

# The Extended UNIQUAC model

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## 1. Introduction

This document contains the equations necessary to implement the Extended UNIQUAC thermodynamic model for electrolyte solutions<sup>1</sup> as an activity coefficient model. Once these equations are implemented in a computer program, they have to be combined with a gibbs energy minimization routine in order to perform speciation equilibrium calculations and phase equilibrium calculations.

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<sup>1</sup> Thomsen K., Rasmussen P.: "Modeling of Vapor-Liquid-Solid Equilibria in Gas - Aqueous Electrolyte Systems. Chemical Engineering Science, 54(1999) 1787-1802.

## 2. Residual part of the UNIQUAC gibbs excess energy function

$$\frac{ng_{Residual}^E}{RT} = -\sum_i n_i q_i \ln \left( \sum_j \theta_j \psi_{ji} \right) = -\sum_i MOL(I) \cdot QPAR(I) \cdot \ln TP(I)$$

$$TP(I) = \sum_j \theta_j \psi_{ji}$$

$$TPI(I) = \frac{1}{TP(I)}$$

$$\theta_j = \frac{n_j q_j}{\sum_l n_l q_l} = MOL(J) \cdot QPAR(J) \cdot DENQ = THETA(J)$$

$$\psi_{ji} = \exp \left( -\frac{a_{ji}}{T} \right) = \exp(-AKI \cdot TKI) = PSI(J, I)$$

$$-\frac{a_{ji}}{T} = -AKI \cdot TKI = LPSI(J, I)$$

$$a_{ji} = u_{ji} - u_{ii} = u_{ji}^0 + u_{ji}^t (T - 298.15) - [u_{ii}^0 + u_{ii}^t (T - 298.15)] = AKI$$

$$\left[ \frac{\partial \left( \frac{ng_{Residual}^E}{RT} \right)}{\partial n_i} \right]_{T,P,n_j} = -q_i \ln TP(I) - \sum_j \frac{n_j q_j}{TP(J)} \left[ \frac{\partial TP(J)}{\partial n_i} \right]_{T,P,n_j}$$

$$\left[ \frac{\partial TP(J)}{\partial n_i} \right]_{T,P,n_j} = \sum_k \left( \frac{\partial \theta_k}{\partial n_i} \psi_{kj} + \theta_k \frac{\partial \psi_{kj}}{\partial n_i} \right)$$

$$\frac{\partial \psi_{kj}}{\partial n_i} = 0$$

$$\frac{\partial \theta_k}{\partial n_i} = q_i \frac{\sum_l n_l q_l - n_i q_i}{\left( \sum_l n_l q_l \right)^2} = QPAR(I) \cdot DENQ (1 - THETA(I)) \text{ for } i = k$$

$$\frac{\partial \theta_k}{\partial n_i} = q_i \frac{-n_k q_k}{\left( \sum_l n_l q_l \right)^2} = -QPAR(I) \cdot DENQ \cdot THETA(K) \text{ for } i \neq k$$

$$\begin{aligned}
\left[ \frac{\partial TP(J)}{\partial n_i} \right]_{T,P,n_j} &= -QPAR(I) \cdot DENQ \\
&\left( \sum_k THETA(K) \cdot PSI(K, J) - THETA(I) \cdot PSI(I, J) - (1 - THETA(J)) \cdot PSI(I, J) \right) \\
&= -QPAR(I) \cdot DENQ \cdot (TP(J) - PSI(I, J)) \\
\left[ \frac{\partial \left( \frac{n g_{Residual}^E}{RT} \right)}{\partial n_i} \right]_{T,P,n_j} &= -QPAR(I) \left( \ln TP(I) - \sum_j \frac{MOL(J) \cdot QPAR(J)}{TP(J)} DENQ \cdot (TP(J) - PSI(I, J)) \right) \\
&= -QPAR(I) \left( \ln TP(I) - \sum_j \frac{THETA(J)}{TP(J)} (TP(J) - PSI(I, J)) \right) \\
&= -QPAR(I) \left( \ln TP(I) - \sum_j THETA(J) + \sum_j \frac{THETA(J) \cdot PSI(I, J)}{TP(J)} \right) \\
&= -QPAR(I) \left( \ln TP(I) - 1 + \sum_j \frac{THETA(J) \cdot PSI(I, J)}{TP(J)} \right) \\
&= QPAR(I) \cdot (1 - LNTP(I) - TPT(I)) = \ln \gamma_i^{Residual}
\end{aligned}$$

$$TPT(I) = \sum_j THETA(J) \cdot PSI(I, J) \cdot TPI(J)$$

### 3. Combinatorial part of the UNIQUAC gibbs excess energy function

$$\frac{n g_{Combinatorial}^E}{RT} = \sum_i n_i \ln \frac{\phi_i}{x_i} - \frac{z}{2} \sum_i q_i n_i \ln \frac{\phi_i}{\theta_i} = \sum_i n_i \ln \frac{n \phi_i}{n_i} - \frac{z}{2} \sum_i q_i n_i \ln \frac{\phi_i}{\theta_i} = BCO - ZCO2 \cdot CCO$$

