Thermodynamic Properties of Aqueous Magnesium Chloride Solutions From 250 to 600 K and to 100 MPa

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A new general model that describes the thermodynamic properties of $MgCl_2(aq)$ has been developed from a global fit to experimental results, including isopiestic molalities, vapor pressure measurements, freezing-point depressions, enthalpies of dilution, heat capacities, and densities, for this system. The model is based on a recent ion-interaction treatment with extended higher-order virial terms, and on experimental results from 240 to 627 K at pressures to 100 MPa and molalities to $25\ mol\cdot kg^{-1}$. © *1998 American Institute of Physics and American Chemical Society.* [S0047-2689(98)00305-5]

Key words: activity coefficient, apparent molar properties, aqueous solutions, density, enthalpy, heat capacity, magnesium chloride, osmotic coefficient, Pitzer equation, thermodynamics, vapor pressure.

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List of Symbols

A_ϕ, A_H, A_J, A_V	Debye–Hückel coefficients for osmotic coefficient, apparent molar enthalpy, apparent molar constant-pressure heat capacity, and apparent molar volume
b	A constant in Pitzer ion-interaction model, chosen to be 1.2 $kg^{1/2} \cdot mol^{-1/2}$
B_{MX}, B^ϕ_{MX}	Second-order parameters in the Pitzer model
B^L_{MX}, B^V_{MX},	Temperature and pressure derivatives of B_{MX}
$C_{MX}, C^\phi_{MX}, C^{(0)}_{MX}, C^{(1)}_{MX}, C^{(2)}_{MX}$	Third-order parameters in the Pitzer model
C^L_{MX}, C^V_{MX}	Temperature and pressure derivatives of C_{MX}
$C_{p,\phi}$	Apparent molar heat capacity at constant pressure
$C^0_{p,2}$	Apparent molar heat capacity at infinite dilution at constant pressure
$D_{MX}, D^\phi_{MX}, D^{(0)}_{MX}, D^{(1)}_{MX}, D^{(2)}_{MX}$	Fourth-order parameters in the Pitzer model
D^L_{MX}, D^V_{MX}	Temperature and pressure derivatives of D_{MX}
G^E	Excess Gibbs energy of a solution
ΔH_{dil}	Enthalpy of dilution
I	Ionic strength, $I = \frac{1}{2}\Sigma_i m_i z_i^2$
K	Ion association constant
L_ϕ	Relative apparent molar enthalpy
m	Molality
P	Pressure, MPa
P_s	Saturation pressure of pure water
R	Gas constant, 8.3144 $J \cdot K^{-1} \cdot mol^{-1}$
T	Temperature, K
V_ϕ	Apparent molar volume
V^0_2	Apparent molar volume at infinite dilution
w_w	Mass of water, kg
z_M, z_X	Charges of the cation and the anion
α_{B1}	A constant in the Pitzer model, chosen to be 2.0 $kg^{1/2} \cdot mol^{-1/2}$
α_{C1}, α_{C2}	Constants in the extended Pitzer model, chosen to be 0.4 and 0.28 $kg \cdot mol^{-1}$, respectively
$\beta^{(0)}_{MX}, \beta^{(1)}_{MX}$	Ion-interaction parameters in the Pitzer model
$\gamma_\pm$	Mean activity coefficient
ϕ	Osmotic coefficient
v_M, v_X	The stoichiometric numbers of M and X ions in the electrolyte $M_{v_M}X_{v_X}$
v	$v_M + v_X$

1. Introduction

A knowledge of thermodynamic properties of aqueous solutions of magnesium chloride is of great interest from both theoretical and practical standpoints. $MgCl_2$ is a typical example of the $2-1$ charge-type electrolyte and is an important component in many natural and industrial waters. Pressurized high-temperature waters containing dissolved magnesium chloride are encountered in the deep earth and ocean as well as in electric power plants where water of various degrees of purity is the heat transfer fluid. Understanding various geochemical processes and industrial problems requires a thorough knowledge of thermodynamic properties of aqueous electrolyte solutions including those of magnesium chloride. Recently, a Pitzer ion-interaction treatment of thermodynamic properties of aqueous solutions of $MgCl_2$ and other alkaline–earth metal chlorides has been made by Holmes *et al.*[1–3] from 255 to 523 K and to pressures of 100 MPa and molalities of 6.17 $mol \cdot kg^{-1}$. The model gives an excellent representation of thermodynamic properties for these electrolyte solutions in the experimental temperature, pressure, and concentration ranges. Additional results of thermodynamic properties for $MgCl_2(aq)$ under extended experimental conditions are available.[4–17] Also, a very comprehensive set of high-temperature, high-pressure volumetric results has been reported[18] after the Holmes *et al.*[2,3] work was published. Models that accurately describe the excess properties of aqueous electrolytes over wide ranges of temperature, pressure, and concentration are essential to an understanding of chemical processes under extreme conditions. It is therefore desirable to extend the model over the full temperature, pressure, and concentration ranges for which data are available.

In this study, we developed a new general model for $MgCl_2(aq)$ solutions based on a recent ion-interaction treatment with extended higher-order virial terms.[19] The model represents experimental results at temperatures from approximately 240 to 627 K, pressures from the vapor pressure of the solution to 100 MPa, and molality to 25 $mol \cdot kg^{-1}$. Comparisons were made for our model with the experimental data and with the model of Holmes *et al.* in the ranges where both models are applicable.

2. Thermodynamic Properties of $MgCl_2(aq)$

2.1. Description of Equations

The Pitzer ion-interaction model[20] has been widely used to describe the thermodynamic properties of electrolyte solutions both for the isothermal or isobaric composition dependence of various thermodynamic functions and for global representation of these quantities over a range of temperatures and pressures. For representing thermodynamic properties of electrolyte solutions to higher concentrations, extended ion-interaction models have been used in a number of investigations. Filippov *et al.*[21] and Anstiss and Pitzer[22] used higher order virial-coefficient (to sixth order) terms, in addition to those for the binary and ternary ion interactions, and obtained satisfactory results for the treatment of activity and osmotic coefficients at 298 K in concentrated single and mixed electrolyte solutions. With these higher order terms, Ananthaswamy and Atkinson[23] fitted activity and osmotic coefficient data as well as thermal property results for $CaCl_2(aq)$ solutions over the temperature range from 273 to 373 K. Alternatively, Archer[24,25] extended the Pitzer model with an ionic strength-dependent third virial-coefficient term, and obtained good fits of the experimental results over the temperature range from 250 to 600 K at pressures to 100 MPa for $NaCl(aq)$[25] and from 260 to 623 K to 150 MPa for $NaBr(aq)$[24] solutions. Archer's extension of the Pitzer ion-interaction model has been used in the modeling of a number of other aqueous electrolyte solutions.[26,27] Very recently, we have presented equations[19] with third, fourth, and higher-order virial coefficients as a function of ionic strength. Our equations have been very effective in representing the complex behaviors of $MgCl_2(aq)$ and of $CaCl_2(aq)$ to solid saturation at 298 K. The ionic strength-dependent formulation in our equations was selected such that at the third virial level, the only difference from the Archer term for the osmotic coefficient is the first power of I instead of $I^{1/2}$ in the exponential expressions. The expressions for Gibbs energy and the activity coefficient are more complex for the Archer term and progressively much more complex for the fourth and higher virials, but the corresponding expressions in our equations are relatively simple and retain the form of the second-virial-coefficient level for all higher-order coefficients. The selection of such an ionic strength-dependent function has been discussed in detail in a separate paper.[19] In the present work, we adopted this new formulation of the Pitzer model, with two ionic strength-dependent terms in the third order coefficient ($C^{(1)}$ and $C^{(2)}$) and an ionic-strength-independent fourth-order term ($D^{(0)}$) to represent thermodynamic properties of the $MgCl_2(aq)$.

The Pitzer equation to the fourth order for the excess Gibbs free energy, G^E, of the solution of an electrolyte $M_{\upsilon_M}X_{\upsilon_X}$ can be written in general form as

$$\frac{G^{\mathrm{E}}}{w_{\mathrm{w}}RT} = -\frac{4IA_{\phi}}{b}\ln(1+b\sqrt{I}) + 2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})m^2B_{\mathrm{MX}} + 2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{3/2}m^3C_{\mathrm{MX}} + 2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^2m^4D_{\mathrm{MX}}, \qquad (1)$$

$$B_{\mathrm{MX}} = \beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(1)}g(x_{B1}) + \beta_{\mathrm{MX}}^{(2)}g(x_{B2})$$
$$(x_{B1} = \alpha_{B1}I^{1/2};\quad x_{B2} = \alpha_{B2}I^{1/2}), \qquad (2)$$

$$C_{\mathrm{MX}} = C_{\mathrm{MX}}^{(0)} + C_{\mathrm{MX}}^{(1)}g(x_{C1}) + C_{\mathrm{MX}}^{(2)}g(x_{C2})$$
$$(x_{C1} = \alpha_{C1}I;\quad x_{C2} = \alpha_{C2}I), \qquad (3)$$

$$D_{\mathrm{MX}} = D_{\mathrm{MX}}^{(0)} + D_{\mathrm{MX}}^{(1)}g(x_{D1}) + D_{\mathrm{MX}}^{(2)}g(x_{D2})$$
$$(x_{D1} = \alpha_{D1}I^{3/2};\quad x_{D2} = \alpha_{D2}I^{3/2}), \qquad (4)$$

$$g(x) = 2[1-(1+x)\exp(-x)]/x^2, \qquad (5)$$

where $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$, $\beta_{\mathrm{MX}}^{(2)}$, $C_{\mathrm{MX}}^{(0)}$, $C_{\mathrm{MX}}^{(1)}$, $C_{\mathrm{MX}}^{(2)}$, $D_{\mathrm{MX}}^{(0)}$, $D_{\mathrm{MX}}^{(1)}$, and $D_{\mathrm{MX}}^{(2)}$ are adjustable parameters (ion-interaction parameters) that are dependent on temperature and pressure, ν_M and ν_X are the stoichiometric numbers of cations and anions formed upon dissociation, z_M and z_X are the charges of the cation and the anion, respectively, w_{w} is the mass of water in kg, m is the molality of the electrolyte in solution, I is the ionic strength, and A_{ϕ} is the Debye–Hückel parameter for the osmotic coefficient. The quantity b is a constant with the value 1.2 $kg^{1/2} \cdot mol^{-1/2}$. Values of α_{B1}, α_{C1}, and α_{C2} were found to give the best global fit when chosen to be 2.0 $kg^{1/2} \cdot mol^{-1/2}$, 0.4 $kg \cdot mol^{-1}$, and 0.28 $kg \cdot mol^{-1}$, respectively. The $\beta^{(2)}$ term was not needed so no α_{B2} value was selected. An ionic strength-independent fourth-order term, $D_{\mathrm{MX}}^{(0)}$, proved to be sufficient in representing the present database, so no α_{D1} and α_{D2} were needed. The Debye–Hückel coefficients used in the present work were calculated from the Archer and Wang dielectric-constant equation[28] and the Hill equation of state for water.[29]

Appropriate differentiation of Eq. (1) leads to the osmotic coefficient, ϕ, the natural logarithm of the mean activity coefficient, $\ln \gamma_{\pm}$, the relative apparent molar enthalpy, L_{ϕ}, the constant-pressure apparent molar heat capacity, $C_{p,\phi}$, and the apparent molar volume, V_{ϕ}:

$$\phi - 1 = |z_{\mathrm{M}}z_{\mathrm{X}}|f^{\phi} + \frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})}{\nu}mB_{\mathrm{MX}}^{\phi} + \frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{3/2}}{\nu}m^2C_{\mathrm{MX}}^{\phi} + \frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^2}{\nu}m^3D_{\mathrm{MX}}^{\phi}, \qquad (6)$$

$$f^{\phi} = -A_{\phi}I^{1/2}/(1+bI^{1/2}), \qquad (7)$$

$$B^{\phi}_{\mathrm{MX}}=\beta^{(0)}_{\mathrm{MX}}+\beta^{(1)}_{\mathrm{MX}}\exp(-x_{B1})+\beta^{(2)}_{\mathrm{MX}}\exp(-x_{B2}), \quad (8)$$

$$C^{\phi}_{\mathrm{MX}}=2[C^{(0)}_{\mathrm{MX}}+C^{(1)}_{\mathrm{MX}}\exp(-x_{C1})+C^{(2)}_{\mathrm{MX}}\exp(-x_{C2})], \quad (9)$$

$$D^{\phi}_{\mathrm{MX}}=3[D^{(0)}_{\mathrm{MX}}+D^{(1)}_{\mathrm{MX}}\exp(-x_{D1})+D^{(2)}_{\mathrm{MX}}\exp(-x_{D2})], \quad (10)$$

$$\ln \gamma_{\pm}=|z_{\mathrm{M}}z_{\mathrm{X}}|f^{\gamma}+\frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})}{\nu}mB^{\gamma}_{\mathrm{MX}} + \frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{3/2}}{\nu}m^2C^{\gamma}_{\mathrm{MX}}+\frac{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{2}}{\nu}m^3D^{\gamma}_{\mathrm{MX}}, \quad (11)$$

$$f^{\gamma}=-A_{\phi}[I^{1/2}/(1+bI^{1/2})+(2/b)\ln(1+bI^{1/2})], \quad (12)$$

$$B^{\gamma}_{\mathrm{MX}}=2\beta^{(0)}_{\mathrm{MX}}+\beta^{(1)}_{\mathrm{MX}}[g(x_{B1})+\exp(-x_{B1})] + \beta^{(2)}_{\mathrm{MX}}[g(x_{B2})+\exp(-x_{B2})], \quad (13)$$

