THERMAL PROPERTIES OF ELECTROLYTE SOLUTIONS

Methods for Calculation of Multicomponent Systems and Experimental Data

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Foreword

This book is the continuation of a number of works dealing with studies, representations and methods of calculation of the physico-chemical properties of binary and multicomponent electrolyte solutions [1—3].

Compared to [3], this book has substantially revised and enlarged data on the thermal properties of electrolyte solutions, in particular, new data on apparent molar heat capacity. Experimental data on heat capacity for the most-used electrolytes are represented in the high-temperature region and at various pressures. This book does not contain experimental data on integral heat of solution in water and enthalpy solution. The data were given in [3].

Section 1 gives the methods of calculation of heat capacity and apparent molar heat capacity and various coefficients of equations to calculate binary and multicomponent solutions.

The list of electrolytes in this book is significantly longer than in [3] (see Table index for Section 2), and the data for the same electrolytes were revised. The logic sequence of reference data is identical to that in [3], and the maximum temperature range and mass content in a solution are given for each electrolyte. Considerable attention is given to high-temperature studies. Experimental data for many electrolytes, which are presented here, were obtained using original experimental techniques, which should make this book popular.

The author will gratefully accept all comments and wishes of the reader.
1

Methods for Calculation of Thermal Properties

Heat Capacity

The heat capacity of a multicomponent solution can be calculated by the formula [1–3]

\[ C_p = C_{p,0} + \sum_{i=1}^{k} \left( B_{1i} + B_{2i} \tilde{c}_i + B_{3i} t + B_{4i} t^2 \right) c_i \]  \hspace{1cm} (1.1)

where \( C_p \) is the heat capacity of the multicomponent solution, J/kg·K; \( C_{p,0} \) is the heat capacity of water, J/kg·K; \( B_{ni} \) are the coefficients (see Table 1.1); \( \tilde{c}_i \) is the mass content of the \( i \)th component in the binary isopiestic solution, %; \( t \) is the temperature, °C; \( c_i \) is the mass content of the \( i \)th component in the multicomponent solution, %; \( k \) is the number of the solution components.

The heat capacity of water (in kJ/kg·K) in the saturation line in the range \( 0 \leq t < 40^\circ C \) is calculated by the formula

\[ C_{p,0} = 4.21703 - 0.068372 t^{0.5} - 0.193808 t^{1.5} + 0.340252 t^2 \]  \hspace{1cm} (1.2)

where \( t' = 0.1t \);

in the range \( 40 \leq t < 250^\circ C \), by the formula

\[ C_{p,0} = 4.178232 - 0.200822 t^{2.5} + 0.551896 t^3 - 0.4335824 t^{3.5} + 0.123167 t^4 \]  \hspace{1cm} (1.3)

in the range \( 250 \leq t \leq 310^\circ C \), by

\[ C_{p,0} = 2.593188 + 0.52937 t^{2.5} - 0.068205 t^{4.5} + 0.002056 t^7 \]  \hspace{1cm} (1.4)
and in the range $310 < t \leq 350^\circ C$, by

$$C_{p,0} = -45.771367 + 6.383903 \, t^{4} - 2.681648 \, t^{5} + 0.147224 \, t^{6.5} \quad (1.5)$$

The total root-mean-square error of the calculation by formulas (1.6–1.9) is 3.95 J/kg·K, and the mean relative error, 0.035%.

The heat capacity of water (in kJ/kg·K) in the temperature range from 0 to 500°C and in the pressure range from 0.01 to 100 MPa is calculated by the following equations:

$$C_{p,0} = 4.24687 + 0.002052 \, t - 0.002988(t + 0.1) - 0.023721 \, t^{0.5} \quad (1.6)$$

in the temperature range $0 \leq t \leq 40^\circ C$ and the pressure range $0.01 \leq p \leq 0.1$ MPa with the root-mean-square error 3.2 J/kg·K or with the mean relative error 0.04%;

$$C_{p,0} = 3.590912 - 0.972858/p + 1.309513/p^{0.5} + 0.00027 \exp(1/p) + 0.138643(t + 0.5) - 9.038999 \cdot 10^{0.3}(t/p)^{0.5} + 0.000299 \, t/p + 0.078149 \, t^{0.5} - 0.000795 \, t^{1.5} \quad (1.7)$$

in the temperature range $0 \leq t \leq 40^\circ C$ and the pressure range $0.1 \leq p \leq 100$ MPa with the root-mean-square error 25.8 J/kg·K or with the mean relative error 0.42%;

