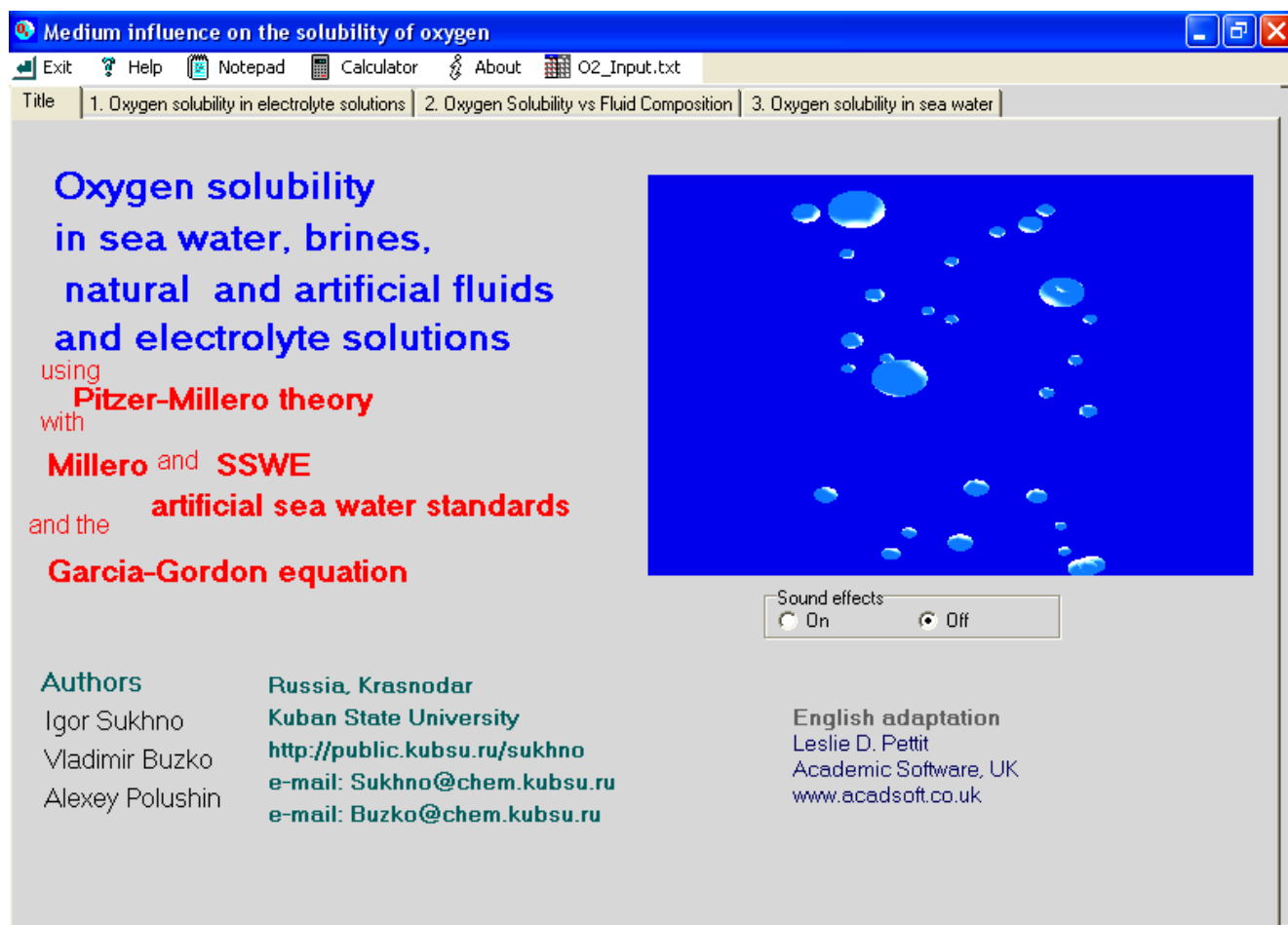


Manual



Introduction

O2_Solubility is a program to calculate the oxygen solubility in sea waters over a range of salinities, natural fluids (mineralized waters, brines) and electrolyte solutions. It employs a Pitzer-Millero type equation to calculate the solubility nonelectrolytes in salt solutions. It also employs three equations to calculate oxygen solubility in sea waters:

1. the Garcia-Gordon equation,
2. the Pitzer-Millero equation using two artificial sea water standards: the SSWE (Synthetic Sea Water for Equilibrium studies) and the ASW – Millero recipe
3. a polynomial equation derived from Millero experimental data.