$$C^{\gamma}_{\mathrm{MX}}=3C^{(0)}_{\mathrm{MX}}+C^{(1)}_{\mathrm{MX}}[g(x_{C1})+2\exp(-x_{C1})]+C^{(2)}_{\mathrm{MX}} \times[g(x_{C2})+2\exp(-x_{C2})], \quad (14)$$

$$D^{\gamma}_{\mathrm{MX}}=4D^{(0)}_{\mathrm{MX}}+D^{(1)}_{\mathrm{MX}}[g(x_{D1})+3\exp(-x_{D1})]+D^{(2)}_{\mathrm{MX}} \times[g(x_{D2})+3\exp(-x_{D2})], \quad (15)$$

$$L_{\phi}=\frac{\nu|z_{\mathrm{M}}z_{\mathrm{X}}|A_H}{2b}\ln(1+bI^{1/2})-2\nu_{\mathrm{M}}\nu_{\mathrm{X}}RT^2[mB^{L}_{\mathrm{MX}} + (\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{1/2}m^2C^{L}_{\mathrm{MX}}+\nu_{\mathrm{M}}\nu_{\mathrm{X}}m^3D^{L}_{\mathrm{MX}}], \quad (16)$$

$$C_{p,\phi}=C^{0}_{p,2}+\frac{\nu|z_{\mathrm{M}}z_{\mathrm{X}}|A_J}{2b}\ln(1+bI^{1/2}) -2\nu_{\mathrm{M}}\nu_{\mathrm{X}}RT^2[mB^{J}_{\mathrm{MX}}+(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{1/2}m^2C^{J}_{\mathrm{MX}} +\nu_{\mathrm{M}}\nu_{\mathrm{X}}m^3D^{J}_{\mathrm{MX}}], \quad (17)$$

$$V_{\phi}=V^{0}_{2}+\frac{\nu|z_{\mathrm{M}}z_{\mathrm{X}}|A_V}{2b}\ln(1+bI^{1/2})+2\nu_{\mathrm{M}}\nu_{\mathrm{X}}RT[mB^{V}_{\mathrm{MX}} + (\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{1/2}m^2C^{V}_{\mathrm{MX}}+\nu_{\mathrm{M}}\nu_{\mathrm{X}}m^3D^{V}_{\mathrm{MX}}], \quad (18)$$

where $\nu=\nu_{\mathrm{M}}+\nu_{\mathrm{X}}$, A_H, A_J and A_V are the Debye–Hückel coefficients for the apparent molar enthalpy, heat capacity, and volume, respectively, $C^{0}_{p,2}$ and V^{0}_{2} are the apparent molar heat capacity and volume, respectively, at infinite dilution, and

$$B^{L}_{\mathrm{MX}}=(\partial B_{\mathrm{MX}}/\partial T)_P=(\partial\beta^{(0)}_{\mathrm{MX}}/\partial T)_P+(\partial\beta^{(1)}_{\mathrm{MX}}/\partial T)_P g(x_{B1}) + (\partial\beta^{(2)}_{\mathrm{MX}}/\partial T)_P g(x_{B2}), \quad (19)$$

$$C^{L}_{\mathrm{MX}}=(\partial C_{\mathrm{MX}}/\partial T)_P=(\partial C^{(0)}_{\mathrm{MX}}/\partial T)_P+(\partial C^{(1)}_{\mathrm{MX}}/\partial T)_P g(x_{C1}) + (\partial C^{(2)}_{\mathrm{MX}}/\partial T)_P g(x_{C2}), \quad (20)$$

$$D^{L}_{\mathrm{MX}}=(\partial D_{\mathrm{MX}}/\partial T)_P=(\partial D^{(0)}_{\mathrm{MX}}/\partial T)_P+(\partial D^{(1)}_{\mathrm{MX}}/\partial T)_P g(x_{D1}) + (\partial D^{(2)}_{\mathrm{MX}}/\partial T)_P g(x_{D2}), \quad (21)$$

$$B^{J}_{\mathrm{MX}}=(\partial^2 B_{\mathrm{MX}}/\partial T^2)_P+(2/T)(\partial B_{\mathrm{MX}}/\partial T)_P, \quad (22)$$

$$C^{J}_{\mathrm{MX}}=(\partial^2 C_{\mathrm{MX}}/\partial T^2)_P+(2/T)(\partial C_{\mathrm{MX}}/\partial T)_P, \quad (23)$$

$$D^{J}_{\mathrm{MX}}=(\partial^2 D_{\mathrm{MX}}/\partial T^2)_P+(2/T)(\partial D_{\mathrm{MX}}/\partial T)_P, \quad (24)$$

$$B^{V}_{\mathrm{MX}}=(\partial B_{\mathrm{MX}}/\partial P)_T, \quad (25)$$

$$C^{V}_{\mathrm{MX}}=(\partial C_{\mathrm{MX}}/\partial P)_T, \quad (26)$$

$$D^{V}_{\mathrm{MX}}=(\partial D_{\mathrm{MX}}/\partial P)_T. \quad (27)$$

2.2. Literature Sources for Thermodynamic Properties

Sources of all of the experimental results used in this study for the global least-squares fit are listed in Table 1. These results were chosen primarily on the basis of their coverage of wide ranges of temperature, pressure, or molality. Thus, in addition to the results[11-13,30-39,41,42,44-64] used by Holmes *et al.*,[2,3] the following high-temperature and/or high-molality results were included: (1) Newly published volumetric data of Obsil *et al.*;[18] (2) vapor pressure data of Lindsay and Liu,[4,5] Urusova and Valyashko,[6-8] and Emons *et al.*;[9] (3) new enthalpy of dilution data of Wang *et al.*[10] and those of Gillespie *et al.*[11] and Simonson *et al.*[12] at temperatures greater than 523 K; and (4) heat capacity data of White *et al.*[13] for $T>499$ K. Additionally, freezing-point depression data of Rodebush[14] and those from the International Critical Tables of Numerical Data (ICT)[15] were also included, together with those of Gibbard and Gossmann,[42] to extend the model down to a temperature of approximately 240 K. Additional data that were considered in the data analysis also included vapor pressure results of Sako *et al.*[43] and Derby and Yngve,[16] isopiestic molalities of Kuschel and Seidel,[40] heat capacity results of Saluja *et al.*,[57] and volumetric results of Romankiw and Chou,[65] Saluja *et al.*[57] and Pepinov *et al.*[17]

For the correct application of the least-squares method, relative weights were assigned to each set of the experimental results to reflect their different variances. The assignment of the weight was based on the compatibility of one set of results with others, the thermodynamic consistency of the data with other properties, and the precision of experimental results as reported by the original investigator. The assigned relative weights are also given in Table 1.

2.3. Temperature and Pressure Dependencies of the Ion-Interaction Parameters

In order to fit simultaneously all of the experimental results listed in Table 1, equations describing the temperature and pressure dependence of the nonzero ion-interaction parameters, $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$, $C^{(1)}_{\mathrm{MX}}$, $C^{(2)}_{\mathrm{MX}}$ and $D^{(0)}_{\mathrm{MX}}$, and V^{0}_{2}, and $C^{0}_{p,2}$ are needed. In the preliminary study of this system, the volumetric data were evaluated and were used to fit Eq. (18) at various temperatures and pressures. The osmotic coefficient, enthalpy, and heat capacity data were then corrected to a single pressure of 17.9 MPa in order to compare the thermodynamic properties at various pressures from different authors. Isothermal fitting of these properties at vari-

TABLE 1. Literature sources for thermodynamic properties of aqueous $MgCl_2$ solutions

Property	Method[a]	T(K)	P(MPa)	m(mol·kg^{-1})	N[b]	Reference	Relative weight[c]
ϕ	iso	298.15	0.1	1.41–5.92	70	Rard and Miller[30]	1.5
ϕ	iso	298.15	0.1	0.11–0.13	4	Rard and Miller[31]	1.5
ϕ	iso	298.15	0.1	0.11–2.02	27	Robinson and Stokes[32]	0.12[d]
ϕ	iso	298.15	0.1	0.31–3.80	26	Robinson and Bower[33]	0.12[d]
ϕ	iso	298.15	0.1	1.14–5.92	24	Stokes[34]	0.12[d]
ϕ	iso	298.15	0.1	0.23–1.15	5	Wu *et al.*[35]	1.5
ϕ	iso	298.15	0.1	0.08–2.76	17	Platford[36]	1.5[d]
ϕ	iso	298.15	0.1	0.39–2.09	10	Saad *et al.*[37]	0.12
ϕ	iso	298.15	0.1	1.10–2.42	6	Frolov *et al.*[38]	0.12
ϕ	iso	298.15	0.1	0.43–2.00	8	Padova and Saad[39]	0.12
ϕ	iso	289.15	0.1	0.75–1.87	6	Kuschel and Seidel[40]	0.12
ϕ	iso	373.45	sat	0.92–6.38	15	Fanghanel and Grjotheim[41]	0.12
ϕ	iso	383–524	sat	0.42–3.95	192	Holmes and Mesmer[2]	1.0
ϕ	fp	255–273	0.1	0.03–2.03	30	Gibbard and Gossmann[42]	0.12
ϕ	fp	240–273	0.1	0.01–2.94	9	ICT[15]	6×10^{-3}
ϕ	fp	240–267	0.1	0.92–2.94	6	Rodebush[14]	6×10^{-3}
ϕ	vp	348–573	sat	1.62–5.15	20	Liu and Lindsay[4]	0.12
ϕ	vp	398–573	sat	0.35	8	Lindsay and Liu[5]	0.12
ϕ	vp	573–623	sat	1.15–25.7	37	Urusova and Valyashko[6]	0.12
ϕ	vp	523.15	sat	1.21–17.9	10	Urusova and Valyashko[7]	0.12
ϕ	vp	523–573	sat	9.25	2	Urusova and Valyashko[8]	0.12
ϕ	vp	402–513	sat	6.94–12.1	72	Emons *et al.*[9]	0.12
ϕ	vp	323–398	sat	2.10–4.10	30	Sako *et al.*[43]	0.12
ΔH_{dil}	cal	473–573	7.0–10.0	0.02–3.52	50	Simonson *et al.*[12]	0.5, 1.0[e]
ΔH_{dil}	cal	523–598	10.3–13.2	0.03–1.04	95	Gillespie *et al.*[11]	1.0
ΔH_{dil}	cal	293	0.1	0.18–5.90	8	Fricke[44]	1.0
ΔH_{dil}	cal	298.15	0.1	0.005–5.70	21	Jahn and Wolf[45]	1.0
ΔH_{dil}	cal	298.15	0.1	0.0001–0.10	10	Lange and Streeck[46]	0.5
ΔH_{dil}	cal	303.15	0.1	0.17–1.21	7	Leung and Millero[47]	1.0
ΔH_{dil}	cal	373–473	sat	0.002–5.43	37	Mayrath and Wood[48]	0.5, 1.0[e]
ΔH_{dil}	cal	523–573	20.5	0.10–1.55	18	Wang *et al.*[10]	1.0
ΔH_{dil}	cal	298.15	0.1	0.003–1.99	13	Snipes *et al.*[49]	0.5, 1.0[e]
$C_{p,\phi}$	cal	353–453	sat	0.22–0.90	24	Likke and Bromley[50]	1.5
$C_{p,\phi}$	cal	349–598	2.33–17.9	0.03–2.26	346	White *et al.*[13]	1.5, 1.0, 0.6[f]
$C_{p,\phi}$	cal	298.15	0.1	0.04–5.52	20	Fedyainov *et al.*[51]	0.3
$C_{p,\phi}$	cal	283–403	sat	0.38–0.95	22	Eigen and Wicke[52]	0.2
$C_{p,\phi}$	cal	298.15	0.1	0.46–5.11	12	Vasilev *et al.*[53]	0.3
$C_{p,\phi}$	cal	298.15	0.1	0.14–5.03	14	Perron *et al.*[54]	6.0
$C_{p,\phi}$	cal	298.15	0.1	0.01–0.34	8	Perron *et al.*[55]	6.0
$C_{p,\phi}$	cal	298–373	0.6	0.11–0.53	20	Saluja *et al.*[56]	1.5
$C_{p,\phi}$	cal	298–373	0.6	0.44–5.19	28	Saluja *et al.*[57]	1.5
$C_{p,\phi}$	cal	298–348	0.1	0.06–6.17	31	Ruskov[58]	0.3
V_ϕ	vib	308–368	0.1	0.35–4.61	67	Connaughton *et al.*[59]	1.0
V_ϕ	pycn/dilat	298.15	0.1	0.001–0.70	6	Dunn[60]	1.0
V_ϕ	vib	298.15	0.1–40.6	0.03–2.95	34	Gates and Wood[61]	1.0
V_ϕ	vib	278–318	0.1	0.01–5.43	144	Lo Surdo *et al.*[62]	1.0
V_ϕ	dilat	323–473	2.03	0.1–1.0	28	Ellis[63]	1.0
V_ϕ	mf	273–323	0.1–100	0.009–0.32	138	Chen *et al.*[64]	1.0
V_ϕ	vib	297–372	0.6	0.44–5.19	28	Saluja *et al.*[57]	1.0
V_ϕ	vib	297–372	0.6	0.11–0.53	20	Saluja *et al.*[56]	1.0

TABLE 1. Literature sources for thermodynamic properties of aqueous $MgCl_2$ solutions—(Continued)

Property	Method[a]	T(K)	P(MPa)	$m(\mathrm{mol\cdot kg^{-1}})$	N[b]	Reference	Relative weight[c]
V_ϕ	vib	298.15	0.1	0.14–5.03	14	Perron *et al.*[54]	1.0
V_ϕ	vib	298.15	0.1	0.004–0.34	9	Perron *et al.*[55]	1.0
V_ϕ	dilat	298.15	0.1	0.46–5.11	12	Vasilev *et al.*[53]	0.01
V_ϕ	dilat	298–348	0.1	0.06–6.17	15	Ruskov[58]	0.01
V_ϕ	vib	369–627	10–30	0.005–3.04	147	Obsil *et al.*[18]	0.5, 1.0[g]
V_ϕ	vib	298–318	0.1	0.54–3.31	30	Romankiw and Chou[65]	1.0

[a] Experimental method: (iso) isopiestic; (fp) freezing point; (vp) vapor pressure; (cal) calorimetric; (vib) vibrating tube; (pycn) pycnometric; (dilat) dilatometric; (mf) magnetic float.