$$\phi_i = \frac{n_i r_i}{\sum_l n_l r_l} = MOL(I) \cdot RPAR(I) \cdot DENR = PHIT(I)$$

$$\frac{\phi_i}{x_i} = \frac{n \phi_i}{n_i} = \frac{n r_i}{\sum_l n_l r_l} = TMOL \cdot RPAR(I) \cdot DENR = PHIT(I)$$

$$\ln(PHIT(I)) = LPHIT(I)$$

$$\left[ \frac{\partial BCO}{\partial n_i} \right]_{T,P,n_j} = \ln \frac{n \phi_i}{n_i} + \sum_j n_j \frac{n_j}{n \phi_j} \frac{\partial (n \phi_j / n_j)}{\partial n_i}$$

$$\frac{\partial (n \phi_j / n_j)}{\partial n_i} = \frac{r_j}{\sum_l n_l r_l} - n r_j \frac{r_i}{\left( \sum_l n_l r_l \right)^2} = \frac{r_j}{\sum_l n_l r_l} \left( 1 - \frac{n r_i}{\sum_l n_l r_l} \right) = \frac{\phi_j}{n_j} \left( 1 - \frac{n \phi_i}{n_i} \right)$$

$$\left[ \frac{\partial BCO}{\partial n_i} \right]_{T,P,n_j} = \ln \frac{n\phi_i}{n_i} + \sum_j n_j \frac{n_j}{n\phi_j} \frac{\phi_j}{n_j} \left( 1 - \frac{n\phi_i}{n_i} \right) = \ln \frac{n\phi_i}{n_i} + \sum_j \frac{n_j}{n} \left( 1 - \frac{n\phi_i}{n_i} \right) = \ln \frac{n\phi_i}{n_i} + 1 - \frac{n\phi_i}{n_i}$$

$$= LPHIT(I) + 1 - PHIT(I)$$

$$\frac{\partial CCO}{\partial n_i} = q_i \ln \frac{\phi_i}{\theta_i} + \sum_j q_j n_j \frac{\partial \ln(\phi_j / \theta_j)}{\partial n_i}$$

$$\frac{\phi_i}{\theta_i} = \frac{n_i r_i}{\sum_l n_l r_l} \frac{\sum_l n_l q_l}{n_i q_i} = \frac{r_i}{q_i} \frac{\sum_l n_l q_l}{\sum_l n_l r_l} = \frac{RPAR(I) \cdot DENR}{QPAR(I) \cdot DENQ} = PHTH(I)$$

$$\ln(PHTH(I)) = LPHTH(I)$$

$$\frac{\partial \ln \frac{\phi_j}{\theta_j}}{\partial n_i} = \frac{\theta_j}{\phi_j} \frac{r_j}{q_j} \left( \frac{q_i}{\sum_l n_l r_l} - \frac{r_i \sum_l n_l q_l}{\left( \sum_l n_l r_l \right)^2} \right) = \frac{\theta_j}{\phi_j} \frac{r_j}{q_j} \frac{1}{\sum_l n_l r_l} \left( q_i - r_i \frac{\sum_l n_l q_l}{\sum_l n_l r_l} \right) = \frac{\theta_j}{\phi_j} \frac{r_j}{q_j} \frac{1}{\sum_l n_l r_l} \left( q_i - q_i \frac{\phi_i}{\theta_i} \right)$$

$$= \frac{\theta_j}{\phi_j} \frac{r_j}{q_j} \frac{q_i}{\sum_l n_l r_l} \left( 1 - \frac{\phi_i}{\theta_i} \right) = \frac{q_i}{\sum_l n_l q_l} \left( 1 - \frac{\phi_i}{\theta_i} \right) = QPAR(I) \cdot DENQ (1 - PHTH(I))$$

$$\frac{\partial CCO}{\partial n_i} = q_i \ln \frac{\phi_i}{\theta_i} + \sum_j q_j n_j \frac{q_i}{\sum_l n_l q_l} \left( 1 - \frac{\phi_i}{\theta_i} \right) = q_i \ln \frac{\phi_i}{\theta_i} + q_i \left( 1 - \frac{\phi_i}{\theta_i} \right) \frac{1}{\sum_l n_l q_l} \sum_j n_j q_j = q_i \left[ \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right]$$

$$= QPAR(I) \cdot (1 + LPHTH(I) - PHTH(I))$$

$$\frac{\partial \frac{ng_{\text{Combinatorial}}^E}{RT}}{\partial n_i} = \ln \frac{n\phi_i}{n_i} + 1 - \frac{n\phi_i}{n_i} - \frac{z}{2} q_i \left[ \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right] =$$

$$= 1 + LPHIT(I) - PHIT(I) - ZCO2 \cdot QPAR(I) \cdot [1 + LPHTH(I) - PHTH(I)] = \ln \gamma_i^{\text{Combinatorial}}$$

