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GIBBS FREE ENERGY-BASED OBJECTIVE FUNCTION FOR ELECTROLYTE ACTIVITY COEFFICIENT MODELS

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Abstract: This paper proposes Gibbs free energy-based objective functions in parameter fitting of activity coefficient and specific heat capacity of ions. The activity coefficient parameters are fitted through the averaged squared error between Gibbs free energy calculated by using the measured activity coefficient data and that by using the model equation. The standard-state heat capacity parameters of ions are fitted through the minimization of the average squared error between Gibbs free energy of dissolution calculated through the saturation activity over a temperature range and that calculated through the standard state chemical potential as a function of temperature via standard state specific heat. This methodology is tested with Bromley and Pitzer models. The proposed methodology reduces the need of experiments and avoids the uncertainty of extrapolation to infinite dilution when determining standard state specific heat of ions. The proposed methodology provides more accurate solubility estimates than the common methodology, except for low temperatures in Pitzer model where the common approach is somehow slightly more accurate. In addition, the proposed methodology enables accurate modeling with limited data: solubility over temperature range, activity coefficient data up to some concentrated range not covering saturation and no ionic specific heat data.

keywords: thermodynamics, electrolyte system, aqueous thermodynamics, objective function, Gibbs

24 free energy, Bromley's method, Pitzer model

25

26 **1. Introduction**

27 Aqueous thermodynamics has an important role in chemical engineering. Many chemical processes
28 involve dissociated solutes in water, such as water purification, mining industry and the currently
29 investigated biorefinery processes. For instance, more accurate thermodynamic modeling would be
30 needed in biorefinery processes, such as the recovery of carboxylic acids or salts through partial wet
31 oxidation of black liquor ¹. The thermodynamics provide equilibrium states and basis for mass
32 balances during process design. The accuracy of thermodynamic models plays critical role in design
33 and evaluation of processes. In aqueous thermodynamics, the accuracy close-to saturation conditions
34 are crucial since the errors would affect the calculated mass balances. However, despite the sharing
35 the same core with the non-electrolyte phase equilibrium thermodynamics, aqueous thermodynamics
36 has differences that can differentiate the methodology and data collection for the model development.
37 As a result, the methodology of aqueous thermodynamics model development should have high
38 accuracy at especially close-to-saturation conditions and facilitate the data collection without
39 compromising from fundamental principles.

40

41 Aqueous electrolyte thermodynamics has the same core basis on thermodynamic laws and
42 equilibrium criteria of the non-electrolyte phase equilibrium thermodynamics: minimum Gibbs free
43 energy, uniform temperature and pressure, and chemical potential of each compound being equal in
44 all phases. Thermodynamic models of multicomponent equilibrium are based on the minimization of
45 Gibbs free energy: this is valid for any thermodynamic model including phase equilibrium, reaction
46 equilibrium and the speciation of ions in aqueous systems. The Gibbs free energy function involves

the standard state chemical potentials, temperature dependences through standard state specific heat expressions, activity coefficients and the composition. The standard state properties of compounds correspond to the pure compound properties for liquid, solid and non-electrolyte solutions. On the other hand, electrolyte thermodynamic model development requires the determination of activity coefficient model and temperature-dependent specific heat expressions of ions.

52

Aqueous electrolyte thermodynamics differs from the non-electrolyte thermodynamics in three aspects of activity coefficient models as well: the convention of activity coefficients, the forms of activity coefficient models, and parameter fitting. The convention is symmetrical for water ($\gamma_w \rightarrow 1$ when mole fraction of water approaches one) and unsymmetrical for the ions ($\gamma_i \rightarrow 1$ under infinite dilution: in molality scale, $m_i \rightarrow 0$), rather than being symmetrical for all components. In other words, the standard state of an electrolyte solution is the hypothetical ideal solution with unit molality. Thus, the determination of standard-state properties of ions require different methods from measuring pure compound properties: activity coefficient and specific heat are in the scope of this study. Regarding the forms of models, conventional thermodynamics can use both correlative (parameter fitting by using data) and predictive (based on molecular structure and quantum chemistry) models whereas aqueous thermodynamics mostly use correlative models due to molecular level complexity of ions in water. Based on the molecular level assumptions, correlative models include Margules models and local composition models ². For aqueous electrolyte thermodynamics, the local composition theory assumes that the distribution of molecules or ions around each molecule depends on sizes and mole fractions. Long-range electrostatic interactions, that are dominant in dilute solutions, are described by Debye-Hückel model. However, concentrated solutions lead to short-range interactions as well, for which some empirical models were developed (such as Bromley and Meissner ³) or the local composition theory-based models were adapted (e.g., e-NRTL, Pitzer and extended UNIQUAC ⁴).

71 The local composition models include ion-specific size and/or ion pair-specific interaction parameters
72 to be fitted by using data. These models can accurately be fitted for high concentrations. However,
73 the model complexity leads to the need of large amount of data of binary and tertiary water-salt
74 systems. In contrast, the empirical models have less complexity due to some simplifications. For
75 instance, Bromley model has one parameter to be fitted for a binary water-salt system. In
76 multicomponent cases, this model considers all ions as whole as a single complex salt by combining
77 salt-water binary interaction parameters of all salts involved in the system to a single parameter. On
78 the other hand, due to the simplifications, these models have limitations regarding the valid range of
79 concentrations and are less accurate than the local composition models. As a result, the choice of
80 activity coefficient model depends on the desired balance between accuracy and complexity.

