**Aspen Pxy/Txy Fitting Assignment**

The assignments set forth in this assignment have several objectives. The overlying objective is to deepen your understanding of how activity coefficients are used in Aspen and how to compare and regress within the Aspen program.

Before you start this assignment, review the tutorial provided on LON-CAPA about the Aspen TDE Engine. This will be a good reference to use during this exercise. For this problem, you will use the local composition methods. It is recommended to work this problem using the Aspen Properties User interface instead of the Aspen Plus user interface. The **Aspen Properties** interface loads only that part of code necessary for properties. Within Aspen **Plus** ver 10, you can switch between the flow sheet simulation and the properties using selector buttons on lower part of the left menu panel.

Below is a summary of the sections of this assignment and the learning objectives. As you work through the assignment, each section header will also provide a cross-reference to the section in the Aspen TDE tutorial pdf.

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| --- | --- |
| Homework Section | Objective |
| B | How to find activity parameter functions within Aspen and recognize how temperature dependent functions relate to the parameters from textbooks. |
| C | How to find experimental phase equilibria data and save data for regression. |
| D | Generating a phase diagram (T-xy or P-xy) using Aspen parameters and comparing with experimental data |
| E-G | Understanding how to perform a regression. While this part of the exercise is ‘contrived’ because we ask you to perform regression of a system that is already fitted, reproducing the steps helps you understand how the regressions are performed. |
| H | Using UNIFAC to estimate VLE and recognizing the limitations of the estimations. |
| I | Retrospective thoughts and feedback |

About saving: When you save a file, unless your case is complicated, consider saving only the backup format. The backup format (.bkp for Aspen, .aprbkp for Aspen Properties) are a small single file that is always upward compatible to newer Aspen versions. The composite or restart format files are not necessary to save unless your case was hard to converge (as in an Aspen Plus case with complicated recycle streams) where the order of your convergence makes a difference. The composite or restart format files can get very large because they keep a record of the sequence of your work, but such detail is usually unnecessary.

Save your file frequently. Aspen is a complex program, and it can crash. By saving your work frequently, you can avoid lost time recreating work from a crash.

To document your work, start a WORD document. As you work through the homework, copy/paste the header and insert the requested information for each section. Through each section, the required output is usually marked with an ‘>’. Comments are requested in some parts and are necessary for assignment of full credit. Note that you can copy most Aspen plots by right-clicking and selecting ‘Copy’. For other screenshots, use the windows snipping tool Start>Enter ’snipping tool’ in search.

1. **Selecting Your Compounds (Aspen tutorial pdf section 4.01-4.02)**

Start **Aspen Properties** (not Aspen Plus) using a template for ‘Chemicals with Metric Units’. The selection of ‘Chemicals’ will default to the NRTL-IG (ideal gas) method. Select compounds to create a pair from different columns. Select a pair with normal boiling points differing by more than 5 C. Boiling points (C) are in parenthesis.

|  |  |  |  |
| --- | --- | --- | --- |
| **Alcohols** | **Esters** | **Ketone** | **Alkanes** |
| Ethanol (78.4) | methyl acetate (57.1) | Acetone (56.1) | Hexane (69) |
| n-propanol (~97) | ethyl acetate (77.1) | methyl ethyl ketone (79.6) | Heptane (96.4) |
| 2-propanol (82.6) |  |  | Octane (~126) |
| n-butanol (117.7) |  |  |  |

Note that you can edit the Component ID in Aspen for your convenience by double clicking in the id column, though the number of characters is limited to about seven.

**B. (5 pt) Finding a VLE Data Set for Your Compounds (Aspen tutorial pdf section 4.04-4.07)**

Use the TDE engine to see if binary data are available for your compounds. Browse to select VLE data *where both x and y data are measured*. Plot the data (use the icons in the tool bar) to make sure the data set do not scatter. The x and y values should change smoothly and there should be sufficient data to perform a regression later.

* **Document:**
1. The binary component IDs and component names
2. The ID number for the data set
3. The citation for the data
4. The type of data set (Pxy or Txy) and the number of data.
5. Add a statement about why you selected this data set.

Save the data set to the data browser as explained in the TDE tutorial. Save the Aspen file.

