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Thermodynamically Traceable Calorimetric Results for Dilute Aqueous Potassium Chloride Solutions at Temperatures from (273.15 to 373.15) K. Part 1. The Quantities Associated with the Partial Molar Enthalpy

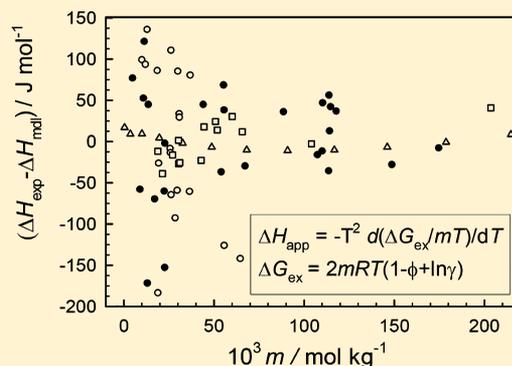
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S Supporting Information

ABSTRACT: In our previous study (Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P., *J. Chem. Eng. Data* 2019, 64, 16–33), we presented a fully traceable two-parameter Hückel equation with parameters B and b_1 for activity and osmotic coefficients in dilute KCl(aq) in the temperature range of (273.15 to 383.15) K. This equation applies within experimental error to almost all thermodynamic data in the literature at least up to a molality of 0.2 mol·kg⁻¹. In our Hückel model, parameter B is treated as a constant, whereas parameter b_1 depends quadratically on the temperature. In the present study, the same model is applied to the molar enthalpies of the components in KCl solutions. No new parameter estimations are necessary for the treatment of these calorimetric data. We also extend now the previous enthalpy results for dilute NaCl solutions (see Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P., *J. Chem. Eng. Data* 2017, 62, 2717–2632) up to 373 K because in that study the treatment of calorimetric data was limited only up to 353 K. In a future publication (Part 2 of this study), it will be shown that this Hückel model applies additionally well to the heat-capacity literature available for dilute KCl solutions. Here, we also consider a second parametrization of the Hückel equation for KCl solutions obtained in a previous work (Partanen, J. I., *J. Chem. Eng. Data* 2016, 59, 286–306). This is seen to apply better to enthalpy data in less dilute KCl solutions up to the saturated solutions in the range of (298 to 303) K. However, the alternative parametrization is not fully traceable and not as accurate as our primary one. Following the success of these Hückel models, we supplement the thermodynamic tables for KCl solutions with the relative apparent and partial molar enthalpies of KCl in these solutions from (273.15 to 373.15) K. We also give here the values of these quantities for NaCl in dilute aqueous NaCl solutions at 373.15 K. We have good reason to believe that the new tables contain the most reliable values available for the enthalpy quantities of dilute NaCl and KCl solutions.



INTRODUCTION

The two-parameter Hückel equation with parameters B and b_1 has been previously proven to be useful when the thermodynamic properties of dilute solutions of pure electrolytes are predicted at the normal reference temperature of 298.15 K.^{1–18} In recent studies,^{19–22} it has been additionally observed that it applies within experimental error to the thermodynamic properties of sodium and potassium chloride solutions at least up to a molality of 0.2 mol·kg⁻¹ in the temperature range of (273 to 383) K. In ref 22, the following approach (parametrization PI) was presented for the determination of the temperature dependence of the parameters in the Hückel equations of NaCl and KCl.

(1) At 298.15 K, the parameter values from ref 3 were utilized.

- (2) At 273.15 K, the parameter values from ref 19 were utilized. These values were determined from the existing freezing-point-depression data.
- (3) The parameter values for NaCl solutions at 348.15 K were determined in ref 20 from the vapor pressure data of Gibbard et al.²³
- (4) Because parameter B had the same value for both NaCl and KCl in operations 1, 2, and 3, these values are accepted, and they are used in all temperatures. These values are $B_{\text{NaCl}} = 1.4 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and $B_{\text{KCl}} = 1.3 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$. For NaCl at temperatures other than the three that were mentioned, a quadratic equation was

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determined in ref 20 for the temperature dependence of parameter b_1 using the three b_1 values.

