

# A USER-FRIENDLY INTERFACE TO COMPUTER PROGRAMS FOR THE DETERMINATION OF THE CHARACTERISTICS OF EQUILIBRIUM SYSTEMS FROM PHYSICOCHEMICAL DATA

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**Abstract:** A Graphical user interface to programs for the determination of equilibrium parameters from physicochemical data (GOLEM) has been worked out. The program converts input data written in common chemical language into the algebraic form required by the programs that do actual computations. This includes translation of chemical equations into algebraic form and building up the history of the preparation of solutions. The program works on PC/DOS platforms and in the current version prepares the data for the program STOICHIO (J. Kostrowicki, A. Liwo, *Comput. Chem.*, 1987, **11**, 195; *Talanta*, 1990, **37**, 645) which determines the stoichiometry and equilibrium constants from physicochemical measurements.

## 1. Introduction

Studying solution equilibria continues to be an important task of physical chemistry. Measuring and processing experimental characteristics of equilibrium systems, such as electromotive force, absorbance, osmotic pressure, etc., allows one to determine the composition and thermodynamic parameters (usually equilibrium constants) of a system. Parameter determination is usually accomplished using the non-linear least-squares method. Complicated equilibrium systems must be treated using general algebraic description, which is hard to digest for a typical solution chemist. Therefore, although software for the determination of equilibrium parameters in a general case

are available, they are difficult to use for a typical chemist, because of the need of switching from common chemical language to algebraic language. A translator from the chemical language into general algebraic formulation of chemical equilibria is therefore necessary. This work describes such a translator developed in our group. It is interfaced to the program STOICHIO [1, 2] that determines the stoichiometry and equilibrium constants from physicochemical measurements by non-linear confluence analysis.

## 2. Determination of equilibrium parameters

### *Matrix representation of chemical equations*

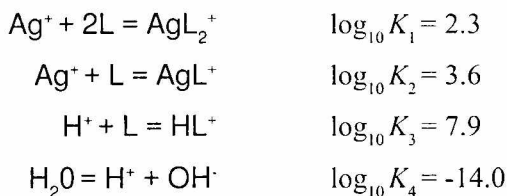
The values of stoichiometric coefficients, equilibrium constants and other important parameters are usually determined from physicochemical measurements. Measured quantities are functions of equilibrium concentrations of the chemical species present in a system. The state of an equilibrium system is described by the vector of equilibrium concentrations of all species,  $C$  [1, 2]:

$$C = [C_1, C_2, C_3, \dots, C_n]^T \quad (1)$$

where  $C_i$  is the concentration of  $i$ -th species.

Chemical reactions can be described as a matrix whose elements are the algebraic stoichiometric coefficients, reactants having been transferred to the right side. This matrix will be called the *stoichiometric matrix*, and identified by symbol  $A$ ;  $a_{ij}$  will denote the stoichiometric coefficient at  $j$ -th species in  $i$ -th reaction. Each  $a_{ij}$  is positive for a product, negative for a substrate and zero for a species that does not take part in the specified reaction. Physically, the stoichiometric coefficients are rational numbers, but for the purpose of optimization it is convenient to treat them as real numbers. Using matrix notation allows for uniform description of various equilibrium schemes, e.g. acid-base, complex formation, redox, etc.

As an example, consider a simple system where equilibrium takes place between  $\text{Ag}^+$  and triethanolamine (denoted by L). Assume that the following equilibria coexist in the system:

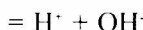


The corresponding stoichiometric matrix is shown below (Figure 1):

$$\begin{bmatrix} [\text{AgL}_2]^+ & [\text{AgL}]^+ & [\text{HL}]^+ & \text{OH}^- & \text{Ag}^+ & \text{L} & \text{H}^+ \\ 1. & 0. & 0. & 0. & -1. & -2. & 0. \\ 0. & 1. & 0. & 0. & -1. & -1. & 0. \\ 0. & 0. & 1. & 0. & 0. & -1. & -1. \\ 0. & 0. & 0. & 1. & 0. & 0. & 1. \end{bmatrix}$$

**Figure 1.** The stoichiometric matrix of silver(I) — triethanolamine system. The components are  $\text{Ag}^+$ , L and  $\text{H}^+$ . Any other species are treated as complexes.