[b] N–number of data points.

[c] Relative weight was assigned such that for the osmotic coefficient, it is the ratio of the weight assigned to a specific data point to the weight assigned to Holmes and Mesmer's data (See Ref. 2) for the enthalpy of dilution data, it is relative to that assigned to Gillespie *et al.* data; (See Ref. 11); for the apparent molar heat capacities, it is relative to those assigned to White *et al.* (See Ref. 15) data; and for the apparent molar volumes, it is relative to those assigned to Perron *et al.* (Refs. 54 and 55) data.

[d] Certain data points were weighted zero, based on the evaluation by Rard and Miller (Ref. 30).

[e] All data at $m<0.1\ \mathrm{mol\cdot kg^{-1}}$ were assigned a relative weight of 0.5.

[f] Data at $m<0.1\ \mathrm{mol\cdot kg^{-1}}$ were assigned a relative weight of 0.6, those at $T\geqslant 549$ K were assigned 1.0, others were 1.5.

[g] Data at $m<0.1\ \mathrm{mol\cdot kg^{-1}}$ and $T\geqslant 573$ K were assigned a relative weight of 0.5, others were assigned 1.0.

ous temperatures at this pressure gave a general indication of the temperature dependence of the ion-interaction parameters. However, the existing experimental volumetric data do not cover the entire temperature and concentration regions where other types of thermodynamic data are available. Therefore, corrections of the thermodynamic properties to a single pressure based on the volumetric fit may be subject to large uncertainties in the ranges where volumetric results do not exist. But these isothermal and isobaric fits in our initial investigation suggested the temperature and pressure dependent forms for the ion-interaction parameters and the apparent molar volumes and heat capacities at infinite dilution, on which our final global fit was based. The optimum forms for these equations are listed below, where T is in K and P in MPa.

$$f^G(T,P)=F_0(T)+F_1(T)\cdot P+F_2(T)\cdot P^2/2, \tag{28}$$

where f^G stands for ion-interaction parameters, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $C^{(0)}_{MX}$, $C^{(1)}_{MX}$, $C^{(2)}_{MX}$, and $D^{(0)}_{MX}$, and

$$F_j(T)=a_{j,1}+a_{j,2}\ \ln T+a_{j,3}T+a_{j,4}T^2+a_{j,5}T^3+a_{j,6}T^{10}$$
$$+a_{j,7}/(647-T)^2 \quad (j=0,1,2), \tag{29}$$

$$V^0_2(T,P)=V_1(T)+V_2(T)\cdot P+V_3(T)\cdot P^2, \tag{30}$$

$$V_i(T)=b_{i,1}+b_{i,2}\ \ln T+b_{i,3}T+b_{i,4}T^2+b_{i,5}T^3+b_{i,6}T^{10}$$
$$+b_{i,7}/(647-T)^2 \quad (i=1,2,3). \tag{31}$$

The expression for $C^0_{p,2}$ follows readily from the relationship

$$(\partial C_P/\partial P)_T=-T\cdot(\partial^2 V/\partial T^2)_P, \tag{32}$$

as

$$C^0_{p,2}(T,P)=J_0(T)+J_1(T)\cdot P+J_2(T)\cdot P^2/2$$
$$+J_3(T)\cdot P^3/3, \tag{33}$$

$$J_i(T)=b_{i,2}/T-2b_{i,4}T-6b_{i,5}T^2-90b_{i,6}T^9-6b_{i,7}T/$$
$$(647-T)^4 \quad (i=1,2,3), \tag{34}$$

$$J_0(T)=c_1+c_2T+c_3T^2+c_4/(647-T)^4. \tag{35}$$

3. Results of Data Analysis

3.1. The Overall Fit

The global least-squares regression, which determined the temperature- and pressure-independent parameters of the model equations, consists of fitting Eqs. (6) and (16)–(18) simultaneously to a total of 2259 experimental points of various types listed in Table 1. Values of adjustable parameters for Eqs. (28)–(31) and (33)–(35) are listed in Table 2, along with their associated standard errors. The standard deviations of the fit over the entire temperature, pressure, and concentration ranges were 1.12 $\mathrm{kJ\cdot mol^{-1}}$ for the enthalpy of dilution, 34.0 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for the apparent molar heat capacities, 0.030 for the osmotic coefficients, and 1.58 $\mathrm{cm^3\cdot mol^{-1}}$ for the apparent molar volumes; while those in the range of $T\leqslant 524$ K were 0.86 $\mathrm{kJ\cdot mol^{-1}}$, 20.0 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$, 0.028, and 0.64 $\mathrm{cm^3\cdot mol^{-1}}$ for the enthalpies of dilution, apparent molar heat capacities, osmotic coefficients, and apparent molar volumes, respectively. Table 3 summarizes the data regression for each type of experimental result at various temperature ranges. Calculated values of ϕ, ln $\gamma_\pm$, L_ϕ, $C_{p,\phi}$, and V_ϕ based on Eqs. (6), (11), and (16)–(18) and parameters listed in Table 2 are given in Tables 4–8, respectively, at the round molalities and at various temperatures and pressures.

3.2. Volumetric Results

Figure 1 shows differences of the experimentally determined V_ϕ from those calculated using the fitted equations at various temperatures and pressures. The only two sources of volumetric data at $T>473$ K are those of Obsil *et al.*[18] and of Pepinov *et al.*[17] Both data sets were measured to a pressure of 30 MPa. However, these two data sets are not consistent with each other. Values of V_ϕ determined by Pepinov *et al.*

TABLE 2. Parameters for Eqs. (28)–(35)[a]

	$\beta^{(0)}$	σ_s	$\beta^{(1)}$	σ_s	$C^{(0)}$	σ_s
$a_{0.1}$	-5.50111455E+01	7.70789E-03	7.21220552E+01	3.92013E-02	5.92428240E+00	1.19829E-03
$a_{0.2}$	1.50130326E+01	1.56371E-03	-1.77145085E+01	8.27895E-03	-1.65126386E+00	2.52317E-04
$a_{0.3}$	-1.58107430E-01	1.29989E-05	1.14397153E-01	2.87792E-05	1.89399822E-02	2.05489E-06
$a_{0.4}$	2.30409919E-04	2.58829E-08			-2.99972128E-05	3.93260E-09
$a_{0.5}$	-1.31768095E-07	1.84907E-11	-1.43588435E-07	1.65808E-11	1.89174291E-08	2.84338E-12
$a_{0.6}$	-1.26699609E-28	1.90820E-32	1.72952766E-27	7.87220E-32		
$a_{0.7}$	2.82197499E+02	5.61996E-02	3.41920714E+03	1.64626E-01	5.49030201E+01	5.30195E-03
$a_{1.1}$					4.50114048E-02	2.90080E-06
$a_{1.2}$			2.28440612E-04	5.20074E-08	-1.08427926E-02	6.84641E-07
$a_{1.3}$	8.39661960E-05	4.08623E-09			7.41041864E-05	4.39843E-09
$a_{1.4}$	-4.60207270E-07	2.19045E-11			-5.99961498E-08	3.46722E-12
$a_{1.5}$	6.21165614E-10	2.92386E-14				
$a_{1.6}$	8.43555937E-31	5.21922E-35	-1.77573402E-29	5.50889E-34		
$a_{1.7}$			-2.29668879E+02	1.00529E-03	-4.60562847E+00	6.73671E-05
$a_{2.1}$						
$a_{2.2}$						
$a_{2.3}$			-2.71485086E-07	1.78194E-11		
$a_{2.4}$						
$a_{2.5}$					-1.39016981E-15	-2.82482E-18
$a_{2.6}$						
$a_{2.7}$	-1.11176553E+00	3.79926E-05	1.01000272E+01	8.33834E-05	1.40556304E-01	3.74694E-06

	$C^{(1)}$	σ_s	$C^{(2)}$	σ_s	$D^{(0)}$	σ_s
$a_{0.1}$					4.08980052E-02	1.51418E-05
$a_{0.2}$	-1.02256042E+00	3.95536E-04				
$a_{0.3}$	3.77018617E-02	1.44366E-05	-2.28040769E-03	1.01829E-06	-2.95119845E-04	1.07475E-07
$a_{0.4}$	-7.91682934E-05	2.96769E-08	1.37425889E-05	4.43055E-09	6.91001227E-07	2.53134E-10
$a_{0.5}$	5.91314258E-08	2.12441E-11	-1.94821902E-08	4.99198E-12	-5.32314849E-10	1.98484E-13
$a_{0.6}$			1.04649784E-28	1.51454E-32	3.97961809E-31	1.80555E-34
$a_{0.7}$	-2.28493084E+02	4.76744E-02				
$a_{1.1}$						
$a_{1.2}$						
$a_{1.3}$	-7.79259941E-05	4.19186E-09				
$a_{1.4}$	4.28675876E-07	2.22100E-11				
$a_{1.5}$	-5.77509662E-10	2.91789E-14				
$a_{1.6}$						
$a_{1.7}$						
$a_{2.1}$	-5.13962051E-04	4.38074E-08				
$a_{2.2}$	9.30761142E-05	7.88383E-09				
$a_{2.3}$						
$a_{2.4}$						
$a_{2.5}$	-7.43350922E-13	4.51204E-17				
$a_{2.6}$						
$a_{2.7}$	1.12721557E+00	3.85461E-05				

	$V^{(0)}$	σ_s		J_0	σ_s
$b_{1.1}$	-1.17446972E+04	1.01242E+00	c_1	-1.85339983E+03	8.30088E-02
$b_{1.2}$	2.86541606E+03	2.51507E-01	c_2	1.00024310E+01	4.56226E-04
$b_{1.3}$	-2.27968076E+01	2.15585E-03	c_3	-1.54388692E-02	6.08434E-07
$b_{1.4}$	3.09897542E-02	3.09045E-06	c_4	-8.54129389E+10	1.72795E+06
$b_{1.5}$	-1.92379975E-05	1.97867E-09			
$b_{1.6}$	1.67447187E-26	3.31428E-30			
$b_{1.7}$	-1.91185804E+06	5.99660E-01			
$b_{2.1}$					
$b_{2.2}$					
$b_{2.3}$	-4.00100143E-04	7.23442E-08			
$b_{2.4}$					
$b_{2.5}$	-2.43204343E-08	1.06579E-12			
$b_{2.6}$	-6.04921882E-28	4.89952E-32			
$b_{2.7}$	1.08024906E+05	4.69334E+00			
$b_{3.1}$					
$b_{3.2}$	1.19091585E-02	7.31144E-07			
$b_{3.3}$	4.19764987E-04	2.59254E-08			
$b_{3.4}$	7.93310194E-07	4.65755E-11			
$b_{3.5}$					
$b_{3.6}$					
$b_{3.7}$	-1.66310231E-03	9.09209E-02			

[a] Values following the parameters are the corresponding standard errors.

TABLE 3. Summary of data regression for experimental results

Property	T/K	P/MPa	m/mol·kg^{-1}	Standard deviation of fit[a]
V_ϕ	273–627	0.1–100	0.001–5.4	**1.58**
	273–298	0.1–100	0.001–5.4	0.53
	303–372	0.1–80	0.015–5.3	0.58
	373–517	2–30	0.015–3.04	1.26
	573	10–30	0.03–3.04	1.55
	627	20–30	0.005–1.15	6.07
ϕ	254–623	0.1–Sat	0.03–25.7	**0.030**
	254–298	0.1	0.03–5.92	0.0078
	323–423	Sat	0.35–9.25	0.035
	425–524	Sat	0.35–17.9	0.031
	548–623	Sat	0.35–25.7	0.049
ΔH_{dil}	292–598	0.1–20.5	0.0001–5.9	**1.12**
	292–303	0.1	0.0001–5.9	0.27
	373–473	Sat–7	0.0016–5.4	0.57
	523–598	7–20.5	0.017–3.5	1.26
$C_{p,\phi}$	283–598	Sat–17.9	0.013–6.17	**34**
	283–298	0.1	0.013–5.8	23
	313–373	Sat–17.7	0.031–6.17	15
	393–499	Sat–17.9	0.031–2.26	18
	549–598	10.1–17.9	0.031–2.26	64

[a] Units are cm^3·mol^{-1} for V_ϕ, kJ·mol^{-1} for ΔH_{dil}, and J·K^{-1}·mol^{-1} for $C_{p,\phi}$.

are about 15% less negative than those of Obsil *et al.* at 573 K. Data of Obsil *et al.* for $T<473$ K are in accordance with the 2 MPa data of Ellis.[63] Thus, the Obsil *et al.* data were included in the fit, while the Pepinov *et al.* data were given zero weight. Values of V_ϕ reported by Vasilev *et al.*[53] at 298 K are systematically higher than those of the others at this temperature. Similar cases were also found for the Ruskov[58] data to 348 K. These data were given a substantially reduced weight. The 298 K, 0.1 MPa values of V_ϕ reported by Gates and Wood,[61] Dunn,[60] Lo Surdo *et al.*,[62] Chen *et al.*,[64] Romankiw and Chou,[65] and Perron *et al.*[54,55] agree within 1%. These data were assigned the same weight in the fit. At higher pressures, the Gates and Wood[61] data differ by less than 4% from those of Chen *et al.*[64] at pressures from 10 to 40 MPa. They were equally weighted at these pressures. Ellis' data covers the intermediate temperature range from 323 to 473 K at a pressure of 2.03 MPa, and are in accordance with high-temperature, high-pressure data of Obsil *et al.* and were assigned the same weight as the Obsil *et al.* data. Obsil *et al.* data at $m<0.1$ mol·kg^{-1} are relatively scattered, and these data, together with their data at $T\gtrsim 573$ K, were assigned a lower weight than their results at higher molalities. Thus, standard deviations of the fit for apparent molar volumes are 0.53 cm^3·mol^{-1} for 273 K$\leq T \leq$298 K (P $=0.1-100$ MPa), 0.58 cm^3·mol^{-1} for 298 K$<T<$373 K ($P=0.1-80$ MPa), 1.26 cm^3·mol^{-1} for 373 K$\leq T<$523 K ($P=2-30$ MPa), 1.55 cm^3·mol^{-1} at $T=573$ K (P $=10-30$ MPa), and 6.07 cm^3·mol^{-1} at $T=627$ K (P $=20-30$ MPa).

