTPUT ( $A^3$ )  
! ACOSMO = MOLECULAR SURFACE AREA FROM COSMO OUTPUT ( $A^2$ ) --THE SUM  
! OF THE INDIVIDUAL PROFILE.  
!

! LITERATURE CITED:

! Klamt, A. Conductor-like Screening Model for Real Solvents: A New Approach to the  
! Quantitative Calculation of Solvation Phenomena. J. Phys. Chem 1995, 99, 2224.  
! Klamt, A.; Jonas, V.; Burger, T.; Lohrenz, J. Refinement and Parameterization of  
! COSMO-RS. J. Phys. Chem A 1998, 102, 5074.  
! Klamt, A.; Eckert, F.; COSMO-RS: A Novel and Efficient Method for the a Priori



! Prediction of Thermophysical Data of Liquids. Fluid Phase Equilibria 2000,  
! 172, 43.  
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! Lin, S.T.; Quantum Mechanical Approaches to the Prediction of Phase Equilibria:  
! Solvation Thermodynamics and Group Contribution Methods, PhD. Dissertation,  
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! Mullins, E. Application of COSMO-SAC to Solid Solubility in Pure and Mixed Solvent  
! Mixtures for Organic Pharmacological Compounds. Thesis, M. S. Virginia Polytechnic  
! Institute and State University, Blacksburg, 2007.

!  
!  
! PROGRAM CURRENTLY SETUP FOR TERNARY MIXTURES ONLY

!\*\*\*\*\*

IMPLICIT NONE

REAL\*8, PARAMETER :: EO = 2.395D-04 ! PERMITTIVITY OF FREE SPACE ( $\epsilon^2$ \*MOL/KCAL/ANG<sup>2</sup>)  
REAL\*8, PARAMETER :: AEFPRIME = 7.5D0 ! ANGSTROMS<sup>2</sup>  
REAL\*8, PARAMETER :: RGAS = 0.001987D0 ! KCAL/(MOL K)  
REAL\*8, PARAMETER :: VNORM = 66.69D0 ! NORMALIZED CAVITY VOLUME, ANGSTROMS<sup>3</sup>  
REAL\*8, PARAMETER :: ANORM = 79.53D0 ! NORMALIZED SURFACE AREA, ANGSTROMS<sup>2</sup>  
INTEGER, PARAMETER :: COORD = 10.0D0 ! COORDINATION NUMBER, Z, KLAMT USED 7.2  
INTEGER, PARAMETER :: COMP = 3 ! NUMBER OF COMPONENTS IN SYSTEM  
INTEGER, PARAMETER :: COMPSEG = 201 ! NUMBER OF INTERVALS FOR THE SIGMA PROFILE (-0.1 TO 0.1)

REAL\*8 :: FPOL, ALPHA, ALPHAPRIME, EPS, SYSTEMP, SIGMAHB, CHB, CION, SIGMAION  
REAL\*8 :: SYSPRES, SIGMAACC, SIGMADON, SUMMATION, DELTAWHB, DELTAWION, DELTAWMF  
REAL\*8 :: N1, N2

REAL\*8, DIMENSION(3) :: VCOSMO, ACOSMO, RNORM, QNORM  
REAL\*8, DIMENSION(3) :: THETA, PHI, LSG, LNGAMMASG, LNGAMMA, GAMMA, SUMGAMMA  
REAL\*8, DIMENSION(:), ALLOCATABLE :: COUNTER, DENOM, PROFILE, NUMER, SEGGAMMA  
REAL\*8, DIMENSION(:), ALLOCATABLE :: SEGGAMMAOLD, CONVERG, VCOSMO1, VCOSMO2, VCOSMO3

```

REAL*8, DIMENSION(:), ALLOCATABLE :: X1, X2, X3, POINT, TEMP, ACOSMO1, ACOSMO2, ACOSMO3,
MOSTNEGDW
REAL*8, DIMENSION(:,:), ALLOCATABLE :: SIGMA, DELTAW, SEGGAMMAPR, SEGGAMMAOLDPR, CONPR, X
REAL*8, DIMENSION(:,:), ALLOCATABLE :: SIGMA1, SIGMA2, SIGMA3, COUNTER1, COUNTER2, COUNTER3
INTEGER :: I, J, K, L, M, MF, COUNT, NUMPOINTS, iSTAT, loopcount
INTEGER, DIMENSION (:), ALLOCATABLE :: FILEUNIT1, FILEUNIT2, FILEUNIT3

```

```

CHARACTER (25), DIMENSION(3) :: SYSCOMP
CHARACTER (256), DIMENSION(:), ALLOCATABLE :: FILENAME1, FILENAME2, FILENAME3
CHARACTER (25), DIMENSION (:), ALLOCATABLE :: SOLV1, SOLV2, SOLV3
CHARACTER (256):: OUTPUTFILE, INPUTFILE

```

!COMPSEG IS BASED ON THE SIGMAAVERAGE FORTRAN CODE UNDER SECTION CALLED "SETTING CHGDEN MATRIX"

EPS = 3.667D0 !DIELECTRIC CONSTANT,(LIN AND SANDLER USE A CONSTANT FPOL WHICH YEILDS EPS=3.68)

SIGMAHB = 0.0084D0 ! HYDROGEN-BONDING INTERACTION CUT-OFF, e/ANG^2

CHB = 85580.0D0 ! HYDROGEN-BONDING INTERACTION CONSTANT, KCAL\*ANG^4/MOL/e^2

SIGMAION = 0.016D0 ! IONIC-BONDING INTERACTION CUT-OFF - VALUE IS ONLY A GUESS

CIION = 85580.0D0 ! IONIC-BONDING INTERACTION CONSTANT - VALUE IS ONLY A GUESS

FPOL = (EPS-1.0D0)/(EPS+0.5D0) !UNITLESS

ALPHA = (0.3D0\*AEFFPRIME\*\*(1.5D0))/(EO) ! KCAL\*ANG^4/MOL/e^2

ALPHAPRIME = FPOL\*ALPHA ! MISFIT ENERGY CONSTANT, KCAL\*ANG^4/MOL/e^2

NUMPOINTS = 10 ![USER SPECIFIED] BASED ON HOW MANY ROWS OF DATA "SETS" YOU HAVE IN YOUR INPUT FILE

```

ALLOCATE (SOLV1(NUMPOINTS), VCOSMO1(NUMPOINTS), SOLV2(NUMPOINTS), VCOSMO2(NUMPOINTS), &
          SOLV3(NUMPOINTS), VCOSMO3(NUMPOINTS), TEMP(NUMPOINTS), X1(NUMPOINTS), &
          X2(NUMPOINTS), X(NUMPOINTS,COMP), FILEUNIT1(NUMPOINTS),
FILEUNIT2(NUMPOINTS),&
          FILEUNIT3(NUMPOINTS), FILENAME1(NUMPOINTS), FILENAME2(NUMPOINTS), &

```

```

FILENAME3(NUMPOINTS), SIGMA1(COMPSEG,NUMPOINTS),
SIGMA2(COMPSEG,NUMPOINTS), &
SIGMA3(COMPSEG,NUMPOINTS), COUNTER1(COMPSEG,NUMPOINTS),
COUNTER2(COMPSEG,NUMPOINTS), &
COUNTER3(COMPSEG,NUMPOINTS), ACOSMO1(NUMPOINTS), ACOSMO2(NUMPOINTS),
ACOSMO3(NUMPOINTS),&

```

```

STAT = iSTAT)

```

```

WRITE (*,*) iSTAT, " ALLOCATION SUCCESSFUL"

```

```

ACOSMO1 = 0.0D0

```

```

ACOSMO2 = 0.0D0

```

```

ACOSMO3 = 0.0D0

```

```

VCOSMO1 = 0.0D0

```

```

VCOSMO2 = 0.0D0

```

```

VCOSMO3 = 0.0D0

```

```

!INPUT SECTION

```

```

![USER SPECIFIED INPUT FILE LOCATION]

```

```

!THIS FILE CAN HAVE MANY ROWS - THE NUMBER OF ROWS IS HOW MANY NUMPOINTS YOU HAVE.

```

```

!THE NAMES OF THE SOLV1, SOLV2,SOLV3, MUST BE THE EXACT NAMES OF THE SIGMA PROFILE TEXT

```

```

FILES YOU HAVE SET UP

```

```

INPUTFILE = "C:\ElectrolyteInput.txt"

```

```

OPEN (UNIT=12, FILE=INPUTFILE, STATUS="OLD", ACTION="READ", POSITION="REWIND")

```

```

DO I = 1, NUMPOINTS

```

```

READ (12,*) SOLV1(I), VCOSMO1(I), SOLV2(I), VCOSMO2(I), SOLV3(I), VCOSMO3(I), TEMP(I), &
X1(I), X2(I)

```

```

!USER MUST SET WHERE THE SIGMAPROFILES ARE LOCATED FOR THE SOLV1, SOLV2, AND SOLV3 IN
THE INPUT FILE

```

```

FILENAME1(I) = "C:\sigmaprofiles\\"//SOLV1(I) ![USER SPECIFIED: COMPONENT 1]

```

```

FILENAME2(I) = "C:\sigmaprofiles\\"//SOLV2(I) ![USER SPECIFIED: COMPONENT 2]