Note that the stoichiometric matrix does not contain water. This is caused by the fact that water is always in excess with respect to all other reactants and therefore its concentration can be considered approximately constant. This means that the last chemical equation can formally be considered a “creation” process (see Figure 1):



### Mass balance and equilibrium equations

Any change in the concentration of  $j$ -th component can be expressed as a product  $a_{ij} \varepsilon_i$  where  $\varepsilon_i$  is the *extent* of  $i$ -th chemical reaction. The total change of concentration of the  $j$ -th species ( $\Delta C_j$ ) is expressed by Eq. (2):

$$\Delta C_j = \sum_{i=1}^m a_{ij} \varepsilon_i \quad (2)$$

where  $m$  is the number of chemical reactions. In matrix notation this can be expressed as:

$$\Delta \mathbf{C} = \mathbf{A}^T \boldsymbol{\varepsilon} \quad (3)$$

where  $\boldsymbol{\varepsilon} = [\varepsilon_1, \varepsilon_2, \dots, \varepsilon_m]^T$  is the vector of the extents of the consecutive reactions.

From Eq. (3) it can be inferred that there exist exactly  $n-m$  linearly independent linear combinations of concentrations that do not change during the course of the reactions. This can easily be demonstrated by multiplying both sides of Eq. (3) by a matrix orthogonal to  $\mathbf{A}$ . This matrix is called the *balance matrix* and is indicated by symbol  $\mathbf{Q}$  [of dimensions  $(n-m) \times m$ ]:

$$\mathbf{Q} \Delta \mathbf{C} = \mathbf{Q} \mathbf{A}^T \boldsymbol{\varepsilon} = 0 \quad (4)$$

Because  $Q\Delta C = 0$  (from Eq. 4), we have:

$$T_i = \sum_{i=1}^n q_i C_i \quad i = 1, 2, \dots, n-m \quad (5)$$

or in matrix notation:

$$Q C = T \quad (6)$$

with

$$T = [T_1, T_2, T_3, \dots, T_{n-m}]^T \quad (7)$$

where  $T$  is a constant vector (its components do not change during the reactions). The constants  $T_1, T_2, \dots, T_{n-m}$  describe the total amounts of selected species present in the system or their linear combinations, i.e. the material balance, and are therefore called *balance constants*.

The equilibrium state must satisfy the mass-action law which for ideal systems can be described by Eq. (8) or, in matrix notation, by Eq. (9):

$$\ln K_i = \sum_{i=1}^n a_{ij} \ln C_j \quad i = 1, 2, \dots, m \quad (8)$$

$$\ln K = A \ln C \quad (9)$$

where  $K_i$  is the equilibrium constant of  $i$ -th reaction and  $K$  is the vector of equilibrium constant.

Because any linear combination of a chemical reaction is a chemical reaction and any linear combination of balance equations is a balance equation, a given system can be described by an infinite number of equivalent stoichiometric and balance matrices. Some standardization is introduced when  $A$  and  $Q$  are expressed in the so-called normal Hermitian form:

$$\begin{aligned} A &= [I_{(n-m)} \ ; \ -P] \\ Q &= [P^T \ ; \ I_{(n-m) \times (n-m)}] \end{aligned} \quad (10)$$

where  $I$  is the unit matrix.

The stoichiometric matrix expressed by Eq. (10) contains reactions of the formation of the first  $m$  species (called *complexes*) from the last  $n-m$  species (called *components*). Each row of the balance matrix in the Hermitian form is the balance equation corresponding to the conservation of the total concentration of the respective component. Matrix  $P$  will be called the *composition matrix*;  $p_{ij}$  denotes the quantity of the

$j$ -th component per one molecule of the  $i$ -th complex; therefore the components of  $i$ -th row of the matrix  $P$  are coefficients in the chemical formula of  $i$ -th complex expressed in terms of the assigned components. Given  $A$ ,  $P$  can be computed from Eq. (11):

$$P = -{}^0A^{-1}A^0 \quad (11)$$

where  ${}^0A$  and  $A^0$  denote the left and right part of the stoichiometric matrix, corresponding to complexes and components, respectively:

$$A = \left[ {}^0A_{n,m} : A_{m,(n-m)}^0 \right] \text{ with } \det {}^0A \neq 0 \quad (12)$$

