C H A P T E R **16**

Basic Calculations

This chapter will introduce basic concepts that are important in running any type of chemical equilibrium problem.

■ *Lesson 1* will bring you through the basic process of setting up a problem, reviewing your equilibrium model, running a calculation, and viewing your output.

■ *Lesson 2* will show you the three ways to address pH in MINEQL+: as a known, fixed value; calculated from the total H^+ concentration; or calculated using electroneutrality.

■ *Lesson 3* will show you how to handle dissolved CO_2, whether as a system that is closed to the atmosphere or open. It will also show you how to estimate the amount of inorganic carbon in the system from pH and alkalinity measurements.

Lesson 1: Performing a Single Calculation

The purpose of this lesson is to demonstrate the process of running a chemical equilibrium problem. The problem has been purposely kept simple so that you can focus on key elements in setting up the problem: reviewing data, running the calculation, and reviewing output.

The System A container of water has the following chemical components:

Parameter	Value
$[Ca^{2+}]_T$	10^{-4} M
$[PO_4^{3-}]_T$	$5x10^{-5}$ M

pH will not be addressed in this lesson. We will use the default pH value of 7.00 in this example.
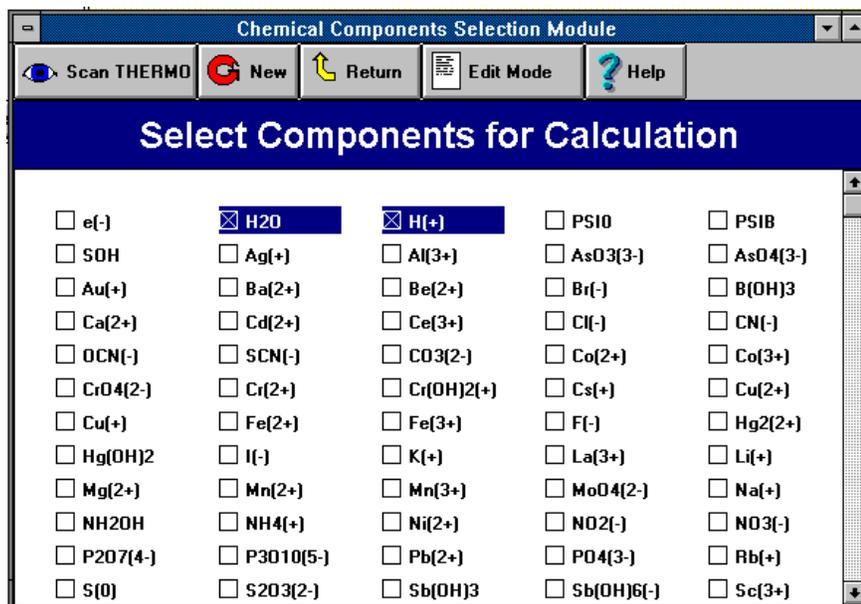
The Goal To set up a simple chemical equilibrium problem and display its output.

Methods Start MINEQL+ by double-clicking on its icon from within the Window's Program Manager. If this is the first time you are running MINEQL+, the *AutoPilot* will be initialize when the program starts up. This in turn will open the *Select Components* tool.

The Select Components Tool

Chemical Components Selection Module

Scan THERMO | New | Return | Edit Mode | Help

Select Components for Calculation

☐ e(-)	☒ H2O	☒ H(+)	☐ PSI0	☐ PSIB
☐ SOH	☐ Ag(+)	☐ Al(3+)	☐ AsO3(3-)	☐ AsO4(3-)
☐ Au(+)	☐ Ba(2+)	☐ Be(2+)	☐ Br(-)	☐ B(OH)3
☐ Ca(2+)	☐ Cd(2+)	☐ Ce(3+)	☐ Cl(-)	☐ CN(-)
☐ OCN(-)	☐ SCN(-)	☐ CO3(2-)	☐ Co(2+)	☐ Co(3+)
☐ CrO4(2-)	☐ Cr(2+)	☐ Cr(OH)2(+)	☐ Cs(+)	☐ Cu(2+)
☐ Cu(+)	☐ Fe(2+)	☐ Fe(3+)	☐ F(-)	☐ Hg2(2+)
☐ Hg(OH)2	☐ I(-)	☐ K(+)	☐ La(3+)	☐ Li(+)
☐ Mg(2+)	☐ Mn(2+)	☐ Mn(3+)	☐ MoO4(2-)	☐ Na(+)
☐ NH2OH	☐ NH4(+)	☐ Ni(2+)	☐ NO2(-)	☐ NO3(-)
☐ P2O7(4-)	☐ P3O10(5-)	☐ Pb(2+)	☐ PO4(3-)	☐ Rb(+)
☐ S(0)	☐ S2O3(2-)	☐ Sb(OH)3	☐ Sb(OH)6(-)	☐ Sc(3+)

