



# Stability Constants

HOW TO ENTER K-VALUES IN TO OLI DATABANKS

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#### Acknowledgement

Several individuals have contributed to the contents of this manual. With special thanks to AJ Gerbino (OLI Systems, Inc. – Cedar Knolls, NJ) who has provided invaluable feedback; Peiming Wang (OLI Systems, Inc. – Cedar Knolls, NJ) who authored the sections on the Mixed Solvent Electrolyte model and regression and finally to Steven Grise (Chemours – Wilmington, DE) for decoding the MSE model and making sense of it for normal humans.

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# Introduction

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## Equilibrium Constant Data

The OLI thermodynamic framework has been developed to encompass most of the important thermodynamic properties of chemicals in water. This framework is valid from -50 to 300 °C, 0 to 1500 atmospheres and ionic strengths up to 30 molal.

Part of the success in predicting the thermodynamic behavior of chemical species in water lies in using a full speciation approach to aqueous chemistry and then predicting the partial molal standard state thermodynamic properties via the Helgeson Equation of State<sup>1</sup>.

A large amount of experimental data is required to regress the equation of state coefficients. This data must span the aforementioned conditions. In addition, the reference state thermodynamic values for the chemical species must also be known<sup>2</sup>. Thanks to the work of Helgeson and others (e.g., OLI researchers) estimation methods can often yield reasonable estimates of the required coefficients.

The reference state thermodynamic values required are:

Gibb's Free Energy	G
Enthalpy	H
Entropy	S
Heat Capacity	Cp
Volume	V

In addition, the seven Helgeson equation of state coefficients ( $w$ ,  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $c_1$ ,  $c_2$ ) are also required.

These values allow the simulation to predict the chemical equilibrium very accurately up to high temperature and pressures.

Unfortunately, it is often the case that most, if not all, of this data is lacking. We may only be able to obtain equilibrium data at a limited set of conditions, frequently not at the reference state. As noted above the OLI software has been

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<sup>1</sup> H.C Helgeson, D.H., Kirkham, G.C. Flowers. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures - Parts I through IV. American Journal of Science 1974, 1976, 1981.

<sup>2</sup> The reference state is defined to be a chemical in its standard state at 298.15 K, 1 bar.

developed so that, if required, estimates can be based upon only the reference state thermodynamic values or on observed stability constants measured in dilute solutions in the presence of a background electrolyte.

To this end, we have developed an easy method of entering such an equilibrium stability constant data into the OLI databooks. This manual will instruct you as to the methodology.

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## Sources of Data

There have been two traditional sources of reference state thermodynamic data available to the public. Each of these sources is now available in electronic form but it is beyond the scope of this manual to explain how to use those forms. Rather, we are assuming that you have access to such data and will be manually entering in the data.

The primary source of reference state thermodynamic data comes from the National Institute for Standards and Technology (NIST). NIST was formerly known as the National Bureau of Standards (NBS). The reference is:

**NBS Tables of Chemical Thermodynamic Properties - Selected Values for Inorganic and C<sub>1</sub>-C<sub>2</sub> Organic substances in SI units. D.D.Wagman, W.H.Evans, V.B.Parker, R.H.Shum, I.Halow, S.M.Bailey, K.L. Churney, and R.L.Nuttal. J.Phys.Chem.Ref.Data. Suppl.No.2. Vol 11(1982)**

The user would look up the Gibb's Free Energy of Formation for each species in the equilibrium and then calculate the equilibrium constant. This is often a tedious job.

Alternatively if the user has published stability constants, these can be entered directly in the OLI software. A common reference for such published equilibrium constants is:

**Critical Stability Constants, Volume 4: Inorganic Complexes. Robert M. Smith and Arthur E. Martell. Plenum Press (1976) pp257.**

This work is often referred to as "Smith and Martell" and is the work we are generally concerned with in this manual.

An electronic version of the "Smith and Martell" compendium is available from the National Institute of Standards and Technology. This is referred to as:

**NIST Standard Reference Database 46.**

**NIST Critically Selected Stability Constants of Metal Complexes Database.**

**Version 8.0 for Windows.**

**United States Department of Commerce  
Technology Administration  
National Institute of Standards and Technology  
Standard Reference Data Program**

**Gaithersburg, MD 20899  
May 2004.**

# Using Published Stability Constants

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## Overview

Using published stability constants in the OLI software requires some explanation. We are generally referring to the published work of Smith and Martell, but other sources can be applied.

Each published source of data is dependent on a mathematical model. Each author makes assumptions about the excess thermodynamic properties used in the experiments to retrieve the infinite dilution values<sup>3</sup>. It is the infinite dilution equilibrium constant that we require in the OLI software. This infinite dilution value is independent of the composition.

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## Representing Smith and Martell Data

Smith and Martell represent their data in a symbolic form. This has been done to reduce the amount of information represented on a page. This method, however, can lead to confusion.

For most of this guide we will be using Smith and Martell's Volume 4 for Inorganic Complexes.

Smith and Martell represent ligands with the letter "L". This ligand is the most fundamental part of the complex and can not donate any more protons or metals. We will be considering the complexes of the chloride ion ( $\text{Cl}^-$ ) as one of the examples in this manual. In Smith and Martell's nomenclature, the letter L = Cl.

From Smith and Martell, Volume 4, page 109<sup>4</sup> for Chloride ion complexes of tin (Sn) we have the following table:

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<sup>3</sup> The term infinite dilution value is misleading. The actual thermodynamic value is the "Hypothetical 1 molal solution thermodynamic property extrapolated from infinite dilution

<sup>4</sup> **Critical Stability Constants, Volume 4: Inorganic Complexes. Robert M. Smith and Arthur E. Martell. Plenum Press (1976) pp257. Page 109**

Table 1 Smith and Martell Constants

Metal Ion	Equilibrium	LogK 25C, 0.5	LogK 25C,1.0	LogK 25C, 0	Delta H 25C,0	Delta S 25C,0
Sn <sup>2+</sup>	ML/M.L			1.51		
		1.08 <sup>D</sup>	1.17 <sup>E</sup> ±0.02	1.45 <sup>F</sup>	(3) <sup>X</sup>	(15) <sup>E</sup>
	ML <sub>2</sub> /M.L <sup>2</sup>			2.25		
		1.72 <sup>D</sup>	1.72 <sup>E</sup> ±0.02	2.35 <sup>F</sup>	(3) <sup>X</sup>	(20) <sup>E</sup>
	ML <sub>3</sub> /M.L <sup>3</sup>			2.0		
		1.5 <sup>D</sup>	1.7 <sup>E</sup> ±0.0	2.5 <sup>F</sup>	(6) <sup>X</sup>	(30) <sup>E</sup>
	ML <sub>4</sub> /M.L <sup>4</sup>	1		1.5		
				2.3 <sup>F</sup>		

<sup>D</sup>25C, 2.0

<sup>E</sup>25C, 3.0

<sup>F</sup>25C, 4.0

<sup>X</sup>0-45C, 3.0

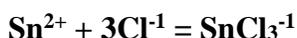
This table has many features which are not immediately apparent. The first column “Metal ion” is the metal that is complexing with the ligand. In this table we are concerned with tin chloride complexes of the form SnCl<sub>x</sub>.

The second column, “Equilibrium” is perhaps the most confusing column to understand. Smith and Martell represent their equilibria as association reactions. This differs in how equilibria are generally represented in the OLI software. The symbolic notation in Smith and Martell is products over reactants.

For example, the equilibrium:



Represents the equilibrium equation:



Notice that the nomenclature for Smith and Martell makes no reference to the charge of the ion.

The next three columns are the common log of the equilibrium constants for the designated equilibrium at 25 °C and either 0.5, 1.0 or 0 molal ionic strength. Some entries have superscripts which denote either temperatures or ionic strengths other than those in the column heading.

In general, the OLI software requires the values in the 25°C, 0 ionic strength column since these are the infinite dilutions values and are independent of activity coefficient models.

The column denoted as Delta H corresponds to the enthalpy of reaction for the stated equilibrium in kilocalories/mole. A value in parenthesis means that Smith and Martell have estimated these values. A superscript denotes conditions different from the column heading.

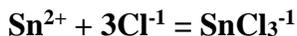
The column denoted as Delta S is similar to Delta H except that this is the entropy of reaction in calories/mole/K.

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## How OLI represents an equilibrium reaction

The OLI software represents an equilibrium reaction in a different manner than does Smith and Martell. OLI represent the equilibrium reactions as dissociation reactions rather than association reactions. This is done purely for historical reasons.

Let's consider the  $\text{SnCl}_3^{-1}$  complex. Smith and Martell use the nomenclature  $\text{ML}_3/\text{M.L}^3$  to represent this equilibrium:



Smith and Martell report an equilibrium constant for this reaction at 25°C and 0.0 molal ionic strength of **Log K = 2.0**

$$\text{Or } \mathbf{K = 1.0 \times 10^2}$$

As mentioned before, OLI prefers to write this equilibrium as a dissociation reaction.



Or in the syntax of OLI, the equation is written as:



Since this is the reciprocal of the Smith and Martell equilibrium we can calculate a new equilibrium constant by:

$$K^{\text{OLI}} = 1/K^{\text{SM}}$$

$$K^{\text{OLI}} = 1 / (1 \times 10^2) = 1.0 \times 10^{-2}$$

$$\mathbf{\text{Log } K^{\text{OLI}} = -2.0}$$

You can see that in Log space OLI's representation of the equilibrium constant is the negative of Smith and Martell's equilibrium constant. This is true for almost all of Smith and Martell's equilibrium. The only exceptions are for solubility products which are written for dissociation reactions.

**Make sure you understand the equilibrium that corresponds to the published equilibrium constant.**

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## Using Equilibrium Constants in OLI's Software

Usually if the user is entering equilibrium constants directly into the databook the user has data as a function of temperature at infinitely dilution conditions. The user will enter the equilibrium constant data in log space following this format:

$$\text{Log } K = A + B/T_K + CT_K + DT_K^2$$

Where Log K is denoted as **KFIT** in the databook and  $T_K$  is the temperature in Kelvin.

If the user has only data from Smith and Martell at 25°C and 0 molal ionic strength, then only the “A” term is entered (in log space). In our example for  $\text{SnCl}_3^{-1}$  the log K (written for OLI) is -2.0. We would enter the KFIT as follows:

**KFIT -2.0 0 0 0**

The corresponding equilibrium would also be written by the user in the **EQUA** line using OLI’s notation.

**EQUA SNCL3ION=SNION+3CLION**

## How does OLI use the published equilibrium constants at conditions other than 25°C and 0 molal ionic strength?

Smith and Martell report data at many conditions other than at 25 °C and 0 molal ionic strength. Using these values directly in the data book assumes that the Authors that Smith and Martell reference have the same activity model that OLI’s uses. This is generally not the case.

OLI has developed a technique for taking the published apparent equilibrium constants and extrapolating the data to infinite dilution conditions, then retrieving the standard state equilibrium constant. This is done automatically in the OLI Databook.

The technique assumes the following: The apparent equilibrium constant is a function of the standard state equilibrium constant (the infinite dilution value) and an excess contribution. We can represent this as:

$$K = K^{\text{inf}} K^{\text{xs}}$$

Where  $K^{\text{inf}}$  is the infinite dilution value we use in the databook,  $K^{\text{xs}}$  is the excess contributions (a function of the activity model) and K is the published apparent equilibrium constant.

We can determine the  $K^{\text{xs}}$  term by using OLI’s proprietary activity coefficient model. We assume that the published apparent equilibrium constant, K, is referenced to a background electrolyte. We default to a background electrolyte of NaCl but this can be changed if required. We know K from the literature and thus we can solve for  $K^{\text{inf}}$  which we enter in the data book.

This can be done for each complex we wish to consider. This, however, can be rather tedious for many complexes. OLI has developed a utility program that can incorporate a large amount of published data on apparent equilibrium constants into the OLI Databook. This will be illustrated in the next chapter.

# Using the Complex Feature

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## Overview

We are now going to provide a short tour on how to enter published equilibrium constant values into the OLI Databook. It will be assumed that the user has some familiarity with OLI Software. The data presented here is from Smith and Martell, Volume 4 page 109 and concerns the chloride complexes of lead ( $\text{PbCl}_x^z$ ).

The data is not at the standard conditions for infinitely dilution equilibrium values. We need to use the <Complex> Actions in the OLI Databook. A tour of the OLI Databook is provided at the end of this manual.

The data from Smith and Martell are:

Metal Ion	Equilibrium	Log K (25 °C, 2.0 molal ionic strength)
$\text{Pb}^{2+}$	ML/M.L	1.02
	$\text{ML}_2/\text{M.L}^2$	1.4
	$\text{ML}_3/\text{M.L}^3$	1.5
	$\text{ML}_4/\text{M.L}^4$	0.7

These correspond to the equilibria:

ML/M.L	$\text{Pb}^{2+} + \text{Cl}^{-1} = \text{PbCl}^{+1}$
$\text{ML}_2/\text{M.L}^2$	$\text{Pb}^{2+} + 2\text{Cl}^{-1} = \text{PbCl}_2^0$
$\text{ML}_3/\text{M.L}^3$	$\text{Pb}^{2+} + 3\text{Cl}^{-1} = \text{PbCl}_3^{-1}$
$\text{ML}_4/\text{M.L}^4$	$\text{Pb}^{2+} + 4\text{Cl}^{-1} = \text{PbCl}_4^{-2}$

Let's start the tour.