It can be noted that the example stoichiometric matrix shown in Figure 1 is in the normal Hermitian form. The corresponding balance matrix  $Q$  is shown below (Figure 2), and the matrix  $P$  is:

$$\begin{bmatrix} \text{Ag}^+ & \text{L} & \text{H}^+ \\ 1. & 2. & 0. \\ 1. & 1. & 0. \\ 0. & 1. & 1. \\ 0. & 0. & -1. \end{bmatrix}$$

$$\begin{bmatrix} [\text{AgL}_2]^- & [\text{AgL}]^- & [\text{HL}]^- & \text{OH}^- & \text{Ag}^+ & \text{L} & \text{H}^+ \\ 1. & 1. & 0. & 0. & 1. & 0. & 0. \\ 2. & 1. & 1. & 0. & 0. & 1. & 0. \\ 0. & 0. & 0. & -1. & 0. & 0. & 1. \end{bmatrix}$$

Figure 2. The mass balance matrix corresponding to the stoichiometric matrix of Figure 1.

### Representation of solutions used in titrations

The solutions used for titrations result from mixing various *intermediate* solutions, which are in turn formed by dissolving or mixing certain reagents. The history of preparing the solutions is represented by an acyclic graph [3]. An example is shown in Figure 3.

Solution 1, with volume  $V_{13}$  and initial concentrations of species given by vector  $C_1$ , and solution 2, with volume  $V_{23}$  and initial concentrations given by vector  $C_2$ , were mixed to give solution 3, with a volume found to be  $W_3$ . Then solution 5 was formed analogously from solutions 3 and 4, and solution 6 from solutions 1, 3, and 5. Solution 6 was the one used in the titrations. From the example presented we can see that vertices of the graph are of three types: *initial*, *intermediate*, and *final*. In the example, the initial vertices are 1, 2, and 4; intermediate are 3 and 5 and the final is vertex 6. The initial vertices need not correspond to solutions; they can also represent solid

reagents. In such a case the „concentrations” are simply the amounts of the respective species per reagent unit.

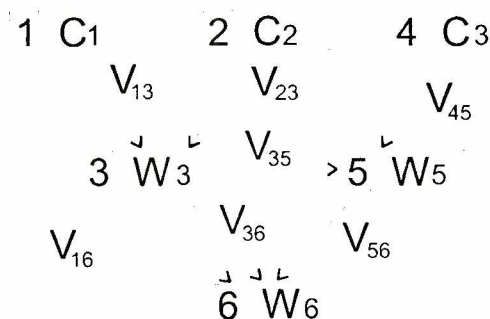


Figure 3. An example of the graph of the history of preparing solutions

### General algorithm for the determination equilibrium parameters

A general algorithm to compute equilibrium parameters has been worked out by J. Kostrowicki and A. Liwo. It minimizes the sum of the weighted squares of the differences between the measured and predicted experimental observables, given by Eq. (13) [1, 2, 3]:

$$\begin{aligned} \phi(x, y, E^0, S, \omega, V) = & \sum_{i=1}^t \left\{ \left( \frac{1}{\sigma_E^i} \right)^2 \sum_{j=1}^{n_i} [\hat{\Psi}_j^i - \Psi(V_j^i, \omega, E_i^0, S_i, x, y)]^2 + \right. \\ & \left. \left( \frac{1}{\sigma_{E^0}^i} \right)^2 \sum_{j=1}^{n_i} (\hat{V}_j^i - V_j^i)^2 + \left( \frac{1}{\sigma_{E^0}^i} \right)^2 (\hat{E}_i^0 - E_i^0)^2 + \left( \frac{1}{\sigma_S^i} \right)^2 (\hat{S}_i - S_i)^2 \right\} \\ & + \sum_{i=1}^u \left( \frac{1}{\sigma_\omega^i} \right)^2 (\hat{\omega}_i - \omega_i)^2 + \sum_{i=1}^p \sum_{j=1}^p (W_y)_{ij} (\hat{y}_i - y_i)(\hat{y}_j - y_j) \end{aligned} \quad (13)$$

where:

$f(x, y, E^0, S, \omega, V)$

– the minimized sum; the vector  $(x, y, E^0, S, \omega, V)$  contains measured quantities;