By default, **H2O** and **H(+)** are always selected for a new problem. Although it is possible to de-select these components, it is not advisable if you are going to use the default thermodynamic database supplied with MINEQL+. In practically all cases you should include these two components.

Since this is a Ca-PO$_4$ system, we will need to include these two components in our problem in addition to **H2O** and **H(+)**. Use the mouse to click on **Ca(2+)** and then **PO4(3-)** from the list of components shown on the screen.

Components Selected
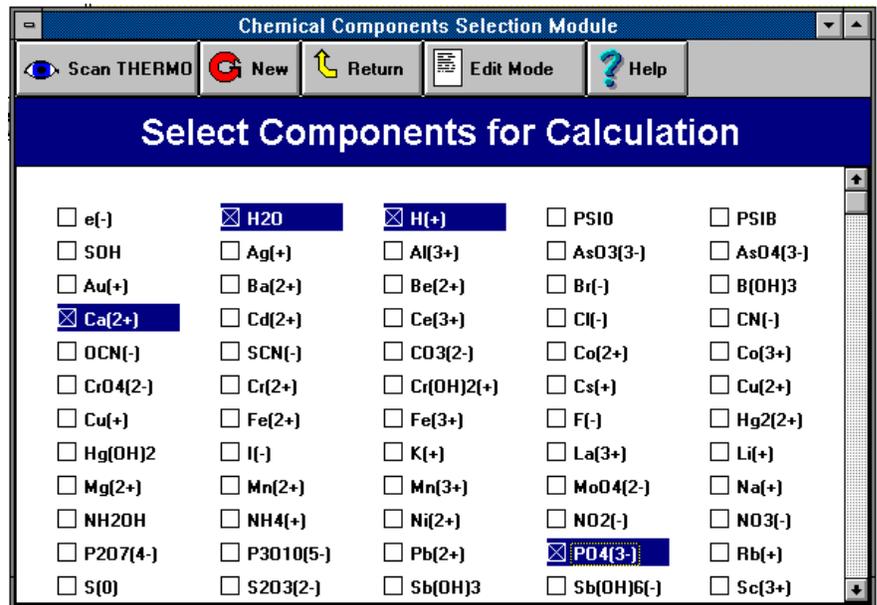
Again, using your mouse, press the **Scan Thermo** button in order to extract the reaction data you'll need to run this problem. The reaction data for chemical species is stored in the default thermodynamic database and the **Scan Thermo** button tells MINEQL+ to extract only those reactions that are appropriate for the components you have selected.

The next screen that appears is the *Tableau* tool for aqueous species. Aqueous species include dissolved complexes and ion pairs in solution. If we wanted to, we could add new species using the *Tableau* tool or delete species that we didn't want in the problem. For this problem, we will just review the data and except the default configuration of species. We could use the *Tableau* tool to input the total concentrations of Ca^{2+} and PO_4^{3-}, however, in this lesson we will use the *Totals Wizard*, which is described later. Press the **Close** button.