#### 4. Excess enthalpy

$$\frac{nh^E}{R} = -T^2 \left[ \frac{\partial (ng^E / RT)}{\partial T} \right]_{P,x} = TK^2 \sum_i MOL(I) \cdot QPAR(I) \cdot TPX(I)$$

$$-\frac{h_i^E}{RT^2} = \left[ \frac{\partial \ln \gamma_i^{\text{Residual}}}{\partial T} \right]_{P,n_j} = -q_i \left( \frac{\partial \ln TP(I)}{\partial T} + \frac{\partial \left( \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \right)}{\partial T} \right)$$

$$\frac{\partial TP(I)}{\partial T} = \sum_j \theta_j \frac{d\psi_{ji}}{dT} = \sum_j \theta_j \psi_{ji} \xi_{ji}$$

$$a_{ji}^t = u_{ji}^t - u_{ii}^t$$

$$\frac{d\psi_{ji}}{dT} = \psi_{ji} \left( \frac{a_{ji}}{T^2} - \frac{a_{ji}^t}{T} \right) = \psi_{ji} \left( \frac{a_{ji} - Ta_{ji}^t}{T^2} \right) = \psi_{ji} \xi_{ji}$$

$$\xi_{ji} = \frac{a_{ji} - Ta_{ji}^t}{T^2} = XI(J, I)$$

$$\frac{\partial \ln TP(I)}{\partial T} = \frac{1}{TP(I)} \frac{\partial TP(I)}{\partial T} = \frac{1}{TP(I)} \sum_j \theta_j \psi_{ji} \xi_{ji} = TPI(I) \sum_j \theta_j \psi_{ji} \xi_{ji} = TPX(I)$$

$$\frac{\partial \left( \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \right)}{\partial T} = \sum_j \left( -\frac{1}{TP(J)^2} \frac{\partial TP(J)}{\partial T} \theta_j \psi_{ij} + \frac{\theta_j \psi_{ij} \xi_{ij}}{TP(J)} \right) = \sum_j \left( -\frac{\theta_j \psi_{ij}}{TP(J)^2} \sum_k \theta_k \psi_{ki} \xi_{ki} + \frac{\theta_j \psi_{ij} \xi_{ij}}{TP(J)} \right)$$

$$= \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left( -\frac{\sum_k \theta_k \psi_{kj} \xi_{kj}}{TP(J)} + \xi_{ij} \right)$$

$$\frac{h_i}{R} = q_i T^2 \left( \frac{\sum_k \theta_k \psi_{ki} \xi_{ki}}{TP(I)} + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} \left( \xi_{ij} - \frac{\sum_k \theta_k \psi_{kj} \xi_{kj}}{TP(J)} \right) \right)$$

$$= QPAR(I) \cdot T^2 \left( TPX(I) + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) \right)$$

$$= QPAR(I) \cdot T^2 (TPX(I) + TPTH(I))$$

$$TPTH(I) = \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) = \sum_j THETA(J) \cdot PSI(I, J) \cdot TPI(J) \cdot (XI(I, J) - TPX(J))$$

## 5. Excess Heat Capacity

$$\frac{nC_p^E}{R} = \frac{d(nh^E / R)}{dT} = \frac{d}{dT} \left( T^2 \left( \sum_i MOL(I) \cdot QPAR(I) \cdot TPX(I) \right) \right)$$

$$= 2T \cdot \sum_i MOL(I) \cdot QPAR(I) \cdot TPX(I) + T^2 \sum_i MOL(I) \cdot QPAR(I) \cdot \frac{dTPX(I)}{dT}$$

$$= 2T \cdot \sum_i MOL(I) \cdot QPAR(I) \cdot TPX(I) + T^2 \sum_i MOL(I) \cdot QPAR(I) \cdot DTPX(I)$$

$$= 2 \cdot TK \frac{nh^E}{R} + TK^2 \sum_i MOL(I) \cdot QPAR(I) \cdot DTPX(I)$$

$$\frac{h_i^E}{R} = -T^2 \left[ \frac{\partial \ln \gamma_i^{\text{Residual}}}{\partial T} \right]_{P, n_j}$$

