Thermodynamics of Aerosols and Droplets Using the Extended Aerosol Inorganics Model (*E-AIM*)

http://www.aim.env.uea.ac.uk/aim/aim.php
or http://www.aim.env.uea.ac.uk

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1. Overview

What is *E-AIM*? It is a web-based computer program for calculating gas/liquid/solid equilibrium in chemical systems of interest to atmospheric chemists. These systems consist of the major inorganic ions (H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^- and Cl^-), and also organic compounds including acids and amines. Calculations can be carried out for:

1. user-specified concentrations of solute species (ions and organic compounds) in water
2. for known amounts (moles) of species and total water in 1 m^3 of atmosphere
3. for known amounts (moles) of species at equilibrium with ambient relative humidity (*RH*) and temperature in 1 m^3 of atmosphere.

There are also calculators on the site for densities and surface tensions of mixtures, and the vapour pressures of pure organic compounds based upon their structure. There are four separate models:

Model I: H^+ - SO_4^{2-} - NO_3^- - Cl^- - Br^- - H_2O (valid from <200 to 330 K).
Model II: H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O (valid from <200 to 330 K).
Model III: H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O (for 298.15 K only).
Model IV: H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O (valid for ≤263 to 330 K, depending on composition).

Each of these models is able to include up to 20 organic compounds (non-dissociating, acids and di-acids, and/or amines and di-amines). These compounds can be selected from a list, or can be defined by the user by filling in a data page for their thermodynamic properties.

Users can register with the site with an email address and password, in the usual way. If they do so, they will be able to save any organic compounds that they define, so that they can be recalled and used in future sessions and shared with colleagues and students.

2. This Presentation

This presentation describes the use of the models on the *E-AIM* website to carry out various aerosol-related calculations. The thermodynamic principles of the model are described in the tutorial, but some basic knowledge is assumed. The tutorial presented at the meeting includes a number of worked examples (shown as recordings). There are draft copies of these on the web, which you can view at any time. The link is given in the final section of these notes.

The *E-AIM* website contains extensive help information, both on how to use the model and on the underlying thermodynamics (with references to the published papers that describe this). In these notes we provide links to that information, supplement it with citations of useful books and papers, and give additional information that will help the user/reader to understand the contents of the presentation and use the model. We do not duplicate here the help information on the website. This document, and the contents of the website, are complementary and are best studied together.

3. How to Get Up and Running Quickly

1. Read the Quick Start Guide (http://www.aim.env.uea.ac.uk/aim/info/quickstart.html). This also links to other pages with important basic information.
2. Read the FAQ (http://www.aim.env.uea.ac.uk/aim/info/faq.html).
3. Do the tutorials, which demonstrate the basic functionality of the model, using simple inorganic systems: http://www.aim.env.uea.ac.uk/aim/tutorial/tutorial.php.
4. Follow the link in section 9 of this document to see the videos of the example calculations shown in the presentation.

4. Summary Descriptions of *E-AIM* Models I-IV

Each of the models is for a different set of common inorganic ions, plus water and organic compounds. The models consist of :

1. A set of equilibrium constants (and their variation with temperature for all models except III), describing the formation of solids, association and dissociation in solution, and the solubilities of gases.
2. Equations to calculate the activities of the water and solute species in aqueous solutions, based on extensive thermodynamic data for pure aqueous solutions and simple mixtures.
3. A mathematical solver to determine the equilibrium state of the system in which all of the equations for the equilibrium constants (in terms of concentrations, activity coefficients, and partial pressures) are obeyed.

The chemical and physical systems that can be modeled on the website, and the methods, are summarized on the Chemical Systems page (http://www.aim.env.uea.ac.uk/aim/info/description.html).

The Description and Abstract link on the home page of each model contains the abstract from the published paper, the citation, a list of the chemical species in the model, and any modifications since the paper was first published:

Model I: http://www.aim.env.uea.ac.uk/aim/model1/descr1.html
Model II: http://www.aim.env.uea.ac.uk/aim/model2/descr2.html
Model III: http://www.aim.env.uea.ac.uk/aim/model3/descr3.html
Model IV: http://www.aim.env.uea.ac.uk/aim/model4/descr4.html

5. *E-AIM* Publications

The full list or papers, and capsule summaries, are given here: http://www.aim.env.uea.ac.uk/aim/info/papers.html. (The link to this page is in the Quick Start Guide on the *E-AIM* home page.)