Tableau Tool with Aqueous Species

Type II – Aqueous Species						
⊕ Insert ✎ Delete ⊤ Move ↻ Close ▦ Wizard ? Help						

Name		H2O	H(+)	Ca(2+)	PO4(3-)	Log K	Delta H
OH–	(–1)	1	–1	0	0	–13.997	13.339
CaOH+	(+1)	1	–1	1	0	–12.697	15.323
CaH2PO4+	(+1)	0	2	1	1	20.923	–1.4348
CaHPO4 (aq)		0	1	1	1	15.035	–0.71780
H2PO4–	(–1)	0	2	0	1	19.573	–4.3828
HPO4–2	(–2)	0	1	0	1	12.375	–3.5858
H3PO4		0	3	0	1	21.721	–2.4148
CaPO4–	(–1)	0	0	1	1	6.4600	3.1808

Total Conc. (M) –>	0.000E+00	0.000E+00	0.000E+00	0.000E+0

The *Tableau* tool will disappear and a software tool will appear that will allow you to choose whether you wish to look at other types of reaction data in your system.
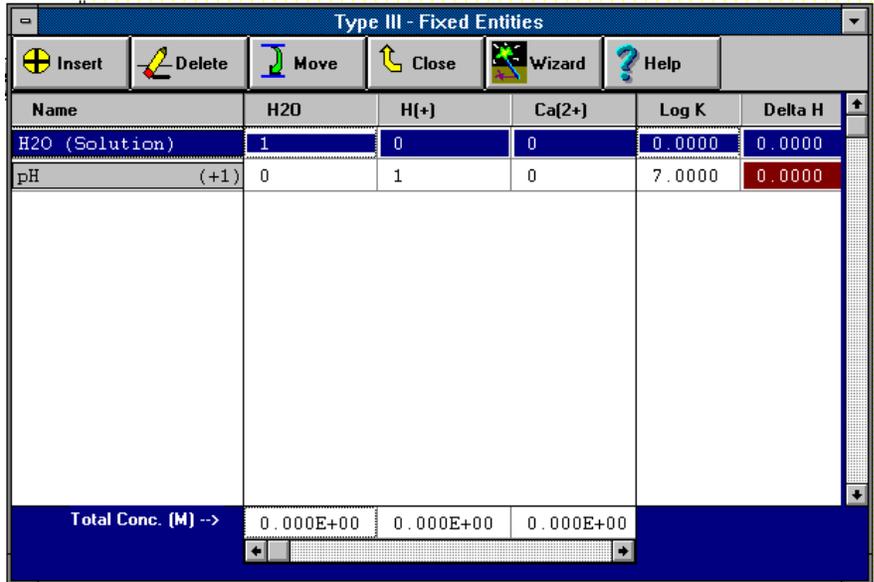
The Tableau Switch
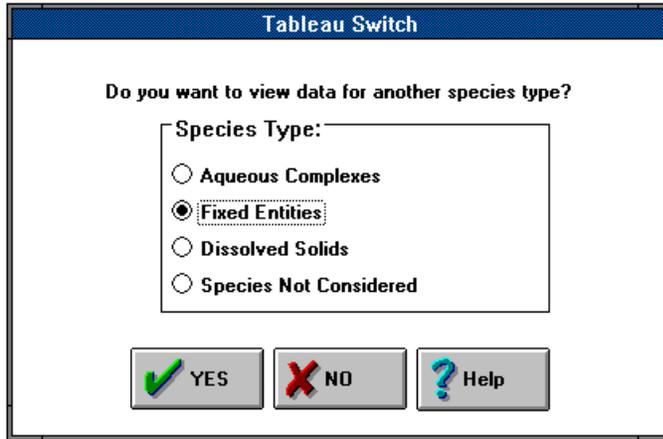
Make sure the **Fixed Entities** button is selected and press the **Yes** button to open the tableau for *Fixed Entities*.
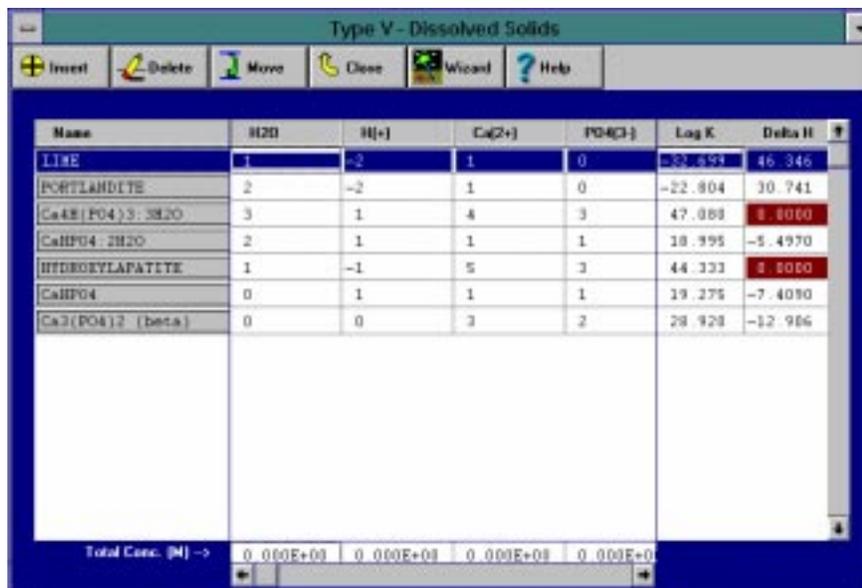
The Tableau Tool with Fixed Entities