3.3. Osmotic Coefficient Results

The osmotic coefficient results used in this study were obtained from three types of measurements. These are isopiestic molalities, vapor pressure decreases, and freezing-point depression.

Goldberg and Nuttall[66] and Rard and Miller[30] reviewed the activity and osmotic coefficient data at 298 K for MgCl$_2$(aq). Rard and Miller also reported a comprehensive set of isopiestic molalities of MgCl$_2$(aq) covering molalities to 5.9 mol·kg^{-1}. Above 2.5 mol·kg^{-1}, the Rard and Miller measurements give significantly higher osmotic coefficients than the earlier data of Stokes.[34] The difference probably arose from contamination with alkali chlorides in those earlier measurements.[30] The Rard and Miller values were adopted for the isopiestic ratios. These and other ϕ values from isopiestic measurements were recalculated using the more recent equations for the reference solutes: Archer[25] for NaCl(aq), Clegg *et al.*[26] for H$_2$SO$_4$(aq), and Pitzer *et al.*[19] for CaCl$_2$(aq). Below 2.5 mol·kg^{-1}, the Rard and Miller[30] and Goldberg and Nuttall[66] evaluations of osmotic coefficients from different sets of measurements are essentially the same. Only the values given large weights in these reviews are significantly weighted in our calculations. A few more recent measurements of Kuschel and Seidel[40] were also included. Earlier freezing-point data of Rodebush[14] and those from ICT[15] differ from those of Gibbard and Gossmann[42] by more than 0.03 in ϕ at 255 K and show a trend of increasing difference with decreasing temperature. Rodebush and ICT data were given reduced weight in the overall fit. Osmotic coefficients from these sources differ from the values calculated using the present model by 0.025 at 255 K, and this difference increases with decreasing temperature.

At higher temperatures, there are several important sets of osmotic coefficient data that go beyond 500 K and cover molality range to 25 mol·kg^{-1} including the isopiestic measurements of Holmes and Mesmer,[2] vapor pressure measurements of Liu and Lindsay,[4,5] Urusova and Valyashko,[6–8] and Emons *et al.*[9] In the Holmes *et al.*[2,3] treatment of MgCl$_2$(aq), the vapor pressure data were not included because those data either could not be fit with their model with an acceptable error of fit[2] or are beyond the upper molality limit of their study. Osmotic coefficients from vapor pressure measurements of Liu and Lindsay[4] and from isopiestic measurements of Holmes *et al.*[2] differ by up to 0.05 with Liu and Lindsay values being greater. On the other hand, values of ϕ at 523 and 573 K from vapor pressure measurements of Liu and Lindsay[4] and of Urusova and Valyashko[6,7] agree reasonably with each other within their experimental uncertainties. However, osmotic coefficients from vapor pressure measurements show relatively large scatter, and therefore were given smaller weights compared with those from isopiestic measurements of Holmes *et al.* under corresponding conditions. The osmotic coefficients of Sako *et al.*[43] at 1.05 mol·kg^{-1} and of Derby and Yngve[16] as calculated from their vapor pressure data were far off those obtained from other data sets in the corresponding temperature, pressure, and concentra-

TABLE 4. Calculated osmotic coefficients of $MgCl_2(aq)$ at saturation pressures using Eq. (6) and parameters in Table 2

$m/\mathrm{mol \cdot kg^{-1}}$	373.15 K	423.15 K	473.15 K	523.15 K	573.15 K	623.15 K
0.001	0.9560	0.9495	0.9404	0.9276	0.9074	0.8626
0.005	0.9161	0.9035	0.8853	0.8595	0.8212	0.7407
0.01	0.8942	0.8781	0.8541	0.8205	0.7722	0.6751
0.02	0.8717	0.8517	0.8211	0.7785	0.7196	0.6093
0.05	0.8460	0.8207	0.7807	0.7253	0.6533	0.5354
0.10	0.8332	0.8034	0.7568	0.6921	0.6105	0.4922
0.20	0.8289	0.7930	0.7403	0.6667	0.5721	0.4441
0.30	0.8344	0.7926	0.7354	0.6557	0.5494	0.4039
0.40	0.8461	0.7984	0.7364	0.6507	0.5335	0.3695
0.50	0.8628	0.8090	0.7416	0.6497	0.5223	0.3418
0.60	0.8835	0.8234	0.7501	0.6515	0.5148	0.3210
0.70	0.9074	0.8409	0.7612	0.6557	0.5103	0.3065
0.80	0.9339	0.8608	0.7743	0.6617	0.5084	0.2977
0.90	0.9623	0.8825	0.7891	0.6692	0.5086	0.2939
1.00	0.9921	0.9057	0.8053	0.6781	0.5106	0.2942
1.20	1.0548	0.9549	0.8407	0.6993	0.5191	0.3042
1.40	1.1201	1.0066	0.8791	0.7243	0.5326	0.3230
1.60	1.1869	1.0599	0.9198	0.7527	0.5505	0.3470
1.80	1.2547	1.1144	0.9626	0.7842	0.5721	0.3736
2.00	1.3235	1.1701	1.0072	0.8187	0.5973	0.4011
2.25	1.4112	1.2414	1.0656	0.8656	0.6333	0.4352
2.50	1.5010	1.3152	1.1269	0.9163	0.6738	0.4681
2.75	1.5935	1.3918	1.1909	0.9704	0.7183	0.4994
3.00	1.6891	1.4715	1.2576	1.0272	0.7661	0.5292
3.25	1.7879	1.5544	1.3269	1.0861	0.8166	0.5577
3.50	1.8900	1.6406	1.3984	1.1466	0.8691	0.5853
3.75	1.9954	1.7300	1.4719	1.2080	0.9231	0.6124
4.00	2.1038	1.8223	1.5471	1.2698	0.9778	0.6393
4.50	2.3289	2.0146	1.7012	1.3928	1.0877	0.6937
5.00	2.5619	2.2145	1.8579	1.5124	1.1956	0.7501
5.50	2.7990	2.4184	2.0149	1.6265	1.2989	0.8090
6.00	3.0357	2.6225	2.1698	1.7337	1.3963	0.8703
6.50	...	2.8229	2.3206	1.8332	1.4868	0.9334
7.00	...	3.0158	2.4656	1.9247	1.5702	0.9975
7.50	...	3.1975	2.6031	2.0080	1.6463	1.0616
8.00	...	3.3643	2.7317	2.0834	1.7154	1.1250
8.50	...	3.5128	2.8498	2.1509	1.7776	1.1870
9.00	...	3.6395	2.9562	2.2107	1.8333	1.2468
9.50	...	...	3.0495	2.2631	1.8828	1.3041
10.00	...	...	3.1284	2.3084	1.9265	1.3585
10.50	...	...	3.1918	2.3466	1.9646	1.4096
11.00	...	...	3.2382	2.3779	1.9975	1.4574
11.50	...	...	3.2665	2.4026	2.0255	1.5017
12.00	...	...	3.2755	2.4208	2.0489	1.5425
13.00	...	...	...	2.4382	2.0828	1.6135
14.00	...	...	...	2.4310	2.1014	1.6707
15.00	...	...	...	2.4003	2.1067	1.7148
16.00	...	...	...	2.3469	2.1009	1.7468
17.00	...	...	...	2.2717	2.0859	1.7676
18.00	...	...	...	2.1755	2.0637	1.7783
19.00	...	...	...	...	2.0363	1.7801
20.00	...	...	...	...	2.0058	1.7742
21.00	...	...	...	...	1.9741	1.7616
22.00	...	...	...	...	1.9433	1.7435
23.00	...	...	...	...	...	1.7213
24.00	...	...	...	...	...	1.6959
25.00	...	...	...	...	...	1.6687

TABLE 5. Calculated ln $\gamma_\pm$ of $MgCl_2(aq)$ at saturation pressures using Eq. (11) and parameters in Table 2

$m/\mathrm{mol\cdot kg^{-1}}$	373.15 K	423.15 K	473.15 K	523.15 K	573.15 K	623.15 K
0.001	−0.1382	−0.1585	−0.1865	−0.2264	−0.2897	−0.4325
0.005	−0.2786	−0.3199	−0.3784	−0.4612	−0.5887	−0.8667
0.01	−0.3661	−0.4209	−0.4997	−0.6108	−0.7784	−1.1345
0.02	−0.4697	−0.5409	−0.6452	−0.7918	−1.0070	−1.4486
0.05	−0.6253	−0.7226	−0.8686	−1.0729	−1.3612	−1.9159
0.10	−0.7498	−0.8705	−1.0532	−1.3084	−1.6595	−2.2965
0.20	−0.8718	−1.0213	−1.2445	−1.5565	−1.9813	−2.7122
0.30	−0.9349	−1.1059	−1.3558	−1.7050	−2.1822	−2.9855
0.40	−0.9694	−1.1591	−1.4309	−1.8098	−2.3300	−3.1963
0.50	−0.9853	−1.1925	−1.4840	−1.8890	−2.4466	−3.3678
0.60	−0.9878	−1.2117	−1.5220	−1.9509	−2.5418	−3.5106
0.70	−0.9801	−1.2201	−1.5486	−2.0002	−2.6215	−3.6309
0.80	−0.9643	−1.2202	−1.5665	−2.0398	−2.6890	−3.7329
0.90	−0.9421	−1.2136	−1.5774	−2.0716	−2.7467	−3.8197
1.00	−0.9147	−1.2017	−1.5827	−2.0971	−2.7964	−3.8939
1.20	−0.8479	−1.1653	−1.5798	−2.1329	−2.8765	−4.0118
1.40	−0.7693	−1.1167	−1.5631	−2.1524	−2.9361	−4.0989
1.60	−0.6822	−1.0590	−1.5358	−2.1590	−2.9795	−4.1638
1.80	−0.5884	−0.9943	−1.5000	−2.1548	−3.0096	−4.2126
2.00	−0.4892	−0.9238	−1.4570	−2.1413	−3.0282	−4.2497
2.25	−0.3584	−0.8283	−1.3945	−2.1131	−3.0376	−4.2841
2.50	−0.2206	−0.7253	−1.3232	−2.0739	−3.0337	−4.3090
2.75	−0.0760	−0.6151	−1.2440	−2.0253	−3.0182	−4.3269
3.00	0.0752	−0.4979	−1.1579	−1.9687	−2.9929	−4.3394
3.25	0.2330	−0.3740	−1.0653	−1.9053	−2.9591	−4.3474
3.50	0.3973	−0.2436	−0.9669	−1.8362	−2.9183	−4.3516
3.75	0.5676	−0.1070	−0.8634	−1.7626	−2.8716	−4.3522
4.00	0.7438	0.0354	−0.7554	−1.6854	−2.8201	−4.3495
4.50	1.1118	0.3355	−0.5280	−1.5235	−2.7064	−4.3344
5.00	1.4968	0.6526	−0.2893	−1.3562	−2.5837	−4.3074
5.50	1.8939	0.9818	−0.0432	−1.1879	−2.4568	−4.2696
6.00	2.2973	1.3181	0.2067	−1.0215	−2.3292	−4.2223
6.50	···	1.6563	0.4571	−0.8593	−2.2034	−4.1671
7.00	···	1.9914	0.7053	−0.7027	−2.0808	−4.1056
7.50	···	2.3185	0.9487	−0.5527	−1.9627	−4.0394
8.00	···	2.6325	1.1849	−0.4098	−1.8497	−3.9700
8.50	···	2.9289	1.4116	−0.2746	−1.7422	−3.8986
9.00	···	3.2030	1.6267	−0.1473	−1.6404	−3.8264
9.50	···	···	1.8284	−0.0279	−1.5445	−3.7542
10.00	···	···	2.0145	0.0833	−1.4544	−3.6828
10.50	···	···	2.1833	0.1863	−1.3701	−3.6129
11.00	···	···	2.3329	0.2810	−1.2916	−3.5450
11.50	···	···	2.4614	0.3675	−1.2186	−3.4794
12.00	···	···	2.5671	0.4458	−1.1511	−3.4164
13.00	···	···	···	0.5778	−1.0318	−3.2991
14.00	···	···	···	0.6771	−0.9322	−3.1942
15.00	···	···	···	0.7442	−0.8506	−3.1023
16.00	···	···	···	0.7796	−0.7851	−3.0231
17.00	···	···	···	0.7839	−0.7338	−2.9563
18.00	···	···	···	0.7577	−0.6945	2.9013
19.00	···	···	···	···	−0.6651	−2.8574
20.00	···	···	···	···	−0.6432	−2.8234
21.00	···	···	···	···	−0.6266	−2.7985
22.00	···	···	···	···	−0.6128	−2.7815
23.00	···	···	···	···	···	−2.7712
24.00	···	···	···	···	···	−2.7664
25.00	···	···	···	···	···	−2.7658

