Part 4. Calculation of activity coefficients in built-in functions of GEM-Selektor code

4.1. Aqueous electrolyte solutions

Possible options for built-in models of aqueous activity coefficients in GEM-Selektor code are summarized in Appendix 4-1.

The chemical potential of j-th aqueous ion or complex is approximated in the GEM IPM algorithm by the following expression in the uniform (mole fraction) scale [Karpov et al., 1997; 2001]:

$$\upsilon_j = \frac{\partial G(x)}{\partial x_j} = \frac{g_j}{RT} + \ln\frac{1000}{M_w} + \ln\frac{x_j}{X_w} + \ln\gamma_j - \ln\frac{x_{j_w}}{X_w} + 1 - \frac{x_{j_w}}{X_w} \qquad (4.1\text{-}1),$$

where $G(x)$ is the total Gibbs energy of the system (in moles); g_j is the partial molal Gibbs energy function of j-th aqueous species at T,P of interest in the molal scale; x_j is the mole quantity of j-th species and x_{j_w} that of the water-solvent. X_w is the total mole quantity of the aqueous phase (including water-solvent), γ_j is the internal asymmetric activity coefficient (in practical scale), and $M_w = 18.0153$ g mol^{-1} is the gram-formula mass of H_2O. The two terms $\ln\frac{1000}{M_w}$ and $-\ln\frac{x_{j_w}}{X_w}$ on the right-hand side convert the standard chemical potential and the activity coefficient from the practical asymmetrical (molality) to the rational (mole fraction) concentration scale. Details of the representation of calculated activities, molalities, and respective "external" activity coefficients are given in Appendix 4-2.

For the water-solvent (H_2O), the following approximation of chemical potential is used:

$$\upsilon_{j_w} = \frac{g_{j_w}}{RT} + \ln\frac{x_{j_w}}{X_w} + \ln\gamma_{j_w} + 2 - \frac{x_{j_w}}{X_w} - \frac{X_w}{x_{j_w}} \qquad (4.1\text{-}2),$$

The internal activity coefficient of water γ_{j_w} is by default taken as unity because the mole amount of water x_{j_w} is adjusted on GEM iterations, resulting in activity: $\exp\left(\upsilon_{j_w} - g_{j_w}/RT\right)$ and mole fraction of H_2O: $\chi_{j_w} = x_{j_w}/X_w$ less than unity at non-zero concentration of dissolved salts. Internal activity coefficients of aqueous species (γ_j in eqn 4.1-1) will be recalculated on all iterations of the GEM algorithm because these values affect chemical potentials and depend on concentrations of dissolved ionic species, which are initially unknown.

4.1.1. Charged aqueous species

Equations for individual aqueous activity coefficients use the *effective ionic strength I* - a measure of a "concentration of charge":

$$I = \frac{1}{2}\sum_{j}^{n(L_w)} m_j z_j^2 \qquad (4.1\text{-}3),$$

where z_j is the formula charge of j-th species and m_j is its molality (in moles per 1 kg H_2O),

$$m_j = \frac{x_j}{x_{j_w}}\frac{1000}{M_w} = 55.508435\frac{x_j}{x_{j_w}} \qquad (4.1\text{-}4),$$

where $M_w = 18.0153$ is the gram-formula mass of H_2O. Note that in ion-association aqueous models, the effective ionic strength, which counts only charged aqueous species, is usually less than the formal ionic strength obtained from the bulk concentration of a dissolved salt.

The theory of Debye and Hückel [1923] relates the activity coefficient of aqueous ion to its charge and the ionic strength of the aqueous electrolyte. This is based on representing the ions as point charges in an ideal structureless dielectric solvent and considering long-range Coulombic forces between charges of opposite sign working against disorder caused by thermal Brownian movement. Derivation of this theory is lengthy, but readily available from textbooks (e.g. [Robinson and Stokes, 1968]). The final result is called the Debye-Hückel equation:

$$\log_{10}\gamma_j^{(r)} = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + \dot{a}B_\gamma \sqrt{I}}$$ (4.1-5).

There, $\dot{a}$ (in 10^{-8} cm) is an average distance of approach of two ions of opposite charge (or the ion-size Kielland's parameter for individual ions), and

$$A_\gamma = 1.82483 \cdot 10^6 \rho_0^{0.5} (\varepsilon_0 \cdot T)^{-1.5}$$ (4.1-6),

$$B_\gamma = 50.2916 \rho_0^{0.5} (\varepsilon_0 \cdot T)^{-0.5}$$ (4.1-7),

where ρ_0 is density ($g \cdot cm^{-3}$) and ε_0 is the dielectric constant of pure water at temperature T (K) and pressure P (bar) of interest. The latter two values are obtained internally from SUPCRT92 subroutines [Johnson et al., 1992] incorporated into the GEMS code. At $T_r = 25$ °C and $P_r = 1$ bar, $A_\gamma \approx 0.5114$ and $B_\gamma \approx 0.3288$.

Note that eqn (4.1-5) defines the asymmetric activity coefficient $\gamma_j^{(r)}$ in rational (mole fraction) scale. Its conversion to practical (molality) scale required for γ_j in eqn (4-1.1) can be performed, according to Helgeson et al. (1981), by adding a term $\Gamma_\gamma = -log_{10}(1 + 0.0180153m_\Sigma)$, where m_Σ is the sum of molalities of all dissolved species (including both charged and neutral ones). Thomsen (2005) defines this conversion as $\gamma_j^{(m)} = \gamma_j^{(r)}\chi_w$ where $\chi_w = x_{jw}/X_w$ is the mole fraction of water solvent. However, using eqn (4.1-4), it can be shown with simple algebraic substitutions that both corrections are equivalent. Therefore, the internal molal γ_j value of the Debye-Hückel activity coefficient eqn (4.1-5) is calculated as

$$\log_{10}\gamma_j = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + \dot{a}B_\gamma \sqrt{I}} + \log_{10}\frac{x_{jw}}{X_w}$$ (4.1-8)

Equation (4.1-5) or (4.1-8) works well at relatively low ionic strength ($0.001 \le I \le 0.1$ m). At low ionic strength ($I < 0.001$ m), the denominator in eqn (4.1-5) approaches unity, converting it effectively into the Debye-Hückel limiting law:

$$\log_{10}\gamma_j \approx -A_\gamma z_j^2 \sqrt{I} + \log_{10}\frac{x_{jw}}{X_w}$$ (4.1-9).

Extension of the Debye-Hückel theory to account for short-range interactions has added a linear term to the extended <u>Debye-Hückel equation</u>:

$$\log_{10}\gamma_j = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + \dot{a}B_\gamma \sqrt{I}} + b_\gamma I + \log_{10}\frac{x_{jw}}{X_w}$$ (4.1-10),

where b_γ is a semi-empirical coefficient, either individual for a given electrolyte ion (in this case, eqn (4.1-10) is also called the Truesdell-Jones equation), or common for all charged aqueous species [Helgeson et al., 1981] in the predominant electrolyte.

The extended equation (4.1-10) is thought to be applicable up to 1-2 molal ionic strength using b_γ =0.064 (NaCl) and it was implemented with common b_γ as a built-in function in GEM-Selektor. This function can be used either with individual Kielland ion-size parameters $\dot{a}_j$ (collected from DComp or ReacDC records) as formerly suggested by Karpov, or with an average value of $\dot{a}$ (in 10^{-8} cm) the same for all ionic species, as proposed in [Helgeson et al., 1981]. In the latter option, well-calibrated models for the pressure and temperature dependence of b_γ for 4 major background electrolytes (NaCl, KCl, NaOH, KOH) can be used [Oelkers and Helgeson, 1990; Pokrovski and Helgeson, 1995; 1997a; 1997b]. The ion-size parameters for these models are 3.72 (NaCl), 4.08 (KCl), 3.31 (NaOH), and 3.67 (KOH), and were derived from the effective electrostatic radii of the ions [Helgeson et al., 1981]. The Kielland's (1936) table of individual effective ionic radii $\dot{a}_j$ can be found in textbooks (e.g. [Nordstrom and Muñoz, 1994; Langmuir, 1997] with recommended defaults for missing ionic species.

Usage of individual Kielland's parameters may be more appropriate at relatively low ionic strength. On the other hand, application of eqn (4.1-9) with the common ion-size parameter $\dot{a}$ seems to be more warranted at higher ionic strength and/or elevated temperatures.

Another built-in function in the GEMS code implements the popular <u>Davies equation</u>:

$$\log_{10}\gamma_j = -A_\gamma z_j^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) + \log_{10}\frac{x_{jw}}{X_w} \qquad (4.1-11).$$

This semi-empirical equation can be used at low temperatures and ionic strength between 0.1 and 0.7 molal; it is thought to be inaccurate at $I < 0.1$ m because it neglects the difference in ion approach parameters. The advantage of the Davies equation is that it uses only the charge as an individual species property. Conversely, all ions of the same charge will have identical activity coefficients (this is also true for eqn 4.1-10 with common $\dot{a}$ parameter). Note that the last (mole fraction to molality correction) term in eqn (4.1-10) is optional in GEMS-PSI code.

4.1.2. Neutral aqueous species (ion pairs, dissolved gases)

To account for the "salting-out" effect, neutral aqueous species (dissolved gases and neutral complexes) require an activity coefficient assumed to be a linear function of ionic strength:

$$\log_{10}\gamma_j = b_g I + \log_{10}\frac{x_{jw}}{X_w} \qquad (4.1-12).$$

In the case of dissolved gases, the empirical b_g coefficient can be obtained from experimental values of the Setchenow coefficient, measured in electrolyte solutions with the assumption that the activity coefficient of a gas dissolved in pure water equals unity. Typical values of b_g lie between 0.02 and 0.2 [Langmuir, 1997], with an average 0.074 [Borisov and Shvarov, 1992]. In GEMS, the b_g values can be automatically collected from DComp or ReacDC records for neutral aqueous species, wherever provided.

Eqn (4.1-12) can also be obtained from eqn (4.1-10) at zero charge (z_j =0), suggesting that the common third parameter b_γ can be used as a generic salting-out coefficient of neutral aqueous complexes, for which the experimental Setchenow coefficient is not known. This option (or

its alternative to leave $\gamma_j = 1$ for neutral complexes) can be set in DComp or ReacDC records in the GEMS chemical thermodynamic database, according to the user's preference.