$\mathbf{x} = [x_1, x_1, x_1, \dots, x_{n_{par}}]^T$

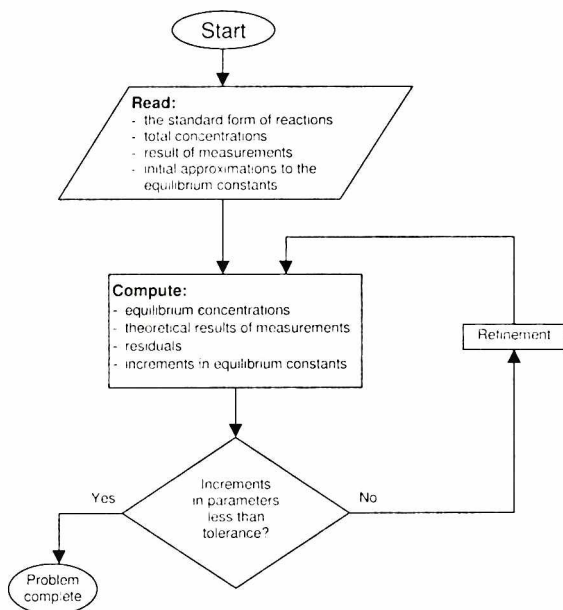
– the vector of the parameters to be determined, e.g. equilibrium constants;

$\mathbf{y} = [y_1, y_1, y_1, \dots, y_{n_{par}}]^T$

– the vector of the parameters that have been determined from other experiments and for which the variance-covariance matrix  $(W_y^{-1})$  is known (e.g., known equilibrium constants);

$E^0 = [E_1^0, E_2^0, E_3^0, \dots, E_t^0]^T$	– the vector of the standard electromotive forces of the subsequent titrations;
$S = [S_1, S_2, S_3, \dots, S_t]^T$	– the vector of the Nernstian slopes of the subsequent titrations;
$\omega = [\omega_1, \omega_2, \omega_3, \dots, \omega_t]^T$	– the vector of characteristics of the composition of the titrants and titrands;
$(V_j^i, E_j^i), j = 1, 2, \dots, r_i, i = 1, 2, \dots, t$	– $j$ th titrant volume and $j$ th electromotive force in $i$ th titration;
$\sigma$	– estimated a priori standard deviations of the respective quantities (e.g. on the basis of the apparatus characteristics);
$t$	– number of titrations;
$r_i$	– number of points in the $i$ th titration;
$u$	– number of composition characteristics;
$p$	– number of parameters determined from earlier measurements;
$\wedge$	– indicates the measured quantity.

Minimization of  $\phi$  is carried out using the iterative Marquardt method [6]. A general flow chart of the program is shown in Figure 4.

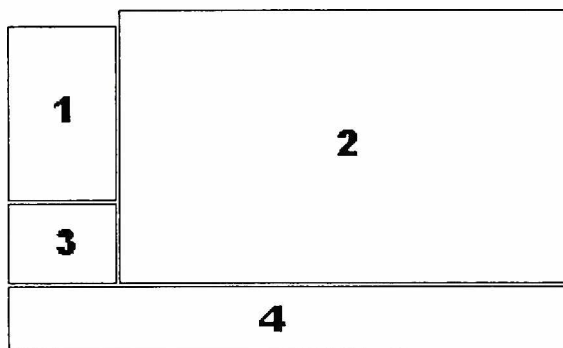


**Figure 4.** General algorithm of equilibrium-parameter determination from experimental data. The main computation is realized in the Compute step. In the Read step the data are read from a data file prepared by GOLEM.

## Introduction to GOLEM

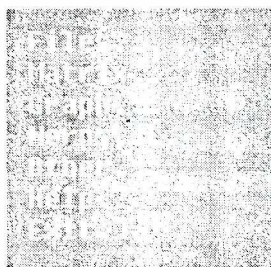
GOLEM is an advanced graphical user friendly interface for preparing data files. It has been implemented on DOS and Windows platforms. All the requirements of program are described in the *Technical information* section.

The main screen of the program is divided into several windows. The general scheme is shown in Figure 5. Area 1 is used by the cascade menu system. The main working area is located in window 2; window 3 is the information window and window 4 is the status and report window.



*Figure 5. Windows placement in application.*

Once the program has started, the main menu is displayed, which is used for choosing the main options and work mode. The initial state of the menu is shown below.



*Figure 6. The initial form of the menu. The "Files..." submenu groups a set of file and directory handling commands; the "Matrix..." submenu serves to input chemical equations; the "Graph..." submenu is used for constructing the graph of the history of preparing the solutions; the "Nernst..." submenu serves to enter general titration data (titrand volume, electrode equation(s), etc.); the "Other..." submenu contains miscellaneous options, such as "Configuration"; "Help..." and "Exit..." are self explanatory.*



The current status of the program is shown in the Information window:

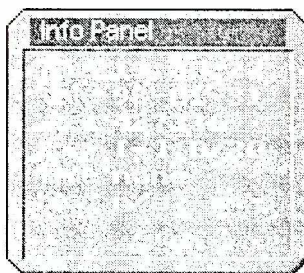


Figure 7. The initial state of the „Information” Window.