These equations allow calculation of the solubility of gaseous O₂ in a precise and convenient way.

O2_Solubility has been developed under the Windows 9x, 2000 and Windows NT/XP operating systems. The 32-bit version was built by Borland Delphi 5.0. The first version program was released on May 15, 2004 as version 1.0.

O2_Solubility program is composed of the following files:

- **O2_solubility.exe** – the program exe-file
- **O2_input.txt** – input file
- **O2_help.chm** – the help file

If you have any suggestions, or know of any models and additional parameters that you would like to see added to the repertoire, please send us an e-mail. We will gladly attend to your comments since we wish to continue development and support of this program.

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The authors express their sincere gratitude to

Dr. Leslie D. Pettit (Academic Software, UK, <http://www.acadsoft.co.uk>)

for his advice on designing this program.

Using the O2_Solubility.exe program

The **O2_Solubility.exe** program has easy point-and-click interface and allows the user to

- Calculate the solubility of gaseous O₂ in pure water at different temperatures
- Calculate the solubility of gaseous O₂ in electrolyte solutions at different temperatures and different concentration ranges (gram per kg water, mole per kg water, mole per liter solution)
- Compare the solubility of gaseous O₂ in different electrolytes at selected conditions
- Calculate the solubility of gaseous O₂ in natural fluids (brines, mine waters, mineralized waters, urine, blood and other physiological liquors) and artificial fluids (artificial sea water, mixed salt solutions, process liquids) with different ionic compositions and at different temperatures taking account the fluid pH
- Calculate the gaseous O₂ solubility in sea waters over a wide salinity range and choose from 2 built-in nonelectrolyte solubility models (using two common Artificial Sea Water standards: ASW and the Millero, SSWE) and compare to experimental data
- Calculate the gaseous O₂ solubility in hypersaline waters up to 200 ‰ using the Garcia-Gordon equation over the temperature range of 0 to 100 °C
- Copy plots directly to the clipboard to use in another Windows application
- Save all results of calculation in Rich Text Format file
- Read simple ASCII data files
- Use comments in input file and in the final RTF output
- Scale, translate, sort, remove and edit data sets by hand similarly to a spreadsheet
- Receive and to keep calculated solubility of gaseous O₂ in a tabular and graphic form.

The **O2_Solubility.exe** program has 3 main tabbed pages:

- ❑ **Oxygen solubility in electrolyte solutions**
- ❑ **Oxygen solubility vs. fluid composition**
- ❑ **Oxygen solubility in sea water**

