

## 36. Aqua Module

	A	B	C	D	E	F	G	H	I	J	K	L		
1	<b>Water Phase Data</b>			Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	H Ideal	H Estimate	Cp Ideal
2		°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	kcal/kg	kcal/kg	kcal/(kg*K)		
3														
4	Water Phase	40	59.19											
5	<b>Water Species Data</b>			Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	AC	AC	Molality
6		°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	Molar Sc.	Molal Sc.	mol/kg		
7	H2O	40	5.55E+01											
8	H(+a)	40	4.05E-08											
9	HS(-a)	40	5.28E-126											
10	HS2(-a)	40	3.34E-221											
11	HSO3(-a)	40	1.49E-42											
12	HSO4(-a)	40	7.29E-07											
13	HSO5(-a)	40	1.37E-28											
14	HS2O3(-a)	40	3.76E-135											
15	Na(+a)	40	1.92E+00											
16	NaSO4(-a)	40	1.63E+00											
17	OH(-a)	40	7.69E-07											
18	S(-2a)	40	4.67E-131											

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## Abstract

Non-ideal aqueous electrolyte models have been added to the HSC software in the newly developed "HSC Aqua module". HSC Chemistry software has up to this point not included non-ideal models for aqueous electrolyte solutions. However, HSC includes an impressive number of standard state data for neutral components and ionic species. For calculation of the excess Gibbs energy of the individual species and mixtures activity coefficient models need to be included in the HSC data bank. Electrolytes have so far been treated as ideal solutions where the activity coefficients of the individual solution species are set to one.

Predictive and semi-empirical models for ionic activities mean that the activity coefficient and osmotic coefficient have been introduced. In addition, an estimation of solution enthalpies and heat capacities is included. These working equations were derived from activity coefficient models. The activity coefficient models available are the Davies model (extended Debye-Hückel), the semi-empirical Pitzer model (with binary interactions only), and Harvie's modification of the Pitzer model (binary and ternary parameters). The Pitzer parameter database can be used for binary electrolyte systems as well as for multi-component solutions<sup>1-6</sup>.

An extensive database has been collected, including temperature-dependent Pitzer binary and ternary ion interaction parameters. The total number of Pitzer parameters in the HSC Aqua database is currently 1031. This includes 425 cation-anion pairs, 114 cation-cation and anion-anion pairs, 199 ternary coefficients, and 293 ion-neutral pairs.

Many of these parameters are tabulated as temperature-dependent functions, thus allowing the derivation of thermodynamic relations for enthalpies and heat capacities. For those species that have good temperature-dependent data, calculations are in agreement with the literature. For systems that do not have temperature-dependent data, enthalpy and heat capacity estimates are consequently less accurate.

A Pitzer activity calculator tool has been tested against literature data. These include binary systems: NaOH, KOH, NaCl, KCl, HCl, LiCl, CaCl<sub>2</sub>, ZnCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, CuSO<sub>4</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub>, MgSO<sub>4</sub>, MnSO<sub>4</sub>, ZnSO<sub>4</sub>, and AgNO<sub>3</sub>, for example.

The Aqua module can be used for the estimation of ion activities, mean activity coefficients, the osmotic coefficient of water, enthalpies, and heat capacities of homogenous (single phase) aqueous electrolyte solutions. In addition, the water vapor pressures of electrolyte solutions, boiling point elevation, freezing point depression, relative humidity and osmotic pressure can be estimated. The Aqua module can be combined with the HSC Equilibrium Module just by checking a box, i.e. multiphase (gas-aqueous-solid) calculations where ion activities and speciation can be taken into account in the water phase.

## 36.1. Introduction

Electrolyte solutions play an important role in a wide spectrum of industrial applications. These include the solubility phenomena of salts and gases in aqueous systems, precipitation, crystallization, desalination, distillation, and extraction. Wastewater, potable water, mine waters, and natural waters are all different types of electrolyte solutions.

Reliable thermodynamic data for ionic species is needed in order to estimate their properties correctly. Ionic systems deviate from ideality even in very dilute solutions. This is due to the long-range electrostatic forces between ions that are significant even in very dilute solutions. Thus electrolyte solutions are non-ideal even at low solute concentrations.

Adequate thermodynamic models are necessary for the determination of the properties of aqueous electrolyte systems. A simulation model should be reliable at a wide range of temperatures and solute concentrations. Despite the decades of effort put into finding a truly predictive fundamental theory for concentrated electrolyte solutions, a perfect theory has not yet been found. For practical applications, it is still necessary to rely on semi-empirical models. One of the most widely used semi-empirical models was developed by Kenneth Pitzer in 1973 and later modified by Harvie in the 1980s<sup>1,2</sup>.

The Pitzer equations form a quite solid and theoretically realistic foundation for the calculation of aqueous system thermodynamics. The model is widely recognized and has been tested frequently for different electrolyte solutions.

Other benefits of the Pitzer formalism include the largest amount of reliable ion interaction parameters that can be extended to evaluate multi-component solutions. However, the Pitzer model is usually valid up to 6 mol/kg.

## 36.2. Aqua Module Interface in HSC

The first step in the implementation of the Pitzer model into the HSC Chemistry software was the creation of the HSC Aqua module. With this module, the user can estimate the activity coefficients, enthalpies and heat capacities of homogenous (single-phase) aqueous electrolyte solutions. The development of the module consisted of two main tasks: the collection of Pitzer parameter data and the development of the calculation routine. The programs used for these tasks were Microsoft Visual Basic, the Formula One chart tool, and Microsoft Excel.

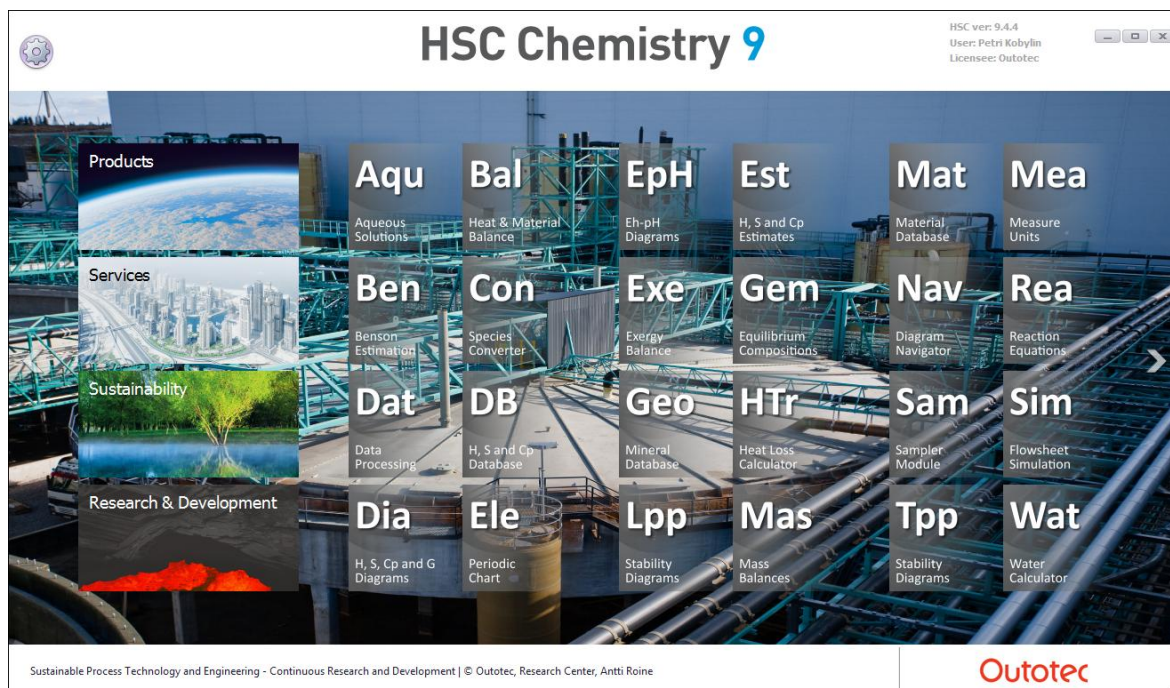


Fig. 1. The main screen of HSC.

## 36.3. Input Sheets

The input sheets for the current HSC Aqua module are opened from the main menu. The input solution of the aqueous electrolyte calculation procedure can be specified on two separate sheets. From the top menu bar of the input sheets, example cases of a calculated electrolyte solution can be opened and saved through the “File” command. The example cases can be saved as \*.aqu8.

Water Phase Data		Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	H Ideal	H Estimate	Cp Ideal
		°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	kcal/kg	kcal/kg	kcal/(kg*K)
Water Phase		40	59.19									
Water Species Data		Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	AC	AC	Molality
		°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	Molar Sc.	Molal Sc.	mol/kg
H2O		40	5.55E+01									
H(+a)		40	4.05E-08									
HS(-a)		40	5.28E-126									
HS2(-a)		40	3.34E-221									
HSO3(-a)		40	1.49E-42									
HSO4(-a)		40	7.29E-07									
HSO5(-a)		40	1.37E-28									
HS2O3(-a)		40	3.76E-135									
Na(+a)		40	1.92E+00									
NaSO4(-a)		40	1.63E+00									
OH(-a)		40	7.69E-07									
S(-2a)		40	4.67E-131									

Fig. 2. Appearance of the Aqua module Water Phase.

The “**Water Phase**” sheet is used to calculate the activity coefficients, enthalpies and heat capacities for an aqueous solution with a selected composition and temperature. The user specifies the system by inserting the ionic or molecular formulas of the solute species in the “**Water Species Data**” column.

1	Water Phase Data											
2	Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	H Ideal	H Estimate	Cp Ideal	
3	°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	kcal/kg	kcal/kg	kcal/(kg*K)	
4	40	59.19	100.00	1.25E+06	-73.71	-73.70	17.69	17.95	-3485.75	-3485.13	0.84	
5	Water Species Data											
6	Temp.	Amount	Amount	Amount	H Ideal	H Estimate	Cp Ideal	Cp Estimate	AC	AC	Molality	
7	°C	kmol	mol-%	g	kcal/mol	kcal/mol	cal/(mol*K)	cal/(mol*K)	Molar Sc.	Molar Sc.	mol/kg	
8	40	5.55E+01	93.77	1.00E+06	-68.05	-68.05	18.01	17.88	1.01	1.01	5.55E+01	
9	40	4.05E-08	0.00	4.08E-05	0.00	0.00	0.00	0.00	0.31	0.29	4.05E-08	
10	40	5.28E-126	0.00	1.74E-121	-4.53	-4.69	-19.57	-14.52	0.73	0.69	5.28E-126	
11	40	3.34E-221	0.00	2.17E-216	-64.13	-63.78	-6.63	-1.58	0.43	0.41	3.34E-221	
12	40	1.49E-42	0.00	1.21E-37	-149.68	-151.02	-0.06	5.00	1.02	0.96	1.49E-42	
13	40	7.29E-07	0.00	7.07E-02	-211.89	-211.69	5.72	10.55	0.67	0.63	7.29E-07	
14	40	1.37E-28	0.00	1.55E-23	-184.86	-184.51	33.37	38.42	0.43	0.41	1.37E-28	
15	40	3.76E-135	0.00	4.25E-130	-153.84	-153.49	4.16	9.22	0.43	0.41	3.76E-135	
16	40	1.92E+00	3.24	4.40E+04	-57.28	-57.06	10.77	16.23	0.47	0.44	1.92E+00	
17	40	1.63E+00	2.75	1.94E+05	-273.31	-272.96	21.21	26.27	0.43	0.41	1.63E+00	
18	40	7.69E-07	0.00	1.31E-02	-55.42	-55.47	-27.29	-5.53	0.76	0.71	7.69E-07	
19	40	4.67E-131	0.00	1.50E-126	7.36	8.74	-40.65	-20.22	0.03	0.03	4.67E-131	

**Fig. 3.** The left-hand part of the "Water Phase" sheet of the HSC Aqua aqueous electrolyte module.

1	Cp Estimate	Osmotic	H2O Vapour	Sol. Vapour	Ionic	pH	Relat.	FP	BP	FP (aw	BP (aw	Osmotic
2	kcal/(kg*K)	Coeff.	Pa	Pa	Strength		Humidity	°C	°C	at 25°C)	at 25°C)	Pressure
3					mol/kg		%			°C	°C	Pa
4	0.85	0.78	7377.08	7004.56	2.06	7.93	94.95	-5.26	101.43	-5.26	101.49	7430735.09
5	MW	Elements:										
6	g/mol	H	Na	O	S	e-						
7	18.02	2.00		1.00								
8	1.01	1.00				-1.00						
9	33.07	1.00			1.00	1.00						
10	65.14	1.00			2.00	1.00						
11	81.07	1.00			3.00	1.00	1.00					
12	97.07	1.00			4.00	1.00	1.00					
13	113.07	1.00			5.00	1.00	1.00					
14	113.14	1.00			3.00	2.00	1.00					
15	22.99		1.00				-1.00					
16	119.05		1.00	4.00	1.00	1.00						
17	17.01	1.00		1.00		1.00						
18	32.07				1.00	2.00						

**Fig. 4.** The right-hand part of the "Water Phase" sheet of the HSC Aqua aqueous electrolyte module.

The water species "H2O" is pre-inserted into the system in each calculation case, because it is compulsory for the calculations. All the neutral and ionic solutes have to be expressed with the suffix (a). For example, the CO<sub>3</sub><sup>2-</sup> ion is inserted as CO3(-2a) and CO<sub>2</sub> is inserted as CO2(a). The suffix defines that the species are contained within the aqueous phase. After the specification of the electrolyte, the listed components are provided with temperature values in degrees Celsius. In addition, the user must specify

the amounts of each species and the solvent (water) in kmol units. Temperature, pressure and energy units can be changed from Units menu.

At this point, the user can also define the model to be used in the calculations. This is done with the help of the Aqua method icon where "Davies", "Pitzer", and "Harvie" can be chosen, which define the model used for estimating the activity coefficients of ions, the mean activity coefficient of binary system, osmotic coefficient of water, excess enthalpies, and heat capacities. By selecting "Harvie," the calculation routine uses all the binary and ternary parameters in the databank and Harvie's modification is used. By selecting "Pitzer," the calculation routine omits all Pitzer (including Harvie's) ternary interaction parameters and calculations are carried out using Pitzer binary parameters only. By selecting the "Davies" option, in turn, all the Pitzer ion interaction parameters are disregarded and the system properties are calculated using Equation (15).

All activity coefficient equations included in the Aqua module should show limiting behavior i.e. activity coefficients  $\gamma_i$  should approach the numerical value 1 as the solution becomes more dilute. This is the Debye-Hückel limiting law. In very dilute solutions (with respect to ions), solution properties, enthalpies and heat capacities should also approach the numerical values of pure water.

The possibility of using different models to calculate system properties greatly adds to the depth of the simulation module, as the user can choose between a simple model and a more rigorous one depending on the case. The simplifications performed by the different model selections are explained to the user when the checkboxes are selected.

If the desired aqueous electrolyte contains species other than water and the cation and anion of the solute salt, HSC Aqua announces that the user has specified the system incorrectly and performs the calculation using only the "Water Phase" sheet. HSC Aqua assumes complete dissociation of the salt into the water phase.

## 36.4. Output Sheets

The output of the HSC Aqua module is included in the input sheets. The calculation routine determines the molalities, molecular weights, amounts in grams, ionic activity coefficients, enthalpies, and heat capacities of the different species and displays them to the user in the different columns of the calculation sheets. The element matrix of the solutes and solvent is also displayed. In addition, the heat capacities and enthalpies are displayed both on a mass and mole basis. The properties of the entire electrolyte solution are displayed in the first row of the “**Water Phase**” sheet.



## 36.5. New features in Aqua



There are three new features in Aqua module: Main Database, Parameter Sets and Density Calculator.

Main Database icon opens a list of Pitzer parameters in the database. It does not show numerical values, see Fig. 5.

