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Stability Constant Estimator User's Guide

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TABLE OF CONTENTS

INTRODUCTION

1.1	PURPOSE	1
1.2	BACKGROUND ...	1
1.2.1	Definition of Stability Constant	1
1.2.2	Utility and Availability of Stability Constant Data	2
1.2.3	Methods for Predicting Stability Constants	3
1.2.3.1	Linear Free Energy Relationships	3
1.2.3.2	Relationships with Physical Properties of Metal Ions	5
1.2.3.3	Parametric Equations	7

OPERATING INSTRUCTIONS

2.1	OVERVIEW	9
2.2	INSTALLATION ..	11
2.3	STARTUP AND SHUTDOWN	12
2.3.1	Starting the Program	12
2.3.2	The Main Screen	12
2.3.3	Exiting the Program	12
2.4	STABILITY CONSTANT ESTIMATION	13
2.4.1	The Metal-Ligand Selection Screen - Starting a Session	13
2.4.1.1	Selecting the Metal-Ligand Species	13
2.4.1.2	Filter Options and Status of Estimation Methods	13

2.4.1.3	Specifying Name of Output File	16
2.4.2	The Estimate Screen	16
2.4.2.1	Automatic vs. Interactive Estimation	16
2.4.2.2	Filters	17
2.4.2.3	LFER Methods	19
2.4.2.4	Physical Property Methods	19
2.4.2.5	Plot Screens	19
2.4.2.6	Hancock Equation	22
2.4.2.7	Brown and Sylva Equation	23
2.5	DATABASE MODIFICATION	24
2.5.1	Metal Ion Parameters	24
2.5.1.1	Viewing Metal Ion Parameters	24
2.5.1.2	Modifying Metal Ion Parameters	24
2.5.1.3	Defining a New Metal Ion	25
2.5.1.4	Description of Parameters	26
2.5.1.5	Deleting a Metal Ion	28
2.5.2	Ligand Parameters	28
2.5.2.1	Viewing Ligand Parameters	28
2.5.2.2	Modifying Ligand Parameters	28
2.5.2.3	Defining a New Ligand	28
2.5.2.4	Description of Ligand Parameters	29
2.5.2.5	Deleting a Ligand	31

2.5.3	Stability Constant Data	31
2.5.3.1	Viewing Stability Constants	32
2.5.3.2	Modifying an Existing Stability Constant	32
2.5.3.3	Adding a New Stability Constant	33
2.5.3.4	Description of Stability Constant Parameters	33
2.5.3.5	Deleting a Stability Constant	34
2.6	FILES AND FILE HANDLING	35
2.6.1	The Output File	35
2.6.2	Database Files	36
2.6.2.1	Default Database	36
2.6.2.2	User Modified Database	36
2.6.3	The Save File Screen	37
2.6.4	The Open Database Screen	37
	VALIDATION OF PERFORMANCE	39
	BIBLIOGRAPHY	41
	APPENDIX A. Example Output File	A-1

FIGURES

1.	Flow Chart for the SCE Program	10
2.	Main Screen as it appears after startup	14
3.	The Metal-Ligand Selection Screen after user has selected Co(II) and acetohydroxamate(-1)	14
4.	Estimate Screen immediately after selection of the magnesium alanate species	18
5.	Estimate Screen after completion of an automatic estimation on the manganisum alanate species	18
6.	Example Plot Screen for a LFER method. This is a plot of $\log K(\text{Yb}(3+)\text{L}_i)$ vs. $\log K(\text{Nd}(3+)\text{L}_i)$ obtained during an estimation of $\log K$ for neodymium acetate by selecting 'Two Metals' under the 'LFER' menu option of the Estimate Screen and selecting Yb(3+) from the metals list in the Plot Screen.	20
7.	Example Plot Screen for a Physical Property method. This is a plot of metal ion ionization potential vs. $\log K(\text{M}_i\text{citrate})$ obtained during an estimation of $\log K$ for nickel citrate by selecting 'Electronegativity' under the 'Physical Property' menu option of the Estimate Screen.	21
8.	Edit Metal Parameter Screen after selection of the silver ion, Ag(+1)	25
9.	Edit Ligand Parameter Screen after selection of acetate	29
10.	Edit Thermo Data Screen after selecting americium aspartate.	32

INTRODUCTION

1.1 PURPOSE

The purpose of the Stability Constant Estimator (SCE) program is to estimate aqueous stability constants for 1:1 complexes of metal ions with ligands by using trends in existing stability constant data. Such estimates are useful to fill gaps in existing thermodynamic databases and to corroborate the accuracy of reported stability constant values.

1.2 BACKGROUND

1.2.1 Definition of Stability Constant

The equilibrium constant involving the formation of a metal complex from the aquo metal ion and the most basic form of the ligand is a standard measure of the effectiveness of the ligand in coordinating metal ions. These constants are called stability constants or formation constants. For a 1:1 complex between a metal ion and a ligand, the stability constant is defined as the quotient of the products of the activities of the metal ion and the ligand divided by the activity of the metal-ligand complex.

Stability constants are usually reported as their logarithms. The logarithm of the stability constant is directly related to the Gibbs free energies of the products of the reaction minus the Gibbs free energies of the reactants in their standard states.

The determination of activities of aqueous species under real conditions and at infinite dilution is a complex and time-consuming operation beyond the interest and capabilities of most coordination chemists. Because concentrations closely parallel activities under carefully controlled conditions involving both temperature and ionic strength, it is the usual practice to determine stability constants in terms of concentration.

Such concentration constants are very close to the true thermodynamic constants of the reaction in the electrolyte medium chosen, because the activity coefficients change very little in going from the finite concentrations used in the measurement of the stability constants, to infinite dilution in the supporting electrolyte. Therefore, very little error is involved in the assumption that the concentration constants measured under controlled conditions and under a controlled ionic atmosphere are very close to the true thermodynamic constants of the reaction, i.e. the change in Gibbs free energy for complex formation can be determined from stability constants expressed in terms of concentration (Martell and Hancock 1996).

1.2.2 Utility and Availability of Stability Constant Data

Stability constants are fundamental to understanding and predicting the behavior of metal ions in aqueous solution. Such understanding is important in a wide variety of areas that include metal ions in biology, biomedical applications, metal ions in the environment, extraction metallurgy, food chemistry, and metal ions in many industrial processes (Dimmock et al. 1995, Martell and Hancock 1996).

Understanding the chemistry of metal ions in aqueous solution requires a detailed analysis of the chemical "speciation" of each metal and ligand present in the system. In this context, speciation is used to denote the chemical form of each metal ion with respect to valence state(s) and the activities of complexes and free aquated metal ion in equilibrium with solid precipitates and minerals. It is not sufficient to merely know the total concentrations of each metal ion and ligand.

In many cases, however, relatively low concentrations coupled with the extremely complicated, and labile, equilibrium processes render speciation in aqueous systems inaccessible to direct analytical measurements. In a complicated mixture, knowledge of thermodynamic stability constants of possible reactions that may occur within that mixture, together with the concentrations of reactants, enables the existence and concentration of resulting species to be determined. The metal-ligand equilibria can be simulated using the laws of mass action and mass balance, defined parameters such as pH, E_h , and total metal and total ligand concentrations, and stability constants for all potentially important metal-ligand complexes.

Clearly, the success of such calculations, and their predictions, requires an accurate thermodynamic database which contains stability constants for all of the potentially important complexes that can form in the system. While a large number of stability constants for the formation of metal complexes with organic ligands have been accumulated (Sillen and Martell 1965, 1975; Martell and Smith 1974, 1977, 1982; Smith and Martell 1975, 1976, 1989; Pettit and Powell 1993), significant omissions are evident which currently prevent calculations of equilibrium concentrations of many species of interest. Speciation codes such as PHREEQE (Parkhurst 1980) and MINTEQA2 (Allison 1991) contain extensive databases for metals and ligands commonly encountered in groundwaters; however, these databases are not fully comprehensive and contain relatively few data on organic ligands and/or trace metal ions.

This situation could be remedied by further measurement of stability constants to fill the gaps in the database. This would be an exceedingly large task. Even if such measurements were carried out, the accuracy of the measurements would be called into question when uncorroborated values are determined by a single investigator or difficult systems are complicated by hydrolysis, redox, or solubility problems. One may conclude that the further measurement of large numbers of stability constants is not an attractive option. Therefore, accurate and reliable methods of predicting stability constants are desirable.