4.1.3. Water solvent

By default, the activity coefficient of water solvent is assumed to be unity and the activity of water is directly calculated from its mole fraction. This is usually a good approximation, as long as total solute concentrations remain moderate. Optionally, when the extended Debye-Hückel activity model for aqueous species after Helgeson et al. [1981] is used, the activity of water can be calculated from the osmotic coefficient:

$$\ln a_{water} = -\frac{\phi\, m_\Sigma}{55.508435} \tag{4.1-13}.$$

where m_Σ is the sum of all species molalities and ϕ is the osmotic coefficient, which is calculated as [Helgeson et al., 1981]:

$$\phi = -\log_{10}\frac{m_C}{m_\Sigma}\left[\frac{\left|Z_+ Z_-\right| A_\gamma \sqrt{I}\, \sigma\!\left(\dot{a}\, B_\gamma \sqrt{I}\right)}{3} + \frac{\psi\, \Gamma_\gamma}{0.0180153\, \nu\, I} - \frac{b_\gamma\, I}{2}\right] \tag{4.1-14}$$

and:

$$\sigma\!\left(\dot{a}\, B_\gamma \sqrt{I}\right) = \frac{3}{\dot{a}^3 B_\gamma^{\,3} I^{3/2}}\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right) \tag{4.1-15}$$

$$\Lambda = 1 + \dot{a}\, B_\gamma \sqrt{I} \tag{4.1-16}$$

Here Z_+ and Z_- are the charges of the completely dissociated electrolyte, ψ is 1 for any 1:1 electrolyte, ν is the stoichiometric number of moles in 1 mole of the electrolyte, m_C and m_Σ are the sums of molalities of charged and all species, respectively.

Note that the quotient m_C/m_Σ is only considered in the seminal paper by Helgeson et al. [1981] but not in later work such as Pokrovskii and Helgeson [1995; 1997a; 1997b]. Ignoring this term results in incorrect calculations for dilute electrolyte solutions with a considerable degree of association, which may cause a failure of the initial approximations in GEM-based equilibrium solvers. Note that although the activity coefficient of water calculated with eqns (4.1-13) to (4.1-16) is usually relatively close to unity, setting it by default to 1.0 is thermodynamically inconsistent because it violates the Gibbs-Duhem relationship.

4.1.4. Specific ion interation theory (SIT) model

The Brønsted-Guggenheim-Scatchard model, also called the SIT (Specific Ion Interaction Theory) model, was also built into the GEM-Selektor code because this model has been extensively used in NEA TDB evaluations [Grenthe and Puigdomenech, 1997] and in compilation of the Nagra-PSI 01/01 chemical thermodynamic database [Hummel et al., 2002]. The SIT model is based on two assumptions.

(1) The asymmetric molal activity coefficient of an ion of charge z_i in solution is given by

$$\log_{10}\gamma_i = -\frac{z_i^2 A_\gamma \sqrt{I}}{1+1.5\sqrt{I}} + \sum_k \varepsilon(i,k)m_k \qquad (4.1\text{-}17)$$

where A_γ is the limiting Debye-Hückel law slope, and $\varepsilon(i,k)$ is an interaction coefficient which describes the specific short-range interaction between the ionic species i and k. The summation extends over all species k with molality m_k present in solution. Value of 1.5 $kg^{1/2} \cdot mol^{-1/2}$ in the denominator corresponds to the product $a_j \cdot B_\gamma$ in the Debye-Hückel term (where a_j is an "effective" ion diameter and B_γ is given by eqn 4.1-7). This value of 1.5 was empirically selected to minimize the ionic strength dependency of a number of electrolytes at $T = 298.15$ K.

The present notation assumes that interaction coefficients $\varepsilon(i,k)$ do not depend on concentration and temperature and are symmetric, i.e. $\varepsilon(i,k) \equiv \varepsilon(k,i)$. If concentration dependency of interaction coefficients needs to be stated explicitly, the NEA series of "Chemical Thermodynamics" [Grenthe and Puigdomenech, 1997] suggests an expression of the form

$$\varepsilon(i,k,I) = \varepsilon_1(i,k) + \varepsilon_2(i,k) \cdot \log_{10}I \qquad (4.1\text{-}18).$$

(2) Interaction coefficients $\varepsilon(i,k)$ for ions of the same sign are zero.

Often, the interaction coefficient for uncharged species ($z_i = 0$) is assumed to be zero, because the DH-term is zero by definition. However, this simplification is not always sensible, and it may well be that the activity coefficient of uncharged species $\gamma_{neutral}$

$$\log_{10}\gamma_{neutral} = \sum_k \varepsilon(neutral,k)m_k \qquad (4.1\text{-}19)$$

significantly differs from unity.

4.1.5. Pitzer ion-interaction Model (*contributed by F.F. Hingerl*)

Virial expansion approach. The Pitzer model consists of a set of equations formulated by Kenneth Pitzer and his associates in the 1970s. The model is tailored for determining excess Gibbs energy of aqueous electrolyte mainly from theoretical considerations. The long-range interactions are accounted for by a Debye-Hückel part, the short-range interactions - by a virial expansion. A general form of the Pitzer equation is [Anderson, 2005]:

$$\frac{G^{EX}}{kg_W RT} = f(I) + \sum_i^{L_i} \sum_j^{L_j} \lambda_{ij} m_i m_j + \sum_i^{L_i} \sum_j^{L_j} \sum_k^{L_k} \mu_{ijk} m_i m_j m_k \qquad (4.1\text{-}20)$$

where kg_W is the number of kilograms of water and m indicate molalities. The indices i,j,k represent any kind of aqueous species. In Eq.(4.1-20), a version of the Debye-Hückel equation stands for $f(I)$, the first virial coefficient. The next term accounts for interactions between two species, and the last one for interaction between three species. The binary interaction coefficient λ_{ij} is a function of ionic strength I; the ternary interaction coefficient μ_{ijk} is considered being independent of ionic strength. It becomes zero if all indices point to ions having charge of the same sign. Inserting parameters and a Debye-Hückel term into the general Pitzer equation for the case of a binary electrolyte leads to the following form of excess Gibbs energy:

$$\frac{G^{EX}}{kg_W RT} = -A^\Phi \left(\frac{4I}{b}\right) ln\left(1+b\sqrt{I}\right) + 2\nu_M \nu_X \left[m^2 B_{MX} + m^3 \nu_M \nu_X C_{MX} \right] \qquad (4.1\text{-}21)$$

where ν_M and ν_X are stochiometry coefficients of the cation and anion in the electrolyte. We note the theoretical expression of the Debye-Hückel parameter (in SI units)

$$A^{\Phi} = \frac{1}{3}\left(2\pi N_0 d_w 1000\right)^{\frac{1}{2}}\left(\frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}\right)^{\frac{3}{2}} \qquad (4.1\text{-}22)$$

with d_w as the density of water (in g per cm^3), e as the electronic charge, N_0 as the Avogadro number, ε and ε_o as the relative permittivity of water or vacuum respectively; T stands for the temperature, and k for the Boltzmann constant.

Virial coefficients. The secondary Pitzer virial coefficient C_{MX} is related to C_{MX}^{Φ} by

$$C_{MX} = \frac{C_{MX}^{\Phi}}{2\sqrt{|z_M z_X|}} \qquad (4.1\text{-}23)$$

where z_M and z_X are charges of cations or anions respectively. Further virial coefficients are:

$$B_{MX}^{\Phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}e^{-\alpha_{MX}\sqrt{I}} + \beta_{MX}^{(2)}e^{-\alpha'_{MX}\sqrt{I}} \qquad (4.1\text{-}24)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}g(\alpha_{MX}\sqrt{I}) + \beta_{MX}^{(2)}g(\alpha'_{MX}\sqrt{I}) \qquad (4.1\text{-}25)$$

$$B_{MX}' = \frac{\partial B_{MX}}{\partial I} = \beta_{MX}^{(1)}\frac{g'(\alpha_{MX}\sqrt{I})}{I} + \beta_{MX}^{(2)}\frac{g'(\alpha'_{MX}\sqrt{I})}{I} \qquad (4.1\text{-}26)$$

B_{MX}^{Φ} is needed for calculation of the osmotic coefficient and the activity of water, B_{MX} for calculation of activity coefficients of cations and anions, and B_{MX}' for the Debye-Hückel term. The functions $g(x)$ and $g'(x)$ are

$$g(x) = 2(1-(1+x)e^{-x})/x^2 \qquad (4.1\text{-}27)$$

$$g'(x) = -2(1-(1+x+\frac{x^2}{2})e^{-x})/x^2 \qquad (4.1\text{-}28)$$

where x substitutes for $\alpha_{MX}\sqrt{I}$ in (4.1-27) and for $\alpha'_{MX}\sqrt{I}$ in (4.1-28). For any salt containing a monovalent ion, $\alpha_{MX} = 2$ and $\alpha'_{MX} = 12$; for 2-2 electrolytes, $\alpha_{MX} = 1.4$ and $\alpha'_{MX} = 12$; for 3-2, 4-2 and electrolytes containing higher valence cations, $\alpha_{MX} = 2.0$ and $\alpha'_{MX} = 50$.

The definition of effective (molal) ionic strength (I) is as usual [see Pitzer, 1991]:

$$I = \frac{1}{2}\sum_{j=1}^{L} z_j^2 m_j \qquad (4.1\text{-}29)$$

where z_j is the charge of species j; m_j its molality, and L is the number of aqueous species.

Activity and osmotic coefficients. From fundamental thermodynamics, G^{ex} and γ_j (and the osmotic coefficient ϕ) are related by

$$\frac{\partial G^{EX}/(kg_W RT)}{\partial m_j} = \mu_j^{ex}/RT = \ln\gamma_j \qquad (4.1\text{-}30)$$

$$\phi - 1 = \frac{\partial G^{EX}/(kg_W RT)}{\partial m_j} \qquad (4.1\text{-}31)$$

From the Pitzer G^{ex} expression, the activity coefficients of ions and the osmotic coefficient for the solvent can be obtained. In GEM-Selektor, the corresponding derivation of the Pitzer formalism according to Harvie et al (1984) is implemented. The activity of water in the solution is calculated as:

$$ln(a_{H_2O}) = -\frac{M_W}{1000} + \sum_{j=1}^{L}(m_j)\phi \qquad (4.1\text{-}32)$$

M_w stands for the molecular mass of water, m_j for the molality of species j and ϕ for the osmotic coefficient. The latter is obtained from following expression:

$$
\begin{aligned}
0.5\sum_{j=1}^{L} m_j(\phi-1) = & \left(-\frac{A^\Phi I^{\frac{3}{2}}}{1+1.2\sqrt{I}}\right) \\
& +\sum_{c=1}^{L_c}\sum_{a=1}^{L_a} m_c m_a \left(B_{ca}^\Phi + ZC_{ca}\right) \\
& +\sum_{c=1}^{L_c}\sum_{c'=c+1}^{L_c} m_c m_{c'}\left(\Phi_{cc'}^\Phi + \sum_{a=1}^{L_a}\Psi_{cc'a}\right) \\
& +\sum_{a=1}^{L_a}\sum_{a'=a+1}^{L_a} m_a m_{a'}\left(\Phi_{aa'}^\Phi + \sum_{c=1}^{L_c}\Psi_{aa'c}\right) \\
& +\sum_{n=1}^{L_n}\sum_{c=1}^{L_c} m_n m_c \lambda_{nc} + \sum_{n=1}^{L_n}\sum_{a=1}^{L_a} m_n m_a \lambda_{na} \\
& +\sum_{n=1}^{L_n}\sum_{c=1}^{L_c}\sum_{a=1}^{L_a} m_n m_c m_a \zeta_{nca}
\end{aligned}
\qquad (4.1\text{-}33)
$$