The subsequent items describe current time and date, the amount of free memory, the number of files used by the program (maximum 20 allowed), preceded by the number of file currently in use ([-] for none), the name of the file currently in use, and the data header.

The status window is designed for information purposes only. It is used for displaying comments, suggestions and warnings produced by program.

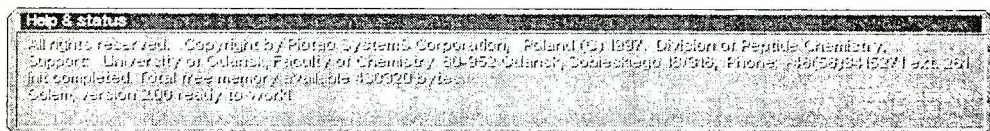


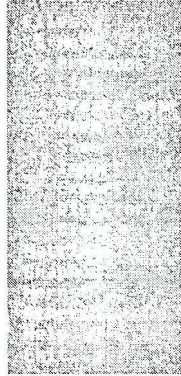
Figure 8. The status window in its initial form.

Depending on individual needs, the message level can be set at errors (for advanced users), errors and warnings (for intermediate users) or full (recommended for novices); this is accomplished using the “Configuration” option of the “Other...” menu.

## Preparing data files with GOLEM

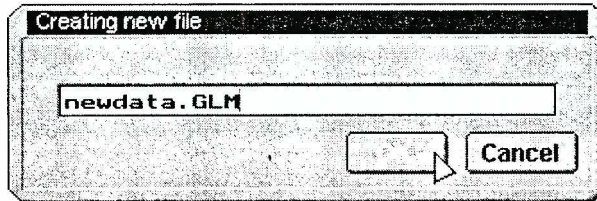
### Creating a new data file

A useful and easy method of data preparation is illustrated here on an example. Assume that we want to determine equilibrium constants in the  $\text{Ag}^+$  — triethanolamine system shown and that the stoichiometry of the first complex, initially guessed to be  $\text{AgL}_2^+$  is to be determined. First, we have to define the name and location of the internal data file used by GOLEM for keeping all entered data. This can be done thorough the “Files...” menu, which is presented in expanded form in Figure 9.



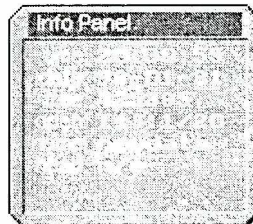
*Figure 9. Expanded file menu. Some of the commands can be inactive. It depends of current situations and program state.*

By clicking on the “Create new” field in the “Files...” menu we are able to enter the name of a new file (see Figure 10 below). After that the program checks if the name is correct and if it corresponds to a new file. A warning message is issued, if any attempt is made to open and, thereby, overwrite an existing file. All comments and warnings can be displayed in the Status window.



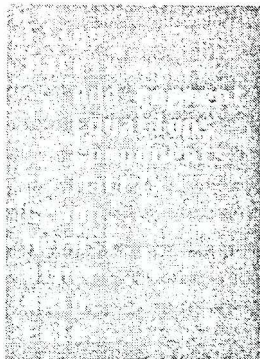
*Figure 10. A small window from “Create new” command. It allows to enter a new data file name.*

If the file name is correct, GOLEM creates an empty data file and allows us to create the first part of the data. Creating a new file is indicated in the “Information” window, as shown in Figure 11.



*Figure11. Information window after creating the first file.*

Subsequently, the “Equations” command from the “Matrix...” menu is used to enter chemical equations (Figure 12).



*Figure 12. The “Matrix...” menu.*

### *Entering chemical equations*

Chemical equations are entered in the “Work” window. Up to 20 reactions can be stored simultaneously. Each of them is placed in a single line. Editing can be done using the keyboard; the mouse is used only for text cursor positioning. Each equation is followed by the logarithm of its equilibrium constant and, optionally, the standard deviation of this equilibrium constant, if known from other measurements.