1.2.3 Methods for Predicting Stability Constants

The SCE program represents a significant step toward filling gaps in the thermodynamic database by providing a tool for the prediction of unknown stability constants from trends in extant stability constant data. This program estimates stability constants for binary complexes, i.e. one metal with one ligand, by utilizing methods that have been reported in the literature. These methods are summarized below.

1.2.3.1 Linear Free Energy Relationships

Linear free energy relationships (LFER) are linear correlations between the free energy change, i.e. $\log K_i$, of one group of reactions with the free energy change, i.e. $\log K_j$, for a second group of reactions. Three types of LFER have been observed for metal-ligand complexes.

(i) The logarithm of the stability constants, $\log K(\text{ML}_i)$, for a series of ligands, L_i , with one metal ion, M , often yield a linear correlation when plotted against the sum of the pK_a 's of each L_i .

$$\log K(\text{ML}_i) = a \cdot \sum \text{pK}_a(\text{L}_i) + b \quad (\text{LFER Method 1})$$

This type of correlation has been reported for: $\text{Mg}(\text{II})$ with oxines (Irving and Rossotti 1956), $\text{Mg}(\text{II})$ to $\text{Ba}(\text{II})$ with aminocarboxylates (Irving and da Silva 1963; Irving and Miles 1966a, 1966b), $\text{Fe}(\text{II})$ with pyridines (da Silva and Calado 1966), $\text{Fe}(\text{III})$ with phenols (Ernst and Herring 1964; Hancock and Marsicano 1980a), $\text{Fe}(\text{III})$ with carboxylic acids (Hancock and Marsicano 1980a), $\text{Co}(\text{II})$ with polyamines (Harris et al. 1978), $\text{Ni}(\text{II})$ with oxines (Jones et al. 1958), $\text{Ni}(\text{II})$ with polyamines (Harris et al. 1978), $\text{Cu}(\text{II})$ with β -diketonates (Calvin and Wilson 1945; da Silva and Calado 1966), $\text{Cu}(\text{II})$ with salicylaldehydes (Calvin and Wilson 1945), $\text{Cu}(\text{II})$ with benzoic acids (May and Jones 1962; da Silva and Calado 1966), $\text{Cu}(\text{II})$ with pyridines (Sun and Brewer 1967), $\text{Cu}(\text{II})$ with oxines (Irving and Rossotti 1956), $\text{Zn}(\text{II})$ with polyamines (Harris et al. 1978), $\text{Zn}(\text{II})$ with aminocarboxylates (Irving and da Silva 1963; Irving and Miles 1966a, 1966b), $\text{Zn}(\text{II})$ with oxines (Jones et al. 1958), $\text{Zn}(\text{II})$ with pyridines (Sun and Brewer 1967), $\text{Ga}(\text{III})$ with aminocarboxylates (Harris and Martell 1976; Motekaitis and Martell 1980), $\text{Ag}(\text{I})$ with pyridines (Da Silva and Calado 1966; Sun and Brewer 1967), $\text{Ag}(\text{I})$ with anilines (da Silva and Calado 1966), $\text{Ag}(\text{I})$ with phenylthioacetic acids (Pettit et al. 1968a), $\text{UO}_2(\text{II})$ with carboxylic acids and phenols (Hancock and Marsicano 1980a).

(ii) The logarithm of the stability constants, $\log K(\text{M}_1\text{L}_i)$, for a series of ligands, L_i , with one metal ion, M_1 , often yield a linear correlation when plotted against the logarithm of the stability constants, $\log K(\text{M}_2\text{L}_i)$, for the same L_i with a second metal ion, M_2 .

$$\log K(\text{M}_1\text{L}_i) = a \cdot \log K(\text{M}_2\text{L}_i) + b \quad (\text{LFER Method 2})$$

This type of correlation has been reported for a wide variety of organic ligands with the following metal ion pairs: $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$ (Irving and Miles 1966b; Hummel 1992), $\text{Na}(\text{I})$ vs $\text{Ca}(\text{II})$ (Hummel 1992), $\text{K}(\text{I})$ vs $\text{Ca}(\text{II})$ (Hummel 1992), $\text{Ca}(\text{II})$ and $\text{Sr}(\text{II})$ (Hummel 1992), $\text{Mg}(\text{II})$ and $\text{Ni}(\text{II})$ (Van Uitert and Fernelius 1954), $\text{Ca}(\text{II})$ and $\text{Ni}(\text{II})$ (Hummel 1992), $\text{Mn}(\text{II})$ and $\text{Ni}(\text{II})$ (Hummel 1992), $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ (Irving and Rossotti 1956; Beck 1970), $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ (Rossotti 1960), $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$ (Hancock et al. 1974; Hancock and Marsicano

1976; Marsicano and Hancock 1978), Cu(II) and Ag(I) (Marsicano and Hancock 1978), Co(II) and Ag(I) (Marsicano and Hancock 1978), Cd(II) and Ag(I) (Hancock et al. 1974; Marsicano and Hancock 1978), Cu(II) and Hg(II) (Hancock and Marsicano 1980a), Fe(III) and Hg(II) (Hancock and Marsicano 1978), Cd(II) and Hg(II) (Hancock and Marsicano 1980a), Ag(I) and Hg(II) (Hancock et al. 1974; Hancock and Marsicano 1976, 1978; Marsicano and Hancock 1978), Hg(II) and Bi(III) (Hancock and Marsicano 1978; Marsicano and Hancock 1978), Ag(I) and Au(I) (Hancock et al. 1974; Hancock and Marsicano 1976; Marsicano and Hancock 1978).

(iii) The logarithm of the stability constants, $\log K(M_iL_1)$, for a series of metals, M_i , with one ligand, L_1 , often yield a linear correlation when plotted against the logarithm of the stability constants, $\log K(M_iL_2)$, for the same M_i with a second ligand, L_2 .

$$\log K(M_iL_1) = a \bullet \log K(M_iL_2) + b \quad (\text{LFER Method 3})$$

This type of correlation has been reported for the ligand types: soft donor ligands and bromide (Misono and Saito 1970), negative oxygen donor ligands and hydroxide (Ashurst and Hancock 1977; Hancock and Nakani 1982; Nakani and Hancock 1984; Evers et al. 1989; Hancock and Martell 1989; Jarvis and Hancock 1991), polyamine ligands and ammonia (Van Uitert and Fernelius 1954; Hancock and McDougall 1977; Hancock et al. 1979; Hancock and Martell 1989), bipyridine and ammonia (Hancock and McDougall 1977, Hancock et al. 1993), phenanthroline and ammonia (Hancock and McDougall 1977), phenanthroline and bipyridine (Nieboer and McBryde 1970), EDTA and cyclohexyl-EDTA (Irving and Rossotti 1956; Rossotti 1960), acetylacetonate and dibenzoylmethane (Irving and Rossotti 1956), oxine and hydroxycinnoline (Irving and Rossotti 1956), phenylthioacetate and phenylselenoacetate (Pettit et al. 1968b), benzamidotetrazole with a series of substituted benzamidotetrazole derivatives (Bowden and Sharma 1991).

1.2.3.2 Relationships with Physical Properties of Metal Ions

The logarithm of the stability constants, $\log K(M_iL)$, for a series of metals, M_i , with one ligand, L , are in some cases correlated with physical properties of the metal ion. A variety of functional dependencies have been observed with metal properties that include the charge (Z), ionic radius (R), electronegativity (EN), and ionization potential (IP). These are summarized below.

(i) Functional forms involving the charge and ionic radius of the metal ion include:

$$\log K(M_iL) = a \cdot [(Z_i)/(R_i + b)] + c \quad (\text{PP Method 1})$$

$$\log K(M_iL) = a \cdot [(Z_i)/(R_i + b)]^2 + c \quad (\text{PP Method 2})$$

where a, b, and c represent adjustable parameters.

Linear correlations are often observed only when the series of metal ions is limited to either the Group 1A, Group 2A, or the lanthanides (Davies 1951; Martell and Calvin 1952; Rossotti 1960; Beck 1970; Hefter 1974; Langmuir 1979).