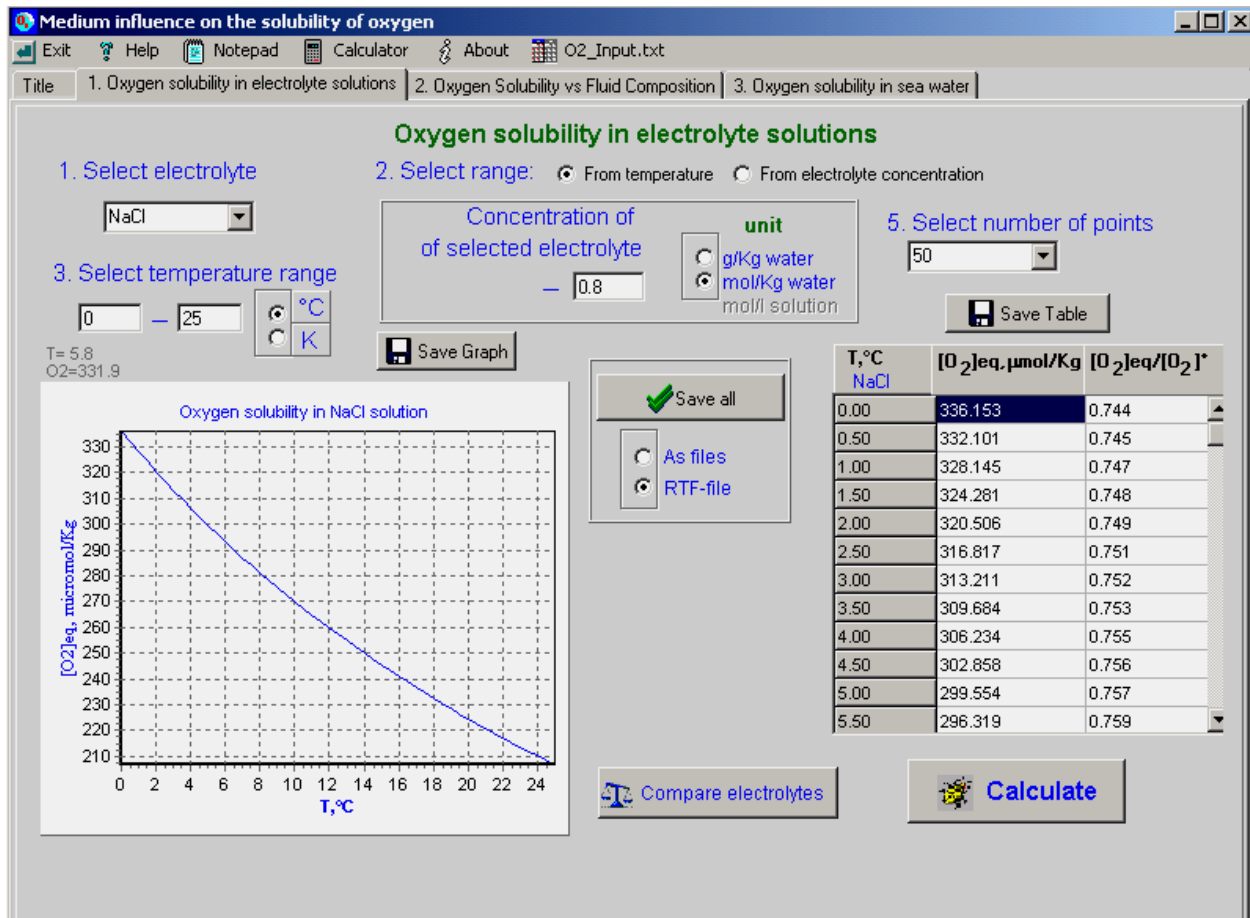
Like all Windows applications, you can also select items off of the menu bar to accomplish certain tasks.

The toolbar gives access to frequently used commands

- ✓ **Exit**
- ✓ **Help**
- ✓ **About**
- ✓ **Notepad**
- ✓ **Calculator**

Oxygen solubility in electrolyte solutions

A ‘Oxygen solubility in electrolyte solutions’ tabbed page is shown below



The solubility of oxygen in individual electrolyte solutions is calculated from equations proposed by Millero in his numerous studies [1-3] devoted the solubility of oxygen in individual and mixed aqueous electrolyte solutions:

$$\ln([O_2]^0/[O_2]) = \ln \gamma(O_2) = Am + Bm^2 \quad (1)$$

or

$$\ln[O_2] = A + Bm + Cm^2 \quad (2)$$

Equation (1) allows calculation of the solubility of gaseous oxygen in aqueous solutions of 18 important electrolytes (LiCl, KCl, RbCl, CsCl, NaF, NaBr, NaI, NaNO₃, KBr, KI, KNO₃, CaCl₂, SrCl₂, BaCl₂, Li₂SO₄, K₂SO₄, Mg(NO₃)₂) at 25 °C with a precision better than ±3.0 μmol/kg water and the calculation of the solubility of gaseous oxygen in aqueous solutions of 4 major sea salts (NaCl, MgCl₂, Na₂SO₄, and MgSO₄) over the 5-45 °C range (for NaCl 0-45 °C range) with precision better ±2.0 μmol/kg water.

The solubility of oxygen in pure water (ln [O₂]⁰ units) is calculated over the temperature range 0-50 °C (273.15-323.15 K) from Millero's experimental data [2] using the equation:

$$[O_2], \mu\text{mol/kg water} = a \cdot \exp(b/(T+c)) \quad (3)$$


where $a=23.7734$, $b=317.7348$, $c=-165.2438$.

Equation (3) allows calculation of the solubility of gaseous oxygen in pure water over the 0-50 °C range with a precision better $\pm 1.15 \mu\text{mol/kg}$ water.

Parameters of equation (1) and equation (2) are in the [O2_input.txt](#) file.