```

```
FILENAME3(I) = "C:\sigmaprofiles\\"//SOLV3(I) ![USER SPECIFIED: COMPONENT 3]
X(I,1) = X1(I)
X(I,2) = X2(I)
X(I,3) = 1.0D0 - X1(I) - X2(I)
FILEUNIT1(I) = 20 + I
FILEUNIT2(I) = 1000 + I
FILEUNIT3(I) = 2000 + I
```

```
OPEN(UNIT=FILEUNIT1(I), FILE=FILENAME1(I), STATUS="OLD", ACTION="READ",
POSITION="REWIND")
OPEN(UNIT=FILEUNIT2(I), FILE=FILENAME2(I), STATUS="OLD", ACTION="READ",
POSITION="REWIND")
OPEN(UNIT=FILEUNIT3(I), FILE=FILENAME3(I), STATUS="OLD", ACTION="READ",
POSITION="REWIND")
```

```
DO J=1, COMPSEG
  READ(FILEUNIT1(I),*) COUNTER1(J,I), SIGMA1(J,I)
  ACOSMO1(I)=ACOSMO1(I)+SIGMA1(J,I)
  READ(FILEUNIT2(I),*) COUNTER2(J,I), SIGMA2(J,I)
  ACOSMO2(I)=ACOSMO2(I)+SIGMA2(J,I)
  READ(FILEUNIT3(I),*) COUNTER3(J,I), SIGMA3(J,I)
  ACOSMO3(I)=ACOSMO3(I)+SIGMA3(J,I)
END DO
```

```
CLOSE(21)
CLOSE(22)
CLOSE(23)
```

```
END DO
CLOSE (12)
!END INPUT SECTION
WRITE(*,*) "INPUT SECTION COMPLETE"
```

```
![USER SPECIFIED OUTPUT FILE LOCATION]
OUTPUTFILE = "C:\ElectrolytePrediction.TXT"
```

```
OPEN(UNIT=11, FILE = OUTPUTFILE, STATUS="REPLACE")
7 FORMAT (1X,A6,1X,A6,1X,A6,1X,A6,1X,A5,1X,A5,1X,A5,1X,A7,1X,A7,1X,A7)
8 FORMAT (1X,A20,1X,A20,1X,A20,1X,E,1X,E,1X,E,1X,E,1X,E,1X,E)
WRITE (11,7) "COMP1","COMP2","COMP3", "TEMP", "X1", "X2", "X3", "GAMMA1", "GAMMA2", "GAMMA3"
WRITE(*,*) "INITIAL OUTPUT FILE CREATED SUCESSFULLY"
```

```
!ALLOCATE ARRAYS USED IN MAIN ITERATIVE LOOP
ALLOCATE(SIGMA(COMPSEG,COMP), COUNTER(COMPSEG), MOSTNEGDW(COMPSEG), PROFILE(COMPSEG),
NUMER(COMPSEG),&
DENOM(COMPSEG), DELTAW(COMPSEG,COMPSEG), SEGGAMMA(COMPSEG),
SEGGAMMAOLD(COMPSEG), &
CONVERG(COMPSEG), SEGGAMMAPR(COMPSEG,COMP), SEGGAMMAOLDPR(COMPSEG,COMP), &
CONPR(COMPSEG,COMP))
WRITE(*,*) "ALLOCATION OF MAIN LOOP ARRAYS SUCESSFUL"
```

```
! BEGIN ITERATION LOOP FOR ALL POINTS, REASSIGNING NEW SIGMA PROFILES FOR EACH ITERATIONS
DO MF = 1, NUMPOINTS !4851 IF USING ENTIRE ARRAY OF POSSIBLE MOLE FRACTION COMBINATIONS
```

```
!RE-ZERO LOOP VARIABLES
SIGMA = 0.0D0
COUNTER = 0.0D0
ACOSMO = 0.0D0
VCOSMO = 0.0D0
SYSTEMP = 0.0D0
PROFILE = 0.0D0
DELTAW = 0.0D0
```

DELTAWHB = 0.0D0  
DELTAWION = 0.0D0  
SEGGAMMA = 1.0D0  
SEGGAMMAOLD = 1.0D0  
CONVERG = 1.0D0  
SEGGAMMAPR = 1.0D0  
SEGGAMMAOLDPR = 1.0D0  
SIGMAACC = 0.0D0  
SIGMADON = 0.0D0  
THETA = 0.0D0  
PHI = 0.0D0  
LSG = 0.0D0  
RNORM = 0.0D0  
QNORM = 0.0D0  
LNGAMMASG = 0.0D0  
SUMGAMMA = 0.0D0  
LNGAMMA = 0.0D0  
GAMMA = 0.0D0  
MOSTNEGDW = 0.0D0

! REASSIGN SIGMA PROFILES, ACOSMO, AND VCOSMO

SYSCOMP(1) = SOLV1(MF)  
SYSCOMP(2) = SOLV2(MF)  
SYSCOMP(3) = SOLV3(MF)  
SIGMA(:,1) = SIGMA1(:,MF)  
SIGMA(:,2) = SIGMA2(:,MF)  
SIGMA(:,3) = SIGMA3(:,MF)  
COUNTER(:) = COUNTER1(:,MF)  
VCOSMO(1) = VCOSMO1(MF)  
ACOSMO(1) = ACOSMO1(MF)  
VCOSMO(2) = VCOSMO2(MF)  
ACOSMO(2) = ACOSMO2(MF)  
VCOSMO(3) = VCOSMO3(MF)

ACOSMO(3) = ACOSMO3(MF)

SYSTEMP = TEMP(MF)

!CALCULATE THE MIXTURE SIGMA PROFILE

DO J =1,COMPSEG

!REPLACE ALL FRAC1,FRAC2 WITH APPROPRIATE X1, X2, OR X3

!THE 3 LINES BELOW CALCULATE THE MIXTURE SIGMA PROFILE BASED ON EQUATION 2.21

ON PAGE 9 OF MILLINS THESIS

NUMER(J) = X(MF,1)\*SIGMA(J,1) + X(MF,2)\*SIGMA(J,2) + X(MF,3)\*SIGMA(J,3)

DENOM(J) = X(MF,1)\*ACOSMO(1) + X(MF,2)\*ACOSMO(2) + X(MF,3)\*ACOSMO(3)

PROFILE(J) = NUMER(J)/DENOM(J)

!WRITE (\*,\*) PROFILE(J)

END DO

WRITE(\*,\*) MF, "MIXTURE SIGMA PROFILE CALCULATION COMPLETE"

!DETERMINE THE EXCHANGE ENERGY, DELTAW, KCAL/MOL (ORIGINAL MODEL MODIFIED FOR ELECTROLYTES)

DO I = 1, COMPSEG

DO K = 1, COMPSEG

! ASSIGN BONDING DONOR AND ACCEPTOR

IF (COUNTER(I)>=COUNTER(K)) THEN

SIGMAACC = COUNTER(I)

SIGMADON = COUNTER(K)

END IF

IF (COUNTER(I)<COUNTER(K)) THEN

SIGMADON = COUNTER(I)

SIGMAACC = COUNTER(K)

END IF

DELTAWMF = ((ALPHAPRIME/2.0)\*(COUNTER(I)+COUNTER(K))\*\*2.0)

!DERTERMINE IF THERE IS HYDROGEN BONDING TO CONTRIBUTE TO DELTAW

```

IF (AND (ABS(SIGMAACC) > SIGMAION , ABS(SIGMADON) > SIGMAION)) THEN
  DELTAWHB = 0
ELSE
  DELTAWHB = CHB * MAX(0.0,(SIGMAACC - SIGMAHB)) * MIN(0.0,(SIGMADON +
SIGMAHB))
END IF

```

```

! DETERMINE IF THERE IS ION-ION BONDING TO CONTRIBUTE TO DELTAW
! The signs of the interaction are taken care of by the signs in "sigmadon" and "sigmaacc"
! If both sigmadon and sigmaacc are positive (or both negative)
! then the DeltaWion is positive, favoring the two segments NOT pairing.
! If one of them is negative and the other positive, this gives a negative
! interaction energy which favors the segments pairing.
! the first term is the attractive interaction and the last 2 are repulsive.

```

```

DELTAWION = CION * MAX(0.0,(SIGMAACC - SIGMAION)) * MIN(0.0,(SIGMADON +
SIGMAION)) + &
CION * MAX(0.0,(SIGMAACC - SIGMAION)) * MAX(0.0,(SIGMADON -
SIGMAION)) + &
CION * MIN(0.0,(SIGMAACC + SIGMAION)) * MIN(0.0,(SIGMADON +
SIGMAION))

```

```

!ORIGINALLY EQUATION 2.7 IN MULLINS THESIS BUT HAS BEEN MODIFIED FOR
ELECTROLYTES

```

```

DELTAW(I,K) = DELTAWMF + DELTAWHB + DELTAWION

```

```

IF (PROFILE(K)>0) THEN
  IF (DELTAW(I,K) < MOSTNEGDW(I)) THEN
    MOSTNEGDW(I)=DELTAW(I,K)
  END IF
END IF

```



```

        END DO

    END DO

    WRITE(*,*) MF, "EXCHANGE ENERGY CALCUATED FOR ALL SEGMENTS"

    !ITERATION FOR SEGMENT ACTIVITY COEFFICIENT (MIXTURE)
    !THIS IS EQUATION 2.6 ON PAGE 6 OF MULLINS THESIS
    SEGGAMMA = 1.0
DO
    SEGGAMMAOLD = SEGGAMMA
    DO I = 1, COMPSEG
        SUMMATION = 0.0
        DO K = 1, COMPSEG

            IF (PROFILE(K) >0) THEN

                IF ((DELTAW(I,K)-MOSTNEGDW(I))/(RGAS*SYSTEMP) < 500 ) THEN
                    SUMMATION = SUMMATION + PROFILE(K)* SEGGAMMAOLD(K)
*DEXP(-(DELTAW(I,K)-MOSTNEGDW(I))/(RGAS*SYSTEMP))
                END IF

            END IF

        END DO

    END DO

    SEGGAMMA(I)=DEXP(-DLOG(SUMMATION))
    !SEGGAMMA(I)=1/SUMMATION
    SEGGAMMA(I)=(SEGGAMMA(I)+SEGGAMMAOLD(I))/2.0

END DO

```

```
DO I=1, COMPSEG
    CONVERG(I)=DABS((SEGGAMMA(I)-SEGGAMMAOLD(I))/SEGGAMMAOLD(I))
END DO
```

```
IF (MAXVAL(CONVERG) <=0.000001) EXIT
```

```
END DO
```

```
!END ITERATION FOR SEGMENT ACTIVITY COEFFICIENT (MIXTURE)
WRITE(*,*) MF, "MIXTURE SEGMENT ACTIVITY COEFFICIENT COMPLETE"
```

```
!ITERATION FOR SEGMENT ACTIVITY COEFFICIENT (PURE SPECIES)
```

```
!THIS EQUATION 2.14 ON PAGE 8 OF MULLINS THESIS
```

```
DO L = 1, COMP
```

```
    SEGGAMMAPR (:,L) = 1.0
```

```
    DO
```

```
        SEGGAMMAOLDPR (:,L) = SEGGAMMAPR (:,L)
```

```
        DO I = 1, COMPSEG
```

```
            SUMMATION = 0.0
```

```
            DO K = 1, COMPSEG
```

```
                IF (SIGMA(K,L)>0) THEN
```

```
                    IF ((DELTA W(I,K)-MOSTNEGDW(I))/(RGAS*SYSTEMP) < 200 ) THEN
```

```
                        SUMMATION = SUMMATION +
```

```
(SIGMA(K,L)/ACOSMO(L))*SEGGAMMAOLDPR(K,L)* DEXP(-(DELTA W(I,K)-MOSTNEGDW(I))/(RGAS*SYSTEMP))
```

```
                    END IF
```

```
                END IF
```

```
            END DO
```

```

        SEGGAMMAPR(I,L)=DEXP(-DLOG(SUMMATION))
        !SEGGAMMAPR(I,L)=1/(SUMMATION)
        SEGGAMMAPR(I,L)=(SEGGAMMAPR(I,L)+SEGGAMMAOLDPR(I,L))/2.0

    END DO

    DO I=1, COMPSEG
        CONPR(I,L)=DABS((SEGGAMMAPR(I,L)-SEGGAMMAOLDPR(I,L))/SEGGAMMAOLDPR(I,L))
    END DO

    IF (MAXVAL(CONPR) <=0.000001) EXIT

    END DO
END DO
!END ITERATION FOR SEGMENT ACITIVITY COEFFICIENT (PURE SPECIES)
WRITE(*,*) MF, "PURE SPECIES SEGMENT ACTIVITY COEFFICIENT COMPLETE"

!THE STAVERMAN-GUGGENHEIM EQUATION
!SEE EQUATION 2.3 AND EXPLANATION ON PAGE 6 OF MULLINS THESIS
DO I = 1,COMP
    RNORM(I) = V COSMO(I)/VNORM
    QNORM(I) = A COSMO(I)/ANORM
END DO

DO I = 1, COMP
    THETA(I) = X(MF,I)*QNORM(1)/(X(MF,1)*QNORM(1) + X(MF,2)*QNORM(2) + X(MF,3)*QNORM(3))
    PHI(I) = X(MF,I)*RNORM(1)/(X(MF,1)*RNORM(1) + X(MF,2)*RNORM(2) + X(MF,3)*RNORM(3))
    LSG(I) = (COORD/2.0)*(RNORM(I)-QNORM(I))-(RNORM(I)-1.0)
END DO

!THIS IS EQUATION 2.3 ON PAGE 6 OF MULLINS THESIS