(ii) Functional forms involving the electronegativity and charge include:

$$\log K(M_iL) = a \cdot EN_i + b \quad (\text{PP Method 3})$$

$$\log K(M_iL) = a \cdot (Z_i \cdot EN_i) + b \quad (\text{PP Method 4})$$

$$\log K(M_iL) = a \cdot (Z_i \cdot EN_i) + b \cdot EN_i^2 + c \quad (\text{PP Method 5})$$

Linear correlations have been obtained with varied groups of metal ions (Van Uitert et al. 1953; Izatt et al. 1955a, 1955b; Rossotti 1960; Beck 1970; Nieboer and McBryde 1973).

(iii) Functional forms involving the ionization potential include:

$$\log K(M_iL) = a \cdot IP_i + b \quad (\text{PP Method 6})$$

Linear correlations have been obtained with varied groups of metal ions (Calvin and Melchior 1948; Rossotti 1960; Beck 1970)

(iv) A functional form which combines all the terms used above is:

$$\log K(M_iL) = a \cdot [(Z_i)/(R_i + b)] + c \cdot [(Z_i)/(R_i + d)]^2 + e \cdot IP_i + f \cdot EN_i + g \cdot EN_i^2 + h \cdot Z_i \cdot EN_i + i \quad (\text{PP Method 7})$$

1.2.3.3 Parametric Equations

Parametric equations are relationships that yield $\log K(\text{ML})$ values as a function of metal and ligand parameters. These parameters have been obtained by fitting the relationships to large sets of $\log K(\text{ML})$ data for subsets of metal ions and ligands; therefore, the parametric equations can only be used to calculate $\log K(\text{ML})$ data for ML complexes formed from within these subsets.

Two types of parametric equations have been developed for metal-ligand complexes.

(i) Hancock's equation has the form:

$$\log K(\text{ML}) = E_M \cdot E_L + C_M \cdot C_L - D_M \cdot D_L$$

where three parameters (E, C, and D) are required for each metal ion and for each ligand. One extensive set of parameters includes E, C, and D values for 31 metal ions and 19 ligands (fluoride, acetate, hydroxide, azide, thiocyanate, ammonia, pyridine, chloride, sulfite, bromide, thiosulfate, iodide, thiourea, thiodiglycol, 3-sulfotriphenylphosphine, 3-sulfotriphenylarsine, 2-hydroxyethyl-diethylphosphine, cyanide) (Hancock and Marsicano 1978, 1980a, 1980b). Another parameter set has been developed for all 14 lanthanides with 22 aminocarboxylate ligands (Carugo and Castellani 1992). Simpler parameteric equations of this type, which only use two parameters per metal and ligand, have also been investigated (Edwards 1954; Misono and Saito 1970; Martell et al. 1985).

(ii) Brown and Sylva's equation has the form:

$$\log K(\text{ML}) = \text{slope} \cdot [g_1 \cdot (Z_M/r_M^2 + g_2)] + \text{int}$$

$$g_1 = [1 + D + E_L^2 \cdot S] \cdot [Z_M + 2]$$

$$g_2 = M \cdot [Z_M - 1] - 0.05 d \cdot [(\partial - 1) \cdot (E_L^4 - 3) - 1] \cdot [N - (3 + 2 \cdot \partial)]^2 \cdot [1 - \partial \cdot Z_M] \cdot (1 - S)$$

where d, D, M, N, S, and Z_M are parameters that can be deduced from the electronic structure of each metal ion, r_M is Shannon's ionic radius of each metal ion, and ∂ , E_L , int, and slope are

parameters for each ligand type. The four ligand-dependent parameters were reported for 20 ligands (hydroxide, fluoride, chloride, bromide, iodide, carbonate, sulfate, nitrate, nitrite, perchlorate, chlorate, bromate, thiosulfate, dihydrogen phosphate, hydrogen phosphate, bicarbonate, iodate, acetate, ammonia, and thiocyanate) (Brown and Sylva 1987). A simpler form of the Brown and Sylva equation has been applied to the hydroxide ion (Brown et al. 1985).

OPERATING INSTRUCTIONS

2.1 OVERVIEW

Figure 1 presents a flow chart describing the operation of the Stability Constant Estimator (SCE).

At start-up, SCE will load two default databases. The first contains stability constant data. The second contains metal ion and ligand parameters. Users have the option of loading their own private databases or modifying the contents of existing databases before proceeding with an estimate.

Stability constant estimations are performed in sessions. A session begins with the selection of an ML species and ends when the user decides to discontinue work on this ML species. At the start of a session, SCE scans the database and reports which estimation methods are available for use with the ML species under consideration.

In the identification of applicable methods, several criteria are used to select appropriate data from the thermodynamic database. The criteria employed are in accordance with those used in the literature for stability constant correlations. Users have the capability to interactively override all or parts of this filtering. Where insufficient data is available to conduct linear free energy and physical properties methods, users have the option of entering additional stability constant data. Where insufficient data is available for parametric equation methods, users have the option of fitting parameters if sufficient thermodynamic data is available.

Estimates can be performed interactively or automatically through the use of linear free energy relationships, correlations with metal ion physical properties, and/or parametric equations.

If users choose to work interactively, they select an applicable method, view the result, and decide whether to keep or reject the $\log K(\text{ML})$ value obtained. If the value is kept, it is written to the screen and a summary of the estimation is written to an output file. The user may make as many estimates as the database will allow. As results are accumulated, they are continually averaged and the current average is reported to the user. Prior to exiting this session, the user may write the average $\log K$ value to the output file.

FIGURE 1. Flow Chart for the SCE Program

If users select the automatic mode, SCE attempts every possible estimation method available for the ML species. During this process, the data used for each estimate and the resulting log K values are written to an output file and reported to the screen. When all possible methods have been tried, the log K values are averaged and the resulting log K estimate is written to the output file and reported to the screen.

Once the session has been completed, the user may start another session by selecting a new ML species or exit the program.

2.2 INSTALLATION

IBM/Windows 3.1/3.11

Run Setup. (Choose "Run" from the "File" menu. Type "A:\SETUP" then click the "OK" button)

IBM/Windows 95

Run Setup. (Choose "Run" from the "Start" menu. Type "A:\setup" in the "Open" input field. Click the "OK" button)

Macintosh

Copy the contents of the installation disk to a folder. This is done by dragging the files from the Floppy Disk icon to a folder created on your Hard Disk drive.

Unix

For a Unix system the File on disk needs to be unzipped using gunzip then compiled using the system compiler. This is done in the following steps:

- (1) Unzip the file. (type "gzip -d sce.tar.gz")
- (2) Tar the file. (type "tar -xf sce.tar")
- (3) Run the makesce script file. (type "source makesce")

2.3 STARTUP AND SHUTDOWN

2.3.1 Starting the Program.

<i>IBM/Windows 3.1/3.11</i>	Double click on the SCE group then double click on the SCE icon
<i>IBM/Windows 95</i>	Click on "Start", choose "Programs", then choose "SCE"
<i>Macintosh</i>	Open the SCE folder and double click the SCE icon.
<i>UNIX</i>	Type SCE and press Return or Enter key.

2.3.2 The Main Screen

The main screen as it appears on startup is shown in Figure 2. This screen consists of a menu bar and a window for reporting a summary of the estimations that have been performed. The menu bar contains three pull down menus titled 'File', 'Edit', and 'Estimate'.

Select options in the 'File' pull-down menu to open or save a user-defined database and to exit the program. Database file handling is discussed in detail in Section 2.6. Select options in the 'Edit' pull-down menu to modify databases. Database modification is discussed in detail in Section 2.5. Select the 'Estimate' pull-down menu to initiate a stability constant estimation session. Stability constant estimation is discussed in detail in Section 2.4.

With the exception of exiting the program, the user will always be returned to the Main-Screen after completion of any task initiated from the main pull-down menus.

2.3.3 Exiting the Program

Choose Exit from the 'File' pull-down menu.