Calculate and save results

To calculate the solubility of gaseous oxygen in aqueous solutions of electrolytes

- ❖ Select electrolyte
- ❖ Select calculation range (from temperature or from electrolyte concentration)
- ❖ Indicate the temperature (Celsius or Kelvin scale) or concentration (g/kg water, mol/kg water, mol/l solution) range
- ❖ Select the number of points
- ❖ Select desired type of "[Plot graph as](#)"
- ❖ Press the " [Calculate](#)" button

Graphs may be plotted using the coordinates

- ❖ $[\text{O}_2]_{\text{equilibrium}}$, micromole/kg water
- ❖ $[\text{O}_2]_{\text{equilibrium}}/[\text{O}_2]^0$ pure water

The user can save

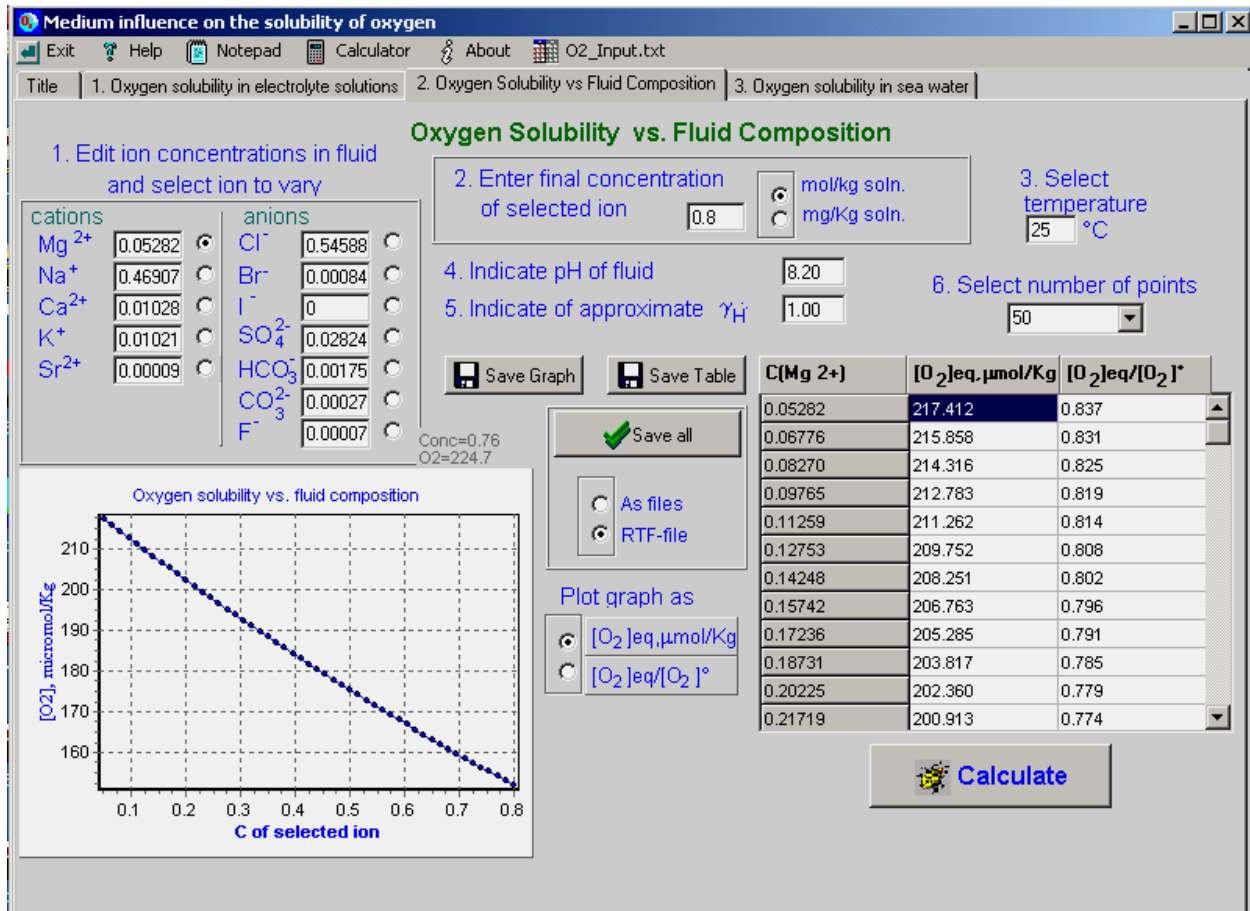
- ❖ the table of the calculated values as a text file (*.txt) and to the clipboard simultaneously
- ❖ the plot as a graphic file (*.bmp) and to the clipboard simultaneously
- ❖ all results together (table, plot, comments) in RTF format