$$\begin{aligned}
\frac{C_{p,i}^E}{R} &= \left[ \frac{\partial h_i^E / R}{\partial T} \right]_{P,n_j} = -2T \left[ \frac{\partial \ln \gamma_i^{\text{Residual}}}{\partial T} \right]_{P,n_j} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{P,n_j} \\
&= 2T \frac{h_i^E}{RT^2} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{P,n_j} = 2 \frac{h_i^E}{RT} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{P,n_j} \\
&\quad - \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{P,n_j} = QPAR(I) \frac{\partial}{\partial T} \left( TPX(I) + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) \right) \\
\frac{d\xi_{ji}}{dT} &= -2 \frac{a_{ji}}{T^3} + \frac{a'_{ji}}{T^2} + \frac{a''_{ji}}{T} = -2 \frac{a_{ji} - Ta'_{ji}}{T^3} = -2 \cdot TKI \cdot XI(J, I) \\
\frac{\partial TPX(I)}{\partial T} &= \frac{\partial}{\partial T} \left( \frac{1}{TP(I)} \sum_j \theta_j \psi_{ji} \xi_{ji} \right) \\
&= -\frac{1}{TP(I)^2} \frac{\partial TP(I)}{\partial T} \sum_j \theta_j \psi_{ji} \xi_{ji} + \frac{1}{TP(I)} \sum_j \theta_j \left( \frac{\partial \psi_{ji}}{\partial T} \xi_{ji} + \frac{\partial \xi_{ji}}{\partial T} \psi_{ji} \right) \\
&= -TPX(I)^2 + \frac{1}{TP(I)} \sum_j \theta_j \left( \psi_{ji} \xi_{ji}^2 - \frac{2}{T} \xi_{ji} \psi_{ji} \right) = -TPX(I)^2 + \frac{1}{TP(I)} \sum_j \theta_j \left( \psi_{ji} \xi_{ji} \left( \xi_{ji} - \frac{2}{T} \right) \right) \\
&= -TPX(I)^2 + \frac{1}{TP(I)} \sum_j THETA(J) (PSI(J, I) \cdot XI(J, I) (XI(J, I) - 2TKI)) \\
&= -TPX(I)^2 + TPI(I) \sum_j THETA(J) (PSI(J, I) \cdot XI(J, I) (XI(J, I) - 2TKI)) = DTPX(I) \\
&\quad \frac{\partial}{\partial T} \left( \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) \right) \\
&= \sum_j \left[ \frac{\partial}{\partial T} \left( \frac{\theta_j \psi_{ij}}{TP(J)} \right) (XI(I, J) - TPX(J)) + \frac{\theta_j \psi_{ij}}{TP(J)} \frac{\partial}{\partial T} (XI(I, J) - TPX(J)) \right] \\
&\quad \frac{\partial}{\partial T} \left( \frac{\theta_j \psi_{ij}}{TP(J)} \right) = \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) \\
&\quad - \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{P,n_j} = QPAR(I) \frac{\partial}{\partial T} \left( TPX(I) + \sum_j \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J)) \right) \\
&= QPAR(I) \left( DTPX(I) + \sum_j \left[ \frac{\theta_j \psi_{ij}}{TP(J)} (XI(I, J) - TPX(J))^2 + \frac{\theta_j \psi_{ij}}{TP(J)} (-2TKI \cdot XI(I, J) - DTPX(J)) \right] \right) \\
&= QPAR(I) \left( DTPX(I) + \sum_j \left[ \frac{\theta_j \psi_{ij}}{TP(J)} \left( (XI(I, J) - TPX(J))^2 - 2TKI \cdot XI(I, J) - DTPX(J) \right) \right] \right) \\
&= QPAR(I) \left( DTPX(I) + \sum_j \left[ THEATA(J) PSI(I, J) \cdot TPI(J) \cdot \left( (XI(I, J) - TPX(J))^2 - 2TKI \cdot XI(I, J) - DTPX(J) \right) \right] \right)
\end{aligned}$$

$$\begin{aligned}
\frac{C_{p,i}^E}{R} &= 2 \frac{h_i^E}{RT} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual}}}{\partial T^2} \right]_{p,n_j} \\
&= 2 \frac{h_i^E}{RT} + T^2 \cdot QPAR(I) \cdot \\
&\quad \left( DTPX(I) + \right. \\
&\quad \left. \sum_j \left[ THETA(J) \cdot PSI(I, J) \cdot TPI(J) \cdot \left( (XI(I, J) - TPX(J))^2 - 2TKI \cdot XI(I, J) - DTPX(J) \right) \right] \right)
\end{aligned}$$

## 6. Composition derivatives of residual part of activity coefficients

$$\begin{aligned}
\frac{\partial \ln \gamma_i^{\text{residual}}}{\partial n_j} &= \frac{\partial}{\partial n_j} QPAR(I) \cdot (1 - LNTP(I) - TPT(I)) \\
&= -QPAR(I) \left( \frac{\partial LNTP(I)}{\partial n_j} + \frac{\partial TPT(I)}{\partial n_j} \right) \\
\frac{\partial LNTP(I)}{\partial n_j} &= \frac{1}{TP(I)} \frac{\partial TP(I)}{\partial n_j} = -\frac{1}{TP(I)} QPAR(J) \cdot DENQ \cdot (TP(I) - PSI(J, I)) \\
&= QPAR(J) \cdot DENQ \left( \frac{PSI(J, I)}{TP(I)} - 1 \right) \\
\frac{\partial TPT(I)}{\partial n_j} &= \frac{\partial}{\partial n_j} \sum_k \frac{THETA(K) \cdot PSI(I, K)}{TP(K)} \\
&= \sum_k \left( \frac{PSI(I, K) \frac{\partial THETA(K)}{\partial n_j} TP(K) - PSI(I, K) \cdot THETA(K) \frac{\partial TP(K)}{\partial n_j}}{TP(K)^2} \right) \\
&= \sum_k \frac{PSI(I, K)}{TP(K)^2} \left( TP(K) \frac{\partial THETA(K)}{\partial n_j} - THETA(K) \frac{\partial TP(K)}{\partial n_j} \right) \\
&= \sum_k \frac{PSI(I, K)}{TP(K)^2} QPAR(J) \cdot THETA(K) \cdot DENQ (-TP(K) + TP(K) - PSI(J, K)) \\
&\quad + \frac{PSI(I, J)}{TP(J)} QPAR(J) \cdot THETA(J) \cdot DENQ + \frac{PSI(I, J)}{TP(J)} QPAR(J) \cdot (1 - THETA(J)) \cdot DENQ \\
&= QPAR(J) \cdot DENQ \left( \frac{PSI(I, J)}{TP(J)} - \sum_k \left( \frac{THETA(K) \cdot PSI(I, K) \cdot PSI(J, K)}{TP(K)^2} \right) \right)
\end{aligned}$$