2.4 STABILITY CONSTANT ESTIMATION

2.4.1 The Metal-Ligand Selection Screen - Starting a Session

A stability constant estimation session begins by choosing 'Estimate' from the 'Estimate' pull-down menu on the Main Screen. Users are presented with the Metal-Ligand Selection Screen shown in Figure 3 where they select the metal-ligand species for which a stability constant estimate is desired, select filter options that control which data will be used in constructing plots, view the status of estimation methods that are available, and specify the name of an output file for writing estimate results. After providing the requisite input, the user clicks on the 'OK' button to proceed with the estimation session.

2.4.1.1 Selecting the Metal-Ligand Species

The metal ion is selected by scrolling through the metal ion list, placing the cursor on the target metal ion, and clicking to highlight the selection. The ligand is selected by scrolling through the ligand list, placing the cursor on the target ligand, and clicking to highlight the selection.

If the thermodynamic database contains a stability constant for the metal-ligand species selected, this value is displayed in the box labeled 'Database log K'. The user may proceed to estimate a value for the metal-ligand species even though a value already exists in the database.

Note that the selection of a given metal-ligand species requires that both the metal ion and the ligand be present in the lists. If the metal ion or ligand of interest is not present, the user can add them to the appropriate list through use of options in the 'Edit' pull-down menu of the Main Screen (see Section 2.5). In this event, users may click on the 'Cancel' button to return to the Main Screen.

2.4.1.2 Filter Options and Status of Estimation Methods

Filter options determine which data in the thermodynamic database may be used to construct the plots that are used in the LFER and Physical Property methods.

Figure 2. Main Screen as it appears after startup.

Choose Metal-Ligand to Evaluate

Cd[+2]	acac[-1]
Ce[+3]	acetate[-1]
Ce[+4]	acetoxyhydroxamate[-1]
Cm[+3]	alanate[-1]
Co[+2]	ammonia[0]

Database log K

LFER Methods

☒ Metals match type ☐ Metals match charge ☒ Ligand match type ☐ Ligand match charge

sum pKa's (# points) M[1] vs M[2] (# plots) L[1] vs L[2] (# plots)

Physical Property Methods (# points)

☒ Metals match type ☒ Metals match charge

Method 1 & 2 (R)	Method 3,4,5 (EN)	Hancock Method
<input type="text" value="4"/>	<input type="text" value="4"/>	<input type="text" value="Current"/>
Method 6 (IP)	Method 7 (R,EN,IP)	Brown and Sylva Method
<input type="text" value="4"/>	<input type="text" value="N/A"/>	<input type="text" value="Current"/>

Figure 3. The Metal-Ligand Selection Screen after user has selected Co(II) and acetoxyhydroxamate(-1).

Four filters are used with LFER methods: (1) metal ions must match the type of the selected metal ion (see Section 2.5 for a definition of metal ion type), and (2) metal ions must match charge of the selected metal ion, (3) ligands must match the type of the selected ligand (see section 2.5 for a definition of ligand type), (4) ligands must match the charge of the selected ligand. The default setting (observed in Figure 3) is with (1) and (3) turned on and (2) and (4) turned off.

Two filters are used with Physical Property methods: (1) metal ions must match the type of the selected metal, (2) metal ions must match charge of the selected metal. The default setting (observed in Figure 3) is with (1) and (2) turned on.

The Metal-Ligand Selection Screen contains a box to report the status of each type of estimation method with respect to the choice of metal-ligand species and the setting of the filters. If a method is not available, the box will contain 'N/A'. If a method is available, the way that status is reported varies with estimation method. The number of points that can be plotted are reported for LFER using sum of pKa's and for all physical property methods. The number of plots that can be made are reported for LFER methods involving two metal ions or two ligands. The parametric equations, i.e. the Brown and Sylva method and the Hancock method, will report a status of 'current' if parameters are available. If parameters are not available, but sufficient data is present in the thermodynamic database, the status of 'fit metal', 'fit ligand', or 'fit both' will indicate which parameters could be fit to allow an estimation.

The settings of the filters can affect both the status of the methods and the accuracy of the estimates. Any of the six filter settings can be reversed by clicking on the appropriate button. The affect of this change on the method status is immediately reported.

Note it is possible that no estimation methods may be available for a selected metal-ligand species regardless of filter settings. This situation is caused by a lack of thermodynamic data for other complexes with the target metal ion and/or the target ligand (LFER methods, Physical Property methods), a lack of physical property parameters for the target metal ion (physical property methods), and/or a lack of parametric equation parameters (the Hancock and the Brown and Sylva methods). If a source for the missing data is available, the user may input the missing data using options in the 'Edit' pull-down menu of the Main Screen (see

Section 2.5). In this event, users may click on the 'Cancel' button to return to the Main Screen.

2.4.1.3 Specifying Name of Output File

Stability constant estimation results may be written to an output file. The current name of this output file is shown in a box at the bottom of the Metal-Ligand Selection Screen. The user may specify the name and path for file after clicking on the button labelled 'Output File' which brings up a standard Save File screen (see Section 2.6). Multiple output files can be generated by assigning a new output file name each time the user starts an estimation session.

If no user-specified name is provided, the program will write results to a file named DEFAULT.OUT which will have the same path as the program executable.

2.4.2 The Estimate Screen

Figure 4 shows an example of the Estimate Screen that appears after the user has clicked the 'OK' button on the Metal-Ligand Selection Screen. When first opened, this screen consists of a menu bar, a box showing the selected metal-ligand species, a box for reporting estimates, boxes for the database value of log K and the literature citation for this value (if they exist), a box for the predicted log K (always at an ionic strength of 0.0), and a box for the predicted log K as a function of ionic strength. Estimates are performed through options chosen in the pull-down menus.

2.4.2.1 Automatic vs. Interactive Estimation

Estimates may be performed interactively or automatically.

Automatic An automatic estimate is initiated by selecting 'Automatic' from the 'Automatic' pull-down menu. The program will then perform all estimates that are possible for the specified metal-ligand species. As each estimate is completed, details on that estimate are written to the output file (see Section 2.6). As estimates are accumulated, the list of estimates, the contents of the predicted log K box, and the log K as a function of ionic strength box are continuously updated. After a minimum of three estimates have been made, the list of

estimates on the screen is updated to show only those estimates that lie within one standard deviation of the mean. All estimates are retained in memory and the mean is re-evaluated each time a new estimate is accumulated. Thus, individual estimates may disappear from the list and later reappear in the list as more data is accumulated. The predicted log K is the mean of all estimates showing in the list. The Davies equation and the predicted log K are used to compute log K as a function of ionic strength. Figure 5 provides an example of the Estimate Screen after an automatic estimation has been completed.

Interactive If users do not choose the automatic option, then the estimate must be performed interactively. In this case, users decide which methods will be used from those available under the 'LFER', 'Physical Property', 'Hancock', and 'Brown and Sylva' pull-down menus. Available options are shown with black text and unavailable options are shown in grey text. When options are based on linear correlations (LFER and Physical Property), the user views the correlations that are obtained and can manipulate the results by removal of suspect data points. The user decides whether individual estimates will be added to the list or rejected. When an estimate is added to the list, details of that estimate are written to the output file. The predicted log K value is the mean of all estimates in the list. The Davies equation and the predicted log K are used to compute log K as a function of ionic strength.

Ending a Session After the user has completed the desired estimations on a selected metal-ligand species the user can return to the Main Screen by selecting the 'Done' button. Prior to exiting the Estimate Screen, the user may choose to write a summary of the estimate to the output file by selecting the 'Write' button.

2.4.2.2 Filters

Filter options that were set in the Metal-Ligand Selection Screen determine which data in the thermodynamic database may be used to construct the plots used in the LFER and Physical Property methods (see Section 2.4.1.2 above). The user may view and/or alter the current settings of these filters by selecting 'Filter' from the 'Filter' pull-down menu of the Estimate Screen. This may be done prior to initiating an automatic estimation or anytime during an interactive estimation.

Estimate

Automatic Filters LFER Physical Property Hancock Brown and Sylva

Summary of estimates on: **Mg(+2):alanate(-1)**

Database log K: 1.960

Predicted log K: N/A

Reference: Smith and Martell, Critical Stability Constants Series

log K as F(ionic strength)

Write Done

Figure 4. Estimate Screen immediately after selection of the magnesium alanate species.