**Main Pitzer Database**

**Pitzer-Harvie activity coefficient equation for cation M(+) and anion X(-)**

$$\ln \gamma_{+,M} = z^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left( 2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) + \sum_{c,c'} \sum_a m_a m_{c'} \Psi_{Maa'c} + Z_c \sum_a \sum_a m_a m_a C_{ca} + 2 \sum_a m_a \lambda_{aM} + \dots$$

$$\ln \gamma_{-,M} = z^2 F + \sum_c m_c (2B_{Xc} + ZC_{Xc}) + \sum_a m_a \left( 2\Phi_{Xa} + \sum_c m_c \Psi_{Xca} \right) + \sum_{c,c'} \sum_a m_c m_{c'} \Psi_{cc'a} + Z_c \sum_a \sum_a m_c m_a C_{ca} + 2 \sum_a m_n \lambda_{nX} + \dots$$

**Equation parameters**

- Gamma: activity coefficient, AC
- z: charge of ion
- m: molality
- Z: sum of (molality x ionic charge) of all ions
- I: ionic strength, function of m and z
- c: cation
- a: anion
- n: neutral species
- B: c-a term, function of b(0), b(1), b(2), I
- C: c-a term, function of C(f), z
- Fil: c-c and a-a term, function of theta, I
- Psi: c-c-a & a-a-c term
- Lambda: n-c & n-a term
- F: Davies term

Cation (+)	Anion (-)	Temperature dependent data			Reported parameter validity range		AC			H			Cp							
		Activity coefficient (AC)	Enthalpy (H)	Specific heat capacity (Cp)	Min T [C]	Max T [C]	Molality / ionic strength [mol/kg]	b(0)	b(1)	b(2)	C(f)	b(0)	b(1)	b(2)	C(f)	b(0)	b(1)	b(2)	C(f)	
Ag(+a)	NO3(-a)	C	*	*	*	*	*	C	C	C										
Al(+3a)	Cl(-a)	T	*	T	*	290	m < 5	T	T	T	T	T	T	T	T	T	T	T	T	T
Al(+3a)	NO3(-a)	C	*	*	*	25	25	C	C	C										
Al(+3a)	SO4(-2a)	C	*	*	*	25	25	C	C	C										
Ba(+2a)	Br(-a)	T	C	*	*	5	45	*	T	T	T	C	C	C						
Ba(+2a)	CH3COO(-a)	C	*	*	*	*	*	C	C	C										
Ba(+2a)	Cl(-a)	T	T	T	*	25	200	*	T	T	T	T	T	T	T	T	T	T	T	T

Fig. 5. List of Main Database Pitzer parameters.

Parameter Sets icon shows parameters for the active system specified by the user in column A of the water phase sheet, see Fig. 6.

**Active Pitzer Parameters**

Pitzer interaction parameters that are currently used from the database based on specified solution and calculation method.

**Temperature dependence of Pitzer parameters**

$$a + \frac{b}{T} + c \cdot \ln(T) + dT + eT^2 + fT^{-2}$$

**Temperature dependence notations**

- T = temperature dependent data available in defined temperature range
- C = Pitzer parameter set defined by constant values at 25 degrees C
- \* = specific parameter data unavailable

**Pitzer Binaries: Cation - Anion Interactions**

Cation (+)	Anion (-)	Temperature dependent data			Reported parameter validity range		AC			H			Cp							
		Activity coefficient (AC)	Enthalpy (H)	Specific heat capacity (Cp)	Min T [C]	Max T [C]	Molality / ionic strength [mol/kg]	b(0)	b(1)	b(2)	C(f)	b(0)	b(1)	b(2)	C(f)	b(0)	b(1)	b(2)	C(f)	
H(+a)	HSO4(-a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
H(+a)	SO4(-2a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	HS(-a)	T	T	T	*	50	I < 1	T	T	T	C	T	T	T	T	T	T	T	T	T
Na(+a)	HSO3(-a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	HSO4(-a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	OH(-a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	SO3(-2a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	SO4(-2a)	T	T	T	*	*	*	T	T	T	T	T	T	T	T	T	T	T	T	T
Na(+a)	S2O3(-2a)	C	*	*	*	*	*	C	C	C										

**Theta: Cation - Cation & Anion - Anion Interactions**

Ion i (+/-)	Ion j (+/-)	Temperature dependent data			Reported parameter validity range		
		Activity coefficient (AC)	Enthalpy (H)	Specific heat capacity (Cp)	Min T [C]	Max T [C]	Molality / ionic strength [mol/kg]
H(+a)	Na(+a)	T	C	*	*	90	I < 1
HSO4(-a)	SO4(-2a)	T	T	T	*	*	*
OH(-a)	SO4(-2a)	C	*	*	*	*	*

Fig. 6. Parameter Sets icon show parameters for the active system specified in column A. It also shows the missing parameters for the active system.

Density Calculator estimates water solution density. The salt concentration unit needs to be given using weight fractions, see **Fig 7**. Estimates are available for only limited salts.

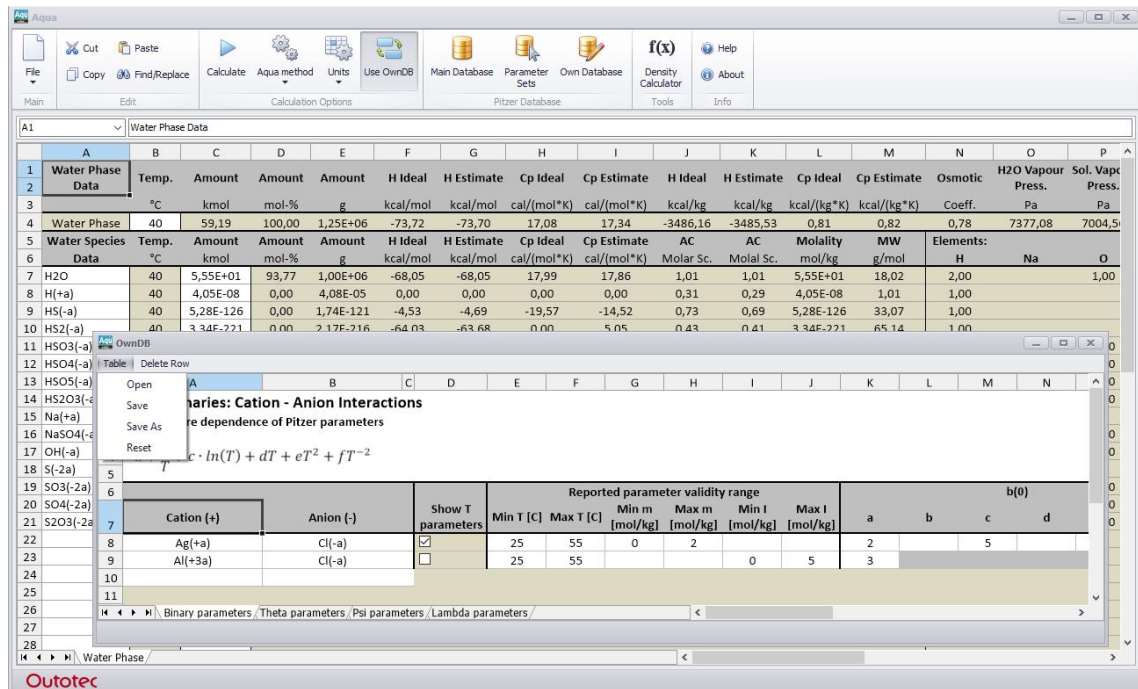
The screenshot shows the 'Density Calculator' application window. The spreadsheet contains the following data:

Density of Aqueous Solution											
Author: Tuukka Kotiranta					H2O density		996.95		kg/m3		
Density database: C:\HSC9\Databases\Aqueous Solution Density.xls					Solution density		1204.371594		kg/m3		
					Temperature		25		°C		
Component in water		Mass fraction		Temperature °C		Selected components		Mass fraction in solution		Validity region violations	
		Min	Max	Min	Max			Mass fraction	Temperature °C		
7	Al2(SO4)3	9.724E-03	0.398	15	95	ZnSO4		0.149			
8	AlCl3	0.0023	0.193556	25	25	H2SO4		0.048			
9	Ba(NO3)2	1.297E-02	8.381E-02	5	95						
10	BaCl2	8.073E-04	0.26	0	140						
11	Ca(CH3CO2)2	2.164E-03	8.766E-02	15	45						
12	Ca(NO3)2	4.438E-02	0.76815	25	60						
13	CaCl2	1.392E-03	0.5132	0	100						
14	CaSO4	7.479E-05	1.003E-03	25	25						
15	Cd(NO3)2	1.168E-02	0.7	15	85						

**Fig 7.** Density Calculator estimates water solution density. In this example, the mass fraction of ZnSO4 and H2SO4 is 0.149 and 0.048, respectively, and rest 0.803 is water.

## 36.6. Own database of Pitzer parameters

Starting from HSC 10, users can create and maintain their own databases of Pitzer parameters. The values of the parameters from the Own Database can be used in the calculations outside the Aqua module, in other modules of HSC, such as Sim and Gem, along with the standard Pitzer parameters from the Main Database. Note that the values of the parameters from the Own Database overwrite those from the Main Database if both databases contain the same parameters.



**Fig 8.** In HSC 10 it is possible to add your own Pitzer parameters in the Aqua module. These Own Pitzer parameters can also be used in the Gem and Sim modules.

Before using the Own Database the user has to fill in the data in the forms of the Own Database and save the database. *Use OwnDB* button makes the parameters from the Own Database visible in the Main Database. At the same time, the parameters from the Main Database are still accessible in the calculations as noted above. When the use of the Own Database is activated in the Aqua module, all the parameters from both databases are listed in the Main Database. The parameters from the Own Database are placed at the top of the forms and marked with a blue color. It is possible to exclude certain parameters from calculations with help of checkboxes in the Main Database. When the *Use OwnDB* button changes its state, the program resets the forms of the parameters, collects the parameters from the databases and resets the checkboxes.

### Main Database of Pitzer parameters

The Main Database displays the parameters available for calculations. It is possible to exclude certain parameters from the calculations using the checkboxes next to the parameters in the forms. When the Own Database is activated using the *Use OwnDB* button, the Main Database lists the parameters from both databases. Four colors are used to distinguish different types of parameters. Black depicts the parameters from the Main Database of HSC. Blue indicates the parameters present in the user's Own Database. Green indicates the parameters that are present in both databases. The parameters from the Own Database are employed in the calculations if not set otherwise using the checkboxes. Red indicates the parameters excluded from the

calculations by setting the value of the respective checkbox to false. The parameters having a numerical value are marked with an X symbol.

Cation (+)	Anion (-)	Active set used in Pitzer calc.	Reported parameter validity range						b(0)								
			Min T [C]	Max T [C]	Min m [mol/kg]	Max m [mol/kg]	Min I [mol/kg]	Max I [mol/kg]	a	b	c	d	e	f	a	b	
Ag(+a)	Cl(-a)	<input checked="" type="checkbox"/>	25	55	0	2			X		X			X		X	
Al(+3a)	Cl(-a)	<input checked="" type="checkbox"/>	25	55				0	5	X	X	X				X	X
Ag(+a)	NO3(-a)	<input checked="" type="checkbox"/>								X						X	
Al(+3a)	NO3(-a)	<input type="checkbox"/>	25	25	3	1				X						X	
Al(+3a)	SO4(-2a)	<input checked="" type="checkbox"/>	25	25				4,5		X						X	
Ba(+2a)	Br(-a)	<input checked="" type="checkbox"/>	5	45						X			X			X	
Ba(+2a)	CH3COO(-a)	<input checked="" type="checkbox"/>								X						X	

Fig 9. The Main Pitzer Database.

## User's Own Database of Pitzer parameters

The user can add and modify the data in the white cells in the forms of the user's Own Database. The *Show T parameters* checkbox disables the temperature-dependent coefficients of Pitzer parameters. When the checkbox is in the 'false' state, only the coefficients independent of temperature are available. The change of state of the checkbox erases the data in the cells. A right click on an active row calls the pop-up icon menu *Delete Row*, which can be used to delete the row. Note that it is important to remove the focus from the cell being edited before saving or closing the forms of the user's Own Database; otherwise the data in the cell will not be saved.

The forms of the user's Own Database are stored locally on the user's computer. The forms are saved every time the forms are closed. If there is a need to reset the forms (delete all the data from the user's Own Database) then the user can click *Reset* in the context menu *Table*. Note that the file containing the data is not deleted in this way; only the link with the file is deleted. The link can be restored by clicking *Open* in the context menu *Table* and selecting the correct file.

## Things to be remembered while using the Own Database:

- Invalid entries to the cells of validity range or the values of the parameters will not be recognised correctly. The invalid entries of the parameter values will be replaced in calculations with zeros.
- *Save as* command in the context menu *Table* creates a new file with the Own Database forms and sets a path to it for the modules of HSC.
- *Save* command in the context menu *Table* saves the data in the existing file. If the file has not been saved before, the command acts in the same way as *Save as*.
- *Open* command from the context menu *Table* sets the path to the database file and loads the forms of the user's Own Database from the file.

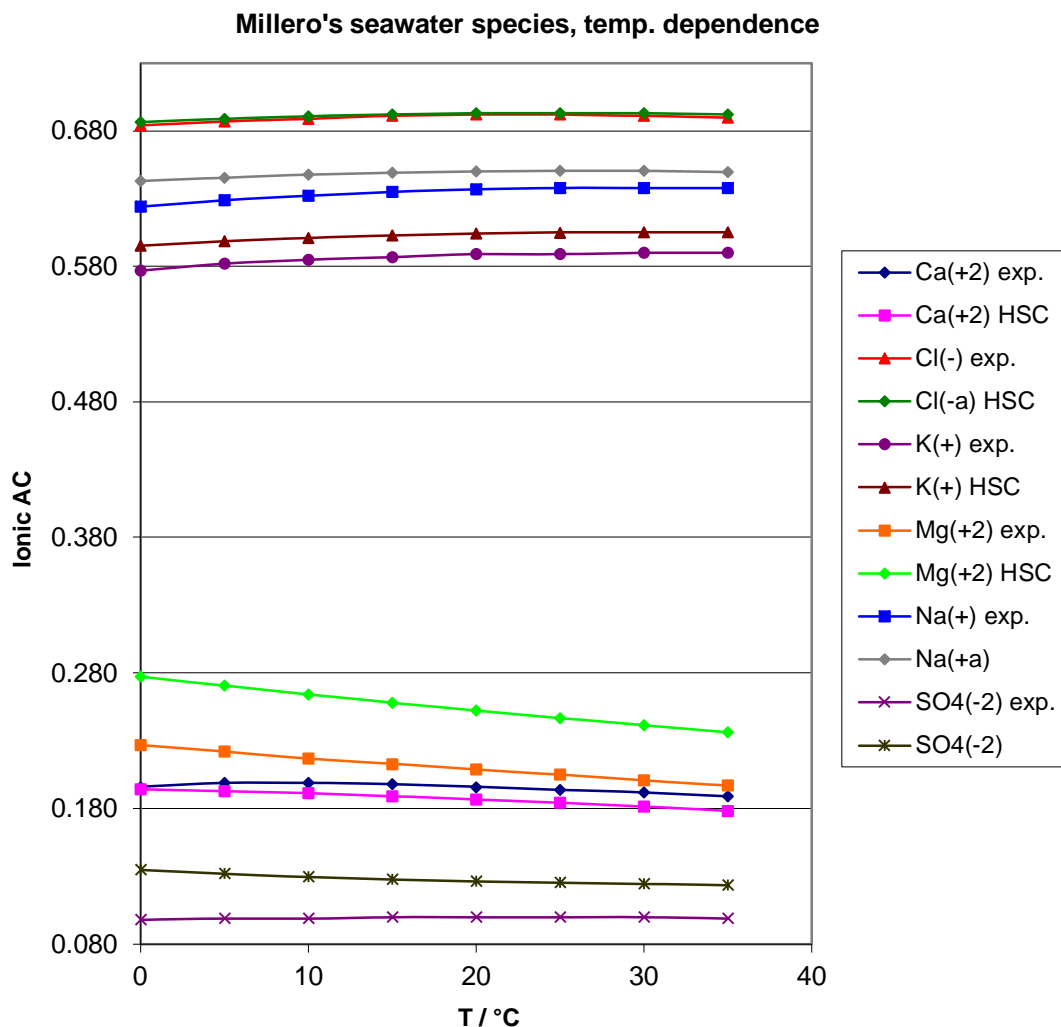
- It is not possible to change the file of the Own Database outside the Aqua module. Using Own Database forms changed for example in MS Excel will not succeed, and the program will return an error message.
- It is obligatory to specify all the species in each active row correctly. The program reads the data from the forms of the Own Database until the first invalid row on each page.
- In order to use the data from the Own Database of the Aqua module in other modules of HSC, such as Gem or Sim, it is enough to create the database file and save it locally. There is no need to activate it with the *Use OwnDB* button. This button only controls the visibility of the parameters from the Own Database in the Main Database. The user can disable the use of the Own Database by clicking Reset in the context menu *Table* of the Own Database.