$$\frac{\partial \ln \gamma_i^{\text{residual}}}{\partial n_j} = -QPAR(I) \cdot QPAR(J) \cdot DENQ \cdot$$

$$\left( PSI(J, I) \cdot TPI(I) - 1 + PSI(I, J) \cdot TPI(J) - \sum_k THETA(K) \cdot PSI(I, K) \cdot PSI(J, K) \cdot TPI(K)^2 \right)$$

$$\frac{\partial \ln \gamma_i^{\text{Combinatorial}}}{\partial n_j} = \frac{\partial}{\partial n_j} (1 + LPHIT(I) - PHIT(I) - ZCO2 \cdot QPAR(I) \cdot [1 + LPHTH(I) - PHTH(I)])$$

$$\frac{\partial PHIT(I)}{n_j} = \frac{PHIT(I)}{TMOL} (1 - PHIT(J))$$

$$\frac{\partial PHTH(I)}{n_j} = PHTH(I) \cdot QPAR(J) \cdot DENQ \cdot (1 - PHTH(J))$$

$$\frac{\partial \ln \gamma_i^{\text{Combinatorial}}}{\partial n_j} = \frac{(1 - PHIT(J))}{TMOL} - \frac{PHIT(I)}{TMOL} (1 - PHIT(J))$$

$$- ZCO2 \cdot QPAR(I) \cdot [QPAR(J) \cdot DENQ \cdot (1 - PHTH(J)) - PHTH(I) \cdot QPAR(J) \cdot DENQ \cdot (1 - PHTH(J))]$$

$$= \frac{(1 - PHIT(J))}{TMOL} (1 - PHIT(I)) - ZCO2 \cdot QPAR(I) \cdot QPAR(J) \cdot DENQ \cdot (1 - PHTH(J)) [1 - PHTH(I)]$$

## 7. Infinite dilution terms

At infinite dilution all MOL(I) different from MOL(W) are equal to zero  
 All THETA(I) different from THETA(W) are equal to zero THETA(W)=1  
 $TP(I) = PSI(W, I)$

$$TP(W) = PSI(W, W) = 1$$

$$\ln \gamma_i^{\text{Residual}, \infty} = QPAR(I) \cdot (1 - LPSI(W, I) - PSI(I, W))$$

At infinite dilution:

$$PHIT(I) = \frac{RPAR(I)}{RPAR(W)}$$

$$PHTH(I) = \frac{RPAR(I) \cdot QPAR(W)}{QPAR(I) \cdot RPAR(W)}$$

$$\ln \gamma_i^{\text{Combinatorial}, \infty} = 1 + \ln \frac{RPAR(I)}{RPAR(W)} - \frac{RPAR(I)}{RPAR(W)}$$

$$- ZCO2 \cdot QPAR(I) \cdot \left[ 1 + \ln \frac{RPAR(I) \cdot QPAR(W)}{QPAR(I) \cdot RPAR(W)} - \frac{RPAR(I) \cdot QPAR(W)}{QPAR(I) \cdot RPAR(W)} \right]$$

$$\frac{\partial \ln \gamma_i^{\text{Residual}, \infty}}{\partial T} = -QPAR(I) \cdot (XI(W, I) + XI(I, W) \cdot PSI(I, W))$$



$$\begin{aligned}
\frac{nh_i^{E,\infty}}{R} &= TK^2 \sum_{\text{SOLUTES}} \text{MOL}(I) \cdot \text{QPAR}(I) \cdot (\text{XI}(W, I) + \text{PSI}(I, W) \cdot \text{XI}(I, W)) \\
-\frac{h_i^{E,\infty}}{RT^2} &= \left[ \frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T} \right]_{P,n_j} = -\text{QPAR}(I) \cdot (\text{XI}(W, I) + \text{PSI}(I, W) \cdot \text{XI}(I, W)) \\
\frac{h_i^{E,\infty}}{R} &= TK^2 \cdot \text{QPAR}(I) \cdot (\text{XI}(W, I) + \text{PSI}(I, W) \cdot \text{XI}(I, W)) \\
\frac{\partial^2 (\ln \gamma_i^{\text{Residual},\infty})}{\partial T^2} &= \frac{\partial \left( \frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T} \right)}{\partial T} \\
&= -\text{QPAR}(I) \cdot \left( \frac{\partial \text{XI}(W, I)}{\partial T} + \frac{\partial \text{XI}(I, W)}{\partial T} \cdot \text{PSI}(I, W) + \text{XI}(I, W) \cdot \frac{\partial \text{PSI}(I, W)}{\partial T} \right) \\
&= -\text{QPAR}(I) \cdot (-2 \cdot \text{TKI} \cdot \text{XI}(W, I) - 2 \cdot \text{TKI} \cdot \text{XI}(I, W) \cdot \text{PSI}(I, W) + \text{XI}(I, W)^2 \cdot \text{PSI}(I, W)) \\
&= \text{QPAR}(I) \cdot (2 \cdot \text{TKI} \cdot (\text{XI}(W, I) + \text{XI}(I, W) \cdot \text{PSI}(I, W)) - \text{XI}(I, W)^2 \cdot \text{PSI}(I, W)) \\
\frac{C_{pi}^{E,\infty}}{R} &= \left[ \frac{\partial h_i^{E,\infty} / R}{\partial T} \right]_{P,n_j} = -2T \left[ \frac{\partial \ln \gamma_i^{\text{Residual},\infty}}{\partial T} \right]_{P,n_j} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2} \right]_{P,n_j} \\
&= 2T \frac{h_i^{E,\infty}}{RT^2} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2} \right]_{P,n_j} = 2 \frac{h_i^{E,\infty}}{RT} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{\text{Residual},\infty}}{\partial T^2} \right]_{P,n_j} \\
&= 2 \frac{h_i^{E,\infty}}{RT} - TK^2 \cdot \text{QPAR}(I) \cdot (2 \cdot \text{TKI} \cdot (\text{XI}(W, I) + \text{XI}(I, W) \cdot \text{PSI}(I, W)) - \text{XI}(I, W)^2 \cdot \text{PSI}(I, W))
\end{aligned}$$