Estimate

Automatic Filters LFER Physical Property Hancock Brown and Sylva

Summary of estimates on: **Mg(+2):alanate(-1)**

1.890 +/- 0.900 Hancock
 1.853 +/- 0.216 Phys. Prop. [Z,EN,EN**2]
 2.500 +/- 1.375 Phys. Prop. [Z,EN]
 2.500 +/- 1.375 Phys. Prop. [EN]
 1.587 +/- 0.297 LFER with picolinate(-1)
 1.453 +/- 0.214 LFER with ida(-2)
 2.468 +/- 0.049 LFER with glycinate(-1)
 1.565 +/- 0.448 LFER with glutamate(-2)

Database log K: 1.960

Predicted log K: 2.064 +/- 0.470

Reference: Smith and Martell, Critical Stability Constants Series

log K as F(ionic strength)
 2.064 @ I= 0.00
 1.615 @ I= 0.10
 1.515 @ I= 0.20
 1.464 @ I= 0.30
 1.437 @ I= 0.40

Write Done

Figure 5 Estimate Screen after completion of an automatic estimation on the magnesium alanate species.

2.4.2.3 LFER Methods

The 'LFER' pull-down menu contains the three stability constant estimation methods described in Section 1.2.3.1. These are linear free energy relationships based on (i) the sum of ligand pKa's, (ii) two metals (M_1 vs. M_2), or (iii) two ligands (L_1 vs. L_2). If viable, an option will appear in black text; otherwise, the option will appear in grey text. Selection of a viable option takes the user to a Plot Screen (see Section 2.4.2.5) where the linear correlation is graphed and the user decides whether to keep or reject the result.

2.4.2.4 Physical Property Methods

The 'Physical Property' pull-down menu contains the estimation methods described in Section 1.2.3.2. These are linear correlations based on the radius, charge, electronegativity, and ionization potential of the metal ion. If viable, an option will appear in black text; otherwise, the option will appear in grey text. Selection of a viable option takes the user to a Plot Screen (see Section 2.4.2.5) where the linear correlation is graphed and the user decides whether to keep or reject the result.

2.4.2.5 Plot Screens

Plot Screens appear after the selection of any of the options under the 'LFER' and 'Physical Property' pull-down menus. All Plot Screens are not identical, but they share many common features. This section provides a discussion of these common features and identifies method dependent differences.

Common Features

Figures 6 and 7 show Plot Screens for representative LFER and Physical Property methods. Both screens contain a title composed of '<X-axis label> vs. <Y-axis label>', graph of the data points showing the best-fit line, a box to the right of the plot that gives information on the regression, a box that contains the log K estimate, a 'Write' button, and a 'Done' button.

When more than 10 data points are present and the linear correlation coefficient is less than 0.9, the program will automatically exclude points from the regression until either (i) the

correlation coefficient exceeds 0.9 or (ii) there are less than 10 data points remaining. A data point should be removed if the overall regression is better after removing the data point and the correlation coefficient is less than 0.9. Data points that were excluded from the regression appear as red '+'s and data points that were included in the regression appear as white 'x's.

Clicking on a point will change an excluded point to an included point and visa-versa. When the status of a point is reversed the regression is repeated and both the line and estimate are updated.

Figure 6. Example Plot Screen for a LFER method. This is a plot of $\log K(\text{Yb}(3+)\text{L})$ vs. $\log K(\text{Nd}(3+)\text{L})$ obtained during an estimation of $\log K$ for neodymium acetate by selecting 'Two Metals' under the 'LFER' menu option of the Estimate Screen and selecting Yb(3+) from the metals list in the Plot Screen.

Figure 7. Example Plot Screen for a Physical Property method. This is a plot of metal ion ionization potential vs. $\log K(M_1\text{citrate})$ obtained during an estimation of $\log K$ for nickel citrate by selecting 'Electronegativity' under the 'Physical Property' menu option of the Estimate Screen.

Holding down the shift-key and clicking on a point will cause a label to appear that identifies the point. For example, in a M_1 vs. M_2 LFER plot each point represents a different ligand and the label would contain the name of the ligand.

Selecting the 'Maximize' button will enlarge the graph to full window size, for easier selection/deselection of data items. Clicking on the 'Ok' button while the graph is maximized will return to the original size graph.

Selecting the 'Print' button will bring up the available printer options for the computer system as well as available printers. This window is the common window used to make printer selections and change print options.

Selecting the 'Write' button will write details of the estimate to the output file and add the estimate to the list on the Estimate Screen.

Selecting the 'Ok' button will return the user to the Estimate Screen.

Method Dependent Features

An additional box is present in Plot Screens that appear when either the 'Two Metals' or 'Two Ligands' options are selected in the LFER pull-down menu. Unlike the other LFER and Physical Property methods, there may be multiple plots possible in these cases and the user must specify which plot to view.

In the 'Two Metals' case, where the program is plotting log K data for M_1 vs. M_2 , the Plot Screen contains a box with a list of possible metal ions. The user must select a metal ion from this list prior to viewing the plot corresponding to that metal ion. The user may select other metal ions from the list to examine all possible plots prior to exiting this Plot Screen.

In the 'Two Ligands' case, where the program is plotting log K data for L_1 vs. L_2 , the Plot Screen contains a box with a list of possible ligands. The user must select a ligand from this list prior to viewing the plot corresponding to that ligand. The user may select other ligands from the list to examine all possible plots prior to exiting this Plot Screen.

2.4.2.6 Hancock Equation

The Hancock pull-down menu contains three options. These are 'Current', 'Fit Metal', and 'Fit Ligand'. Viable options will appear in black text. Unavailable options will appear in grey text.

A viable 'Current' option indicates that parameters are available to estimate a log K using the Hancock equation described in Section 1.2.3.3. Selecting this option yields a Report Screen which contains a box reporting the log K estimate, a 'Write' button that causes the estimate to be written to an output file and to the log K list on the Estimate Screen, and a 'Done' button that closes the Report Screen and returns the user to the Estimate Screen.

If either 'Fit Metal' or 'Fit Ligand' are viable, this indicates that sufficient data is available in the current thermodynamic database to fit the metal parameters E_M , C_M and D_M or to fit the ligand parameters E_L , C_L and D_L . After fitting a set of parameters the Report screen will appear with the new results.

The parameter fitting options may be available even when the parameters are extant in the program. In this situation, choosing to fit parameters may alter the estimate. The reason is that the set of Hancock parameters provided with the program were fit simultaneously using thermodynamic data for all metal ions and all ligands currently in the database whereas the fitting options provided under the Hancock pull-down menu fit only fit the three parameters for the metal ion or the three parameters for the ligand using a limited subset of the thermodynamic data..

2.4.2.7 Brown and Sylva Equation

The Brown and Sylva pull-down menu contains two options. These are 'Current' and 'Fit Ligand'. Viable options will appear in black text. Unavailable options will appear in grey text.

A viable 'Current' option indicates that parameters are available to estimate a log K using the Brown and Sylva equation described in Section 1.2.3.3. Selecting this option yields a Report Screen which contains a box reporting the log K estimate, a 'Write' button that causes the estimate to be written to an output file and to the log K list on the Estimate Screen, and a 'Done' button that closes the Report Screen and returns the user to the Estimate Screen.

If 'Fit Ligand' is viable, this indicates that sufficient data is available in the current thermodynamic database to fit the ligand parameters d , E_L , int, and slope. After fitting a set of parameters the Report screen will appear with the new results.

The parameter fitting option may be available even when the parameters are extant in the program. In this situation, choosing to fit parameters may alter the estimate. The reason is that the default set of Brown and Sylva parameters provided with the program were fit for each ligand using all data available for that ligand at the time of fitting. If the user has altered thermodynamic database, different parameters may be obtained after fitting.

2.5 DATABASE MODIFICATION

The SCE program uses two types of data. These are (i) stability constant data and (ii) the parameters associated with the metal ions and the ligands. An image of these data are loaded into program memory from two database files (see Section 2.6) and this image is used in all subsequent operations carried out by SCE. The user may modify this database image through use of the Edit pull-down menu of the Main Screen. Modifications can be saved to a user-defined database files for later use (see Section 2.6).

The Edit pull-down menu of the Main Screen contains three options. These are 'Metal', 'Ligand', and 'Thermo'. These options allow the user to define a new metal ion or edit the parameters of an existing metal ion, to define a new ligand or edit the parameters of an existing ligand, and to add a new stability constant or change an existing stability constant, respectively.