## 36.7. Multi-Component Examples

The testing of the HSC Aqua module with multi-component electrolytes was much more complicated than with binary systems, because there was not as much data available in the literature about these kinds of solutions. Especially when considering enthalpies and heat capacities, the number of multi-component electrolyte systems was really small. Nevertheless, the HSC Aqua model was tested for the activity coefficients for some experimental systems. Examples of seawater simulation results are shown in **Table 1** and **Fig. 10**.

**Table 1.** Ionic properties of solutes in seawater, Millero's seawater recipe, salinity 35 at 298.15K, Harvie's model (Clegg and Whitfield, 413).<sup>12</sup>

Water Phase	Temp / °C	Amount / mol	Activity coefficient		H / cal/mol		C <sub>P</sub> /cal/Kmol		Molality
			Exp.	Calc.	Ideal	Calc.	Stand.	Calc.	
		5.667E-02			-68.071	-68.070	17.359	17.420	
H2O	25	5.551E-02	1.001	1.002	-68.315	-68.315	17.980	17.940	55.50844
Br(-a)	25	8.700E-07	0.716	0.719	-29.040	-28.865	-30.174	-24.554	0.00087
Ca(+2a)	25	1.064E-05	0.194	0.184	-129.800	-129.282	-7.402	5.937	0.01064
Cl(-a)	25	5.658E-04	0.692	0.693	-39.933	-39.931	-29.217	-24.134	0.56579
F(-a)	25	6.000E-08	0.281	0.299	-80.150	-80.038	-26.952	-15.884	0.00006
HCO3(-a)	25	2.410E-06	0.605	0.590	-164.898	-164.727	-8.284	-4.947	0.00241
K(+a)	25	1.058E-05	0.589	0.605	-60.270	-60.299	2.040	7.828	0.01058
Mg(+2a)	25	5.519E-05	0.205	0.247	-111.616	-110.839	-5.119	-3.037	0.05519
Na(+a)	25	4.853E-04	0.638	0.650	-57.433	-57.440	9.168	14.706	0.48525
SO4(-2a)	25	2.927E-05	0.100	0.125	-217.400	-217.120	-63.323	-72.444	0.02927
Sr(+2a)	25	9.000E-08	0.175	0.223	-131.670	-131.092	-9.871	2.494	0.00009

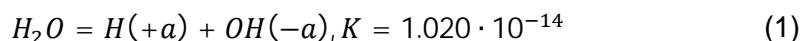


**Fig. 10.** The activity coefficients of different ionic species of seawater at different temperatures. Millero's seawater recipe, S=35. (Clegg and Whitfield, 413).<sup>12</sup>

**36.8. Aqueous Equilibria**

Equilibrium calculations of aqueous solutions can be made in a similar manner as presented above for non-electrolyte solutions. However, some points need special attention:

1. Always remember to add water to the aqueous phase. It must be the first species in the Aqua module calculations. For example, 55.509 mol (= 1 kg) is a good selection if the amount of ions is some 0.01 - 5 moles.
2. Add some charged species (electrons) to the system, for example, by 0.001 mol OH(-a) and the same amount of H(+a). Be sure to maintain the electronic neutrality of the system if you carry out the calculations with the Gibbs solver.
3. If you are calculating, for example, the dissolution of 1 mole of CaCO<sub>3</sub> in water and you have stoichiometric raw material amounts, please also add a small amount of O<sub>2</sub>(g) to the gas phase, for example, 1E-5 moles. If you have stoichiometric NaCl in the system, please add a minor amount of Cl<sub>2</sub>(g) to the gas phase (1E-5 mol). These tricks help the GIBBS solver to find the equilibrium composition in cases of fully stoichiometric overall compositions.
4. HSC converts the entropy values of aqueous components from the molality scale to the mole fraction scale if the Mixing Entropy option is selected. Therefore, the entropy values in the results1 sheet are not the same as those in the HSC database, see Chapter 13 (sections 13.4. and 13.6). Identical results will be achieved if the Raoultian activity coefficients of the aqueous species are changed to 55.509/x(H<sub>2</sub>O), which converts the Raoultian activity scale to the aqueous activity scale.
5. For some aqueous species only G values are available at 25 °C. These can be saved in the database as H values if S = 0. Please note, however, that these can only be used in the calculations at 25 °C.
6. You can check the equilibrium results by doing simple element balance checks or comparing the equilibrium constants. For example, you can calculate the equilibrium constant for Equation (1) using the Reaction Equations option at 25 °C:



You can also calculate the same equilibrium constant from the equilibrium results of the GIBBS program (CaCO<sub>3</sub>.gem9) using Equation (11) in Chapter 8 Introduction. You can read the necessary molal concentrations, for example, in the equilibrium results1 sheet. This calculation should give nearly the same results as the Reaction Equation option.

$$K = \frac{[H(+a)] \cdot [OH(-a)]}{[H_2O]} = \frac{4.9015 \cdot 10^{-10} \cdot 20.858 \cdot 0.055584}{55468.3299} = 1.023 \cdot 10^{-14} \quad (2)$$



## 36.9. General Calculation Principles for Water Systems

In ionic solutions, interactions between ions are so strong that an ideal assumption can be made only in a very dilute solution (less than 0.001 mol/kg). The chemical potential of a species  $i$  (partial molar Gibbs energy) of a solute in a solution is related to its activity  $a_i$  by:

$$\mu_i = \mu_i^\ominus + RT \ln a_i \quad (3)$$

The activity is related to the molality by:

$$a_i = \frac{\gamma_i m_i}{m^\ominus} \quad (4)$$

where activity coefficient  $\gamma_i$  depends on the composition, molality, temperature, and to a lesser degree on pressure. The  $m^\ominus = 1$  mol/kg standard state simply cancels the units of molality in the equation. As the solution approaches ideality at low molalities, the activity coefficient approaches the numerical value 1.

$$\gamma_i \rightarrow 1 \text{ and } a_i \rightarrow \frac{m_i}{m^\ominus} \text{ as } m_i \rightarrow 0 \quad (5)$$

The chemical potential can be written in an ideal and non-ideal part as:

$$\mu_i = \mu_i^\circ + RT \ln \frac{m_i}{m^\circ} + RT \ln \gamma_i = \mu_i^\circ + RT \ln(m_i \gamma_i) \quad (6)$$

where  $\mu_i^\circ$  is the standard chemical potential in J/mol.

The chemical potential ( $G_m = \mu$ ) of a salt  $M_{v+}X_{v-}$  that dissolves to give  $v_+M^+$  cations and  $v_-X^-$  anions is:

$$G_m = v_+\mu_+ + v_-\mu_- = \mu_+^\circ + \mu_-^\circ + v_+RT \ln(m_+\gamma_+) + v_-RT \ln(m_-\gamma_-) = G_m^\circ + RT \ln(m_\pm \gamma_\pm) \quad (7)$$

where  $\gamma_\pm$  is the mean activity coefficient defined as:

$$\gamma_\pm = (\gamma_+^{v_+} \gamma_-^{v_-})^{1/(v_++v_-)} \quad (8)$$

The chemical potential of each ion can be written using a mean activity coefficient:

$$\mu_i = \mu_i^\circ + RT \ln(m_\pm \gamma_\pm) \quad (9)$$

The mean activity coefficient is usually used in binary systems only. In multi-component solutions, the chemical potential of an individual species  $i$  is written as:

$$\mu_i = \mu_i^\circ + RT \ln(m_i \gamma_i) \quad (10)$$

The osmotic coefficient of water is related to the activity coefficients that can be derived from activity coefficient relations.<sup>4,6</sup>

## 36.10. Excess Enthalpy and Heat Capacities

Excess Gibbs energy yields other thermodynamic properties such as excess enthalpies and heat capacities determined by appropriate differentiation. The enthalpy of the entire electrolyte solution can then be calculated by the addition of the partial enthalpies multiplied by the solute species amounts in moles. Furthermore, the partial heat capacity of a solute can be determined by further differentiation of the excess enthalpy function. This means that the equations of all the relevant thermodynamic properties of the aqueous system species can be led back to the equations of the logarithmic activity coefficient expressions. The excess enthalpy is derived from the temperature dependency of the activity coefficient function as follows:

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = -\frac{H_{m,i}^{ex}}{vRT^2} \quad (11)$$

Excess enthalpy is often noted as  $L$  and it is related to apparent molar enthalpy as follows:

$$\phi_L = \frac{L - n_1 L_1^\circ}{n_2} = \frac{L}{n_2} \quad (12)$$

The second derivative of excess Gibbs energy and the first derivative of enthalpy yields the following expression for heat capacity:

$$C_{P,m} = \left(\frac{\partial H_m}{\partial T}\right)_P = C_{P,m}^\circ + \left(\frac{\partial L_m}{\partial T}\right)_P \quad (13)$$

The apparent molar heat capacity,  ${}^\phi C_P$  (J/Kmol), is derived as follows:

$$\phi C_P = \frac{C_P - n_1 C_{P1}^\circ}{n_2} \quad (14)$$

In equations (12)-(14):

${}^\phi L$  is the apparent relative molal enthalpy of a solution, J/mol

$L$  is the relative enthalpy of a solution (is excess enthalpy), J

$L_1^\circ$  is the excess enthalpy of water, J/mol

$C_{P,m}$  is the specific heat capacity, J/Kmol

$H_m$  is the enthalpy, J/mol

$T$  is temperature, K

$L_m$  is the molar excess enthalpy, J/mol

$C_{P,m}^\circ$  is the standard molar heat capacity, J/Kmol.

$C_P$  is the heat capacity, J/K

$C_{P1}^\circ$  is the infinite dilute partial molal heat capacity of the solvent, J/Kmol and

$n_1$  and  $n_2$  are the molar amounts of the solvent and the solute, mol

## 36.11. Summary of the Equations Used in HSC Aqua

**Davies:**

$$\ln \gamma_i = -A_\phi \left( \frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right) \quad (15)$$

(not actually the Davies equation but called Davies here).

**Pitzer:**

$$\ln \gamma_{+,M} = z_+^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + 2 \sum_n m_n \lambda_{nM} \quad (16)$$

$$\ln \gamma_{-,M} = z_-^2 F + \sum_c m_c (2B_{Xc} + ZC_{Xc}) + 2 \sum_n m_n \lambda_{nM} \quad (17)$$

The mean activity coefficient of a dissolved salt (in the Pitzer formalism without ternaries):

$$\ln \gamma_\pm = z_+ |z_-| f^\gamma + \frac{v_+ v_-}{\nu} m (2B_{+-}^\phi + 2B_{+-} + 3ZC_{+-}) \quad (18)$$

The osmotic coefficient of water (in the Pitzer formalism without ternaries):

$$\phi - 1 = -A_\phi z_+ |z_-| \frac{\sqrt{I}}{(1 + b\sqrt{I})} + 2 \frac{v_+ v_-}{\nu} m (B_{+-}^\phi + ZC_{+-}) \quad (19)$$

Parameters used in the Pitzer option in the calculations:

$$\beta_{MX}^{(0)}, \beta_{MX}^{(1)}, \beta_{MX}^{(2)}, C_{MX}^\phi, \lambda_{nM}$$

**Harvie:**

$$\begin{aligned} \ln \gamma_{+,M} = & z_+^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \left( 2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) \quad (20) \\ & + \sum_{a < a'} \sum m_a m_{a'} \Psi_{Maa'} + Z_+ \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nM} + \dots \end{aligned}$$

$$\begin{aligned} \ln \gamma_{-,M} = & z_-^2 F + \sum_c m_c (2B_{Xc} + ZC_{Xc}) + \sum_a m_a \left( 2\Phi_{Xa} + \sum_c m_c \Psi_{Xca} \right) \quad (21) \\ & + \sum_{c < c'} \sum m_c m_{c'} \Psi_{cc'X} + Z_- \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{nX} + \dots \end{aligned}$$

Parameters used in the Harvie option in the calculations:

$$\beta_{MX}^{(0)}, \beta_{MX}^{(1)}, \beta_{MX}^{(2)}, C_{MX}^\phi, \theta_{ij} \text{ and } \Psi_{ijk}.$$

**The Number of Pitzer Parameters on the Database is:**

- The interaction parameter data was collected from the available literature. At present, the database is not visible to the user but the parameter species pairs that exist on the database are listed in Appendix B.

All the parameters of the HSC Aqua Pitzer database were then fitted to the same temperature-dependent equation (22):

$$F = a + \frac{b}{T} + c \cdot \ln(T) + dT + eT^2 + fT^{-2} \quad (22)$$

where  $T$  is the solution temperature in Kelvin and  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  and  $f$  are adjustable parameters.

In many cases only data at a standard temperature, 25 °C, exists. In such cases, the parameters were included on the database as constant terms (“a” parameters), which are shown as the first term in the function.

## Osmotic Coefficient and Activity of Water

The osmotic coefficient of pure water has a numerical value of 1,000. The osmotic coefficient differs if any other components are dissolved in water, including salts. The osmotic coefficient is related to the vapor pressure of the water and is thermodynamically related to ion activities in the solution. The osmotic coefficient and activity of water are related through the following equation<sup>2</sup>:

$$\ln(a_w) = -\frac{W}{1000} \left( \sum m_i \right) \phi \quad (23)$$

The activity of water can further be used to calculate important properties like water activity and vapor pressure (24), and relative humidity (25). The pure water vapor pressure in Equation (24) was calculated from the vapor pressure values listed in the “Measure Units” database of HSC. The pressure values were fitted to polynomial regression curves in order to match the experimental pressure values as well as possible.

In order to increase the accuracy of the fit, the temperature range was split into two parts above and below 160 °C, see Appendix A. The vapor pressures, osmotic coefficients, and relative humidities (water activities) are calculated in the new “Osmcalc” subroutine of the AquaDLL.dll calculation routine.

$$a_w = \frac{p}{p_0} \quad (24)$$

$$RH(\%) = \frac{p}{p_0} \cdot 100\% \quad (25)$$

$$p_0 = (-3.10432954399391 \cdot 10^{-21} \cdot T^{10} + 1.00959411100662 \cdot 10^{-18} \cdot T^9 - 5.88099024207425 \cdot 10^{-17} \cdot T^8 - 3.18476754457404 \cdot 10^{-14} \cdot T^7 + 6.55612456912702 \cdot 10^{-12} \cdot T^6 + 2.25575938350116 \cdot 10^{-9} \cdot T^5 + 2.99998801482107 \cdot 10^{-7} \cdot T^4 + 2.57849258952755 \cdot 10^{-5} \cdot T^3 + 1.43776358189044 \cdot 10^{-3} \cdot T^2 + 4.51730065352071 \cdot 10^{-2} \cdot T + 0.599030194123347) \cdot \text{din equations (23)-(25):}$$

$a_w$  is water activity

$W$  is the molar mass of water, g/mol

$m_i$  is the molality of a solute species  $i$ , mol/kg

$RH(\%)$  is the relative humidity

$p$  is the solution vapor pressure and

$p_0$  is the vapor pressure of pure water, see Appendix A.

