

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

### 4.1. Individual aqueous species

Possible options for built-in calculation 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]:

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

where  $G(x)$  is the total Gibbs energy of the system (in moles);  $g_j$  is the partial molal apparent 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);  $\gamma_j$  is the activity coefficient (in rational scale); and  $M_w = 18.0153 \text{ g mol}^{-1}$  is the gram-formula mass of  $\text{H}_2\text{O}$ . The last three terms on the right side represent the conversion from the practical asymmetrical (i.e. molal) to the rational (i.e. mole fraction) concentration scale.

For the water-solvent ( $\text{H}_2\text{O}$ ), the following approximation of chemical potential is used:

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

the activity coefficient of water  $\gamma_{j_w}$  is by default taken as unity because the mole quantity of water  $x_{j_w}$  will be adjusted on GEM iterations, resulting in both activity  $\exp\left(v_{j_w} - \frac{g_{j_w}}{RT}\right)$

and mole fraction of  $\text{H}_2\text{O}$   $x_{j_w} = \frac{x_{j_w}}{X_w}$  less than unity at non-zero concentration of dissolved salts. Optionally, when the extended Debye-Hückel activity model for aqueous species after Helgeson (1981) is used (see details below), the activity coefficient of water solvent can be calculated from equations given in Pokrovski & Helgeson (1997a). Furthermore, it is possible to write a Phase definition script for calculation of  $\gamma_{j_w}$  if needed.

Activity coefficients of aqueous species ( $\gamma_j$  in eqn 4.1-1) will be re-calculated 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. Equations for aqueous activity coefficients use the *effective ionic strength*  $I$  - a measure of a “concentration of charge”:

$$I = \frac{1}{2} \sum_j^{n(L_w)} m_j z_j^2 \quad (4.1-3),$$

where  $z_j$  is the formula charge of  $j$ -th species and  $m_j$  is its molality (in moles per 1 kg  $\text{H}_2\text{O}$ ),

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

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 physical 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:

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

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

$$A_\gamma = 1.82483 \cdot 10^6 \rho_0^{0.5} (\epsilon_0 \cdot T)^{-1.5} \quad (4.1-6),$$

$$B_\gamma = 50.2916 \rho_0^{0.5} (\epsilon_0 \cdot T)^{-0.5} \quad (4.1-7),$$

where  $\rho_0$  is density ( $g \cdot cm^{-3}$ ) and  $\epsilon_0$  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  $B_\gamma \approx 0.3288$ .

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

$$\log \gamma_j \approx -A_\gamma z_j^2 \sqrt{I} \quad (4.1-8).$$

Extension of the Debye-Hückel theory to account for the polarization of solvent molecules in the vicinity of ionic charges has added a linear term to the extended Debye-Hückel equation:

$$\log \gamma_j = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + \dot{a} B_\gamma \sqrt{I}} + b_\gamma \cdot I \quad (4.1-9),$$

where  $b_\gamma$  is a semi-empirical coefficient, either individual for a given electrolyte ion (in this case, eqn (4.1-9) is also called the Truesdell-Jones equation), or common for all minor aqueous species [Helgeson et al., 1981] in the predominant electrolyte.

The extended equation (4.1-9) is thought to be applicable up to 1-2 molal ionic strength using  $b_\gamma = 0.064$  (NaCl) and it was implemented with common  $b_\gamma$  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  $b_\gamma$  for 4 major background electrolytes (NaCl, KCl, NaOH, KOH) can be used [Oelkers & Helgeson, 1990; Pokrovski & 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 default values 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  $\bar{a}$  seems to be more warranted at higher ionic strength and/or elevated temperatures.

Another built-in function in the GEMS code implements the popular Davies equation:

$$\log \gamma_j = -A_\gamma z_j^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (4.1-10).$$

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 Davies equation is that it uses only the charge as an individual species property; conversely, all ions of the same charge (e.g. +2 and -2) will have identical activity coefficients (this is also true for eqn 4.1-9 with common  $\bar{a}$  parameter).