2.5.1 Metal Ion Parameters

Figure 8 shows the Edit Metal Parameter Screen obtained by selecting 'Metal' from the 'Edit' pull-down menu of the Main Screen. This screen can be used to view parameters associated with each metal ion, alter the parameters associated with a metal ion, and define a new metal ion.

2.5.1.1 Viewing Metal Ion Parameters

To view parameters associated with a metal ion, select a metal ion from the current list of metal ions in the upper left of the screen. An empty parameter box indicates that the database does not currently contain a value for that parameter. Select the 'Cancel' button to return to the Main Screen.

2.5.1.2 Modifying Metal Ion Parameters

To modify a parameter associated with a metal ion, click in the box to locate the cursor, delete the old value, and enter a new value. An error message will appear if the new value is out of

range. Select the 'OK' button to enter the modifications into program memory and return to the Main Screen. Select the 'Cancel' button to return to the Main Screen without entering any modifications.

Current Metal Ions	Symbol	Type
Ag(+1)	Ag	Hard
Al(+3)		Borderline
Am(+3)		Soft
Au(+1)		
Ba(+2)		
Be(+2)		

Charge: 1

Radius: 1.150
angstroms

Electronegativity: 1.930

Ionization Potential: 0.731
MJ/mol

Hancock Parameters

E: -1.516 C: 0.143 D: 0.000

Brown and Sylva Parameters

d: 10 D: 1 M: 1 N: 4 S: 0 Radius: 0.670
angstroms

Ok Cancel Delete Metal

Figure 8. Edit Metal Parameter Screen after selection of the silver ion, Ag(+1).

2.5.1.3 Defining a New Metal Ion

To define a new metal ion, click in the boxes and enter the appropriate information. Definition of a new metal ion requires that the user provide a minimum of the name, the charge, and the type. Entries of other parameters is optional. Select the 'OK' button to enter the new metal ion type into program memory and return to the Main Screen. Select the 'Cancel' button to return to the Main Screen without entering any modifications. The new metal ion will now appear in the metal ion lists found in the Edit Metal Parameters Screen and the Metal-Ligand Selection Screen.

2.5.1.4 Description of Parameters

Symbol

The metal ion symbol is a character string limited to 6 characters in length. If the user enters a symbol that is longer than 6 characters, the symbol will be truncated to the first 6 characters. This information must be entered when defining a new metal ion.

Charge

SCE uses metal ion charge as a filter criteria when selecting thermodynamic data for LFER and Physical Property methods. The charge must be entered as a positive integer between 1 and 5, i.e. all metal ions in the metal ion list must be cations. Metal ion species that have negative charges, e.g. chromate or pertechnetate, are defined as ligands in the context of this program. If the user enters a value that is out of range, a warning message will appear. This parameter must be entered when defining a new metal ion.

Type

SCE uses metal ion type as a filter criteria when selecting thermodynamic data for LFER and Physical Property methods. Metal ions are assigned a type based on a hard - borderline - soft classification scheme (Pearson 1968). A type must be selected from the type list when defining a new metal ion.

Radius

The radius parameter is used in some Physical Property methods. Values in the database are Shannon's ionic radii (IR values for coordination number = 6 from Table 1 in Shannon 1976). The radius is entered as a real number that must be between 0 and 2 Å. If the user enters a number that is out of range, a warning message will appear. Leave this box blank if unknown.

Electronegativity

The electronegativity is used in some Physical Property methods. Values in the database are taken from Pauling's electronegativity scale (from Table 4.8 in Huheey 1978). The electronegativity is entered as a real number that must be between 0 and 3. Leave this box blank if unknown.

Ionization Potential

The ionization potential is used in some Physical Property methods. Values in the database are given in units of MJ/mol (from Table 2.4A in Huheey 1978). The ionization potential is entered as a real number that must be between 0 and 15 MJ/mol. Leave this box blank if unknown.

Hancock Metal Ion Parameters

The Hancock metal ion parameters are the E_M , C_M , and D_M values used in the Hancock equation (see Section 1.2.3.3). These parameters are entered as real numbers and may take any value. All default values provided with SCE have been fit simultaneously with the ligand parameters using all the stability constant data provided with SCE to provide an internally consistent set. Leave these boxes blank if unknown.

Brown and Sylva Metal Ion Parameters

The Brown and Sylva metal ion parameters are the d , D , M , N , S , Z_M , and r_M values used in the Brown and Sylva equation (see Section 1.2.3.3). Default values are taken from the literature (Brown and Sylva 1985). The parameters d , D , M , N , S , and Z_M are entered as integers. The value of r_M is entered as a real number with units of angstroms. Leave these boxes blank if unknown.

Note that although Brown and Sylva took their values of r_M from the same source as that used for the radius parameter described previously in this section, they sometimes took radii corresponding to coordination numbers other than six. Therefore, the values in the 'radius' box and the ' r_M ' box may differ.

2.5.1.5 Deleting a Metal Ion

After choosing a metal on the Edit Metal screen, the user can delete this metal ion by clicking on the 'Delete Metal' button. A conformation box will appear before the metal is deleted.

2.5.2 Ligand Parameters

Figure 9 shows the Edit Ligand Parameter Screen obtained by selecting 'Ligand' from the 'Edit' pull-down menu of the Main Screen. This screen can be used to view parameters associated with each ligand, alter the parameters associated with a ligand, and define a new ligand.

2.5.2.1 Viewing Ligand Parameters

To view parameters associated with a ligand, select a ligand from the current list of ligands in the upper left of the screen. An empty parameter box indicates that the database does not currently contain a value for that parameter. Select the 'Cancel' button to return to the Main Screen.

2.5.2.2 Modifying Ligand Parameters

To modify a parameter associated with a ligand, click in the box to locate the cursor, delete the old value, and enter a new value. An error message will appear if the new value is out of range. Select the 'OK' button to enter the modifications into program memory and return to the Main Screen. Select the 'Cancel' button to return to the Main Screen without entering any modifications.

2.5.2.3 Defining a New Ligand

To define a new ligand, click in the boxes and enter the appropriate information. Definition of a new ligand requires that the user provide the name, the charge, and the type. Entries of other parameters is optional. Select the 'OK' button to enter the new metal ion type into program memory and return to the Main Screen. Select the 'Cancel' button to return to the Main Screen without entering any modifications. The new ligand will now appear in the

ligand lists found in the Edit Ligand Parameters Screen and the Metal-Ligand Selection Screen.

Figure 9. Edit Ligand Parameter Screen after selection of acetate.

2.5.2.4 Description of Ligand Parameters

Name

The ligand name is a character string limited to 26 characters in length. If the user enters a name that is longer than 26 characters, the name will be truncated to the first 26 characters. This information must be entered when defining a new ligand.

Charge

SCE uses ligand charge as a filter option when selecting thermodynamic data for LFER and Physical Property methods. The charge must be entered as an integer between -6 and 6. If the user enters a value that is out of range, a warning message will appear. This parameter must be entered when defining a new ligand.

Type

SCE uses ligand type as a filter criteria when selecting thermodynamic data for LFER and Physical Property methods. Ligands are assigned a type based on donor group functionality. The default types include oxygen donor, aliphatic amine, aromatic amine, sulfur donor, amino acid, or other. A type must be selected from the type list when defining a new ligand.

The user may add additional types to the type list. This is done by selecting the 'Add Type' button at the bottom of the Edit Ligand Screen. This will bring up the Add Type Screen. Enter the name of the new type and select OK to return to the Edit Ligand Screen. The new type will be added to the bottom the type list.

Sum of pKa's

SCE uses this parameter in the sum of the pKa's LFER method. The sum of the pKa's is a real number that must be greater than zero. Leave this box blank if data is unavailable.

The default values provided with SCE were obtained as indicated below from literature pKa values (Martell and Smith 1974, 1977, 1982; Smith and Martell 1975, 1976, 1989).

Oxygen and sulfur donor ligands: Start from the current protonation state of the ligand and use the sum the pKa's associated with bringing the ligand to a charge neutral state, e.g. two protons must be added to phthalate(-2) and the sum of pKa's is $4.87 + 2.99 = 7.86$.