81

82 Parameter fitting introduces a major difference between non-electrolyte thermodynamics and aqueous
83 electrolyte thermodynamics. When developing an activity coefficient model, the model parameters
84 are fitted to the measured data. However, in aqueous electrolyte thermodynamics, it is hardly possible
85 to change only one ion amount when collecting data: the amount of ions with the opposite sign would
86 change as well because of the electroneutrality. Therefore, the activity coefficients of ions are
87 expressed as the mean molal activity coefficient in practice, rather than individual activity coefficient
88 of ions, due to the influence of electroneutrality phenomenon on the data collection process. The ionic
89 activity coefficients are measured by potentiometric methods, such as Harned cell ⁵: calculating the
90 activity by using the measured electromotive force values, thus providing the mean activity
91 coefficient of ions. Thomsen (2009) summarized the activity coefficient measurement methods ⁴. In
92 addition, Rockwood (2015) described the method of measuring individual ionic activity coefficient
93 through contact potentials of two sides of a cell separated by a metal plate: one side with the
94 investigated concentration and other side as the reference ⁶. However, the method requires

95 measurements of contact potentials at series of concentrations in the reference side and extrapolation
96 to zero concentration, i.e. numerous experiments for each data point and uncertainty of extrapolation.
97 Nevertheless, individual ionic activity coefficient could play a critical role in the applications where
98 pH is important since pH measurement determines the activity of hydrogen ion (not concentration) ⁶.
99 In addition, individual ionic activity coefficient can be useful in the special cases where
100 electroneutrality is broken during a transient stage, e.g., electrospray ionization in mass spectrometry,
101 charging the plates of a capacitor and some biological functions based on unbalanced charge transfer
102 between cellular compartments separated by membranes ⁶. Then, the activity coefficient models
103 express the individual ionic activity coefficient and mean molal activity coefficient as a function of
104 composition and temperature. Since more data is available in mean molal activity coefficient due to
105 practical measurement, the mean molal activity coefficient is involved in the electrolyte models and
106 the interaction parameters are fitted based on this coefficient.

107

108 The objective function in parameter fitting has a significant role on the accuracy of the model;
109 therefore, it should be defined properly based on the use of activity coefficient correlation in the phase
110 equilibrium model. Activity coefficient alone has no meaning in terms of thermodynamic properties.
111 Instead, activity coefficient composes the total Gibbs free energy together with composition and
112 temperature. The multi-component equilibrium models determine the speciation based on minimizing
113 the total Gibbs free energy of the system. For instance, the error in activity coefficient around the
114 saturation concentration is more critical compared to the error in a dilute solution since it affects the
115 solubility estimate and the speciation result. Thus, defining objective functions based on the total
116 Gibbs free energy would spontaneously provide the proper weighting factors of activity coefficient
117 values with respect to temperature and composition. However, activity-coefficient based objective
118 functions (e.g. least squared error in natural logarithm of mean activity coefficient as shown in

Equation 1) are very common in the literature:

$$OF = \frac{1}{NP} \sum_1^{NP} (\ln \gamma_{\pm, meas.}^m - \ln \gamma_{\pm, calc.}^m)^2 \quad \text{and } NP: \text{ the number of data points} \quad (1)$$

where $\gamma_{\pm, meas.}^m$ represents the mean molal activity coefficient obtained through experimental measurements and $\gamma_{\pm, calc.}^m$ represents the calculated value through an activity coefficient model. Alternatively, Thomsen et al. (1996) used an objective function that includes the relative squared error of activity coefficients, heat of dilution, specific heat and saturation indexes in order to address the limitations on available activity coefficient data by using different types of data in parameter fitting⁷.

Another important aspect required for multicomponent models is to determine the temperature-dependence parameters of the standard-state specific heats of ions. On the other hand, it is impossible to measure the standard-state specific heat of ions due to the standard state of hypothetically ideal solution with unit molality. The current determination of standard-state heat capacities of ions involves measuring the apparent molar heat capacity in dilute solutions and extrapolation of these measurements to infinite dilution^{4, 8, 9}. However, this approach requires numerous experiments for each salt and each temperature condition. As a result, temperature dependence of standard-state heat capacities of ions is rarely available in the literature: measurement data are available only for few salts, such as sodium chloride, but unavailable for many salts, such as the salts of carboxylic acids.

This study proposes new approaches in parameter fitting for activity coefficient models and temperature dependence of standard state specific heat. For activity coefficient model parameters, this paper introduces the objective function as the least squared error between Gibbs free energy values calculated by using measured and predicted values of activity coefficients. For specific heat,

142 this study introduces parameter fitting based on the Gibbs free energy of dissociation at the saturation
 143 concentration. Then, in order to determine temperature-dependent standard state specific heat of ions,
 144 it would be sufficient to measure the concentration and activity coefficients at saturation points at
 145 different temperatures, rather than numerous measurements with dilute solutions and extrapolations.
 146 This paper illustrates the proposed approaches with Bromley model as simple one and Pitzer model
 147 as advanced model. The results are composed of parameter fitting for activity coefficients, solubility
 148 estimates and parameter fitting for standard state specific heat of ions.

149

150 **2. Model Development with the Gibbs Free Energy-Based Objective Functions**

151 The equilibrium state is determined through the minimization of total Gibbs free energy function in
 152 Equation 2 with respect to the composition, on the constraints of component mass balances as in
 153 Equation 3 assuming complete dissociation to ions when dissolving:

$$154 \quad G = n_w \mu_w + \sum_i^{ions} n_i \mu_i \quad (2)$$

$$155 \quad n_{i \text{ total}} = n_{i \text{ ion}} + n_{i \text{ in solid}} \quad (3)$$

156 where n_w and n_i represents the mole numbers of water and the dissolved ion i , and μ_w and μ_i represents
 157 the chemical potential of water and the dissolved ion i . Equation 4 and Equation 5 show the chemical
 158 potential of water and each ion i :

$$159 \quad \mu_i = \mu_i^o + RT \ln(m_i \gamma_i) \quad (4)$$

$$160 \quad \mu_w = \mu_w^o + RT \ln(x_w \gamma_w) \quad (5)$$

161 where μ_i^o and μ_w^o represent the standard state chemical potential of the ion i and water, m_i represents
 162 the molal concentration of the ion i , x_w represents the mole fraction of water, γ_i is the molal activity
 163 coefficient of the ion i and γ_w is the activity coefficient of water in mole fraction scale. The standard
 164 state is defined as unit molal ideal solution. Consequently, the standard state chemical potential of
 165 water corresponds to molar Gibbs free energy of formation of pure water and that of an ion

corresponds to the partial molar Gibbs free energy at the standard state. The standard state chemical potentials are listed in NBS tables under 0.1 MPa and 298.15 K ⁸. The temperature dependence is expressed through specific heat capacity as shown in Equation 6:

$$\mu_i^o = \Delta_f H_i^o(298.15 K) + \int_{298.15 K}^T c_{pi}^o dT - T \left(\Delta_f S_i^o(298.15 K) + \int_{298.15 K}^T c_{pi}^o d \ln T \right) \quad (6)$$