The buttons in the “Work” window allow including the reactions from a previously created file in the current set of chemical equations, or exporting them to several formats (plain text or  $\text{T}_\text{E}\text{X}$ ). The default equation type is “normal” (indicated by an “N”) and it is not needed to set. Reactions whose equilibrium constants correspond to solvent ionic product or solute solubility product are identified as “creation” (C) or “annihilation” (A) processes, respectively. The user can mark a reaction with (U) to indicate that its stoichiometry is unknown; in this case the displayed coefficients are only initial guesses to the “true” stoichiometry, as shown in Figure 13.

Once all chemical equations have been entered, the correctness test can be invoked by clicking on the “Test” button. Erroneous equations will be ignored. The “Other...” and “Configuration” menu command can configure test types. Some “soft” errors (e.g. incorrect species names) can usually be ignored. All equations are tested in one pass. Results of the tests are reported in the Status window. It is also possible to save all errors and/or warnings to a report file (useful, if verbose messages are analyzed after).

Chemical Equation	Equilibrium Constant (K)	Other Value
$1\text{Ag}^+ + 2\text{L} \rightleftharpoons 1\text{AgL}_2$	2.3	
$1\text{Ag}^+ + 1\text{L} \rightleftharpoons 1\text{AgL}^+$	3.6	
$1\text{H}^+ + 1\text{L} \rightleftharpoons 1\text{HL}^+$	7.9	
$1\text{H}^+ + 1\text{OH}^- \rightleftharpoons 1\text{H}_2\text{O}$	-14.0	

Figure 13. Work window containing the entered chemical equations.

### Choosing the components

In this step we have to choose  $n-m$  component species. The formulas of any of the  $m$  remaining species (the complexes) must be expressed in terms of these components, which means that the part of the stoichiometric matrix corresponding to complexes must be non-singular. If there are any complexes with unknown stoichiometry, they must also be marked in this step, as shown in Figure 14. Obviously, no unknown species can be chosen as a component.

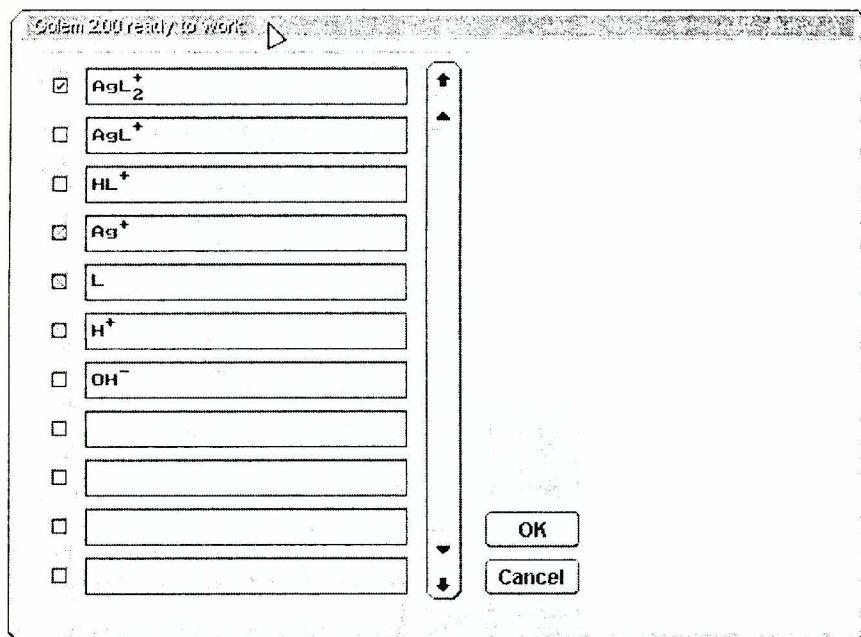


Figure 14. Defining the set of components (marked with ☒) and complexes with unknown stoichiometry (marked with ☑). The type of species can be selected from small context menu by clicking the right mouse button on the square check box).

### Generating the stoichiometric matrix

Creation of the stoichiometric matrix is invoked by choosing the “Matrix” command from the “Matrix...” menu. The stoichiometric matrix is displayed in Figure 15 below. The matrix can be exported to a text or as a table in the T<sub>E</sub>X format.