```

```

DO I = 1, COMP
  LNGAMMASG(I) = DLOG(PHI(I)/X(MF,I))+(COORD/2)*QNORM(I)*DLOG(THETA(I)/PHI(I))+LSG(I)- &
    (PHI(I)/X(MF,I))*(X(MF,1)*LSG(1) + X(MF,2)*LSG(2) + X(MF,3)*LSG(3))
END DO

```

```

!END STAVERMAN-GUGGENHEIM EQUATION CALCULATIONS
WRITE(*,*) MF, "STAVERMAN-GUGGENHEIM EQUATION CLACULATIONS COMPLETE"

```

!THIS CALCULATES THE FIRST PART (THE SUMMATION PART) OF EQUATION 2.15 ON PAGE 8 OF MULLINS  
 THESIS

```

SUMGAMMA = 0.0D0
DO I = 1, COMPSEG
  SUMGAMMA(1) = SUMGAMMA(1)
+((SIGMA(I,1)/AEFFPRIME)*(DLOG(SEGGAMMA(I)/(SEGGAMMAPR(I,1))))))
  SUMGAMMA(2) = SUMGAMMA(2)
+((SIGMA(I,2)/AEFFPRIME)*(DLOG(SEGGAMMA(I)/(SEGGAMMAPR(I,2))))))
  SUMGAMMA(3) = SUMGAMMA(3)
+((SIGMA(I,3)/AEFFPRIME)*(DLOG(SEGGAMMA(I)/(SEGGAMMAPR(I,3))))))
END DO

```

```

WRITE(*,*) MF, "FRIST PART EQUATION 2.15 CLACULATIONS COMPLETE"

```

!THIS CALCULATES THE ACTIVITY COEFFICIENT BASED ON EQUATION 2.15 ON PAGE 8 OF MULLIN  
 THESIS

```

GAMMA(1) = DEXP(SUMGAMMA(1) + LNGAMMASG(1))
GAMMA(2) = DEXP(SUMGAMMA(2) + LNGAMMASG(2))
GAMMA(3) = DEXP(SUMGAMMA(3) + LNGAMMASG(3))
WRITE(*,*) GAMMA(1), "GAMMA1"
WRITE(*,*) GAMMA(2), "GAMMA2"
WRITE(*,*) GAMMA(3), "GAMMA3"

```

```

!LNGAMMA(1) = DLOG(GAMMA(1))
!LNGAMMA(3) = DLOG(GAMMA(3))
      !LNGAMMA(2) = DLOG(GAMMA(2))

      WRITE(11,8) SYSCOMP(1),SYSCOMP(2),SYSCOMP(3),SYSTEMP,X(MF,1), X(MF,2), X(MF,3), GAMMA(1),
GAMMA(2), GAMMA(3)

      END DO

END PROGRAM GAMMA1electrolyte

```

### ***Appendix B: Sample Materials Studio output files and sample sigma profile for an Electrolyte***

We present the Accelrys Materials Studio output and sigma profile of OH<sup>-</sup> as a sample electrolyte. In the sigma profile, the value of the screening charge density range from -0.1 e/Å<sup>2</sup> – 0.1 e/Å<sup>2</sup>. The files, sigma profile, COSMO calculation output, geometry optimization output, and energy calculation output, are in simple TXT file format.

**Table 10: Example electrolyte sigma profile for OH<sup>-</sup>.**

Component Name	Hydroxide ion
Chemical Formula	OH-
CAS Number	14280-30-9
<u>Screening Charge Density, <math>\sigma_m</math> (e/Å<sup>2</sup>)</u>	<u>Sigma Profile, P(<math>\sigma</math>)A(<math>\sigma</math>), (Å<sup>2</sup>)</u>
-0.1	0.00E+00
-9.90E-02	0.00E+00
-9.80E-02	0.00E+00
-9.70E-02	0.00E+00
-9.60E-02	0.00E+00
-9.50E-02	0.00E+00
-9.40E-02	0.00E+00
-9.30E-02	0.00E+00
-9.20E-02	0.00E+00
-9.10E-02	0.00E+00

-9.00E-02	0.00E+00
-8.90E-02	0.00E+00
-8.80E-02	0.00E+00
-8.70E-02	0.00E+00
-8.60E-02	0.00E+00
-8.50E-02	0.00E+00
-8.40E-02	0.00E+00
-8.30E-02	0.00E+00
-8.20E-02	0.00E+00
-8.10E-02	0.00E+00
-8.00E-02	0.00E+00
-7.90E-02	0.00E+00
-7.80E-02	0.00E+00
-7.70E-02	0.00E+00
-7.60E-02	0.00E+00
-7.50E-02	0.00E+00
-7.40E-02	0.00E+00
-7.30E-02	0.00E+00
-7.20E-02	0.00E+00
-7.10E-02	0.00E+00
-7.00E-02	0.00E+00
-6.90E-02	0.00E+00
-6.80E-02	0.00E+00
-6.70E-02	0.00E+00
-6.60E-02	0.00E+00
-6.50E-02	0.00E+00
-6.40E-02	0.00E+00
-6.30E-02	0.00E+00
-6.20E-02	0.00E+00
-6.10E-02	0.00E+00
-6.00E-02	0.00E+00
-5.90E-02	0.00E+00
-5.80E-02	0.00E+00
-5.70E-02	0.00E+00

-5.60E-02	0.00E+00
-5.50E-02	0.00E+00
-5.40E-02	0.00E+00
-5.30E-02	0.00E+00
-5.20E-02	0.00E+00
-5.10E-02	0.00E+00
-5.00E-02	0.00E+00
-4.90E-02	0.00E+00
-4.80E-02	0.00E+00
-4.70E-02	0.00E+00
-4.60E-02	0.00E+00
-4.50E-02	0.00E+00
-4.40E-02	0.00E+00
-4.30E-02	0.00E+00
-4.20E-02	0.00E+00
-4.10E-02	0.00E+00
-4.00E-02	0.00E+00
-3.90E-02	0.00E+00
-3.80E-02	0.00E+00
-3.70E-02	0.00E+00
-3.60E-02	0.00E+00
-3.50E-02	0.00E+00
-3.40E-02	0.00E+00
-3.30E-02	0.00E+00
-3.20E-02	0.00E+00
-3.10E-02	0.00E+00
-3.00E-02	0.00E+00
-2.90E-02	0.00E+00
-2.80E-02	0.00E+00
-2.70E-02	0.00E+00
-2.60E-02	0.00E+00
-2.50E-02	0.00E+00
-2.40E-02	0.00E+00
-2.30E-02	0.00E+00

-2.20E-02	0.00E+00
-2.10E-02	0.00E+00
-2.00E-02	0.00E+00
-1.90E-02	0.00E+00
-1.80E-02	0.00E+00
-1.70E-02	0.00E+00
-1.60E-02	0.00E+00
-1.50E-02	0.00E+00
-1.40E-02	0.00E+00
-1.30E-02	0.00E+00
-1.20E-02	0.00E+00
-1.10E-02	0.00E+00
-1.00E-02	0.00E+00
-9.00E-03	0.00E+00
-8.00E-03	0.00E+00
-7.00E-03	0.00E+00
-6.00E-03	0.00E+00
-5.00E-03	0.00E+00
-4.00E-03	0.00E+00
-3.00E-03	0.00E+00
-2.00E-03	0.00E+00
-1.00E-03	0.154864596
0.00E+00	0.296575404
1.00E-03	0.00E+00
2.00E-03	0.914548619
3.00E-03	1.695941381
4.00E-03	0.00E+00
5.00E-03	0.00E+00
6.00E-03	0.00E+00
7.00E-03	0.00E+00
8.00E-03	0.00E+00
9.00E-03	0.00E+00
1.00E-02	0.70652729
1.10E-02	1.831377996



1.20E-02	1.875919062
1.30E-02	0.257565652
1.40E-02	0.00E+00
1.50E-02	0.00E+00
1.60E-02	0.00E+00
1.70E-02	0.00E+00
1.80E-02	9.84E-02
1.90E-02	1.622446716
2.00E-02	1.97E-02
2.10E-02	0.00E+00
2.20E-02	0.00E+00
2.30E-02	0.759369934
2.40E-02	2.323522156
2.50E-02	1.14468791
2.60E-02	0.897932551
2.70E-02	2.706424437
2.80E-02	2.20759277
2.90E-02	3.311849626
3.00E-02	4.651299869
3.10E-02	0.581152761
3.20E-02	10.10414764
3.30E-02	2.064790347
3.40E-02	0.00E+00
3.50E-02	0.00E+00
3.60E-02	0.00E+00
3.70E-02	0.00E+00
3.80E-02	0.00E+00
3.90E-02	0.00E+00
4.00E-02	0.00E+00
4.10E-02	0.00E+00
4.20E-02	0.00E+00
4.30E-02	0.00E+00
4.40E-02	0.00E+00
4.50E-02	0.00E+00