The user can also compare

- ❖ the solubility of oxygen in different electrolytes "[Compare electrolytes](#)":
 - as plots (up to 5 electrolytes)
 - as tabular data (2 electrolytes)

Oxygen Solubility vs. Fluid Composition

A ‘Oxygen solubility vs. fluid composition’ tabbed page is shown below



The oxygen solubility is calculated depending on fluid composition. “Fluid” means natural (brines, mine waters, mineralized waters, urine, blood and other physiological liquors) or artificial (artificial sea water, mixed salt solutions, process liquids) solutions. The fluid composition is set per ion and takes into account the major ions of natural and artificial solutions (cations: Na^+ , Mg^{2+} , K^+ , Na^+ , Ca^{2+} , Sr^{2+} , anions: Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , Br^- , F^- , I^-). The user must take the pH of fluid into account. The activity coefficient of H^+ is also used if it is known.

The oxygen solubility is calculated by the γ_{O_2} coefficient – ratio of solubility of oxygen in pure water to solubility of oxygen in electrolyte solution [4]:

$$\ln\{[\text{O}_2]^0/[\text{O}_2]\} = \ln\gamma(\text{O}_2) \quad (4)$$

Interactions between ions which are components of a fluid are accounted for using the Pitzer type equations [1,4-5]:

$$\ln\gamma_{\text{O}_2} = 2\sum_c \lambda_{\text{O}_2\text{c}} m_c + 2\sum_a \lambda_{\text{O}_2\text{a}} m_a + 2\sum_N \lambda_{\text{O}_2\text{N}} m_N + \sum_c \sum_a m_c m_a \zeta_{\text{O}_2\text{ca}} \quad (5)$$

where

$\lambda_{\text{O}_2\text{i}}$ is a parameter that accounts for the interaction of O_2 with cations (c) and anions (a),

$\zeta_{\text{O}_2\text{ca}}$ accounts for interactions for O_2 with the cation and anion (c-a).

The component N is used to denote the interactions between O_2 with neutral species (e.g., the MgSO_4 ion pair).

As shown elsewhere [2], the Pitzer equations (5) yield reliable estimates of the solubility of oxygen in artificial brines and mixtures of the major sea salts at 25 °C. The solubility of oxygen in the binary mixtures without complex formation agree to within $\pm 5 \mu\text{mol/kg}$, whereas for the binary mixtures with complex formation (e.g. Na_2SO_4 and MgCl_2) agreement decreases to $\pm 10 \mu\text{mol/kg}$ [1]. This can be related to the formation of ion pairs in the mixture [2]. Calculations of the solubility of O_2 in seawater and artificial seawater with this model were found to be in good agreement with the measured values ($\pm 5 \mu\text{mol/kg}$.) [1-2].

The ionic Pitzer salting-out coefficients for the major natural salts should allow one to make a reliable estimates of the solubility of oxygen in mixed electrolyte solutions over a wide range of temperatures and concentrations.

We used the values of λ_{O_2} for the interactions of Na^+ , Mg^{2+} , SO_4^{2-} and $\xi_{\text{O}_2, \text{ca}}$ for the interactions of NaCl , Na_2SO_4 , MgCl_2 and MgSO_4 with O_2 as temperature-dependent functions from 5 to 45 °C (T/K). These have been fitted to equations of the form ($\lambda_{\text{O}_2 \text{ Cl}} = 0$) [2]:

$$\lambda_{\text{O}_2 \text{ ion}} (\xi_{\text{O}_2, \text{ca}}) = a_0 + a_1/T + a_2 \cdot \ln T \quad (6)$$

All coefficients a_0 , a_1 , a_2 for the ions discussed are taken from [2].

Because other ions Ca^{2+} , K^+ , Sr^{2+} , Br^- , I^- , HCO_3^- , CO_3^{2-} , F^- and H^+ , along with the prevailing natural ions Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , are the major components of most natural waters, it is desirable to have reliable solubility data for them over a wide range of temperature and ionic strength and it is essential to account for interaction between O_2 and Ca^{2+} , K^+ , Sr^{2+} , Br^- , I^- , HCO_3^- , CO_3^{2-} and F^- . Unfortunately, to the best of our knowledge, data for those ions over a wide range of temperatures and ionic strengths are be lacking. For the more significant ions such as Ca^{2+} and K^+ we used the following approximations to calculate ionic Pitzer salting-out coefficients for Ca^{2+} and K^+ ions at different temperature:

