Tools of the Trade

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Adjustment, Estimation, and Uses of Equilibrium Reaction Constants in Aqueous Solution

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Environmental scientists, chemical engineers, chemists, and specialists in related fields need software to treat quantitatively the dependence of equilibrium constants and activity coefficients on ionic strength and on the presence of dissolved gases. IUPAC has been actively involved in this problem for many years and is now able to provide several software tools.

In 2006, the project Adjustment, Estimation, and Uses of Equilibrium Reaction Constants in Aqueous Solution <www.iupac.org/projects/2006/2006-010-1-500.html> was initiated as an extension of project 2000-003-1-500, Ionic Strength Corrections for Stability Constants. The aim of this project is to prepare a suite of programs to correct stability constants for ionic strength changes and temperature changes, for the calculation of gas solubilities, for speciation calculations, and for titration simulations.

Overview of the Suite of Programs

The software package (*Aq_Solutions.exe*) for the quantitative treatment of equilibria in solution consists of a suite of programs that will be regularly extended and updated. Currently, the suite of programs includes those developed under project 2000-003-1-500, but these are now being extended. Programs already available include:

SIT: This corrects stability constants for changes in ionic strength using Specific Interaction Theory (SIT) and estimates SIT parameters, with full statistics. It contains an editable database of published SIT parameters. It also provides routines to inter-convert MolaRity (c) and MolaLity (m), and lg K_c and lg K_m values. A version of the SIT program to correct stability constants for changes in seawater salinity and in electrolyte mixtures is currently being tested.

Electrolytes: This calculates electrolyte activity coefficients, osmotic coefficients, and the activity of water for 315 electrolyte solutions using the Pitzer and Lin-Tseng-Lee equations. It also calculates

- ionic activity coefficients using the Millero-Pitzer and Lin-Tseng-Lee methods
- ionic activity coefficients for 77 ions in various electrolyte solutions ($NaClO_4$, KCl, NaCl, etc.) using the Pitzer-Millero method
- ionic activity coefficients for the most important 28 ions in seawater, using the Millero ion pairing model and the Lund-Jonsson -Padersen method

Acid-base: This calculates the composition of acid-base systems at equilibrium in electrolyte solutions and seawater. It also calculates the following:

- equilibrium protonation constants of the 8 most important and widespread inorganic acids, 14 carboxylic acids, 9 aminoacids, 4 nuclotide-5'-phosphoric acids, 10 phenolic compounds, and 5 bio-logically activity organic amines at different salinity (chlorinity) at different temperatures
- the equilibrium molar fractions of free acid and free base ionic forms as a function of pH
- p*K*w values and the H^+ activity coefficient in seawater at different salinity (chlorinity) and tempera-tures using the Culberson-Pytkowicz-Dickson-Riley-Hansson, Millero, Sammartano-De Robertis, and Millero ion pairing models
- H^+ activity coefficients for correction of pa_H to $p[H^+]$ in different ionic media (KBr, KNO_3, KCl, NaCl, $NaClO_4$) at 298 K
- dissociation constants of 28 organic acids at different concentration of background electrolytes (KNO_3, $NaNO_3$, KCl, NaCl) at 18 and 25 °C, using simplified Pitzer theory
- equilibrium molar fraction of free ionic forms of 247 polycarboxylic (mono-, di-, tri-, tetra-) acids and the equilibrium molar fraction of weak complexes of ionic forms of polycarboxylic acids as a function of ion background electrolyte at different pH

The program also helps predict the influence of background electrolyte on thermodynamic protonation constants.

Temperature effects: This calculates and models the thermodynamic properties (lg K°_{298}, ΔH°_{298}, ΔS°_{298}, $\Delta C_p{}^\circ_{298}$, $d(\Delta C_p{}^\circ_{298})/dT$, $d2(\Delta C_p{}^\circ_{298})/dT^2$) from temperature dependence of equilibrium constant using eight thermodynamic equations: Van't Hoff, Isobar, Extended Isobar, Clarke-Glew, Extended Clarke-Grew, DQUANT, Valentiner, and Blandamer-Robertson-Scott equations. It also predicts the temperature dependence of lg *K*. Full statistics are included.