4.60E-02	0.00E+00
4.70E-02	0.00E+00
4.80E-02	0.00E+00
4.90E-02	0.00E+00
5.00E-02	0.00E+00
5.10E-02	0.00E+00
5.20E-02	0.00E+00
5.30E-02	0.00E+00
5.40E-02	0.00E+00
5.50E-02	0.00E+00
5.60E-02	0.00E+00
5.70E-02	0.00E+00
5.80E-02	0.00E+00
5.90E-02	0.00E+00
6.00E-02	0.00E+00
6.10E-02	0.00E+00
6.20E-02	0.00E+00
6.30E-02	0.00E+00
6.40E-02	0.00E+00
6.50E-02	0.00E+00
6.60E-02	0.00E+00
6.70E-02	0.00E+00
6.80E-02	0.00E+00
6.90E-02	0.00E+00
7.00E-02	0.00E+00
7.10E-02	0.00E+00
7.20E-02	0.00E+00
7.30E-02	0.00E+00
7.40E-02	0.00E+00
7.50E-02	0.00E+00
7.60E-02	0.00E+00
7.70E-02	0.00E+00
7.80E-02	0.00E+00
7.90E-02	0.00E+00

8.00E-02	0.00E+00
8.10E-02	0.00E+00
8.20E-02	0.00E+00
8.30E-02	0.00E+00
8.40E-02	0.00E+00
8.50E-02	0.00E+00
8.60E-02	0.00E+00
8.70E-02	0.00E+00
8.80E-02	0.00E+00
8.90E-02	0.00E+00
9.00E-02	0.00E+00
9.10E-02	0.00E+00
9.20E-02	0.00E+00
9.30E-02	0.00E+00
9.40E-02	0.00E+00
9.50E-02	0.00E+00
9.60E-02	0.00E+00
9.70E-02	0.00E+00
9.80E-02	0.00E+00
9.90E-02	0.00E+00
0.1	0.00E+00

**Table 11: Accelrys MS Geometry Optimization Task Output (OUTMOL file) for OH<sup>-</sup> sample electrolyte.**

```

=====
Materials Studio DMol^3 version 4.0
compiled on Dec 19 2005 03:11:22
=====
Density Functional Theory Electronic Structure Program
Copyright (c) 2005, Accelrys Inc. All rights reserved.
Cite work using this program as:
B. Delley, J. Chem. Phys. 92, 508 (1990).
B. Delley, J. Chem. Phys. 113, 7756 (2000).
DMol^3 is available as part of Materials Studio.
=====

```

DATE: Jan 18 12:39:23 2008

Basis set is read from file:  
 C:\PROGRA~1\Accelrys\MSMODE~1.0\DMol3\..\Data\Resources\Quantum\DMol3\BASFILE\_v400

Message: License checkout of MS\_dmol successful  
 Message: Number of licenses checked out 1

Geometry is read from file: OH-.car

INCOOR, atomic coordinates in au (for archive):  
 \_\_\_\_\_>8

```

$coordinates
H      -2.35837773705952    1.29438471002747    0.00024574941618
O      -4.45574038274650    1.32565515491389   -0.00048979996871
$end
_____>8

```

N\_atoms = 2 N\_atom\_types = 2

INPUT\_DMOL keywords (for archive):  
 \_\_\_\_\_>8

```

# Task parameters
Calculate optimize <--
Opt_energy_convergence 1.0000e-005 <--
Opt_gradient_convergence 2.0000e-003 A <--
Opt_displacement_convergence 5.0000e-003 A <--
Opt_iterations 50 <--
Opt_max_displacement 0.3000 A <--

```

```

Symmetry                on                                <--
Basis_Version    v4.0.0                                <--
# Electronic parameters                                <--
Spin_polarization    unrestricted                       <--
Charge                -1                               <--
Basis                 dnp                              <--
Pseudopotential      none                             <--
Functional            vwn-bp                          <--
Aux_density           octupole                        <--
Integration_grid     fine                            <--
Occupation            fermi                           <--
Cutoff_Global        3.3000 angstrom                  <--
Scf_density_convergence    1.0000e-006                <--
Scf_charge_mixing     0.2000                          <--
Scf_spin_mixing       0.5000                          <--
Scf_iterations        50                               <--
Scf_diis              6 pulay                         <--
# Print options                                           <--
Print                 eigval_last_it                  <--
# Calculated properties                                     <--

```

---

>8

```

Density functional:
  Becke 1988 exchange
    gradient corrected exchange potential used in SCF
  P91_gradients for COSMO run
    gradient corrected correlation potential used in SCF
  VWN local correlation (p91-pwc)

```

Calculation is spin\_unrestricted

```

Molecule has been put into center of mass coordinate system
Molecule has been rotated to standard orientation

```

Symmetry group of the molecule: c\*v

```

** GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES **
  Searching for a Minimum
  Optimization Cycle:  0

```

-----  
Input Coordinates (Angstroms)  
-----

	ATOM	X	Y	Z
1	H	0.000000	0.000000	0.555000
2	O	0.000000	0.000000	-0.555000

---

Message: Generating delocalized internals

Total number of primitive bonds: 1  
 Total number of primitive angles: 0  
 Total number of primitive dihedrals: 0

Total number of primitive internals: 1

Message: Generation of delocalized internals is successful

Specifications for basis set selection:

Hydrogen nbas= 1, z= 1, nrfn= 5, rcut= 6.24, e\_ref= -0.043556 Ha  
 n=1 L=0 occ= 1.00 e= -0.227151Ha -6.1811eV  
 n=1 L=0 occ= 0.00 e= -0.844683Ha -22.9850eV  
 n=2 L=1 occ= 0.00 e= -0.144025Ha -3.9191eV  
 n=2 L=1 occ= 0.00 e= -1.999949Ha -54.4214eV eliminated  
 n=1 L=0 occ= 0.00 e= -8.000000Ha -217.6912eV eliminated  
 Oxygen nbas= 2, z= 8, nrfn= 10, rcut= 6.24, e\_ref= -0.059893 Ha  
 n=1 L=0 occ= 2.00 e= -18.900536Ha -514.3100eV  
 n=2 L=0 occ= 2.00 e= -0.870453Ha -23.6862eV  
 n=2 L=1 occ= 4.00 e= -0.323270Ha -8.7966eV  
 n=2 L=0 occ= 0.00 e= -2.144910Ha -58.3660eV  
 n=2 L=1 occ= 0.00 e= -1.591974Ha -43.3198eV  
 n=3 L=2 occ= 0.00 e= -1.385418Ha -37.6992eV  
 n=2 L=1 occ= 0.00 e= -3.124998Ha -85.0356eV eliminated  
 n=1 L=0 occ= 0.00 e= -12.500000Ha -340.1425eV eliminated  
 n=3 L=2 occ= 0.00 e= -2.722144Ha -74.0733eV eliminated  
 n=2 L=1 occ= 0.00 e= -6.125000Ha -166.6698eV eliminated

Point group symmetry c4v symmetry orbital prototypes generated (SYMDEC)

Symmetry orbitals

n	norb	representation
1	9	A1.1
2	1	B1.1
3	1	B2.1
4	4	E.1
5	4	E.2

total number of valence orbitals: 19

molecule charge= -1.0 active electron number= 10.0

including core= 10.0 (without charge= 9.0)  
 Integration points and checksum: 1474 9.000013 51  
 extra disk use on option Direct\_scf off= 2.8Mbytes

-----  
 Memory Stack Information  
 -----

	Number of elements	Mbytes
integer arrays	13488	0.1
real arrays	855842	6.5
total	869330	6.5

-----

Default spin density on atom H( 1), L= 0 was used on start: M\_s= 0.5

+++ Entering Optimization Section +++  
 Message: Entering optimization section

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
 Message: Start SCF iterations

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -76.0711152  | -0.4928304     | 0.27E+00    | 0.020    | 1    |
| Ef | -75.9051319  | -0.3268471     | 0.13E+00    | 0.021    | 2    |
| Ef | -75.8416573  | -0.2633725     | 0.99E-01    | 0.022    | 3    |
| Ef | -75.7972479  | -0.2189632     | 0.46E-01    | 0.024    | 4    |
| Ef | -75.7887219  | -0.2104372     | 0.14E-01    | 0.026    | 5    |
| Ef | -75.7891306  | -0.2108459     | 0.19E-01    | 0.027    | 6    |
| Ef | -75.7887333  | -0.2104486     | 0.39E-02    | 0.029    | 7    |
| Ef | -75.7887899  | -0.2105052     | 0.17E-02    | 0.030    | 8    |
| Ef | -75.7888372  | -0.2105525     | 0.85E-03    | 0.032    | 9    |
| Ef | -75.7888300  | -0.2105453     | 0.49E-03    | 0.033    | 10   |
| Ef | -75.7888278  | -0.2105431     | 0.32E-03    | 0.035    | 11   |
| Ef | -75.7888264  | -0.2105417     | 0.15E-03    | 0.036    | 12   |
| Ef | -75.7888267  | -0.2105420     | 0.39E-04    | 0.038    | 13   |
| Ef | -75.7888268  | -0.2105421     | 0.25E-04    | 0.039    | 14   |
| Ef | -75.7888279  | -0.2105432     | 0.99E-05    | 0.041    | 15   |
| Ef | -75.7888279  | -0.2105432     | 0.39E-05    | 0.043    | 16   |
| Ef | -75.7888283  | -0.2105436     | 0.21E-05    | 0.044    | 17   |
| Ef | -75.7888282  | -0.2105435     | 0.77E-06    | 0.046    | 18   |

Message: SCF converged

Energy of Highest Occupied Molecular orbital 0.14800Ha 4.027ev  
HOMO is orbital number 10  
LUMO is orbital number 11

| state |   |   | eigenvalue |            | occupation |       |
|-------|---|---|------------|------------|------------|-------|
|       |   |   | (au)       | (ev)       |            |       |
| 1     | - | 1 | A1.1       | -18.368384 | -499.829   | 1.000 |
| 2     | + | 1 | A1.1       | -18.368384 | -499.829   | 1.000 |
| 3     | - | 2 | A1.1       | -0.427141  | -11.623    | 1.000 |
| 4     | + | 2 | A1.1       | -0.427141  | -11.623    | 1.000 |
| 5     | - | 3 | A1.1       | 0.009152   | 0.249      | 1.000 |
| 6     | + | 3 | A1.1       | 0.009152   | 0.249      | 1.000 |
| 7     | - | 1 | E.1        | 0.147997   | 4.027      | 1.000 |
| 8     | - | 1 | E.2        | 0.147997   | 4.027      | 1.000 |
| 9     | + | 1 | E.1        | 0.147998   | 4.027      | 1.000 |
| 10    | + | 1 | E.2        | 0.147998   | 4.027      | 1.000 |
| 11    | + | 4 | A1.1       | 0.313347   | 8.527      | 0.000 |
| 12    | - | 4 | A1.1       | 0.313347   | 8.527      | 0.000 |
| 13    | + | 2 | E.1        | 0.529271   | 14.402     | 0.000 |
| 14    | + | 2 | E.2        | 0.529271   | 14.402     | 0.000 |
| 15    | - | 2 | E.1        | 0.529271   | 14.402     | 0.000 |
| 16    | - | 2 | E.2        | 0.529271   | 14.402     | 0.000 |
| 17    | + | 5 | A1.1       | 0.645187   | 17.556     | 0.000 |
| 19    | + | 6 | A1.1       | 0.851709   | 23.176     | 0.000 |
| 22    | + | 7 | A1.1       | 1.008223   | 27.435     | 0.000 |
| 25    | + | 3 | E.1        | 1.024287   | 27.872     | 0.000 |
| 26    | + | 3 | E.2        | 1.024287   | 27.872     | 0.000 |
| 27    | + | 1 | B2.1       | 1.182071   | 32.166     | 0.000 |
| 28    | - | 1 | B2.1       | 1.182071   | 32.166     | 0.000 |
| 29    | + | 1 | B1.1       | 1.182072   | 32.166     | 0.000 |
| 30    | - | 1 | B1.1       | 1.182072   | 32.166     | 0.000 |