Neutral aqueous species (dissolved gases and neutral complexes) require a simpler form of activity coefficient that can be assumed a linear function of ionic strength (the "salting-out" effect):

$$\log \gamma_j = b_g \cdot I \quad (4.1-11).$$

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 under an 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 will be automatically collected from DComp or ReacDC records for neutral aqueous species, wherever provided.

Eqn (4.1-11) can also be obtained from eqn (4.1-9) at zero charge ( $z_j = 0$ ), suggesting that the common third parameter  $b_\gamma$  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.

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 activity coefficient of an ion of charge  $z_i$  in solution is given by

$$\log_{10} \gamma_i = -\frac{z_i^2 \cdot A_\gamma \cdot \sqrt{I}}{1 + 1.5 \cdot \sqrt{I}} + \sum_k \varepsilon(i, k) \cdot m_k \quad (4.1-12)$$

where  $A_\gamma$  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  $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  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  $B_\gamma$  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  $T = 298.15 \text{ K}$ .

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

$$\varepsilon(i,k,I) = \varepsilon_1(i,k) + \varepsilon_2(i,k) \cdot \log_{10} I \quad (4.1-13).$$

(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  $\gamma_{neutral}$

$$\log_{10} \gamma_{neutral} = \sum_k \varepsilon(neutral,k) \cdot m_k \quad (4.1-14)$$

significantly differs from unity.

## 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 4-2.

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]:

$$v_j = \frac{g_{j,T,P}}{RT} + \ln \chi_j + \ln \gamma_j \quad (4.2-1),$$

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  $X_\alpha = \sum_j x_j$ ,  $j \in L_\alpha$  is the total mole quantity in the  $\alpha$ -th phase), and  $\gamma_j$  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:

$$\begin{aligned} a_j &= X_j \gamma_j, \quad \gamma_j \neq 1, \quad j \in L_\alpha; \\ \Delta S_d &= -R \sum_j \chi_j \ln a_j; \\ \Delta V_d &\neq 0; \quad \Delta H_d \neq 0; \\ \Delta G_d &= \Delta H_d + RT \sum_j \chi_j \ln a_j \end{aligned}$$

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:

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

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

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

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

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

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

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]):

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

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

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

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  $\chi_j$  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:

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

where  $\chi_1$  and  $\chi_2$  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<sup>-1</sup>), in general, functions of *T* and *P* but not of  $\chi$ :

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

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:

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

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

Eqns (4.2-12) and (4.2-13) comprise the so-called “subregular” or “asymmetric” Margules mixing model. Asymptotically (e.g. at  $\chi_1 \rightarrow 1$  and  $\chi_2 \rightarrow 0$ ), the activity coefficient of the “major” end-member  $\ln \gamma_1 \rightarrow 0$  and that of the “trace” end-member  $\ln \gamma_2 \rightarrow W_2/(RT)$ . Likewise, at  $\chi_1 \rightarrow 0$  and  $\chi_2 \rightarrow 1$ ,  $\ln \gamma_1 \rightarrow W_1/(RT)$  and  $\ln \gamma_2 \rightarrow 0$ . 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:

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

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

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]:

$$\ln \gamma_1 = a\chi_2^2 \quad (4.2-16),$$

$$\ln \gamma_2 = a\chi_1^2 \quad (4.2-17).$$

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

$$W = W_U - TW_S + PW_V = W_H - TW_S \quad (4.2-18).$$

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],

$$a_T \approx \frac{2T_c}{T} \quad (4.2-19),$$

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 following 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):

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

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:

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

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:

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

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

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

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 quaternary case, six binary plus four ternary plus one quaternary 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,...):

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

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

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

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

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

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. Holland & Powell [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:

$$G_{EX} = \sum_{i=1}^{n-1} \sum_{j>i}^n x_i x_j W_{ij} \quad (4.2-29)$$

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

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

in which  $q_i = 1 - x_i$  when  $i = k$  and  $q_i = -x_i$  when  $i \neq k$ . The  $W_{ij}$  are the 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 & 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 & Powell, 2003) for gas mixtures. Holland & 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:



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

where

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

Here,  $\alpha_i$  and  $\alpha_j$  are the size parameters (one per end-member). The  $\phi_i$  terms are size-parameter adjusted mole fractions:

$$\phi_i = \frac{x_i \alpha_i}{\sum_{j=1}^n x_j \alpha_j} \quad (4.2-33)$$

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

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

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

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

Note that  $\alpha_k$  is the size parameter for the end-member for which the activity coefficient is calculated, whereas  $\alpha_i$  and  $\alpha_j$  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]:

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

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

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

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

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:

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

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

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

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 free energy is expressed as:

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

where

$$L_{ij} = {}^0L_{ij} + {}^1L_{ij} (x_i - x_j) + {}^2L_{ij} (x_i - x_j)^2 + {}^3L_{ij} (x_i - x_j)^3 \quad (4.2-42)$$

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.

### 4.3. 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 4-3.

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:

$$PV = nRT \quad (4.3-1)$$

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:

$$\Delta S = -R \ln(P) \quad (4.3-2)$$

$$\Delta G = RT \ln(P) \quad (4.3-3)$$

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:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad (4.3-4)$$

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:

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{0.5} V(V+b)} \quad (4.3-5)$$

Several modifications have been proposed, including the modified Redlich-Kwong (MRK) EoS by Kerrick & Jacobs [1981] developed for the H<sub>2</sub>O-CO<sub>2</sub> system:

$$P = \frac{RT(1+y+y^2-y^3)}{V(1-y)^3} - \frac{a(P,T)}{T^{0.5} V(V+b)} \quad (4.3-6)$$

In this equation,  $y = b/4V$  (constant  $b$  term), whereas the attractive term  $a$  becomes a function of temperature and volume:

$$a(P,T) = c(T) + d(T)/V + e(T)/V^2 \quad (4.3-7)$$

$$z(T) = z_1 + z_2 T + z_3 T^3$$

Holland & Powell [1991] have proposed a further modification of the Redlich-Kwong EoS, which involves the addition of up to 3 virial terms at higher pressures. This compensated Redlich-Kwong (CORK) model has found wide application in metamorphic petrology. It is foreseen to implement one modified Redlich-Kwong EoS model in forthcoming versions of GEM-Selektor.

The Peng-Robinson 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:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)+b(V-b)} \quad (4.3-8)$$

The attractive and repulsive terms are then expressed as:

$$a = (0.457235 R^2 T_C^2 / P_C) \alpha \quad (4.3-9)$$

$$b = 0.077796 RT_C / P_C \quad (4.3-10)$$

$$\alpha = \left[ 1 + \kappa (1 - T_R^{0.5}) \right]^2 \quad (4.3-11)$$

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<sub>2</sub>O required further improvement. One modification, the PRSV

model [Stryjek & Vera, 1986a], has become quite popular in geochemistry and is now implemented in GEM-Selektor. The PRSV model has introduced a further correction term:

$$\kappa = \kappa_0 + \kappa_1 (1 + T_R^{0.5}) (0.7 - T_R) \quad (4.3-12)$$

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

$$\kappa = \kappa_0 + [\kappa_1 + \kappa_2 (\kappa_3 - T_R) (1 - T_R^{0.5})] (1 + T_R^{0.5}) (0.7 - T_R) \quad (4.3-13)$$

The  $\kappa_0$  term is then a function of the Pitzer acentric factor  $\omega$ , a measure of the non-centric nature of the gas molecules:

$$\kappa_0 = 0.378893 + 1.4897153 \omega - 0.17131848 \omega^2 + 0.0196544 \omega^3 \quad (4.3-14)$$

The PRSV model represents  $P$ - $V$ - $T$  properties of many gases, including  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , 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:

$$b_{\text{mix}} = \sum_{j=1}^m x_j b_j \quad (4.3-15)$$

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

$$a_{\text{mix}} = \sum_{j=1}^m \sum_{k=1}^m x_j x_k a_{jk} \quad (4.3-16)$$

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

$$a_{jk} = (a_j a_k)^{0.5} \quad (4.3-17)$$

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

$$a_{jk} = (a_j a_k)^{0.5} (1 - k_{jk}) \quad (4.3-18)$$

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 & 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.