Name	H2O	H(+)	Ca(2+)	Log K	Delta H
H2O (Solution)	1	0	0	0.0000	0.0000
pH (+1)	0	1	0	7.0000	0.0000
Total Conc. (M) -->	0.000E+00	0.000E+00	0.000E+00		

The *Tableau* tool is open again, this time showing only the chemical species that will be held at a fixed concentration. In our case this includes H_2O, which has a fixed activity of 1, and pH which will be set at the default value of 7.00. For more information about pH and pH calculations see Lesson 2.

Press the **Close** button. Make sure the **Dissolved Solids** button is selected and once again press the **Yes** button to look at the tableau for *Dissolved Solids*. This tableau contains a list of solids that have the potential to precipitate if their solubility constraints are exceeded. In effect, they are a database of solids which may or may not participate in the equilibrium solution, and their participation will depend upon the conditions of solubility in the system. Once again, we will accept these default species for our problem.

The Tableau Tool with Dissolved Solids

Name	H2O	H^{+}	Ca(2+)	PO4(3-)	Log K	Delta H
LIME	1	-2	1	0	-32.699	46.346
PORTLANDITE	2	-2	1	0	-22.804	30.741
Ca4H(PO4)3:3H2O	3	1	4	3	47.088	0.0000
CaHPO4:2H2O	2	1	1	1	18.995	-5.4970
HYDROXYLAPATITE	1	-1	5	3	44.333	0.0000
CaHPO4	0	1	1	1	19.275	-7.4090
Ca3(PO4)2 (beta)	0	0	3	2	28.928	-12.986

Total Conc. [M] -->	0.000E+00	0.000E+00	0.000E+00	0.000E+00

Click on the **Close** button and this time press the **No** button to stop opening the *Tableau* tool.

The *RunTime Manager* will open at this point. We need to set the total molar concentration of calcium and phosphate for our system. Press the **Wizard** button located at the bottom of the *RunTime Manager*.

The RunTime Manager
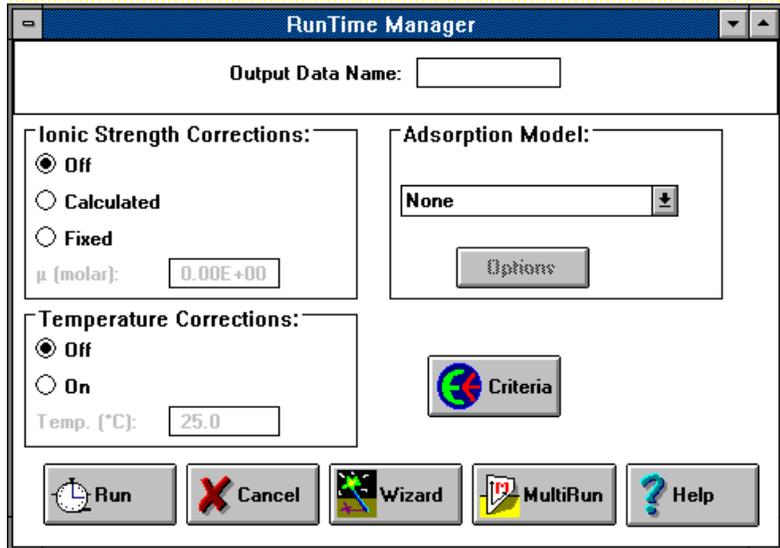
The *Totals Wizard* will appear. Type in 1E-4 for *Ca(2+)* and 5E-5 for *PO4(3-)*.