which is expressed in the similar way for water and solid salt as well. It should be noted that NBS tables provide entropy value of the species, not the entropy difference of formation; therefore, $\Delta_f S_i^o(298.15 K)$ values must be calculated through formation reaction of each species from the stable elements. The equilibrium constants are derived from the criterion of a species having equal chemical potential in each phase at saturation conditions. The chemical potential of solid, i.e. the Gibbs free energy of formation of the solid, is equal to the sum of the chemical potential of dissociation products. For instance, for a salt-water binary system, Equation 7 shows an example of an anhydrous salt dissociation, and Equation 8 and Equation 9 shows the equilibrium criterion and equilibrium constant:

$$\mu_{C_c A_{a(s)}}^o = c \left[\mu_{C(aq)}^o + RT \ln \left(m_{C(aq)} \gamma_{C(aq)} \right) \right] + a \left[\mu_{A(aq)}^o + RT \ln \left(m_{A(aq)} \gamma_{A(aq)} \right) \right] \quad (8)$$

$$K = \exp \left(-\frac{\Delta G_r^o}{RT} \right) = \left(m_{C(aq)} \right)^c \left(m_{A(aq)} \right)^a \left(\gamma_{\pm}^m \right)^{a+c} \text{ and } \Delta G_r^o = c \mu_{C(aq)}^o + a \mu_{A(aq)}^o - \mu_{C_c A_{a(s)}}^o \quad (9)$$

where $\mu_{C(aq)}^o$ and $\mu_{A(aq)}^o$ represent the standard state chemical potential of cation C and anion A, $\mu_{C_c A_{a(s)}}^o$ represents the standard state chemical potential of solid salt (equal to Gibbs free energy formation of the salt), $m_{A(aq)}$ and $m_{C(aq)}$ represents the molal concentrations, and $\gamma_{C(aq)}$ and $\gamma_{A(aq)}$ represent the molal activity coefficients of cation and anion.

185

The thermodynamic model development for aqueous electrolyte systems has three steps: selection or development of an activity coefficient model, fitting the activity coefficient model parameters and fitting the temperature dependence of specific heat of ions. The selection of activity coefficient model depends on the compromise between the desired accuracy and computational complication, as

190 mentioned before. This study illustrates the calculations with an empirical model and a local
191 composition theory-based model, namely Bromley and Pitzer models. Regarding the accuracy, even
192 though it is important to have a model accurate from 0 to saturation concentration, the errors in dilute
193 solutions do not affect the speciation conclusion whereas the errors in close-to-saturation solutions
194 becomes more critical in terms of speciation result. For instance, 0.1 m or 1 m NaCl in water will be
195 concluded as all NaCl being dissolved, even though the calculated values of activity coefficients and
196 Gibbs free energy can slightly differ. However, if the concentration is close to saturation, those slight
197 differences become more critical since it will affect the calculated solid and dissolved amounts, thus
198 affecting mass balance of a process under investigation. On the other hand, some salts can be
199 concentrated and some can be dilute in multi-component systems. Therefore, the model should be
200 very accurate at high concentrations and at least fairly accurate for dilute concentrations. In other
201 words, even a small compromise in accuracy of dilute solutions is acceptable with the award of
202 remarkable improvement in accuracy of high concentrations. In the thermodynamic model
203 development, the objective functions in the parameter fitting steps can adjust higher weights for the
204 errors of high concentrations. Consequently, this study proposes Gibbs free energy-based objective
205 functions in the parameter fitting steps, i.e. based on the ultimate property calculated with activity
206 coefficients and specific heats. These steps should be applied separately in order to provide
207 independent fitting of specific heat and activity coefficient model parameters, rather than
208 compensation among these parameters.

209

210 The activity coefficient parameters are determined by using mean activity coefficient data under
211 various concentrations and temperature conditions. The objective function in data fitting is based on
212 the squared error in the total Gibbs free energy in each datum. The total Gibbs free energy of the
213 system is calculated as shown in Equation 2-6 and the objective function is:

$$OF_Y = \frac{1}{NP} \sum_d^{NP} (G_{meas.} - G_{calc.})^2 \quad (10)$$

$$OF_Y = \frac{1}{NP} \sum_d^{NP} [m_w (RT \ln \gamma_{w,meas.} - RT \ln \gamma_{w,calc.}) + \sum_i^{ions} m_i (RT \ln \gamma_{\pm,meas.}^m - RT \ln \gamma_{\pm,calc.}^m)]^2 \quad (11)$$

$$OF_Y = \frac{1}{NP} \sum_d^{NP} \sum_i^{ions} (m_i RT \ln \gamma_{\pm,meas.}^m - m_i RT \ln \gamma_{\pm,calc.}^m)^2 \quad (12)$$

$$OF_Y = \frac{1}{NP} \sum_d^{NP} (m_w RT \ln \gamma_{w,meas.,d} - m_w RT \ln \gamma_{w,calc.,d})^2 \quad (13)$$

where m_w represents the moles of water per kg (equal to 55.51), $G_{meas.}$ represents the total Gibbs free energy of the system when the measured activity coefficients are used and $G_{calc.}$ represents the total Gibbs free energy when the calculated activity coefficients are used in the model. Equation 11 is obtained by substituting the chemical potential expressions to Equation 10. Thus, Equation 11 presents the proposed objective function for fitting both water activity and mean molal ion activity. In case of fitting only mean activity coefficient of ions, the objective function can be expressed as in Equation 12. Similarly, Equation 13 presents the objective function in case of fitting only water activity. In case of fitting individual ionic activity coefficient, Equation 12 can be adapted as the deviation of Gibbs free energy resulting from only the individual ion: including a single ion and using individual activity coefficient of the involved ion. The scope of this paper covers the parameter fitting of mean molal activity coefficients.

Water activity is another aspect of multicomponent thermodynamic models as in Equation 2-6. Water activity is usually determined through vapor pressure measurements with varying solute concentration and temperature. Since water activity and mean activity coefficient of ions are linked through Gibbs-Duhem equation, activity coefficient models include expressions for water activity as well by using the same interaction parameters. For instance, Pitzer interaction coefficients of sodium acetate were determined through fitting the parameters to water activity data obtained with vapor pressure measurements¹⁰⁻¹¹. However, Bromley's method includes an empirical method for water activity with B parameter determined by fitting only to mean activity coefficient of ions: water

activity calculations of Bromley method becomes inaccurate with increasing concentration. Nevertheless, the literature data usually includes both osmotic coefficients and mean molal activity coefficients of ions, which can be used together in parameter fitting step. Consequently, this study uses Equation 12 (only the mean activity coefficient) for fitting Bromley model and Equation 11 (both water activity and the mean activity coefficient) for fitting Pitzer model.