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## A tour of entering equilibrium constants into the OLI Databook.

We first need to start the OLI software. This can be done in several ways. If you selected the default install options, you can double click the OLI icon on the Windows desktop. Alternatively, you can use the *Start* button by selecting *Programs/OLI/ OLI Software*.

After starting the OLI software, you should see a figure like this:

*If you have used OLI before you will notice some new options.*

- 1. There are scroll bars at the right and bottom sides. You can use these to resize the window, but this is not recommended.*
- 2. The action line is now active on the main menu. You can change your working directory here*
- 3. The current working directory is displayed at the bottom of the screen.*

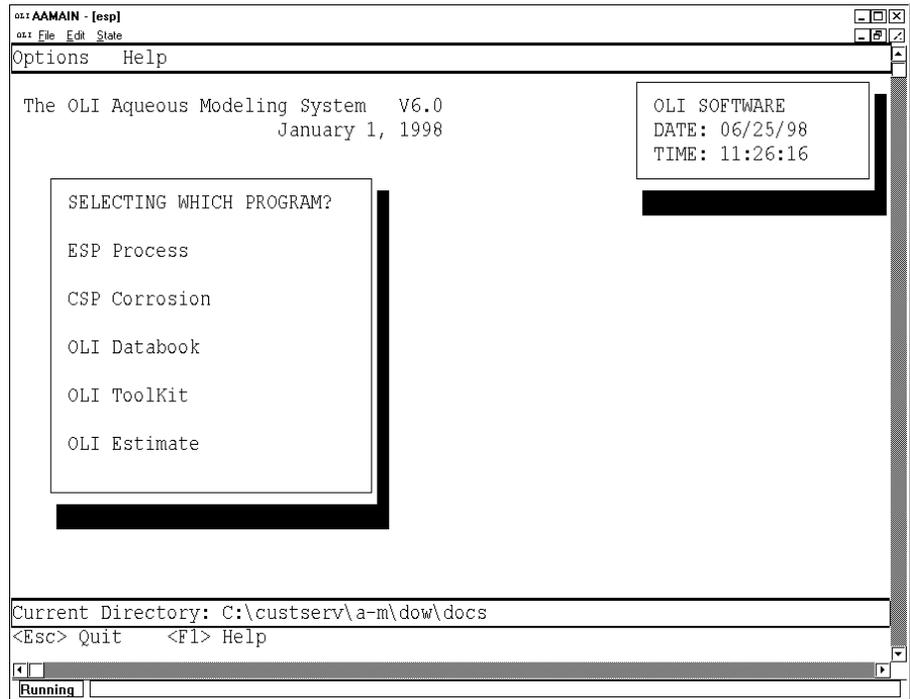


Figure 3-1 OLI Main Menu

- o Position the cursor on **OLI Databook** and press <Enter> or use the mouse to double-click on the **OLI Databook** field.

The program will pause for a moment and then load the OLI Databook menu. There may be many databooks displayed on this screen. OLI now provides several databooks with the ESP software.

*OLI now provides several databooks. On this screen the databooks ALLOYS, CERAMICS, CORROSIO, GEOCHEM, HEATPUMP, LAB, LOWTEMP, PUBLIC are provided by OLI. The other databooks are private databooks that exist in the working directory.*

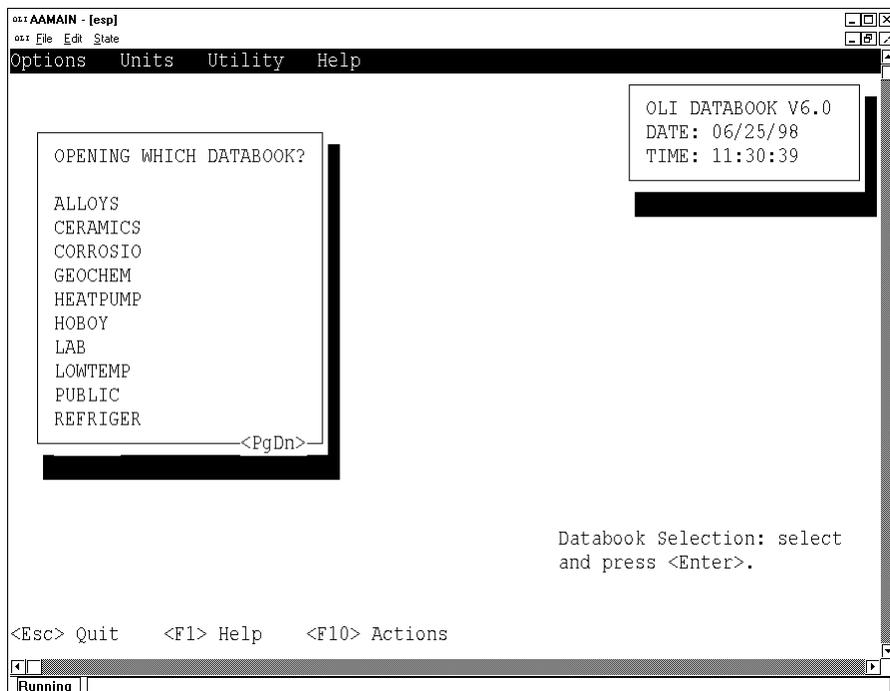


Figure 3-2 The OLI Databook Menu, top half

- o We need to create a private databook for this tour. In practice we could use one of the existing databooks. The option to create a new databook is not on this screen. Press the <PgDn><sup>5</sup> key till **New Databook** is present on the screen. Alternatively, you could use the mouse and double-click on the <PgDn> box.
- o Position the cursor on **New Databook** and press enter (or double-click on **New Databook**).

<sup>5</sup> This is the Page Down Key. You could also use the down-arrow key.

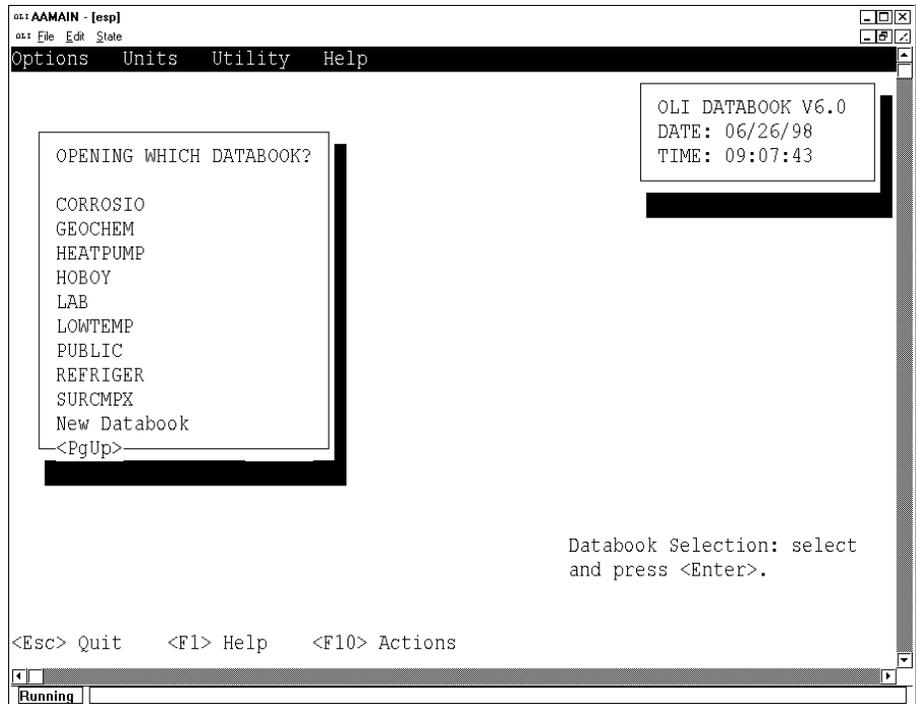


Figure 3-3 Finding New Databook on the Databook menu

- o You will be prompted for a name of a new databook. We recommend the name **newcomp** for this tour. You may use any name that you desire. Enter **newcomp** in the highlighted box and press <Enter>

*Although we are using most of the Windows architecture for the internals of ESP we are still limited by the old DOS conventions for file names. This was done to maintain compatibility with older software. The databook name must be limited to 8 characters and the first 3 characters must unique in this directory.*

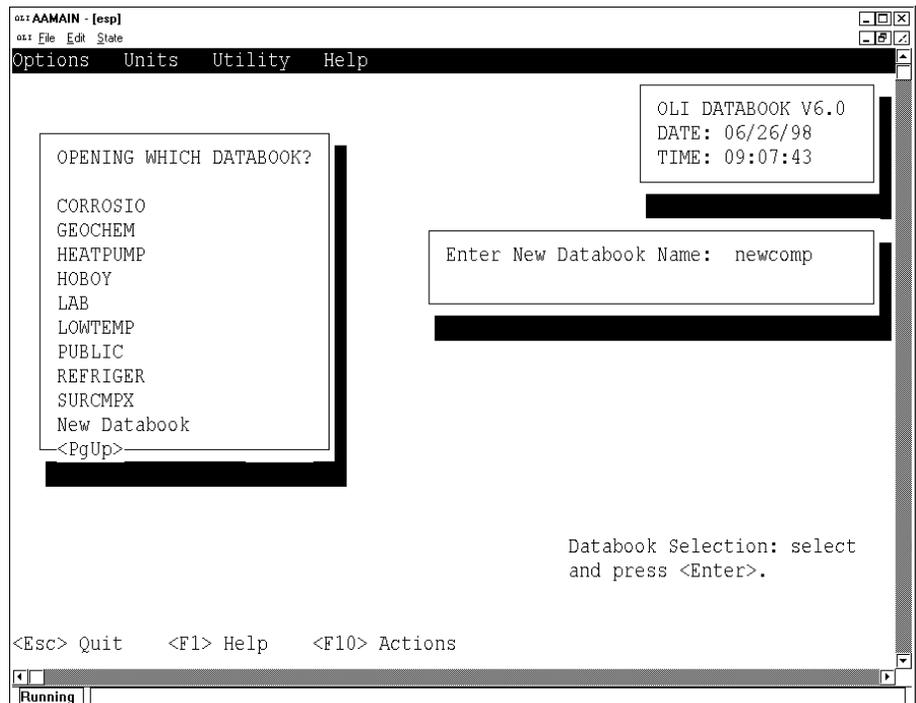


Figure 3-4 Entering the name of the new databook

The program will begin to create all the required files for the databook. On most computers there will be 39 files created. Some will have the format **Newcomp.\*** where the asterisk represents file extensions of DIC, DDB, NDX, etc. Some files will have the format **New\*.\*\***, where the asterisk has truncated the name and replaced it with names such as COMP, RAW, MATC, and the double asterisk is new file extensions. Normally the user does not have to concern themselves with this operation. The following figure shows you that something is happening.

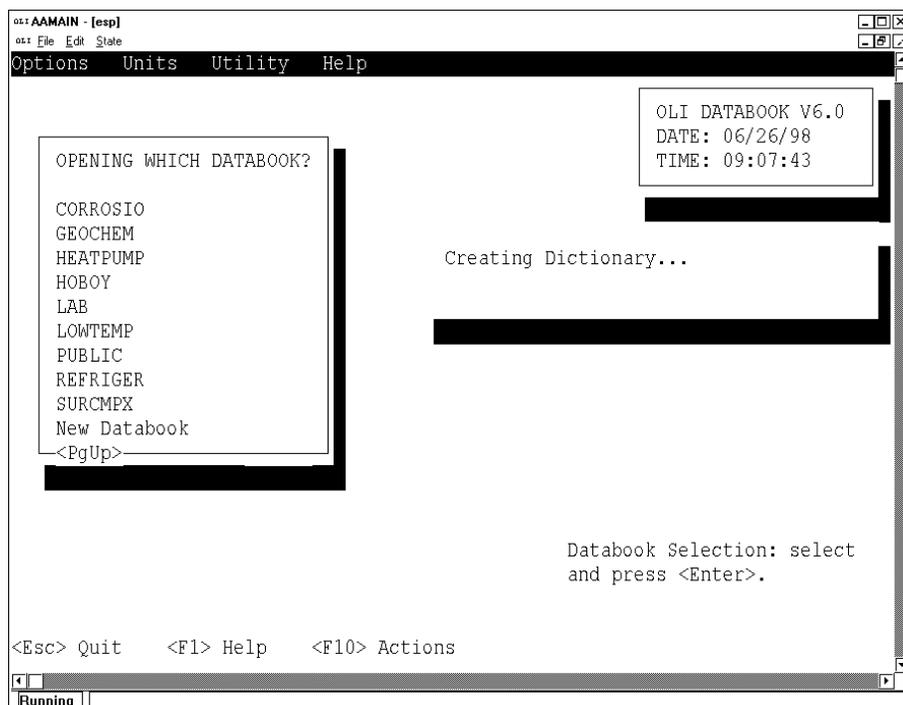


Figure 3-5 Waiting to create the databook

Once the program has finished completing the file creations you will be placed at the Chapter Menu in the Databook. The contents of these chapters have been described elsewhere and we will not dwell on them here.<sup>6</sup>

We are primarily concerned with the individual species data thus the **Species** chapter is most important to us.