The osmotic coefficient of water was added to the “Water phase” listing for multi-component solution systems.

## Osmotic Pressure

The osmotic coefficient can also be used to determine the osmotic pressure of an electrolyte solution. Osmotic pressure has units of pressure and gives a pressure difference compared to pure water. It is an important property in membrane systems, when considering processes like reverse osmosis, for example. The osmotic pressure value is calculated in HSC Aqua using Equation (26)<sup>6</sup>.

In the first version of the calculation code, the temperature-dependent water density function Equation (27) required for the calculation was taken from McCutcheon et al.<sup>14</sup>. The osmotic pressure is calculated in the "Osmcalc" subroutine of AquaDLL.dll.

$$\pi = -\frac{RT}{v_w} \ln(a_w) = -\frac{RT\rho_w}{M_w} \ln(a_w) \quad (26)$$

$$\rho_w = 1000 \cdot \left(1 - \frac{T_c + 288.9414}{508929.2 \cdot (T_c + 68.12963)} \cdot (T_c - 3.9863)^2\right) \quad (27)$$

$$\rho_w = 1000 \cdot \left(1 - \frac{(T_c + 288.9414)}{508929.2 \cdot (T_c + 68.12963)} \cdot (T_c - 3.9863)^2\right)$$

In equations (26)-(27):

$a_w$  is the water activity,

$R$  is the molar gas constant, J/(mol K)

$T$  is the solution temperature, K

$v_w$  is the partial molar volume of the solvent, m<sup>3</sup>/mol

$\pi$  is the osmotic pressure, Pa

$M_w$  is the molecular weight of the solvent, kg/mol

$\rho_w$  is the density of the solvent, kg/m<sup>3</sup> and

$T_c$  is the solution temperature, °C.

## Boiling Point Elevation and Freezing Point Depression

Since the vapor pressure of the solution and freezing point of a liquid are directly related to the phase equilibrium, the water activity can be further related to estimating important solution properties, namely boiling point elevation and freezing point depression.

The derivation of the boiling and freezing point changes begin with the definition of chemical potential. Because the calculation of the freezing point depression is analogous to the boiling point elevation, only the freezing point depression will be considered here in detail. At the solid-liquid equilibrium point, the chemical potential of the solvent is equal between the solid and the liquid phase. The chemical potential of the different phases may, in turn, be expressed with Equations (28)-(29). Since the activity of the pure solid solvent is unity and because the chemical potentials of the phases are equal, the Gibbs free energy of fusion can be expressed with Equation (30). When the Gibbs-Helmholz equation is applied to expression (30), the relation (31) is obtained<sup>15</sup>.

$$\mu_{liq}(T, P) = \mu_{liq}^o(T, P) + RT \cdot \ln(a_{liq}(T, P, m)) \quad (28)$$

$$\mu_{sol}(T, P) = \mu_{sol}^o(T, P) + RT \cdot \ln(a_{sol}(T, P)) \quad (29)$$

$$\Delta G_o^{fus} = \mu_{liq}^o - \mu_{sol}^o = -RT \cdot \ln(a_{liq}) \quad (30)$$

$$\frac{d\ln(a_{liq})}{dT} = \frac{\Delta H_T^{fus}}{RT^2} \quad (31)$$

In equations (28)-(31):

$\mu_{liq}$  and  $\mu_{sol}$  are the chemical potential of the liquid solvent (water) and solid solvent (ice),

$\mu_{liq}^0$ ,  $\mu_{liq}^\circ$  and  $\mu_{sol}^\circ$  are the chemical potential of the pure liquid solvent and pure solid solvent,

$T$ ,  $P$ , and  $R$  are temperature, pressure and molar gas constant,

$m$  is the solute molality,

$a_{liq}$ ,  $\mathbf{a}_{liq}$  and  $\mathbf{a}_{sol}$  are the activity of the liquid solvent and solid solvent,

$\Delta G_0^{fus}$ ,  $\Delta G_0^{fus}$  and  $\Delta H_T^{fus}$  are the Gibbs free energy of fusion and the enthalpy of fusion.

$\Delta H_T^{fus}$  Because of the relatively large freezing point depressions of some salts, the enthalpy of fusion term of Eq. (31) is often not constant. In most cases, a linear temperature dependency related to the heat capacity change of the phase transition (32) is assumed. By integrating Eq. (31) and combining it with Eq. (32), an expression for the temperature change of the freezing point depression Eq. (33) is obtained. By approximating the logarithmic function with the first two terms of the Taylor series, the freezing point Equation (34) used in AquaDLL.dll is derived. The boiling point elevation is similar to this expression, although the enthalpies and heat capacity changes of fusion are replaced by those of vaporization<sup>15</sup>.

$$\Delta H_T^{fus} = \Delta H_{0,T_F}^{fus} + \Delta C_P^{fus}(T - T_F) = \Delta H_{0,T_F}^{fus} - (C_P^{liq} - C_P^{sol})\theta_F \quad (32)$$

$$R \cdot \ln(a_{liq}) = \Delta H_{0,T_F}^{fus} \left( \frac{1}{T_F} - \frac{1}{T_F - \theta_F} \right) + \Delta C_P^{fus} \left( \ln \left( \frac{T_F - \theta_F}{T_F} \right) + \frac{T_F}{T_F - \theta_F} \right) \quad (33)$$

$$\theta_F = \frac{\Delta H_{0,T_F}^{fus} - 2RT_F \ln(a_{liq}) - \sqrt{2\Delta C_P^{fus} T_F^2 R \ln(a_{liq}) + (\Delta H_{0,T_F}^{fus})^2}}{2 \cdot \left( \frac{\Delta H_{0,T_F}^{fus}}{T_F} + 0.5\Delta C_P^{fus} - R \ln(a_{liq}) \right)} \quad (34)$$

$$\theta_B = \frac{\Delta H_{0,T_B}^{vap} - 2RT_B \ln(a_{liq}) - \sqrt{2\Delta C_P^{vap} T_B^2 R \ln(a_{liq}) + (\Delta H_{0,T_B}^{vap})^2}}{2 \cdot \left( \frac{\Delta H_{0,T_B}^{vap}}{T_B} + 0.5\Delta C_P^{vap} - R \ln(a_{liq}) \right)} \quad (35)$$

where

$T$  is the freezing temperature of the solution,

$T_F$  and  $T_B$  are the (normal) freezing and boiling temperatures of the pure solvent,

$\Delta H_T^{fus}$  is the enthalpy change of fusion of the solution,

$\Delta H_{0,T_F}^{fus}$ ,  $\Delta H_{0,T_F}^{fus}$  is the enthalpy change of fusion of the pure solvent at  $T_F$ ,

$\Delta H_{0,T_B}^{vap}$ ,  $\Delta H_{0,T_B}^{vap}$  is the enthalpy change of vaporization of the pure solvent at  $T_B$ ,

$\Delta C_P^{fus}$ ,  $\Delta C_P^{fus}$  is the heat capacity difference between the liquid and solid phases at  $T_F$ ,

$\Delta C_P^{vap}$ ,  $\Delta C_P^{vap}$  is the heat capacity difference between the vapor and liquid phases at  $T_B$ ,

$C_P^{liq}$ ,  $C_P^{liq}$  is the real heat capacity of the liquid solvent,

$C_P^{sol}$   $C_P^{sol}$  is the heat capacity of the solid solvent,  
 $C_P^{vap}$   $C_P^{vap}$  is the heat capacity of the solvent vapor,  
 $R$  is the molar gas constant,  
 $a_{liq}$   $a_{liq}$  is the activity of the liquid solvent,  
 $\theta_F$  and  $\theta_B$  are the freezing point depression and boiling point elevation.

The new “Colligcalc” subroutine was developed for boiling point elevation and freezing point depression calculations. The heat capacities and water activities of Equations (32)-(35) were calculated at the boiling and freezing points of an ideal solution (i.e., pure water). In order to do this, a new subroutine called “CPPitzer” was created. Essentially, this is just a scaled-down version of the “Pitzer\_AC” subroutine. The calculation of the activity coefficients has been removed and only the osmotic coefficient and its temperature derivatives are calculated.

In addition to the expressions related directly to water activity, other important expressions were included in the new software version. The ionic strength  $I$  of the solution Equation (36) is an essential denominator in the Pitzer formalism and it was therefore already included in the previous versions of the HSC Aqua calculation algorithm. However, this quantity is now also visible on the results sheet for both binary and multi-component systems, since a printing command was added to the “Istrength” subroutine of AquaDLL.dll. In addition, molar activity coefficients displayed in HSC Aqua next to the molal activity coefficients have been calculated with the Pitzer formalism. These activity coefficients were derived through Eq. (37) and were displayed because the HSC Gibbs calculation routine uses the molar activity coefficients in the “**Equilibrium Compositions**” module user interface. The new calculations were included in AquaDLL.dll.

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (36)$$

$$\gamma_x = \frac{\gamma_m}{x(H_2O)} \quad (37)$$

In equations (36)-(37):

$I$  is the ionic strength of the solution,  
 $m_i$  is the molality of a solute species  $i$  (mol/kg) and  
 $z_i$  is the charge of solute species  $i$ .  
 $x_i$  is the mole fraction of solute species  $i$ ,  
 $\gamma_x$  and  $\gamma_m$  are the molar and the molal activity coefficient of solute species  $i$ .

Another extremely essential property of the aqueous solution is the pH value of the solution. Because the pH is the 10-base logarithm of the hydrogen ion activity in the solution (38), this quantity can also readily be determined with HSC Aqua. The ability to simulate the pH value of different solutions is crucial to the software development, because pH is a very common and independent measurement, which can be performed in fairly simple laboratory conditions. It is therefore an important and easily perceived reference point for the accuracy of the calculations. The pH of the solution is calculated in the new “pHcalc” subroutine of AquaDLL.dll. If the hydrogen ion has not been specified as an aqueous species by the user, the pH values are not calculated. In the future development of the calculations, some kind of notification about the hydrogen ion specification could be included in the code.

$$pH = -\log(a_{H^+}) = -\log(\gamma_{H^+} \cdot m_{H^+}) \quad (38)$$

in Equation (38):

$a_{H^+}$  is the hydrogen ion activity,  
 $\gamma_{H^+}$  is the hydrogen ion (molal) activity coefficient and  
 $m_{H^+}$  is the hydrogen ion molality.

All the new calculation results of HSC Aqua have been included in the multi-component sheet ("Water Phase"). Furthermore, the enthalpy of dilution is calculated from the apparent relative molal enthalpies (39). The enthalpy of dilution of a binary system is calculated from one molal concentration to another and the calculation principle has been presented by Silvester and Pitzer<sup>7</sup>.

The enthalpy of dilution can be calculated as the difference of relative apparent molar enthalpies  $\phi_L$  between two molalities:

$$\Delta H_D(m_1 \rightarrow m_2) = \phi_{L_2} - \phi_{L_1} \quad (39)$$

where

$\Delta H_D$  is the enthalpy of dilution, J/Kmol,  
 $m_1$  and  $m_2$  are the initial molality of the solution and the final molality of the dilution, mol/kg,  
 $\phi_{L_1}$  and  $\phi_{L_2}$  are the apparent relative molal enthalpies of initial and final solution, J/mol.

## Data Validation and Database Development

New data was added to the database and verified against literature data using HSC Aqua, i.e., the new data was validated by comparing the calculation results with experimental or other calculated values. Through this testing, not only the validity of the parameter sets but also the capabilities of the calculation tool are determined in a more rigorous way than just by cross-referencing parameter values. In this study, previous testing of the software was expanded with further binary salts and some new solution properties. The experimental data was derived from different literary sources.

Based on the test results, tabulation errors in the Pitzer parameter database were corrected and some parameter sets were also replaced or modified. In addition, new parameter entries were also made.



## 36.12. Conclusions

The HSC Chemistry software has been expanded with the HSC Aqua module, which deals with non-ideal electrolyte solutions. It estimates the activity coefficients, enthalpies, and heat capacities of binary and multi-component aqueous solutions. The module was also tested with several aqueous binary electrolytes and some multi-component examples.

The enthalpies yield satisfactory results, but the heat capacities, being the 2nd derivatives of Pitzer functions, show a greater deviation from experimental data. This estimation should be used as guidance only and the direct measurement of heat capacities for the most important process solutions is recommended.

From the test cases it is clear that the HSC Aqua aqueous electrolyte module is a capable tool for the modeling of different thermodynamic properties of aqueous electrolyte ionic species with respect to temperature and composition.

The various example systems examined in this work clearly show that aqueous electrolyte systems differ considerably from ideal systems. Even at low solute molalities, the activity coefficients, molal enthalpies, and molal heat capacities are greatly affected by the ion interactions between the different solute species.

It can therefore be stated that accurate aqueous solution calculations in HSC Chemistry definitely require a model for the estimation of corrections to ideal solution properties. This module will be developed and improved further.

## 36.13. References

1. K. S. Pitzer, Thermodynamics of electrolytes. 1. Theoretical basis and general equations, *J. Phys. Chem.*, **77**, (1973) 268-277.
2. C. Harvie, N. Møller, and J. Weare, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system to high ionic strengths at 25°C, *Geochim. Cosmochim. Acta.*, **48** (1984) 723-751.
3. Debye and E. Huckel, The theory of electrolytes. I. Lowering of freezing point and related phenomena, *Physik. Z.* **24** 185, 334 (1923). Ref. from H. Harned and B. Owen, *The Physical Chemistry of Electrolyte Solutions*, 2<sup>nd</sup> edition, Reinhold Publishing Corp. 1950, p.18.
4. K. S. Pitzer, *Thermodynamics*, 3<sup>rd</sup> edition, McGraw-Hill, 1995.
5. K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*, CRC Press, Boca Raton, Florida, USA, 1979.
6. Prausnitz, R. Lichtenthaler, and E. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3<sup>rd</sup> edition, Prentice-Hall, 1999.
7. Silvester, Pitzer, Thermodynamic of electrolytes. X. Enthalpy and the effects of temperature on the activity coefficients, *J. Sol. Chem.*, **7** No 5 (1978) 327-337.
8. C. M. Criss and J. F. Millero., *J. Phys. Chem.* **100** (1996), 1288-1294.
9. Zemaitis et al., *Handbook of aqueous electrolyte thermodynamics. Theory and application*, New York, 1986
10. Wagman, et al., The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data.* **5**, 10 (1982).
11. R. T. Pabalan and K.S. Pitzer, Apparent molar heat capacity and other thermodynamic properties of aqueous KCl solutions to high temperatures and pressures, *J. Chem. Eng. Data*, **33** (1988a) 354-362.
12. Clegg and Whitfield, Activity coefficients in Electrolyte Solutions, 2<sup>nd</sup> ed., K.S. Pitzer, ed., CRC Press, Boca Raton, 1991, p.413.
13. Malatesta et al., Activity and osmotic coefficients from the emf of liquid-membrane cells. VII: Co(ClO<sub>4</sub>)<sub>2</sub>, Ni(ClO<sub>4</sub>)<sub>2</sub>, K<sub>2</sub>SO<sub>4</sub>, CdSO<sub>4</sub>, CoSO<sub>4</sub>, and NiSO<sub>4</sub>. *J. Sol. Chem.* **28** No 5 (1999) 593-619.
14. McCutcheon S. C., Martin J. L. & Barnwell T. O. Jr. (1993) Water Quality. In: Maidment D. R. (editor) (1993) Handbook of Hydrology. McGraw-Hill, New York, NY. 1424 p.
15. Ge X. & Wang X. Estimation of Freezing Point Depression, Boiling Point Elevation, and Vaporization Enthalpies of Electrolyte Solutions. *Ind. Eng. Chem. Res.*, **48** (2009) 2229–2235.