Orbital occupation is:

|   |                  |   |             |
|---|------------------|---|-------------|
| 3 | A1( 1) alpha and | 3 | A1( 1) beta |
| 0 | B1( 1) alpha and | 0 | B1( 1) beta |
| 0 | B2( 1) alpha and | 0 | B2( 1) beta |
| 1 | E( 2) alpha and  | 1 | E( 2) beta  |

Total number electrons: 10.0

| df |   | ATOMIC COORDINATES (au) |          |          | DERIVATIVES (au) |          |          |
|----|---|-------------------------|----------|----------|------------------|----------|----------|
| df | x | y                       | z        | x        | y                | z        |          |
| df | H | 0.000000                | 0.000000 | 1.048798 | 0.000000         | 0.000000 | 0.070834 |



df o 0.000000 0.000000 -1.048798 0.000000 0.000000 -0.070834

-----  
Total E (au) Binding E (au) Convergence Time (m) Iter  
-----  
Ef -75.7888282 -0.2105435 0.77E-06 0.047 19  
binding energy -0.210544Ha -5.72918ev -132.121kcal/mol -552.793kJ/mol  
-----

~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*  
Searching for a Minimum  
Optimization cycle: 1

Input Coordinates (Angstroms)  
-----  
ATOM X Y Z  
1 H 0.000000 0.000000 0.555000  
2 O 0.000000 0.000000 -0.555000  
-----

Startup Hessian in Internal Coordinates

The size of active space is : 1  
There are : 1 degrees of freedom  
There are : 1 primitive internals

opt== Cycle Total Energy Energy change Max Gradient Max Displacement  
opt== tolerance:..... 0.0000100 0.001058 0.009449  
opt== 1 -75.7888282 0.0000000 0.070834 0.069467

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
Integration points and checksum: 1474 9.000013 51  
Message: Start SCF iterations

-----  
Total E (au) Binding E (au) Convergence Time (m) Iter  
-----  
Ef -75.7976493 -0.2193646 0.34E-01 0.049 1  
Ef -75.7967060 -0.2184212 0.14E-01 0.051 2  
Ef -75.7966083 -0.2183236 0.70E-02 0.052 3

|    |             |            |          |       |   |
|----|-------------|------------|----------|-------|---|
| Ef | -75.7965874 | -0.2183027 | 0.83E-03 | 0.053 | 4 |
| Ef | -75.7965884 | -0.2183036 | 0.43E-03 | 0.055 | 5 |
| Ef | -75.7965874 | -0.2183026 | 0.73E-04 | 0.057 | 6 |
| Ef | -75.7965872 | -0.2183024 | 0.75E-05 | 0.058 | 7 |
| Ef | -75.7965871 | -0.2183024 | 0.56E-05 | 0.059 | 8 |
| Ef | -75.7965871 | -0.2183024 | 0.58E-06 | 0.061 | 9 |

Message: SCF converged

Energy of Highest Occupied Molecular Orbital 0.148775Ha 4.048ev  
HOMO is orbital number 10  
LUMO is orbital number 11

| state |   |   |      | eigenvalue |          | occupation |
|-------|---|---|------|------------|----------|------------|
|       |   |   |      | (au)       | (ev)     |            |
| 1     | - | 1 | A1.1 | -18.357975 | -499.546 | 1.000      |
| 2     | + | 1 | A1.1 | -18.357975 | -499.546 | 1.000      |
| 3     | - | 2 | A1.1 | -0.438527  | -11.933  | 1.000      |
| 4     | + | 2 | A1.1 | -0.438527  | -11.933  | 1.000      |
| 5     | - | 3 | A1.1 | 0.008026   | 0.218    | 1.000      |
| 6     | + | 3 | A1.1 | 0.008026   | 0.218    | 1.000      |
| 7     | - | 1 | E.1  | 0.148775   | 4.048    | 1.000      |
| 8     | - | 1 | E.2  | 0.148775   | 4.048    | 1.000      |
| 9     | + | 1 | E.1  | 0.148775   | 4.048    | 1.000      |
| 10    | + | 1 | E.2  | 0.148775   | 4.048    | 1.000      |
| 11    | + | 4 | A1.1 | 0.332504   | 9.048    | 0.000      |
| 12    | - | 4 | A1.1 | 0.332504   | 9.048    | 0.000      |
| 13    | + | 2 | E.1  | 0.538296   | 14.648   | 0.000      |
| 14    | + | 2 | E.2  | 0.538296   | 14.648   | 0.000      |
| 15    | - | 2 | E.1  | 0.538296   | 14.648   | 0.000      |
| 16    | - | 2 | E.2  | 0.538296   | 14.648   | 0.000      |
| 17    | + | 5 | A1.1 | 0.645072   | 17.553   | 0.000      |
| 20    | + | 6 | A1.1 | 0.889118   | 24.194   | 0.000      |
| 22    | + | 7 | A1.1 | 1.027773   | 27.967   | 0.000      |
| 25    | + | 3 | E.1  | 1.029923   | 28.026   | 0.000      |
| 26    | + | 3 | E.2  | 1.029923   | 28.026   | 0.000      |
| 27    | + | 1 | B2.1 | 1.182239   | 32.170   | 0.000      |
| 28    | - | 1 | B2.1 | 1.182239   | 32.170   | 0.000      |
| 29    | + | 1 | B1.1 | 1.182239   | 32.170   | 0.000      |
| 30    | - | 1 | B1.1 | 1.182239   | 32.170   | 0.000      |

Orbital occupation is:

|   |                  |   |             |
|---|------------------|---|-------------|
| 3 | A1( 1) alpha and | 3 | A1( 1) beta |
| 0 | B1( 1) alpha and | 0 | B1( 1) beta |
| 0 | B2( 1) alpha and | 0 | B2( 1) beta |
| 1 | E( 2) alpha and  | 1 | E( 2) beta  |

Total number electrons: 10.0

| df |   | ATOMIC COORDINATES (au) |          |           | DERIVATIVES (au) |          |           |
|----|---|-------------------------|----------|-----------|------------------|----------|-----------|
| df |   | x                       | y        | z         | x                | y        | z         |
| df | H | 0.000000                | 0.000000 | 0.979331  | 0.000000         | 0.000000 | 0.037098  |
| df | O | 0.000000                | 0.000000 | -0.979331 | 0.000000         | 0.000000 | -0.037098 |

|                | Total E (au) | Binding E (au) | Convergence      | Time (m)       | Iter |
|----------------|--------------|----------------|------------------|----------------|------|
| Ef             | -75.7965871  | -0.2183024     | 0.58E-06         | 0.062          | 10   |
| binding energy | -0.218302Ha  | -5.94031ev     | -136.990kcal/mol | -573.164kJ/mol |      |

~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*

Searching for a Minimum

Optimization Cycle: 2

Input Coordinates (Angstroms)

|   | ATOM | X        | Y        | Z         |
|---|------|----------|----------|-----------|
| 1 | H    | 0.000000 | 0.000000 | 0.518240  |
| 2 | O    | 0.000000 | 0.000000 | -0.518240 |

| opt== | Cycle | Total Energy | Energy change | Max Gradient | Max Displacement |
|-------|-------|--------------|---------------|--------------|------------------|
|       | 2     | -75.7965871  | -0.0077589    | 0.037098     | 0.074684         |

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
Integration points and checksum: 1474 9.000013 51  
Message: Start SCF iterations

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -75.7993005  | -0.2210158     | 0.40E-01    | 0.064    | 1    |
| Ef | -75.7980629  | -0.2197782     | 0.17E-01    | 0.066    | 2    |
| Ef | -75.7978972  | -0.2196125     | 0.82E-02    | 0.067    | 3    |
| Ef | -75.7978672  | -0.2195825     | 0.99E-03    | 0.069    | 4    |
| Ef | -75.7978683  | -0.2195836     | 0.57E-03    | 0.071    | 5    |

|    |             |            |          |       |    |
|----|-------------|------------|----------|-------|----|
| Ef | -75.7978673 | -0.2195826 | 0.76E-04 | 0.072 | 6  |
| Ef | -75.7978671 | -0.2195823 | 0.77E-05 | 0.074 | 7  |
| Ef | -75.7978671 | -0.2195823 | 0.49E-05 | 0.076 | 8  |
| Ef | -75.7978671 | -0.2195823 | 0.11E-05 | 0.077 | 9  |
| Ef | -75.7978671 | -0.2195823 | 0.82E-06 | 0.078 | 10 |