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**Appendix 4-1.** Built-in options for calculation of activity coefficients for aqueous species (GEM-Selektor v.2.2.0 PSI).

Code	Model	Equations	Input parameters
<b>D</b>	Davies	4.1-10	Ionic strength $I$ (eqn 4.1-3, computed automatically on each GEM IPM iteration)
<b>3</b>	Extended Debye-Hückel (Kielland)	4.1-9, 4.1-11	$I$ ; individual ion-size parameter $\bar{a}$ (Kielland, collected from DComp/ReacDC records); common $b_\gamma$ (third) parameter (default 0.064)
<b>H</b>	Extended Debye-Hückel (Helgeson)	4.1-9, 4.1-11	$I$ ; common ion-size parameter $\bar{a} = 3.72$ (parameters from DComp/ReacDC records ignored); common $b_\gamma$ parameter (default 0.064)
<b>2</b>	Debye-Hückel	4.1-5	$I$ ; individual ion-size parameter $\bar{a}$ (Kielland, collected from DComp/ReacDC records);
<b>1</b>	Debye-Hückel limiting law	4.1-8	$I$ – ionic strength only (eqn 4.1-3)
<b>S</b>	SIT (BGS) model	4.1-12	$I$ ; one interaction coefficient per cation-anion pair (to enter into <b>ph_cf</b> array of Phase record)

**Appendix 4-2.** Built-in options for activity coefficients for end members of condensed non-electrolyte solution phases (GEMS v.2.2.0-PSI).

Code	Model	Equations	Interaction parameters (to enter into <b>ph_cf</b> array)
<b>G</b>	Redlich-Kister model (binary)	4.2-36 to 4.2-38	3 constant binary interaction parameters
<b>M</b>	Subregular model (binary)	4.2-10 to 4.2-13	2 binary interaction parameters, each represented with 3 coefficients as $a + b \cdot T + c \cdot P$
<b>T</b>	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 $a + b \cdot T + c \cdot P$
<b>R</b>	Regular model (multicomponent)	4.2-29, 4.2-30	1 binary interaction parameter per pair of components, represented as $a + b \cdot T + c \cdot P$
<b>V</b>	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 <b>dc_cf</b> array
<b>K</b>	Redlich-Kister model (multicomponent)	4.2-41, 4.2-42	4 binary interaction parameters per pair of components, represented as $a + b \cdot T + c \cdot T \cdot \ln(T) + d \cdot P$
<b>U</b>	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.2.2.0-PSI).

Code	Model	Equations	Parameters
<b>F</b>	CG EoS (Churakov and Gottschalk, 2003)	Section 3	4 to 12 parameters per species, collected from DComp records
<b>P</b>	PRSV (Peng-Robinson-Stryjek-Vera)	4.3-8 to 4.3-14	6 parameters per species, collected from DComp records 1 constant binary interaction parameter per pair (to enter into <b>ph_cf</b> 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.** 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<sub>4</sub> and celestite SrSO<sub>4</sub>) 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  $\text{SrSO}_4$  end member must be marked as “major” (‘M’ in the **PHDCC** column on Page 1 of the Phase window) and  $\text{BaSO}_4$  as “junior” (‘J’), and in the second phase, the  $\text{SrSO}_4$  end member is marked as “junior” (‘J’) and  $\text{BaSO}_4$  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  $g^\circ$  values (17 to 20 kJ mol<sup>-1</sup>) 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  $g^\circ$  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 convergence, in GEMS-PSI versions starting from 2.1, some additional automatic “no-simplex” IPM 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.