243

Another core step of thermodynamic modelling is the determination of temperature-dependent standard state specific heat expression for ions. This study proposes fitting the parameters for specific heat by using saturation data. For each salt, specific heat parameters are to be fitted by minimizing the squared error of Gibbs free energy of dissociation calculated by saturation activity data and standard-state chemical potentials. The Gibbs free energy of dissociation can be calculated by using saturation concentration and activity coefficient data under various temperature conditions as in Equation 14. This represents the measured Gibbs free energy of dissociation. In addition, Gibbs free energy of dissociation can be calculated by using chemical potential expressions as shown in Equation 15 and Equation 16. This represents the calculated Gibbs free energy of dissociation. Specific heat for water is expressed as in Equation 17, of which the parameters are listed in DIPPR 801, and specific heat for ions is expressed as in Equation 18 ⁷. Finally, the sum of the temperature-dependent specific heat parameters of ions is fitted through minimization of the objective function in Equation 19. Then, in order to determine the specific heat parameters of individual ions, the specific heat of hydrogen ion is assumed to be zero at any temperature as the reference and that of other ions can be calculated relative to hydrogen ion specific heat by using the data of an acid as well.

$$\Delta G_{r\text{ meas.}}^o = -RT \ln \left(m_{C(aq)}^c m_{A(aq)}^a (\gamma_{\pm}^m)^{a+c} \right) \quad (14)$$

$$\Delta G_{r\text{ calc.}}^o = c\mu_{C(aq)}^o + a\mu_{A(aq)}^o - \mu_{C_a(s)}^o \quad (15)$$

$$\mu_i^o = \Delta_f H_i^o(298.15\text{ K}) + \int_{298.15\text{ K}}^T c_{pi}^o dT - T \left(\Delta_f S_i^o(298.15\text{ K}) + \int_{298.15\text{ K}}^T c_{pi}^o d \ln T \right) \quad (16)$$

$$c_{p_w}^o = a_w + b_w T + c_w T^2 + d_w T^3 + e_w T^4 \quad (17)$$

$$c_{p_i}^o = a_i + b_i T + \frac{c_i}{T-200} \quad (18)$$

$$OF_{cp} = \frac{1}{NP} \sum_d^{NP} (\Delta G_{r_{meas.}}^o - \Delta G_{r_{calc.}}^o)^2 \quad (19)$$

265

266 As a typical case, if the available data involves the solubility and activity coefficient up to some
 267 certain molality (rather than up to saturation), the measured saturation molality and the estimated
 268 activity coefficient can be used in Equation 14. However, extrapolating the calculations far beyond
 269 the data range can affect the accuracy of the activity coefficients. Nevertheless, activity coefficient
 270 data up to saturation eliminates the need of numerous apparent molal heat capacity measurements in
 271 dilute solutions as well as ensuring the accuracy of activity calculations.

272

273 After fitting the parameters of activity coefficient and standard state specific heat of ions, the
 274 thermodynamic model is constructed as in Equation 2-6 for speciation calculations. This model is
 275 solved by minimizing the Gibbs free energy with respect to the composition.

276

277 **3. Results and Discussion**

278 The proposed objective function is compared with the typical one shown in Equation 1 by using the
 279 same set of data specified in Table 1. Table 1 shows the references of the data used in this study as
 280 well as the remarks and concentration and temperature ranges. Further data about salt solutions can
 281 be collected from a databank listing the literature references¹². The comparison involves the accuracy
 282 of parameter fitting for activity coefficient models, the determination of temperature-dependent
 283 standard state specific heat expressions and solubility estimates. Bromley and Pitzer models used in

284 this comparison are described in Appendix 1 ¹³⁻¹⁴.

285 Table 1. The list of salts and data used for parameter fitting in this study

Salt	Reference for data	Remarks
NaCl	$\gamma_{\pm}^m$ and γ_w : Clarke and Glew (1985) ¹⁵ Solubility: Clarke and Glew (1985) ¹⁵ K_{sp} : Saturation data and Equation 9 $C_{p\ NaCl(aq)}$: Clarke and Glew (1985) ¹⁵	m: 0 to saturation T: 273.15 to 373.15 K
KCl	$\gamma_{\pm}^m$ and γ_w : Marques et al. (2006) ¹⁶ , Hamer and Wu (1972) ¹⁷ , Snipes et al. (1975) ¹⁸ Solubility: Yaws (2012) ¹⁹ K_{sp} : Solubility data and estimated activity coefficient substituted to Equation 9	m: 0 to saturation at 298.15 K, 0 to 4 molal at other temperatures T: 283.15 to 353.15 K data: only mean molal activity coefficient at some points and both activity and osmotic coefficients at some points
KBr	$\gamma_{\pm}^m$ and γ_w : Hamer and Wu (1972) ¹⁷ , Robinson and Stokes (1959) ²⁰ Solubility: Yaws (2012) ¹⁹ K_{sp} : Solubility data and estimated activity coefficient substituted to Equation 9	m: 0 to 5.5 molal at 298.15 K, 0 to 4 molal at other temperatures T: 298.15 K and 333.15-373.15 K

286

287 3.1 Parameter Fitting for Activity Coefficient Models

288 The parameter fitting step involves the determination of model parameters by using the activity
 289 coefficient data. The procedure might depend on the selected activity coefficient model and available
 290 data. For Bromley model, the parameters of temperature dependence of interaction parameters (B^* ,
 291 B_1 , B_2 and B_3) are fitted directly at once for a binary salt-water system by using the whole data of
 292 mean molal activity coefficient versus concentration at all temperature values, i.e. using Equation 12
 293 as the objective function. In Pitzer model, the expressions for temperature dependence of β and C^ϕ
 294 parameters include six p parameters, i.e. twenty four parameters in total or eighteen parameters in

case of excluding β_2 for salts including a univalent ion. Therefore, instead of fitting at once to the whole data set, this study conducts fitting in two steps for Pitzer model to clarify the procedure. Firstly, fitting β_0 , β_1 , β_2 and C^ϕ parameters for each temperature separately by using both osmotic coefficient and mean molal activity coefficient data, i.e. using Equation 11 as the objective function. Then, p parameters in the temperature dependence expressions are fitted separately to the sixth order polynomial relation with the parameter value and temperature in Kelvin through trend line option in Excel. This procedure prevents the compensation among numerous parameters and reduces uncertainty of fitting results due to initial values.