Message: SCF converged

Energy of Highest Occupied Molecular Orbital 0.14899Ha 4.054ev  
HOMO is orbital number 10  
LUMO is orbital number 11

| state |   |   | eigenvalue |            | occupation |       |
|-------|---|---|------------|------------|------------|-------|
|       |   |   | (au)       | (ev)       |            |       |
| 1     | - | 1 | A1.1       | -18.345851 | -499.216   | 1.000 |
| 2     | + | 1 | A1.1       | -18.345851 | -499.216   | 1.000 |
| 3     | - | 2 | A1.1       | -0.455043  | -12.382    | 1.000 |
| 4     | + | 2 | A1.1       | -0.455043  | -12.382    | 1.000 |
| 5     | - | 3 | A1.1       | 0.006917   | 0.188      | 1.000 |
| 6     | + | 3 | A1.1       | 0.006917   | 0.188      | 1.000 |
| 7     | - | 1 | E.1        | 0.148995   | 4.054      | 1.000 |
| 8     | - | 1 | E.2        | 0.148995   | 4.054      | 1.000 |
| 9     | + | 1 | E.1        | 0.148995   | 4.054      | 1.000 |
| 10    | + | 1 | E.2        | 0.148995   | 4.054      | 1.000 |
| 11    | + | 4 | A1.1       | 0.351429   | 9.563      | 0.000 |
| 12    | - | 4 | A1.1       | 0.351429   | 9.563      | 0.000 |
| 13    | + | 2 | E.1        | 0.547974   | 14.911     | 0.000 |
| 14    | + | 2 | E.2        | 0.547974   | 14.911     | 0.000 |
| 15    | - | 2 | E.1        | 0.547974   | 14.911     | 0.000 |
| 16    | - | 2 | E.2        | 0.547974   | 14.911     | 0.000 |
| 17    | + | 5 | A1.1       | 0.646992   | 17.606     | 0.000 |
| 19    | + | 6 | A1.1       | 0.922858   | 25.112     | 0.000 |
| 23    | + | 3 | E.1        | 1.035729   | 28.184     | 0.000 |
| 24    | + | 3 | E.2        | 1.035729   | 28.184     | 0.000 |
| 26    | + | 7 | A1.1       | 1.069920   | 29.114     | 0.000 |
| 27    | + | 1 | B2.1       | 1.182067   | 32.166     | 0.000 |
| 28    | - | 1 | B2.1       | 1.182067   | 32.166     | 0.000 |
| 29    | + | 1 | B1.1       | 1.182067   | 32.166     | 0.000 |
| 30    | - | 1 | B1.1       | 1.182067   | 32.166     | 0.000 |

Orbital occupation is:

|                         |                  |      |             |
|-------------------------|------------------|------|-------------|
| 3                       | A1( 1) alpha and | 3    | A1( 1) beta |
| 0                       | B1( 1) alpha and | 0    | B1( 1) beta |
| 0                       | B2( 1) alpha and | 0    | B2( 1) beta |
| 1                       | E( 2) alpha and  | 1    | E( 2) beta  |
| Total number electrons: |                  | 10.0 |             |

| df | df | ATOMIC COORDINATES (au) |          |           | DERIVATIVES (au) |          |           |
|----|----|-------------------------|----------|-----------|------------------|----------|-----------|
|    |    | x                       | y        | z         | x                | y        | z         |
| df | H  | 0.000000                | 0.000000 | 0.904647  | 0.000000         | 0.000000 | -0.026844 |
| df | O  | 0.000000                | 0.000000 | -0.904647 | 0.000000         | 0.000000 | 0.026844  |

|                | Total E (au) | Binding E (au) | Convergence      | Time (m)       | Iter |
|----------------|--------------|----------------|------------------|----------------|------|
| Ef             | -75.7978671  | -0.2195823     | 0.82E-06         | 0.079          | 11   |
| binding energy | -0.219582Ha  | -5.97514ev     | -137.793kcal/mol | -576.525kJ/mol |      |

~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*  
 Searching for a Minimum  
 Optimization cycle: 3

| Input Coordinates (Angstroms) |      |          |          |           |
|-------------------------------|------|----------|----------|-----------|
|                               | ATOM | X        | Y        | Z         |
| 1                             | H    | 0.000000 | 0.000000 | 0.478719  |
| 2                             | O    | 0.000000 | 0.000000 | -0.478719 |

| opt== | Cycle | Total Energy | Energy change | Max Gradient | Max Displacement |
|-------|-------|--------------|---------------|--------------|------------------|
|       | 3     | -75.7978671  | -0.0012799    | 0.026844     | 0.031231         |

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
 Integration points and checksum: 1474 9.000012 51  
 Message: Start SCF iterations

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -75.7988304  | -0.2205457     | 0.18E-01    | 0.081    | 1    |
| Ef | -75.7985523  | -0.2202676     | 0.70E-02    | 0.082    | 2    |
| Ef | -75.7985121  | -0.2202274     | 0.34E-02    | 0.084    | 3    |
| Ef | -75.7985102  | -0.2202255     | 0.41E-03    | 0.086    | 4    |
| Ef | -75.7985100  | -0.2202252     | 0.13E-03    | 0.087    | 5    |
| Ef | -75.7985097  | -0.2202250     | 0.31E-04    | 0.089    | 6    |

```

Ef      -75.7985098      -0.2202251      0.29E-05      0.090      7
Ef      -75.7985098      -0.2202251      0.22E-05      0.092      8
Ef      -75.7985098      -0.2202251      0.16E-06      0.093      9

```

Message: SCF converged

```

Energy of Highest Occupied Molecular orbital  0.14898Ha  4.054ev
HOMO is orbital number 10
LUMO is orbital number 11

```

| state |   |   |      | eigenvalue |          | occupation |
|-------|---|---|------|------------|----------|------------|
|       |   |   |      | (au)       | (ev)     |            |
| 1     | + | 1 | A1.1 | -18.351035 | -499.357 | 1.000      |
| 2     | - | 1 | A1.1 | -18.351035 | -499.357 | 1.000      |
| 3     | + | 2 | A1.1 | -0.447565  | -12.179  | 1.000      |
| 4     | - | 2 | A1.1 | -0.447565  | -12.179  | 1.000      |
| 5     | - | 3 | A1.1 | 0.007371   | 0.201    | 1.000      |
| 6     | + | 3 | A1.1 | 0.007371   | 0.201    | 1.000      |
| 7     | + | 1 | E.1  | 0.148977   | 4.054    | 1.000      |
| 8     | + | 1 | E.2  | 0.148977   | 4.054    | 1.000      |
| 9     | - | 1 | E.1  | 0.148977   | 4.054    | 1.000      |
| 10    | - | 1 | E.2  | 0.148977   | 4.054    | 1.000      |
| 11    | + | 4 | A1.1 | 0.343782   | 9.355    | 0.000      |
| 12    | - | 4 | A1.1 | 0.343782   | 9.355    | 0.000      |
| 13    | + | 2 | E.1  | 0.543963   | 14.802   | 0.000      |
| 14    | + | 2 | E.2  | 0.543963   | 14.802   | 0.000      |
| 15    | - | 2 | E.1  | 0.543963   | 14.802   | 0.000      |
| 16    | - | 2 | E.2  | 0.543963   | 14.802   | 0.000      |
| 17    | + | 5 | A1.1 | 0.645846   | 17.574   | 0.000      |
| 20    | + | 6 | A1.1 | 0.910486   | 24.776   | 0.000      |
| 21    | + | 3 | E.1  | 1.033339   | 28.119   | 0.000      |
| 22    | + | 3 | E.2  | 1.033339   | 28.119   | 0.000      |
| 26    | + | 7 | A1.1 | 1.048906   | 28.542   | 0.000      |
| 27    | + | 1 | B2.1 | 1.182176   | 32.169   | 0.000      |
| 28    | - | 1 | B2.1 | 1.182176   | 32.169   | 0.000      |
| 29    | + | 1 | B1.1 | 1.182177   | 32.169   | 0.000      |
| 30    | - | 1 | B1.1 | 1.182177   | 32.169   | 0.000      |

Orbital occupation is:

```

3  A1( 1) alpha and 3  A1( 1) beta
0  B1( 1) alpha and 0  B1( 1) beta
0  B2( 1) alpha and 0  B2( 1) beta
1  E( 2) alpha and 1  E( 2) beta
Total number electrons: 10.0

```

df                    ATOMIC    COORDINATES (au)                    DERIVATIVES (au)

| df |   | x        | y        | z         | x        | y        | z         |
|----|---|----------|----------|-----------|----------|----------|-----------|
| df | H | 0.000000 | 0.000000 | 0.935879  | 0.000000 | 0.000000 | 0.004432  |
| df | O | 0.000000 | 0.000000 | -0.935879 | 0.000000 | 0.000000 | -0.004432 |

|                | Total E (au) | Binding E (au) | Convergence      | Time (m)       | Iter |
|----------------|--------------|----------------|------------------|----------------|------|
| Ef             | -75.7985098  | -0.2202251     | 0.16E-06         | 0.094          | 10   |
| binding energy | -0.220225Ha  | -5.99263ev     | -138.196kcal/mol | -578.212kJ/mol |      |

~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*  
 Searching for a Minimum  
 Optimization Cycle: 4

Input Coordinates (Angstroms)

|   | ATOM | X        | Y        | Z         |
|---|------|----------|----------|-----------|
| 1 | H    | 0.000000 | 0.000000 | 0.495246  |
| 2 | O    | 0.000000 | 0.000000 | -0.495246 |

| opt== | Cycle | Total Energy | Energy change | Max Gradient | Max Displacement |
|-------|-------|--------------|---------------|--------------|------------------|
|       | 4     | -75.7985098  | -0.0006427    | 0.004432     | 0.004425         |

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
 Integration points and checksum: 1474 9.000012 51  
 Message: Start SCF iterations

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -75.7985363  | -0.2202516     | 0.24E-02    | 0.097    | 1    |
| Ef | -75.7985343  | -0.2202495     | 0.99E-03    | 0.098    | 2    |
| Ef | -75.7985349  | -0.2202502     | 0.48E-03    | 0.099    | 3    |
| Ef | -75.7985345  | -0.2202498     | 0.56E-04    | 0.100    | 4    |
| Ef | -75.7985346  | -0.2202499     | 0.61E-05    | 0.102    | 5    |
| Ef | -75.7985346  | -0.2202499     | 0.45E-05    | 0.103    | 6    |
| Ef | -75.7985346  | -0.2202499     | 0.40E-06    | 0.104    | 7    |

Message: SCF converged

Energy of Highest Occupied Molecular Orbital 0.14899Ha 4.054ev  
 HOMO is orbital number 10  
 LUMO is orbital number 11

| state |   |   |      | eigenvalue |          | occupation |
|-------|---|---|------|------------|----------|------------|
|       |   |   |      | (au)       | (ev)     |            |
| 1     | - | 1 | A1.1 | -18.350310 | -499.338 | 1.000      |
| 2     | + | 1 | A1.1 | -18.350310 | -499.338 | 1.000      |
| 3     | + | 2 | A1.1 | -0.448574  | -12.206  | 1.000      |
| 4     | - | 2 | A1.1 | -0.448574  | -12.206  | 1.000      |
| 5     | - | 3 | A1.1 | 0.007306   | 0.199    | 1.000      |
| 6     | + | 3 | A1.1 | 0.007306   | 0.199    | 1.000      |
| 7     | - | 1 | E.1  | 0.148986   | 4.054    | 1.000      |
| 8     | + | 1 | E.1  | 0.148986   | 4.054    | 1.000      |
| 9     | - | 1 | E.2  | 0.148986   | 4.054    | 1.000      |
| 10    | + | 1 | E.2  | 0.148986   | 4.054    | 1.000      |
| 11    | - | 4 | A1.1 | 0.344892   | 9.385    | 0.000      |
| 12    | + | 4 | A1.1 | 0.344892   | 9.385    | 0.000      |
| 13    | - | 2 | E.1  | 0.544536   | 14.818   | 0.000      |
| 14    | - | 2 | E.2  | 0.544536   | 14.818   | 0.000      |
| 15    | + | 2 | E.1  | 0.544536   | 14.818   | 0.000      |
| 16    | + | 2 | E.2  | 0.544536   | 14.818   | 0.000      |
| 17    | + | 5 | A1.1 | 0.645975   | 17.578   | 0.000      |
| 20    | + | 6 | A1.1 | 0.912415   | 24.828   | 0.000      |
| 23    | + | 3 | E.1  | 1.033681   | 28.128   | 0.000      |
| 24    | + | 3 | E.2  | 1.033681   | 28.128   | 0.000      |
| 26    | + | 7 | A1.1 | 1.051573   | 28.615   | 0.000      |
| 27    | + | 1 | B2.1 | 1.182164   | 32.168   | 0.000      |
| 28    | - | 1 | B2.1 | 1.182164   | 32.168   | 0.000      |
| 29    | + | 1 | B1.1 | 1.182164   | 32.168   | 0.000      |
| 30    | - | 1 | B1.1 | 1.182164   | 32.168   | 0.000      |