The Totals Wizard

Calculation Wizard				
✔ OK	✖ Cancel	❓ Help		
Totals	pH	CO2	Solids Mover	Redox

Component	Total C (M):
Ca(2+)	1.000E-04
PO4(3-)	5.000E-05

Press the **OK** button when you're finished.
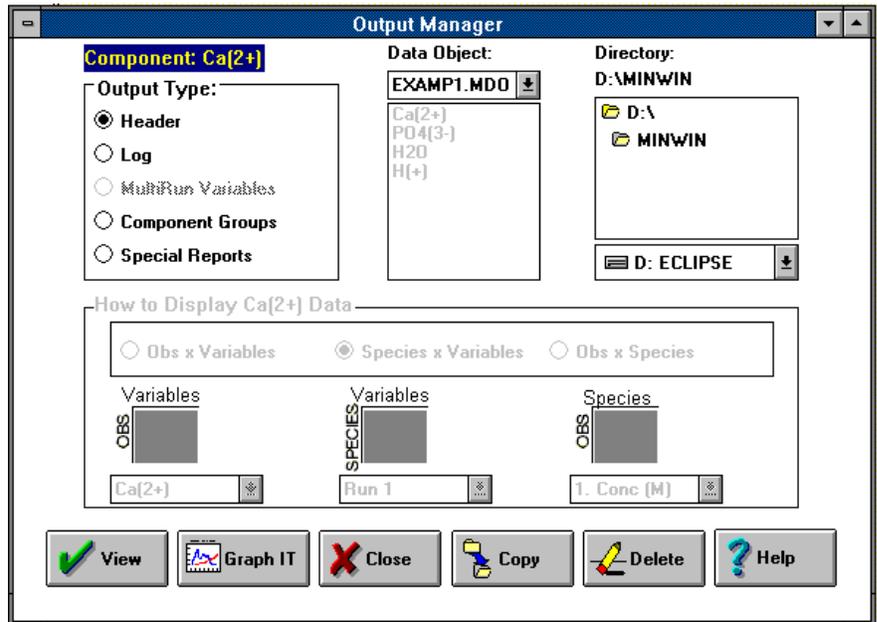
At the top of the *RunTime Manager*, there is a field labeled *Output Data Name*.
Use your mouse to select this field and type in the name **EXAMP1.** Now click the
Run button to perform the calculation.

Output Data Name: EXAMP1

After a second or two, the calculation will be completed and the *Output Manager* will appear.

The Output Manager

The Output   Press the **GraphIT** button at the bottom of the *Output Manager*. The *Graphics Manager* will appear.

The Graphics Manager

```
┌─────────────────────────────────────────────────────────────────┐
│ ▬                        Graphics Manager                         │
├─────────────────────────────────────────────────────────────────┤
│           Object File: EXAMP1.MDO      Run Type: SINGLE RUN       │
│                                                                   │
│  Graph Title: [                                                 ] │
│                                                                   │
│                                                                   │
│          Graph Type:  [Bar Chart    ▩]   X Axis: [None      ▩]    │
│          Component:   [Ca(2+)        ▼]   Y Axis:                 │
│          Observation: [Run 1         ▼]   ☐ 1: Ca(2+)         ▲   │
│          Units:       [% Total       ▩]   ☐ 2: CaOH +    (+1)     │
│                                           ☐ 2: CaHPO4 AQ          │
│                                           ☐ 4: Ca5OH(PO4)3        │
│                                           ☐ 5: PORTLANDITE        │
│          [✔ Plot]  [✘ Cancel]  [? Help]   ☐ 5: LIME              │
│                                           ☐ 5: CaHPO4        ▼    │
│                                                                   │
└─────────────────────────────────────────────────────────────────┘
```

This tool will allow you to display a horizontal bar chart that represents the distribution of chemical species for a given component. Move the mouse to the *Component* combo box and select **PO4(3-)**. Press the **Plot** button to display the graph.