$$\frac{\lambda_{\text{O}_2 \text{ Ca}} (T/K)}{\lambda_{\text{O}_2 \text{ Ca}} (298.15)} = \frac{\lambda_{\text{O}_2 \text{ Mg}} (T/K)}{\lambda_{\text{O}_2 \text{ Mg}} (298.15)}, \quad \frac{\lambda_{\text{O}_2 \text{ K}} (T/K)}{\lambda_{\text{O}_2 \text{ K}} (298.15)} = \frac{\lambda_{\text{O}_2 \text{ Na}} (T/K)}{\lambda_{\text{O}_2 \text{ Na}} (298.15)} \quad (7)$$

$$\frac{\xi_{\text{O}_2 \text{ CaCl}_2} (T/K)}{\xi_{\text{O}_2 \text{ CaCl}_2} (298.15)} = \frac{\xi_{\text{O}_2 \text{ MgCl}_2} (T/K)}{\xi_{\text{O}_2 \text{ MgCl}_2} (298.15)}, \quad \frac{\xi_{\text{O}_2 \text{ KCl}} (T/K)}{\xi_{\text{O}_2 \text{ KCl}} (298.15)} = \frac{\xi_{\text{O}_2 \text{ NaCl}} (T/K)}{\xi_{\text{O}_2 \text{ NaCl}} (298.15)} \quad (8)$$


$$\frac{\xi_{\text{O}_2 \text{ CaSO}_4} (T/K)}{\xi_{\text{O}_2 \text{ CaSO}_4} (298.15)} = \frac{\xi_{\text{O}_2 \text{ MgSO}_4} (T/K)}{\xi_{\text{O}_2 \text{ MgSO}_4} (298.15)}, \quad \frac{\xi_{\text{O}_2 \text{ K}_2\text{SO}_4} (T/K)}{\xi_{\text{O}_2 \text{ K}_2\text{SO}_4} (298.15)} = \frac{\xi_{\text{O}_2 \text{ Na}_2\text{SO}_4} (T/K)}{\xi_{\text{O}_2 \text{ Na}_2\text{SO}_4} (298.15)} \quad (9)$$

For the others ions Sr^{2+} , Br^- , I^- , HCO_3^- , CO_3^{2-} , F^- and H^+ ionic Pitzer salting-out coefficients were assumed to be temperature-independent. Ionic values of the Pitzer coefficients for oxygen for ions at 25 °C were taken from [3-4], except for values for HCO_3^- , CO_3^{2-} , H^+ and OH^- which were taken from [5].

Calculate and save results

To calculate the solubility of gaseous oxygen in fluids

- ❖ Enter ion concentrations of fluid and indicate desired ion (default it is used the fluid composition corresponding the Millero data for natural sea water at 35 ‰ [6-7])
- ❖ Enter final concentration of selected ion
- ❖ Indicate the temperature (from -5 to 50 °C).
- ❖ Indicate the pH of fluid if it is possible (default it is used the pH corresponding the Millero data for natural sea water at 35 ‰ [6-7])
- ❖ If possible, enter the activity coefficient of H^+ (default $\gamma_{\text{H}^+}=1$)

- ❖ Indicate the number of points
- ❖ Indicate desired type of "**Plot graph as**"
- ❖ Press the "  **Calculate** " button