Orbital occupation is:

|   |                  |   |             |
|---|------------------|---|-------------|
| 3 | A1( 1) alpha and | 3 | A1( 1) beta |
| 0 | B1( 1) alpha and | 0 | B1( 1) beta |
| 0 | B2( 1) alpha and | 0 | B2( 1) beta |
| 1 | E( 2) alpha and  | 1 | E( 2) beta  |

Total number electrons: 10.0

| df |   | ATOMIC COORDINATES (au) |          |           | DERIVATIVES (au) |          |           |
|----|---|-------------------------|----------|-----------|------------------|----------|-----------|
| df |   | x                       | y        | z         | x                | y        | z         |
| df | H | 0.000000                | 0.000000 | 0.931453  | 0.000000         | 0.000000 | 0.000415  |
| df | O | 0.000000                | 0.000000 | -0.931453 | 0.000000         | 0.000000 | -0.000415 |



```

-----
Total E (au)      Binding E (au)      Convergence      Time (m)      Iter
-----
Ef      -75.7985346      -0.2202499      0.40E-06      0.106      8
binding energy -0.220250Ha      -5.99331ev      -138.212kcal/mol      -578.277kJ/mol
-----

```

~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*

Searching for a Minimum

Optimization Cycle: 5

```

-----
Input Coordinates (Angstroms)
-----
ATOM      X      Y      Z
1  H      0.000000      0.000000      0.492904
2  O      0.000000      0.000000      -0.492904
-----

```

```

opt==  Cycle      Total Energy      Energy change      Max Gradient      Max Displacement
5      -75.7985346      -0.0000248      0.000415      0.000458

```

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

```

-----
Integration points and checksum:      1474      9.000012      51
Message: Start SCF iterations

```

```

-----
Total E (au)      Binding E (au)      Convergence      Time (m)      Iter
-----
Ef      -75.7985348      -0.2202500      0.25E-03      0.108      1
Ef      -75.7985350      -0.2202503      0.10E-03      0.109      2
Ef      -75.7985351      -0.2202504      0.50E-04      0.111      3
Ef      -75.7985351      -0.2202504      0.58E-05      0.112      4
Ef      -75.7985351      -0.2202504      0.63E-06      0.113      5

```

Message: SCF converged

```

Energy of Highest Occupied Molecular Orbital      0.14899Ha      4.054ev
HOMO is orbital number      10
LUMO is orbital number      11

```

| state |   |   | eigenvalue |            | occupation |       |
|-------|---|---|------------|------------|------------|-------|
|       |   |   | (au)       | (ev)       |            |       |
| 1     | - | 1 | A1.1       | -18.350236 | -499.336   | 1.000 |
| 2     | + | 1 | A1.1       | -18.350236 | -499.336   | 1.000 |
| 3     | + | 2 | A1.1       | -0.448679  | -12.209    | 1.000 |
| 4     | - | 2 | A1.1       | -0.448679  | -12.209    | 1.000 |
| 5     | - | 3 | A1.1       | 0.007299   | 0.199      | 1.000 |
| 6     | + | 3 | A1.1       | 0.007299   | 0.199      | 1.000 |
| 7     | + | 1 | E.1        | 0.148987   | 4.054      | 1.000 |
| 8     | + | 1 | E.2        | 0.148987   | 4.054      | 1.000 |
| 9     | - | 1 | E.1        | 0.148987   | 4.054      | 1.000 |
| 10    | - | 1 | E.2        | 0.148987   | 4.054      | 1.000 |
| 11    | - | 4 | A1.1       | 0.345006   | 9.388      | 0.000 |
| 12    | + | 4 | A1.1       | 0.345006   | 9.388      | 0.000 |
| 13    | + | 2 | E.1        | 0.544596   | 14.819     | 0.000 |
| 14    | + | 2 | E.2        | 0.544596   | 14.819     | 0.000 |
| 15    | - | 2 | E.1        | 0.544596   | 14.819     | 0.000 |
| 16    | - | 2 | E.2        | 0.544596   | 14.819     | 0.000 |
| 17    | + | 5 | A1.1       | 0.645989   | 17.578     | 0.000 |
| 20    | + | 6 | A1.1       | 0.912611   | 24.833     | 0.000 |
| 21    | + | 3 | E.1        | 1.033716   | 28.129     | 0.000 |
| 23    | + | 3 | E.2        | 1.033716   | 28.129     | 0.000 |
| 26    | + | 7 | A1.1       | 1.051854   | 28.622     | 0.000 |
| 27    | + | 1 | B2.1       | 1.182162   | 32.168     | 0.000 |
| 28    | - | 1 | B2.1       | 1.182162   | 32.168     | 0.000 |
| 29    | + | 1 | B1.1       | 1.182163   | 32.168     | 0.000 |
| 30    | - | 1 | B1.1       | 1.182163   | 32.168     | 0.000 |

Orbital occupation is:

|   |                  |   |             |
|---|------------------|---|-------------|
| 3 | A1( 1) alpha and | 3 | A1( 1) beta |
| 0 | B1( 1) alpha and | 0 | B1( 1) beta |
| 0 | B2( 1) alpha and | 0 | B2( 1) beta |
| 1 | E( 2) alpha and  | 1 | E( 2) beta  |

Total number electrons: 10.0

| df |   | ATOMIC COORDINATES (au) |          |           | DERIVATIVES (au) |          |           |
|----|---|-------------------------|----------|-----------|------------------|----------|-----------|
| df |   | x                       | y        | z         | x                | y        | z         |
| df | H | 0.000000                | 0.000000 | 0.930996  | 0.000000         | 0.000000 | -0.000009 |
| df | O | 0.000000                | 0.000000 | -0.930996 | 0.000000         | 0.000000 | 0.000009  |

---

|              |                |             |          |      |
|--------------|----------------|-------------|----------|------|
| Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|--------------|----------------|-------------|----------|------|

---

Ef            -75.7985351            -0.2202504            0.63E-06            0.113            6  
binding energy -0.220250Ha    -5.99332eV    -138.212kcal/mol    -578.279kJ/mol

-----  
~~~~~ End Computing SCF Energy/Gradient ~~~~~

\*\* GEOMETRY OPTIMIZATION IN DELOCALIZED COORDINATES \*\*  
Searching for a Minimum  
Optimization Cycle: 6

| Input Coordinates (Angstroms) |      |          |          |           |
|-------------------------------|------|----------|----------|-----------|
|                               | ATOM | X        | Y        | Z         |
| 1                             | H    | 0.000000 | 0.000000 | 0.492662  |
| 2                             | O    | 0.000000 | 0.000000 | -0.492662 |

| opt== | Cycle | Total Energy | Energy change | Max Gradient | Max Displacement |
|-------|-------|--------------|---------------|--------------|------------------|
|       | 6     | -75.7985351  | -0.0000005    | 0.000009     | 0.000010         |

+++ Entering Properties Section +++  
Message: DMol3 job finished successfully  
time all done        0.11m        6.81s  
Message: License checkin of MS\_dmol successful

**Table 12: Accelrys MS Energy Calculation Task Output (OUTMOL file) for OH<sup>-</sup> electrolyte. The energy calculation task output calculates atomic coordinates, total energy, and molecular cavity dimensions. The energy calculation task runs simultaneously with the COSMO calculation for a condensed phase molecule.**

```

=====
Materials Studio DMol^3 version 4.0
compiled on Dec 19 2005 03:11:22
=====
Density Functional Theory Electronic Structure Program
Copyright (c) 2005, Accelrys Inc. All rights reserved.
Cite work using this program as:
B. Delley, J. Chem. Phys. 92, 508 (1990).
B. Delley, J. Chem. Phys. 113, 7756 (2000).
DMol^3 is available as part of Materials Studio.
=====

```

DATE: Jan 18 12:40:54 2008

Basis set is read from file:  
C:\PROGRA~1\Accelrys\MSMODE~1.0\DMol3\..\Data\Resources\Quantum\DMol3\BASFILE\_v400

Message: License checkout of MS\_dmol successful  
Message: Number of licenses checked out 1

Geometry is read from file: OH-.car

INCOOR, atomic coordinates in au (for archive):

```

----->8
$coordinates
H      -2.47615714673327    1.29614073223318    0.00020444378553
O      -4.33796097307275    1.32389913270818   -0.00044849433805
$end

```

N\_atoms = 2 N\_atom\_types = 2

INPUT\_DMOL keywords (for archive):

```

----->8

```

# Task parameters

Calculate energy  
Symmetry on

Basis\_Version v4.0.0

```

<--
<--
<--
<--
<--
<--
<--

```

```

# Environment Keywords <--
Cosmo on <--
Cosmo_Grid_Size 1082 <--
Cosmo_Segments 92 <--
Cosmo_Solvent_Radius 1.300000 <--
Cosmo_A-Matrix_Cutoff 7.000000 <--
Cosmo_Radius_Incr 0.000000 <--
Cosmo_A-Constant 1.882190 <--
Cosmo_B-Constant 0.010140 <--
Cosmo_RadCorr_Incr 0.150000 <--
Cosmo_Atomic_Radii <--
  1 1.300
  6 2.000
  7 1.830
  8 1.720
  9 1.720
 15 2.120
 16 2.160
 17 2.050
 35 2.160
 53 2.320
# Electronic parameters <--
Spin_polarization unrestricted <--
Charge -1 <--
Basis dnp <--
Pseudopotential none <--
Functional vwn-bp <--
Aux_density octupole <--
Integration_grid fine <--
Occupation fermi <--
Cutoff_Global 3.3000 angstrom <--
Scf_density_convergence 1.0000e-006 <--
Scf_charge_mixing 0.2000 <--
Scf_spin_mixing 0.5000 <--
Scf_iterations 50 <--
Scf_diis 6 pulay <--
# Print options <--
Print eigval_last_it <--
# Calculated properties <--

```

---

>8