The initial values are adjusted in the way that the interaction parameter value would be equal to the value at 25 °C reported in the literature and parameters in temperature-dependent terms are set to zero. For instance, the initial value B_2 is set to 0.0574 and other parameters are set to zero when fitting NaCl-water data with Bromley model ¹³. Similarly, p_0 terms of the parameters β_0 , β_1 and C^ϕ are set to 0.0765, 0.2264 and 0.00127 as the initial values, respectively ¹⁴. The other p parameters are set to zero. Appendix 2 shows the parameters fitted with both the common (Equation 1) and the proposed (Equation 12 for Bromley and Equation 11 for Pitzer model) objective functions. There can be some other ways to define the initial values; however, the manual trials did not result in significant improvement in the objective function values. Wide range of initial values are tried manually for NaCl-water system with Bromley model, resulting in only negligible reduction in the objective function value. In addition, as another trial, the parameters obtained with the common approach are used as the initial values for the proposed approach when modeling NaCl-water system with Pitzer model. This trial resulted in negligible improvement as well: in the magnitude of 10^{-5} or even less. Consequently, this study uses the reported values of interaction parameters at 25 °C as initial values as described before, in order to clarify the procedure.

319

320

Table 2. The accuracy comparisons: OF values for both fitting approaches

Salt	Bromley model		Pitzer model	
	The proposed approach: Fitting with OF_γ as in Eq. 12	The common approach: Fitting with OF as in Eq. 1	The proposed approach: Fitting with OF_γ as in Eq. 11	The common approach: Fitting with OF as in Eq. 1
NaCl	$OF_\gamma = 0.1161$ $OF = 4.152 \times 10^{-4}$	$OF_\gamma = 0.1668$ $OF = 3.523 \times 10^{-4}$	$OF_\gamma = [8.698 \times 10^{-8}, 2.264 \times 10^{-5}]$ $OF = [4.509 \times 10^{-8}, 3.623 \times 10^{-6}]$	$OF_\gamma = [1.784 \times 10^{-7}, 2.642 \times 10^{-5}]$ $OF = [1.836 \times 10^{-8}, 2.520 \times 10^{-6}]$
KCl	$OF_\gamma = 0.01029$ $OF = 4.980 \times 10^{-5}$	$OF_\gamma = 0.006352$ $OF = 6.277 \times 10^{-5}$	$OF_\gamma = [7.162 \times 10^{-9}, 6.420 \times 10^{-3}]$ $OF = [3.868 \times 10^{-8}, 2.082 \times 10^{-5}]$	$OF_\gamma = [6.018 \times 10^{-8}, 6.424 \times 10^{-3}]$ $OF = [3.561 \times 10^{-8}, 2.064 \times 10^{-5}]$
KBr	$OF_\gamma = 0.02860$ $OF = 2.968 \times 10^{-4}$	$OF_\gamma = 0.04755$ $OF = 2.457 \times 10^{-4}$	$OF_\gamma = [1.212 \times 10^{-5}, 3.494 \times 10^{-5}]$ $OF = [8.370 \times 10^{-7}, 7.254 \times 10^{-6}]$	$OF_\gamma = [4.766 \times 10^{-5}, 1.143 \times 10^{-4}]$ $OF = [3.077 \times 10^{-7}, 9.967 \times 10^{-7}]$

321

322 Table 2 determines the fitting accuracy for both common (OF) and the proposed (OF_γ) objective
323 functions. OF represents the activity coefficient accuracy and OF_γ represents the Gibbs free energy
324 accuracy: the lower value the more accurate is the fitting. Since the data is fitted separately at each
325 temperature, Table 2 reports the minimum and maximum values of the objective functions for Pitzer
326 model. As in Table 2, the proposed approach results in significantly lower value in OF_γ and negligibly
327 higher value in OF compared to the common fitting approach. In other words, the proposed objective

functions give more accurate fitting with respect to Gibbs free energy without significant effect on the activity coefficient accuracy. For instance, Bromley model results in OF_γ value of 0.1161 for the proposed approach and 0.1668 for the common approach for fitting NaCl-water parameters; therefore, the proposed approach is more accurate in Gibbs free energy. In addition, the OF value of the proposed approach is slightly higher than the common approach, i.e. only minor loss in activity coefficient accuracy. Similarly, the results in Pitzer model confirm the higher accuracy of the proposed approach in Gibbs free energy as well: smaller values of OF_γ for the proposed fitting approach. Thus, it can be concluded that Gibbs free energy is calculated more accurately with the proposed objective functions, with negligible decrease in the accuracy of activity coefficient values. Nevertheless, the accuracy of a thermodynamic model is determined by Gibbs free energy calculation, rather than the activity coefficient alone.

Moreover, it is more important to improve the accuracy near the saturation concentration because that condition includes the phase equilibrium, thus affecting the speciation results. In other words, improving the accuracy around saturation point provides more accurate solubility estimations. (Section 3.3 compares the solubility estimations.) Instead, the error in low concentrations is less critical for speciation results. Figure 1 shows the activity coefficient data versus estimations of sodium chloride-water binary system with both Bromley model. The standard error of mean molal activity coefficient is 0.00068 at 25 °C and saturation concentration while the error is 0.01 with the common approach and 0.005 with the proposed approach. In other words, the accuracy improvement is more dominant than the uncertainty of data. Even though the accuracy of both approaches are very close, the proposed approach improves the accuracy especially towards the saturation for Bromley model, thus improving the accuracy of speciation results. Figure 2 shows the activity coefficient and osmotic coefficient as the comparison of data with the common and proposed fitting with the Pitzer model. In

352 Pitzer model, water activity and mean activity coefficient are linked and this model is more advanced
 353 than Bromley. Despite no improvement in the accuracy of activity coefficient or osmotic coefficient
 354 alone, the proposed approach aims at improving the Gibbs free energy accuracy. Figure 3 shows the
 355 deviation of excess Gibbs free energy calculated with the modelled activity and osmotic coefficients
 356 from that calculated with the measured activity and osmotic coefficients. Even though the common
 357 fitting approach can be more accurate at low and moderate concentrations, the proposed approach is
 358 usually more accurate at concentrations around saturation. This is demonstrated by R^2 values as well.
 359 Table 3 shows the fractions of unexplained variance ($1 - R^2$) of excess Gibbs free energy obtained
 360 from measured activity and osmotic coefficients from that obtained from calculated coefficients.