Print

Help

Distribution of Phosphate Species for a Single Run.

```
PO4(3-)   (5.74E-11 M)
CaH2PO4+  (3.63E-08 M)
CaHPO4 (aq)  (4.70E-07 M)
H2PO4-    [XXXXXXXXXXXXXX]  (2.15E-05 M)
HPO4-2    [XXXXXXX]  (1.36E-05 M)
H3PO4     (3.02E-10 M)
CaPO4-    (1.25E-08 M)
HYDROXYLAPAT  [XXXXXXX]  (4.80E-06 M)

          0        20        40
                 Percent
```
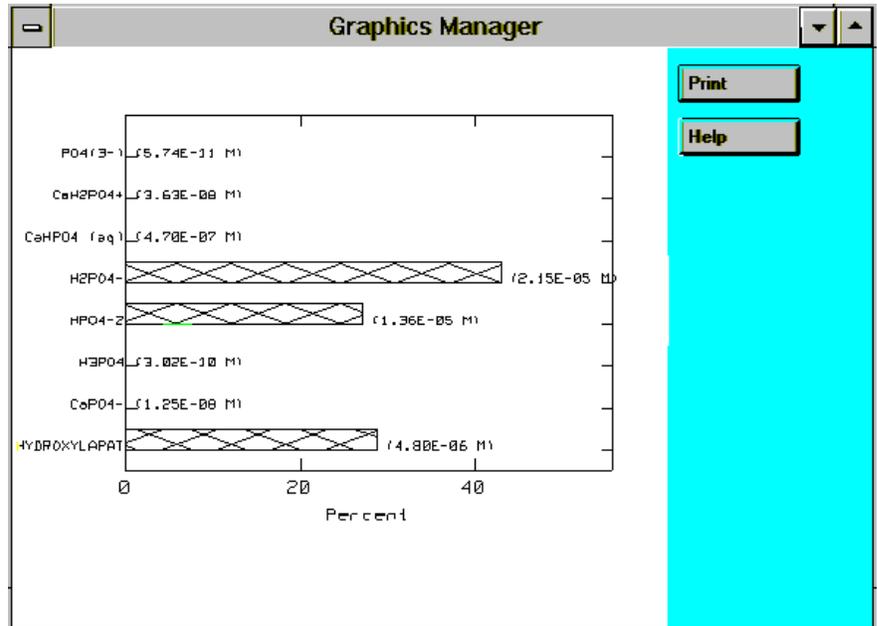
At a glance, we can see that most of the PO_4 is contained in $H_2PO_4^-$, HPO_4^{2-}, $Ca_5OH(PO_4)_3$ (which is a solid phase).

Output Type:
- ○ Header
- ○ Log
- ○ MultiRun Variables
- ◉ Component Groups
- ○ Special Reports

Alternatively, we could display the output in tabular form. Using the *Output Manager*, select the **Component Groups** button, then select **PO4(3-)** from the list of components in the middle of the screen. Press the **View** button to see the data.

```
Ca(2+)
PO4(3-)
H2O
H(+)
```

Notice that all the PO$_4$ species are presented in one table. The name of each species is listed in the 3rd column of this table. The 4th column has the species type listed. Types 1 and 2 refer to dissolved species; Type 3 are fixed entities and Type 4 are precipitated solids. Type 5 are solids that had the potential to precipitate but did not and therefore are not included in the calculation. Type 6 are species that are not considered in the calculation. Type 7 is a pseudo-species since it refers to the total dissolved concentration of that component in solution. This number may be different than the total concentration that you entered at the beginning of the problem because it does not include solids that have precipitated.

The 5th column contains the molar concentration of each species.   The 6th column shows the log of the concentration.