```

Density functional:
  Becke 1988 exchange
  gradient corrected exchange potential used in SCF

```

P91\_gradients for COSMO run  
gradient corrected correlation potential used in SCF  
VWN local correlation (p91-pwc)

Warning: Current COSMO implementation can not use symmetry

Calculation is spin\_unrestricted

Molecule has been put into center of mass coordinate system  
Molecule has been rotated to standard orientation

Symmetry group of the molecule: c\*v  
Molecule has been snapped to exact symmetry

Specifications for basis set selection:

|          |       |      |      |    |              |     |       |       |             |              |
|----------|-------|------|------|----|--------------|-----|-------|-------|-------------|--------------|
| Hydrogen | nbas= | 1,   | z=   | 1, | nrfn=        | 5,  | rcut= | 6.24, | e_ref=      | -0.043556 Ha |
| n=1      | L=0   | occ= | 1.00 | e= | -0.227151Ha  |     |       |       | -6.1811ev   |              |
| n=1      | L=0   | occ= | 0.00 | e= | -0.844683Ha  |     |       |       | -22.9850ev  |              |
| n=2      | L=1   | occ= | 0.00 | e= | -0.144025Ha  |     |       |       | -3.9191ev   |              |
| n=2      | L=1   | occ= | 0.00 | e= | -1.999949Ha  |     |       |       | -54.4214ev  | eliminated   |
| n=1      | L=0   | occ= | 0.00 | e= | -8.000000Ha  |     |       |       | -217.6912ev | eliminated   |
| Oxygen   | nbas= | 2,   | z=   | 8, | nrfn=        | 10, | rcut= | 6.24, | e_ref=      | -0.059893 Ha |
| n=1      | L=0   | occ= | 2.00 | e= | -18.900536Ha |     |       |       | -514.3100ev |              |
| n=2      | L=0   | occ= | 2.00 | e= | -0.870453Ha  |     |       |       | -23.6862ev  |              |
| n=2      | L=1   | occ= | 4.00 | e= | -0.323270Ha  |     |       |       | -8.7966ev   |              |
| n=2      | L=0   | occ= | 0.00 | e= | -2.144910Ha  |     |       |       | -58.3660ev  |              |
| n=2      | L=1   | occ= | 0.00 | e= | -1.591974Ha  |     |       |       | -43.3198ev  |              |
| n=3      | L=2   | occ= | 0.00 | e= | -1.385418Ha  |     |       |       | -37.6992ev  |              |
| n=2      | L=1   | occ= | 0.00 | e= | -3.124998Ha  |     |       |       | -85.0356ev  | eliminated   |
| n=1      | L=0   | occ= | 0.00 | e= | -12.500000Ha |     |       |       | -340.1425ev | eliminated   |
| n=3      | L=2   | occ= | 0.00 | e= | -2.722144Ha  |     |       |       | -74.0733ev  | eliminated   |
| n=2      | L=1   | occ= | 0.00 | e= | -6.125000Ha  |     |       |       | -166.6698ev | eliminated   |

Symmetry orbitals

|   |      |                |
|---|------|----------------|
| n | norb | representation |
| 1 | 19   | a              |

total number of valence orbitals: 19

|                  |      |                         |      |
|------------------|------|-------------------------|------|
| molecule charge= | -1.0 | active electron number= | 10.0 |
| including core=  | 10.0 | (without charge=        | 9.0) |

Integration points and checksum: 8028 9.000012 302

extra disk use on option Direct\_scf off= 4.7Mbytes

Memory Stack Information

|                | Number of elements | Mbytes |
|----------------|--------------------|--------|
| integer arrays | 20096              | 0.1    |
| real arrays    | 927063             | 7.1    |
| total          | 947159             | 7.1    |

COSMO input

In this run the solvent is an ideal conductor

Dielectric Constant = infinity  
 Basic Grid Size = 1082  
 Number of Segments = 92  
 Solvent Radius = 1.30  
 A - Matrix Cutoff = 7.00  
 Radius Increment = 0.00  
 Radius Increase for Outlying Charge corr. = 0.15  
 Non-Electrostatic Energy = A+B\*area  
 A = 1.88219 B = 0.01014

van der waals radius

| atomic number | vdw  | vdw+raddc |
|---------------|------|-----------|
| 1             | 1.30 | 1.30      |
| 2             | 1.72 | 1.72      |

The program will read COSMO basic grid from file:

C:\PROGRA~1\Accelrys\MSMODE~1.0\DMol3\..\Data\Resources\Quantum\DMol3\COSGRID

nps(usual segment ) = 92  
 nps(hydrogen segment) = 32

Total number of COSMO charges: 113

Default spin density on atom H( 1), L= 0 was used on start: M\_s= 0.5

+++ Entering SCF Section +++  
 Message: Entering SCF section

~~~~~ Start Computing SCF Energy/Gradient ~~~~~

-----  
 Message: Start SCF iterations

|    | Total E (au) | Binding E (au) | Convergence | Time (m) | Iter |
|----|--------------|----------------|-------------|----------|------|
| Ef | -76.0960335  | -0.5177488     | 0.28E+00    | 0.034    | 1    |
| Ef | -75.9790382  | -0.4007534     | 0.13E+00    | 0.041    | 2    |
| Ef | -75.9503934  | -0.3721086     | 0.88E-01    | 0.048    | 3    |
| Ef | -75.9498952  | -0.3716105     | 0.42E-01    | 0.055    | 4    |
| Ef | -75.9462289  | -0.3679442     | 0.10E-01    | 0.062    | 5    |
| Ef | -75.9467726  | -0.3684879     | 0.15E-01    | 0.067    | 6    |
| Ef | -75.9465711  | -0.3682864     | 0.31E-02    | 0.073    | 7    |
| Ef | -75.9466545  | -0.3683698     | 0.29E-02    | 0.080    | 8    |
| Ef | -75.9466358  | -0.3683511     | 0.52E-03    | 0.085    | 9    |
| Ef | -75.9466380  | -0.3683533     | 0.32E-03    | 0.092    | 10   |
| Ef | -75.9466397  | -0.3683550     | 0.22E-03    | 0.099    | 11   |
| Ef | -75.9466393  | -0.3683545     | 0.13E-03    | 0.106    | 12   |
| Ef | -75.9466407  | -0.3683560     | 0.45E-04    | 0.113    | 13   |
| Ef | -75.9466410  | -0.3683562     | 0.17E-04    | 0.120    | 14   |
| Ef | -75.9466410  | -0.3683563     | 0.71E-05    | 0.128    | 15   |
| Ef | -75.9466410  | -0.3683563     | 0.53E-05    | 0.135    | 16   |
| Ef | -75.9466411  | -0.3683563     | 0.23E-05    | 0.142    | 17   |
| Ef | -75.9466410  | -0.3683563     | 0.11E-05    | 0.148    | 18   |
| Ef | -75.9466410  | -0.3683563     | 0.72E-06    | 0.155    | 19   |

Message: SCF converged

Energy of Highest Occupied Molecular Orbital -0.13576Ha -3.694ev  
HOMO is orbital number 10  
LUMO is orbital number 11

| state | eigenvalue |      | occupation                |
|-------|------------|------|---------------------------|
|       | (au)       | (ev) |                           |
| 1     | +          | 1 a  | -18.630011 -506.949 1.000 |
| 2     | -          | 1 a  | -18.630011 -506.949 1.000 |
| 3     | +          | 2 a  | -0.730265 -19.872 1.000   |
| 4     | -          | 2 a  | -0.730265 -19.872 1.000   |
| 5     | +          | 3 a  | -0.271194 -7.380 1.000    |
| 6     | -          | 3 a  | -0.271194 -7.380 1.000    |
| 7     | +          | 4 a  | -0.135798 -3.695 1.000    |
| 8     | -          | 4 a  | -0.135798 -3.695 1.000    |
| 9     | +          | 5 a  | -0.135756 -3.694 1.000    |
| 10    | -          | 5 a  | -0.135756 -3.694 1.000    |
| 11    | -          | 6 a  | 0.108141 2.943 0.000      |
| 12    | +          | 6 a  | 0.108141 2.943 0.000      |
| 14    | +          | 7 a  | 0.299221 8.142 0.000      |
| 16    | +          | 8 a  | 0.299304 8.144 0.000      |
| 18    | +          | 9 a  | 0.376641 10.249 0.000     |
| 20    | +          | 10 a | 0.639481 17.401 0.000     |



|    |   |    |   |          |        |       |
|----|---|----|---|----------|--------|-------|
| 21 | + | 11 | a | 0.747092 | 20.329 | 0.000 |
| 23 | + | 12 | a | 0.747107 | 20.330 | 0.000 |
| 25 | + | 13 | a | 0.787261 | 21.422 | 0.000 |
| 28 | + | 14 | a | 0.890438 | 24.230 | 0.000 |
| 30 | + | 15 | a | 0.890472 | 24.231 | 0.000 |

Orbital occupation is:  
 5 a (1) alpha and 5 a (1) beta  
 Total number electrons: 10.0

|                | Total E (au) | Binding E (au) | Convergence      | Time (m)       | Iter |
|----------------|--------------|----------------|------------------|----------------|------|
| Ef             | -75.9466410  | -0.3683563     | 0.53E-06         | 0.164          | 20   |
| binding energy | -0.368356Ha  | -10.02349ev    | -231.152kcal/mol | -967.139kJ/mol |      |

#### DMol3/COSMO Results

Total energy (au) [TE]  
 {including COSMO solvation energy, Eq.2} = -75.946641  
 Dielectric energy (au)  $\{1/2\langle q|U\rangle\}$  [DE] = -0.150041

Total energy corrected (au) [TE(corr)]  
 {TE(corr) = TE + DE(corr) - DE} = -75.953966  
 Dielectric energy corrected (au) [DE(corr)]  
 {DE(corr) =  $(q+q'')A(q+q'')$ } = -0.157365

{U is the potential on the inner cavity  
 it depends on the accurate density}

Sum of polarization charges {q} = 0.97476  
 Sum of polarization charges(corrected)  
 {q+q''} = 0.99925

Total surface area (Angstrom\*\*2) = 40.22658  
 Total volume of cavity (A\*\*3) = 23.51747

Nonelectrostatic Solvation Energy (kcal/mol) = 2.290088

Total energy (au) [TE]  
 + Non-Electrostatic Energy = -75.942993  
 Total energy corrected (au) [TE(corr)]  
 + Non-Electrostatic Energy = -75.950317

~~~~~ End Computing SCF Energy/Gradient ~~~~~