362 Figure 1. Measured vs. calculated mean molal activity coefficients with Bromley model

Figure 2. Measured vs. calculated mean molal activity coefficients and osmotic coefficients with Pitzer model

Figure 3. The deviations in Gibbs free energy calculations in kJ

Table 3. Fractions of unexplained variance ($1-R^2$) of excess Gibbs free energy for NaCl-water system and Pitzer model

	25 °C and the whole concentration range	25 °C and from 5 m to saturation	80 °C and the whole concentration range	80 °C and from 5 m to saturation
through OF_γ (proposed)	8.27×10^{-8}	7.62×10^{-8}	3.04×10^{-9}	3.03×10^{-9}
through OF (common)	1.29×10^{-7}	9.37×10^{-8}	9.94×10^{-9}	8.92×10^{-9}

3.2 Parameter Fitting for Standard State Specific Heat of Ions

The standard-state heat capacity parameters of ions can be fitted through thermodynamic relations shown in Equation 14-19, provided that the solubility product data is available under various temperatures. The specific heat of ions are equalized to the literature value at 25 °C as the initial guess of the fitting: a_i is set to the standard state specific heat value (e.g. 0.09 for sodium chloride ions), and b_i and c_i are set to zero in Equation 18 as the initial values. The measured data available for sodium chloride-water system includes both solubility and mean molal activity coefficient at saturation under temperature range of 0-100 °C. Figure 4 shows the plot of the extrapolated values of dilute measurements from different references ^(15, 21, 22), and the plot of the fitted specific heat through Equation 18 to one data set by the least squared error compared to the fitted specific heat through minimizing the squared error in Gibbs free energy of reaction as the proposed approach for sodium chloride example. Since the data is collected as the extrapolation of dilute concentration measurements to infinite dilution, the data from different sources can vary significantly. In contrast, the proposed method uses more precisely measurable data (i.e., saturation concentration and activity coefficient) and the fundamental thermodynamic relations to obtain the standard-state specific heat of ions. In addition, there is no temperature dependence between the differences in calculated specific

388 heats and literature values. Thus, this proposed method reduce the need of experiments dramatically
 389 by eliminating numerous dilute measurements and the extrapolation to infinite dilution.
 390
 391 Furthermore, Table 4 shows the OF_{Cp} values for fitting the specific parameters to the data (the
 392 common approach) and the Gibbs free energy-based fitting at saturation (the proposed approach). For
 393 the salts of which the activity coefficient data is unavailable at saturation, Equation 14 uses the
 394 measured saturation molality and estimated activity coefficient at the saturation molality. It is evident
 395 that the need of experiments for measuring specific heat can be eliminated by fitting the standard-
 396 state specific heat parameters based on Gibbs free energy of reaction and the saturation data.

397
 398 Figure 4. The standard state specific heat versus temperature
 399

Table 4. The accuracy of standard state specific heat of ions: the parameters in Equation 18 and the objective function in Equation 19

Salt (Cp in kJ/molK)	The proposed approach	The common approach
NaCl (Cp _{Na+} + Cp _{Cl-})	a = 0.839 b = -0.00182 c = -38.24 OF _{Cp} = 2.707 x 10 ⁻⁵	a = 1.085 b = -0.00244 c = -43.75 OF _{Cp} = 1.101 x 10 ⁻⁴
KBr (Cp _{K+} + Cp _{Br-})	a = -30.589 b = 0.0707 c = 918.28 OF _{Cp} = 0.00378	not available
KCl (Cp _{K+} + Cp _{Cl-})	a = 58.86 b = -0.128 c = -2117.33 OF _{Cp} = 0.04684	not available

The proposed approach can be validated by enthalpy measurements as well. For instance, standard-state enthalpy of solution refers to the enthalpy change due to the dissolution of unit molal solute at infinite dilution. Similar to standard state specific heat of ions, this property involves a hypothetically ideal standard state. Nevertheless, data are available despite the uncertainty. As a comparison, the standard-state enthalpy of solution is calculated as in Equation 20 by using the ionic specific heat parameters obtained with the proposed method as well. Figure 5 shows the literature values of standard-state enthalpy of solution as well as the calculations through Equation 20 by using the ionic specific heat parameters fitted with the proposed and common approaches. The results are consistent and verifying the proposed method for the standard-state specific heat parameters of ions.

$$\Delta H_{sol}^o = \sum_i^{ions} \left[\Delta_f H_i^o(298.15 K) + \int_{298.15 K}^T c_{pi}^o dT \right] - \left[\Delta_f H_{C_c A_a(s)}^o(298.15 K) + \int_{298.15 K}^T c_{p C_c A_a(s)}^o dT \right] \quad (20)$$

Figure 5. Standard state enthalpy of solution versus temperature

3.3 Solubility Estimates

The solubility estimates through the proposed approaches are compared for both Pitzer and Bromley models. For Bromley model, the solubility of salts are estimated by adjusting the molality to equalize the equilibrium constant calculated through molality and composition-dependent activity coefficient to that calculated through the measured solubility and activity coefficient at saturation. Figure 6 (top) shows the solubility data and the estimates when using the interaction parameter of the common fitting and the proposed fitting. This simple way is dictated by the inaccurate calculations of water activity with Bromley model. Solubility values are estimated by the minimization of Gibbs free energy for a salt-water binary system as in Equation 2-6 when Pitzer model is used for activity coefficients. This is more proper test for further use of the model in multicomponent systems and in various applications. The proposed fitting approaches are tested by using the activity coefficient and ionic specific heat parameters fitted with common approaches and with proposed approaches. For instance, Figure 6 (bottom) shows the solubility estimate of sodium chloride in water, 8 moles of

428 NaCl and 1 kg of water of which the speciation is solved by Gibbs free energy minimization. The
429 common approach uses the activity coefficient parameters fitted through Equation 1 and the standard
430 state ionic specific heat parameters fitted the data. In contrast, the proposed approach uses the activity
431 coefficient parameters fitted through Equation 11 and the standard state ionic specific heat parameters
432 through Equation 19.