Graphs may be plotted using the coordinates

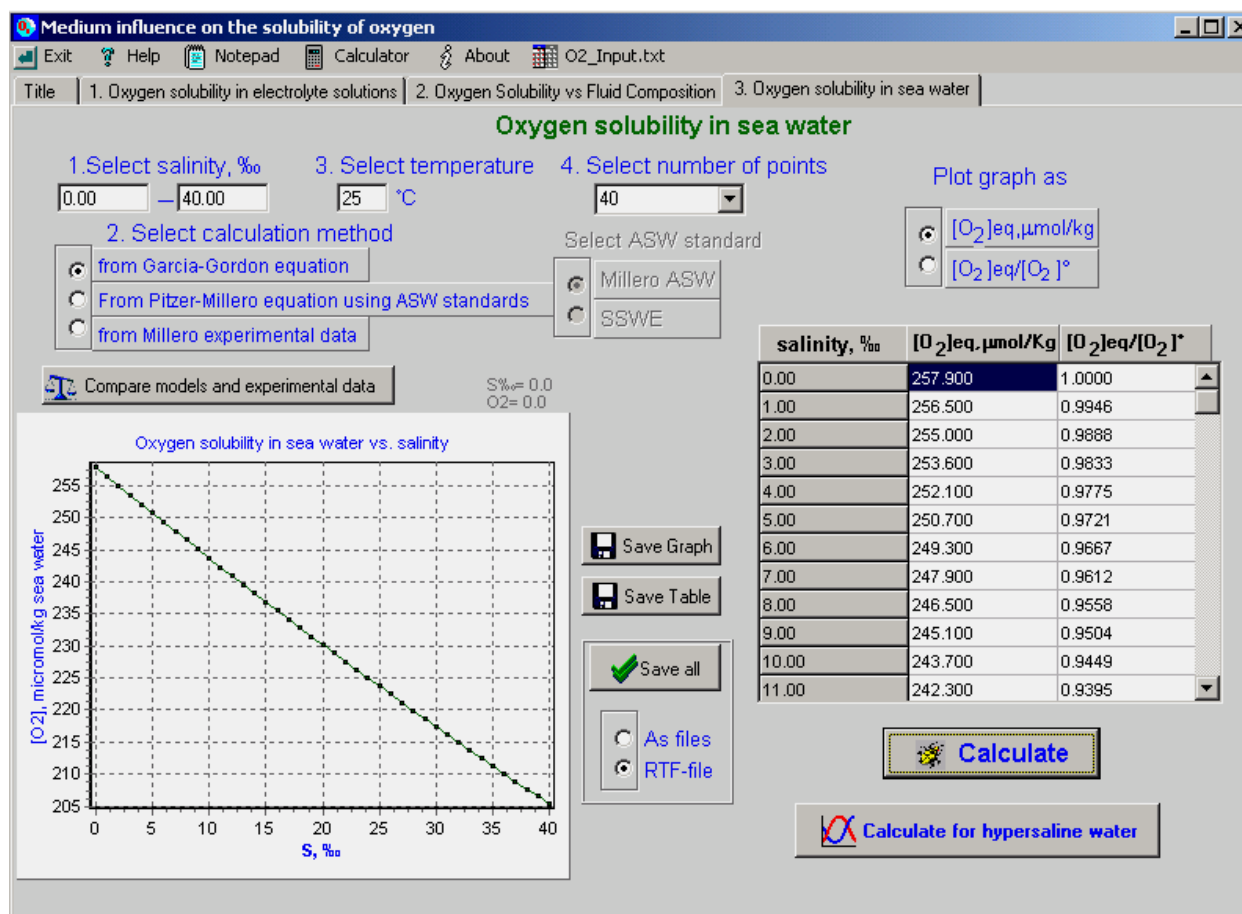
- ❖ $[O_2]_{\text{equilibrium}}$, micromole/kg water
- ❖ $[O_2]_{\text{equilibrium}}/[O_2]^0$ pure water

It is possible to save

- ❖ the table of the calculated values as a text file (*.txt) and to the clipboard simultaneously
- ❖ the plot as a graphic file (*.bmp) and to the clipboard simultaneously
- ❖ all results together (table, plot, comments) in RTF format

Oxygen solubility in sea water

A ‘Oxygen solubility in sea water’ tabbed page is shown below



The oxygen solubility in seawater is calculated using the equation proposed by Garcia and Gordon [8]. This equation yields values for the solubility of oxygen in water and seawater over the temperature range 0 to 40°C and salinity range 0 to 40 ‰. This gives agreement to within 0.5 μmol/kg with the experimental data of Benson and Krause [9]. For the wider temperature range from 0 to 100°C and salinity range 0 to 200 ‰ the Garcia and Gordon equation gives an approximate estimation oxygen solubility in sea water which agrees to within ± 10 μmol/kg [8].

It is also used another way. At temperature 25°C and salinity range 0 to 45 ‰ the oxygen solubility in sea water is calculated from values proposed by Millero [1].

The third way to calculate the oxygen solubility in sea water at different salinity and temperature is using the Pitzer equation type (5) and artificial sea water standards (ASW) with a known ionic concentration composition. The ionic values of the Pitzer coefficients for oxygen for the ions discussed are taken from [2-5].

The Artificial Sea Water (ASW) recipe proposed by Millero [6-7] and Synthetic Sea Water for Equilibrium studies (SSWE) standard proposed by De Stefano-Foti-Sammartano-Gianguzza [10-11] are used.