Subscripts *n, c* and *a* indicate neutral species, cations or anions, respectively. The activity coefficients of a cation (γ_M) with index M and $z_M \geq 1$, anions (γ_X) with index X and $z_A \leq -1$, and neutral species (γ_N) with index N and $z_N=0$, are computed as:

$$
\begin{aligned}
ln\,\gamma_M = & \; z_M^2 F \\
& +\sum_{a=1}^{L_a} m_a\left(2B_{Ma} + ZC_{Ma}\right) \\
& +\sum_{c=1}^{L_c} m_c\left(2\Phi_{Mc} + \sum_a m_a\Psi_{Mca}\right) \\
& +\sum_{a=1}^{L_a}\sum_{a'=a+1}^{L_a} m_a m_{a'}\Psi_{aa'M} \\
& +|z_M|\sum_{c=1}^{L_c}\sum_{a=1}^{L_a} m_c m_a C_{ca} \\
& +2\sum_{n=1}^{L_n} m_n \lambda_{nM}
\end{aligned}
\qquad (4.1\text{-}34)
$$

$$ln\,\gamma_X = z_X^2 F$$

$$+\sum_{c=1}^{L_c} m_c (2B_{cX} + ZC_{cX})$$

$$+\sum_{a=1}^{L_a} m_a (2\Phi_{Xa} + \sum_{c=1}^{L_c} m_c \Psi_{Xac})$$

$$+\sum_{c}^{L_c} \sum_{c'=c+1}^{L_c} m_c m_{c'} \Psi_{cc'X}$$

$$+|z_X| \sum_{c=1}^{L_c} \sum_{a=1}^{L_a} m_c m_a C_{ca}$$

$$+2\sum_{n=1}^{L_n} m_n \lambda_{nX}$$

(4.1-35)

$$ln\,\gamma_N = \sum_{a=1}^{L_a} m_a (2\lambda_{na})$$

$$+\sum_{c=1}^{L_c} m_c (2\lambda_{nc})$$

$$+\sum_{n=1}^{L_n} m_n \zeta_{Nca}$$

(4.1-36)

The *F*-factor used in computation of γ_M and γ_X is defined as follows:

$$F = -A^{\Phi} \left(\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} ln(1+1.2\sqrt{I}) \right)$$

$$+\sum_{c=1}^{L_c} \sum_{c'=c+1}^{L_c} m_c m_{c'} \Phi'_{cc'}$$

$$+\sum_{a=1}^{L_a} \sum_{a'=a+1}^{L_a} m_a m_{a'} \Phi'_{aa'}$$

$$+\sum_{c=1}^{L_c} \sum_{a=1}^{L_a} m_c m_a B'_{ca}$$

(4.1-37)

The *Z* term comes from:

$$Z = \sum_{j=1}^{L} |z_j| m_j$$

(4.1-38)

It is used in the terms for calculation of activity coefficients and of the osmotic coefficient.

The ionic strength-dependent parameters $\Phi_{cc}^{\Phi}, \Phi_{aa}^{\Phi}, \Phi'_{cc}, \Phi'_{aa}, \Phi_{cc}, \Phi_{aa}$ account for interactions between like-sign ion pairs.

$$\Phi_{ij}^{\Phi} = \theta_{ij} + {}^E\theta_{ij}(I) + I\,{}^E\theta'_{ij}(I)$$

(4.1-39)

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I)$$

(4.1-40)

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I)$$
(4.1-41)

The parameters ${}^{E}\theta'_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ are computed according to Pitzer (1991) by Harvie's method (application of Chebyshev polynomial approximations to solve the used integrals instead of numerical integration). ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ terms account for the electrostatic unsymmetrical mixing effects. Ψ_{cca} and Ψ_{caa} ternary ion-interaction coefficients and ζ_{nca} account for ternary interactions between charged species of different sign with neutral species.

4.1.6. Extended UNIQUAC (EUNIQUAC) model (*contributed by F.F. Hingerl*)

The Extended UNIQUAC (UNIversal QUAasi-Chemical) model [Nicolaisen et al., 1993; Thomsen et al., 1996; Thomsen and Rasmussen, 1999]) combines a Debye-Hückel term for long-range electrostatic interactions with a standard UNIQUAC local composition term [Abrams and Prausnitz, 1975] for short-range interactions.

Conventions, concentration and standard states. The implemented version of the EUNIQUAC model is internally formulated based on the mole fraction concentration scale. The standard state chemical potential of water solvent μ_W^0 and the associated activity coefficient γ_W, follow the symmetric (Raoultian) convention (x_W is the mole fraction of water):

$$\mu_W = \mu_W^0 + RT\,ln\left(x_W\gamma_W\right)$$
(4.1-42)

The corresponding formulation of the chemical potential of the solute is expressed in mole fraction scale taken in the asymmetric (Henryan) convention.

$$\mu_j = \mu_j^* + RT\,ln\left(x_j\gamma_j^*\right)$$
(4.1-43)

The asymmetric mole fraction activity coefficient is

$$\gamma_j^* = \gamma_j / \gamma_j^{\infty}$$
(4.1-44)

where γ_j^* is the activity coefficient taken in the asymmetric convention; γ_j the activity coefficient in the symmetric convention; and γ_j^{∞} is the infinite dilution activity coefficient in the symmetric convention. Conversion of aqueous species activity coefficients to the molality scale for compatibility with the standard state convention used for aqueous species in the GEM-Selektor code is performed through the the following correction term:

$$\gamma_j^m = \gamma_j^* x_W$$
(4.1-45)

The EUNIQUAC equations. The asymmetric term for the excess Gibbs energy (per mole of solution and normalized over *RT*) is expressed as follows:

$$g^{E*} / RT = g_{D-H}^{E*} / RT + g_C^{E*} / RT + g_R^{E*} / RT$$
(4.1-46)

In this formulation, g_{D-H}^{E*} is the long-range-interaction contribution which is represented by a Debye-Huckel term. The short-range interactions are separated into a combinatorial (entropic) term g_C^{E*} and a residual (enthalpic) term g_R^{E*}. The former is independent of temperature (and pressure) and varies only with changes in relative size of the involved species. The latter represents the temperature dependence of the short-range-interactions and is proportional to

excess enthalpy. Currently, the pressure dependence of short-range interactions is not explicitly included in the functional form of the EUNIQUAC equations.

The rational scale, symmetrical-convention activity coefficient is derived from the molar excess Gibbs energy using standard thermodynamic relationships:

$$ln\,\gamma_j = \left[\frac{\partial \left(ng^E / RT\right)}{\partial n_j} \right]_{P,T,n_{j\neq i}}$$

(4.1-47)

Long-range contributions. The Debye Huckel (D-H) term is calculated as:

$$G^{E,D-H} / (RT) = -x_W M_W 4A \left[ln\left(1 + bI^{\frac{1}{2}}\right) - bI^{\frac{1}{2}} + 0.5b^2 I \right] / b^3$$

(4.1-48)

where M_W is the molar mass of water (0.018015 kg/mol), b is a parameter with the value 1.5 $(kg/mol)^{1/2}$, and I is the true ionic strength:

$$I = 0.5\sum_j m_j z_j^2 = 0.5\sum_j x_j z_j^2 / (x_W M_W)$$

(4.1-49)

Here m_j stands for the molality of species j, z_j is the charge of species j, and x_j is the mole fraction of species j. A is the Debye-Huckel parameter, which can be approximated (for water as solvent) by the empirical relationship:

$$A = \left[1.131 + 1.335 \cdot 10^{-3} \cdot (T - T_0) + 1.164 \cdot 10^{-5} \cdot (T - T_0)^2 \right]$$

(4.1-50)

Note that this simple polynomial approximation is only valid for the temperature range 273.15-383.15 K. T_0 is the reference temperature of 273.15 K. A more general expression for the Debye-Huckel parameter A that explicity accounts for temperature and pressure dependence is:

$$A = c \frac{d^{\frac{1}{2}}}{(DT)^{\frac{3}{2}}}$$

(4.1-51)

The parameter c has a value of $1.3287*10^5$ $K^{3/2}m^{3/2}mol^{-1/2}$, d is the density of water in kg/m^3 and D is the dielectric constant of water.

Derivation of the D-H contribution to the excess Gibbs energy with respect to n_j (j stands for any solute and water) results in equations for the D-H contribution to the activity coefficient of species j (γ_j^{D-H}) or water (γ_W^{D-H}), respectively. The D-H term for aqueous species follows the asymmetric convention and the term for water follows the symmetric convention:

$$ln\,\gamma_j^{*D-H} = -z_j^2 AI^{\frac{1}{2}} / \left(1 + bI^{\frac{1}{2}}\right)$$

(4.1-52)

$$ln\,\gamma_W^{D-H} = M_W 2A \left[1 + bI^{\frac{1}{2}} - \left(1 + bI^{\frac{1}{2}}\right)^{-1} - 2\,ln\left(1 + bI^{\frac{1}{2}}\right) \right] / b^3$$

(4.1-53)

Short-range contributions - combinatorial (entropic) term. The combinatorial contribution to the excess Gibbs energy is described as:

$$G^{E,C} / (RT) = \sum_j x_j \ln\left(\phi_j / x_j\right) - 5.0 \sum_j q_j x_j \ln\left(\phi_j / \theta_j\right)$$

(4.1-54)

where ϕ_j is the volume fraction calculated from the volume parameters r_j:

$$\phi_j = x_j r_j / \sum_i x_i r_i$$

(4.1-55)

and θ_j are the surface area fractions calculated from the surface area parameters q_j.

$$\theta_j = x_j q_j / \sum_i x_i q_i$$

(4.1-56)

Derivation of the combinatorial part of the excess Gibbs energy function (4.1-54) results in the corresponding contributions to activity coefficients:

$$\ln \gamma_j^C = \ln\left(\phi_j / x_j\right) + 1 - \phi_j / x_j - 5.0 q_j \left[\ln\left(\phi_j / \theta_j\right) + 1 - \phi_j / \theta_j\right]$$

(4.1-57)

Because this former expression gives a symmetric activity coefficient term, the infinite dilution term is used to obtain the respective asymmetric terms. This is done by setting $x_W = 1$ in equation (4.1-57), which results in:

$$\ln \gamma_j^{C,\infty} = \ln\left(r_j / r_w\right) + 1 - r_j / r_w - 5.0 q_j \left[\ln\left(r_j q_w / r_w q_j\right) + 1 - \left(r_j q_w / r_w q_j\right)\right]$$

(4.1-58)