*We are no longer referring to double-clicks. You can always use the double-click method to enter a section*

- o Position the cursor on **SPECIES** and press <Enter>

<sup>6</sup> See the OLI reference manual and the OLI Aqueous Workshop notes

Position the cursor on  
*SPECIES* and press <Enter>

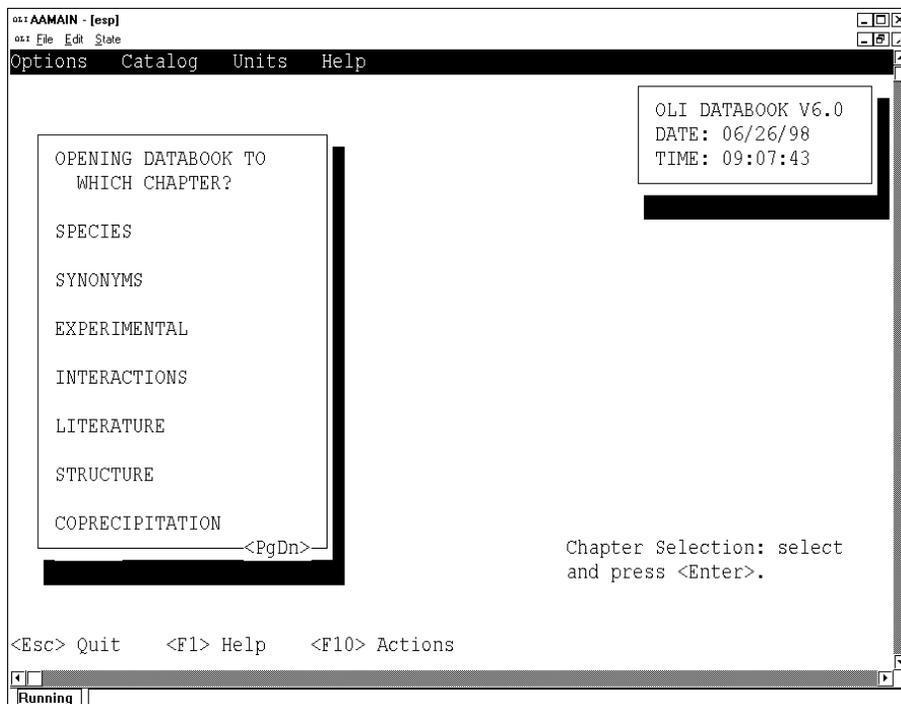


Figure 3-6 Selecting the *SPECIES* chapter

We are now ready to enter our first species. The lead chloride data contains aqueous species information for 4 complexes. These complexes are:



We can only enter this data if the underlying species of these complexes are present in the OLI PUBLIC Databook. These underlying species are called base ions. In this case, the base ions are the Lead ion ( $Pb^{2+}$ , PBION) and the chloride ion ( $Cl^{-1}$ , CLION).

It is generally better to start entering data for the highest order complex for which you have data. In this case it would be for  $PbCl_4^{2-}$ . We must enter the data in the OLI syntax which is PBCL4ION.

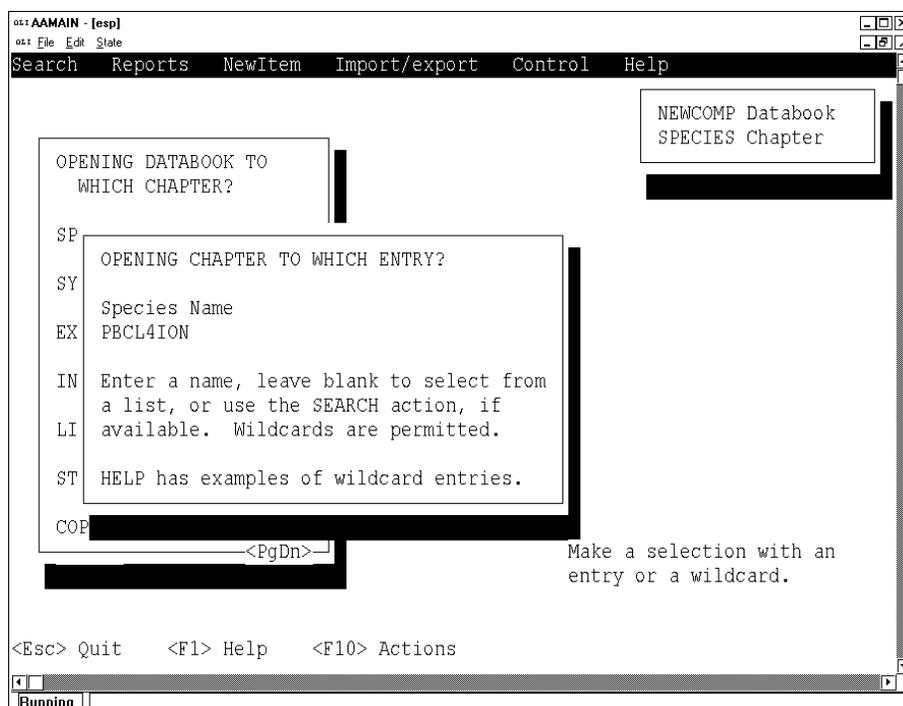


Figure 3-7 Entering the name PBCL4ION

*Note: This selection requires you to press <Enter>, using the mouse does not work!*

*You may enter the name in either upper or lower case. The databook converts the name as required.*

- o Enter the name **PBCL4ION** on the blank line and press <Enter>.
- o You will be warned that you are entering a species that does not exist in the databook. Sometimes you will be editing a species and have mistyped the name. In that case you would select NO to the message. In this case select YES, we are truly entering a new species.

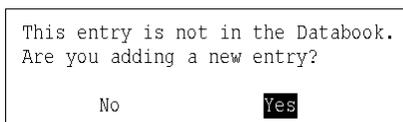


Figure 3-8 Select Yes, we are entering a new species

- o You will now see the Species data screen. This screen will allow you to enter data for the species. Normally we would have to enter the molecular weight and stoichiometry but that

will be automatically done for us using this technique. Position the cursor on **Aqueous Phase** and press <Enter>.

```

SELECT WHICH PART OF THE DATA?

General Information
Aqueous Phase
Vapor Phase
Solid Phase
  
```

Figure 3-9 The "Empty" Data screen

The following screen is displayed. Notice that all field are either blank or have 0.0 entered.

*Notice that the red box contains the chapter name (SPECIES) and our name for the complex (PBCL4ION). It also reminds us that we are viewing the aqueous section.*

```

o: AAMAIN - [esp]
o: File Edit State
View Edit Units Evaluate Complex Help

SPECIES Chapter
PBCL4ION Species
Aqueous Phase

Last Modification Date
[Redacted]
-18 Lines

DATE
GREF 0.0
HREF 0.0
SREF 0.0
VREF 0.0
CPRE 0.0
ZRAC
HKF
HTYP
EQUA
CHAR
IONC
KEIT
IONT

Data display: position cursor and select an action, or <Esc> to quit.
<Esc> Quit <F1> Help <F10> Actions

Running
  
```

Figure 3-10 The blank Aqueous species screen

*To remind you, the action line is the white line at the top of the screen. Do not get confused with the Windows Action line which is normally gray.*

- o We will now begin to enter the information on the complex. Use the action key (normally <F10>) or the mouse and select **Complex** from the action line. Press <Enter> to select.

We are entering the data for our Species  $\text{PbCl}_4^{2-}$ . The following screens should be filled out.

*The <TAB> key can be used to move from one field to the next.*

```
Aqueous Complex Data Entry

(M)etal: PBION
(L)igand:CLION
Background electrolyte: NACL

Maximum order for Metal : 1
Maximum order for Ligand: 4

Temperature, C :25           Ionic Strength: 2.0_
Temperature, C :           Ionic Strength:
(The second temperature is optional)
```

Figure 3-11 Specifying the order and conditions of the species

There are several important features on this screen. First is the metal and ligand fields. The metal (PBION) and the ligand (CLION) must be in the PUBLIC databook.

Next, the number of metal species should be entered. In this case there is only one (1) lead ion. There are four (4) chloride ions and this should be entered.

The temperature of the data is 25 C and is the only temperature available. The ionic strength was 2.0 molal. The background electrolyte was assumed to be NACL.

- o Enter the appropriate values and then press <Enter> to move to the next screen.

By default, the OLI Databook assumes step-wise dissociation reactions for the complexes. This means that instead of the complete dissociations (as in  $\text{PBCL}_4\text{ION}=\text{PBION}+4\text{CLION}$ ) we are assuming that the dissociations are of the kind;  $\text{PBCL}_4\text{ION}=\text{PBCL}_3\text{ION}+\text{CLION}$ .

Since the Smith and Martell data is usually represented as associations we have reversed the equation in our entry form. In this case you would see;  $\text{CLION}+\text{PBCL}_3\text{ION}=\text{PBCL}_4\text{ION}$ .

This is illustrated in the next figure.

Aqueous Complex Data Entry

Chemical Equilibrium Association Equation(s) for the Complex

Log K	Delta H, cal	Complex equation(s)
		PBION+CLION=PBCLION CLION+PBCLION=PBCL2AQ CLION+PBCL2AQ=PBCL3ION CLION+PBCL3ION=PBCL4ION

Temperature, C : 25

Figure 3-12 The default associates are shown

- o The data we have from Smith and Martell are for the complete associations and therefore we must modify the equations in the data entry screen. Modify the screen to look like the example in the following figure:

*The data entry screen is set to overstrike mode. This means that you will have to use the <SpaceBar> to remove any unwanted characters.*

*Failure to clean up the screen will result in a fatal error (crash!).*

Aqueous Complex Data Entry

Chemical Equilibrium Association Equation(s) for the Complex

Log K	Delta H, cal	Complex equation(s)
1.02		PBION+CLION=PBCLION
1.4		2CLION+PBION=PBCL2AQ
1.5		3CLION+PBION=PBCL3ION
0.7		4CLION+PBION=PBCL4ION
-		

Temperature, C : 25

Figure 3-13 The correct Log K and associations

We had to modify the associations to match the reactions used to represent the literature data. Pressing <Enter> on the last field will start the calculation.

An ElectroChem calculation will now be made to get the infinite delution K value

Cancel

Figure 3-14 Press <Enter> on Continue to start

The OLI Software will automatically perform the following calculations.

1. The software will create a chemistry model which will contain all the lead chloride complexes including  $\text{Pb}^{2+}$ ,  $\text{PbCl}^{+1}$ ,  $\text{PbCl}_2^0$ ,  $\text{PbCl}_3^{-1}$ ,  $\text{PbCl}_4^{2-}$ .
2. An equilibrium calculation will be performed, holding the ionic strength constant at 2.0 molal.
3. The infinite dilution equilibrium constants for all the complexes will be determined based upon the entered equilibria.
4. The NEWCOMP databook will automatically be updated with equations, equilibrium constants, molecular weights, reference state thermodynamic properties and stoichiometric coefficients.

This may take several minutes. You may be prompted to <Press Any Key> to continue. If so, press the <Enter> key. Normally the program will return you to the next figure.

*Notice that the Gibb's free energy and enthalpy have been calculated. We are missing data for heat capacity, volume and entropy.*

**Caution: Due to the limited data, you should limit your use of the NEWCOMP databook to isothermal calculations near 25 C and 1 atmosphere.**



Figure 3-15 The completed screen for PBCL4ION

- o Press the <Esc> key or right click the mouse to return to the Data Screen. You will notice that some sections have now been filled out.

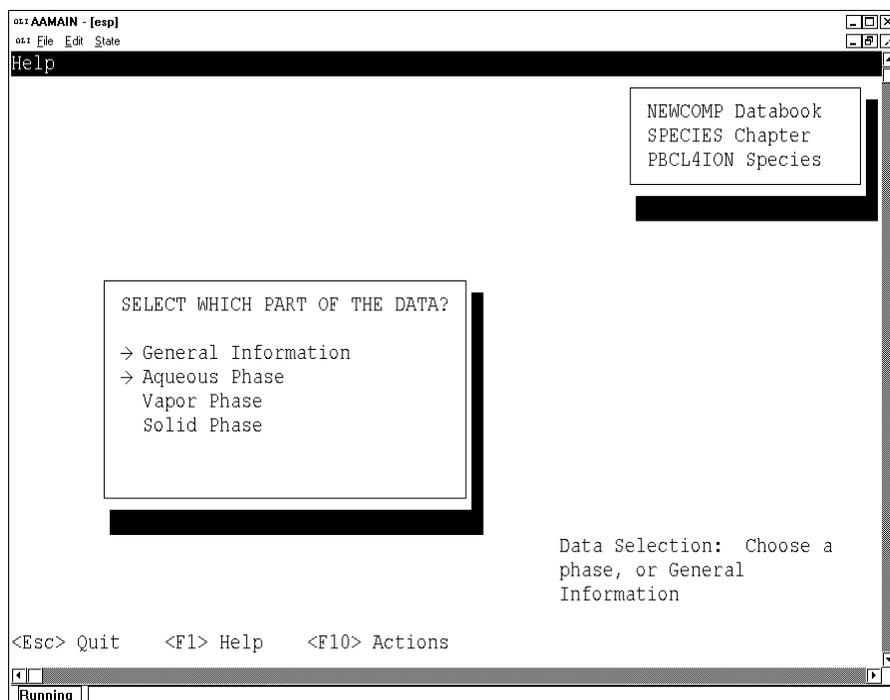


Figure 3-16 The data screen showing some sections have been entered

- o Press the <Esc> key once more to return to the **OPENING CHAPTER TO WHICH ENTRY?** Screen. The name PBCL4ION may be present. Press the <SpaceBar> to blank out the names and then press <Enter>.