## 8. The Debye-Hückel contribution

$$\begin{aligned}
\frac{ng_{\text{Debye-Hückel}}^E}{RT} &= -n_w M_w \frac{4A}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right] \\
I &= 0.5 \cdot \sum_{\text{ions}} m_i z_i^2 \\
m_i &= \frac{n_i}{n_w M_w} \\
\frac{dm_i}{dn_w} &= -\frac{n_i}{(n_w M_w)^2} M_w = -\frac{n_i}{n_w^2 M_w} = -\frac{m_i}{n_w} \\
\frac{dI}{dn_w} &= 0.5 \cdot \sum \frac{dm_i}{dn_w} z_i^2 = -0.5 \cdot \sum \frac{m_i}{n_w} z_i^2 = -\frac{0.5}{n_w} \sum m_i z_i^2 = -\frac{I}{n_w} \\
\frac{dI}{dn_i} &= \frac{0.5}{n_w M_w} \cdot z_i^2
\end{aligned}$$

$$\frac{\partial \left( \frac{n g_{Debye-Hückel}^E}{RT} \right)}{\partial n_w} = -M_w \frac{4A}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right] - n_w M_w \frac{4A}{b^3} \left[ \frac{\partial \ln(1 + bI^{1/2})}{\partial n_w} - b \frac{\partial I^{1/2}}{\partial n_w} + \frac{b^2}{2} \frac{\partial I}{\partial n_w} \right]$$

$$\frac{\partial I^{1/2}}{\partial n_w} = \frac{0.5}{I^{1/2}} \frac{\partial I}{\partial n_w} = -\frac{0.5}{I^{1/2}} \frac{I}{n_w} = -\frac{0.5}{n_w} I^{1/2}$$

$$\frac{\partial \ln(1 + bI^{1/2})}{\partial n_w} = \frac{b}{1 + bI^{1/2}} \frac{\partial I^{1/2}}{\partial n_w} = -\frac{0.5b}{1 + bI^{1/2}} \frac{I^{1/2}}{n_w}$$

$$\frac{\partial \left( \frac{n g_{Debye-Hückel}^E}{RT} \right)}{\partial n_w} = -M_w \frac{4A}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} - \frac{0.5bI^{1/2}}{1 + bI^{1/2}} + 0.5bI^{1/2} - \frac{b^2 I}{2} \right]$$

$$= -M_w \frac{2A}{b^3} \left[ 2 \ln(1 + bI^{1/2}) - bI^{1/2} - \frac{bI^{1/2}}{1 + bI^{1/2}} \right]$$

$$= -M_w \frac{2A}{b^3} \left[ 2 \ln(1 + bI^{1/2}) - 1 - bI^{1/2} + 1 - \frac{bI^{1/2}}{1 + bI^{1/2}} \right]$$

$$= -M_w \frac{2A}{b^3} \left[ 2 \ln(1 + bI^{1/2}) - 1 - bI^{1/2} + \frac{1 + bI^{1/2} - bI^{1/2}}{1 + bI^{1/2}} \right]$$

$$= M_w \frac{2A}{b^3} \left[ 1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] = \ln \gamma_w^{DH}$$

$$\frac{\partial \left( \frac{n g_{Debye-Hückel}^E}{RT} \right)}{\partial n_i} = -n_w M_w \frac{4A}{b^3} \left[ \frac{\partial \ln(1 + bI^{1/2})}{\partial n_i} - b \frac{\partial I^{1/2}}{\partial n_i} + \frac{b^2}{2} \frac{\partial I}{\partial n_i} \right]$$

$$\frac{\partial I^{1/2}}{\partial n_i} = \frac{0.5}{I^{1/2}} \frac{\partial I}{\partial n_i} = \frac{0.5}{I^{1/2}} \cdot \frac{0.5}{n_w M_w} z_i^2$$