Short-range contributions - residual (enthalpic) term. The temperature-dependent term of the residual term of the excess Gibbs energy function is given as:

$$G^{E,R} / (RT) = -\sum_j x_j q_j \ln\left(\sum_i \theta_i \psi_{ij}\right)$$

(4.1-59)

with:

$$\psi_{ij} = \exp\left[-\left(u_{ij} - u_{jj}\right) / T\right]$$

(4.1-60)

$$u_{ij} = u_{ij}^0 + u_{ij}^t \left(T - 298.15\right)$$

(4.1-61

The parameters u_{ij}^0 and u_{ij}^t characterize the energetic interaction between species i an j. They are considered symmetrical ($u_{ji} = u_{ij}$). Equation (4.1-61) gives their temperature dependence. The derivation of equation (4.1-59) with respect to species j results in the corresponding expression for the residual part of the symmetrical-convention activity coefficient:

$$\ln \gamma_j^R = q_j \left[1 - \ln\left(\sum_l \theta_l \psi_{lj}\right) - \sum_i \left(\theta_i \psi_{ji} / \sum_l \theta_l \psi_{li}\right)\right]$$

(4.1-62)

The associated infinite dilution correction term is given by:

$$\ln \gamma_j^{R,\infty} = q_j [1 - \ln \psi_{wj} - \psi_{jw}]$$

(4.1-63)

The asymmetric-convention activity coefficient of the solute species. In order to get activity coefficients consistent with the asymmetric convention, the symmetric activity coefficients

have to be divided by the corresponding infinite dilution terms (see equation 4.1-44). Since the Debye-Huckel part is already considered asymmetric, this conversion is only applied to the combinatorial and redidual terms of the short-range contributions. According to equation (4.1-46), the final asymmetric activity coefficient is then obtained by summation of the corrected parts:

$$ln\,\gamma_j^* = ln\left(\gamma_j^C / \gamma_j^{C,\infty}\right) + ln\left(\gamma_j^R / \gamma_j^{R,\infty}\right) + ln\,\gamma_j^{*D-H}$$

(4.1-64)

The symmetric-convention activity coefficient of the solvent. The activity coefficient of water is always calculated consistent with the symmetric convention:

$$ln\,\gamma_W = ln\,\gamma_W^C + ln\,\gamma_W^R + ln\,\gamma_W^{D-H}$$

(4.1-65)

The osmotic coefficient. From the activity coefficient of water, the corresponding practical osmotic coefficient (in the Lewis-Randall scale) can be calculated:

$$\Phi \equiv \frac{-ln\,a_w}{M_w v m_s} = -\frac{n_w}{v n_s} ln\left(\gamma_w x_w\right)$$

(4.1-66)

In this definition, a complete dissociation of the electrolyte is assumed, which is reflected by the stoichiometric coefficient v (actually, the sum over the stoichiometric units forming due to dissociation) given a fixed value independent of the actual degree of dissociation of the salt. According to Thomsen (1997), osmotic coefficients for bisulfate salts, as well as bicarbonate salts, can be found in the literature either as osmotic coefficients for 2-1 or 1-1 electrolytes.

4.2. Solid solutions, melts and liquid mixtures

Possible options for built-in calculation of activity coefficients for end members of condensed phases in GEM-Selektor code are summarized in Appendix 4-3.

Treatment of solid (and any condensed non-electrolyte) solutions in GEM-Selektor code is based on the following expression for the chemical potential of a j-th end member [Karpov et al., 1997; 2001]:

$$\upsilon_j = \frac{g_{j,T,P}}{RT} + ln\,\chi_j + ln\,\gamma_j$$

(4.2-1),

where $g_{j,T,P}$ is the molar apparent Gibbs energy function at T,P of interest; $\chi_j = \frac{x_j}{X_\alpha}$ is the mole fraction (x_j is the mole quantity of j-th species and $X_\alpha = \sum x_j$, $j \in L_\alpha$ is the total mole quantity in the in the α-th phase), and γ_j is an activity coefficient.

If all $\gamma_j = 1$ then eqn (4.2-1) reduces to the Raoult's law of ideal mixing, where the activity of j-th end-member equals its mole fraction. This definition of ideal mixing is rather narrow because, in a broader sense, ideal solutions can be defined as having zero enthalpy and volume of dissolution [Oates, 1966; Anderson and Crerar, 1993]. Further complications include regular solutions (with non-zero enthalpy of dissolution) and non-ideal solutions where enthalpy, volume and entropy of dissolution are non-zero for an end-member. In general, one can write for the dissolution properties:

$$a_j = X_j \gamma_j, \quad \gamma_j \neq 1, \quad j \in L_\alpha;$$
$$\Delta S_d = -R \sum_j \chi_j \ln a_j;$$

$$\Delta V_d \neq 0; \quad \Delta H_d \neq 0;$$

$$\Delta G_d = \Delta H_d + RT \sum_j \chi_j \ln a_j$$

Here, a_j stands for the activity of j-th end-member and the subscript d refers to the difference of a particular property between a non-ideal solution and a mechanical mixture of its pure end-members [Anderson and Crerar, 1993]. In practice, the excess thermodynamic functions of mixed non-electrolyte phases are usually considered:

$$V_{EX} = V_{real} - \sum_j \chi_j V_j^o \qquad (4.2\text{-}2),$$

$$H_{EX} = H_{real} - \sum_j \chi_j H_j^o \qquad (4.2\text{-}3),$$

$$S_{EX} = S_{real} - \left(\sum_j \chi_j S_j^o - R \sum_j \chi_j \ln \chi_j \right) \qquad (4.2\text{-}4),$$

$$G_{EX} = G_{real} - \left(\sum_j \chi_j G_j^o + RT \sum_j \chi_j \ln \chi_j \right) \qquad (4.2\text{-}5),$$

where the subscript *real* refers to an experimentally measurable property in the real system. Likewise, for one end-member, an excess partial property can be defined as a difference between the real and the ideal partial molar property. For instance, the excess partial Gibbs energy of j-th end-member (counted relative to Raoultian ideal mixing) is

$$\overline{G}_j^{EX} = \mu_{j,real} - \mu_{j,ideal} = \mu_j^o + RT \ln \chi_j \gamma_j - \mu_j^o - RT \ln \chi_j = RT \ln \gamma_j \qquad (4.2\text{-}6).$$

The excess partial molar entropy, enthalpy, and volume can then be found by differentiating the $\overline{G}_j^{EX}$ over temperature and pressure (see details in e.g. [Anderson and Crerar, 1993]):

$$\overline{S}_j^{EX} = -R \ln \gamma_j - RT \left(\frac{\partial \ln \gamma_j}{\partial T} \right)_{P,\chi} \qquad (4.2\text{-}7);$$

$$\overline{H}_j^{EX} = -RT^2 \left(\frac{\partial \ln \gamma_j}{\partial T} \right)_{P,\chi} \qquad (4.2\text{-}8);$$

$$\overline{V}_j^{EX} = -RT \left(\frac{\partial \ln \gamma_j}{\partial P} \right)_{T,\chi} \qquad (4.2\text{-}9).$$

Thus, to describe real non-electrolyte solutions, it is sufficient to know (partial) molar properties of all end-members at T,P of interest plus functional dependencies of their activity coefficients on T,P and composition (i.e. on mole fractions χ_j of all end-members).

There is no general solution to this problem, though a great variety of semi-empirical models have been developed and parameterized for binary-, ternary-, … symmetric and asymmetric systems. Some of the most frequently used mixing models are described below and implemented as built-in functions in the GEM-Selektor code (see text below and Appendix 4-2). In addition to those built-in mixing models, any arbitrary mixing model can be written by the user in a Phase definition script to calculate activity coefficients of end-members, which will be stored in the database and automatically executed on GEM iterations.

4.2.1. Regular and subregular (Margules) models

The Margules binary mixing model is most frequently used (see e.g.[Anderson and Crerar, 1993]). It is based on the "subregular" expression for the excess Gibbs energy of mixture:

$$G_{EX} = \chi_1(W_2\chi_1\chi_2) + \chi_2(W_1\chi_1\chi_2) \tag{4.2-10},$$

where χ_1 and χ_2 are mole fractions of the first and second end member ($\chi_1 + \chi_2 = 1$) and W_1, W_2 are Margules parameters (in J mol^{-1}), in general, functions of T and P but not of χ:

$$W_j = W_{U,j} - TW_{S,j} + PW_{V,j} \tag{4.2-11},$$

where W_U, W_S, and W_V are empirical parameters related to excess internal energy, entropy and volume of the mixture; they can be evaluated from experimental data. Next, the following expressions for partial excess Gibbs energies and activity coefficients can be obtained:

$$RT\ln\gamma_1 = \overline{G}_1^{EX} = (2W_2 - W_1)\chi_2^2 + 2(W_1 - W_2)\chi_2^3 \tag{4.2-12},$$

$$RT\ln\gamma_2 = \overline{G}_2^{EX} = (2W_1 - W_2)\chi_1^2 + 2(W_2 - W_1)\chi_1^3 \tag{4.2-13}.$$

Eqns (4.2-12) and (4.2-13) comprise the so-called "subregular" or "asymmetric" Margules mixing model. Asymptotically (e.g. at $\chi_1 \to 1$ and $\chi_2 \to 0$), the activity coefficient of the "major" end-member $\ln\gamma_1 \to 0$ and that of the "trace" end-member $\ln\gamma_2 \to W_2/(RT)$. Likewise, at $\chi_1 \to 0$ and $\chi_2 \to 1$, $\ln\gamma_1 \to W_1/(RT)$ and $\ln\gamma_2 \to 0$. This asymptotic behavior simplifies modeling calculations when co-precipitation of trace components into host mineral is considered.

Eqns (4.2-12) and (4.2-13) are often used with dimensionless interaction parameters:

$$\ln\gamma_1 = (2a_2 - a_1)\chi_2^2 + 2(a_1 - a_2)\chi_2^3 \tag{4.2-14},$$

$$\ln\gamma_2 = (2a_1 - a_2)\chi_1^2 + 2(a_2 - a_1)\chi_1^3 \tag{4.2-15},$$

where $a_1 = W_1/RT$; $a_2 = W_2/RT$. If $a_1 = a_2 = a$ then eqns (4.2-14) and (4.2-15) reduce to the "regular" or "symmetric" Margules mixing model, typically used for carbonate or sulfate solid solutions [Lippmann, 1980; Glynn, 2000]:

$$\ln\gamma_1 = a\chi_2^2 \tag{4.2-16},$$

$$\ln\gamma_2 = a\chi_1^2 \tag{4.2-17}.$$

In general, the binary interaction parameter $W = RT \cdot a$ is also a function of T,P but not χ:

$$W = W_U - TW_S + PW_V = W_H - TW_S \tag{4.2-18}.$$

At $a > 2$, the symmetric binary mixture should exsolve into two co-existing phases of different composition along the *binodal solvus* curve [cf. Glynn, 2000]. The width of the miscibility gap depends on temperature; according to Lippmann [1980],

$$a_T \approx 2T_c/T \tag{4.2-19},$$

where T_c is the critical temperature (or the highest temperature of melting) for the ionic solid. At ambient temperatures, the values of a range from nearly zero to maximum 13-14 in various ionic binary mixtures, i.e. from complete miscibility to $\chi_1 \leq n \cdot 10^{-6}$ [Glynn, 2000]. If experimental compositions of two phases co-existing within the miscibility gap are known then the value of interaction parameter a can be retrieved. In case of the binary symmetric gap, the fol-

lowing relation can be derived from equating chemical potentials of end-member A at both phase compositions ($\chi_A < 0.5$ is mole fraction of A in one of the phases):

$$a = \frac{\ln \chi_A - \ln(1 - \chi_A)}{2\chi_A - 1}$$ (4.2-20).