TABLE 6. Calculated L_ϕ of $MgCl_2(aq)$ at various temperatures and pressures using Eq. (16) and parameters in Table 2[a]

m	373.15 K				473.15 K			
$mol \cdot kg^{-1}$	P_s	5 MPa	10 MPa	20 MPa	P_s	5 MPa	10 MPa	20 MPa
0.001	0.82	0.81	0.80	0.78	2.52	2.48	2.41	2.31
0.005	1.67	1.65	1.63	1.60	5.36	5.27	5.16	4.95
0.01	2.22	2.20	2.18	2.13	7.31	7.20	7.05	6.79
0.02	2.90	2.87	2.84	2.79	9.83	9.70	9.52	9.19
0.05	3.99	3.96	3.93	3.86	14.17	14.01	13.78	13.37
0.10	5.00	4.97	4.93	4.86	18.22	18.03	17.76	17.25
0.20	6.26	6.23	6.19	6.12	22.87	22.62	22.27	21.62
0.30	7.21	7.18	7.14	7.06	25.86	25.56	25.15	24.37
0.40	8.03	7.99	7.95	7.87	28.14	27.80	27.33	26.45
0.50	8.76	8.72	8.68	8.59	30.03	29.66	29.15	28.20
0.60	9.45	9.40	9.35	9.26	31.70	31.31	30.76	29.75
0.70	10.10	10.04	9.99	9.89	33.22	32.81	32.24	31.18
0.80	10.71	10.66	10.60	10.49	34.64	34.21	33.62	32.53
0.90	11.31	11.25	11.19	11.07	35.99	35.54	34.93	33.82
1.00	11.89	11.82	11.75	11.63	37.27	36.81	36.19	35.07
1.20	13.01	12.93	12.86	12.71	39.71	39.23	38.58	37.43
1.40	14.10	14.02	13.93	13.77	42.02	41.51	40.83	39.64
1.60	15.18	15.08	14.99	14.81	44.21	43.67	42.96	41.72
1.80	16.24	16.14	16.03	15.84	46.30	45.73	44.98	43.68
2.00	17.30	17.19	17.08	16.87	48.30	47.70	46.91	45.53
2.25	18.61	18.49	18.37	18.15	50.68	50.04	49.19	47.71
2.50	19.92	19.79	19.67	19.43	52.94	52.26	51.35	49.77
2.75	21.22	21.09	20.96	20.71	55.11	54.39	53.43	51.76
3.00	22.52	22.38	22.24	21.98	57.19	56.45	55.45	53.71
3.25	23.80	23.66	23.52	23.25	59.20	58.45	57.44	55.65
3.50	25.07	24.92	24.78	24.51	61.16	60.41	59.41	57.63
3.75	26.32	26.18	26.03	25.75	63.08	62.36	61.39	59.67
4.00	27.56	27.42	27.27	26.98	64.98	64.30	63.40	61.80
0.001	4.67	4.41	4.22	4.06	10.55	10.17	9.08	8.27
0.005	9.75	9.25	8.90	8.60	21.43	20.67	18.51	16.92
0.01	13.14	12.52	12.08	11.70	28.31	27.32	24.52	22.47
0.02	17.43	16.67	16.15	15.69	36.58	35.31	31.79	29.24
0.05	24.58	23.66	23.04	22.50	49.34	47.67	43.11	39.91
0.10	31.11	30.08	29.39	28.79	60.17	58.16	52.80	49.14
0.20	38.67	37.46	36.66	35.97	72.50	70.11	63.83	59.65
0.30	43.67	42.30	41.38	40.59	81.02	78.34	71.36	66.76
0.40	47.55	46.03	45.01	44.12	87.94	85.02	77.42	72.43
0.50	50.82	49.16	48.04	47.07	93.90	90.77	82.62	77.25
0.60	53.69	51.90	50.70	49.65	99.18	95.86	87.20	81.49
0.70	56.27	54.38	53.11	52.00	103.9	100.4	91.3	85.29
0.80	58.65	56.67	55.33	54.17	108.3	104.6	95.1	88.75
0.90	60.88	58.81	57.41	56.20	112.2	108.4	98.5	91.94
1.00	62.98	60.83	59.38	58.12	115.9	112.0	101.8	94.90
1.20	66.89	64.59	63.03	61.69	122.5	118.4	107.6	100.3
1.40	70.50	68.05	66.40	64.96	128.3	124.0	112.8	105.3
1.60	73.89	71.28	69.52	67.99	133.6	129.2	117.6	109.9
1.80	77.08	74.32	72.44	70.81	138.4	133.8	122.1	114.3
2.00	80.11	77.19	75.20	73.46	142.7	138.2	126.4	118.6
2.25	83.68	80.58	78.44	76.57	147.8	143.2	131.5	123.9
2.50	87.03	83.77	81.51	79.52	152.4	147.9	136.4	129.2
2.75	90.19	86.80	84.44	82.36	156.5	152.1	141.2	134.5
3.00	93.16	89.69	87.28	85.13	160.3	156.1	145.9	139.9
3.25	95.95	92.48	90.06	87.90	163.6	159.6	150.4	145.5
3.50	98.59	95.18	92.81	90.69	166.5	162.8	154.8	151.1
3.75	101.1	97.82	95.56	93.54	168.9	165.6	159.1	156.7
4.00	103.4	100.4	98.4	96.50	170.8	168.1	163.2	162.5

[a] The unit of L_ϕ is $kJ \cdot mol^{-1}$.

TABLE 7. Calculated $C_{p,\phi}$ of $MgCl_2(aq)$ at various temperatures and pressures using Eq. (17) and parameters in Table 2[a,b]

m	373.15 K			473.15 K			523.15 K			598.15 K
mol·kg^{-1}	5 MPa	10 MPa	17.9 MPa	5 MPa	10 MPa	17.9 MPa	5 MPa	10 MPa	17.9 MPa	17.9 MPa
0.001	−271	−266	−258	−611	−587	−555	−1030	−948	−855	−3337
0.005	−259	−254	−247	−580	−556	−526	−965	−889	−803	−2947
0.01	−251	−247	−240	−559	−536	−506	−925	−852	−770	−2717
0.02	−241	−236	−229	−531	−509	−480	−878	−809	−731	−2462
0.05	−223	−218	−212	−484	−462	−433	−809	−744	−670	−2129
0.10	−207	−203	−197	−439	−418	−390	−752	−691	−619	−1912
0.20	−191	−188	−183	−388	−367	−340	−686	−627	−558	−1719
0.30	−183	−179	−175	−354	−334	−308	−637	−582	−515	−1592
0.40	−177	−174	−170	−329	−310	−285	−596	−544	−480	−1483
0.50	−172	−170	−166	−308	−290	−266	−560	−511	−450	−1385
0.60	−168	−165	−162	−290	−272	−249	−528	−481	−424	−1295
0.70	−164	−161	−158	−275	−257	−235	−500	−455	−400	−1215
0.80	−160	−157	−154	−261	−244	−222	−474	−432	−380	−1143
0.90	−156	−153	−150	−248	−231	−210	−450	−410	−361	−1078
1.00	−151	−149	−146	−236	−220	−199	−428	−391	−344	−1021
1.20	−143	−141	−137	−214	−199	−179	−389	−356	−314	−923
1.40	−135	−133	−129	−195	−180	−162	−355	−325	−288	−842
1.60	−128	−126	−122	−177	−163	−146	−324	−297	−264	−773
1.80	−121	−119	−115	−161	−148	−132	−295	−271	−241	−711
2.00	−115	−112	−109	−145	−134	−119	−268	−246	−220	−651
2.25	−107	−105	−102	−128	−118	−106	−236	−217	−193	−577
2.50	−101	−99	−96	*−113*	*−104*	*−93*	*−207*	*−189*	*−167*	···
2.75	−95	−93	−90	*−99*	*−91*	*−82*	*−181*	*−163*	*−140*	···
3.00	−89	−87	−84	*−86*	*−79*	*−71*	*−157*	*−138*	*−114*	···
3.25	−83	−81	−78	*−75*	*−68*	*−61*	*−137*	*−116*	*−88*	···
3.50	−77	−75	−72	*−65*	*−58*	*−51*	*−121*	*−96*	*−63*	···
3.75	−71	−69	−66	*−56*	*−49*	*−41*	*−109*	*−79*	*−38*	···
4.00	−65	−62	−59	*−48*	*−39*	*−30*	*−101*	*−64*	*−15*	···

[a] The unit of $C_{p,\phi}$ is J·K^{-1}·mol^{-1}.

[b] Values in italic are extrapolated above the molality range of experimental data.

tion ranges, and were assigned zero weight in the fit.

Figure 2 shows comparisons of the experimental and calculated osmotic coefficients at various temperatures from different sources. The fit is reasonably good and is within the experimental uncertainties. The standard deviations of the fit are 0.0078 for $T \leq 298$ K, 0.035 for 323 K$\leq T \leq$423 K, 0.031 for 423$<T\leq$524 K, and 0.049 for $T>$524 K.

At 298 K or lower temperatures, the present model shows systematic cyclic deviations which were not seen in our recent treatment of $MgCl_2(aq)$ and $CaCl_2(aq)$ systems exclusively at 298.15 K using the same equation.[19] This is due to the extension of the model to a wide temperature range. An improved representation of experimental results at low temperatures ($T \leq 298$ K) may be obtained if the parameters α_{B1}, α_{C1}, and α_{C2} in the present model are chosen to be functions of temperature, but this will result in complex equations for the enthalpy and the heat capacity. The guiding consideration in the development of the present model was to treat all available results with an acceptable level of accuracy while retaining the simplest possible forms for the temperature, pressure, and composition dependence of all measured properties.

3.4. Enthalpy of Dilution Results

The calorimetric results from Simonson *et al.*,[12] Wang *et al.*,[10] Gillespie *et al.*[11] and Mayrath and Wood[48] provide a comprehensive database for the enthalpy of dilution of $MgCl_2(aq)$ at high temperatures and pressures covering the molality range to 5.4 mol·kg^{-1}. Most of these results show acceptable agreement with each other, and consistency with those at near 298 K and with other thermodynamic functions. However, it is worth noting that in both the Simonson *et al.* and Gillespie *et al.* measurements, a small amount of HCl was added in order to suppress the hydrolysis of Mg^{2+} in dilute solutions of this electrolyte. While Simonson *et al.* added equal amounts of the acid (0.02 mol·kg^{-1}) into both streams to cancel out the dilution effect of HCl, Gillespie *et al.* added ~0.01 mol·kg^{-1} HCl only to solutions of $MgCl_2(aq)$ before mixing. The addition of HCl into the solutions of $MgCl_2(aq)$ complicates the treatment due to the enhanced ion association of Mg^{2+} with Cl^-, and due to the changing extent of association of HCl with changing ionic strength. There are large uncertainties in the association constant for the ion pair $MgCl^+$ at high temperatures, as will be discussed in Sec. 4.1, and any assumption of the association constants will lead to ambiguities in the calculated speciation. The effect of ion association on enthalpies of dilution is especially large in dilute solutions at high temperatures. Results below 0.1 mol·kg^{-1} were given lower weights. A few points from Simonson *et al.* at 573 K in 0.05 mol·kg^{-1} HCl were not included in the calculation because they are signifi-

TABLE 8. Calculated V_{ϕ} of $MgCl_2(aq)$ at various temperatures and pressures using Eq. (18) and parameters in Table 2[a]

m	373.15 K				473.15 K				573.15 K			623.15 K	
mol·kg^{-1}	2 MPa	10 MPa	20 MPa	30 MPa	2 MPa	10 MPa	20 MPa	30 MPa	10 MPa	20 MPa	30 MPa	20 MPa	30 MPa
0.001	9.09	9.24	9.83	10.86	−32.51	−29.17	−25.45	−22.24	−219.7	−159.7	−139.7	−824.4	−479.8
0.005	9.71	9.84	10.41	11.41	−30.40	−27.19	−23.60	−20.48	−205.7	−149.7	−131.7	−749.1	−443.0
0.01	10.09	10.21	10.76	11.76	−29.15	−26.02	−22.48	−19.40	−197.7	−144.1	−127.1	−702.4	−419.2
0.02	10.53	10.64	11.17	12.15	−27.76	−24.68	−21.19	−18.12	−188.9	−138.2	−122.1	−647.5	−390.2
0.05	11.14	11.22	11.72	12.67	−25.77	−22.75	−19.27	−16.15	−177.1	−130.7	−115.5	−567.5	−346.1
0.10	11.58	11.61	12.07	12.98	−24.06	−21.08	−17.57	−14.38	−167.8	−125.1	−110.0	−505.8	−311.4
0.20	12.01	11.99	12.38	13.23	−21.70	−18.80	−15.32	−12.09	−155.6	−117.3	−102.2	−441.9	−276.8
0.30	12.36	12.31	12.65	13.46	−19.70	−16.92	−13.55	−10.37	−145.2	−110.2	−95.45	−398.5	−253.4
0.40	12.75	12.66	12.98	13.76	−17.91	−15.27	−12.03	−8.95	−135.9	−103.6	−89.45	−361.9	−232.5
0.50	13.17	13.07	13.37	14.14	−16.30	−13.81	−10.72	−7.76	−127.6	−97.77	−84.18	−329.4	−212.4
0.60	13.63	13.53	13.82	14.59	−14.85	−12.51	−9.57	−6.74	−120.3	−92.58	−79.60	−300.4	−193.4
0.70	14.11	14.01	14.31	15.09	−13.53	−11.33	−8.54	−5.84	−113.7	−87.99	−75.59	−275.0	−176.0
0.80	14.60	14.51	14.83	15.62	−12.32	−10.25	−7.61	−5.04	−107.9	−83.90	−72.05	−253.6	−160.9
0.90	15.10	15.02	15.36	16.16	−11.19	−9.25	−6.76	−4.31	−102.5	−80.19	−68.86	−236.3	−148.8
1.00	15.59	15.53	15.89	16.72	−10.12	−8.31	−5.95	−3.63	−97.62	−76.77	−65.93	−223.5	−140.2
1.20	16.54	16.51	16.92	17.80	−8.11	−6.52	−4.42	−2.33	−88.66	−70.50	−60.58	−212.0	−135.2
1.40	17.41	17.43	17.89	18.82	−6.18	−4.80	−2.93	−1.05	−80.45	−64.64	−55.54	···	···
1.60	18.20	18.26	18.77	19.76	−4.29	−3.10	−1.44	0.26	−72.70	−58.99	−50.63	···	···
1.80	18.90	19.00	19.56	20.60	−2.44	−1.41	0.07	1.61	−65.39	−53.54	−45.81	···	···
2.00	19.51	19.65	20.26	21.35	−0.65	0.25	1.59	3.01	−58.64	−48.39	−41.17	···	···
2.25	20.17	20.36	21.03	22.19	1.49	2.26	3.48	4.78	−51.29	−42.70	−35.87	···	···
2.50	20.74	20.97	21.72	22.95	3.41	4.13	5.28	6.54	−45.66	−38.26	−31.50	···	···
2.75	21.22	21.52	22.35	23.66	5.05	5.76	6.93	8.23	−42.31	−35.60	−28.47	···	···
3.00	21.66	22.04	22.95	24.36	6.32	7.10	8.37	9.78	−41.78	−35.18	−27.20	···	···

[a] The unit of V_{ϕ} is cm^3·mol^{-1}.

cantly less negative than the other results in the same range of molality, and the results could be affected significantly by ion pairing.