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Figure 6. Solubility estimates versus temperature for NaCl salt

443

444 The results show that the proposed methodology has sufficient accuracy in solubility estimates as
445 well as facilitating the determination of specific heat parameters of ions. The impact of objective
446 function in parameter fitting is very clear for Bromley model as in Figure 6 (top). The accuracy has
447 improved at the whole temperature range. Furthermore, for an advanced model, the proposed
448 approach slightly improves the accuracy at high temperatures and is fairly accurate at low
449 temperatures despite being less accurate than the common approach, as shown in Figure 6 (bottom).
450 The 6th order polynomial fitting of β and C^ϕ temperature dependences have average squared errors
451 at the magnitude of 10^{-8} or less, i.e. sufficient fitting. However, the lower accuracy of the proposed
452 methodology at low temperatures can result from the decreasing trend of OF_γ from 2.26×10^{-5} at 5°C
453 to 1.21×10^{-7} at 60°C , rather than being random. It can be future aspect to try another activity
454 coefficient model or to develop one which represents the temperature dependences of interactions
455 more accurately. In other words, the sufficient accuracy in solubility estimates validate the proposed
456 approach: Gibbs free energy-based objective functions in parameter fitting and using saturation data
457 in fitting of specific heat parameters of ions. Regarding the activity coefficient fitting, the proposed
458 approach potentially improves the accuracy of speciation mass balances in real applications only by
459 replacing the objective function with Gibbs free energy-based expression, without additional
460 computation. Regarding the specific heat parameters, the proposed approach can eliminate the
461 numerous measurements for extrapolation to infinite dilution at each temperature condition.
462 Considering the uncertainties in measurements of dilute solutions and extrapolation, the proposed
463 approach provides thermodynamically more consistent method of determining the standard state
464 specific heat parameters of ions.

Figure 7. Solubility estimates for KBr salt by the minimization of Gibbs free of the system with 1 kg water and 10 moles of KBr salt

Constructing a thermodynamic model in case of limited data is also possible when mean molal activity coefficient and osmotic coefficient data are available up to concentrated ranges at different temperatures. For instance, the KBr-water data used in this study includes mean molal activity coefficients and osmotic coefficients up to 5.5 molal at 298.15 K and up to 4 molal at other temperatures. In other words, the utilized data does not include activity at saturation and standard state specific heat of ions. First, the parameters of activity coefficient model are fitted with the available data through the proposed objective function (Equation 11 for Pitzer model). Then, the standard state specific heat parameters are fitted with the molality data and estimated activity coefficient at saturation by using Equation 19. Finally, the thermodynamic model is constructed as in

Equation 2-6 for speciation, the minimization of the total Gibbs free energy. Figure 7 shows the solubility estimates of KBr with Pitzer model. The results are accurate enough to confirm the validity of the proposed approaches of the parameter fitting in case of limited available activity data and in the absence of standard state specific data for ions as well.

4. Conclusion

The objective function has a significant impact on the accuracy of the model, thus requiring proper determination. The recent studies presented activity coefficient-based objective functions when fitting the interaction parameters in the activity coefficient models. However, activity coefficient alone does not represent any thermodynamic property and not the ultimate purpose of the model. The ultimate target of a thermodynamic model is to calculate Gibbs free energy and then to determine the equilibrium state by minimizing this thermodynamic property. In addition, the common method for defining standard state specific heat of ions involve numerous measurements on dilute solutions and extrapolation to infinite dilution.

Consequently, this study proposes a new objective function for the model development. Activity coefficients are fitted through minimizing the averaged squared error in Gibbs free energy when calculated by activity coefficient data and by the model equation. This objective function provides proper weight factors based on the concentrations of ions and temperature. The standard-state specific heat parameters of ions is determined through fitting with respect to Gibbs free energy of dissolution reaction. This would eliminate the need of numerous experiments measuring apparent molal heat capacity at low concentrations and numerical method-dependent extrapolation to infinite dilution for each salt and each temperature. The proposed methodology for parameter fitting would provide more

501 accurate speciation by improving the model accuracy especially at high concentrations and reduce
502 the need of measurements within the fundamental principles. However, the common method is more
503 accurate than the proposed for Pitzer model at low temperature. Thus, the future scope can include
504 comparing various activity coefficient models as well.

505

506 As the future aspect, the specific heat of hydrated solid salts can be calculated by using the saturation
507 data of hydrated salts as well, which are not available in the literature, after determining the specific
508 heat of ions through the saturation of anhydrous solid forms dissolved in water. Furthermore, the
509 proposed approach to objective function can be applied to non-electrolyte thermodynamics as well.
510 Despite the differences, the core of all thermodynamic models is the calculation of Gibbs free energy.
511 Therefore, it can be expected that Gibbs free energy-based objective function would lead to more
512 accurate fitting and speciation calculations for any multicomponent system.

513

514 Regarding the industrial applicability, the proposed approach improves the precision and validity of
515 simulations and thermodynamic models used for design and operation of chemical processes.
516 Furthermore, this approach reduces the need of costly experiments in process development; for
517 instance, sufficient data can be collected with fewer measurements for new applications, e.g. organic
518 salts in the current development of new biomass processing concepts.

519

520 **References**

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TOC Graphics

Supporting Information

Appendix 1. The Activity Coefficient Models

A1.1 Bromley Model

The individual activity coefficient is calculated as:

$$\log \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + \sqrt{I}} + F_i \quad (A1)$$

$$F_i = \sum_j \dot{B}_{ij} Z_{ij} m_j \quad (j \text{ refers to the ions having opposite charge of } i) \quad (A2)$$

$$Z_{ij} = \frac{z_i + z_j}{2} \quad (A3)$$

$$\dot{B}_{ij} = \frac{0.06 + 0.6 B_{ij}}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ij} \quad (A4)$$

$$I = \frac{1}{2} \sum_i^{ions} m_i z_i^2 \quad (A5)$$

586 where z_i represents the number of charge of i , B_{ij} represents the interaction parameter between
 587 opposite-charged ions, I represents the ionic strength and A is Debye-Hückel constant. A and B_{ij} are
 588 temperature-dependent parameters. Equation A6 gives the temperature dependence of B_{ij} .

$$589 \quad B_{ij} = B^* \ln\left(\frac{T-243}{T}\right) + \frac{B_1}{T} + B_2 + B_3 \ln T \quad (\text{A6})$$

590 Equation A7 gives the temperature dependence of A in natural logarithm scale. Then, it is converted
 591 to logarithm of 10 base by equation A8.