If a miscibility gap is expected to occur in the solid solution system then more than one mixed phase definition must be inserted into the GEMS chemical system definition (CSD), and a special mode of automatic initial approximation has to be specified (Appendix 4-4) to ensure that the two-phase region is reproduced at appropriate bulk compositions.

The Margules model can be relatively easily expanded to ternary, quaternary, … mixture systems. However, the number of interaction parameters increases dramatically, making a much higher demand to experimental data needed for parameterization, and expressions for excess properties become very cumbersome. For instance, the ternary Margules model can be obtained from summation of G_{EX} for three binary models with common end-members:

$$G_{EX} = \left(W_{23}\chi_2^2\chi_3 + W_{32}\chi_3^2\chi_2\right) + \left(W_{13}\chi_1^2\chi_3 + W_{31}\chi_3^2\chi_1\right) + \left(W_{12}\chi_1^2\chi_2 + W_{21}\chi_2^2\chi_1\right) + \\ + W_{123}\chi_1\chi_2\chi_3$$ (4.2-21).

The ternary interaction parameter W_{123} is often neglected [e.g. Anderson and Crerar, 1993]. Full theoretical expressions for sub-regular activity coefficients can be found in [Helffrich and Wood, 1989]. Assuming the regular mixing ($W_{ij} = W_{ji}$), one obtains for activity coefficients:

$$RT\ln\gamma_1 = W_{12}\chi_2(1 - \chi_1) + W_{13}\chi_3(1 - \chi_1) - W_{23}\chi_2\chi_3 + \\ W_{123}\chi_2\chi_3(1 - 2\chi_1)$$ (4.2-22),

$$RT\ln\gamma_2 = W_{23}\chi_3(1 - \chi_2) + W_{12}\chi_1(1 - \chi_2) - W_{13}\chi_1\chi_3 + \\ W_{123}\chi_1\chi_3(1 - 2\chi_2)$$ (4.2-23),

$$RT\ln\gamma_3 = W_{13}\chi_1(1 - \chi_3) + W_{23}\chi_2(1 - \chi_3) - W_{12}\chi_1\chi_2 + \\ W_{123}\chi_1\chi_2(1 - 2\chi_3)$$ (4.2-24).

Thus, compared to the binary regular model (eqns 4.2-10 to 4.2-13), four Margules parameters are needed instead of one (or, including T,P dependence of mixing, 12 parameters are necessary instead of 3). In the quarternary case, six binary plus four ternary plus one quarternary Margules parameters (in total 11) would be necessary just for a regular approximation. This is why, in practice, full mixing models of the order above ternary are very seldom. Built-in Margules mixing models available in GEM-Selektor are limited to binary subregular and multicomponent regular cases.

Various simplifications can be used to reduce the number of interaction parameters, for instance, it can be shown that some binaries in a multi-component mixture are ideal. One can also assume [Kulik et al., 2000] that in reality, two of six end-members together comprise more than 96% of the mixture (major end-members), and the remaining four are minor end-members, each less than 1% mole fraction ($\chi_j < 0.01$). Then activity coefficients of major end-members (1 and 2) can be considered as independent of mole fractions of minor end-members (indexed 3,4,…):

$$RT\ln\gamma_1 \approx W_0(1 - \chi_1)^2$$ (4.2-25),

$$RT\ln\gamma_2 \approx W_0\chi_1^2$$ (4.2-26).

For minor end-members, all minor-minor, ternary, quaternary, … parameters can be neglected in the two major end-members (1 and 2) case:

$$RT \ln \gamma_3 \approx W_{31}\chi_1 + W_{32}\chi_2 - W_0\chi_1\chi_2 \qquad (4.2\text{-}27)$$

$$RT \ln \gamma_4 \approx W_{41}\chi_1 + W_{42}\chi_2 - W_0\chi_1\chi_2 \qquad (4.2\text{-}28)$$

and so on. Thus, in a regular mixture with two major and several minor end-members, one major binary parameter W_0 is needed, as well as two binary Margules parameters per minor end-member (for both minor-major binaries). This simplified model appears to be practically useful for trace metal co-precipitation in host carbonates and sulfates.

4.2.2. Multi-component regular model (symmetric formalism)

Many naturally occurring rock-forming minerals are complex solid-solutions composed of many end-members. Examples include amphiboles, chlorite, muscovite, biotite, pyroxenes and many others. For such cases the regular model can be consistently extended to multi-component systems. Powell and Holland [1993] have derived general expressions for the excess properties and activity coefficients for multi-component regular solid-solutions, which have been termed the symmetric formalism. It needs to be taken into account that the available experimental data for such complex mineral phases usually do not justify to fit them with more than one interaction parameter per binary system. Therefore, using a regular (symmetric) mixing model with only binary interaction parameters is probably as far as we can get with many multi-component phases. The excess Gibbs free energy for the multi-component case is expressed as:

$$G_{EX} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \chi_i \chi_j W_{ij} \qquad (4.2\text{-}29)$$

where the summation takes place over all species 1 to n. The activity coefficient for each end-member k is then calculated as:

$$RT \ln \gamma_k = -\sum_{i=1}^{n-1} \sum_{j>i}^{n} q_i q_j W_{ij} \qquad (4.2\text{-}30)$$

in which $q_i = 1 - \chi_i$ when i = k and $q_i = -\chi_i$ when $i \neq k$. The W_{ij} are binary regular interaction parameters. The binary interaction parameters W_{ij} can be simple functions of temperature and pressure: $W_{ij} = a + bT + cP$ (no excess heat capacity term is considered). The other excess properties (entropy, enthalpy, volume) can be obtained as partial derivatives of the excess Gibbs free energy expression, eq. (4.2-29).

4.2.3. Multi-component Van Laar model (asymmetric formalism)

Although a regular model is suitable as a first-order representation of the mixing properties of many solid-solutions, there is a considerable number of systems that can not be well described in this way. Most importantly, it is known from phase equilibria studies that certain systems display an asymmetric solvus, i.e. the solubility of end-member A in B is considerably higher than the solubility of B in A. Such effects are very pronounced at low temperatures, because the energetic effects of ideal mixing become weaker with decreasing temperature. Prominent examples for systems that are asymmetric are the alkali feldspars (albite-microcline), halite-sylvite, white mica (muscovite-paragonite) and calcite-dolomite.

In order to describe the mixing properties of asymmetric systems, a diverse range of thermodynamic formulations of variable complexity have been developed. Recently, Holland and Powell [2003] have derived a modification of the regular (symmetric) formalism that is suitable for multi-component asymmetric systems. This asymmetric formalism is based on a model that was originally developed by Van Laar (see reference in Holland and Powell, 2003) for gas mixtures. Holland and Powell [2003] have modified the model to be suitable for solid-solutions. The asymmetric formalism retains one binary interaction parameter per pair of end-members, but it adds one scaling parameter (size parameter) per end-member. The excess Gibbs free energy is then expressed as:

$$G_{EX} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \phi_i \phi_j B_{ij}$$
(4.2-31)

where

$$B_{ij} = \frac{2 \sum_{j=1}^{n} \chi_j \alpha_j}{\alpha_i + \alpha_j} W_{ij}$$
(4.2-32)

Here, α_i and α_j are the size parameters (one per end-member). The ϕ_i terms are size-parameter adjusted mole fractions:

$$\phi_i = \frac{\chi_i \alpha_i}{\sum_{j=1}^{n} \chi_j \alpha_j}$$
(4.2-33)

The activity coefficients are now calculated in a way quite similar to the regular (symmetric) formalism:

$$RT \ln \gamma_k = -\sum_{i=1}^{n-1} \sum_{j>i}^{n} q_i q_j W_{ij}^*$$
(4.2-34)

where $q_i = 1 - \phi_i$ when i = k and $q_i = -\phi_i$ when i ≠ k . The W_{ij}^* are size parameter adjusted interaction parameters, defined as:

$$W_{ij}^* = W_{ij} \frac{2\alpha_k}{\alpha_i + \alpha_j}$$
(4.2-35)

Note that α_k is the size parameter for the end-member for which the activity coefficient is calculated, whereas α_i and α_j in the denominator are the size parameters for the respective interaction, which can include species k, but can also be other species than k. As for the symmetric formalism, the W_{ij} can be functions of temperature and pressure: $W_{ij} = a + bT + cP$.

4.2.4. Redlich-Kister (Guggenheim) model

The Redlich-Kister mixing model is a frequently used alternative to the Margules-type models, especially for binary mixtures. It is based on Guggenheim's expansion series for the excess Gibbs energy of mixing [cf. Glynn, 2000]:

$$G_{EX} = RT\chi_1\chi_2[a_0 + a_1(\chi_1 - \chi_2) + a_2(\chi_1 - \chi_2)^2 + ...]$$
(4.2-36),

where a_0, a_1, a_2 … are dimensionless fitting parameters (an equivalent form of eqn 4.2-36 uses $L_j = RT{\cdot}a_j$ parameters in J·mol⁻¹). From the above equation, the following activity coefficients can be obtained in the binary case:

$$\ln \gamma_1 = \chi_2^2[a_0 + a_1(3\chi_1 - \chi_2) + a_2(\chi_1 - \chi_2)(5\chi_1 - \chi_2) + ...]$$
(4.2-37);

$$\ln \gamma_2 = \chi_1^2[a_0 - a_1(3\chi_2 - \chi_1) + a_2(\chi_2 - \chi_1)(5\chi_2 - \chi_1) - ...]$$
(4.2-38).

The first two terms in eqns (4.2-36) to (4.2-38) are generally sufficient to represent experimental data. In this case, the last two equations calculate the same curves as the subregular Margules model (eqns 4.2-12 and 4.2-13), with the following relations between parameters:

$$W_{12} = RT(a_0 - a_1); \quad W_{21} = RT(a_0 + a_1)$$
(4.2-39).

Further reduction to the regular mixing model by setting $a_1=0$ and $a_2 = 0$ yields

$$W = RT \cdot a = RT \cdot a_0$$
(4.2-40).

In GEM-Selektor, equations (4.2-37) and (4.2-38) with three parameters are implemented as a built-in function for the binary Redlich-Kister mixing model. Reduction to subregular and regular mixing models can be done easily by setting unnecessary coefficients to zero.