## Appendix A. Vapor pressure of pure water

$$p_0 = (a \cdot T^{10} + b \cdot T^9 + c \cdot T^8 + d \cdot T^7 + e \cdot T^6 + f \cdot T^5 + g \cdot T^4 + h \cdot T^3 + i \cdot T^2 + j \cdot T + k) \cdot 1000 \quad (\text{A1})$$

$$p_0 = (1.11982860630743 \cdot 10^{-18} \cdot T^{10} - 4.04920519596997 \cdot 10^{-15} \cdot T^9 + 6.08290457531376 \cdot 10^{-12} \cdot T^8 - 5.12897992812743 \cdot 10^{-9} \cdot T^7 + 2.7240831169274 \cdot 10^{-6} \cdot T^6 - 9.59696050004219 \cdot 10^{-4} \cdot T^5 + 0.228254919514224 \cdot T^4 - 36.311462374836 \cdot T^3 + 3706.72828793979 \cdot T^2 - 219658.499462442 \cdot T + 5746593.5787401) \cdot dT < 160 \text{ } ^\circ\text{C}$$

$$a = -3.10432954399391 \cdot 10^{-21}$$

$$b = 1.00959411100662 \cdot 10^{-18}$$

$$c = -5.88099024207425 \cdot 10^{-17}$$

$$d = -3.18476754457404 \cdot 10^{-14}$$

$$e = 6.55612456912702 \cdot 10^{-12}$$

$$f = 2.25575938350116 \cdot 10^{-9}$$

$$g = 2.99998801482107 \cdot 10^{-7}$$

$$h = 2.57849258952755 \cdot 10^{-5}$$

$$i = 1.43776358189044 \cdot 10^{-3}$$

$$j = 4.51730065352071 \cdot 10^{-2}$$

$$k = 0.599030194123347$$

### $T \geq 160 \text{ } ^\circ\text{C}$

$$a = 1.11982860630743 \cdot 10^{-18}$$

$$b = -4.04920519596997 \cdot 10^{-15}$$

$$c = 6.08290457531376 \cdot 10^{-12}$$

$$d = -5.12897992812743 \cdot 10^{-9}$$

$$e = 2.7240831169274 \cdot 10^{-6}$$

$$f = -9.59696050004219 \cdot 10^{-4}$$

$$g = 0.228254919514224$$

$$h = -36.311462374836$$

$$i = 3706.72828793979$$

$$j = -219658.499462442$$

$$k = 5746593.5787401$$

## Appendix B. HSC Aqua thermodynamic database

The Pitzer parameter sets of the HSC Aqua database are presented in this appendix. Because some of the parameter sets have a temperature dependency presented in Equation (22) and some parameters have only been tabulated as constant values, the temperature dependencies of the parameter sets are presented here as well. As the logarithmic activity coefficient expression is differentiated to calculate the enthalpies and heat capacities, the constant terms and first order terms of Equation (22) are eliminated. Therefore, the temperature dependencies of the  $H$  and  $C_p$  expressions have to be considered separately.

The total number of entries in the HSC Aqua database for each sheet of Pitzer parameters is displayed below. The entries of the previous Pitzer parameter database, which was used as a template for the HSC Aqua database, are given in parentheses. These old parameter set amounts also include sets that have been replaced with new parameter entries in the new HSC Aqua database. This data can also be found when the user selects the Main Database icon in the Aqua module.

- Binary ion pairs (Beta and C parameters): **425**
- Cation-cation and anion-anion (Theta parameter) pairs: **114**
- Ternary (Psi) ion interaction parameters: **199**
- Neutral-ion (Lambda parameter) pairs: **293**

Total amount of entries: **1031**

**Table B1.** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Ag(+a)	NO3(-a)	N	N		N								
Al(+3a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Al(+3a)	NO3(-a)	N	N		N								
Al(+3a)	SO4(-2a)	N	N	N	N								
Ba(+2a)	Br(-a)	Y	Y		Y	N	N		N				
Ba(+2a)	CH3COO(-a)	N	N		N								
Ba(+2a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Ba(+2a)	ClO4(-a)	N	N		N								
Ba(+2a)	HSO4(-a)	N	Y				N						
Ba(+2a)	I(-a)	N	N		N								
Ba(+2a)	NO3(-a)	Y	Y			N	N						
Ba(+2a)	OH(-a)	N	N										
Ba(+2a)	SO4(-2a)	Y	Y	Y		Y	Y	Y		N	N	N	
Be(+2a)	SO4(-2a)	N	N		N								
Ca(+2a)	B(OH)4(-a)	Y	Y	Y		N	N	Y				N	
Ca(+2a)	Br(-a)	Y	Y		N	N	N						
Ca(+2a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	N		Y
Ca(+2a)	ClO4(-a)	Y	Y		Y	N	N		N				
Ca(+2a)	HCO3(-a)	N	N										
Ca(+2a)	HS(-a)	N	N										
Ca(+2a)	HSO3(-a)	N	N										
Ca(+2a)	HSO4(-a)	N	N										
Ca(+2a)	I(-a)	N	N		N								
Ca(+2a)	NO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Ca(+2a)	OH(-a)	N	N	N									
Ca(+2a)	PbCl3(-a)	N	N										
Ca(+2a)	PbCl4(-2a)	N			N								
Ca(+2a)	SO4(-2a)	Y	Y	Y		Y	Y	Y		N	N	N	
CaB(OH)(+a)	Cl(-a)	N											
Cd(+2a)	Br(-a)	N	N		N								
Cd(+2a)	Cl(-a)	N	N		N								
Cd(+2a)	ClO4(-a)	N	N		N								
Cd(+2a)	I(-a)	N	N		N								
Cd(+2a)	NO2(-a)	N	N		N								
Cd(+2a)	NO3(-a)	N	N		N								
Cd(+2a)	SO3(-2a)	N	N	N									
Cd(+2a)	SO4(-2a)	Y	Y	Y	Y	N	N	N	N				
Ce(+3a)	Cl(-a)	N	N		N								

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
CH3NH3(+a)	Cl(-a)	N	N		N								
(CH3)2NH2(+a)	Cl(-a)	N	N		N								
CH3NH3(+a)	NO3(-a)	N	N		N								
(CH3)2NH2(+a)	NO3(-a)	N	N		N								
(CH3)3NH(+a)	NO3(-a)	N	N		N								
CH6N3(+a)	Br(-a)	N	N		N								
CH6N3(+a)	ClO4(-a)	N	N		N								
CH6N3(+a)	F(-a)	N	N		N								
CH6N3(+a)	I(-a)	N	N		N								
CH6N3(+a)	NO3(-a)	N	N		N								
(CH3)4CH6N3(+a)	Br(-a)	N	N		N								
(CH3)4CH6N3(+a)	Cl(-a)	N	N		N								
(CH3)4CH6N3(+a)	ReO4(-a)	N	N		N								
(CH3)4CH6N3(+a)	H2NSO3(SFAA)(-a)	N	N		N								
C6H14N4O2H(ARG)(+a)	Cl(-a)	N	N		N								
C6H9N3O2H(HIS)(+a)	Cl(-a)	N	N										
C6H14N2O2H(LYS)(+a)	Cl(-a)	N	N		N								
Cm(+3a)	Cl(-a)	N	N		N								
CmCO3(+a)	Cl(-a)	N	N		N								
Co(+2a)	Br(-a)	N	N		N								
Co(+2a)	Cl(-a)	Y	Y		Y	N	N		N				
Co(+2a)	ClO4(-a)	N	N		N								
Co(+2a)	I(-a)	N	N		N								
Co(+2a)	NO3(-a)	N	N		N								
Co(+2a)	SeO4(-2a)	N	N		N								
Co(+2a)	SO3(-2a)	N	N	N									
Co(+2a)	SO4(-2a)	N	N	N	N								
Cr(+3a)	Cl(-a)	N	N		N								
Cr(+3a)	NO3(-a)	N	N		N								
Cs(+a)	Br(-a)	Y	Y		N	N	N						
Cs(+a)	CH3COO(-a)	N	N		N								
Cs(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Cs(+a)	F(-a)	Y	Y		N	N	N						
Cs(+a)	HSO4(-a)	Y	N		Y	Y			Y	N			N
Cs(+a)	I(-a)	Y	Y		N	N	N						
Cs(+a)	NO2(-a)	N	N		N								
Cs(+a)	NO3(-a)	N	N										
Cs(+a)	OH(-a)	N	N										
Cs(+a)	S2O8(-2a)	N	N										

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Cs(+a)	SO4(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Cu(+2a)	Br(-a)	N	N		N								
Cu(+2a)	Cl(-a)	Y	Y		N	N	N						
Cu(+2a)	ClO4(-a)	N	N		N								
Cu(+2a)	CuCl3(-a)	N	N		N								
Cu(+2a)	CuCl4(-2a)	N	N	N	N								
Cu(+2a)	HSO4(-a)	N	N										
Cu(+2a)	NO3(-a)	N	N		N								
Cu(+2a)	SO4(-2a)	Y	Y	Y	Y	N	N	N	N				
CuCl(+a)	Cl(-a)	N	N		N								
CuCl(+a)	CuCl3(-a)	N	N		N								
CuCl(+a)	CuCl4(-2a)	N	N		N								
CuCl(+a)	SO4(-2a)	N	N										
Dy(+3a)	Cl(-a)	N	N		N								
Dy(+3a)	ClO4(-a)	N	N		N								
Dy(+3a)	NO3(-a)	N	N		N								
Er(+3a)	Cl(-a)	N	N		N								
Er(+3a)	ClO4(-a)	N	N		N								
Er(+3a)	NO3(-a)	N	N		N								
Eu(+3a)	Cl(-a)	N	N		N								
Eu(+3a)	NO3(-a)	N	N		N								
Fe(+2a)	Cl(-a)	N	N		N								
Fe(+2a)	HSO4(-a)	N	N										
Fe(+2a)	SO4(-2a)	N	N	N	N								
Fe(+3a)	Cl(-a)	N	N		N								
Ga(+3a)	Cl(-a)	N	N		N								
GaOH(+3a)	Cl(-a)	N	N										
Ga(+3a)	ClO4(-a)	N	N		N								
Gd(+3a)	Cl(-a)	N	N		N								
Gd(+3a)	ClO4(-a)	N	N		N								
Gd(+3a)	NO3(-a)	N	N		N								
H(+a)	Br(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
H(+a)	C7H8O3S(4MBSA)(-a)	N	N		N								
H(+a)	C8H9O3S(25DMBSA)(-a)	N	N		N								
H(+a)	CF3O3S(-a)	N	N		N								
H(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
H(+a)	ClO4(-a)	Y	Y		Y	N	N		N				
H(+a)	CuCl3(-a)	N	N		N								
H(+a)	CuCl4(-2a)	N	N		N								
H(+a)	F(-a)	N	N		N								

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
H(+a)	HF2(-a)	N	N		N								
H(+a)	HSO4(-a)	Y	Y			Y	Y			Y	N		
H(+a)	I(-a)	Y	Y		Y	N	N		N				
H(+a)	NO3(-a)	Y	Y		Y	Y	N		Y	N			N
H(+a)	H2NSO3(SFAA)(-a)	N	N		N								
H(+a)	PbCl3(-a)	N	N										
H(+a)	PbCl4(-2a)	N											
H(+a)	ReO4(-a)	N	N		N								
H(+a)	SO4(-2a)	Y			Y	Y			Y	Y			Y
H(+a)	SO2Cl(-a)	N	N										
Hf(+4a)	Cl(-a)	N	N		N								
HfOH(+3a)	Cl(-a)	N	N										
Hg(+2a)	ClO4(-a)	N	N		N								
HgCl(+a)	ClO4(-a)	N			N								
HgOH(+a)	ClO4(-a)	N	N		N								
Hg2OH(+3a)	ClO4(-a)	N	N		N								
Ho(+3a)	Cl(-a)	N	N		N								
Ho(+3a)	ClO4(-a)	N	N		N								
Ho(+3a)	NO3(-a)	N	N		N								
In(+3a)	Cl(-a)	N	N										
K(+a)	(CH2COO)2(-2a)	N	N										
K(+a)	Al(OH)4(-a)	N	N		N								
K(+a)	AsO4(-3a)	N	N		N								
K(+a)	B(OH)4(-a)	Y	Y		Y	N	N		N				
K(+a)	B3O3(OH)(-a)	N											
K(+a)	B4O5(OH)4(-2a)	N											
K(+a)	Br(-a)	Y	Y		Y	Y	Y		N	N	N		
K(+a)	BrO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	CH3COO(-a)	N	N		N								
K(+a)	CCl3COO(-a)	N	N		N								
K(+a)	CF3O3S(3FMSFOA)(-a)	N	N		N								
K(+a)	CH4O3S(MSA)(-a)	N	N		N								
K(+a)	C5H8N4(GLU)(-a)	N	N		N								
K(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	ClO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	CNS(-a)	Y	Y		Y	N	N		N				
K(+a)	Co(CN)6(-3a)	N	N		N								
K(+a)	CO3(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	Cr2O7(-2a)	N	N	N	N								



**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
K(+a)	CrO4(-2a)	N	N		N								
K(+a)	F(-a)	Y	Y		Y	N	N		N				
K(+a)	Fe(CN)6(-3a)	Y	Y		Y	N	N		N				
K(+a)	Fe(CN)6(-4a)	Y	Y		Y	N	N		N				
K(+a)	H2AsO4(-a)	N	N										
K(+a)	H2P2O7(-2a)	N	N		N								
K(+a)	H2PO4(-a)	Y	Y		Y	N	N		N				
K(+a)	HasO4(-2a)	N	N		N								
K(+a)	HCO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	HOOC(CH2)2COO(-a)	N	N		N								
K(+a)	HOOC(CH2)4COO(-a)	N	N										
K(+a)	HOOCCH2COO(-a)	N	N		N								
K(+a)	H3CSO4(-a)	N	N		N								
K(+a)	H2NSO3(SFAA)(-a)	N	N		N								
K(+a)	HPO4(-2a)	N	N		N								
K(+a)	HS(-a)	Y			N	Y				Y			
K(+a)	HSO4(-a)	Y	Y		Y	Y	Y		Y	Y	Y		N
K(+a)	I(-a)	Y	Y		Y	N	N		N				
K(+a)	IO3(-a)	N	N										
K(+a)	NH2C6H4SO3(4ABSA)(-a)	N	N		N								
K(+a)	NO2(-a)	N	N		N								
K(+a)	NO3(-a)	Y	Y		Y	N	N		N				
K(+a)	OH(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
K(+a)	PbCl4(-2a)	N											
K(+a)	P3O9(-3a)	N	N		N								
K(+a)	PtF6(-a)	N	N										
K(+a)	PO4(-3a)	N	N		N								
K(+a)	Pt(CN)4(-2a)	N	N		N								
K(+a)	SCN(-a)	N	N		N								
K(+a)	SO4(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
La(+3a)	Cl(-a)	Y	Y		Y	N	N		N				
La(+3a)	ClO4(-a)	Y	Y		Y	N	N		N				
La(+3a)	NO3(-a)	Y	Y		Y	N	N		N				
Li(+a)	B4O7(-2a)	N	N	N	N								
Li(+a)	B4O5(OH)4(-2a)	N	N		N								
Li(+a)	Br(-a)	Y	Y		Y	N	N		N				
Li(+a)	BrO3(-a)	N	N		N								
Li(+a)	BrO3(-a)	N	N										
Li(+a)	CF3O3S(3FMSFOA)(-a)	N	N		N								