$$C_{p,0} = 3.918854 - 0.749179/p + 0.99031/p^{0.5} + 0.000209 \exp(1/p) + 0.000049 \, t^{1.5} \quad (1.8)$$

in the temperature range $40 < t \leq 90^\circ C$ and the pressure range $0.1 \leq p \leq 100$ MPa with the root-mean-square error 14.9 J/kg·K or with the mean relative error 0.25%;

$$C_{p,0} = 4.067187 - 0.64521/p^{0.5} + 0.032742 \exp(1/p) + 0.000712 \, t - 0.001599 \, p - 0.002323 \, t/p + 0.086116(t/p)^{0.5} \quad (1.9)$$

in the temperature range $40 < t \leq 150^\circ C$ and the pressure range $0.5 \leq p \leq 100$ MPa or in the temperature range $150 < t \leq 170^\circ C$ and the pressure range $1 \leq p \leq 100$ MPa with the root-mean-square error 15.4 J/kg·K or with the mean relative error 0.21%;

$$C_{p,0} = -10.531987 + 3.131961/p - 23.631297/p^{0.5} + 6.724561 \exp(1/p) - 0.075355 \, t + 1.999182(t/p)^{0.5} - 0.084543 \, t/p + 0.209343 \exp(t/100) + 1.490491/t^{0.5} \quad (1.10)$$

at $170 < t \leq 210^\circ C$ and $2 \leq p \leq 100$ MPa, $210 < t \leq 220^\circ C$ and $2.5 \leq p \leq 100$ MPa, $220 < t \leq 230^\circ C$ and $3 \leq p \leq 100$ MPa, $230 < t \leq 250^\circ C$ and $4 \leq p \leq 100$ MPa, $250 < t \leq 260^\circ C$ and $5 \leq p \leq 100$ MPa, $260 < t \leq 270^\circ C$ and $6 \leq p \leq 100$ MPa, $270 < t \leq 280^\circ C$ and $7 \leq p \leq 100$ MPa, $280 < t \leq 290^\circ C$ and $7.5 \leq p \leq 100$ MPa, and $290 < t \leq 300^\circ C$ and $9 \leq p \leq 100$ MPa with the root-mean-square error 63.8 J/kg·K and the mean relative error 0.98%;

$$C_{p,0} = -2096.2192 - 0.031519 \, p + 9458.883063/p + 31.63026 \, t/p + 307.417756/t^{0.5} + 2.104763(t/p)^{0.5} - 12.670213 \, t + 0.043842(t/p)^{0.5} + 63.26731(t/100)^{2} - 1096.659064 \, t^{0.5}/p \quad (1.11)$$
at 300 ≤ t ≤ 310°C and 10 ≤ p ≤ 100 MPa, 310 < t ≤ 320°C and 12 ≤ p ≤ 100 MPa, 320 < t ≤ 330°C and 13 ≤ p ≤ 100 MPa, 330 < t ≤ 340°C and 15 ≤ p ≤ 100 MPa, and 340 < t < 350°C and 17 ≤ p ≤ 100 MPa with the root-mean-square error 43.5 J/kg·K and the mean relative error 0.54%;

\[ C_{p,0} = -26.607532 - 3759.07163/p + 1079.075726/p^{0.5} + 15.319892 tp - 28.247262(tp)^{0.7} + 1.441955(tp/100)^2 - 1.211939 tp/p^{0.5} \]  
(1.12)

at 350 ≤ t ≤ 360°C and 20 ≤ p ≤ 100 MPa or 360 ≤ t < 400°C and 40 ≤ p ≤ 100 MPa with the root-mean-square error 7.15 J/kg·K or with the mean relative error 0.84%;

\[ C_{p,0} = -76.628507 + 1539.736275p - 28.240246tp + 84.051161(tp)^{0.5} + 1.021508(tp)^2 - 60205.98/p^2 \]  
(1.13)

at 400 ≤ t ≤ 430°C and 40 ≤ p < 78 MPa with the root-mean-square error 123.8 J/kg·K or with the mean relative error 0.94%;

\[ C_{p,0} = 2472.171315 + 1719.741955/p - 325.099801p^{0.5} - 15099.46/l^{0.5} - 512.643134/f^{0.2} + 0.000031 \exp(tp) \]  
(1.14)

at 430 < t < 440°C and 44 ≤ p < 78 MPa or at 440 ≤ t ≤ 460°C and 50 ≤ p ≤ 78 MPa with the root-mean-square error 6.2 J/kg·K or with the mean relative error 0.58%; and

\[ C_{p,0} = -2.079829 + 543.667042/p + 3.370496tp + 1.003937 f - 0.042255 t + 0.135484(tp/100)^2 - 86.427556 f^{0.5}/p \]  
(1.15)

at 400 ≤ t ≤ 500°C and 78 ≤ p < 100 MPa with the root-mean-square error 41.5 J/kg·K or with the mean relative error 0.61%.