*By default, ESP remembers the last name of the species entered. Just blank out the name with the space bar to pull up a list of all species in the databook. Press <Enter>*

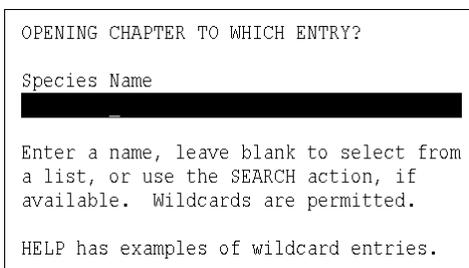


Figure 3-17 Blank out the name if present then press <Enter>

Pressing <Enter> on a blank species line is the equivalent to selecting with an asterisk (\*) to see all species. In this case we have only entered one species, PBCL4ION but we had informed the program that there were 4 possible complexes possible. We entered equilibrium constants for all 4 complexes and the program generated databook entries for each. The following figure shows the species created.

4 LINES

MAKE A SELECTION FROM THIS LIST

PBCL2  
PBCL3ION  
PBCL4ION

*Figure 3-18 The species present in the databook*

It is left up to the user to review the data for these species. This concludes the tour of entering equilibrium constants for complexes into the OLI Databook.

# Entering a New Complex.

---

## Overview

The preceding tour assumes that all of the underlying species are present in the PUBLIC databook. In that case the underlying ions of  $\text{Pb}^{2+}$  and  $\text{Cl}^{-1}$  were in the public databook. It is common that one or more of these underlying ions are not in the PUBLIC databook but could be entered in a private databook.

We will consider entering a new complex into the Private Databook **Newcomp** that we created in the previous chapter. This complex is an acid with many different acid groups.

This acid is *diethylenetriaminepeta(methylenephosphonic) acid* which has the chemical formula:  $\text{C}_9\text{H}_{28}\text{N}_3\text{P}_5\text{O}_{15}$ . Eight (8) of the hydrogens are involved in the acid dissociations typical of most organic acids.

Smith and Martell, volume 2, report stability constants for the following reactions.<sup>7</sup>

---

<sup>7</sup> **Critical Stability Constants, Volume 2: Amino Complexes.** Robert M. Smith and Arthur E. Martell. Plenum Press (1976) pp400. P325

Reaction	Log K
$\text{H}_7\text{DTPMP}^- + \text{H}^+ = \text{H}_8\text{DTPMP}$	2.8
$\text{H}_6\text{DTPMP}^{2-} + \text{H}^+ = \text{H}_7\text{DTPMP}^-$	4.45
$\text{H}_5\text{DTPMP}^{3-} + \text{H}^+ = \text{H}_6\text{DTPMP}^{2-}$	5.50
$\text{H}_4\text{DTPMP}^{4-} + \text{H}^+ = \text{H}_5\text{DTPMP}^{3-}$	6.38
$\text{H}_3\text{DTPMP}^{5-} + \text{H}^+ = \text{H}_4\text{DTPMP}^{4-}$	7.17
$\text{H}_2\text{DTPMP}^{6-} + \text{H}^+ = \text{H}_3\text{DTPMP}^{5-}$	8.15
$\text{HDTPMP}^{7-} + \text{H}^+ = \text{H}_2\text{DTPMP}^{6-}$	10.10
$\text{DTPMP}^{8-} + \text{H}^+ = \text{HDTPMP}^{7-}$	12.04

Where DTPMP is the base ion of the acid ( $\text{C}_9\text{H}_{20}\text{N}_3\text{P}_5\text{O}_{15}^{8-}$ ).

---

## Entering a new Complex and a New Base Ion.

We will begin to enter a new base ion and a new complex into the existing databook. You can, of course, use any existing database other than a databook provided by OLI Systems. For this Tour we will assume that you are using the private databook **NEWCOMP**. If you have left the program, then perform the following steps:

- o Double-Click the OLI Icon on the desktop - or -
- o Select the OLI program option from the Start Menu.
- o Unix users should type ESP at a command prompt to start the program.
- o Select the OLI/Databook from the ESP main menu
- o Select the database **NEWCOMP** (or any existing databook).

Before we can enter the actual stability constant data for this new complex, we need to inform the Databook about the base ions involved. In this case one of the base ions is the hydrogen ion.

The hydrogen ion is already in the PUBLIC databook and we do not need to discuss it any farther. The other base ion is new. This is the ion  $\text{DTPMP}^{8-}$ . We have shortened the name so that it is easier to discuss. Just remember that the base ion does not further dissociate.

Each species in the databook is composed of specific materials. In general, these are the atoms that make up the species. We need to inform the databook about these atoms.

On occasion, it is more practical to group many atoms species together. These groups of atoms do not further react. This simplifies the mass balance relationships in the OLI program. We will group all the atoms,  $C_9H_{28}N_3P_5O_{15}$  into two groups.

The first group will be the acid protons and there are 8 of them. This leaves us with the second group of  $C_9H_{20}N_3P_5O_{15}$  and we will call this group DTPMP. The molecular weight of this group is 565.133 grams/mole.

Each group, whether it be an individual atom or a group such as DTPMP, requires a unique code. These codes are arbitrary but are required to establish the mass balances in the calculations. For this example, we have chosen the number 8500 for the group DTPMP.

## Entering Mat Code information

To add the new base ion into the databook we first start by entering the codes for the material groups in the species. This group is DTPMP and it does not exist in our databook.

- o Select the Literature chapter from the **NEWCOMP** databook.

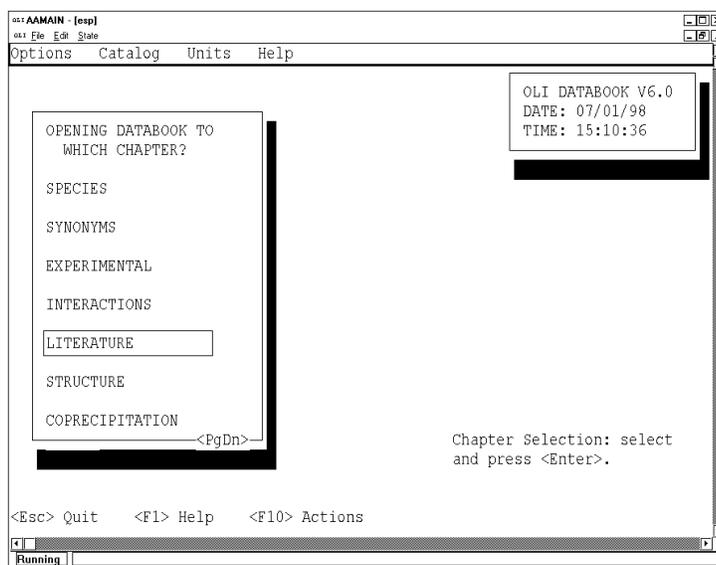


Figure 4-1 Selecting the Literature Chapter

- o The Literature chapter has four sections. We could enter information about the references, equations, material and ions codes. At the moment, we only have information about the material codes. Select MATERIAL CODES from the screen.

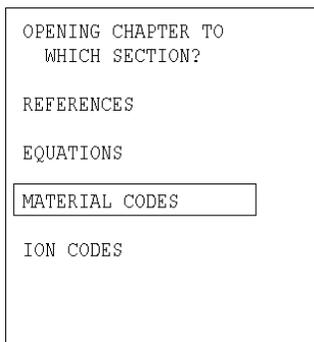


Figure 4-2 Selecting Material Codes

- o You will now see a blank screen. Enter the number **8500** on this screen. Remember that this is the code for DTPMP.

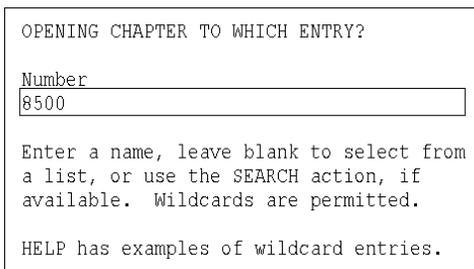


Figure 4-3 Entering the Code for DTPMP

- o You will now see an empty Material Code screen. We must now enter the number, symbolic reference, charge (oxidation state) and molecular weight.

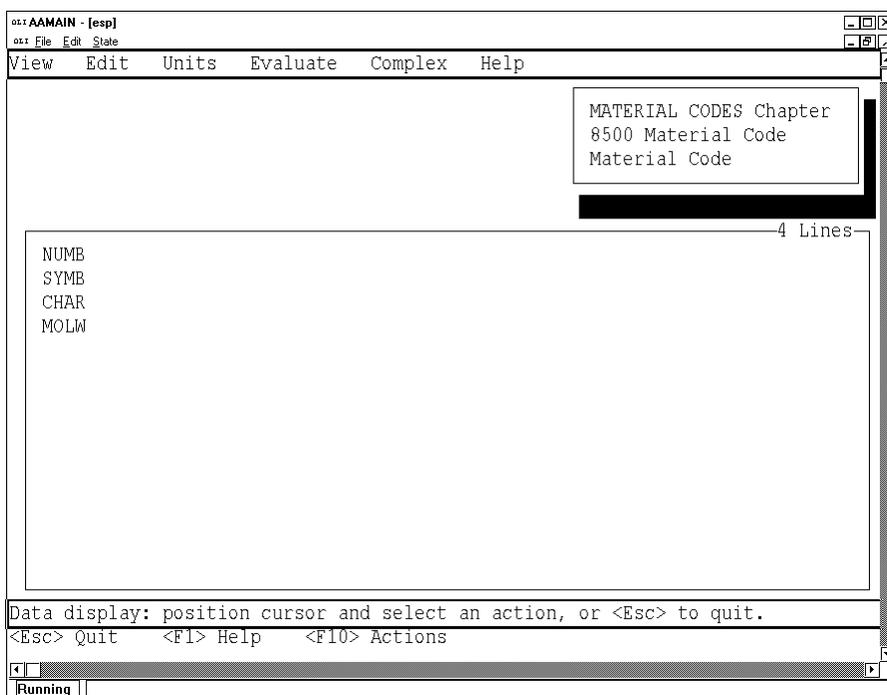


Figure 4-4 The blank Material Code Screen for Code 8500

- o The number is 8500, the symbol will be DTPMP, the charge is -8, and the molecular weight is 565.33

Use the <Action> key or the mouse and select Edit from the action line.

The first line should turn black. Enter the information on the next figure. Each line must be followed by pressing the <Enter> key. This updates the line and informs the databook that the data has changed. You will have to position the cursor on the next line by using the down arrow key.

The assignment of material codes is simple. The codes from 8001 to 9000 are assigned for user use. OLI promises not to use these codes in the commercial databook.

Simply pick a code that you find convenient.

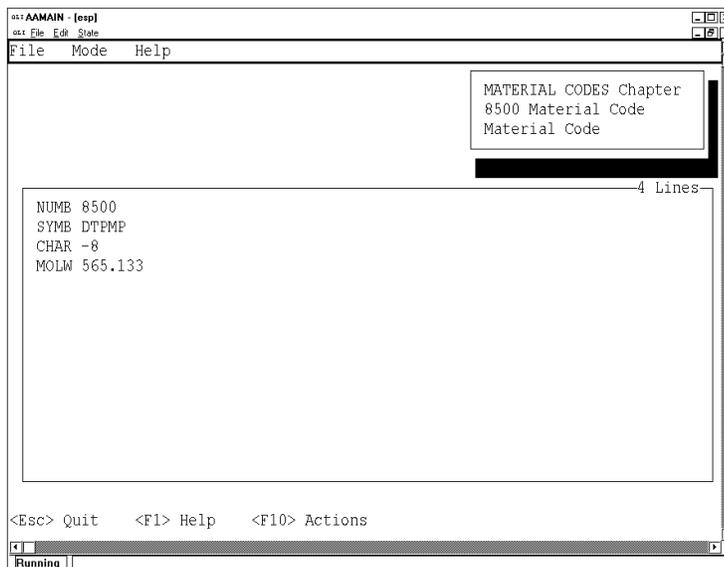


Figure 4-5 Entering the material Code data

- o When you have finished entering the data, use the <Action> key or the mouse to select **File** from the Action Line. This will display the **File** pull-down menu. Select **Exit** to save and exit this screen.