$$\frac{\partial \ln(1 + bI^{1/2})}{\partial n_i} = \frac{b}{1 + bI^{1/2}} \frac{\partial I^{1/2}}{\partial n_i} = \frac{b}{1 + bI^{1/2}} \cdot \frac{0.5}{I^{1/2}} \cdot \frac{0.5}{n_w M_w} z_i^2$$

$$\frac{\partial \left( \frac{n g_{Debye-Hückel}^E}{RT} \right)}{\partial n_i} = -z_i^2 \frac{A}{b^3} \left[ \frac{b}{1 + bI^{1/2}} \cdot \frac{1}{I^{1/2}} - \frac{b}{I^{1/2}} + b^2 \right] = -z_i^2 \frac{A}{b^2 I^{1/2}} \left[ \frac{1}{1 + bI^{1/2}} - 1 + bI^{1/2} \right]$$

$$= -z_i^2 \frac{A}{b^2 I^{1/2}} \left[ \frac{1 - 1 - bI^{1/2} + bI^{1/2} + b^2 I}{1 + bI^{1/2}} \right] = -z_i^2 \frac{A}{b^2 I^{1/2}} \left[ \frac{b^2 I}{1 + bI^{1/2}} \right] = -z_i^2 \frac{AI^{1/2}}{1 + bI^{1/2}} = \ln \gamma_i^{*,DH}$$

The asterisk on  $\gamma$  signifies the unsymmetric mole fraction activity coefficient. The asterisk is omitted in the following due to the identity of the temperature derivatives.

### Debye-Hückel contribution to excess enthalpy

$$\frac{nh^{E,DH}}{R} = -T^2 \left[ \frac{\partial (ng^E / RT)}{\partial T} \right]_{P,x} = T^2 \frac{dA}{dT} n_w M_w \frac{4}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right]$$

$$-\frac{h_i^{E,DH}}{RT^2} = \left[ \frac{\partial \ln \gamma_i^{DH}}{\partial T} \right]_{P,n_j} = -z_i^2 \frac{I^{1/2}}{1 + bI^{1/2}} \frac{dA}{dT}$$

$$-\frac{h_w^{E,DH}}{RT^2} = \left[ \frac{\partial \ln \gamma_w^{DH}}{\partial T} \right]_{P,n_j} = M_w \frac{2}{b^3} \left[ 1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] \frac{dA}{dT}$$

$$A = \left[ 1.131 + 1.335 \cdot 10^{-3} \cdot (T - 273.15) + 1.164 \cdot 10^{-5} \cdot (T - 273.15)^2 \right] (\text{kg mol}^{-1})^{1/2}$$

$$\frac{dA}{dT} = 1.335 \cdot 10^{-3} + 2 \cdot 1.164 \cdot 10^{-5} T (\text{kg mol}^{-1})^{1/2} K^{-1}$$

$$\frac{h_i^{E,DH}}{R} = T^2 z_i^2 \frac{I^{1/2}}{1 + bI^{1/2}} \frac{dA}{dT} = -\frac{\ln \gamma_i^{*,DH}}{A} T^2 \frac{dA}{dT}$$

$$\frac{h_w^{E,DH}}{R} = -T^2 M_w \frac{2}{b^3} \left[ 1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] \frac{dA}{dT} = -\frac{\ln \gamma_w^{*,DH}}{A} T^2 \frac{dA}{dT}$$

### Debye-Hückel contribution to excess heat capacity

$$\frac{nC_p^{E,DH}}{R} = \frac{d(nh^{E,DH} / R)}{dT} = \frac{d}{dT} \left( T^2 \frac{dA}{dT} n_w M_w \frac{4}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right] \right)$$

$$= \left( \frac{2}{T} \frac{dA}{dT} + \frac{d^2 A}{dT^2} \right) T^2 n_w M_w \frac{4}{b^3} \left[ \ln(1 + bI^{1/2}) - bI^{1/2} + \frac{b^2 I}{2} \right] = \left( \frac{2}{T} \frac{dA}{dT} + \frac{d^2 A}{dT^2} \right) \frac{nh^{E,DH}}{R} / \frac{dA}{dT}$$

$$\frac{d^2 A}{dT^2} = 2 \cdot 1.164 \cdot 10^{-5} (\text{kg mol}^{-1})^{1/2} K^{-2}$$

$$\frac{C_{p,i}^{E,DH}}{R} = \left[ \frac{\partial h_i^{E,DH} / R}{\partial T} \right]_{P,n_j} = -2T \left[ \frac{\partial \ln \gamma_i^{DH}}{\partial T} \right]_{P,n_j} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{DH}}{\partial T^2} \right]_{P,n_j}$$

$$= 2T \frac{h_i^{E,DH}}{RT^2} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{DH}}{\partial T^2} \right]_{P,n_j} = 2 \frac{h_i^{E,DH}}{RT} - T^2 \left[ \frac{\partial^2 \ln \gamma_i^{DH}}{\partial T^2} \right]_{P,n_j}$$

$$\left[ \frac{\partial^2 \ln \gamma_i^{DH}}{\partial T^2} \right]_{P,n_j} = -z_i^2 \frac{I^{1/2}}{1 + bI^{1/2}} \frac{d^2 A}{dT^2}$$