\( \tilde{c}_i \) is calculated by the formula

\[ \tilde{c}_i = E_i^{-1} \sum_{i=1}^k E_j c_i \]  
(1.16)

where \( E_i \) is the coefficient, which characterizes the vapor pressure over the solution and is calculated by the expression [2]

\[ E_i = (1 - a_{w}^{*})/c_f \]  
(1.17)

where \( a_{w}^{*} \) and \( c_f \) are the water activity and the mass content of the saturated solution of an individual component of the system analyzed (in kg of substance per 1 kg of solution) at a given temperature.

The water activity is calculated by the thermodynamic relation

\[ a_w = P/P_0 \]  
(1.18)

where \( P \) is the pressure of water vapor over the solution, Pa; \( P_0 \) is the pressure of water vapor over pure water, Pa.
The water vapor pressure over the solution is calculated with the root-mean-square error 39.54 J/kg·K and the mean relative error 0.006% by the formula

\[ P_0 = P_{cr} \exp B \]  
(1.19)

where \( P_{cr} \) is the critical pressure \((2.2064 \cdot 10^7 \text{ Pa})\), and \( B \) is equal to

\[ B = T_{cr} A/T \]  
(1.20)

where \( T_{cr} \) is the critical temperature \((647.14 \text{ K})\); \( T \) is the temperature in K; and the quantity \( A \) is calculated by the following expressions:

\[ A = A_0 + A_1 \cdot T_s^{1.5} + A_2 \cdot T_s^2 + A_3 \cdot T_s^{3.5} \]  
(1.21)

where \( A_0 = -0.595684, A_1 = -11.039345, A_2 = 17.449275, \) and \( A_3 = -16.028445 \) from 0 to 100°C;

\[ A = A_0 + A_1 \cdot T_s + A_2 \cdot T_s^{1.5} + A_3 \cdot T_s^3 + A_4 \cdot T_s^{4.5} \]  
(1.22)

where \( A_0 = -0.018527, A_1 = -7.284175, A_2 = 0.407838, A_3 = -4.200201, \) and \( A_4 = 1.005549 \) from 100 to 250°C;

\[ A = A_0 + A_1 \cdot T_s + A_2 \cdot T_s^{1.5} + A_3 \cdot T_s^3 + A_4 \cdot T_s^{3.5} + A_5 \cdot T_s^4 \]  
(1.23)

where \( A_0 = -0.001096, A_1 = -7.891114, A_2 = 2.024116, A_3 = -22.917717, A_4 = 60.32581, \) and \( A_5 = -50.818889 \) from 250 to 350°C.

In Eqs. (1.21–1.23), \( T_s \) is

\[ T_s = 1 - T/T_{cr} \]  
(1.24)

The water vapor pressure over a binary electrolyte solution is calculated by the expression

\[ P = P_0 \exp(m \cdot P_s/0.434295) \]  
(1.25)

where \( P_s \) is calculated by the equation

\[ P = W + W_1 \cdot t + W_2 \cdot m + W_3 \cdot t^2 + W_4 \cdot t^2 \cdot m + W_5 \cdot t^2 \cdot m^2 \]  
(1.26)

where the coefficients \( W_i \) for some electrolytes are given in Table 1.2.

The mass content of the saturated solution of an individual component of the system analyzed can be calculated, with a satisfactory error for practical calculations of heat capacity, by the formula

\[ c^i = \alpha \cdot \exp(\beta \cdot t) \]  
(1.27)

where \( \alpha \) and \( \beta \) are the coefficients of the equation to describe the saturation line, which are given for some electrolytes in Table 1.3.

**Example.** Calculate the heat capacity of a MgCl₂-NaCl-H₂O solution at 25°C. The mass contents in the solution are \( m_{\text{MgCl}_2} = 1.9806 \text{ mol/kg H}_2\text{O} \) and \( m_{\text{NaCl}} = 2.5 \text{ mol/kg} \).
H₂O. The experimental \( C_p = 3058.1 \, \text{J/kg-K} \) [4]. The molecular masses are \( M_{\text{MgCl}_2} = 95.211 \) and \( M_{\text{NaCl}} = 58.443 \).