Several analytical and geometric schemes for the extension of the Redlich-Kister formalism (and other binary solid-solution models) to higher-order (multicomponent) systems have been proposed, including methods by Kohler, Toop and Muggianu. It has been shown that the Muggianu geometric scheme is formally equal to the more simple analytical expression [Hillert, 1998]. Based on this formalism, a 4-term (^0L-^3L) Redlich-Kister multicomponent model has been implemented in GEM-Selektor. The respective excess Gibbs energy is expressed as:

$$G_{EX} = \sum_{i=1}^{n-1} \sum_{j>i}^{n} \chi_i \chi_j L_{ij}$$
(4.2-41)

where

$$L_{ij} = {}^0L_{ij} + {}^1L_{ij}(\chi_i - \chi_j) + {}^2L_{ij}(\chi_i - \chi_j)^2 + {}^3L_{ij}(\chi_i - \chi_j)^3$$
(4.2-42)

The full expression for the activity coefficient can be found in [Hillert, 1998]. It has to be noted that this equation depends on the order between species (end-members) i and j. Therefore, in setting up models using the multicomponent Redlich-Kister formalism, the sign of each interaction term with odd number, i.e., the terms $^1L_{ij}$ and $^3L_{ij}$ in equation (4.2-42), changes to negative if the order between i and j is reversed. The binary interaction parameters L_{ij} can be a function of temperature and pressure: $^kL_{ij} = a + bT + cT \ln(T) + dP$. The logarithmic term in this expression accounts for excess heat capacity.

4.2.5. NRTL (non-random two-liquid) model

The NRTL model (Renon and Prausnitz, 1968), along with the Wilson and UNIQUAC (universal quasichemical) equations, belongs to a class of models for the excess Gibbs free energy that are based on the concept of local composition. These models are traditionally used to model liquid-liquid equilibria, but are increasingly applied to electrolyte solutions. The basic assumption of local composition models is the existence of distinct subcells in liquid mixtures where each molecule type is surrounded by a compositionally different environment. A major advantage of the local composition models is that the properties of multicomponent mixtures can be successfully modeled from well-calibrated binary systems, without requiring additional ternary and higher-order interaction terms. For binary systems the excess Gibbs energy is given by [Prausnitz et al., 1997]:

$$\frac{g^{EX}}{RT} = \chi_1 \chi_2 \left[\frac{\tau_{21} G_{21}}{\chi_1 + \chi_2 G_{21}} + \frac{\tau_{12} G_{12}}{\chi_2 + \chi_1 G_{12}} \right]$$
(4.2-43),

where

$$\tau_{12} = \frac{\Delta g_{12}}{RT} = \frac{g_{12} - g_{22}}{RT}$$ (4.2-44),

$$\tau_{21} = \frac{\Delta g_{21}}{RT} = \frac{g_{21} - g_{11}}{RT}$$ (4.2-45),

are the normalized differences in the interaction energies between molecule pairs 1-1, 2-2, and 1-2 [Prausnitz et al., 1997]. The G terms in equation (4.2-43) are then given by:

$$G_{12} = \exp(-\alpha_{12}\tau_{12})$$ (4.2-46),

$$G_{21} = \exp(-\alpha_{12}\tau_{21})$$ (4.2-47),

The expressions for the activity coefficients are then obtained as:

$$\ln \gamma_1 = (\chi_2)^2 \left[\tau_{21} \left(\frac{G_{21}}{\chi_1 + \chi_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(\chi_2 + \chi_1 G_{12})^2} \right]$$ (4.2-48),

$$\ln \gamma_2 = (\chi_1)^2 \left[\tau_{12} \left(\frac{G_{12}}{\chi_2 + \chi_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(\chi_1 + \chi_2 G_{21})^2} \right]$$ (4.2-49),

The model is readily expanded to multicomponent systems, with the excess Gibbs energy given as [Prausnitz et al., 1997]:

$$\frac{g^{EX}}{RT} = \sum_{i=1}^{N} \chi_i \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} \chi_j}{\sum_{k=1}^{N} G_{ki} \chi_k}$$ (4.2-50),

Activity coefficients are then computed as [Prausnitz et al., 1997]:

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} \chi_j}{\sum_{k=1}^{N} G_{ki} \chi_k} + \sum_{j=1}^{N} \frac{\chi_j G_{ij}}{\sum_{k=1}^{N} \chi_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{l=1}^{N} \chi_l \tau_{lj} G_{lj}}{\sum_{k=1}^{N} \chi_k G_{kj}} \right)$$ (4.2-51),

The other excess properties (enthalpy, entropy, heat capacity) are obtained from partial derivatives of the excess Gibbs energy function and standard thermodynamic relations, which yields for enthalpy:

$$h^{EX} = -RT^2 \frac{\partial (g^{EX}/RT)}{\partial T}$$ (4.2-52),

The model as originally formulated assumes that the energy terms are constant, whereas empirical series expansions in temperature are now commonly used to improve the model fit of liquid-liquid equilibria data:

$$\Delta g_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \ln T$$ (4.2-53),

$$\tau_{ij} = A_{ij} + B_{ij}/T + C_{ij} T + D_{ij} \ln T$$ (4.2-54),

$$\alpha_{ij} = E_{ij} + F_{ij}(T - 273.15) \tag{4.2-55},$$

The parameters of both equivalent forms of the temperature dependence, eqs. (4.2-53) and (4.2-54), can be easily converted by noting the definition of τ_{ij} in eq. (4.2-44). The model implementation in GEM-Selektor uses the temperature dependence from eqs. (4.2-54) and (4.2-55). This conforms to the most common industry standard as e.g. used by DECHEMA and other process simulation software. The NRTL model involves no pressure dependence of the interaction energies.

4.2.6. Wilson model

The Wilson model is suited to represent the properties of liquid mixtures that are moderately nonideal, but not for highly nonideal systems that exhibit liquid-liquid immicibility (Renon and Prausnitz, 1968). It has the advantage of requiring only two parameters per binary pair compared to three that are needed for the more complex NRTL model. For binary systems the excess Gibbs energy is given by [Prausnitz et al., 1997]:

$$\frac{g^{EX}}{RT} = -\chi_1 \ln(\chi_1 + \Lambda_{12}\chi_2) - \chi_2 \ln(\chi_2 + \Lambda_{21}\chi_1) \tag{4.2-56},$$

where Λ_{12} and Λ_{21} are the two binary interaction parameters. The activity coefficients are calculated as:

$$\ln \gamma_1 = -\ln(\chi_1 + \Lambda_{12}\chi_2) + \chi_2 \left(\frac{\Lambda_{12}}{\chi_1 + \Lambda_{12}\chi_2} - \frac{\Lambda_{21}}{\chi_2 + \Lambda_{21}\chi_1} \right) \tag{4.2-57},$$

$$\ln \gamma_2 = -\ln(\chi_2 + \Lambda_{21}\chi_1) - \chi_2 \left(\frac{\Lambda_{12}}{\chi_1 + \Lambda_{12}\chi_2} - \frac{\Lambda_{21}}{\chi_2 + \Lambda_{21}\chi_1} \right) \tag{4.2-58},$$

The model is readily expanded to multicomponent systems, with the excess Gibbs energy given as [Prausnitz et al., 1997]:

$$\frac{g^{EX}}{RT} = -\sum_{i=1}^{N} \chi_i \ln \sum_{j=1}^{N} \chi_j \Lambda_{ij} \tag{4.2-59},$$

Activity coefficients are then computed as [Prausnitz et al., 1997]:

$$\ln \gamma_i = 1 - \ln \sum_{j=1}^{N} \chi_j \Lambda_{ij} - \sum_{k=1}^{N} \frac{\chi_k \Lambda_{ki}}{\sum_{j=1}^{N} \chi_j \Lambda_{kj}} \tag{4.2-60},$$

All other excess properties (enthalpy, entropy, heat capacity) are obtained from partial derivatives of the excess Gibbs energy function and standard thermodynamic relations. The binary interaction parameters are now commonly expressed as a simple series expansion in temperature, either directly or in exponential form:

$$\Lambda_{ij} = A_{ij} + B_{ij}/T + C_{ij}T + D_{ij}\ln T \tag{4.2-61},$$

$$\Lambda_{ij} = \exp\left(A_{ij} + B_{ij}/T + C_{ij}T + D_{ij}\ln T\right) \tag{4.2-62},$$

The model implementation in GEM-Selektor uses the exponential temperature dependence from eq. (4.2-62), which conforms to the most common industry standard as e.g. used by the DECHEMA database.

4.3. Models for gases and fluids

Possible options for built-in calculation of fugacity- and activity coefficients for end members of non-ideal fluids in GEM-Selektor code are summarized in Appendix 4-4.

The simplest representation of the P-V-T properties of gases and fluids is the ideal gas law, which is a reasonable approximation at low pressures. The conceptual model of the ideal gas assumes that the gas molecules have zero volume and do not interact with each other. The ideal gas law is given by:

$$P V = n R T \tag{4.3-1}$$

where n is the mole amount of the ideal gas. For gases and fluids, two different standard states are generally used, which are the pure ideal gas at T of interest and 1 bar pressure, and the pure ideal gas at T and P of interest [Anderson, 2006]. The GEM-Selektor code uses the 1 bar standard state throughout, consistent with the standard state convention adopted by the SUPCRT92 computer code and database [Johnson et al., 1992]. A change in pressure of the ideal gas from 1 bar to P of interest results in a change in entropy and Gibbs free energy of:

$$\Delta S = -R \ln\left(P\right) \tag{4.3-2}$$

$$\Delta G = R T \ln\left(P\right) \tag{4.3-3}$$

With increasing pressure, the properties of nearly all gases diverge significantly from the prediction of the ideal gas law. Therefore, a considerable number of (mostly empirical) equation of states (EoS) have been developed to describe the *P-V-T* properties of gases and fluids more accurately. One of the most popular family of EoS models are the cubic equations of state, which are derived from the Van der Waals equation:

$$P = \frac{R T}{\left(V - b\right)} - \frac{a}{V^2} \tag{4.3-4}$$

The Van der Vaal EoS corrects the ideal gas law for attractive (term *a*) and repulsive (term *b*) forces between the gas molecules. The repulsive term *b* (termed the co-volume) is also viewed as a correction for the finite (non-zero) volume of gas molecules. Although the Van der Waals EoS represents a considerable improvement of the ideal gas law, it is still not accurate enough for real geochemical applications at moderate to high pressures. Therefore, many improved cubic EoS were developed, with the most common types being based on the Redlich-Kwong and Peng-Robinson models. The original form of the Redlich-Kwong EoS is given by:

$$P = \frac{R T}{\left(V - b\right)} - \frac{a}{T^{0.5} V \left(V + b\right)} \tag{4.3-5}$$

Several modifications have been proposed, one of the most common versions is that by Soave [1972] which is implemented into GEM-Selektor. The basic equation of the Soave-Redlich-Kwong (SRK) EoS model is:

$$P = \frac{R T}{V - b} - \frac{a\left(T\right)}{V \left(V + b\right)} \tag{4.3-6}$$

The attractive and repulsive terms are expressed as:

$$a = 0.42747 \frac{R^2 T_C^2}{P_C} \alpha \qquad (4.3\text{-}7)$$

$$b = 0.08664 \frac{R T_C}{P_C} \qquad (4.3\text{-}8)$$

$$\alpha = \left[1 + m \left(1 - T_R^{0.5} \right) \right]^2 \qquad (4.3\text{-}9)$$

where m is a function of the acentric factor ω, a measure of the non-centric nature of the gas molecules:

$$m = 0.48 + 1.574\,\omega - 0.176\,\omega^2 \qquad (4.3\text{-}10)$$

Many modifications of the Redlich-Kwong EoS have been propsed, including the version by Kerrick and Jacobs [1981] for the CO_2-H_2O system at high pressures. Holland and Powell [1991] have proposed a modification which corrects the behavior of the Redlich-Kwong EoS by the addition of up to 3 virial terms at higher pressures. This compensated Redlich-Kwong (CORK) model has found wide application in metamorphic petrology.