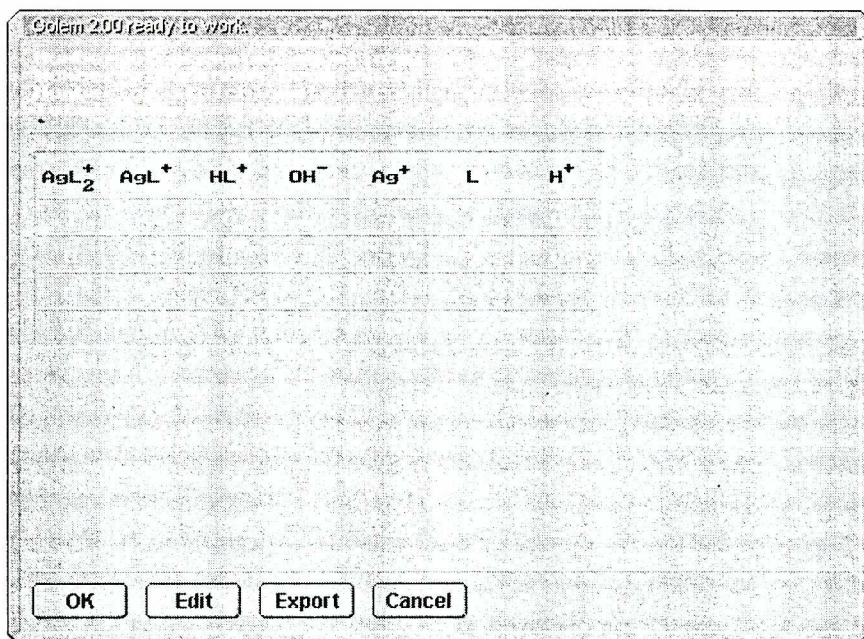
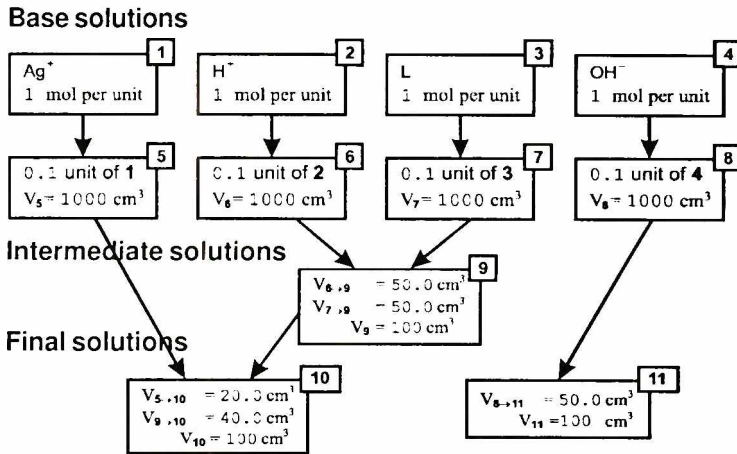


Figure 15. The stoichiometric matrix as shown in the Work window.

### *Defining the graph of the history of the preparation of the solutions*

Solutions used in potentiometric measurements are divided into three groups: base, intermediate, and final, as described in section "Representation of solutions used in titrations". Now the history of mixing the solutions is created. In our example the titrand is 0.02 M in  $\text{Ag}^+$  and  $\text{HL}^+$  and the titrant is 0.5 M in  $\text{OH}^-$ . These solutions are prepared from reagents that contain 1 mol of  $\text{Ag}^+$ ,  $\text{H}^+$ ,  $\text{L}$ , and  $\text{OH}^-$ , respectively, per unit. The reagents are numbered as "solutions" 1–4. Stock solutions of all reagents (with numbers 5–8) of concentrations 0.1, 0.1, 0.1, and 1 M, respectively, are then prepared. Then, solution 9 containing  $\text{HL}^+$  is prepared from stock solutions 5 and 6. Finally, the titrand is prepared by mixing appropriate amounts of stock solution 4 and solution 9 and the titrant is prepared by diluting stock solution 8. The details of the procedure are illustrated in the graph on the next page.



The appearance of the graph when working with GOLEM is shown in Figure 16. The graph is constructed by activating the "Graph..." menu, positioning the rectangles representing solutions or base substances on the screen and drawing lines between them.