$$592 \quad A_{ln} = 1.131 + 1.335 * 10^{-3} * (T - 273.15) + 1.164 * 10^{-5} * (T - 273.15)^2 \quad (\text{A7})$$

$$593 \quad A = \log(\exp(A_{ln})) \quad (\text{A8})$$

594 The mean molal activity coefficient is calculated based on individual coefficients as:

$$595 \quad \log \gamma_m = \frac{\sum_i^{ions} m_i \log \gamma_i}{\sum_i^{ions} m_i} \quad (\text{A9})$$

596 **A1.2 Pitzer Model**

597 The osmotic coefficient and mean molal activity coefficient are calculated as:

$$598 \quad \varphi - 1 = |z_C z_A| f^\varphi + m \left(\frac{2v_C v_A}{v_C + v_A} \right) B_{CA}^\varphi + m^2 \frac{2(v_C v_A)^{3/2}}{v_C + v_A} C_{CA}^\varphi \quad (\text{A10})$$

$$599 \quad \ln \gamma_\pm^m = |z_C z_A| f^\gamma + \left(\frac{2v_C v_A}{v_C + v_A} \right) B_{CA}^\gamma + m^2 \frac{2(v_C v_A)^{3/2}}{v_C + v_A} C_{CA}^\gamma \quad (\text{A11})$$

$$600 \quad f^\gamma = -A_\varphi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \quad (\text{A12})$$

$$601 \quad f^\varphi = -A_\varphi \frac{I^{1/2}}{1 + bI^{1/2}} \quad (\text{A13})$$

$$602 \quad B_{CA}^\gamma = 2\beta_{CA}^0 + \frac{2\beta_{CA}^1}{\alpha^2 I} \left[1 - e^{-\alpha I^{1/2}} (1 + \alpha I^{1/2} - 0.5\alpha^2 I) \right] \quad (\text{A14})$$

$$603 \quad B_{CA}^\varphi = \beta_{CA}^0 + \beta_{CA}^1 e^{-\alpha I^{1/2}} \quad (\text{A15})$$

$$604 \quad C_{CA}^\gamma = 1.5 C_{CA}^\varphi \quad (\text{A16})$$

605 where β_{CA}^0 , β_{CA}^1 and C_{CA}^φ are the interaction parameters fitted to the data. α and b have the values of 2
606 and 1.2, respectively. The temperature dependence of these parameters are expressed as:

607
$$\beta \text{ or } C = p_6T^6 + p_5T^5 + p_4T^4 + p_3T^3 + p_2T^2 + p_1T^1 + p_0 \tag{A17}$$

608 **Appendix 2. The Model Parameters Determined Through Parameter Fitting**

609 **A2.1 Bromley Model**

610 Table A1. The parameters of Bromley model

Salt in water as binary system	The proposed approach	The common approach
NaCl	$B^* = 0.03969$ $B_1 = 2.7225$ $B_2 = 0.6350$ $B_3 = -0.09108$	$B^* = 0.04073$ $B_1 = 2.6586$ $B_2 = 0.6021$ $B_3 = -0.08503$
KBr	$B^* = 0.05241$ $B_1 = 6.4688 \times 10^{-5}$ $B_2 = 0.3648$ $B_3 = -0.04344$	$B^* = 0.05274$ $B_1 = 4.1543$ $B_2 = 0.2404$ $B_3 = -0.02389$
KCl	$B^* = 0.03269$ $B_1 = 0.0004599$ $B_2 = 0.2419$ $B_3 = -0.02857$	$B^* = 0.03056$ $B_1 = 8.0462 \times 10^{-5}$ $B_2 = 0.1427$ $B_3 = -0.01180$

621 **A2.2 Pitzer Model**

622 Table A2. The parameters of Pitzer with the common approach

Salt in water as binary system	β_{CA}^0	β_{CA}^1	C_{CA}^φ	
NaCl	6.2188E-15	-3.8303E-13	-1.057E-15	p ₆
	-1.0394E-11	7.7115E-10	1.8096E-12	p ₅
	6.7051E-09	-6.4616E-07	-1.219E-09	p ₄
	-1.9805E-06	0.0002885	3.9703E-07	p ₃
	0.0002047	-0.07240	-5.821E-05	p ₂
	0.01868	9.6867	0.001455	p ₁
	-4.0634	-539.76	0.3338	p ₀
KBr	0	0	0	p ₆
	-1.7731E-12	0	-1.5152E-11	p ₅
	2.7270E-09	-1.2537E-09	2.583E-08	p ₄
	-1.5794E-06	1.4618E-06	-1.7598E-05	p ₃
	0.0004100	-0.00060400	0.005991	p ₂
	-0.04103	0.1027	-1.0191	p ₁
	0.3311	-5.5143	69.32	p ₀
KCl	-8.2769E-12	0	0	p ₆
	1.5840E-08	-1.987E-09	-1.6344E-11	p ₅
	-1.2615E-05	3.1974E-06	2.6570E-08	p ₄
	0.005352	-0.002055	-1.7252E-05	p ₃
	-1.2757	0.6594	0.005593	p ₂
	161.97	-105.63	-0.9051	p ₁
	-8558.5	6758.5	58.50	p ₀

636

Table A2. The parameters of Pitzer with the proposed approach

Salt in water as binary system	β_{CA}^0	β_{CA}^1	C_{CA}^φ	
NaCl	-1.6320E-14	-2.5784E-13	3.5505E-15	p6
	3.3379E-11	5.2789E-10	-7.1441E-12	p5
	-2.8675E-08	-4.4950E-07	6.0231E-09	p4
	1.3255E-05	0.0002038	-2.7247E-06	p3
	-0.003482	-0.05192	0.0006981	p2
	0.4942	7.0473	-0.09624	p1
	-29.61	-398.19	5.5906	p0
KBr	0	0	0	p6
	0	0	0	p5
	-4.3921E-09	0	3.4807E-10	p4
	6.0219E-06	-2.0493E-07	-4.6482E-07	p3
	-0.003097	0.0002223	0.0002337	p2
	0.7082	-0.07833	-0.05248	p1
	-60.71	9.2596	4.4406	p0
KCl	0	9.9799E-12	0	p6
	-1.2429E-10	-2.0257E-08	2.224E-11	p5
	1.9968E-07	1.7082E-05	-3.5218E-08	p4
	-0.0001281	-0.007661	2.2263E-05	p3
	0.04099	1.9274	-0.007023	p2
	-6.5456	-257.92	1.1056	p1
	417.23	14343.32	-69.49	p0

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