Noted that complex formation between Mg^{2+} with SO_4^{2-} is taken into account using parameters from [1].


Sea water densities used for intermediate calculation are from the Millero & Poisson equation [12].

P.S.

Note that the conversion of oxygen content from milliliter/liter (ml/l) to $\mu\text{mol/kg}$ may be made by multiplying the oxygen content in ml/l by the molar volume of oxygen (44.660 $\mu\text{mol/l}$) and dividing by the potential density expressed in kg/l [13].

Calculate and save results

To calculate the solubility of gaseous oxygen in sea water

- ❖ Select salinity range
- ❖ Select calculation method (in Pitzer-Millero case indicate also the ASW standard)
- ❖ Indicate the temperature
- ❖ Indicate the number of points
- ❖ Indicate desired type of "**Plot graph as**"
- ❖ Press the "  **Calculate** " button

Graphs may be plotted using the coordinates

- ❖ $[\text{O}_2]_{\text{equilibrium}}$, micromole/kg sea water
- ❖ $[\text{O}_2]_{\text{equilibrium}}/[\text{O}_2]^0$

It is possible to save

- ❖ the table of the calculated values as text file (*.txt) and to a clipboard simultaneously
- ❖ the plot as a graphic file (*.bmp) and to a clipboard simultaneously
- ❖ all results together (table, plot, comments) as a protocol in RTF format

It is also possible to

- ❖ compare the solubility of oxygen in sea water for different calculation methods "**Compare models and experimental data**"
- ❖ calculate the gaseous O_2 solubility in hypersaline waters up to 200 ‰ using the Garcia-Gordon equation for the temperature range of 0 to 100 °C

Input file

The **O2_input.txt** file contains **A**, **B** parameters for equation (1), maximum valid molality of the equation used **MaxMolality**, and molar mass **Mr** of salt. Below is an example of this section:

```
-----
<Used equation type: ln {[O2]owater/[O2]solution}=A*m+B*m*m>
<Salt  MaxMolality  A          B          Mr>
NaCl   5.0    0.2949    -0.009986    58.44
        (0.3135)    (-0.006071)
NH4Cl  1.1    0.2484    -0.00054     53.49
        (0.2850)    (-0.00234)
LiCl   12.5   0.1894    -0.00456     42.39
        (0.2074)    (-0.00244)
KCl    4.7    0.2802    -0.01804     74.55
        (0.3076)    (-0.01177)
RbCl   2.5    0.2725    -0.03356     120.92
        (0.3071)    (-0.01885)
CsCl   1.7    0.2935    -0.08271     168.36
        (0.3334)    (-0.05359)
MgCl2  5.5    0.4797    -0.01658     95.21
        (0.4938)    (-0.004153)
CaCl2  4.1    0.5164    -0.02507     110.99
        (0.5352)    (-0.00919)
SrCl2  2.6    0.5683    -0.02798     158.53
        (0.5886)    (-0.00058)
-----
```

In brackets there are coefficients to calculate oxygen solubility in electrolyte solutions in molarity scale of electrolyte concentration.

The **O2_input.txt** file also contains **A**, **B**, **C** parameters for equation (2), maximum valid molality of used equation **MaxMolality**, and temperature. Below is an example of this section:

```
-----
<Used equation type: ln [O2]solution=A+B*m+C*m*m>
<Salt  t,°C  A      B      C      MaxMolality>
[NaCl]  0    6.1152 -0.3869 0.01751    6.1
        5    5.9850 -0.3537 0.01285    6.0
        10   5.8544 -0.3339 0.01235    6.0
        15   5.7550 -0.3223 0.01160    6.1
        20   5.6511 -0.3123 0.01234    5.9
        25   5.5608 -0.2991 0.01139    5.0
        30   5.4759 -0.2917 0.01224    6.2
        35   5.3982 -0.2794 0.01088    5.7
        40   5.3303 -0.2742 0.01171    6.2
        45   5.2300 -0.2782 0.01206    6.3
[Na2SO4] 5    5.9825 -0.9664 0.14617    0.5
        15   5.7462 -0.8768 0.10244    1.0
        25   5.5473 -0.8423 0.10277    1.5
        35   5.3962 -0.7855 0.08114    1.8
        45   5.2447 -0.7537 0.09040    2.6
-----
```

The user can edit and add to the input file. Note that the columns need only be separated by tab (\rightarrow |). Comments may be interspersed freely within the data files provided they are contained between angle brackets $<>$.

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