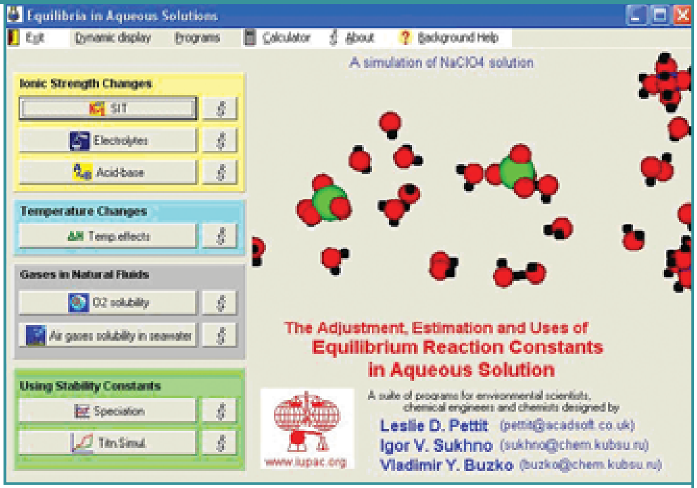
O_2 solubility: This calculates the solubility of gaseous O_2 in pure water at different temperatures, pressures, altitudes, humidities, and for different concentration ranges using Millero experimental data, the Garcia-Gordon equation, and recommended tabular data. It also calculates O_2 solubility in:

- 22 electrolyte solutions at different temperatures, pressures, and concentration ranges
- natural fluids (brines, mine waters, mineralized waters, urine, blood and other physiological media) and artificial fluids (artificial sea water, mixed salt solutions, process liquids) for different ionic compositions at different temperatures, pressures, humidities, and concentration ranges, taking account of the fluid pH
- seawaters over a range of salinities at different temperatures, pressures, humidities, and concentration ranges

It employs three equations to calculate oxygen solubility in seawaters: Garcia-Gordon, Pitzer-Millero (using two artificial seawater standards SSWE) and the ASW Millero polynomial equation derived from Millero experimental data. It uses the Garcia-Gordon equation to predict O_2 solubility in hypersaline waters up to 200 ‰ salinity, over the temperature range 0 to 100°C.

Atmospheric Gas solubility in seawater: A program to calculate air gas (N_2, Ar, CO_2) equilibrium concentrations in pure water and seawaters vs. temperature, pressure, and depth is being tested.

Speciation: This calculates and displays species distribution curves for complexes (including insoluble species). Speciation may be displayed as a function of pH, pL (any reactant), or total reactant concentration, and as either percentages or as species concentrations (log values). When insoluble phases are present, lg *s* values may also be plotted. The sensitivity of speciation curves to errors in lg *K* values may be demonstrated graphically.



A simulation of NaClO4 solution

The Adjustment, Estimation and Uses of
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A suite of programs for environmental scientists,
chemical engineers and chemists designed by
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Titration simulations: This simulates M-L titration curves in real time and displays speciation dynamically. Species L, HL, H_2L, ML, ML_2, MHL and $MH_{-1}L$ may be included and stability constants adjusted in real time.

Availability

A preliminary version of the programs (a zip file) may be downloaded from <www.iupac.org/projects/2006/2006-010-1-500.html> or from <http://public.kubsu.ru/aquasolsoft>.

Please send comments and suggestions to the authors.

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www.iupac.org/projects/2006/2006-010-1-500.html

The **Tools of the Trade** series, coordinated by Kip Powell, past president of the IUPAC Analytical Chemistry Division, provides a forum for views and discussion on one of the Union's goals: "IUPAC will facilitate the advancement of research in the chemical sciences through the tools that it provides for international standardization and scientific discussion." If you wish to contribute, please contact <kip.powell@canterbury.ac.nz>.