The Peng-Robinson (PR) EoS, which is widely used in chemical engineering and now also in geochemistry, has improved the Van der Waals EoS by modifying the repulsive term. The basic Peng-Robinson EoS is given by:

$$P = \frac{R T}{\left(V - b \right)} - \frac{a}{V \left(V + b \right) + b \left(V - b \right)} \qquad (4.3\text{-}11)$$

The attractive and repulsive terms are then expressed as:

$$a = 0.457235 \frac{R^2 T_C^2}{P_C} \alpha \qquad (4.3\text{-}12)$$

$$b = 0.077796 \frac{R T_C}{P_C} \qquad (4.3\text{-}13)$$

$$\alpha = \left[1 + \kappa \left(1 - T_R^{0.5} \right) \right]^2 \qquad (4.3\text{-}14)$$

where T_C and P_C are critical temperature and pressure, and T_R is the reduced temperature (T/T_C). The Peng-Robinson EoS is a quite good model for nonpolar gases, but application to polar gases such as HCl or H_2O required further improvement. One modification, the PRSV model [Stryjek and Vera, 1986a], has become quite popular in geochemistry and is now implemented in GEM-Selektor. The PRSV model has introduced a further correction term:

$$\kappa = \kappa_0 + \kappa_1 \left(1 + T_R^{0.5} \right) \left(0.7 - T_R \right) \qquad (4.3\text{-}15)$$

An extended version (PRSV-2) uses three correction terms [Stryjek and Vera, 1986b]:

$$\kappa = \kappa_0 + \left[\kappa_1 + \kappa_2 \left(\kappa_3 - T_R \right) \left(1 - T_R^{0.5} \right) \right] \left(1 + T_R^{0.5} \right) \left(0.7 - T_R \right) \qquad (4.3\text{-}16)$$

The κ_0 term is then a function of the Pitzer acentric factor ω:

$$\kappa_0 = 0.378893 + 1.4897153\,\omega - 0.17131848\,\omega^2 + 0.0196544\,\omega^3 \qquad (4.3\text{-}17)$$

The PRSV model represents P-V-T properties of many gases, including H_2O and CO_2, up to moderate pressures.

The basic EoS models described above are used to represent the properties of pure gases. For gas mixtures, additional mixing rules need to be applied. The most simple is the Lewis fugacity rule [Anderson, 2006], which assumes ideal mixing of non-ideal gases (represented by the EoS models above). The Lewis fugacity rule works reasonably for mixtures of gases with very similar properties, but is extremely inaccurate for mixtures of polar and non-polar gases. For such dissimilar mixtures, a large number of mixing rules have been developed, with the most simple (and most general) one proposed by Van der Waals. Here, the repulsive parameter b is expressed as simple average over all gas species:

$$b_{mix} = \sum_{j=1}^{m} \chi_j b_j \qquad (4.3\text{-}18)$$

The attractive term is calculated as sum of the contributions from all possible binary interactions:

$$a_{mix} = \sum_{j=1}^{m} \sum_{k=1}^{m} \chi_j \chi_k a_{jk} \qquad (4.3\text{-}19)$$

The binary interactions a_{jk} are then calculated from the combining rule, which in the simplest case is given by the geometric mean:

$$a_{jk} = \left(a_j a_k\right)^{0.5} \qquad (4.3\text{-}20)$$

Nonideality effects can then be expressed by different corrections to the combining rules, e.g. by applying one binary interaction parameter:

$$a_{jk} = \left(a_j a_k\right)^{0.5}\left(1 - k_{jk}\right) \qquad (4.3\text{-}21)$$

The current implementation of the PRSV model in GEM-Selektor uses the Van der Waals mixing rules with one binary interaction parameter.

Recent development of EoS models for gases and fluids was focused on more physical models, i.e. models that are based on fundamental properties of the molecules such as molecular potentials, dipole- and quadrupole effects, and polarizability. These models have much better extrapolative capabilities than the more empirical cubic EoS and require less parameters. The Churakov-Gottschalk fluid model [Churakov and Gottschalk, 2003a; b] that is implemented in the GEM-Selektor code represents one such model (see detailed description in the accompanying document "TPX-corrections-CG-EoS"). One drawback of such models is that they are computationally very expensive and therefore currently less suitable for coupled reactive mass transport models. It is expected though that with ever increasing computer power such models will be more universally used in the future.

4.4. References

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Appendix 4-1. Built-in options for calculation of activity coefficients for aqueous species (GEM-Selektor v.2.2 PSI).

Code	Model	Equations	Input parameters
D	Davies	4.1-10	Ionic strength I (eqn 4.1-3, computed automatically on each GEM IPM iteration); molality correction optional
3	Extended Debye-Hückel (Kielland)	4.1-9, 4.1-11	I; individual ion-size parameter $\mathring{a}$ (Kielland, collected from DComp/ReacDC records); common b_γ (third) parameter (default 0.064)
H	Extended Debye-Hückel (Helgeson)	4.1-9, 4.1-11	I; common ion-size parameter $\mathring{a} = 3.72$ (parameters from DComp/ReacDC records ignored); common b_γ parameter (default 0.064)
2	Debye-Hückel	4.1-5a	I; individual ion-size parameter $\mathring{a}$ (Kielland, collected from DComp/ReacDC records);
1	Debye-Hückel limiting law	4.1-8	I – ionic strength only (eqn 4.1-3)
S	SIT (BGS) model	4.1-12	I; one interaction coefficient per cation-anion pair (to enter into **ph_cf** array of Phase record)
Z	Pitzer (HMW) model	4.1-32 to 4.1-36	I; several sorts of binary and ternary interaction coefficients (in **ph_cf** array of Phase record)
Q	EUNIQUAC model	4.1-42 to 4.1-66	I; volumen and surface parameter per species; binary interaction coefficients (in **ph_cf** array of Phase record)

4. GEMS Built-In Activity Coefficients v.2.3 (D. Kulik and T. Wagner, with contribution by U. Berner & F.Hingerl)

Appendix 4-2. Built-in options for activity coefficients for end members of condensed (solid and liquid) non-electrolyte solution phases (GEMS v.2.2-PSI).

Code	Model	Equations	Interaction parameters (to enter into `ph_cf` array)
G	Redlich-Kister model (binary)	4.2-36 to 4.2-38	3 constant binary interaction parameters
M	Subregular model (binary)	4.2-10 to 4.2-13	2 binary interaction parameters, each represented with 3 coefficients as $a - b{\cdot}T + c{\cdot}P$
T	Regular model (ternary)	4.2-21 to 4.2-24	1 binary interaction parameter per pair and 1 ternary interaction parameter, each represented with 3 coefficients as $a - b{\cdot}T + c{\cdot}P$
R	Regular model (multicomponent)	4.2-29, 4.2-30	1 binary interaction parameter per pair of components, represented as $a + b{\cdot}T + c{\cdot}P$
V	Van Laar model (multicomponent)	4.2-31 to 4.2-35	1 binary interaction parameter per pair of components, represented as $a + b{\cdot}T + c{\cdot}P$ 1 size parameter per component (end member) in `dc_cf` array
K	Redlich-Kister model (multicomponent)	4.2-41, 4.2-42	4 binary interaction parameters per pair of components, represented as $a + b{\cdot}T + c{\cdot}T{\cdot}\ln(T) + d{\cdot}P$
L	NRTL model (multicomponent)	4.2-50, 4.2-51	2 normalized binary interaction energies per pair of components, represented as $A + B/T + C{\cdot}T + D{\cdot}\ln(T)$ 1 parameter α per pair of components: $E + F{\cdot}(T\text{-}273.15)$
W	Wilson model (multicomponent)	4.2-59, 4.2-60	2 binary interaction energies per pair of components, represented as $\exp[\,A + B/T + C{\cdot}T + D{\cdot}\ln(T)\,]$
U	User-defined		Must be provided as Phase scripts and parameters

Appendix 4-3. Built-in options for mixed non-ideal gas/fluid phases (GEMS v.2.2-PSI).

Code	Model	Equations	Parameters
F	CG (Churakov-Gottschalk) EoS	Section 3	4 to 12 parameters per species, collected from DComp records
P	PRSV (Peng-Robinson-Stryjek-Vera) EoS	4.3-11 to 4.3-17	6 parameters per species, collected from DComp records 1 constant binary interaction parameter per pair (to enter into **ph_cf** array)
E	SRK (Soave-Redlich-Kwong) EoS	4.3.6 to 4.3-10	3 parameters per species, collected from DComp records 1 constant binary interaction parameter per pair (to enter into **ph_cf** array)

Note: Codes should be selected in Phase Wizard upon remake of Phase records. The codes are visible in **p_solt[0,0]** field on Phase screen form (Page 3).

Appendix 4-4. Representation of activities and activity coefficients of aqueous species and water in the output of GEM-Selektor v.2.2.4 and above.

The primal chemical potential of aqueous species is defined in GEM-Selektor as (Karpov et al., 2001; see also eqn. 4.1-1):

$$\upsilon_j = \frac{g_j}{RT} + \ln\frac{1000}{M_w} + \ln\frac{x_j}{X_w} + \ln\gamma_j - \ln\frac{x_{j_w}}{X_w} + 1 - \frac{x_{j_w}}{X_w} \tag{A4-1}$$

and that of water-solvent as:

$$\upsilon_{j_w} = \frac{g_{j_w}}{RT} + \ln\frac{x_{j_w}}{X_w} + \ln\gamma_{j_w} + 2 - \frac{x_{j_w}}{X_w} - \frac{X_w}{x_{j_w}} \tag{A4-2}$$

The non-logarithmic asymmetry correction terms on the right-hand side of these two equations (i.e., $1 - x_{j_w}/X_w$ and $2 - x_{j_w}/X_w - X_w/x_{j_w}$) were derived by Karpov (pers.comm.) by partial differentiation of the total Gibbs energy of asymmetric aqueous solution with molality concentration scale for dissolved species and mole fraction scale for water. These terms become significant at total molalities above 0.7 and greatly speed up convergence of GEM IPM at first iterations after the automatic initial approximation, where the mole fraction of water can be less than 0.001. To our knowledge, these asymmetry correction terms were not discussed in the documentation of other GEM or LMA speciation codes.