1. **(5 pt) Recording Binary Interaction Parameters (Aspen tutorial pdf section 4.03)**

 Access the binary interaction parameter values NRTL-1 as in section 4.03 of the handout.

* **Record:**
1. **IMPORTANT-** indicate which component is i and which is j
2. The source of the parameters
3. The parameter values (you can copy/paste and add a header row)
4. Click – Regression information. Record how many data points were used.

Note: the acronyms VLE mean vapor-liquid data regression, LLE means liquid-liquid regression. The vapor phase fugacity method follows the dash: IG means ideal gas phase, RK, HOC mean vapor fugacity coefficients using the Redlich-Kwong EOS and Hayden-O’Connell models, respectively. LIT means the parameters were taken from the literature, but not tested.

> Click in the column for ‘Source’, select another set of parameters. Repeat the documentation for the second set of parameters. Based on the regression information, select a parameter set to use for your subsequent work, and document why you selected the set.

**D. (5 pt) Comparing Experimental Data with Aspen Model (Aspen tutorial pdf section 4.08-4.11)**

 Make a single plot that compares the model and the data.

If you have P-xy data, then overlay a calculated P-xy diagram at the same T. If you have T-xy, overlay the diagrams at the same pressure. The TDE handout sections 4.08-4.11 show more diagrams that are NOT required. Be careful with the x-axis component and the y-axis units before merging. There is no ‘undo’ for a merge. You are always merging ‘from’ the active plot ON TO another selected plot.

The y-axis should be properly merged. The data should be points only and the model should be a solid line without points. The TDE handout shows how to configure the plot.

> Right-click on the merged plot and select ‘Copy’. Paste toyour documentation file. Comment on the comparison of the data. Be critical in your comparison about regions that are good and not so good. A good fit will pass right through the data points or the data will scatter evenly about the line. Save the Aspen File.

Use a solid line for the model and points without lines for the data.

**E. (10 pt) Determining New Parameters Using Regression (Aspen tutorial pdf section 4.15 step 3-4)**

Aspen has generalized the parameters shown in the textbook to use temperature dependent *functions* with additional parameters. The next few parts will ask you to do a regression using fewer parameters. The form of the parameters in the literature is:

Gij=exp(-αijτij), where τij = Δgij/(RT)

The ASPEN equation format is:

Gij=exp(-αijτij), where τij = Aij + Bij/T, and αij = Cij

Within the parameter tables, Aij is NRTL/1 (NRTL parameter 1), Bij is NRTL/2, Cij is NRTL/3. For a complete list of parameters, use F1 to open help and then use the INDEX tab and search for 'NRTL' and select 'property model'. Below is a summary from Aspen documentation:



1. We will perform a regression using only the parameters *Bij* and *Bji*. Go back to the parameter folder, and set the parameters for *Aij* and *Aji* to zero. *This is important* because we will only use *Bij* and *Bji* in your regression. *Aspen will ‘pull’ values from the selected parameter set during a regression if they are not specified in the regression input form.* If your case already has *Aij* and *Aji* of zero, change the value of *Cij*­ a small amount. The normal range of *Cij* is 0.2-0.5, with a default value of 0.3. You will not adjust *Cij* further.
2. Create a Regression as in the tutorial handout section 4.15 (step3) on pg 15. The name for the regression is not important. When prompted for the data set for regression, select the set that you saved from the TDE database. In the regression dialog (as shown on the handout pg 16), **configure the following settings (NOTE: Do not ‘copy’ the Aspen Tutorial settings. The settings in the Aspen tutorial are different than the settings used for this assignment):**

Type: **Binary Parameter**; Name: **NRTL**; Element (we will regress Bij, and Bji, which are NRTL/2): **2**; For the 'Component or Group' boxes, select the components. The **first component will be 'i'**, and the **second 'j'**. *Use the same component order as you listed in your component list, which will make copying/pasting easier in subsequent steps.*

Usually you can leave the remaining fields blank and default guesses will be used: Initial value, Lower Bound, Upper Bound, Scale factor.

After you have set up one column, add a second column to flip the order of components. This will create the 'j+i' parameter.