For further calculations, we convert the mass contents of the components from mol/kg to %:

\[
\begin{align*}
C_{\text{MgCl}_2} &= \frac{100mM}{1000 + \sum_{k=1}^{2} mM} \\
&= \frac{100 \cdot 1.9806 \cdot 95.211}{1000 + 1.9806 \cdot 95.211 + 2.5 \cdot 58.443} = 14.1288 \% \\
C_{\text{NaCl}} &= \frac{100 \cdot 2.5 \cdot 58.443}{1000 + 2.5 \cdot 58.443 + 1.9806 \cdot 95.211} = 10.9470 \%
\end{align*}
\]

To calculate the mass content of each component in the binary isopiestic solution, we use the formulas (1.16–1.21) and (1.24–1.27). The \( \alpha \) and \( \beta \) values for MgCl₂ and NaCl are in Table 1.3:

\[
\alpha = 33.8807 \text{ and } \beta = 3.6523 \cdot 10^{-3} \text{ for MgCl}_2 \text{ and} \\
\alpha = 24.8537 \text{ and } \beta = 1.4882 \cdot 10^{-3} \text{ for NaCl}
\]

Using (1.27), we calculate the mass content of the components MgCl₂ and NaCl in the binary isopiestic solution:

\[
\begin{align*}
C_{\text{MgCl}_2} &= 33.8807 \exp(3.6523 \cdot 10^{-3}) = 37.12 \% \\
C_{\text{NaCl}} &= 24.8537 \exp(1.4882 \cdot 10^{-3}) = 25.80 \%
\end{align*}
\]

Using Eqs. (1.18–1.21) and (1.24), we calculate the water vapor pressure over pure water:

\[
T = 273.15 + 25 = 298.15 \, \text{K}
\]

The reduced temperature, according to (1.24), equals

\[
T_r = 1 - \frac{298.15}{647.14} = 0.5392805
\]

From (1.21), \( A \) is

\[
A = -0.595684 - 11.039345 \cdot 0.5392505^{1.5} + 17.449275 \cdot 0.5392805^3 - 16.028445 \cdot 0.5392805^{3.5} = -4.076919
\]

The quantity \( B \) is calculated by (1.20):

\[
B = 647.14 \cdot (-4.076919)/298.15 = -8.849028
\]

We calculate the water vapor pressure over pure water by Eq. (1.19):
\[ P_0 = 2.2064 \cdot 10^7 \exp(-8.849028) = 3166.652 \text{ Pa} \]

We convert the mass content of the components in the saturated solution from % to mol/kg H\(_2\)O:

\[
m_{\text{MgCl}_2} = \frac{1000c_i^s}{M(100-c_i^s)} = \frac{1000 \cdot 37.12}{95.211(100-37.12)} = 6.20 \text{ mol/kg} \\
m_{\text{NaCl}} = \frac{1000 \cdot 25.8}{58.443(100-25.8)} = 5.95 \text{ mol/kg} 
\]

We find the coefficients \(W\) for MgCl\(_2\) and NaCl from Table 1.2.

For MgCl\(_2\),

\[
W = -4.3224 \cdot 10^{-3} \quad W_1 = -1.678 \cdot 10^{-4} \quad W_2 = -14.2181 \cdot 10^{-3} \\
W_3 = 8 \cdot 10^{-7} \quad W_4 = 6.85 \cdot 10^{-5} \quad W_5 = -2 \cdot 10^{-7}
\]

For NaCl,

\[
W = -1.505 \cdot 10^{-2} \quad W_1 = -5.08 \cdot 10^{-5} \quad W_2 = -8.033 \cdot 10^{-4} \\
W_3 = 4 \cdot 10^{-7} \quad W_4 = 6.8 \cdot 10^{-6} \quad W_5 = -0.34 \cdot 10^{-7}
\]

The value of \(P_0\) for MgCl\(_2\) and NaCl is calculated by (1.26):

\[
P_{\text{MgCl}_2} = -4.3224 \cdot 10^{-3} - 1.678 \cdot 10^{-4} \cdot 25 - 14.2181 \cdot 10^{-3} \cdot 6.2 + 8 \cdot 10^{-7} \cdot 25^2 + \\
6.85 \cdot 10^{-5} \cdot 25 - 6.2 - 2 \cdot 10^{-7} \cdot 25^2 - 6.2 = -8.632711 \cdot 10^{-2}
\]

\[
P_{\text{NaCl}} = -1.505 \cdot 10^{-2} - 5.08 \cdot 10^{-5} \cdot 25 - 8.033 \cdot 10^{-4} \cdot 5.95 + 4 \cdot 10^{-7} \cdot 25^2 + \\
6.8 \cdot 10^{-6} \cdot 25 - 5.95 - 0.34 \cdot 10^{-7} \cdot 25^2 - 5.95 = -1.996457 \cdot 10^{-2}
\]

The water vapor pressure over the binary solution of each component is calculated by (1.25):

\[
P_{\text{MgCl}_2} = 3166.652 \exp(-8.632711 \cdot 10^{-2} \cdot 6.2/0.434295) = 923.364 \text{ Pa} \\
P_{\text{NaCl}} = 3166.652 \exp(-1.996457 \cdot 10^{-2} \cdot 5.95/0.434295) = 2408.86 \text{ Pa}
\]

The water activity over the binary saturated solution of each component is calculated by (1.18).