$$\left[ \frac{\partial \ln \gamma_w^{DH}}{\partial T} \right]_{P,n_j} = M_w \frac{2}{b^3} \left[ 1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] \frac{d^2 A}{dT^2}$$

$$\frac{C_{p,i}^{E,DH}}{R} = 2 \frac{h_i^{E,DH}}{RT} + T^2 z_i^2 \frac{I^{1/2}}{1 + bI^{1/2}} \frac{d^2 A}{dT^2} = \left( \frac{2}{T} + \frac{d^2 A}{dT^2} / \frac{dA}{dT} \right) \frac{h_i^{E,DH}}{RT}$$

$$\frac{C_{p,w}^{E,DH}}{R} = 2 \frac{h_w^{E,DH}}{RT} - T^2 M_w \frac{2}{b^3} \left[ 1 + bI^{1/2} - \frac{1}{1 + bI^{1/2}} - 2 \ln(1 + bI^{1/2}) \right] \frac{d^2 A}{dT^2} = \left( \frac{2}{T} + \frac{d^2 A}{dT^2} / \frac{dA}{dT} \right) \frac{h_w^{E,DH}}{RT}$$

### Composition derivatives of Debye-Hückel contribution to activity coefficients

$$\begin{aligned} \frac{\partial \ln \gamma_i^{*,DH}}{\partial n_w} &= -z_i^2 A \frac{\partial}{\partial n_w} \frac{I^{1/2}}{1+bI^{1/2}} = -z_i^2 A \frac{(1+bI^{1/2}) \frac{\partial}{\partial n_w} I^{1/2} - bI^{1/2} \frac{\partial}{\partial n_w} I^{1/2}}{(1+bI^{1/2})^2} = -z_i^2 A \frac{\frac{\partial}{\partial n_w} I^{1/2}}{(1+bI^{1/2})^2} \\ &= -z_i^2 A \frac{-\frac{0.5}{n_w} I^{1/2}}{(1+bI^{1/2})^2} = -\frac{0.5}{(1+bI^{1/2})n_w} \ln \gamma_i^{*,DH} \end{aligned}$$

$$\begin{aligned} \frac{\partial \ln \gamma_i^{*,DH}}{\partial n_j} &= -z_i^2 A \frac{\partial}{\partial n_j} \frac{I^{1/2}}{1+bI^{1/2}} = -z_i^2 A \frac{(1+bI^{1/2}) \frac{\partial}{\partial n_j} I^{1/2} - bI^{1/2} \frac{\partial}{\partial n_j} I^{1/2}}{(1+bI^{1/2})^2} = -z_i^2 A \frac{\frac{\partial}{\partial n_j} I^{1/2}}{(1+bI^{1/2})^2} \\ &= -z_i^2 A \frac{\frac{0.5}{I^{1/2}} \cdot \frac{0.5}{n_w M_w} z_j^2}{(1+bI^{1/2})^2} = -\frac{A z_i^2 z_j^2}{4n_w M_w I^{1/2} (1+bI^{1/2})^2} \end{aligned}$$

$$\begin{aligned} \frac{\partial \ln \gamma_w^{DH}}{\partial n_w} &= M_w \frac{2A}{b^3} \left[ \frac{\partial}{\partial n_w} (1+bI^{1/2}) + \frac{1}{(1+bI^{1/2})^2} \frac{\partial}{\partial n_w} (1+bI^{1/2}) - \frac{2}{1+bI^{1/2}} \frac{\partial}{\partial n_w} (1+bI^{1/2}) \right] \\ &= M_w \frac{2A}{b^3} \left[ 1 + \frac{1}{(1+bI^{1/2})^2} - \frac{2}{1+bI^{1/2}} \right] \frac{\partial}{\partial n_w} (1+bI^{1/2}) = M_w \frac{2A}{b^3} \frac{b^2 I}{(1+bI^{1/2})^2} bI^{1/2} \frac{-1}{2n_w} = -\frac{M_w A I^{3/2}}{n_w (1+bI^{1/2})^2} \end{aligned}$$

$$\begin{aligned} \frac{\partial \ln \gamma_w^{DH}}{\partial n_j} &= M_w \frac{2A}{b^3} \left[ \frac{\partial}{\partial n_j} (1+bI^{1/2}) + \frac{1}{(1+bI^{1/2})^2} \frac{\partial}{\partial n_j} (1+bI^{1/2}) - \frac{2}{1+bI^{1/2}} \frac{\partial}{\partial n_j} (1+bI^{1/2}) \right] \\ &= M_w \frac{2A}{b^3} \left[ 1 + \frac{1}{(1+bI^{1/2})^2} - \frac{2}{1+bI^{1/2}} \right] \frac{\partial}{\partial n_j} (1+bI^{1/2}) = M_w \frac{2A}{b^3} \frac{b^2 I}{(1+bI^{1/2})^2} b \frac{0.5}{I^{1/2}} \cdot \frac{0.5}{n_w M_w} z_j^2 \\ &= \frac{A I^{1/2} z_j^2}{2n_w (1+bI^{1/2})^2} \end{aligned}$$