Aliphatic and aromatic amines: Start from the current protonation state of the ligand and use the sum of pKa's associated with protonating each donor atom in the ligand, e.g. two protons must be added to diaminoethane(0) and the sum of pKa's is $9.93 + 6.85 = 16.78$.

Amino acids: Start from the current protonation state of the ligand and use the sum of pKa's associated with protonating the ligand to a +1 charge, e.g. two protons must be added to glycinate(-1) and the sum of pKa's is $9.78 + 2.35 = 12.13$.

Hancock Ligand Parameters

The Hancock ligand parameters are the E_L , C_L , and D_L values used in the Hancock equation (see Section 1.2.3.3). These parameters are entered as real numbers and may take any value. All default values provided with SCE have been fit simultaneously with the metal ion parameters using all the stability constant data provided with SCE to provide an internally consistent set. Leave these boxes blank if unknown.

Brown and Sylva Ligand Parameters

The Brown and Sylva ligand parameters are the d , E_L , int , and slope values used in the Brown and Sylva equation (see Section 1.2.3.3). The parameter d is an integer that may take the value of 0 or 1. The parameters E_L , int , and slope are real numbers and may take any value. All default values provided with SCE have been fit to the stability constant data provided with SCE. Leave these boxes blank if unknown.

2.5.2.5 Deleting a Ligand

After choosing a ligand on the Edit Ligand screen, the user can delete this ligand by clicking on the 'Delete Ligand' button. A conformation box will appear before the ligand is deleted.

2.5.3 Stability Constant Data

Figure 10 shows the Edit Thermo Data Screen obtained by selecting 'Thermo' from the 'Edit' pull-down menu of the Main Screen. This screen can be used to view stability constants associated with each metal-ligand species, alter current stability constants, and add more stability constants.

Edit Thermo

Metal	Ligand
Ag[+1]	acac[-1]
Al[+3]	acetate[-1]
Am[+3]	acetoxyhydroxamate[-1]
Au[+1]	alanate[-1]
Ba[+2]	ammonia[0]
Be[+2]	aspartate[-2]
Bi[+3]	benzoate[-1]
Ca[+2]	bipyridyl[0]
Cd[+2]	bromide[-1]
Ce[+3]	i-butanoate[-1]

log K log K @ I=0

6.158 6.158

Ionic Strength

0.000

Reference (limit 60 characters)

Smith and Martell, Critical Stability Constants Series

OK Cancel Delete Thermo

Figure 10. Edit Thermo Data Screen after selecting americium aspartate.

2.5.3.1 Viewing Stability Constants

To view the current value of a stability constant for a metal-ligand species, select the metal ion from the metal list and select the ligand from the ligand list. If available, the log K value will appear in both the 'log K' box and the 'log K at I=0' box, the 'ionic strength' box will read zero, and the 'reference' box will contain a literature citation to the source of the data. If a log K value for this species does not exist, then these four boxes will remain blank. Select the 'Cancel' button to return to the Main Screen.

2.5.3.2 Modifying an Existing Stability Constant

To modify an existing stability constant, view the stability constant as above, then click in the 'log K' box to locate the cursor, delete the old value, and type in the new value. Next, click in the 'ionic strength' box and enter the ionic strength at which the new log K value was

measured. The ionic strength must be in the range of 0 to 1. An error message will appear if the ionic strength value exceeds 1.0. The log K at an ionic strength of zero will automatically be computed and appear in the 'log K at I=0' box. Stability constant values are always stored at an ionic strength of zero. Click in the 'reference' box and enter the literature citation to the source of the data. Select the 'OK' button to enter the modification into program memory and return to the Main Screen. Select the 'Cancel' button to return to the Main Screen without entering any modifications.

2.5.3.3 Adding a New Stability Constant

Adding a new stability constant to the database is the same as modifying an existing stability constant except that the input boxes will all be empty to start with. Note that to add a stability constant for a metal-ligand species, the metal ion and the ligand must be present in the metal list and ligand list, i.e. they must be defined (see Section 2.5.1 and Section 2.5.2 above).

2.5.3.4 Description of Stability Constant Parameters

log K

This box is used to enter experimental log K data. After selection of a metal-ligand species, this box will be empty when there is no stability constant data available or this box will contain the current log K at an ionic strength of zero when the stability constant is available. In the former case, the user would add a log K value to the database by entering it in this box. In the latter case, the user would modify an existing log K value by deleting the old value and entering a new value in this box.

Ionic Strength

This box is used to enter the ionic strength corresponding to the log K value found in the 'log K' box. After selection of a metal-ligand species, this box will be empty when the 'log K' box is empty or this box will contain a value of 0.0 when the 'log K' box contains a value. This box will accept a number between 0.0 and 1.0 when the user alters the contents of the 'log K' box.

log K at I=0

This box always reports the log K at an ionic strength of zero. After selection of a metal-ligand species, this box will be empty when there is no stability constant data available or this box will contain the current log K value when the stability constant is available. If the user adds a log K value or modifies an existing log K value, the values in the 'log K' box and the 'Ionic Strength' box are used to predict the log K at zero ionic strength in accordance with the Davies equation.

Reference

This box is used to enter a literature citation for the log K data. It can accept a character string up to 60 characters in length. This box will be empty when there is no stability constant data available or when a citation has not been entered for a stability constant value. Otherwise, this box will display a literature citation for the stability constant currently in the database.

2.5.2.5 Deleting a Stability Constant

After choosing a metal ion and ligand on the Edit Thermo screen, the user can delete the stability constant by clicking on the 'Delete Thermo' button. A confirmation box will appear before the stability constant is deleted.

2.6 FILES AND FILE HANDLING

2.6.1 The Output File

A record of the estimation results is saved in an output file (see Appendix A). There will always be an open output file during operation of SCE program. DEFAULT.OUT is the name of the output file that is opened on startup of the program. At the start of each stability constant estimation session, the user has the option of closing the current output file and opening a new output file. This is accomplished by selecting the 'Output File' button in the Metal-Ligand Selection Screen.

When performing an automatic stability constant estimate, details of each individual estimate are written to this file. When doing an interactive stability constant estimate, details for an estimate are written only after the user selects the 'Write' buttons that occur in the Plot Screens from LFER and physical property methods, the report screens for parametric equation methods, and the Estimate Screen.

The written output for an estimation session consists of a header identifying the metal ion and the ligand, details of each estimate, and a summary of all estimates performed.

Details for estimates made with LFER methods include a title identifying the method, a list of all data points used to construct the plot, the slope, intercept, and correlation coefficient from the linear regression, the value of the x variable used obtain the log K estimate, and the log K estimate. Details for estimates made with physical property methods include a title identifying the method, the function, the values for the adjustable parameters obtained either by linear or non-linear regression, a list of all data points used to construct the plot, the known values for the physical properties of the metal ion, and the log K estimate. Details for each of the parametric equation methods are limited to a title identifying the method and the log K estimate.

The summary of all estimates first presents a complete list of estimates that have been performed and the mean log K value. The summary then presents a list of estimates that remain after removing values that lie outside one standard deviation from the mean. The predicted log K value is the mean of this second list of estimates. The summary also contains

a table of the log K as a function of ionic strength and, if available, reports the experimental log K value from the database.

2.6.2 The Database Files

2.6.2.1 Default Database

The default database consists of two files that are provided with the program executable. These are named DEFAULT.THM which contains the stability constant data and DEFAULT.PAR which contains metal ion and ligand parameters.

DEFAULT.THM currently contains a total of 1418 stability constants for 1:1 metal-ligand complexes taken from three sources. These were the EPA MINTEQA2 database (Allison et al. 1991), the Critical Stability Constants series (Martell and Smith 1974, 1977, 1982; Smith and Martell 1975, 1976, 1989), and Hydrolysis of Cations (Baes and Mesmer 1976). All values in this database are at an ionic strength of zero.

DEFAULT.PAR currently contains parameters for 74 metal ions and 88 ligands. Parameters were taken from a variety of sources as described above in Sections 2.5.1 and 2.5.2.

2.6.2.2 User Modified Database

On startup, the program will always load an image of the database from the files DEFAULT.THM and DEFAULT.PAR. The user may modify the database image in two ways.