For MgCl\(_2\), \(a_w = 923.364/3166.652 = 0.292\).

For NaCl, \(a_w = 2408.86/3166.652 = 0.7607\).

The coefficients \(E_i\) for each component are calculated by (1.17).

For MgCl\(_2\), \(E_1 = (1 - 0.292)/0.3712 = 1.9073\).

For NaCl, \(E_1 = (1 - 0.7607)/0.258 = 0.9276\).

The mass content of each component in the binary isopiestic solution is found from the dependence (1.16).

For MgCl\(_2\), \(c_{\text{MgCl}_2} = \frac{1}{1.907} (1.907 \cdot 14.1288 + 0.9276 \cdot 10.9470) = 19.454\).
For NaCl, \( \bar{\epsilon}_{\text{NaCl}} = \frac{1}{0.9276} (0.9276 \cdot 10.9470 + 1.907 \cdot 14.1288) = 39.994. \)

The heat capacity of water is calculated by (1.2):

\[
t' = 0.01 \cdot 25 = 0.25
\]

\[
C_{p,0} = 4.21703 - 0.068372 \cdot 0.25^{0.5} - 0.193808 \cdot 0.25^{1.5} + \\
+ 0.340252 \cdot 0.25^2 = 4.17988 \text{ kJ/kg·K.}
\]

The coefficients \( B_m \) for MgCl\(_2\) and NaCl are in Table 1.1.

For MgCl\(_2\), \( B_1 = -66.15; B_2 = 15.4995 \cdot 10^{-2}; B_3 = 43.2114 \cdot 10^{-2}; B_4 = -1.0464 \cdot 10^{-3} \)

For NaCl, \( B_1 = -61.25; B_2 = 27.7534 \cdot 10^{-2}; B_3 = 97.7758 \cdot 10^{-2}; B_4 = -2.3599 \cdot 10^{-3} \)

The heat capacity of the solution is calculated by (1.1):

\[
C_p = 4179.88 + (-66.15 + 15.4995 \cdot 10^{-2} \cdot 19.454 + 43.2114 \cdot 25 - \\
- 1.0464 \cdot 10^{-3} 25^2) \cdot 14.1288 + (-61.25 + 27.7534 \cdot 10^{-2} \cdot 39.994 + 97.7758 \cdot 25 - \\
- 2.3599 \cdot 10^{-3} \cdot 25^2) 10.947 = 3133.7 \text{ J/kg·K, \(2.47\%\).}
\]

**Apparent Molar Heat Capacity**

Apparent molar heat capacity is calculated by the thermodynamic formula

\[
\phi_c = \frac{1000(C_p - C_{p,0})}{m} + C_p M
\]  \hspace{1cm} (1.28)

where \( \phi_c \) is the apparent molar heat capacity, J/K·mol; \( C_p \) and \( C_{p,0} \) are the heat capacities of the solution and water, respectively, kJ/kg·K.

By substituting % for mol/kg in the mass content of components in Eq. (1.28), we obtain the following formula

\[
\phi_c = M \left[ \frac{(C_p - C_{p,0})(100 - c)}{c} + C_p \right]
\]  \hspace{1cm} (1.29)

**Example.** Calculate the apparent molar heat capacity of an AlCl\(_3\)–H\(_2\)O solution at 35°C. The mass content of AlCl\(_3\) in the solution is \( c = 10\% \), and its molecular mass, \( M = 134.34 \). The experimental \( C_p = 3.5338 \text{ J/kg·K.} \)

The heat capacity of water is calculated by (1.2):

\[
C_{p,0} = 4.21703 - 0.068372 \cdot 0.35^{0.5} - 0.193808 \cdot 0.35^{1.5} + \\
+ 0.340252 \cdot 0.35^2 = 4.178131 \text{ kJ/kg·K.}
\]

Then, the apparent molar heat capacity is calculated by (1.29):

\[
\phi_c = 134.34 \left[ \frac{(3.5338 - 4.178131)(100 - 10)}{10} + 3.5338 \right] = -302.0 \text{ J/K·mol}
\]
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