6. Useful Thermodynamics Textbooks

There are many text books that cover the thermodynamics of aqueous solutions, in various degrees of detail. In our work over the years we have found the following to be particularly useful:

A. N. Campbell and N. O. Smith (1951) *The Phase Rule and Its Applications*, 9th Edn., Dover Publications (reprint).
K. Denbigh (1981) *The Principles of Chemical Equilibrium*, 4th Edn., Cambridge University Press.
Philip Fletcher (1993) *Chemical Thermodynamics for Earth Scientists*, Longman Scientific and Technical, London.
H. S. Harned and B. B. Owen (1958) *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York.
F. J. Millero (2001) *Physical Chemistry of Natural Waters*, Wiley Interscience, New York.
K. S. Pitzer (1995) *Thermodynamics*, 3rd Edn., McGraw-Hill, Inc.
R. A. Robinson and R. H. Stokes (1972) *Electrolyte Solutions*, 2nd Revised Edition, Butterworths, London. (Reprinted by Dover in 2002.)
K. S. Pitzer (1991) *Activity Coefficients in Electrolyte Solutions*, 2nd Ed., CRC Press, Boca Raton. These two chapters are especially relevant:
    Ion Interaction Approach: Theory and Data Correlation, by K. S. Pitzer (pages 75 to 153)
    Activity Coefficients in Natural Waters, by S. L. Clegg and M. Whitfield (pages 279 to 434)
P. A. Rock (1983) *Chemical Thermodynamics*, University Science Books (Oxford University Press).
W. Stumm and J. J. Morgan (1996) *Aquatic Chemistry*, 3rd Edn., Wiley Interscience.

7. Notes

In this section we summarise some information that is not covered in detail in the presentation, and is helpful when reading the published papers describing the *E-AIM* models.

(a) Two Further Types of E-AIM Calculation

1. Equilibrating to the vapour pressure of water over ice. This option is available on the Comprehensive Calculations page for each model. It is used to calculate the properties of aqueous solutions saturated with respect to ice (and which are therefore in equilibrium with the vapour pressure over ice).
2. Equilibrating a fixed total amount of water between gas and condensed phases. This option is available on the Comprehensive Calculations page for each model. In this calculation the user enters the total moles of water present in the system volume (1.0 m^3). This water is then allowed to equilibrate between the vapour phase and condensed phase. In this case one of the outputs of the model will be the relative humidity (*RH*).

(b) Concentrations

Mole fractions of solvent and solutes in *E-AIM* are calculated on the basis of individual ions as species (and not electrolytes). So, for example, in aqueous H_2SO_4 solutions the mole fraction of H^+ would be given by:

$$x\mathrm{H}^+ = m\mathrm{H}^+ / (m\mathrm{H}^+ + m\mathrm{HSO_4}^- + m\mathrm{SO_4}^{2-} + (1/\mathrm{M_w}))$$

where prefix *m* indicates molality, and $\mathrm{M_w}$ (0.0180152 kg) is the molar mass of water. The concentrations of sulphate and bisulphate, which are governed by a dissociation equilibrium, are determined by the *E-AIM* model.

(c) Densities

The densities of electrolyte mixtures are calculated from those of the individual pure (single solute) aqueous solutions using methods described by Semmler et al. (2006). The densities of pure aqueous solutions of organic compounds are estimated by assuming a constant molar volume (equal to that of the liquid organic compound) in all solutions.

Reference:
M. Semmler, B. P. Luo, and T. Koop (2006) *Atmos. Environ.* **40**, 467-483.

(d) Activity Coefficients, Equilibrium constants, and Concentration Scales

Equilibrium constants for the inorganic systems in Models I to III are presented on a mole fraction basis in the original papers describing the models (Carslaw et al., 1995; Clegg et al. 1998a,b). The paper by Friese and Ebel (2010) on Model IV lists Gibbs energies and enthalpies of formation of species for some reactions, and molality based equilibrium constants for others. The equilibrium constants that the user enters for organic compounds on the *E-AIM* site are <u>all</u> on a molality basis, because they are more often tabulated that way.

It is straightforward to convert both equilibrium constants and activity coefficients between molality and mole fraction scales. The process is explained, and formulae are given, in chapter 2 (Basic Concepts and Definitions) of Robinson and Stokes (1972). Remember that effective Gibbs energies of formation (G^o) vary with the concentration scale used, as do the equilibrium constants (K), since the two are related by the familiar equation:

$$K = \exp(-\Delta G^o / RT),$$

see section 3.4 of Wexler and Clegg (2002).