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Li(+a)	CH3COO(-a)	N	N		N								
Li(+a)	CCl3COO(-a)	N	N		N								
Li(+a)	CH4O3S(MSA)(-a)	N	N		N								
Li(+a)	Cl(-a)	Y	Y		Y	N	N		Y				Y
Li(+a)	ClO3(-a)	N	N		N								
Li(+a)	ClO4(-a)	Y	Y		Y	N	N		N				
Li(+a)	CuCl3(-a)	N	N										
Li(+a)	CuCl4(-2a)	N	N										
Li(+a)	HSO4(-a)	Y	Y		Y	Y	Y		Y	N	N		Y
Li(+a)	H2NSO3(SFAA)(-a)	N	N		N								
Li(+a)	I(-a)	N	N										
Li(+a)	IO3(-a)	N	N		N								
Li(+a)	NO2(-a)	N	N		N								
Li(+a)	NO3(-a)	N	N		N								
Li(+a)	OH(-a)	N	N										
Li(+a)	ReO4(-a)	N	N		N								
Li(+a)	SO4(-2a)	Y	Y		Y	N	N		N				
Lu(+3a)	Cl(-a)	N	N		N								
Lu(+3a)	ClO4(-a)	N	N		N								
Lu(+3a)	NO3(-a)	N	N		N								
Mg(+2a)	B(OH)4(-a)	Y	Y	Y		N	N	Y				N	
Mg(+2a)	Br(-a)	Y	Y		N	Y	Y			N	N		
Mg(+2a)	CH3COO(-a)	N	N		N								
Mg(+2a)	Cl(-a)	Y	Y		Y	Y	Y		Y	N	N		N
Mg(+2a)	ClO4(-a)	Y	Y		Y	N	N		N				
Mg(+2a)	CuCl3(-a)	N	N										
Mg(+2a)	CuCl4(-2a)	N	N	N									
Mg(+2a)	F(-a)	N	N		N								
Mg(+2a)	HCO3(-a)	N	N										
Mg(+2a)	HPO4(-2a)	N	N										
Mg(+2a)	H2PO4(-a)	N	N										
Mg(+2a)	HS(-a)	N	N		N								
Mg(+2a)	HSO3(-a)	N	N		N								
Mg(+2a)	HSO4(-a)	N	N										
Mg(+2a)	I(-a)	N	N		N								
Mg(+2a)	NO3(-a)	Y	Y		N	N	N						
Mg(+2a)	PbCl3(-a)	N	N										
Mg(+2a)	PbCl4(-2a)	N											
Mg(+2a)	SeO4(-2a)	N	N		N								
Mg(+2a)	SO3(-2a)	N	N	N									

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Mg(+2a)	SO4(-2a)	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
MgB(OH)4(+a)	Cl(-a)	N											
MgOH(+a)	Cl(-a)	N	N										
Mn(+2a)	Br(-a)	N	N		N								
Mn(+2a)	Cl(-a)	N	N		N								
Mn(+2a)	ClO4(-a)	N	N		N								
Mn(+2a)	SO3(-2a)	N	N	N									
Mn(+2a)	SO4(-2a)	N	N	N	N								
N(C2H5)4(+a)	Cl(-a)	N	N		N								
N(C3H7)4(+a)	Cl(-a)	N	N		N								
N(C4H9)4(+a)	Br(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
N(C4H9)4(+a)	Cl(-a)	N	N		N								
N(CH3)4(+a)	Cl(-a)	N	N		N								
Na(+a)	Al(OH)4(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	AsO4(-3a)	N	N		N								
Na(+a)	B(OH)4(-a)	Y	Y		Y	N	N		N				
Na(+a)	B3O3(OH)4(-a)	N	N										
Na(+a)	B4O5(OH)4(-2a)	N	N										
Na(+a)	BF4(-a)	Y	Y		Y	Y	Y		Y	N	N		N
Na(+a)	BO2(-a)	N	N		N								
Na(+a)	Br(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	BrO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	(CH2COO)2(-2a)	N	N		N								
Na(+a)	(CHCOO)2(cis)(-2a)	N	N		N								
Na(+a)	(CHCOO)2(trans)(-2a)	N	N		N								
Na(+a)	C6H5O7(CAC)(-3a)	N	N		N								
Na(+a)	H(C6H5O7(CAC))(-2a)	N	N		N								
Na(+a)	H2(C6H5O7(CAC))(-a)	N	N		N								
Na(+a)	CF3O3S(3FMSFOA)(-a)	N	N		N								
Na(+a)	C2H5COO(-a)	N	N		N								
Na(+a)	CH3COO(-a)	N	N		N								
Na(+a)	CH4O3S(MSA)(-a)	N	N		N								
Na(+a)	C12H17O3S(25IPBSA)(-a)	N	N										
Na(+a)	C8H9O3S(24DMBSA)(-a)	N	N		N								
Na(+a)	C10H13O3S(2M5IPBSA)(-a)	N	N		N								
Na(+a)	C5H8N4(GLU)(-a)	N	N		N								
Na(+a)	C7H5O2(BA)(-a)	N	N		N								
Na(+a)	C7H6O3(SA)(-a)	N	N		N								
Na(+a)	C8H9O3(3MSA)(-a)	N	N		N								
Na(+a)	C13H20O3(35DIPSA)(-a)	N	N		N								

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Na(+a)	C2O4(-2a)	N	N		N								
Na(+a)	CoC2O2(-2a)	N	N		N								
Na(+a)	HC2O4(-a)	N	N		N								
Na(+a)	MnC2O2(-2a)	N											
Na(+a)	NiC2O2(-2a)	N	N		N								
Na(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	ClO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	ClO4(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	Cm(CO3)2(-a)	N	N		N								
Na(+a)	Cm(CO3)3(-3a)	N	N		N								
Na(+a)	Cm(CO3)4(-5a)	N	N		N								
Na(+a)	CNS(-a)	Y	Y		N	N	N						
Na(+a)	CoC6H5O7(CAC)(-3a)	N	N		N								
Na(+a)	CO3(-2a)	Y	Y		N	N	N						
Na(+a)	CrO4(-2a)	N	N		N								
Na(+a)	CuCl3(-a)	N	N		N								
Na(+a)	CuCl4(-2a)	N	N		N								
Na(+a)	F(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	HAsO4(-2a)	N	N		N								
Na(+a)	H2AsO4(-a)	N	N										
Na(+a)	H2PO4(-a)	N	N		N								
Na(+a)	H2SiO4(-2a)	N	N										
Na(+a)	H3SiO4(-a)	N	N										
Na(+a)	HCO3(-a)	Y	Y			N	N						
Na(+a)	HCOO(-a)	N	N		N								
Na(+a)	HOOC(CH2)2COO(-a)	N	N		N								
Na(+a)	HOOC(CH2)4COO(-a)	N	N										
Na(+a)	HOOCCH2COO(-a)	N	N		N								
Na(+a)	H3CSO4(-a)	N	N		N								
Na(+a)	Hf(OH)6(-2a)	N	N		N								
Na(+a)	HgCl3(-a)	N			N								
Na(+a)	HgCl4(-2a)	N			N								
Na(+a)	H2NSO3(SFAA)(-a)	N	N		N								
Na(+a)	HPO4(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	HS(-a)	Y			N	Y				Y			
Na(+a)	HSO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	HSO4(-a)	Y	Y		Y	Y	Y		N	N	Y		
Na(+a)	I(-a)	Y	Y		Y	N	N		N				
Na(+a)	Mg(CO3)2(-2a)	N	N		N								
Na(+a)	NH2C6H4SO3(4ABSA)(-a)	N	N		N								

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Na(+a)	NiC6H5O7(CAC)(-a)	N	N		N								
Na(+a)	NO2(-a)	N	N		N								
Na(+a)	NO3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	OH(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	PbCl3(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	PbCl4(-2a)				N								
Na(+a)	PO4(-3a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	ReO4(-a)	N	N		N								
Na(+a)	Si2O3(OH)4(-2a)	N	N										
Na(+a)	Si3O6(OH)3(-3a)	N	N										
Na(+a)	Si3O5(OH)5(-3a)	N	N										
Na(+a)	Si4O8(OH)4(-4a)	N	N										
Na(+a)	Si4O6(OH)6(-2a)	N	N										
Na(+a)	Si4O7(OH)6(-4a)	N	N										
Na(+a)	Si6O15(-6a)	N	N										
Na(+a)	S2O3(-2a)	N	N		N								
Na(+a)	S2O6(-2a)	N	N										
Na(+a)	S2O8(-2a)	N	N										
Na(+a)	SO3(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	SO4(-2a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Na(+a)	SO2Cl(-a)	N	N										
Na(+a)	Th(CO3)(-6a)	N	N										
Na(+a)	WO4(-2a)	N	N		N								
Nd(+3a)	Cl(-a)	N	N		N								
Nd(+3a)	ClO4(-a)	N	N		N								
Nd(+3a)	NO3(-a)	N	N		N								
NH4(+a)	Br(-a)	N	N		N								
NH4(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
NH4(+a)	ClO4(-a)	N	N										
NH4(+a)	CNS(-a)	N	N		N								
NH4(+a)	F(-a)	Y	N		N	Y				Y			
NH4(+a)	H2PO4(-a)	Y	Y		Y	N	N		N				
NH4(+a)	HCO3(-a)	N	N										
NH4(+a)	HPO4(-2a)	N	N		N								
NH4(+a)	I(-a)	N	N		N								
NH4(+a)	NO3(-a)	N	N		N								
NH4(+a)	SO4(-2a)	N	N		N								
Ni(+2a)	Br(-a)	N	N		N								
Ni(+2a)	Cl(-a)	Y	Y		Y	N	N		N				
Ni(+2a)	ClO4(-a)	N	N		N								

Empty cell = no parameter value

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Ni(+2a)	HSO4(-a)	N	Y				N						
Ni(+2a)	NO3(-a)	N	N		N								
Ni(+2a)	SeO4(-2a)	N	N		N								
Ni(+2a)	SO3(-2a)	N	N	N									
Ni(+2a)	SO4(-2a)	Y	Y	Y	Y	N	N	N	N				
Pb(+2a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Pb(+2a)	ClO4(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Pb(+2a)	HSO4(-a)	Y	N			Y				Y			
Pb(+2a)	NO3(-a)	N	N		N								
Pb(+2a)	SO4(-2a)	N	Y	Y			N	Y				Y	
PbCl(+a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
PbCl(+a)	ClO4(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Pr(+3a)	Cl(-a)	N	N		N								
Pr(+3a)	ClO4(-a)	N	N		N								
Pr(+3a)	NO2(-a)	N	N		N								
Pr(+3a)	NO3(-a)	N	N		N								
Ra(+2a)	HSO4(-a)	N	Y				N						
Ra(+2a)	SO4(-2a)	N	Y	Y			N	N					
Rb(+a)	Br(-a)	Y	Y		N	N	N						
Rb(+a)	CH3COO(-a)	N	N		N								
Rb(+a)	Cl(-a)	Y	Y		N	N	N						
Rb(+a)	F(-a)	Y	Y		N	N	N						
Rb(+a)	I(-a)	Y	Y		N	N	N						
Rb(+a)	NO2(-a)	N	N		N								
Rb(+a)	NO3(-a)	N	N		N								
Rb(+a)	S2O8(-2a)	N	N										
Rb(+a)	SO4(-2a)	Y	Y		N	N	N						
Sc(+3a)	Cl(-a)	N	N		N								
Sm(+3a)	Cl(-a)	N	N		N								
Sm(+3a)	ClO4(-a)	N	N		N								
Sm(+3a)	NO3(-a)	N	N		N								
Sr(+2a)	B(OH)4(-a)	Y	Y	Y		N	N	Y				N	
Sr(+2a)	Br(-a)	Y	Y		N	N	N						
Sr(+2a)	Cl(-a)	Y	Y		Y	Y	Y		Y	Y	Y		Y
Sr(+2a)	ClO4(-a)	Y	Y		Y	N	N		N				
Sr(+2a)	HCO3(-a)	N	N										
Sr(+2a)	HSO3(-a)	Y	Y		Y	N	N		N				
Sr(+2a)	HSO4(-a)	N	N										
Sr(+2a)	I(-a)	N	N		N								
Sr(+2a)	NO3(-a)	Y	Y		N	N	N						

**Table B1 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Binary parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep., AC				T dep., H				T dep., Cp			
Cation	Anion	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$
Sr(+2a)	OH(-a)	N	N		N								
Sr(+2a)	SO4(-2a)	Y	Y	Y		Y	Y	Y		N	N	N	
Tb(+3a)	Cl(-a)	N	N		N								
Tb(+3a)	ClO4(-a)	N	N		N								
Tb(+3a)	NO3(-a)	N	N		N								
Tl(+a)	Cl(-a)	N	N										
Tl(+a)	NO2(-a)	N	N		N								
Tl(+a)	CH3COO(-a)	N	N		N								
Tl(+a)	ClO4(-a)	N	N										
Tl(+a)	NO3(-a)	N	N										
Tm(+3a)	Cl(-a)	N	N		N								
Tm(+3a)	ClO4(-a)	N	N		N								
Tm(+3a)	NO3(-a)	N	N		N								
UO2(+2a)	Cl(-a)	N	N		N								
UO2(+2a)	ClO4(-a)	N	N		N								
UO2(+2a)	NO3(-a)	N	N		N								
UO2(+2a)	SO4(-2a)	N	N		N								
Y(+3a)	Cl(-a)	N	N		N								
Y(+3a)	NO3(-a)	N	N		N								
Yb(+3a)	Cl(-a)	N	N		N								
Yb(+3a)	ClO4(-a)	N	N		N								
Yb(+3a)	NO3(-a)	N	N		N								
Zn(+2a)	Br(-a)	N	N		N								
Zn(+2a)	Cl(-a)	N	N		N								
Zn(+2a)	ClO4(-a)	Y	Y		Y	N	N		N				
Zn(+2a)	F(-a)	N	N										
Zn(+2a)	HSO4(-a)	N	N		N								
Zn(+2a)	I(-a)	N	N		N								
Zn(+2a)	NO3(-a)	N	N		N								
Zn(+2a)	SeO4(-2a)	N	N		N								
Zn(+2a)	SO4(-2a)	Y	Y	Y	Y	N	N	N	N				

**Table B2.** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Theta parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep. AC	T dep. H	T dep. Cp
Al(+3a)	Ca(+2a)	N		
Al(+3a)	Cu(+2a)	N		
Al(+3a)	Fe(+2a)	N		
Al(+3a)	H(+a)	N		
Al(+3a)	K(+a)	N		
Al(+3a)	Mg(+2a)	N		
Al(+3a)	Ni(+2a)	N		
Al(+3a)	Na(+a)	N		
Al(OH)4(-a)	OH(-a)	N		
Ba(+2a)	Ca(+2a)	N		
Ba(+2a)	Cs(+a)	N		
Ba(+2a)	H(+a)	Y	N	
Ba(+2a)	K(+a)	N		
Ba(+2a)	Li(+a)	N		
Ba(+2a)	Na(+a)	N		
B(OH)4(-a)	Cl(-a)	Y	Y	N
B(OH)4(-a)	SO4(-2a)	N		
B3O3(OH)4(-a)	Cl(-a)	N		
B3O3(OH)4(-a)	HCO3(-a)	N		
B3O3(OH)4(-a)	SO4(-2a)	N		
B4O5(OH)4(-2a)	Cl(-a)	N		
B4O5(OH)4(-2a)	HCO3(-a)	N		
B4O5(OH)4(-2a)	SO4(-2a)	N		
B4O7(-2a)	Cl(-a)	N		
Br(-a)	Cl(-a)	N		
Br(-a)	Cr2O7(-2a)	N		
Br(-a)	OH(-a)	N		
Ca(+2a)	Co(+2a)	N		
Ca(+2a)	H(+a)	Y	N	
Ca(+2a)	K(+a)	N		
Ca(+2a)	Mg(+2a)	N		
Ca(+2a)	Mg(+a)	N		
Ca(+2a)	Na(+a)	N		
Ca(+2a)	PbCl(+a)	N		
Cl(-a)	AsO4(-3a)	N		
Cl(-a)	B4O5(OH)4(-2a)	N		
Cl(-a)	CH3COO(-a)	N		
Cl(-a)	CO3(-2a)	N		
Cl(-a)	Cr2O7(-2a)	N		
Cl(-a)	CuCl3(-a)	N		
Cl(-a)	CuCl4(-2a)	N		
Cl(-a)	F(-a)	N		