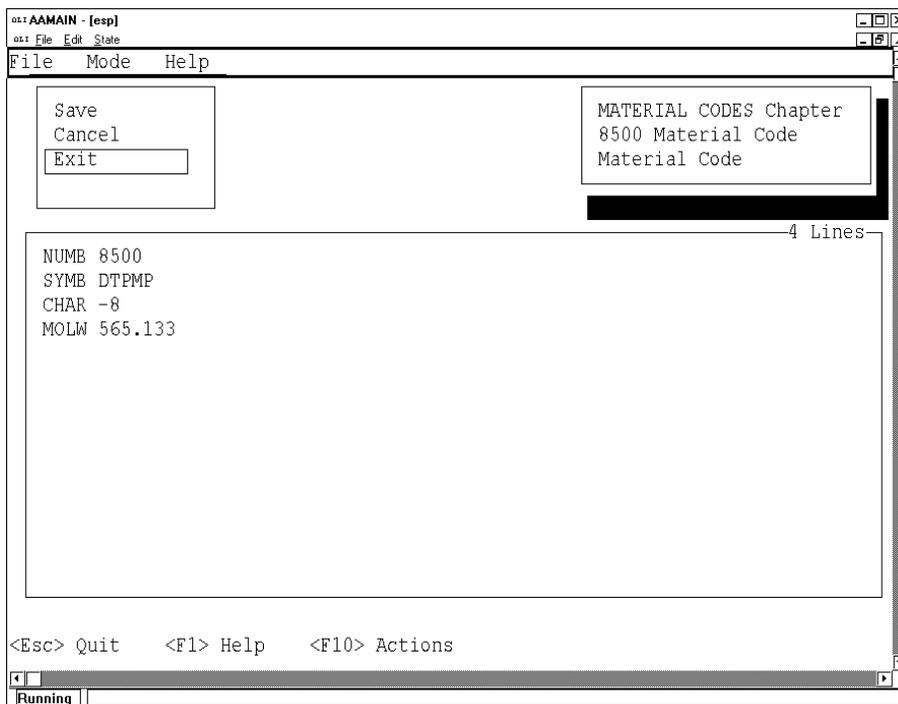


Figure 4-6 Select Exit to Save and leave this screen

- o You will now have to press the <Esc> key (or right click the mouse) to return to the "OPENING DATABOOK TO WHICH CHAPTER" Screen. Select SPECIES.

```

OPENING DATABOOK TO
WHICH CHAPTER?

SPECIES
SYNONYMS
EXPERIMENTAL
INTERACTIONS
LITERATURE
STRUCTURE
COPRECIPIATION
<PgDn>

```

Figure 4-7 Select species to begin

- o As we did in the previous tour, we will now enter a species name. If the species does not appear in the database we will be prompted to accept our entry. In this case, select YES when appropriate. Enter the name DTPMPION on the blank line.

*For this technique we could have actually used any species in the DTPMP chain. It is just simpler to start at one end of the chain.*

```

OPENING CHAPTER TO WHICH ENTRY?

Species Name
DTPMPION

Enter a name, leave blank to select from
a list, or use the SEARCH action, if
available. Wildcards are permitted.

HELP has examples of wildcard entries.

```

Figure 4-8 Entering The Species Name

- o As in the previous tour, select YES to allow us to enter a new species. We need to start out entering some general information about the species. From the SELECT WHICH PART OF THE DATA SCREEN, select **General Information**

```

SELECT WHICH PART OF THE DATA?

General Information
Aqueous Phase
Vapor Phase
Solid Phase

```

Figure 4-9 Selecting General Information

- o As with the Material Code screens, this screen starts off Blank. In the previous tour we went directly to the Complex action. We can not do that here since the program does not yet have any information for the base ion DTPMPION.

This information can be entered by using the Edit Action. Use the <Action> key or the mouse to select Edit.

Use the Edit Action to enter data into the general section.

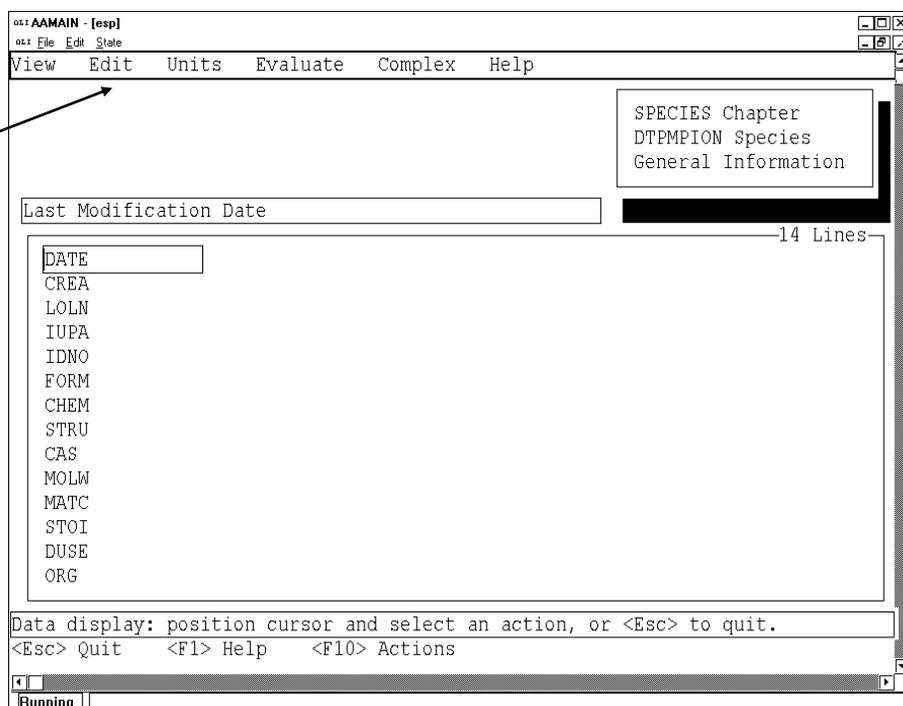


Figure 4-10 Select Edit to start

- o Position the cursor on MOLW. This is the molecular weight of the base ion. Enter 565.133 and press the <Enter> key. This will inform the databook that some data has changed. You should now position the cursor on the next line. Enter MATC and STOI (stoichiometric coefficients) as shown in the next figure.

*The only information that is essential in this section is the Molecular Weight, Material Code and the stoichiometric coefficients. All other information is supplemental.*

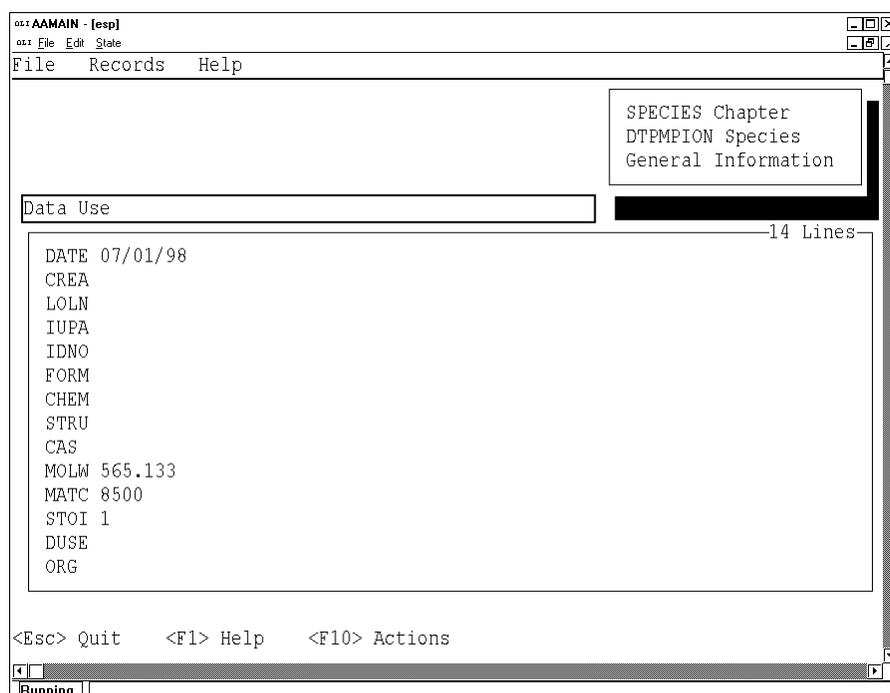


Figure 4-11 Entering the essential data for the base ion

- o When you have finished entering data. Use the <Action> Key or the mouse to select File/Exit. This will save your data and leave this screen.  
 Press the <Esc> key to return to the "...WHICH DATA" screen and select Aqueous Phase.
- o The aqueous information is missing. We will have to enter some essential data for this base ion. First we need to verify our units. Use the <Action> key or the mouse to select Units.  
 Select the METRIC unit system.
- o We are now ready to enter some data. The reference state thermodynamics properties for the base ion have been estimated. The Gibb's Free energy of formation (GREF) is 29744 calories/mole. The Enthalpy of formation (HREF) is -52450 calories/mole, and the entropy is 124.34 calories/mole/K. The charge is -8.  
 Using the Edit action, enter these values as shown in the next figure.

*Why enter thermodynamics? We will ultimately be providing equilibrium constants. The software has been designed to use an entered equilibrium constant over the entered thermodynamics. This fine as long as we only consider isothermal calculations. If any temperature dependence is required, we need some enthalpy data.*

*This data was estimated by doubling the energies for diethylamine. This doubling has almost the same molecular weigh and stoichiometry. It is not the best, but it is the best possible approach when data is lacking.*

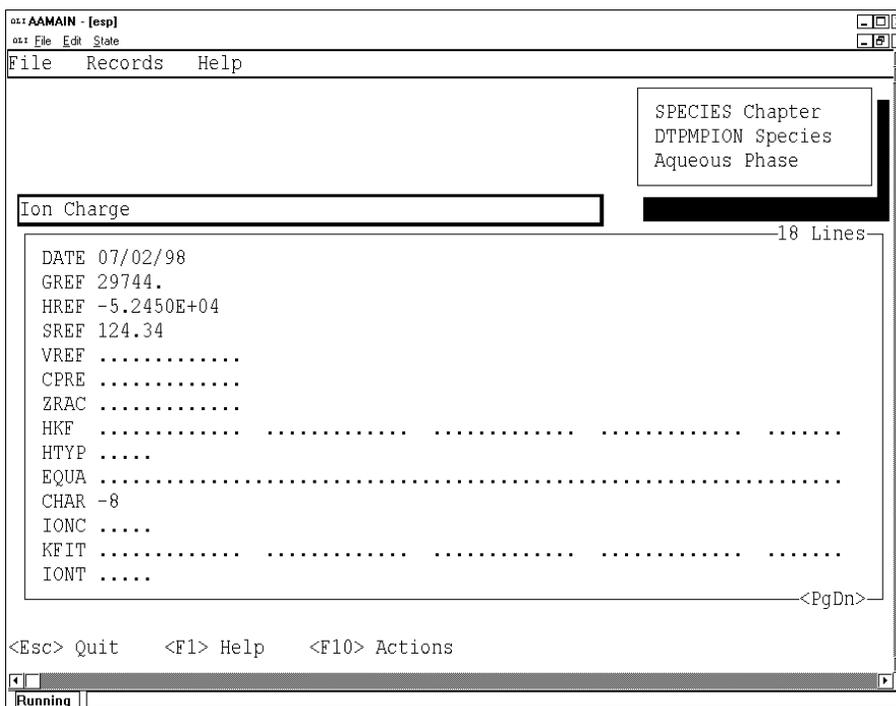


Figure 4-12 Entering data in METRIC units

- o When you are done entering the data, use the <Action> key or the mouse to select **File/Exit**. This will save your data and leave the screen.

- o We are now ready to start the complex estimation. On the Aqueous Phase screen, use the <Action> key or the mouse to select Complex. This is similar to the tour in Chapter 3.
- o. You will be asked to set up the complex calculation. This particular data set of stability constants allows for 8 protons to associate with the base ion. The data is at 20°C in a 0.1 molal ionic strength solution. The background electrolyte was potassium chloride.

Enter the data on the following figure:

Aqueous Complex Data Entry

(M)etal:   
 (L)igand:   
 Background electrolyte:

Maximum order for Metal :   
 Maximum order for Ligand:

Temperature, C :       Ionic Strength:   
 Temperature, C :       Ionic Strength:   
 (The second temperature is optional)

Figure 4-13 Defining the number of complexes

- o Press the <Enter> key when you are done. You will now have to enter the association data. Unlike the previous tour, we will use the associations directly. Enter the data on the next screen:

Aqueous Complex Data Entry

Chemical Equilibrium Association Equation(s) for the Complex

Log K	Delta H, cal	Complex equation(s)
<input type="text" value="2.8"/>	<input type="text"/>	HION+DTPMPION=HDTPMPION
<input type="text" value="4.45"/>	<input type="text"/>	HION+HDTPMPION=H2DTPMPION
<input type="text" value="5.5"/>	<input type="text"/>	HION+H2DTPMPION=H3DTPMPION
<input type="text" value="6.38"/>	<input type="text"/>	HION+H3DTPMPION=H4DTPMPION
<input type="text" value="7.17"/>	<input type="text"/>	HION+H4DTPMPION=H5DTPMPION
<input type="text" value="8.15"/>	<input type="text"/>	HION+H5DTPMPION=H6DTPMPION
<input type="text" value="10.10"/>	<input type="text"/>	HION+H6DTPMPION=H7DTPMPION
<input type="text" value="12.02"/>	<input type="text"/>	HION+H7DTPMPION=H8DTPMPION

Temperature, C : 20

Figure 4-14 Entering association constants

The program will now ask you to begin. Select Continue when appropriate.