Comparisons of the experimental and the calculated enthalpies of dilution from various sources are shown in Fig. 3. Standard deviations of the fit are 0.27 kJ·mol^{-1} for $T < 373$ K, 0.57 kJ·mol^{-1} for $373 \text{ K} \leq T < 523$ K, and 1.26 kJ·mol^{-1} for $T \geq 523$ K.

3.5. Heat Capacity Results

The published heat capacity results cover temperature, pressure, and concentration ranges of 283–598 K, 0.1–17.9 MPa, and 0.01–6.2 mol·kg^{-1}, respectively. Results of Eigen and Wicke,[52] Ruskov,[58] Vasilev *et al.*,[53] and Fedyainov *et al.*[51] were assigned lower weights due to the inconsistency with other results under the corresponding conditions, especially for $m < 1$ mol·kg^{-1}. Points at $m < 0.1$ mol·kg^{-1} from the White *et al.*[13] data set were also given lower weights due to the large scattering. Figure 4 shows the deviation plots for the heat capacity results at various temperatures and pressures as a function of $m^{1/2}$. Standard deviations of the fit are 23 J·mol^{-1}·K^{-1} for $T \leq 298$ K, 15 J·mol^{-1}·K^{-1} for $298 \text{ K} < T \leq 373$ K, 18 J·mol^{-1}·K^{-1} for $373 \text{ K} < T \leq 500$ K, and 64 J·mol^{-1}·K^{-1} for $T > 500$ K.

3.6. Comparison with Holmes *et al.* Model

As the calculated values of thermodynamic properties agree reasonably well with experimental results (Figs. 1–4), it is interesting to compare the calculated values from the model presented in this work with those from the Holmes *et al.* model.[1,2] Figures 5 and 6 show the calculated ϕ and $\ln \gamma_{\pm}$ of $MgCl_2(aq)$, respectively, at various temperatures at saturation pressure as a function of $m^{1/2}$. The agreement between values calculated from the two models is good for the osmotic coefficients. Constant differences in $\ln \gamma_{\pm}$ calculated from the two models are observed at 473 and 523 K at molalities to 6 mol·kg^{-1}. The present model and that of Holmes *et al.* are based on essentially the same set of experimental results in this temperature range. However, the available osmotic coefficient data at these temperatures do not extend to sufficiently low molalities to permit unambiguous calculation of $\ln \gamma_{\pm}$ through Gibbs–Duhem integration, and the relation between $\ln \gamma_{\pm}$ and ϕ is therefore dependent to a degree on the temperature-integrated treatment of the dilution enthalpy results. The combination of additional emphasis on an accurate fit of the available dilution enthalpies at low molalities and assumed similarity of the behavior of $MgCl_2(aq)$ and $CaCl_2(aq)$ led Holmes *et al.* to introduce a term in $\beta^{(2)}$ which gives rise to the differences observed in $\ln \gamma_{\pm}$ between their work and the present model. This term also has a significant effect on the extrapolation of L_{ϕ} values to infinite dilution at high temperatures; this point will be discussed below in more detail. Further data of high precision at low molalities are needed to resolve fully the differences between the representations.

Figures 7–9 show the calculated L_{ϕ}, $C_{p,\phi}$, and V_{ϕ}, respectively, as functions of $m^{1/2}$ at various temperatures and

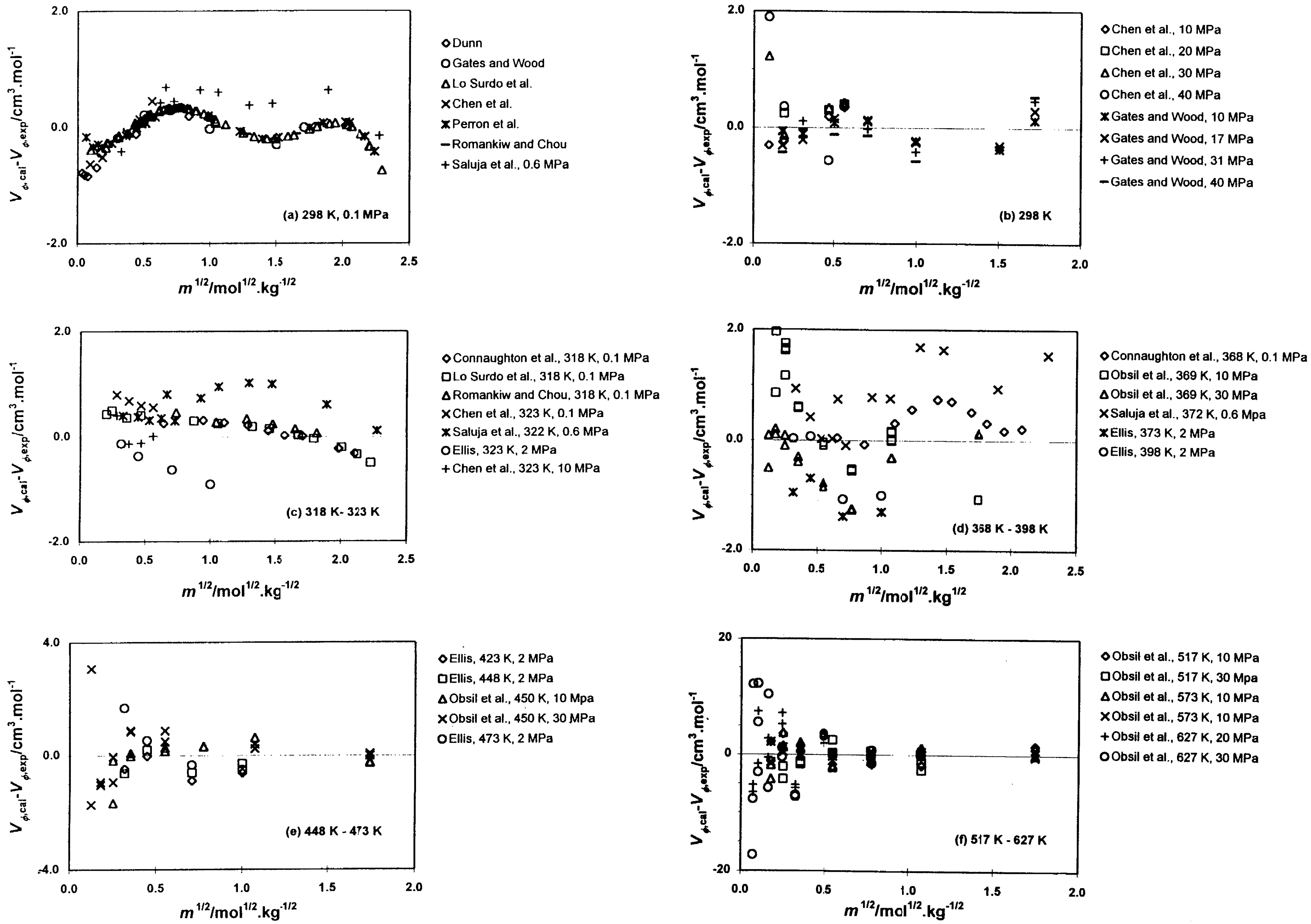

FIG. 1. Deviations for the apparent molar volumes of $MgCl_2(aq)$ at various temperatures and pressures as a function of $m^{1/2}$.

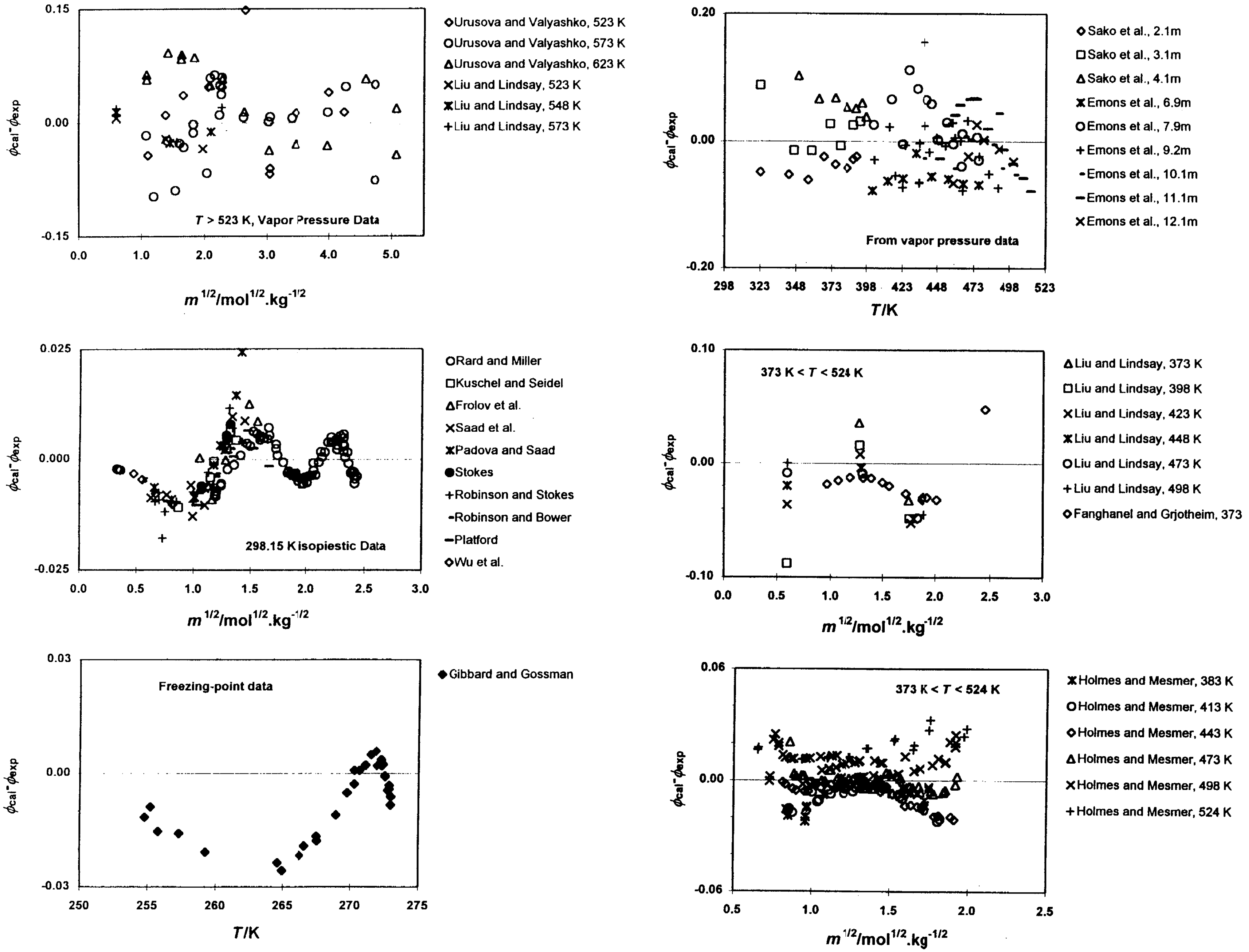

FIG. 2. Differences between the experimental and calculated osmotic coefficients of $MgCl_2(aq)$ solutions at various temperatures and pressures.