**Table B2 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Theta parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

	<b>IONS</b>	<b>T dep. AC</b>	<b>T dep. H</b>	<b>T dep. Cp</b>
Cl(-a)	HAsO4(-2a)	N		
Cl(-a)	H2AsO4(-a)	N		
Cl(-a)	H2PO4(-a)	N		
Cl(-a)	HCO3(-a)	N		
Cl(-a)	HPO4(-a)	N		
Cl(-a)	HSO4(-a)	N		
Cl(-a)	NO3(-a)	N		
Cl(-a)	OH(-a)	Y	Y	N
Cl(-a)	PO4(-3a)	N		
Cl(-a)	SO3(-2a)	N		
Cl(-a)	SO4(-2a)	Y	N	
ClO4(-a)	CO3(-2a)	N		
ClO4(-a)	HCO3(-a)	N		
ClO4(-a)	Th(CO3)(-6a)	N		
Cm(+3a)	Na(+a)	N		
Co(+2a)	H(+a)	Y	N	
Co(+2a)	Mg(+2a)	N		
Co(+2a)	Na(+a)	N		
Co(+2a)	Zn(+2a)	N		
CO3(-2a)	F(-a)	N		
CO3(-2a)	HCO3(-a)	N		
CO3(-2a)	NO2(-a)	N		
CO3(-2a)	NO3(-a)	N		
CO3(-2a)	OH(-a)	N		
CO3(-2a)	SO4(-2a)	N		
Cr2O7(-2a)	SO4(-2a)	N		
Cs(+a)	H(+a)	N		
Cs(+a)	K(+a)	N		
Cs(+a)	Li(+a)	N		
Cs(+a)	Na(+a)	Y	Y	Y
Cu(+2a)	CuCl(+a)	N		
Cu(+2a)	H(+a)	N		
Cu(+a)	Na(+a)	N		
Cu(+2a)	Na(+a)	N		
CuCl(+a)	H(+a)	N		
CuCl(+a)	Na(+a)	N		
CuCl3(-a)	CuCl4(-2a)	N		
F(-a)	HF2(-a)	N		
F(-a)	NO3(-a)	N		
F(-a)	OH(-a)	N		
H(+a)	K(+a)	Y	N	

**Table B2 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Theta parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS		T dep. AC	T dep. H	T dep. Cp
H(+a)	Li(+a)	N		
H(+a)	Mg(+2a)	Y	N	
H(+a)	Mn(+2a)	N		
H(+a)	Na(+a)	Y	N	
H(+a)	NH4(+a)	N		
H(+a)	Ni(+2a)	Y	N	
H(+a)	Sr(+2a)	Y	N	
H(+a)	UO2(+2a)	N		
HCO3(-a)	SO4(-2a)	N		
HSO4(-a)	SO4(-2a)	Y	Y	Y
K(+a)	Li(+a)	N		
K(+a)	Mg(+2a)	N		
K(+a)	Na(+a)	Y	Y	Y
K(+a)	Sr(+2a)	N		
Li(+a)	Na(+a)	N		
Mg(+2a)	Na(+a)	Y	N	
Mg(+2a)	Ni(+2a)	N		
Mg(+2a)	PbCl(+a)	N		
Mn(+2a)	Na(+a)	N		
Na(+a)	La(+3a)	N		
Na(+a)	Pb(+2a)	N		
Na(+a)	PbCl(+a)	N		
Na(+a)	Sr(+2a)	N		
Na(+a)	UO2(+2a)	N		
Na(+a)	Zn(+2a)	N		
Ni(+2a)	Zn(+2a)	N		
NO2(-a)	PO4(-3a)	N		
NO3(-a)	SO4(-2a)	N		
OH(-a)	PO4(-3a)	N		
OH(-a)	SO4(-2a)	N		

**Table B3.** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Psi parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS			T dep. AC	T dep. H	T dep. Cp
Al(+3a)	Ca(+2a)	SO4(-2a)	N		
Al(+3a)	Cu(+2a)	SO4(-2a)	N		
Al(+3a)	Fe(+2a)	SO4(-2a)	N		
Al(+3a)	H(+a)	Cl(-a)	Y	Y	Y
Al(+3a)	K(+a)	Cl(-a)	Y	Y	Y
Al(+3a)	Mg(+2a)	SO4(-2a)	N		
Al(+3a)	Na(+a)	Cl(-a)	Y	Y	Y
Al(+3a)	Ni(+2a)	SO4(-2a)	N		
Al(OH)4(-a)	OH(-a)	K(+a)	N		
Al(OH)4(-a)	OH(-a)	Na(+a)	N		
Ba(+2a)	Ca(+2a)	Cl(-a)	N		
Ba(+2a)	Cs(+a)	Cl(-a)	N		
Ba(+2a)	H(+a)	Br(-a)	N		
Ba(+2a)	H(+a)	Cl(-a)	Y	N	
Ba(+2a)	K(+a)	Cl(-a)	N		
Ba(+2a)	Li(+a)	Cl(-a)	N		
Ba(+2a)	Na(+a)	Cl(-a)	N		
B(OH)4(-a)	Cl(-a)	Ca(+2a)	N		
B(OH)4(-a)	Cl(-a)	Na(+a)	N		
B(OH)4(-a)	Cl(-a)	Mg(+2a)	N		
B3O3(OH)4(-a)	Cl(-a)	Na(+a)	N		
B4O5(OH)4(-2a)	Cl(-a)	Na(+a)	N		
B4O7(-2a)	Cl(-a)	Li(+a)	N		
Br(-a)	Cl(-a)	K(+a)	N		
Br(-a)	Cl(-a)	Na(+a)	N		
Br(-a)	Cr2O7(-2a)	K(+a)	N		
Br(-a)	OH(-a)	K(+a)	N		
Br(-a)	OH(-a)	Na(+a)	N		
Ca(+2a)	Co(+2a)	Cl(-a)	N		
Ca(+2a)	H(+a)	Br(-a)	N		
Ca(+2a)	H(+a)	Cl(-a)	Y	N	
Ca(+2a)	K(+a)	Cl(-a)	Y	Y	Y
Ca(+2a)	K(+a)	SO4(-2a)	N		
Ca(+2a)	Mg(+2a)	Cl(-a)	N		
Ca(+2a)	Mg(+2a)	NO3(-a)	N		
Ca(+2a)	Mg(+2a)	SO4(-2a)	N		
Ca(+2a)	Na(+a)	Cl(-a)	N		
Ca(+2a)	Na(+a)	NO3(-a)	N		
Ca(+2a)	Na(+a)	SO4(-2a)	N		
Cl(-a)	AsO4(-3a)	Na(+a)	N		
Cl(-a)	B4O5(OH)4(-2a)	K(+a)	N		

**Table B3 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Psi parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS			T dep. AC	T dep. H	T dep. Cp
Cl(-a)	B4O5(OH)4(-2a)	Li(+a)	N		
Cl(-a)	B4O5(OH)4(-2a)	Na(+a)	N		
Cl(-a)	CO3(-2a)	K(+a)	N		
Cl(-a)	CO3(-2a)	Na(+a)	N		
Cl(-a)	Cr2O7(-2a)	K(+a)	N		
Cl(-a)	CuCl3(-a)	Cu(+2a)	N		
Cl(-a)	CuCl4(-2a)	Cu(+2a)	N		
Cl(-a)	CuCl3(-a)	CuCl(+a)	N		
Cl(-a)	CuCl4(-2a)	CuCl(+a)	N		
Cl(-a)	CuCl3(-a)	H(+a)	N		
Cl(-a)	CuCl3(-a)	Na(+a)	N		
Cl(-a)	CuCl4(-a)	Na(+a)	N		
Cl(-a)	F(-a)	Na(+a)	N		
Cl(-a)	HAsO4(-2a)	Na(+a)	N		
Cl(-a)	H2AsO4(-a)	Na(+a)	N		
Cl(-a)	H2PO4(-a)	K(+a)	N		
Cl(-a)	H2PO4(-a)	Na(+a)	N		
Cl(-a)	HCO3(-a)	Mg(+2a)	N		
Cl(-a)	HCO3(-a)	Na(+a)	N		
Cl(-a)	HPO4(-2a)	Na(+a)	N		
Cl(-a)	HSO4(-a)	H(+a)	N		
Cl(-a)	HSO4(-a)	Na(+a)	N		
Cl(-a)	NO3(-a)	Ca(+2a)	N		
Cl(-a)	NO3(-a)	K(+a)	N		
Cl(-a)	NO3(-a)	Li(+a)	N		
Cl(-a)	NO3(-a)	Mg(+2a)	N		
Cl(-a)	NO3(-a)	Na(+a)	N		
Cl(-a)	OH(-a)	Ca(+2a)	N		
Cl(-a)	OH(-a)	K(+a)	N		
Cl(-a)	OH(-a)	Na(+a)	N		
Cl(-a)	PO4(-3a)	Na(+a)	N		
Cl(-a)	SO3(-2a)	Na(+a)	N		
Cl(-a)	SO4(-2a)	Ca(+2a)	N		
Cl(-a)	SO4(-2a)	Co(+2a)	N		
Cl(-a)	SO4(-2a)	Cu(+2a)	N		
Cl(-a)	SO4(-2a)	K(+a)	Y	Y	Y
Cl(-a)	SO4(-2a)	Li(+a)	N		
Cl(-a)	SO4(-2a)	Mg(+2a)	N		
Cl(-a)	SO4(-2a)	Na(+a)	Y	Y	N
Cl(-a)	SO4(-2a)	Ni(+2a)	N		
ClO4(-a)	CO3(-2a)	Na(+a)	N		
ClO4(-a)	HCO3(-a)	Mg(+2a)	N		

**Table B3 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Psi parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS			T dep.	ACT dep.	HT dep.	Cp
ClO4(-a)	HCO3(-a)	Na(+a)	N			
Cr(+3a)	Na(+a)	Cl(-a)	N			
Co(+2a)	Ca(+2a)	Cl(-a)	N			
Co(+2a)	H(+a)	Cl(-a)	Y	N		
Co(+2a)	Mg(+2a)	SeO4(-2a)	N			
Co(+2a)	Na(+a)	Cl(-a)	N			
Co(+2a)	Na(+a)	SO4(-2a)	N			
Co(+2a)	Rb(+a)	SO4(-2a)	N			
Co(+2a)	Zn(+2a)	SeO4(-2a)	N			
CO3(-2a)	F(-a)	Na(+a)	N			
CO3(-2a)	HCO3(-a)	K(+a)	N			
CO3(-2a)	HCO3(-a)	Na(+a)	N			
CO3(-2a)	OH(-a)	K(+a)	N			
CO3(-2a)	OH(-a)	Na(+a)	N			
CO3(-2a)	SO4(-2a)	K(+a)	N			
CO3(-2a)	SO4(-2a)	Na(+a)	N			
Cr2O7(-2a)	SO4(-2a)	K(+a)	N			
Cs(+a)	H(+a)	Cl(-a)	N			
Cs(+a)	K(+a)	Cl(-a)	N			
Cs(+a)	Li(+a)	Cl(-a)	N			
Cs(+a)	Na(+a)	Cl(-a)	N			
Cu(+2a)	CuCl(+a)	Cl(-a)	N			
Cu(+2a)	CuCl(+a)	CuCl3(-a)	N			
Cu(+2a)	CuCl(+a)	CuCl4(-2a)	N			
Cu(+2a)	H(+a)	Cl(-a)	N			
Cu(+2a)	H(+a)	CuCl3(-a)	N			
Cu(+2a)	H(+a)	CuCl4(-2a)	N			
Cu(+2a)	H(+a)	HSO4(-a)	N			
Cu(+2a)	Na(+a)	Cl(-a)	N			
Cu(+2a)	Na(+a)	CuCl3(-a)	N			
Cu(+2a)	Na(+a)	CuCl4(-2a)	N			
Cu(+2a)	Na(+a)	SO4(-2a)	N			
Cu(+2a)	Ni(+2a)	NO3(-a)	N			
CuCl(+a)	H(+a)	Cl(-a)	N			
CuCl(+a)	H(+a)	CuCl3(-a)	N			
CuCl(+a)	H(+a)	CuCl4(-2a)	N			
CuCl(+a)	Na(+a)	Cl(-a)	N			
CuCl(+a)	Na(+a)	CuCl3(-a)	N			
CuCl(+a)	Na(+a)	CuCl4(-2a)	N			
CuCl3(-a)	CuCl4(-2a)	Cu(+2a)	N			
CuCl3(-a)	CuCl4(-2a)	CuCl(+a)	N			
CuCl3(-a)	CuCl4(-2a)	H(+a)	N			

**Table B3 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Psi parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS			T dep. AC	T dep. H	T dep. Cp
CuCl3(-a)	CuCl4(-2a)	Na(+a)	N		
F(-a)	HF2(-a)	H(+a)	N		
F(-a)	NO3(-a)	Na(+a)	N		
F(-a)	OH(-a)	Na(+a)	N		
Fe(+2a)	H(+a)	HSO4(-a)	N		
Ga(+3a)	H(+a)	Cl(-a)	N		
H(+a)	K(+a)	Br(-a)	N		
H(+a)	K(+a)	Cl(-a)	N		
H(+a)	K(+a)	HSO4(-a)	N		
H(+a)	K(+a)	SO4(-2a)	N		
H(+a)	Li(+a)	Br(-a)	N		
H(+a)	Li(+a)	Cl(-a)	N		
H(+a)	Li(+a)	ClO4(-a)	N		
H(+a)	Mg(+2a)	Br(-a)	N		
H(+a)	Mg(+2a)	Cl(-a)	Y	N	
H(+a)	Mg(+a)	Cl(-a)	N		
H(+a)	Mg(+a)	HSO4(-a)	N		
H(+a)	Mn(+2a)	Cl(-a)	N		
H(+a)	Na(+a)	Br(-a)	N		
H(+a)	Na(+a)	Cl(-a)	N		
H(+a)	Na(+a)	ClO4(-a)	N		
H(+a)	Na(+a)	HSO4(-a)	N		
H(+a)	Na(+a)	NO3(-a)	N		
H(+a)	Na(+a)	SO4(-2a)	N		
H(+a)	NH4(+a)	Br(-a)	N		
H(+a)	NH4(+a)	Cl(-a)	N		
H(+a)	Ni(+2a)	Br(-a)	N		
H(+a)	Ni(+2a)	Cl(-a)	Y	N	
H(+a)	Sr(+2a)	Br(-a)	N		
H(+a)	Sr(+2a)	Cl(-a)	Y	N	
H(+a)	UO2(+2a)	ClO4(-a)	N		
H(+a)	UO2(+2a)	NO3(-a)	N		
HCO3(-a)	SO4(-2a)	Mg(+2a)	N		
HCO3(-a)	SO4(-2a)	Na(+a)	N		
HSO4(-a)	SO4(-2a)	K(+a)	N		
HSO4(-a)	SO4(-2a)	Mg(+2a)	N		
HSO4(-a)	SO4(-2a)	Na(+a)	Y	Y	Y
K(+a)	Mg(+2a)	Cl(-a)	Y	Y	Y
K(+a)	Mg(+2a)	SO4(-2a)	N		
K(+a)	Mg(+a)	Cl(-a)	N		
K(+a)	Mg(+a)	SO4(-2a)	N		
K(+a)	Na(+a)	B4O5(OH)4(-2a)	N		

**Table B3 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Psi parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