First, the user can modify the default database image by altering current values or by adding more data using features found in the 'Edit' pull-down menu of the Main Screen. These modifications can be saved prior to exiting the code by selecting the 'Save Database As' option from the 'File' pull-down menu of the Main Screen.

Second, the user can completely replace the default database image by loading a previously saved database. This is done by selecting the 'Open Database' option from the 'File pull-down

menu of the Main Screen. If the user always desires to use their own database, this step can be avoided by renaming the user defined database files to DEFAULT.THM and DEFAULT.PAR.

2.6.3 The Save File Screen

The Save File Screen is used to specify the name and path for a file generated by SCE. It appears when the user selects 'Output File' from the Metal-Ligand Selection Screen or when the user selects the 'Save Database As' option from the 'File' pull-down menu of the Main Screen. The user enters the name of the output file or database, specifies the directory where it will be placed, and clicks on the 'Save' button to return to the previous screen.

Note that a user defined database consists of two files that are assigned the same name with different extensions. When saving a user modified database, the user supplies only the name. The program automatically writes the thermodynamic database to <name>.thm and writes the metal and ligand parameter set to <name>.par.

2.6.4 The Open Database Screen

The Open Database Screen is used to load a user modified database. It appears when the user selects 'Open Database' from the 'File' pull-down menu of the Main Screen. The user selects the directory, enters the name of the database, and clicks on the 'Open' button to load the database and return to the Main Screen.

VALIDATION OF PERFORMANCE

How accurate are the estimations provided by SCE? One approach toward answering this question is to compare predicted and measured stability constant values. With this goal in mind, the program was modified to run an automatic estimate on every stability constant currently in the database. During this process, the database stability constant for a given metal-ligand species was not used in any of the estimations conducted for that species.

The results of this validation were as follows. SCE was able to perform estimates on 1407 of the 1418 stability constants in the database. The average error 0.46 log K units and the root mean squared error was 0.77 log K units. In general, better agreement with experiment is obtained when sufficient data are available to perform multiple estimates.

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APPENDIX A

The following is an example output file obtained through an interactive stability constant estimation on aluminum catechol. Default filter options were specified. This output file was constructed to illustrate the format used to report the details of each of the estimation methods.

ESTIMATION RESULTS FOR THE COMPLEX

METAL: Al (+3)
LIGAND: catechol (-2)

LFER sum of pKa's

DATA:

#	M	L	sum pKa	log K
(1)	Al (+3)	sulfate (-2)	1.987	3.020
(2)	Al (+3)	n-butanoate (-1)	4.730	2.498
(3)	Al (+3)	n-propanoate (-1)	4.874	2.608
(4)	Al (+3)	tartrate (-2)	7.402	7.156
(5)	Al (+3)	citrate*1H (-2)	7.889	6.558
(6)	Al (+3)	phthalate (-2)	8.358	5.103
(7)	Al (+3)	malonate (-2)	8.540	7.785
(8)	Al (+3)	acac (-1)	8.990	8.600
(9)	Al (+3)	acetohydroxamate (-1)	9.360	8.624
(10)	Al (+3)	hydroxide (-1)	13.998	9.008
(11)	Al (+3)	citrate (-3)	14.285	10.002
(12)	Al (+3)	salicylate (-2)	16.710	14.248

RESULTS:

slope = 0.739 +/- 0.101
intercept = 0.501 +/- 0.991
r = 0.918

known x = 22.200
 estimated log K = 16.913 +/- 2.449

LFER with Fe(+3)

DATA:

#	L	log K (Fe(+3)*L)	log K (Al(+3)*L)
(1)	sulfate(-2)	3.920	3.020
(2)	n-propanoate(-1)	4.318	2.608
(3)	n-butanoate(-1)	5.560	2.498
(4)	tartrate(-2)	7.838	7.156
(5)	citrate*1H(-2)	8.048	6.558
(6)	succinate(-2)	8.803	5.123
(7)	malonate(-2)	9.443	7.785
(8)	oxalate(-2)	9.453	7.936
(9)	acac(-1)	9.800	8.600
(10)	hydroxide(-1)	11.808	9.008
(11)	acetohydroxamate(-1)	12.094	8.624
(12)	citrate(-3)	13.522	10.002
(13)	salicylate(-2)	17.440	14.248

RESULTS:

slope = 0.844 +/- 0.073
 intercept = -0.755 +/- 0.735
 r = 0.961

known x = 21.348
 estimated log K = 17.257 +/- 1.723

LFER with acac(-1)

DATA:

L1 = acac(-1)

L2 = catechol(-2)

#	M	log K (M*L1)	log K (M*L2)
(1)	Mg(+2)	3.650	6.599
(2)	Mn(+2)	4.210	8.619
(3)	La(+3)	5.614	10.808
(4)	Ni(+2)	6.000	9.819
(5)	Pr(+3)	6.024	11.658
(6)	Nd(+3)	6.034	11.848

(7)	Sm(+3)	6.344	12.408
(8)	Gd(+3)	6.574	12.548
(9)	Eu(+3)	6.614	12.518
(10)	Dy(+3)	6.734	12.688
(11)	Ho(+3)	6.744	12.768
(12)	Er(+3)	6.754	12.778
(13)	Tm(+3)	6.814	12.908
(14)	Lu(+3)	6.824	12.658
(15)	Yb(+3)	6.854	13.018
(16)	UO2(+2)	7.700	16.799
(17)	Sc(+3)	8.000	18.388
(18)	VO(+2)	8.680	18.599
(19)	Ga(+3)	9.400	20.248
(20)	Fe(+3)	9.800	21.348

RESULTS:

slope = 2.486 +/- 0.139
 intercept = -3.375 +/- 0.965
 r = 0.973

known x = 8.600
 estimated log K = 18.005 +/- 1.539

Physical Properties Method 5

$\log K = a \cdot Z \cdot EN + b$

Parameters a and b fit by linear regression:

a = 4.140 +/- 0.404
 b = -2.261 +/- 1.603
 r = 0.943

DATA:

#	M	EN	Z	log K
(1)	La(+3)	1.100	3	10.808
(2)	Pr(+3)	1.130	3	11.658
(3)	Nd(+3)	1.140	3	11.848
(4)	Sm(+3)	1.170	3	12.408
(5)	Eu(+3)	1.185	3	12.518
(6)	Gd(+3)	1.200	3	12.548
(7)	Lu(+3)	1.270	3	12.658
(8)	Dy(+3)	1.220	3	12.688
(9)	Ho(+3)	1.230	3	12.768
(10)	Er(+3)	1.240	3	12.778

(11)	Tm(+3)	1.250	3	12.908
(12)	Yb(+3)	1.260	3	13.018
(13)	Sc(+3)	1.360	3	18.388
(14)	Ga(+3)	1.810	3	20.248
(15)	Fe(+3)	1.960	3	21.348

RESULTS:

known EN = 1.610
known Z = 3

estimated log K = 17.735 +/- 2.525

Hancock Method

RESULTS:

estimated log K = 17.338 +/- 0.900

Brown and Sylva Method

RESULTS:

estimated log K = 16.474 +/- 0.713

SUMMARY OF ESTIMATION

Complete list of estimates:

METHOD	log K	Std. Dev.
LFER Sum of pKa's	16.913 +/-	2.449
LFER with Fe(+3)	17.257 +/-	1.723
LFER with acac(-1)	18.005 +/-	1.539
Phys. Prop. (Z,EN)	17.735 +/-	2.525
Hancock	17.338 +/-	0.900
Brown & Sylva	16.474 +/-	0.713

Average log K = 17.287 +/- 1.096

Estimates remaining after removing outliers:

METHOD	log K	Std. Dev.
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LFER Sum of pKa's	16.913 +/-	2.449
LFER with Fe(+3)	17.257 +/-	1.723
Phys. Prop. (Z,EN)	17.735 +/-	2.525
Hancock	17.338 +/-	0.900

Predicted log K = 17.311 +/- 1.118

Ionic Strength	log K
0.000	17.311
0.100	15.963
0.200	15.665
0.300	15.513
0.400	15.430
0.500	15.388
1.000	15.475

An experimental value for this log K is available!!!.

log K (I=0): 17.64800

Citation: Smith and Martell, Critical Stability Constants Series