After a few moments, the program will begin to automatically create a chemistry model. When that operation is complete, the program will then determine the infinite dilution equilibrium constants. The databook is then finally updated.

- o When the operation is complete, you will be returned to the same aqueous screen from which you started. Press the <Esc> key twice to return to the "OPENING CHAPTER TO WHICH ENTRY" screen. Press the <SpaceBar> to delete the name that

is currently displayed and then press <Enter>. You should see this screen.

```
13 LINES
MAKE A SELECTION FROM THIS LIST
DTEMPION
PBCL2
PBCL3ION
PBCL4ION
PBCLION
HDTEMPION
H2DTEMPION
H3DTEMPION
H4DTEMPION
H5DTEMPION
<PgDn>
```

Figure 4-15 Current Databook Content

- o the databook now contains all the new DTPMP species, from H<sub>0</sub> to H<sub>8</sub>. As with the previous tour, the user can now examine all these species.

The databook is now ready for use.

# Using a Private Databook

---

## Overview

Using private databooks in the OLI software is essential for using new and updated data. The OLI software is only released on a periodic schedule. You may require updated data long before the scheduled release. The only method of using updated data is with a private Databook.

These instructions are for use with the ESP software. If you are using the OLI Studio or OLI Flowsheet software, you will need to seek other instructions:

[OLI Studio](#)

[OLI Flowsheet](#)

Some databooks are provided by OLI when you obtain the software. These are GEOCHEM, CORROSIO, HEATPUMP, ALLOYS, LAB, etc. These private databooks are specialized for specific applications. Using these databooks or a user created data base is the same.

---

## Using a private database

We are going to assume that you are using the same **NEWCOMP** database that has been developed in this manual. The procedure to use other databases is the same.

- o. Access the main OLI/Software menu shown in the next figure. This may require pressing the <Esc> key or restarting the software.

*You may not have all these options installed. All users should have the OLI/Toolkit option installed.*

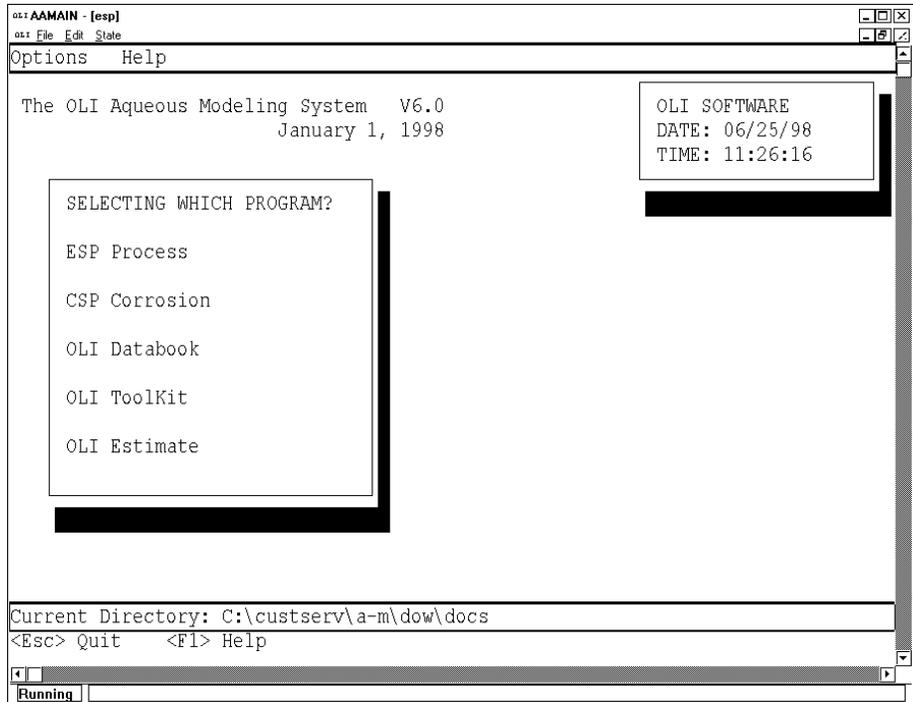


Figure 5-1 The OLI/Software main menu.

- o Position the cursor on OLI Toolkit and press <Enter> or use the mouse and double-click on OLI Toolkit.
- o You will be asked to select a tool. Select the OLI Express tool.

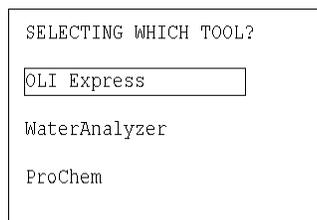


Figure 5-2 Selecting OLI Express

- o You will now have the option of creating new stream or using a stream previously defined in the OLI/Software. For this tour select NEW STREAM.

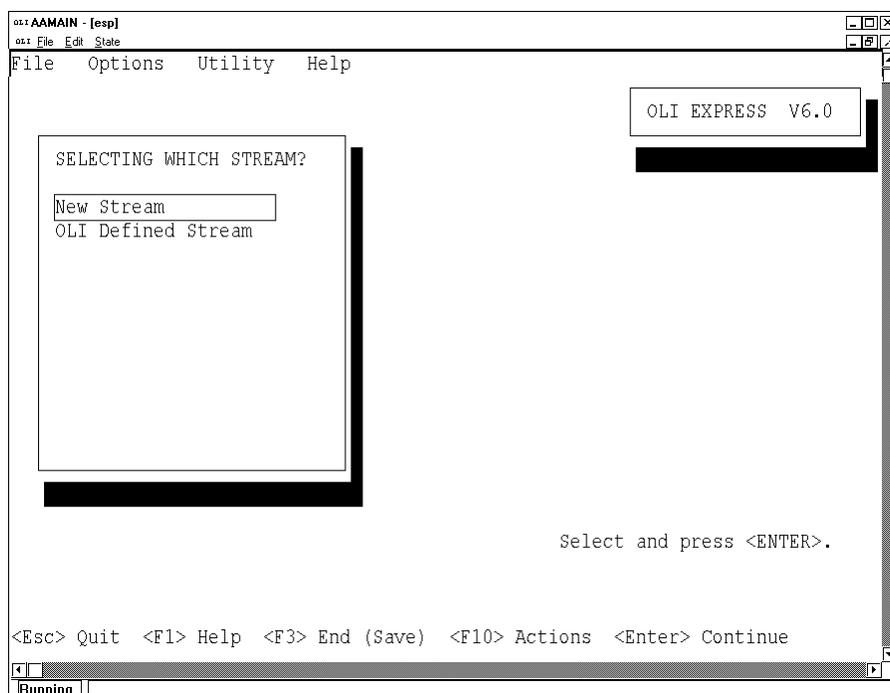


Figure 5-3 Selecting a new stream

- o All streams in the OLI software require names. The names may contain alphanumeric characters and spaces. Enter a name for the stream and press enter. We recommend the name MODTEST.

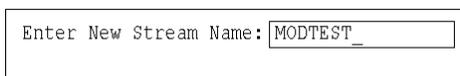


Figure 5-4 Entering the stream name MODTEST

- o We will now be asked to “Work in Which Mode?”. We want to define a new chemistry model so select that option.

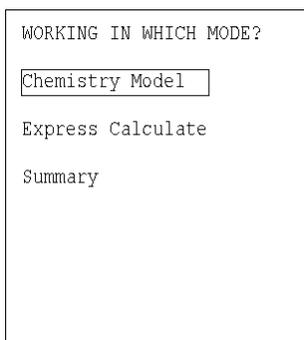


Figure 5-5 Selecting Chemistry Model.

- o We will have to define a new chemistry model. This is a file separate from either the databooks or the stream name. The names do not have to be the same.

Select New Model then enter a name for the new model. We recommend MODTEST

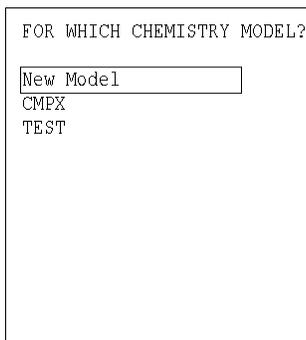


Figure 5-6 Selecting a New Model, any existing models are listed here

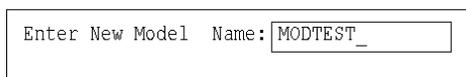


Figure 5-7 Entering the model name

- o We will now begin to enter the species that we wish to simulate. We will be using the species we developed in the previous chapter. The actual name of our large organic acid is H8DTPMP. To learn how to find the name please consult the OLI Manuals or the Aqueous Modeling Workshop notes.

H2O is already entered, enter the name of our acid, H8DTPMP and press <Enter>

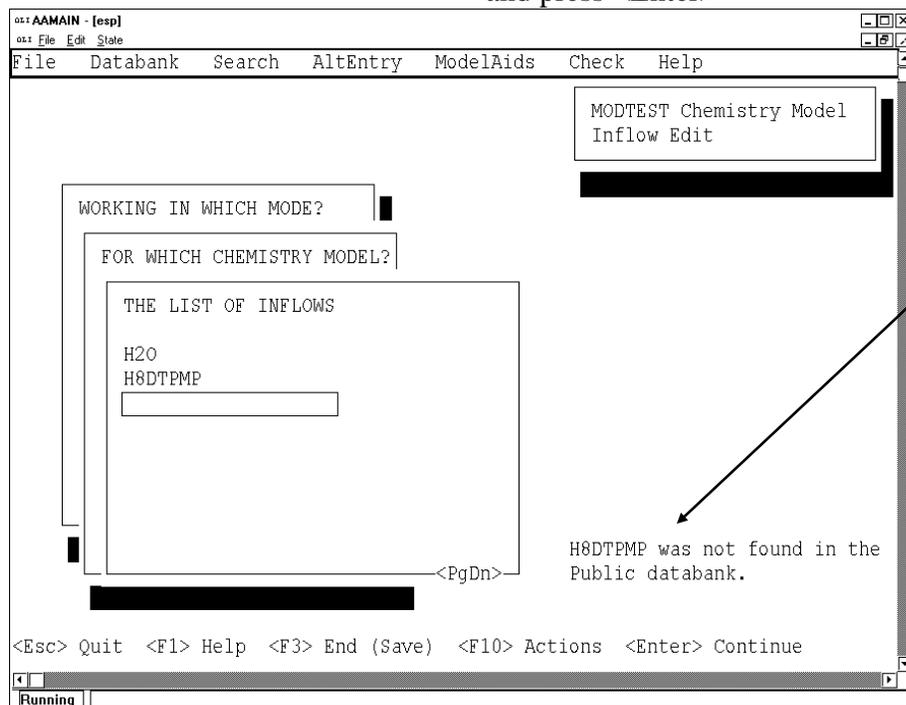


Figure 5-8 Entering species information

**Wait!** There is a warning displayed in the lower right hand-side of the screen. H8DTPMP is not found in the PUBLIC databook.

This is true, we just created the species H8DTPMP in our private databook, NEWCOMP. We need to inform the program that we want to use our private databook.

- o Use the <Action> key or the mouse to select Databank from the action line.
- o. A pull-down menu will appear with a blank line for the databank name. Enter the name NEWCOMP.

*More than one databank can be specified. Up to 10 databanks can be specified.*

*The higher in the list, the higher the priority the database has. For example, if PBCL2 appears in our private database NEWCOMP and we also specify the database GEOCHEM (second line) which also contains PBCL2, then the data in NEWCOMP takes priority.*

*The PUBLIC databank is the lowest priority.*

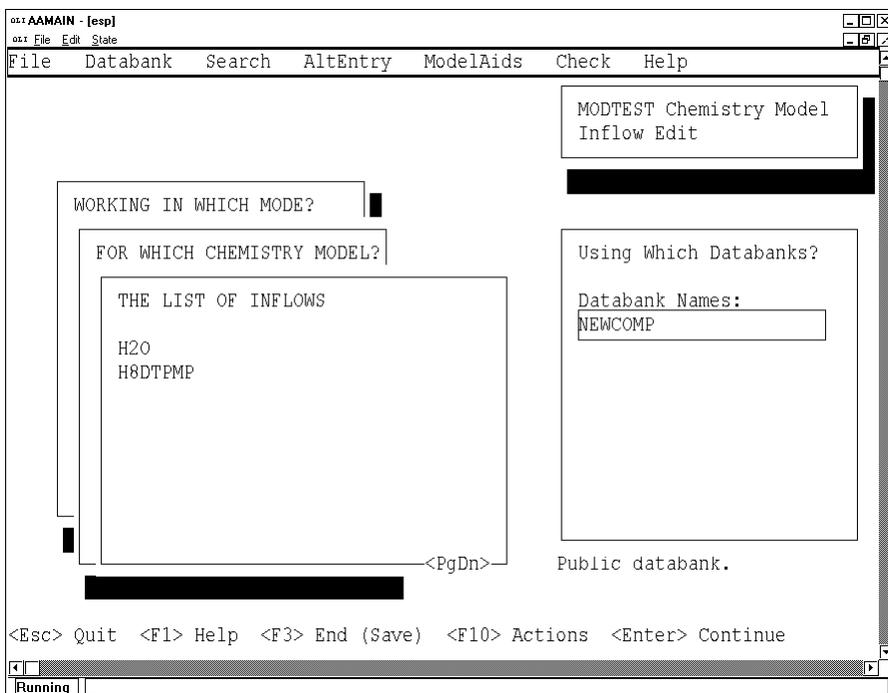


Figure 5-9 Entering the Private databank name

- o At this point, press the <Enter> key to accept NEWCOMP. Finish generating the chemistry model as normal.  
When the generation is complete, select Exit from the screen.