IONS			T dep. AC	T dep. H	T dep. Cp
K(+a)	Na(+a)	Br(-a)	N		
K(+a)	Na(+a)	Cl(-a)	Y	Y	Y
K(+a)	Na(+a)	CO3(-2a)	N		
K(+a)	Na(+a)	H2PO4(-a)	N		
K(+a)	Na(+a)	HCO3(-a)	N		
K(+a)	Na(+a)	NO3(-a)	N		
K(+a)	Na(+a)	SO4(-2a)	Y	Y	Y
K(+a)	Sr(+2a)	Cl(-a)	N		
La(+3a)	Na(+a)	ClO4(-a)	N		
Li(+a)	K(+a)	B4O5(OH)4(-2a)	N		
Li(+a)	K(+a)	Cl(-a)	N		
Li(+a)	Na(+a)	B4O5(OH)4(-2a)	N		
Li(+a)	Na(+a)	CH3COO(-a)	N		
Li(+a)	Na(+a)	Cl(-a)	N		
Li(+a)	Na(+a)	ClO4(-a)	N		
Li(+a)	Na(+a)	NO3(-a)	N		
Mg(+2a)	MgOH(+a)	Cl(-a)	N		
Mg(+2a)	Na(+a)	Cl(-a)	Y	N	
Mg(+2a)	Na(+a)	SO4(-2a)	N		
Mg(+2a)	Ni(+2a)	SeO4(-2a)	N		
Mn(+2a)	Na(+a)	Cl(-a)	N		
Na(+a)	Ni(+2a)	Cl(-a)	N		
Na(+a)	Ni(+2a)	SO4(-2a)	N		
Na(+a)	Sr(+2a)	Cl(-a)	N		
Na(+a)	UO2(+2a)	ClO4(-a)	N		
Na(+a)	UO2(+2a)	NO3(-a)	N		
Na(+a)	Zn(+2a)	SO4(-2a)	N		
Ni(+2a)	Zn(+2a)	SeO4(-2a)	N		
NO2(-a)	PO4(-3a)	Na(+a)	N		
NO3(-a)	SO4(-2a)	Na(+a)	N		
OH(-a)	PO4(-3a)	Na(+a)	N		
OH(-a)	SO4(-2a)	K(+a)	N		
OH(-a)	SO4(-2a)	Na(+a)	N		

**Table B4.** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
Ar(a)	Br(-a)	N		
Ar(a)	Ca(+2a)	N		
Ar(a)	H(+a)	N		
Ar(a)	HCO3(-a)	N		
Ar(a)	K(+a)	N		
Ar(a)	Mg(+2a)	N		
Ar(a)	Na(+a)	N		
Ar(a)	OH(-a)	N		
Ar(a)	SO4(-2a)	N		
B(OH)3(a)	Cl(-a)	N		
B(OH)3(a)	H(+a)	N		
B(OH)3(a)	K(+a)	N		
B(OH)3(a)	Na(+a)	N		
B(OH)3(a)	SO4(-2a)	N		
CCl4(a)	Br(-a)	N		
CCl4(a)	Ca(+2a)	N		
CCl4(a)	H(+a)	N		
CCl4(a)	HCO3(-a)	N		
CCl4(a)	K(+a)	N		
CCl4(a)	Mg(+2a)	N		
CCl4(a)	Na(+a)	N		
CCl4(a)	OH(-a)	N		
CCl4(a)	SO4(-2a)	N		
C2H2(a)	Br(-a)	N		
C2H2(a)	Ca(+2a)	N		
C2H2(a)	H(+a)	N		
C2H2(a)	HCO3(-a)	N		
C2H2(a)	K(+a)	N		
C2H2(a)	Mg(+2a)	N		
C2H2(a)	Na(+a)	N		
C2H2(a)	OH(-a)	N		
C2H2(a)	SO4(-2a)	N		
C2H4(a)	Br(-a)	N		
C2H4(a)	Ca(+2a)	N		
C2H4(a)	H(+a)	N		
C2H4(a)	HCO3(-a)	N		
C2H4(a)	K(+a)	N		
C2H4(a)	Mg(+2a)	N		
C2H4(a)	Na(+a)	N		
C2H4(a)	OH(-a)	N		
C2H4(a)	SO4(-2a)	N		
C2H6(a)	Br(-a)	N		



**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
C2H6(a)	H(+a)	N		
C2H6(a)	HCO3(-a)	N		
C2H6(a)	K(+a)	N		
C2H6(a)	Mg(+2a)	N		
C2H6(a)	Na(+a)	N		
C2H6(a)	OH(-a)	N		
C2H6(a)	SO4(-2a)	N		
C6H6(a)	Br(-a)	N		
C6H6(a)	Ca(+2a)	N		
C6H6(a)	Cl(-a)	N		
C6H6(a)	H(+a)	N		
C6H6(a)	HCO3(-a)	N		
C6H6(a)	K(+a)	N		
C6H6(a)	Li(+a)	N		
C6H6(a)	Mg(+2a)	N		
C6H6(a)	Na(+a)	N		
C6H6(a)	OH(-a)	N		
C6H6(a)	SO4(-2a)	N		
C7H6O22(BA)(a)	Cl(-a)	N		
C7H6O22(BA)(a)	K(+a)	N		
C7H6O22(BA)(a)	Li(+a)	N		
C7H6O22(BA)(a)	Na(+a)	N		
CF4(a)	Br(-a)	N		
CF4(a)	Ca(+2a)	N		
CF4(a)	H(+a)	N		
CF4(a)	HCO3(-a)	N		
CF4(a)	K(+a)	N		
CF4(a)	Mg(+2a)	N		
CF4(a)	Na(+a)	N		
CF4(a)	OH(-a)	N		
CF4(a)	SO4(-2a)	N		
CH3COOH(a)	Cl(-a)	N		
CH3COOH(a)	CH3COO(-a)	N		
CH3COOH(a)	H(+a)	N		
CH3COOH(a)	K(+a)	N		
CH3COOH(a)	Na(+a)	N		
CH3NO2(a)	Cl(-a)	N		
CH3NO2(a)	K(+a)	N		
CH3NO2(a)	Li(+a)	N		
CH3NO2(a)	Na(+a)	N		
CH4(a)	Br(-a)	N		

**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
CH4(a)	Ca(+2a)	N		
CH4(a)	H(+a)	N		
CH4(a)	HCO3(-a)	N		
CH4(a)	K(+a)	N		
CH4(a)	Mg(+2a)	N		
CH4(a)	Na(+a)	N		
CH4(a)	OH(-a)	N		
CH4(a)	SO4(-2a)	N		
CO(a)	Br(-a)	N		
CO(a)	Ca(+2a)	N		
CO(a)	H(+a)	N		
CO(a)	HCO3(-a)	N		
CO(a)	K(+a)	N		
CO(a)	Mg(+2a)	N		
CO(a)	Na(+a)	N		
CO(a)	OH(-a)	N		
CO(a)	SO4(-2a)	N		
CO2(a)	Al(+3a)	Y	Y	Y
CO2(a)	AlO(+a)	Y	Y	Y
CO2(a)	AlOH(+2a)	Y	Y	Y
CO2(a)	Ca(+2a)	Y	Y	Y
CO2(a)	Cl(-a)	Y	Y	Y
CO2(a)	ClO4(-a)	N		
CO2(a)	H(+a)	Y	Y	Y
CO2(a)	HSO4(-a)	N		
CO2(a)	K(+a)	Y	Y	Y
CO2(a)	Mg(+2a)	Y	Y	Y
CO2(a)	Na(+a)	Y	Y	Y
CO2(a)	NH4(+a)	Y	Y	Y
CO2(a)	SO4(-2a)	Y	Y	Y
CoC2O4(a)	Cl(-a)	N		
CuCl2(a)	Cl(-a)	N		
CuCl2(a)	Cu(+2a)	N		
CuCl2(a)	CuCl(+a)	N		
CuCl2(a)	CuCl3(-a)	N		
CuCl2(a)	CuCl4(-2a)	N		
CuCl2(a)	Na(+a)	N		
He(a)	Br(-a)	N		
He(a)	Ca(+2a)	N		
He(a)	H(+a)	N		
He(a)	HCO3(-a)	N		
He(a)	K(+a)	N		

**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
He(a)	Mg(+2a)	N		
He(a)	Na(+a)	N		
He(a)	OH(-a)	N		
He(a)	SO4(-2a)	N		
HgCl2(a)	Na(+a)	N		
Hg(OH)2(a)	Na(+a)	N		
HgOHCl(a)	Na(+a)	N		
H2C2O4(a)	Cl(-a)	N		
H2C2O4(a)	HSO4(-a)	N		
H2C2O4(a)	Na(+a)	N		
H2C2O4(a)	NO3(-a)	N		
HF(a)	Cl(-a)	N		
HF(a)	F(-a)	N		
HF(a)	H(+a)	N		
HF(a)	HF2(-a)	N		
HF(a)	Na(+a)	N		
H2(a)	Br(-a)	N		
H2(a)	Ca(+2a)	N		
H2(a)	H(+a)	N		
H2(a)	HCO3(-a)	N		
H2(a)	K(+a)	N		
H2(a)	Mg(+2a)	N		
H2(a)	Na(+a)	N		
H2(a)	OH(-a)	N		
H2(a)	SO4(-2a)	N		
H4SiO4(a)	Na(+a)	N		
H3PO4(a)	Cl(-a)	N		
H3PO4(a)	H(+a)	N		
H3PO4(a)	K(+a)	N		
H3PO4(a)	Mg(+2a)	N		
H3PO4(a)	Na(+a)	N		
(HOCH2)3CNH2(a)	Ca(+2a)	N		
(HOCH2)3CNH2(a)	Cl(-a)	N		
(HOCH2)3CNH2(a)	K(+a)	N		
(HOCH2)3CNH2(a)	Mg(+2a)	N		
(HOCH2)3CNH2(a)	Na(+a)	N		
H2S(a)	Br(-a)	N		
H2S(a)	Ca(+2a)	N		
H2S(a)	Cl(-a)	N		
H2S(a)	H(+a)	N		
H2S(a)	HCO3(-a)	N		
H2S(a)	K(+a)	N		

**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
H2S(a)	Mg(+2a)	N		
H2S(a)	Na(+a)	N		
H2S(a)	OH(-a)	N		
H2S(a)	SO4(-2a)	N		
H2S(a)	Sr(+2a)	N		
Kr(a)	Br(-a)	N		
Kr(a)	Ca(+2a)	N		
Kr(a)	H(+a)	N		
Kr(a)	HCO3(-a)	N		
Kr(a)	K(+a)	N		
Kr(a)	Mg(+2a)	N		
Kr(a)	Na(+a)	N		
Kr(a)	OH(-a)	N		
Kr(a)	SO4(-2a)	N		
MgHPO4(a)	Na(+a)	N		
MgCO3(a)	ClO4(+a)	N		
MgCO3(a)	Na(+a)	N		
N2(a)	Br(-a)	N		
N2(a)	Ca(+2a)	N		
N2(a)	H(+a)	N		
N2(a)	HCO3(-a)	N		
N2(a)	K(+a)	N		
N2(a)	Mg(+2a)	N		
N2(a)	Na(+a)	N		
N2(a)	OH(-a)	N		
N2(a)	SO4(-2a)	N		
NaNO2(a)	CO3(-2a)	Y	Y	Y
Ne(a)	Br(-a)	N		
Ne(a)	Ca(+2a)	N		
Ne(a)	H(+a)	N		
Ne(a)	HCO3(-a)	N		
Ne(a)	K(+a)	N		
Ne(a)	Mg(+2a)	N		
Ne(a)	Na(+a)	N		
Ne(a)	OH(-a)	N		
Ne(a)	SO4(-2a)	N		
NH3(a)	Br(-a)	N		
NH3(a)	Ca(+2a)	N		
NH3(a)	Cl(-a)	N		
NH3(a)	CO3(-2a)	N		
NH3(a)	F(-a)	N		
NH3(a)	H(+a)	N		

**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. H	T dep. Cp
NH3(a)	K(+a)	N		
NH3(a)	Mg(+2a)	N		
NH3(a)	Na(+a)	N		
NH3(a)	SO4(-2a)	N		
NH3(a)	Sr(+2a)	N		
NiC2O4(a)	Cl(-a)	N		
N2O(a)	Br(-a)	N		
N2O(a)	Ca(+2a)	N		
N2O(a)	H(+a)	N		
N2O(a)	HCO3(-a)	N		
N2O(a)	K(+a)	N		
N2O(a)	Mg(+2a)	N		
N2O(a)	Na(+a)	N		
N2O(a)	OH(-a)	N		
N2O(a)	SO4(-2a)	N		
NO(a)	Br(-a)	N		
NO(a)	Ca(+2a)	N		
NO(a)	H(+a)	N		
NO(a)	HCO3(-a)	N		
NO(a)	K(+a)	N		
NO(a)	Mg(+2a)	N		
NO(a)	Na(+a)	N		
NO(a)	OH(-a)	N		
NO(a)	SO4(-2a)	N		
O2(a)	Br(-a)	N		
O2(a)	Ca(+2a)	N		
O2(a)	Cl(-a)	N		
O2(a)	CO3(-2a)	N		
O2(a)	H(+a)	N		
O2(a)	HCO3(-a)	N		
O2(a)	K(+a)	N		
O2(a)	Mg(+2a)	N		
O2(a)	Na(+a)	N		
O2(a)	OH(-a)	N		
O2(a)	SO4(-2a)	N		
PbCl2(a)	Ca(+2a)	N		
PbCl2(a)	Cl(-a)	Y	Y	Y
PbCl2(a)	ClO4(-a)	Y	Y	Y
PbCl2(a)	Na(+a)	N		
PbCl2(a)	Mg(+2a)	N		
Rn(a)	Br(-a)	N		
Rn(a)	Ca(+2a)	N		

**Table B4 (continued).** The parameter sets and the parameter temperature dependencies of the HSC Aqua Pitzer database Lambda parameter sheet. (HSC Aqua 2009)

Y = the parameter set has at least one temperature-dependent term

N = the parameter set is defined by constant values

Empty cell = no parameter value

NEUTRAL	ION	T dep. AC	T dep. HT	T dep. Cp
Rn(a)	H(+a)	N		
Rn(a)	HCO3(-a)	N		
Rn(a)	K(+a)	N		
Rn(a)	Mg(+2a)	N		
Rn(a)	Na(+a)	N		
Rn(a)	OH(-a)	N		
Rn(a)	SO4(-2a)	N		
SF6(a)	Br(-a)	N		
SF6(a)	Ca(+2a)	N		
SF6(a)	H(+a)	N		
SF6(a)	HCO3(-a)	N		
SF6(a)	K(+a)	N		
SF6(a)	Mg(+2a)	N		
SF6(a)	Na(+a)	N		
SF6(a)	OH(-a)	N		
SF6(a)	SO4(-2a)	N		
SiO2(a)	Al(+3a)	Y	Y	Y
SiO2(a)	AlO(+a)	Y	Y	Y
SiO2(a)	AlOH(+2a)	Y	Y	Y
SiO2(a)	Ca(+2a)	Y	Y	Y
SiO2(a)	Cl(-a)	N		
SiO2(a)	H(+a)	Y	Y	Y
SiO2(a)	HCO3(-a)	Y	Y	Y
SiO2(a)	K(+a)	Y	Y	Y
SiO2(a)	Li(+a)	N		
SiO2(a)	Mg(+2a)	Y	Y	Y
SiO2(a)	Na(+a)	Y	Y	Y
SiO2(a)	NO3(-a)	Y	Y	Y
SiO2(a)	OH(-a)	N		
SiO2(a)	SO4(-2a)	Y	Y	Y
SO2(a)	Cl(-a)	N		
SO2(a)	Na(+a)	N		
SO2(a)	Mg(+2a)	N		
Xe(a)	Br(-a)	N		
Xe(a)	Ca(+2a)	N		
Xe(a)	H(+a)	N		
Xe(a)	HCO3(-a)	N		
Xe(a)	K(+a)	N		
Xe(a)	Mg(+2a)	N		
Xe(a)	Na(+a)	N		
Xe(a)	OH(-a)	N		
Xe(a)	SO4(-2a)	N		