Although not shown in the tabular output above, the following columns can be accessed by scrolling the table to the right. The 7th column shows the log K value. This is the value that is used in the calculation after temperature and ionic strength corrections have been performed, which may be different than the 25 °C and $\mu =$ 0.0 log K displayed in the tableau. The 8th column shows the percentage of the total concentration distributed in each species. The 9th column shows the stoichiometric coefficient of the component in a particular species. For instance, if there is a species with two PO$_4^{3-}$ present, then the value listed in this column would be 2.

Try selecting a different component from the component list in the *Output Manager* and pressing **View** button. This allows you to view the species data for each component separately. This is a fairly powerful feature of the *Output Manager* and will be discussed further in Lesson 4.

Sometimes you may not want to have the speciation data broken into separate component tables; for example, you may want to group all the speciation data together, which can be accomplished using one of the special reports. Use the mouse to click off the **Special Reports** option and press the **View** button. A software tool will appear that will allow you to select the type of report you want to use.

Output Type:
- Header
- Log
- MultiRun Variables
- Component Groups
- ● Special Reports

Use the combo box to select the last report called **Summary of All Species for a Single Run**. Press the **OK** button to generate the report.

A Summary Report which Compiles Speciation Output for All Components

```
┌──────────────────────────────────────────────────────────────────────────┐
│ ▬        Summary of All Species for a Single Run              ▼  ▲         │
├──────────────────────────────────────────────────────────────────────────┤
│ Save  │ Print │ Clip Board │ Help │                                       │
├──────────────────────────────────────────────────────────────────────────┤
│ MINEQL+ Ver 4.5                                      Page 1               │
│ Data Extracted from : TEST.MDO                                            │
│                       SINGLE RUN SUMMARY                                  │
│ ──────────────────────────────────────────────────────────────          │
│ This report compiles the output data (concentration, Log C,              │
│ Log K) for all species within a single run.                              │
│ ──────────────────────────────────────────────────────────────          │
│ ~                                                                        │
│ MINEQL+ Ver 4.5                                      Page 2               │
│ Data Extracted from : TEST.MDO                                            │
│ Run: 1                                                                    │
│      ID              Species        Conc.      Log C       Log K          │
│ ──────────────────────────────────────────────────────────────          │
│                                                                          │
│ Type I - COMPONENTS                                                       │
│       2 H2O                         1.000E+00    0.000      0.000         │
│       3 H(+)                        1.000E-07   -7.000      0.000         │
│      16 Ca(2+)                      7.550E-05   -4.122      0.000         │
│      54 PO4(3-)                     5.740E-11  -10.241      0.000         │
│                                                                          │
│ Type II - COMPLEXES                                                       │
│    3800 OH-              (-1)       1.010E-07   -6.997    -14.000         │
│    7300 CaOH+            (+1)       1.520E-10   -9.819    -12.700         │
│   28403 CaH2PO4+         (+1)       3.630E-08   -7.440     20.920         │
│   28700 CaHPO4 (aq)                 4.700E-07   -6.328     15.040         │
│   41000 H2PO4-           (-1)       2.150E-05   -4.668     19.570         │
│   41100 HPO4-2           (-2)       1.360E-05   -4.866     12.380         │
│   41200 H3PO4                       3.020E-10   -9.520     21.720         │
│   71902 CaPO4-           (-1)       1.250E-08   -7.903      6.460         │
│                                                                          │
│ Type III - FIXED ENTITIES                                                 │
│    3801 H2O (Solution)                                      0.000         │
│                                                                     ▼     │
│ ← │                                                               │ →     │
└──────────────────────────────────────────────────────────────────────────┘
```

The report shows the concentration, log C, and log K values for all species broken down by species type for a single run.

Summary

In this lesson, we have shown

■ How to define a chemical equilibrium problem by selecting components
■ How to review your input reaction data using the *Tableau* tool
■ How to set the total concentration of a component using the *Calculation Wizard*
■ How to set an output name and run a calculation using the *RunTime Manager*
■ How to display a horizontal bar chart for a single run
■ How to display speciation data for a single component using tabular format
■ How to group speciation data together into a single report using the **Special Reports** option