- (5) For KCl solutions, the value of parameter b_1 at 353.15 K was determined in ref 20 from the isopiestic data of Moore et al.²⁴ against NaCl solutions using the quadratic equation for $b_{1,\text{NaCl}}$.
- (6) In ref 22, a quadratic equation of b_1 for KCl solutions was determined using the values of this parameter at 273.15, 298.15, and 353.15 K.

The resulting equations from this six-step approach were tested in refs 20, 21, and 22 against all existing thermodynamic data for NaCl solutions and in ref 22 against the thermodynamic data obtained at equilibrium in a constant or in an almost constant temperature for KCl solutions. In these tests, it was observed that this fully traceable approach applies to dilute solutions of both electrolytes at temperatures extending up to 383 K. In the present study, we show that the suggested approach also applies to all enthalpy data measured for dilute KCl solutions up to 373 K. In a forthcoming study, the experimental heat-capacity data for KCl solutions will be investigated in the same way.

In the second calculation method considered in ref 19 and identified here and previously^{20–22} as parametrization PII, the B_{NaCl} and B_{KCl} values were identical to those used in PI. In PII, the quadratic temperature dependence of parameter b_1 was mainly determined from the amalgam-cell data of Harned and Nims³⁵ and Harned and Cook²⁶ for NaCl and KCl solutions, respectively. These electrochemical data cover the temperature range from (273.15 to 313.15) K and extend at each temperature up to a molality of 4.0 mol·kg⁻¹. Because amalgam-electrode data are not as accurate as the data used in the estimations of PI, the resulting models are less reliable than those based on PI. However, it was observed in refs 19 and 20 that PII applies quite well at temperatures up to 353 K also to more concentrated NaCl and KCl solutions.

In this article, both PI and PII are thoroughly tested against the heats of dilution and solution available in literature for KCl solutions and also against other literature values of the quantities associated closely with these heats. The calorimetric tests of this study are analogous to those presented in ref 20 for NaCl solutions. Also for NaCl(aq), some previous and new results are considered here to make comparisons and to extend the previous results up to 373 K because in ref 20 the treatment of calorimetric data were limited only up to a temperature 353 K. As in ref 21 for NaCl solutions, the wide amount of the heat-capacity data for KCl solutions will be later considered in a separate study.

THEORY

In our previous studies,^{2–22} the following Hückel equations

$$\ln \gamma = -\frac{\alpha|z_+z_-|\sqrt{I_m}}{1 + B\sqrt{I_m}} + b_1\left(\frac{m}{m^\circ}\right) \quad (1)$$

$$\varphi = 1 - \frac{\alpha|z_+z_-|}{B^3I_m} \left[(1 + B\sqrt{I_m}) - 2 \ln(1 + B\sqrt{I_m}) - \frac{1}{1 + B\sqrt{I_m}} \right] + \frac{b_1}{2} \left(\frac{m}{m^\circ}\right) \quad (2)$$

have been used for the mean activity coefficient (γ) of the electrolyte and for the osmotic coefficient (φ) of water in

aqueous solutions of many electrolytes at least up to an ionic strength (I_m) of 1 mol·kg⁻¹. In eqs 1 and 2, m is the molality, m° is 1 mol·kg⁻¹, z_+ is the charge number of the cation, and z_- is that of the anion, and the electrolyte-dependent parameters are B and b_1 . The values of the Debye–Hückel parameter α at 101.325 kPa and at various temperatures are given in Table 1 of ref 20 and were taken from ref 27. For a 1:1 electrolyte such as KCl, $|z_+z_-|$ is 1 and I_m is the same as molality m . The excess Gibbs energy of the system (G_{ex}) on the molality scale in salt solutions is related to the activity and osmotic coefficient by equation

$$\Delta G_{\text{ex}} = 2mRT(1 - \varphi + \ln \gamma) \quad (3)$$

where T is the temperature in Kelvin. For all further energy quantities, the molality scale is used and the mass of water is considered to be 1 kg. The apparent molar enthalpy of salt (symbol 2) is $H_{\text{app},2}$ and it is now defined by equation