You are now ready to begin simulations using your private databook.



# Warnings!

---

## Limitations

### Data consistency

We have assumed that data compilations, such as Smith and Martell's, contain consistent data. In the tour in chapter 3, the apparent equilibrium constants were obtained from 19 separate sources. Each source most likely used several techniques to obtain their values.

The user should verify that the values obtained match other thermodynamic values. A check of the third law of thermodynamics should be performed to ensure that the new databook is consistent with the OLI PUBLIC databook.

### Temperature Limits

In general, only 25°C data is entered. This allows us to retrieve the equilibrium constant at the reference state. From the equilibrium constant we can get the Gibbs Free Energy of Formation and an estimate of the enthalpy of formation for the species. This is not sufficient to perform simulations at temperatures other than at or near 25°C.

It is recommended that only isothermal calculations be performed. When enthalpy of reaction data is available and provided, temperatures up to approximately 50 °C can be considered.

### Density Limits

This technique does not provide any information about the molar volume of the species. Therefore, any calculations in density for solutions with high concentrations of the estimated complexes are to be suspect. Any transport properties are also suspect. The user should expand the data if these properties are required.

### Excess Properties

These species do not contain any information about the concentration dependence on the equilibria. We have assumed that each species will interact with other charged species in an ideal manner.

This assumption is valid if the concentration of the species remains low. Thus, these species are valid for dilute solutions. Calculations at elevated ionic strengths may have poor results for heats of dilution.

---

## What you should know about this technique?

### ElectroChem

ElectroChem is OLI's older software. To evaluate the infinite dilution equilibrium value, software calls are made to the ElectroChem solvers. Specifically, a new variable is defined called  $K_{\text{apparent}}$ . This value is fixed at a value as reported by the literature.

The ionic strength is held constant at the published value by adjust the amount of the background electrolyte. The OLI  $K$ -value is then adjusted such that the combination of the activity model times the OLI  $K$ -value equals the  $K_{\text{apparent}}$ .

This can generate infinite dilution values which may appear quite different from the published equilibrium constant value.

The results of this calculation can be found in the ElectroChem results file **cmpx.oue**. This file can be difficult to read, and it is beyond the scope of this manual.

## Zero Ionic Strength

This technique can not be used to develop complexes for which the published equilibrium values were obtained at 0.0 molal ionic strength. The program will try to adjust the ionic strength to 0.0 which results in an underflow condition. The program may crash or abort abnormally.



# A Tour of the OLI Databook.

---

## OLI/Databook

The following instructions are designed to take you on a tour through some of the interesting features of OLI Databook.

OLI Systems provides five standard databases that can be used in generating a chemistry model. These databases are:

PUBLIC	This is used in every chemistry model
GEOCHEM	This contains minerals of geological interest
LOWTEMP	Species that exist below ambient conditions are included in this database
CORROSIO	A database to support oxidation/reduction chemistry
LAB	A database containing only molecular weights that supports the WaterAnalyzer Program.

## Overview

In this tour we will review some of the important species data for the mineral  $\text{CaSO}_3$  and the gas carbon dioxide ( $\text{CO}_2$ ).

## The Tour Starts Here ...

- o Please start **ESP**, if you have not done so.

```

Options  Help
The OLI Aqueous Modeling System  V6.2-F
                                July 1, 1999
                                OLI SOFTWARE
                                DATE: 08/25/2000
                                TIME: 10:52:16

SELECTING WHICH PROGRAM?
ESP Process
CSP Corrosion
OLI Databook
OLI ToolKit
OLI Estimate

Current Directory: C:\oli\course
<Esc> Quit    <F1> Help

```

Figure 7-1 ESP Main Menu

- o You will now see the initial window of ESP - "**Selecting Which Program**". You should see that **ESP Process** is highlighted with the cursor bar.

Use the down arrow key to select **OLI Databook**. Press **<Enter>** to select this program. (The up and down **<Arrow Keys>** should be used whenever you would like to move the cursor bar to another line).

```

OPENING WHICH DATABOOK?
ALLOYS
CERAMICS
CMPLX
CORROSIO
GEOCHEM
HEATPUMP
LAB
LOWTEMP
PUBLIC
REFRIGER
                                <PgDn>

```

Figure 7-2 Some of the OLI Provided databooks

- o You will now see the initial window of the OLI Databook - "**Opening Which Databook**". If the PUBLIC database is not

visible, press **the <Down Arrow>** key to find it. When the **PUBLIC** Databank is highlighted press **<Enter>** to continue.

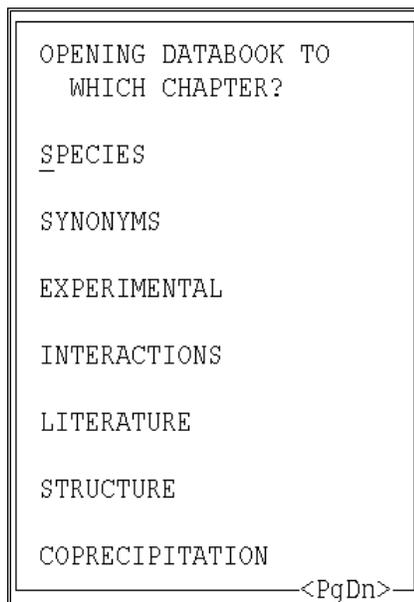


Figure 7-3 List of chapters in databook.

- o You will now be given a choice of several different Chapters. Open OLI Databook to the **SPECIES** Chapter (which is currently highlighted) by pressing **<Enter>**.

## Searching for a Species Via the Periodic Table ...

*In fact, remembering the name of an organic species can be rather difficult. This option is recommended for finding our name for a particular organic species.*

- o ESP now invites you to enter a particular Species Name. Let us suppose that we do not remember the name of the species we are seeking and all we remember is that the species we are looking for contains both calcium (Ca) and sulfur (S).

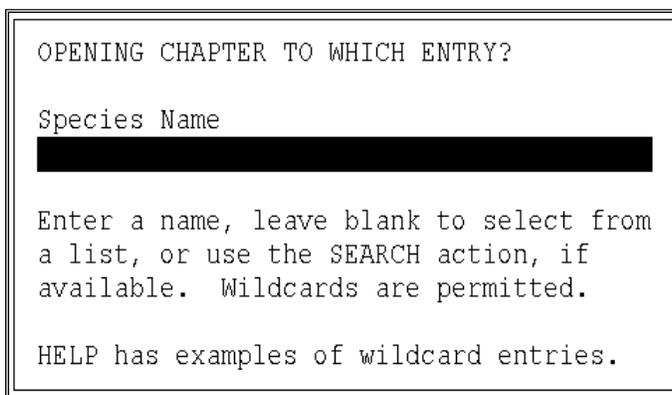


Figure 7-4 Species Entry Screen

The next step should be to press <F10>, the **Action Key**. The Action Key is used throughout ESP as the means of reaching the Action Bar. The first field on the Action Bar, **Search**, will now be highlighted. At this point press <Enter> to select Search.

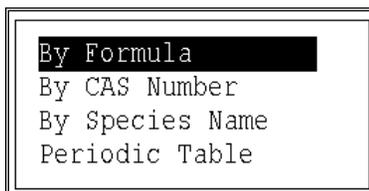


Figure 7-5 Search by screen

- o A pull down menu will now present a series of Search options. Use the down arrow to highlight the **Periodic Table** as the Search option. Once this is done, press <Enter> and the periodic table will be displayed.



```

File  Sort  Help
PUBLIC Databook
SPECIES Chapter
Formula Selection

-12 ENTRIES-
C2Ca2H2O10S  CaO4S
CCaH2O3S     CaS
CCaH2O7S
CaH2O6S2
CaH2O8S2
CaH2S2
CaH4O5S
CaH4O6S
CaHO3.5S
CaO3S
* = duplicate formulas for different compounds

Position and select (press <ENTER>) for data display, or choose an action.
<Esc> Quit   <F1> Help   <F10> Actions

```

Figure 7-7 Search Results

Sometimes there will be several species with the same stoichiometry. An asterisk (\*) will be displayed next to the formula to indicate a duplication.

- o At this point, you will see a display of all species containing both Ca and S. Use the down arrow to highlight CaO3S.

**CaO3S**, is Calcium Sulfite. Press **<Enter>** to access information stored in OLI Databook for this species.

```

SELECT WHICH PART OF THE DATA?

-> General Information
  -> Aqueous Phase
    -> Vapor Phase
      -> Solid Phase

```

Figure 7-8 Calcium Sulfite

## Looking at the Information Stored for Calcium Sulfite ...

The “>” symbol indicates that there is information available. All species have “General Information:

- o We now see that there is General Information as well as Solid Phase data available in the Databank for this solid species. Using the down arrow, you can highlight the **Solid Phase** and press <Enter> to select it.
- o Several data items for the Solid Phase are displayed. Move the cursor bar with the down arrow to the line beginning with **SREF** (Reference State Entropy).

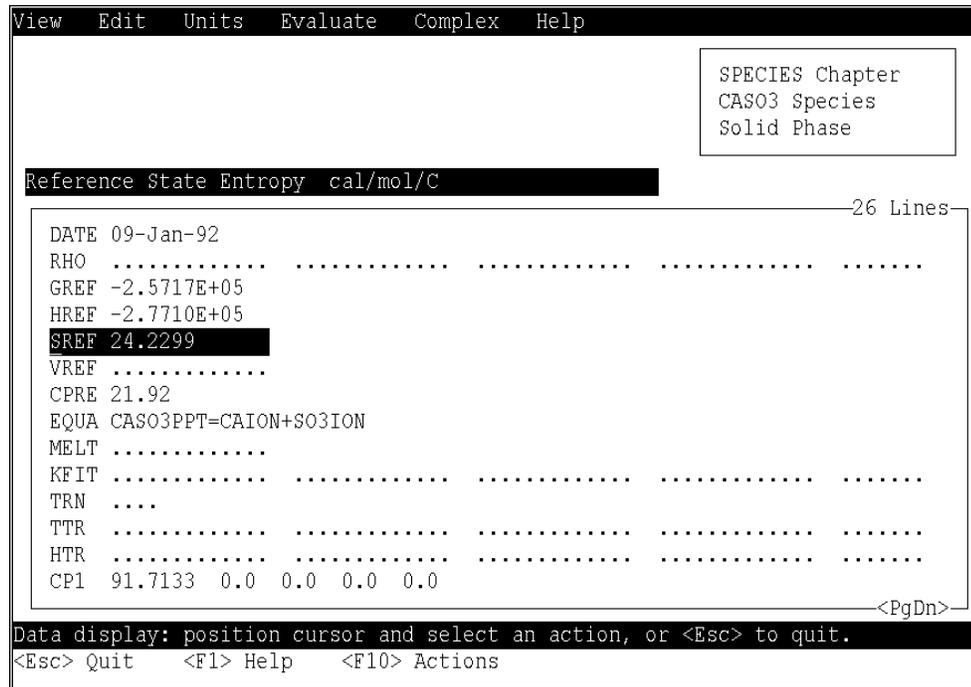


Figure 7-9 Reference State Thermodynamic Data for Calcium Sulfite

The <F1> Help key sometimes is not very helpful.

- o At this point, we can take a small excursion in the tour looking at ESP's online help system. Press <F1>, the **Help Key**, and peruse the description of SREF.

Now, press <Esc>, the Quit Key, to return us to where we were before we selected help. (This is the general convention in ESP for moving back to the just previous step).

- o Continuing the tour of the data, press the **Action Key** to move to the Action Bar. The first field on the Action Bar, **View**, will now be highlighted. Press <Enter> for a pull down menu of View options.

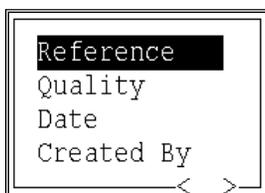


Figure 7-10 View List Items

- o You can now view various information about this data entry. Since the **Reference** option is highlighted, press **<Enter>** to review the detailed reference.

Note that since this reference is a Multi-volume compilation of data, the ESP reference includes the specific volume and page number on which the data appears. To continue the tour, press **<Enter>** to return to the choices on the View menu.

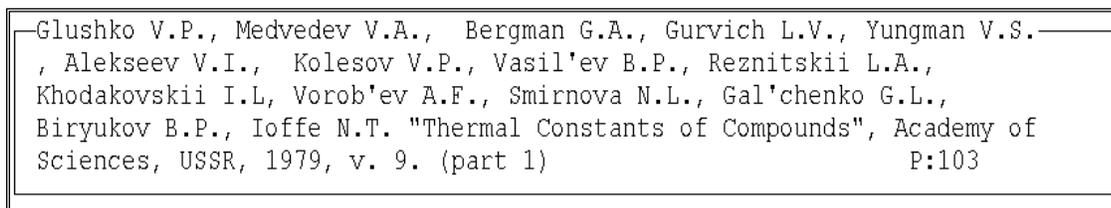


Figure 7-11 The infamous Russian Handbook

*The data is stored in SI units (or nearly so) and therefore the units on the uncertainty is Joule/Mole/K*

- o Now highlight the **Quality** option, and press **<Enter>** to look at the information on uncertainty. When you are ready to continue, press **<Enter>** again to go back to the View menu.