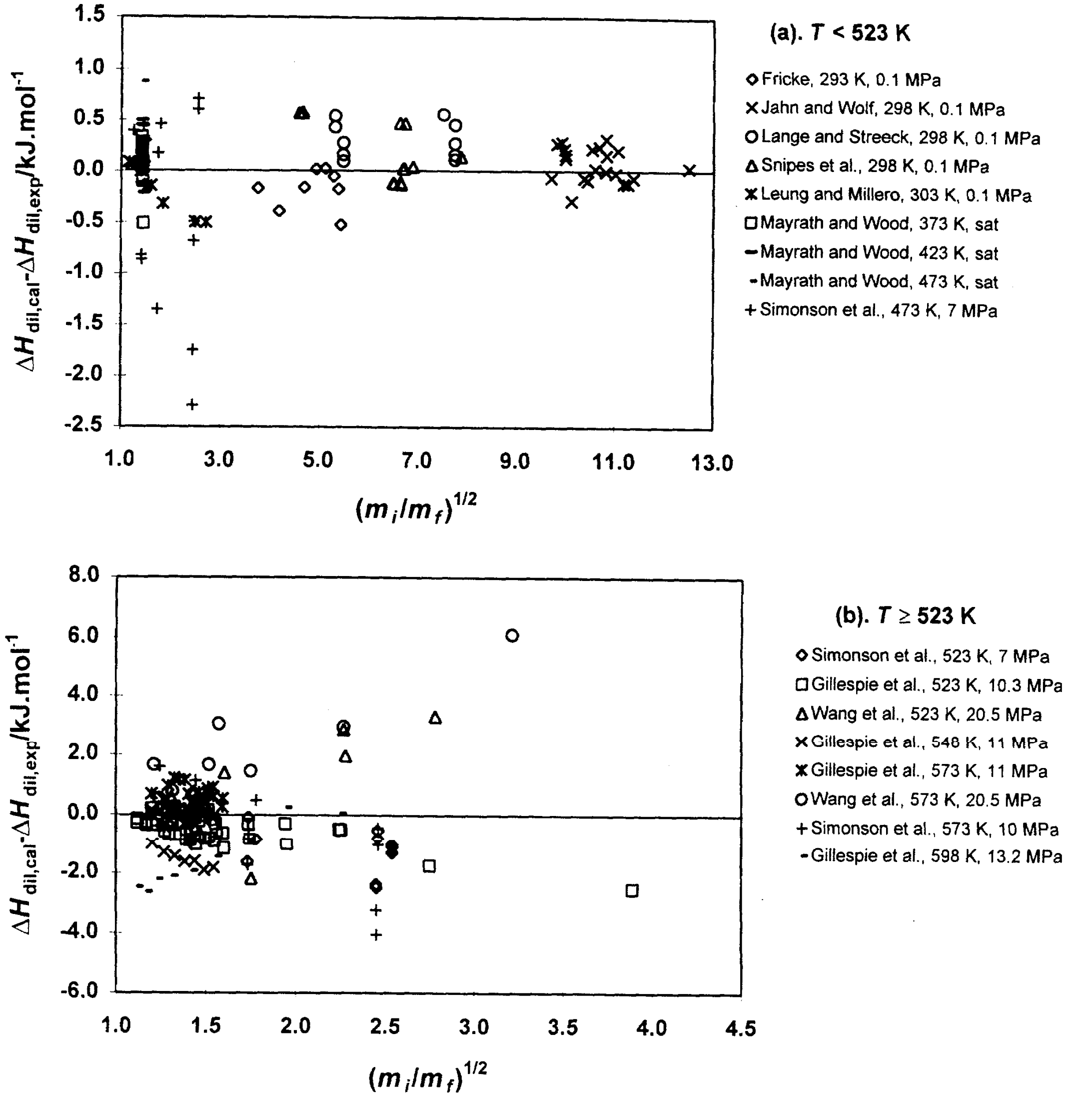

FIG. 3. Differences between the experimental and calculated heat of dilution of $MgCl_2(aq)$ at various temperatures and pressures.

at saturation and higher pressures. Comparisons are also given in these figures of values calculated from our model with those from the Holmes *et al.* model. It is noted that the agreement between the two models is good at $T \leq 473$ K for the three properties. The differences in V_ϕ and $C_{p,\phi}$ at 523 K were primarily due to the required extrapolation of Holmes *et al.* model. Data regression in our treatment included additional high-temperature, high-pressure volumetric results of Obsil *et al.*[18] which were unavailable to Holmes *et al.* Heat capacity results of White *et al.* above 499 K were not included in the Holmes *et al.* treatment as the next higher temperature investigated in the experimental work (549 K) was well beyond the 523 K limit of the earlier treatment. Thesehigher-temperature data were included in the present correlation. It is interesting to note the relatively good agreement of the two treatments for $C_{p,\phi}$ at 523 K for $m \geq 0.25$ mol·kg^{-1}. The stronger dependence of $C_{p,\phi}$ on concentration at low molalities predicted from the Holmes *et al.* treatment is essentially compensated by the more negative extrapolated values of $C^0_{p,2}$. However, this agreement is probably somewhat fortuitous, and values of $C_{p,\phi}$ calculated from the present model should be preferred over those extrapolated from the treatment of Holmes *et al.* at temperatures significantly above 499 K.

Below 0.01 mol·kg^{-1}, the L_ϕ values calculated from the Holmes *et al.* model decrease more rapidly with decreasing molality than those calculated from our model, especially at 523 K. Values of L_ϕ are largely determined by the ion-association properties in this region. It has been noted[67] that

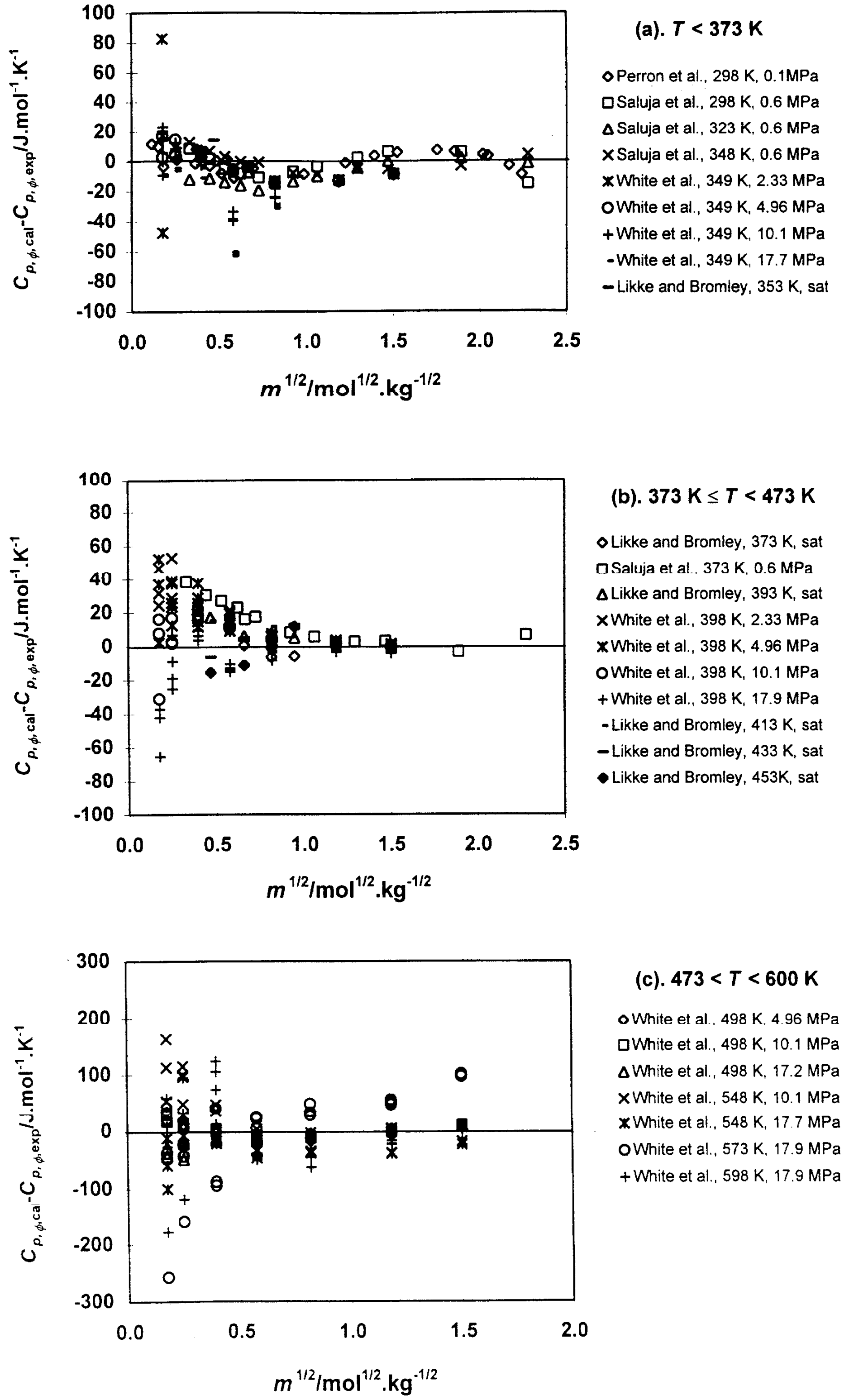

FIG. 4. Differences between the experimental and calculated apparent molar heat capacities of MgCl$_2$(aq) at various temperatures and pressures.

in the very dilute region, the extrapolated L_ϕ values for HCl(aq) calculated using the $\beta^{(2)}$ model have a much less steep dependence on molality compared with those calculated using speciation models, and that ion-association constants calculated from the $\beta^{(2)}$ model are smaller than the corresponding quantities in the speciation models. The trend in Fig. 7 for L_ϕ is therefore expected. In the Holmes *et al.* model, ion pairing in the dilute region was treated by intro-

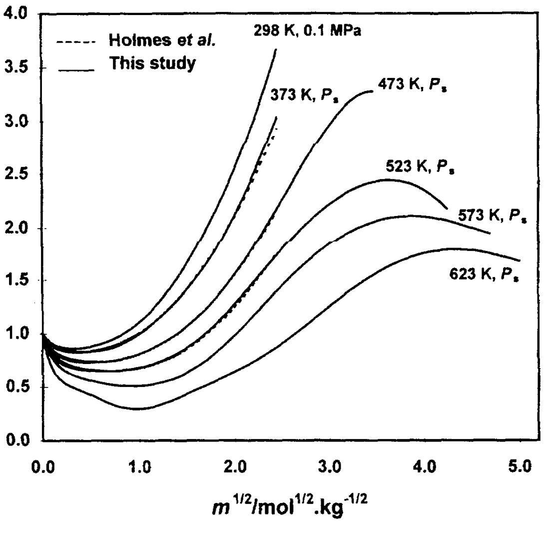

FIG. 5. Osmotic coefficients of $MgCl_2(aq)$ solutions at P_s and various temperatures as a function of $m^{1/2}$. Dashed lines were calculated using Holmes *et al.* model (Refs. 1 and 2), solid lines were calculated using Eq. (6) and parameters listed in Table 2.

ducing a $\beta^{(2)}$ parameter based on the ion-association constant for $CaCl^+$ as extrapolated from Frantz and Marshall,[68] while our model simplified the treatment by assuming no ion association of Mg^{2+} with Cl^-. Since enthalpy of dilution data are not available at molalities below 0.01 $mol \cdot kg^{-1}$ at $T \geq 523$ K, and the ion-association constant for $MgCl^+$ is not well known at high temperatures due to complications arising from hydrolysis of $Mg^{2+}(aq)$, determination of reliable values of L_ϕ in the dilute solutions, although needed, is beyond the scope of the present database.

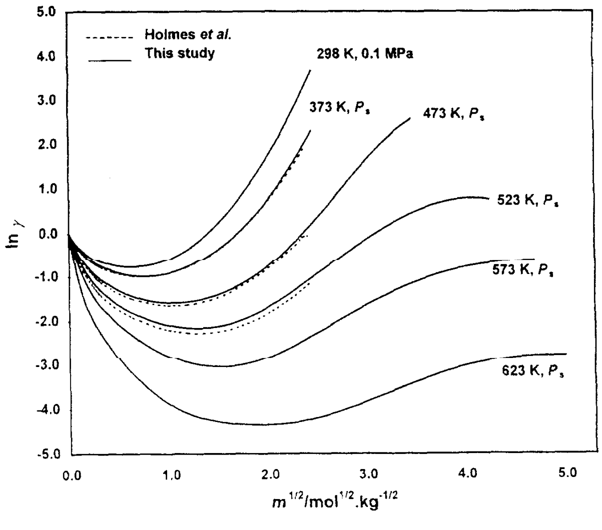

FIG. 6. Values of ln $\gamma_\pm$ for $MgCl_2(aq)$ at P_s and various temperatures as a function of $m^{1/2}$. Dashed lines were calculated using Holmes *et al.* model (Refs. 1 and 2), solid lines were based on Eq. (11) and parameters listed in Table 2.

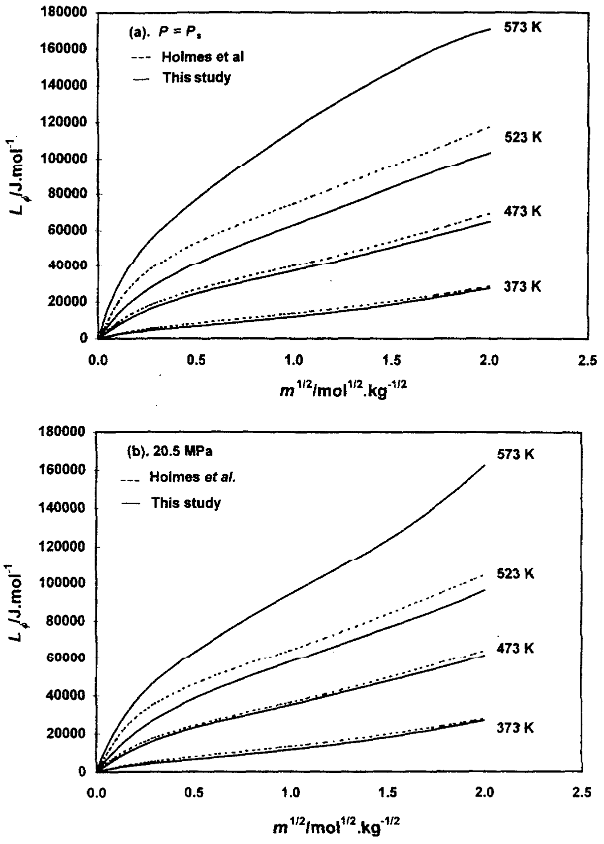

FIG. 7. Relative apparent molar enthalpy, L_ϕ, of $MgCl_2(aq)$ as a function of $m^{1/2}$ at P_s and 20.5 MPa and at various temperatures. Dashed lines were calculated using Holmes *et al.* model (Refs. 1 and 2), solid lines were calculated using Eq. (16) and parameters listed in Table 2.