When you complete this step, you should have **two columns.**

1. On the 'Algorithm' tab, verify that the **'Maximum Likelihood'** method is selected.
2. On the Report tab, **include GAMMA**
3. Click Run. When prompted for the regression to run, select the regression that you have configured.
4. If the regression was successful, select the dialog box button to overwrite your values in the parameter folder. Be sure to indicate 'i' and 'j'.

**NOTE:** Not all regressions are successful. You must look at a plot of results to evaluate the regression as discussed next. It is good practice to try some different initial values for the parameter values in the range of -500 to 500 to see if the regression is finding a local minimum.

1. Visit the parameter folder to confirm that the regression values were updated properly. If not, use the ‘source’ dropdown to select the regression and confirm that the values are correct.

> Documentation for this section includes the parameter values (with labels) and uncertainty. Comment on the uncertainty in the parameters and any challenges you encountered with regression.

**F. (10 pt) Generating Gamma Plot from Regressed Parameters**

A direct comparison of the fit within the regression results is not possible when using the maximum-likelihood method. The maximum-likelihood method can adjust the temperature more than reasonable. You must reinsert the parameters and do an evaluation. Return to the regression input form.

1. On the regression Setup tab, set the Calculation type to **'Evaluation'**
2. **Replace the values** in the regression parameter table initial value boxes to the parameter values to those obtained in the regression (Bij and Bji). On the data browser panel that is found in the left panel of folders, select the regression results folder. Copy and paste values onto the input form. Be careful about parameter order.
3. On the 'Report' Tab, verify that the GAMMA property to the 'Selected Properties' box.
4. **Run the regression again.** It won't really regress- it will just generate data to plot a comparison of the model and data.
5. Go to the Profile tab, create a 'Custom' plot, and plot the estimated *and* experimental gammas (y-axis) for *both* components vs experimental liquid composition of one component (x-axis). After merging the y-axis, clean up to plot so that data are points without a line and the model is a line without points. **Save the gamma graph.**
6. Because the phase diagram is shown only in the area where data exist, you will replot the phase diagram in step (G) to create a better graph.
7. Save your Aspen File.

>Your documentation for this section includes the gamma graph. Use solid lines for the model and points without lines for the data.

**G. (20 pt) Comparing Experimental Data with Regressed Data**

The profile tab from a regression creates a comparison at only the compositions were data are available. Here, we ask you to create a better plot.

>Repeat part (D) using your regressed parameters, including comments about how your fit compares to the experimental data as requested in part (D). Use solid lines for the model and points without lines for the model.

**H.** **(10 pt)** **Using UNIFAC to estimate Txy/Pxy Data**

UNIFAC can be a powerful method to predict phase behavior, but results can sometimes be significantly in error. This section asks you to compare the UNIFAC predictions with the experimental data.

Change the thermodynamic method in the Methods tab on the left panel of folders to **UNIFAC**. Look in the HOME ribbon in the Analysis group for 'Binary'. Prepare a binary P-x-y or T-x-y system to match the same type of data (Txy or Pxy), and either the temperature or pressure of your data set. Set the x-axis to be the same component listed first in the data set. Edit the y-axis to use the same units as the data you saved previously.

Navigate to the data folder and plot the experimental data. After verifying that the y-axes have the same units and the x-axis is the same component, **merge the plots and y-axes** as done in part (D), and clean up the plot to use points without lines for data and lines without points for the model.

Comments on using the ‘Analysis’ tools:
The ‘Analysis’ tools provide a quick way to view model predictions for T-xy and P-xy behavior. First review the folder Methods>Parameters>Binary Interaction>NRTL-1 to confirm that the NRTL parameters source are set to the desired values. Then create a *new* analysis using the ‘Binary’ button in the Home ribbon. Within analysis, on the ‘Calculations Options’ tab, select NRTL. VLLE or VLE can be selected in the calculation options. Browsing to the Analysis folder provides even more options for analysis.

>Save your merged plot and comment on the capabilities of UNIFAC for your system compared to use of NRTL. Be critical in your comparison.

**I. (5 pt)** **Comparing Parameters**

Compare the numerical values of τij from (B) and (E) at the average temperature of the fit. These are NOT the values of *Aij* and *Bij*. Comment on whether they are close or quite different. If the system is modeled well with NRTL, they should be about the same because they should be independent of the regression.

**J. (5 pt) Feedback**

What worked well in this exercise? What could be improved in this exercise?