We have now completed our excursion into calcium sulfite data.

## Perusing the Data on the Vapor Pressure of CO<sub>2</sub> ...

*By this time in the tour we hope you are comfortable with the <Esc> key and the <Action> key to move around. We will be providing less and less illustrations as we progress.*

- o To continue the tour, we now use **<Esc>** repetitively to work back to the page of OLI Databook, - "**Opening Chapter to Which Entry**", where we describe the species of interest.
- o The cursor will now be on the field which invites us to Enter a species name. Please Enter **CO<sub>2</sub>** (all caps) being sure that the

entry is followed by all blank characters. At this point press **<Enter>** so that the data for CO<sub>2</sub> can be made available.

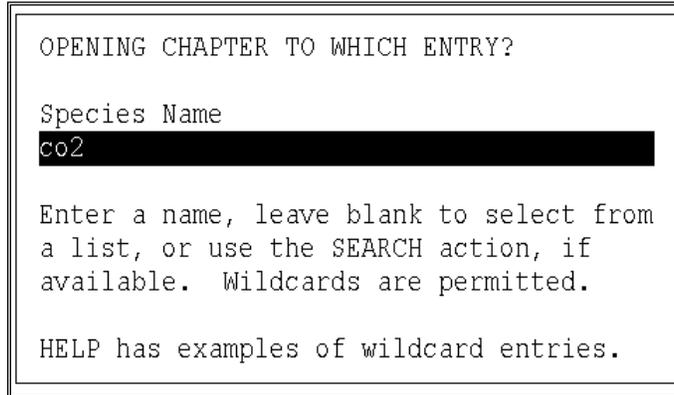


Figure 7-12 Entering CO<sub>2</sub>

- o The next step is to highlight the **Vapor Phase** information. Once this is done, pressing **<Enter>** will give us access to this information.



Figure 7-13 Reference State thermodynamic values for CO<sub>2</sub> in the vapor phase

*Vapor pressure (as well as heat capacity) are functions of temperature. Any record in the database with more than one value in it is most likely a temperature dependent function.*

- o To access more information about the vapor pressure, highlight the line that begins with **"VP"**. This line contains the curve fit coefficients for vapor pressure.

Using **Action Key** we can activate the Action Bar. The **View** facility will be highlighted; press **<Enter>** to display the alternatives offered on the corresponding pull down menu.

- o Since the **Reference** option of the pull down menu is already highlighted, press **<Enter>** to look at the reference. Press **<Enter>**, then **<Esc>** to return to the Action Bar.
- o Using the right arrow key, move to the **Evaluate** facility and press **<Enter>**. The Evaluate Action will prompt for a value for temperature at which to evaluate the vapor pressure equation. Fill in any value for temperature, press **<Enter>**, and the corresponding calculated value will be computed and displayed.

```

Y=EXP(a+b/T+c*LN(T)+d*T**e)           Trange: -56.57
                                           To 31.06      C
Enter Temp: 25 C
Calc'd Value:          atm              (Calcs in SI units)

```

Figure 7-14 The evaluate action, enter 25 C

*If the temperature entered is outside the displayed temperature range for the fit of vapor pressure, a warning message will be displayed on the message line at the bottom of the screen.*

- o Enter 25 C and press **<Enter>**

```

Y=EXP(a+b/T+c*LN(T)+d*T**e)           Trange: -56.57
                                           To 31.06      C
Enter Temp: 25. C
Calc'd Value: 63.6357 atm              (Calcs in SI units)

```

Figure 7-15 The results of the evaluate action

## Dynamically Changing the Units for OLI Databook Displays ...

- o We can now press the **Quit Key (<Esc>)** and return to the Action Bar. To continue the tour, you should use the left arrow key to highlight the **Units** facility on the Action Bar. Press **<Enter>** to pop up the window which allows changes to the display units.
- o The cursor will be active on the field which allows entire default systems of units to be set. Using the right arrow, toggle to **ENGLISH** units and press **<Enter>** to activate these units.

*The coefficients in the temperature dependent equations and not always just a function of temperature so we do not change the scalar values during this operation.*

At this point, all scalar values should be changed to the new system of units. If you press the Action Key to go back to the Action Bar and then, the right arrow to go back to **Evaluate** and then, <Enter> to reactivate the calculator mode, you will now see the displayed temperature range for the fit in the new units.

You can now repeat the earlier type of calculation, but in the new system of units. When done, press <Esc> repetitively to back out to the Chapter Selection window of OLI Databook.

## Viewing the Experimental Data for the CO<sub>2</sub> Vapor Pressure ...

*There is a very large amount of experimental data that OLI has used to fit these components that has not yet been incorporated into the database. Contact OLI for more information*

In addition to providing a Reference for the curve fit coefficients for the CO<sub>2</sub> vapor pressure (which we examined earlier), OLI Databook allows us to access the several data sets upon which the fit was based.

- o To begin this excursion, please highlight the **Experimental Chapter** line on the current display and press <Enter>. At this point, OLI Databook is opened to the Experimental Chapter.
- o You should now see a window which allows you to access the actual experimental data sets used for the coefficient fits for those particular properties which are a function of temperature. The highlight should be on **Vapor Pressure**, so just press <Enter>.

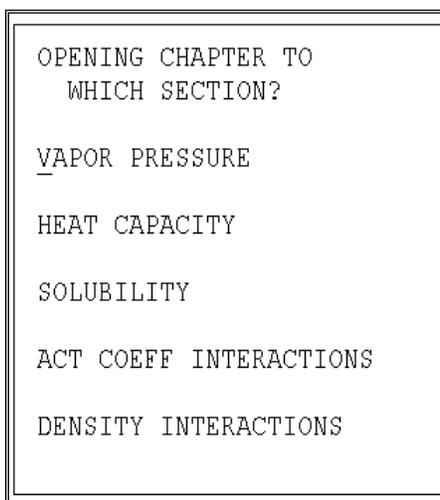


Figure 7-16 Experimental Chapters

If the name is not entered, just enter the name.

Why the fourth? This is the data set actually used by OLI (and it looks the best)

- o The next window, which requests the Species Name, will already have **CO2** filled in, so press **<Enter>** to continue.
- o We now see five data set choices displayed. These are the five actual experimental data sets upon which the coefficients for VP are based.

Let's **highlight the fourth** of these data sets. At this point, press the **Action Key** and the **View** facility on the Action Bar will be highlighted. Press **<Enter>** to pull down the View menu.

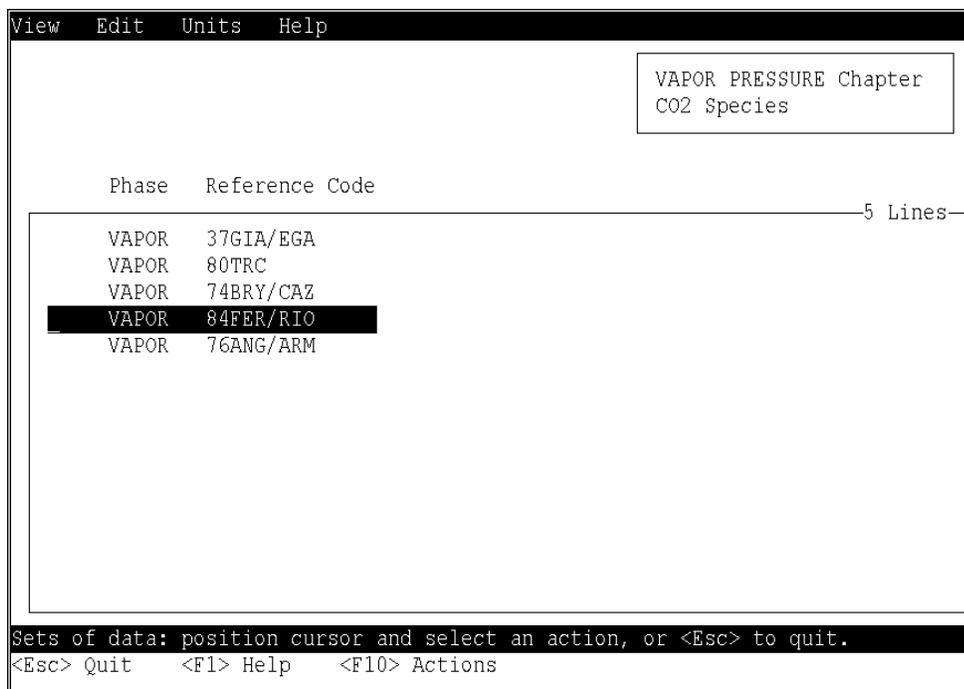


Figure 7-17 Data sets for CO2 vapor pressure

- o The **Reference** option will be highlighted. Pressing **<Enter>** will allow us to look at the reference. Pressing **<Enter>** again will bring us back to the pull down menu for View.
- o Continue by highlighting the **Data** option of the pull down menu. By pressing **<Enter>**, we will be able to peruse the experimental data.

*You may notice that some of the experimental data sets are beyond the range of the coefficients for the OLI model. This is because the data in the Experimental Chapter includes the DIPPR pure component data for that property.*

## Plotting the Experimental Data ...

- o The next excursion on our tour through the Databook will be to look at a plot of the data. We do this by using the **Action Key** and moving to the Action Bar. By using the right arrow, we can move to the **Plot** facility on the Action Bar and then press **<Enter>** to obtain a plot of the stored data versus the plot based upon the curve fit.

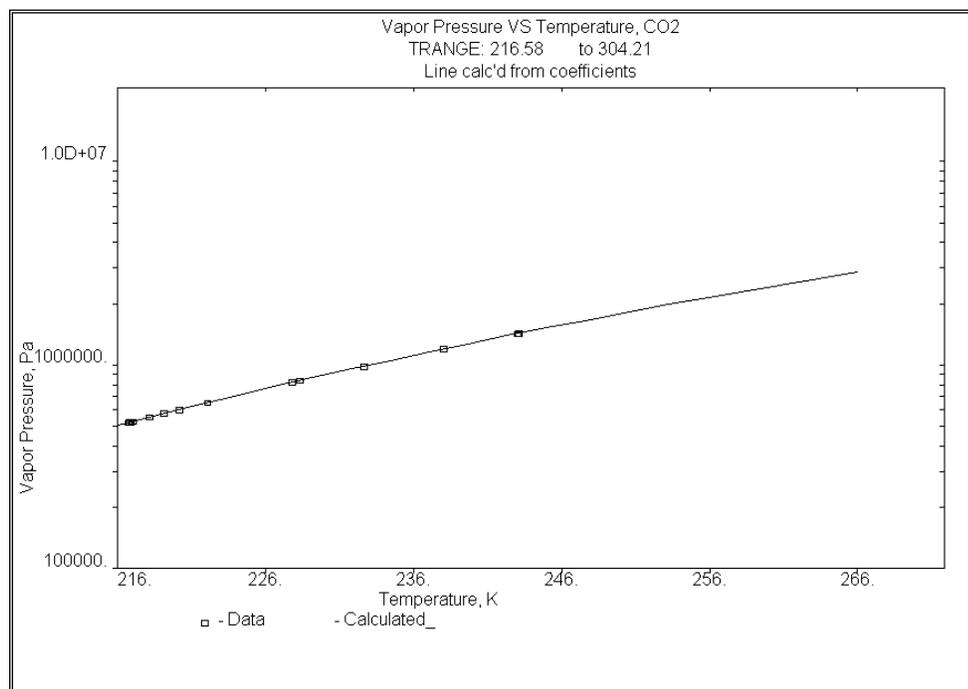


Figure 7-18 A plot of the vapor pressure of CO<sub>2</sub> v. Temperature. The fitted range is at the top of the figure.

- o By pressing **<Esc>** repetitively, we can now go back to the Chapter Selection Menu.

## Viewing the Structure of an Organic Species ...

- o The final excursion on our tour through the Databook will be to look at the structural drawing for an organic species. Start by selecting the **Structure Chapter**. After highlighting this Chapter, press **<Enter>** to open this Chapter of the Databook.
- o To find an interesting organic species to display, type in the wildcard species name: **BENZ\***. The first screen of a list of all of

the species containing BENZ at the start of their name will be displayed.

OPENING CHAPTER TO WHICH ENTRY?

Species Name  
Benz\*

Enter a name, leave blank to select from a list, or use the SEARCH action, if available. Wildcards are permitted.

HELP has examples of wildcard entries.

Figure 7-19 Using a Wildcard '\*'

*The structure is displayed with out any of the hydrogen atoms (which clutter the screen). The user is left to remember their organic chemistry to fill in the missing H's.*

**Highlight the species *Benzidine*** and then press <Enter>. The structure, headed by the ESP internal name, BENZIDINE, is then displayed.