The normalized chemical potential of any compound is computed in GEM-Selektor in a quite general way from the dual solution vector u (the chemical potential of elements) and the compound stoichiometry:

$$\eta_j = \sum_{i \in N} a_{ji} u_i \tag{A4-3}$$

This leads to an uniform calculation of activity (fugacity) of the j-th component:

$$\ln a_j = \eta_j - \frac{g_j^o}{RT} \tag{A4-4}$$

regardless of whether the j-th component is actually present in the mass balance or not (Kulik, 2006). This activity will be expressed in the same concentration scale as g_j^o, i.e. molality scale for aqueous species. In the GEM-Selektor, the calculated value is called "dual-thermodynamic activity" and is displayed either as $\log_{10}a_j$ or a_j, depending on the dialog.

Combining eqs (A4-1) and (A4-3) leads to:

$$\ln a_j = \ln\frac{1000}{M_w} + \ln\frac{x_j}{x_{jw}} + \ln\gamma_j + 1 - \frac{x_{j_w}}{X_w} \tag{A4-5}$$

The formal definition of (molal) activity is $\ln a_j = \ln m_j + \ln y_j$. Using the definition of molality $m_j = \frac{1000}{M_w}\frac{x_j}{x_{j_w}}$ (eqn 4.1-4), it follows that $\ln a_j = \ln m_j + \ln\gamma_j + 1 - \frac{x_{j_w}}{X_w}$.

There is some ambiguity where to attach the asymmetry correction term in order to satisfy the formal definition of molal activity ($\ln a_j = \ln m_j + \ln y_j$). In GEM-Selektor v.2.2.3 or older,

this ambiguity was rather arbitrarily resolved by considering the term $1 - x_{j_w}/X_w$ as part of the dual-thermodynamic activity term, displayed as:

$$\ln a_j = \eta_j - \frac{g_j^o}{RT} - \left(1 - \frac{x_{jw}}{X_w}\right) \qquad\qquad \text{(A4-6)}$$

Conversely, the direct multiplication of molality m_j by the internal activity coefficient γ_j calculated from one of eqs (4.1-5) – (4.1-12) would satisfy the definition of molal activity. Likewise, the asymmetry term for water-solvent (eqn A4-2) was also added into its dual-thermodynamic activity term as:

$$\ln a_{jw} = \eta_{jw} - \frac{g_{jw}^o}{RT} - \left(2 - \frac{x_{jw}}{X_w} - \frac{X_w}{x_{jw}}\right) \qquad\qquad \text{(A4-7)}$$

However, some recent tests (provided by B. Lothenbach) at elevated salt concentrations showed that this assignment of asymmetry term to activity was not quite correct. For instance, any equilibrium constant, e.g. a solubility product of a stable phase, should be reproducible from calculated activities independently of ionic strength, both from dual-thermodynamic $\ln a_j$ values or from the products $\ln(m_j\gamma_j)$. Comprehensive tests showed that this was not the case, and recalculated solubility products deviated slightly from the theoretical ones at $I<0.3$ but increasingly with increasing ionic strength.

This led to important corrections since GEM-Selektor version 2.2.4. The only accurate and consistent assignment of the asymmetry term was found to be in the "external" molal activity coefficient $\ln y_j$ and not in the dual-thermodynamic $\ln a_j$ term. For any aqueous species, the (dual-thermodynamic) activity is now displayed strictly as $\ln a_j = \eta_j - g_j^o/RT$ (eqn A4-3) (or exponent of this, or in decimal logarithm, where appropriate). Thus calculated a_j value is at any ionic strength equal (up to 6th digit) to the product $m_j y_j$ where the "external" molal activity coefficient is computed as

$$\ln y_j = \ln \gamma_j + 1 - \frac{x_{j_w}}{X_w} \qquad\qquad \text{(A4-8)}.$$

There is an important consequence of this correction for neutral aqueous species present in the mass balance. Even if the internal activity coefficient is set to $\gamma_{jn} =1$, the external activity coefficient will be equal to $y_{jn} = \exp\left(1 - x_{jw}/X_w\right)$ which is 1 only in pure water. The table below shows numerical values of y_{jn} as function of total dissolved molality m_Σ. These values also give an impression of the bias in $\log_{10}a_j$ and γ_j results displayed by GEMS versions 2.2.3 or older at various dissolved salt concentrations.

m_Σ	0.001	0.01	0.1	0.2	0.4	0.6	1.0	2.0	4.0	6.0	10.0
y_{jn}	1.000	1.000	1.002	1.004	1.007	1.011	1.018	1.035	1.07	1.10	1.165
$\log_{10} y_{jn}$	7.8e-6	7.8e-5	.00078	.0016	.0031	.0046	.0077	.0151	.0292	.0423	.0663

After corrections, the equilibrium constants can be restored (to a numerical precision of ca. 1e-6 in ln scale) either from $\ln a_j$ or from $m_j y_j$ values, or their combination. For the water-

solvent, the dual-thermodynamic activity is now displayed strictly from eqn (A4-3) and the "external" asymmetric mole-fraction activity coefficient as:

$$\ln y_{jw} = \ln \gamma_{jw} + 2 - \frac{x_{j_w}}{X_w} - \frac{X_w}{x_{jw}} \tag{A4-9}.$$

The table below shows values of y_{jw} as a function of m_Σ (assuming that $\gamma_{jw} = 1$).

m_Σ	0.001	0.01	0.1	0.2	0.4	0.6	1.0	2.0	4.0	6.0	10.0
y_{jw}	1.000	1.000	1.000	1.000	.9999	.9999	.9997	.9987	.9952	.9895	.9729
$\log_{10} y_{jw}$	-1e-10	-1.4e-8	-1.4e-6	-5.6e-6	-2.2e-5	-5e-5	.0001	.0005	.0021	.0046	.0119

As follows from eqn (A4-8), there is a small difference between the "external" molal activity coefficient y_j and the "internal" molal activity coefficient γ_j. The former is displayed (as "gamma" in screen forms or as "external activity coefficient" in the "Single thermodynamic system" dialog) in GEMS output together with molality m_j (concentration in the "Single thermodynamic system" dialog) but not used in any internal calculations in GEM IPM, where only the "internal" activity coefficient $\ln \gamma_j$ (displayed as "lnGam" in screen forms) is recalculated at each IPM iteration from eqs (4.1-5) – (4.1-12). The same, but smaller, difference (see eqn A4-9) applies for "external" y_{jw} and "internal" γ_{jw} activity coefficients of water-solvent.

Appendix 4-5. How to reproduce miscibility gaps in GEM-Selektor calculations

The GEM method based on dual thermodynamics has a rigorous theoretical basis – the Karpov-Kuhn-Tucker necessary and sufficient conditions of minimum of the total Gibbs energy function and, hence, of chemical equilibrium speciation in a *multisystem*. The latter is understood as a heterogeneous chemical system that can include simultaneously aqueous electrolyte, gas mixture, many mixtures with two or more end-members, many sorption phases, and any number of stoichiometrically feasible pure substance phases. All multi-component phases may be non-ideal, and the total number of phases initially included in the mass balance may far exceed the number of phases predicted by the Gibbs' phase rule. A unique solution corresponding to the global minimum of total Gibbs energy function is ensured when all phases are ideal or moderately non-ideal.

The GEM IPM algorithm can also produce correct equilibrium speciation in highly non-ideal systems where the *miscibility gaps* are possible within some phase mixing models, but a careful chemical system definition and a special initial approximation are required in such cases.

If the system bulk composition is such that the solid solution phase is likely to exsolve into two mixture phases, but only one such phase is included into the GEM system definition, a metastable solution of the equilibrium problem is *guaranteed* because one phase will be located in the two-phase composition region. Therefore, if a binary solid solution has a miscibility gap then *two* (identical or not) binary mixture phase definitions must be included. If a ternary mixture has a miscibility gap along one binary then two ternary phase definitions need to be included; and so on.

Two cases are now possible. If the equilibrium composition of the mixture falls outside the miscibility gap then the "multiplicated" solution phases will have the same composition (mole fractions of end members), but may be present in different amounts, up to that only one phase is retained. However, in the case when the whole mixture composition falls into a miscibility gap, but all "copy" phases have received the same end member mole fractions after the simplex (automatic) initial approximation, the GEM result will be most probably incorrect because the phase "copies" will have the same (metastable) composition. This problem, however, can be easily solved by application of the following initial approximation procedure.

Suppose there is a binary mixture (e.g. barite $BaSO_4$ and celestite $SrSO_4$) known to have a miscibility gap at low temperatures, manifested by a regular Redlich-Kister parameter $\alpha_0 > 2.0$. In this case, two definitions of solid solution phases, called e.g. "Ba-Celestite" and "Sr-Barite", need to be inserted into the GEM chemical system definition. Thermodynamic data for the end-members and the mixing model equations are identical in both phase definitions. The only difference is that in the first phase definition, the $SrSO_4$ end member must be marked as "major" ('M' in the `PhDCC` column on Page 1 of the Phase window) and $BaSO_4$ as "junior" ('J'), and in the second phase, the $SrSO_4$ end member is marked as "junior" ('J') and $BaSO_4$ as "major" ('M'). These declarations are used only to obtain such automatic initial approximation that the initial composition of all "copy" solution phases fall outside the miscibility gap, before entering the main GEM IPM algorithm.

At the beginning, large positive increments to standard g^o values (17 to 20 kJ mol^{-1}) will be assigned to all "junior" end members in order to make them relatively unstable with respect to the "major" end members. After the simplex initial approximation, both solid solution phases will enter the main GEM IPM process with different compositions, in particular, "junior" end-members with very small mole fractions. At this point, the g^o increments are removed. After the main IPM algorithm has finished, the two (or more) phases will have different binodal compositions only when these are located on both sides of the miscibility gap and both phases co-exist at equilibrium. Note that even in this case, the activity of an end-member in all

"copy" solution phases will be the same, only its mole fraction and activity coefficient different. Otherwise, the IPM will converge either with two phases of the same composition (usually, one of them in trace quantity), or one of these solid-solution phases eliminated. If there is no need to consider a solid solution system with a miscibility gap then it is sufficient to introduce only one solid-solution phase definition into the model chemical system.

Note also that there is no way to reproduce spinodal compositions in GEM forward calculations, unless simulating them with a "less non-ideal" mixing model.

In the region near the critical point, the convergence of GEM IPM was found to be slow and difficult, most probably due to the fact that the $G(x)$ function surface in this area is almost flat. To improve on quality of results, especially near the critical point of the mixed phase, in GEMS-PSI versions starting from 2.1, some additional automatic "no-simplex" IPM refinement loops can be invoked by setting their number (as negative, from -1 to -30) in the `Pa_PRD[0,1]` cell on the "Project:: Numerical and Configuration Settings" window, accessible via "Numerical Controls" button from the "Gibbs Energy Minimization Modelling Project" dialog.