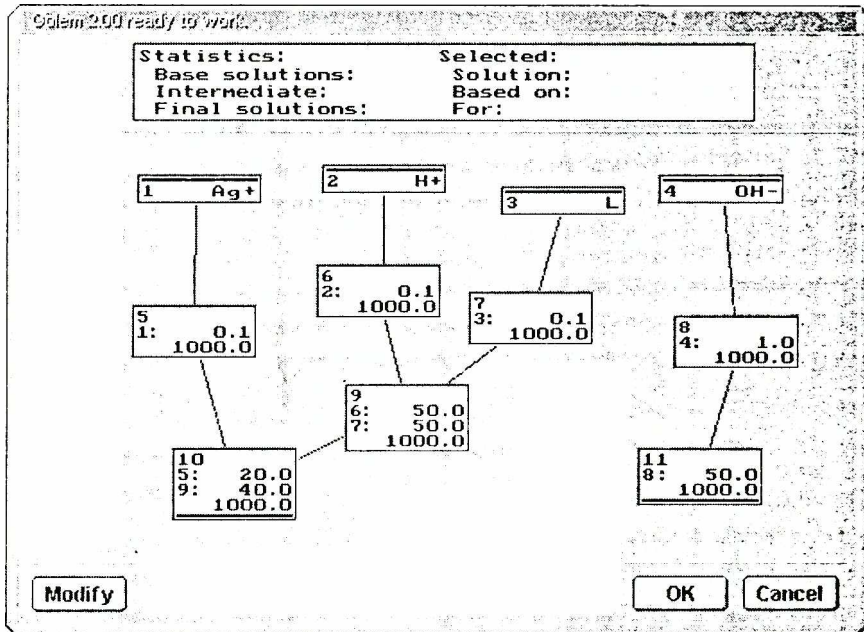


Figure 16. The appearance of the graph of the history of solution preparation.

A dark line at the top marks a base substance and a black line at the bottom marks a final solution. Clicking the left button of the mouse on a particular solution initiates displaying full information regarding this solution. Modifying is allowed after the "Modify"

button is pressed. Only one box can be edited at a time. Clicking on any rectangle will display a short context menu with a set of useful options (e.g. change type, change volume, etc.).

Entering information about preparing the solutions is finished by clicking the "OK" button. The program will check whether the graph is a directed acyclic one, which is the only type of graph that can represent the history of preparing solutions. Errors detected at this stage cannot be ignored.

### ***Entering other data***

The other data include the coefficients of the Nernst equation, volumes of the titrand(s), and the results of titrations (e.g. the pairs of volume and electromotive force). These data are entered manually in text mode or are acquired directly from the apparatus.

Manual entering of the titration data can be accomplished using any text editor or using the GOLEM built-in editor. In the latter case GOLEM prompts the user to enter appropriate data, e.g. electrode characteristics, volume — e.m.f. pairs, etc.

### **Producing data files**

The data, which have been prepared by GOLEM, are often saved to an internal data file, from which they can easily be restored. GOLEM can export these data to files of several types: plain text, T<sub>E</sub>X source or STOICHIO input data files. This is accomplished by choosing the "Export" option from the "Files..." menu.

The first part of the data (including the history of preparing the solutions) corresponding to the example discussed throughout the paper exported to the STOICHIO format is shown on the next page.



```

# Generated by GOLEM, v. 2.0, at 10.02.1998
7  4  3  1  1  2  0  3  1  1
AgL2+
AgL+
HL+
OH-
Ag+
L
H+
-1.0 -2.0 0.0 2.3
0  1  0  0 -1 -1  0  3.6
0  0  1  0  0 -1 -1  7.9
0  0  0  1  0  0  1 -14.0
2
1  5
      1.0      0.01
1      7
      1.0      0.01
1  6
      1.0      0.01
1  4
      1.0      0.01
1  0  1000.0
1  0  1000.0
1  0  1000.0
1  0  1000.0
1  0  100.0
1  0  100.0
1  0  100.0
0
1  5  0  0.1
2  6  0  0.1
3  7  0  0.1
4  8  0  1.0
6  9  0  50.0
7  9  0  50.0
5  10 0  20.0
9  10 0  40.0
8  11 0  50.0
0

```

## Technical information

### *Systems requirements*

GOLEM-2 is a DOS-based program, which works under DOS based systems (6. + versions) or under the MS Windows 95+ shell (better). Running under Windows 3.x is not recommended. All major and specific properties are presented on the next page.

**Table 1.** System requirements

Property/Parameter	Minimal	Recommended
Operating system:	MS DOS 6.0	MS Windows 95
Memory:	450 kB	620 kB
Disk:	500 kB	500 kB
Video:	VGA compatible	VESA support, 512 kB or more
Display:	any VGA-compatible adapter	15" 800x600 NI monitor
Mouse:	MS Series or compatible	
Start-up configuration:	no	yes
Disk buffering:	no	yes
Language:	English	English

## References

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