Activity coefficients calculated using UNIFAC (for the organics + water components of the aqueous solution or hydrophobic liquid phase) are for a pure liquid reference state. That is to say, the activity coefficient for each component is unity in the pure liquid. For solute species (ie, everything except water) these are converted within the models to a reference state of infinite dilution (f^*) with respect to the solvent (water) by dividing by the value of the activity coefficient of the component (relative to the pure liquid reference state) at infinite dilution in water (f^∞):

$f^* = f / f^\infty$, where

f^* = mole fraction based activity coefficient of the component in the system of interest, relative to a reference state of infinite dilution in water.
f = mole fraction based activity coefficient of the component in the system of interest, relative to a pure liquid reference state.
f^∞ = mole fraction based activity coefficient of the component at infinite dilution in water, but relative to a pure liquid reference state.

References:
Carslaw K. S., Clegg S. L. and Brimblecombe P. (1995) *J. Phys. Chem.* **99**, 11557-11574.
S. L. Clegg, P. Brimblecombe, and A. S. Wexler (1998a) *J. Phys. Chem. A*, **102**, 2137-2154.
S. L. Clegg, P. Brimblecombe, and A. S. Wexler (1998b) *J. Phys. Chem. A* **102**, 2155-2171.
E. Friese and A. Ebel (2010) *J. Phys. Chem. A* **114**, 11595-11631.
R. A. Robinson and R. H. Stokes (1972) *Electrolyte Solutions*, 2nd Revised Edition, Butterworths, London. (Reprinted by Dover in 2002.)
A. S. Wexler, and S. L. Clegg (2002) *J. Geophys. Res.* **107**, No. D14, art. no. 4207, 14 pages.

(e) Gibbs Energy Minimisation

This is the method used to solve the model to find the equilibrium state of the system, and is described by Wexler and Clegg (2002). The method used is sequential quadratic programming (from a commercial library), subject to the linear constraints of charge and mole (or mass) balance. The use of Gibbs energy minimization avoids the problems that would be encountered if the equilibria were solved directly. For example, if the equilibrium state were a dry particle the equilibria involving a liquid phase would not apply, but this would not necessarily be known at the start of the calculation.

Reference:
A. S. Wexler, and S. L. Clegg (2002) *J. Geophys. Res.* **107**, No. D14, art. no. 4207, 14 pages.

(f) Gibbs' Phase Rule

The phase rule is easy to state, but can be hard to apply in systems with many reactions occurring. This can make it difficult to determine the number of independently variable components *C*. Good books on the subject tend to be old rather than modern, because they contain the most complete and in-depth explanations. The best I have found, which provides many practical examples, is by Campbell and Smith (1951).

Reference:
A. N. Campbell and N. O. Smith (1951) *The Phase Rule and Its Applications*, 9th Edn., Dover Publications (reprint).

8. Organic Compounds in *E-AIM*

(a) Organic Compound Data Input Pages

Each organic compound has, associated with it, a set of thermodynamic properties consisting of equilibrium constants, methods for estimating activity coefficients, and choices regarding the liquid phase(s) that it can exist in. These are all entered on a single page on the website. A complete description of all the possible entries is given in the main 'help' page, which should be printed out for reference: http://www.aim.env.uea.ac.uk/aim/phpmain/edit_help.html. Information on this page duplicates and supplements that on the model description page that is linked to below.

(b) Activity Coefficients

E-AIM is able to model liquid phases that contain both ions (for which activity coefficients are calculated using the Pitzer-Simonson-Clegg equations), and uncharged organic solutes (which use generally UNIFAC, or assume Raoult's law at the choice of the user). The different options are described here: www.aim.env.uea.ac.uk/aim/info/description.html #section3.

The method of combining the results of the two models to obtain thermodynamically self consistent solvent and solute activities is described in the paper by Clegg, Seinfeld, and Brimblecombe (2001). The method is summarized on the *E-AIM* website here: http://www.aim.env.uea.ac.uk/aim/info/description.html#section3c.
It is elaborated further, in the context of the Zdanovskii, Stokes, Robinson equation for water activities of mixtures (Stokes and Robinson, 1966) by Clegg and Seinfeld (2006).

The treatment of organic ions (which come from dissociation of organic acids (yielding anions), and the reactions of H^+ amines present (to produce aminium cations)) in the aqueous phase is described here: http://www.aim.env.uea.ac.uk/aim/info/description.html#section3a.

References
S. L. Clegg, J. H. Seinfeld, and P. Brimblecombe (2001) *J. Aerosol Sci.* **32**, 713-738.
S. L. Clegg and J. H. Seinfeld (2006) *J. Phys. Chem. A* **110**, 5718-5734.
R. H. Stokes and R. A. Robinson (1966) *J. Phys. Chem.* **70**, 2126-2131.

9. Example *E-AIM* Model Runs (the videos in the presentation)

Descriptive annotations have been added to the sixteen videos shown in the presentation. They are all available for viewing from this page: http://www.aim.env.uea.ac.uk/aim/info/videos.html. Watch them and then try the examples yourselves.