4. Discussion

4.1. Uncertainties in Ion Association and Hydrolysis Constants

Ion association and hydrolysis in $MgCl_2(aq)$ solutions have been reported by a number of investigators at temperatures greater than 523 K. Gillespie *et al.*[11] reported values of $K(MgCl^+)$ from 523 to 598 K from their measurements of enthalpy of dilution of $MgCl_2(aq)$ and enthalpy of mixing of $MgCl_2(aq)$ with HCl(aq) at 10–13 MPa by a nonlinear least-squares analysis. It has been pointed out[27] that the $K(MgCl^+)$ values derived by Gillespie *et al.* may not be unique because of the high covariance of the derived reaction enthalpy and the small equilibrium constant values when determined simultaneously from calorimetric results. Obsil *et al.*[18] also derived values of $K(MgCl^+)$ from 369 to 573 K, which seem to be consistent with those of Gillespie *et al.* However, their K values were obtained based on the assumption that the activity coefficient of the $MgCl^+$ ion pair is the same as that of NaCl, and the mean-activity coefficient of $MgCl_2$ in their calculation was obtained from the earlier isopiestic data of Holmes *et al.*[69] which were questioned by Emons *et al.*[9] and were superseded by later work.[2] Thus, the

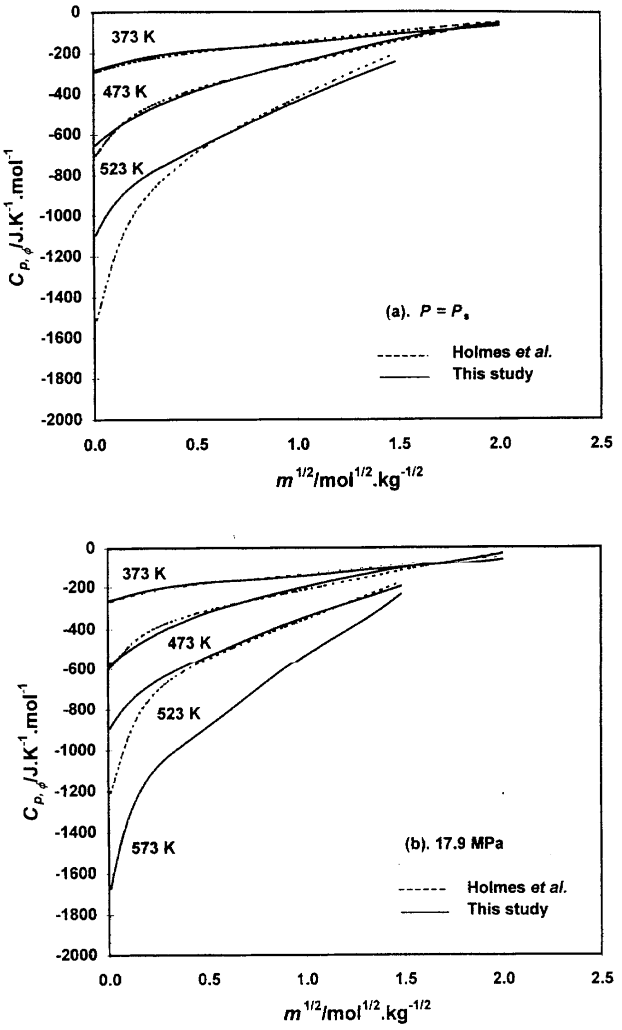

FIG. 8. Apparent molar heat capacity, $C_{p,\phi}$, of $MgCl_2(aq)$ as a function of $m^{1/2}$ at P_s and 17.9 MPa and at various temperatures. Dashed lines were calculated using Holmes *et al.* model (Refs. 1 and 2), solid lines were based on Eq. (17) and parameters listed in Table 2.

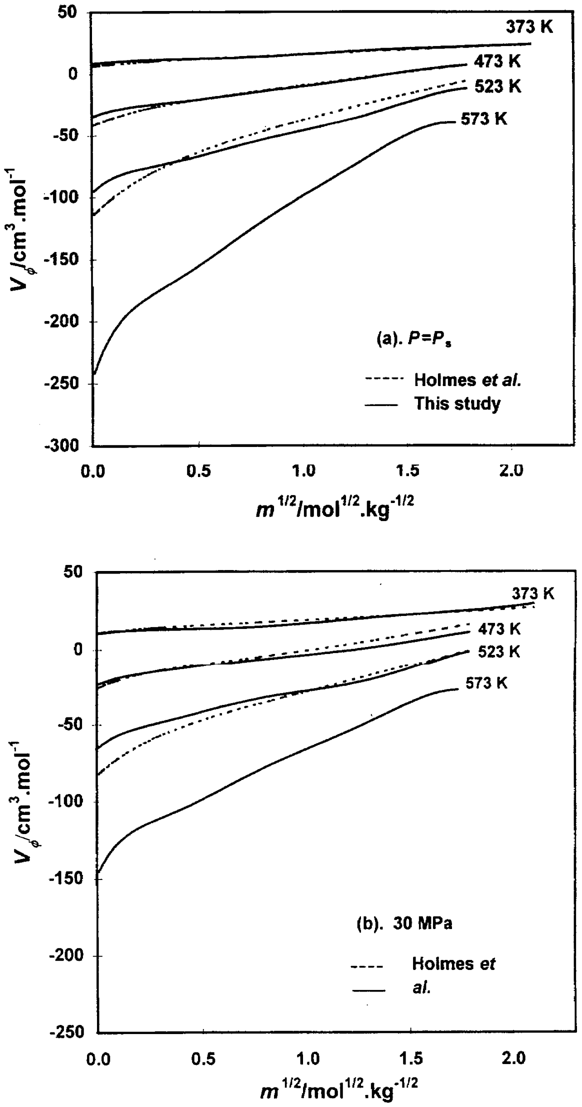

FIG. 9. Apparent molar volume, V_ϕ, of $MgCl_2(aq)$ as a function of $m^{1/2}$ at P_s and 30 MPa and at various temperatures. Dashed lines were calculated using Holmes *et al.* model. (Refs. 1 and 2) solid lines were calculated using Eq. (18) and parameters listed in Table 2.

K values reported by Obsil *et al.* may be less reliable. Saccocia and Seyfried[70] determined values of $K(MgCl^+)$ from their solubility measurements for the assemblage (talc+quartz) in the temperature range 573–673 K at 50 MPa using an iterative approach that gave the best fit of the experimental fluid compositions. The derivation of the association constant from solubility measurements requires estimation of activity coefficients for the various species assumed to be present. When the association constant is small, the derived K values are highly dependent on the assumed functional form of the nonideal behavior for activity coefficients, i.e., derived K values depend strongly on the activity coefficient model. Consequently, the determination of equilibrium constant values for a specific reaction from measurements in mixed electrolyte solutions is often ambiguous, model dependent, and probably not meaningful. Frantz and Marshall[68] measured the electrical conductivities of $CaCl_2(aq)$ and $MgCl_2(aq)$ solutions in the temperature range 298–873 K, and obtained equations for $K(CaCl^+)$ and $K(MgCl^+)$ valid from 673 to 873 K, assuming no hydrolysis of Ca^{2+} and Mg^{2+}. Holmes *et al.*[1,2] used a different K equation based on the ionization constants from Frantz and Marshall in the fitting of the high-temperature, low-molality enthalpy of dilution results for $CaCl_2(aq)$, $MgCl_2(aq)$, and other alkaline earth metal chlorides. But their equation has been tested through fitting to experimental results only to 523 K, and at 523 K, K values calculated from their equation are about 0.5 log unit lower than those of Gillespie *et al.* and 1.0 log unit higher than those extrapolated from Frantz and Marshall. These differences become larger as temperature decreases. Also, values of $K(MgCl^+)$ obtained by Gillespie *et al.*, Obsil *et al.*, and Saccocia and Seyfried are considerably higher than both Holmes *et al.*'s and those extrapolated from the equation given by Frantz and Marshall. Thus, large uncertainties exist in the association constant for the ion pair $MgCl^+$ at high temperatures.

Hydrolysis of Mg^{2+} ion in high-temperature aqueous solutions has been studied by Walther[71] from 573 to 873 K and hydrolysis constants were determined from their solubility measurements. It was indicated that $MgOH^+$ ion is dominant over Mg^{2+} at $T > 633$ K at 100 MPa. Brown *et al.*[72] used potentiometric titration in a study of hydrolysis of Mg^{2+} from 333 to 473 K and determined formation constants of $Mg(OH)_2(s)$ in 0.1 and 1.0 mol·kg^{-1} NaCl media. Palmer and Wesolowski[73] also made potentiometric measurements and derived values for the first hydrolysis constants of the Mg^{2+} ion from 273 to 523 K. Using the hydrolysis constants obtained in their own study and those reported by Walther at higher temperatures and pressures, Palmer and Wesolowski obtained an equation representing $K(MgOH^+)$ to 823 K with the uncertainty being claimed to be 0.5 log units.

The thermodynamics of $MgCl_2(aq)$ solutions at high temperatures are challenging due to the simultaneous existence of ion association and hydrolysis of Mg^{2+}. It has been pointed out[70] that the ion-association constants obtained without considering the hydrolysis of Mg^{2+} need to be modified to take account of $MgOH^+$. This appears to be the same in the reversal case, i.e., the hydrolysis constants derived without taking account of ion pairing at elevated temperatures need to be re-evaluated.

In the initial stage of this study, we introduced the parameter $\beta^{(2)}$ to account for ion association in the dilute region at high temperatures.[20] However, inclusion of this parameter did not seem to improve significantly the results of our global fit including those in the relatively dilute range at high temperatures ($T > 523$ K), such as the enthalpy of dilution results of Simonson *et al.*[12] The dilution enthalpy measurements of Simonson *et al.*[12] in 0.02 mol·kg^{-1} HCl solution are essentially consistent with the assumption of complete dissociation of $MgCl_2$, extending to low molalities. However, their further results in more concentrated acid solution (0.05 mol·kg^{-1} HCl) show a marked departure which is not consistent with a simple mixing effect. Two effects, both arising from ion pairing, contribute to the observed enthalpies of dilution in these mixed solutions. Hydrochloric acid, which is known to associate relatively strongly at high temperatures,[67] becomes increasingly ion paired as the diluent stream is mixed with the $MgCl_2$ stock solution. This effect is endothermic, and effectively decreases the observed (exothermic) enthalpy of dilution. Concurrently, $MgCl^+$ ion pairs in the $MgCl_2(aq)$ stock solution tend to dissociate on dilution, adding a potentially significant exothermic enthalpy of dissociation to the observed dilution enthalpy. In the case of the experiments in 0.02 mol·kg^{-1} HCl the effects essentially cancel, and the results are apparently consistent with complete dissociation of all solutes. However, in the more concentrated acid solutions the contribution to the observed enthalpy from the association of HCl is larger than that for dissociation of $MgCl^-$, and the net result is an apparent shift in the enthalpy of dilution toward less negative values for a given dilution. Quantitative representation of these competing effects requires the application of a fully speciated model for the mixed electrolyte $\{MgCl_2 + HCl\}(aq)$ which is beyond the scope of the available experimental results. Using any assumed association constants to explicitly express the ion association could result in unnecessary complexity introduced by the assumption of additional species of ambiguous molalities; therefore we prefer to use an alternate and simpler description of the thermodynamic properties. The model presented here thus represents a workable approximation for the behavior of these solutions at high temperatures which represents the widest set of available results with minimal assumptions concerning the speciation of the solutes in solution.

4.2. Relationship to Solid Properties

The properties of $MgCl_2$ hydrates, $MgCl_2 \cdot nH_2O$, in equilibrium with saturated solutions are related through the activities of $MgCl_2$ and of H_2O at saturation molalities by Eq. (36).

$$-\frac{\Delta G^0}{RT} = \nu_M \ln m_M + \nu_X \ln m_X + \nu \ln \gamma_\pm + n \ln a_w, \quad (36)$$

where ΔG^0 is the Gibbs free energy change for the dissolution reaction

$$M_{\nu_M} X_{\nu_X} \cdot nH_2O = \nu_M M^{+z_M} + \nu_X X^{-z_X} + nH_2O, \quad (37)$$

where m_M and m_X represent molalities of the cation and anion, respectively, in saturated solution, and a_w is the activity of water. The calculation for $MgCl_2 \cdot 6H_2O$ at 298.15 K is given by Cox *et al.*[74] Substitution of our present values for the activity and osmotic coefficients would make no significant change. But even at 298.15 K thermodynamic properties, such as the enthalpy and Gibbs free energy of the dissolution reaction for the solid $MgCl_2 \cdot nH_2O$, have large uncertainties. Cox *et al.* found that much more accurate values for the standard-state enthalpies and free energies of formation of $Mg^{2+}(aq)$ can be obtained via $MgSO_4 \cdot 6H_2O$ and $Mg(OH)_2$. At higher temperatures, the uncertainties for standard-state dissolution properties of the solid hydrates of $MgCl_2$ are even greater; hence, they are not useful sources of values of the activity and osmotic coefficients of aqueous $MgCl_2$. Instead, the present results could be combined with solubility data to give new estimates for the solid properties.

5. Acknowledgments

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