$$H_{\text{app},2} = \frac{H - (w_1/M_1)H_{m,1}^*}{mw_1} = \frac{H - H_1^*}{m} \quad (4)$$

where H is enthalpy of the system, $H_{m,1}^*$ is the molar enthalpy of pure water (symbol 1), H_1^* is enthalpy of the mass of 1 kg water ($= w_1$), M_1 is the molar mass of water ($= 0.018015 \text{ kg}\cdot\text{mol}^{-1}$), and in the last term “kg” is omitted from the unit for simplicity (as now generally) because the molality scale is always used. The relative apparent molar enthalpy (ΔH_{app}) of salt in these solutions is associated with the excess Gibbs energy by the following thermodynamic identity

$$\Delta H_{\text{app}} = H_{\text{app},2} - H_{m,2}^\infty = -T^2 \frac{\partial \left(\frac{\Delta G_{\text{ex}}}{mT} \right)}{\partial T} \quad (5)$$

where $H_{m,2}^\infty$ is the partial molar enthalpy of the salt at infinite dilution. In this presentation, we simplify and make clearer the previous notations, and quantity $H_{\text{app},2}$ is now exactly the same as $\Delta H_{\text{ex}}/m$ in ref 20. The salt's relative partial molar enthalpy ($\Delta H_{m,2}$) can be calculated from the apparent one using

$$\Delta H_{m,2} = H_{m,2} - H_{m,2}^\infty = \Delta H_{\text{app}} + m \frac{\partial (\Delta H_{\text{app}})}{\partial m} \quad (6)$$

As mentioned above, it was observed previously²² that the constant value of $B = B_{\text{KCl}} = 1.3 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ can be used in dilute KCl solutions at all temperatures from (273 to 383) K. The following three traceable values have been suggested for parameter b_1 : $b_1(273.15 \text{ K}) = -0.0515$, $b_1(298.15 \text{ K}) = 0.011$, and $b_1(353.15 \text{ K}) = 0.044$. With these values, the quadratic equation

$$b_{1,\text{KCl}} = -0.0515 + 3.09375 \times 10^{-3} \left(\frac{T - T_0}{\text{K}} \right) - 23.75 \times 10^{-6} \left(\frac{T - T_0}{\text{K}} \right)^2 \quad (7)$$

where T_0 is 273.15 K, was deduced for the temperature dependence of parameter $b_{1,\text{KCl}}$. This equation was tested in ref 22 using all relevant experimental data that have been published for dilute KCl solutions up to 383 K (without the calorimetric data considered now and later). For NaCl solutions, $B = B_{\text{NaCl}} = 1.4 \text{ (mol}\cdot\text{kg}^{-1})^{-1/2}$ and the corresponding quadratic equation is

Table 1. Parameter Values for the Quadratic Equation of Excess Molar Gibbs Energy Divided by T with Respect to the Temperature (eq 10 in the Text) for KCl Solutions Obtained by Using Parameterization PI

$(m/m^\circ)^a$	$u/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$10^3v/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$10^6w/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-3}$	$10^3(s_G)^b/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
0.001	-0.38460	-0.50436	-3.385	0.036
0.002	-0.53753	-0.68905	-4.848	0.050
0.005	-0.83072	-1.01468	-7.862	0.076
0.01	-1.14588	-1.31800	-11.446	0.105
0.02	-1.56646	-1.63516	-16.875	0.144
0.05	-2.32542	-1.8930	-28.99	0.21
0.10	-3.08146	-1.6203	-44.96	0.28
0.15	-3.60373	-1.0252	-58.99	0.33
0.20	-4.01150	-0.2721	-72.07	0.36
0.30	-4.63955	1.4925	-96.67	0.42
0.40	-5.12353	3.4554	-120.07	0.46
0.50	-5.52134	5.5398	-142.78	0.49
0.60	-5.86126	7.7008	-164.98	0.52
0.70	-6.15949	9.9210	-186.85	0.54
0.80	-6.42617	12.184	-208.45	0.56
0.90	-6.66811	14.480	-229.83	0.59
1.00	-6.89012	16.806	-251.08	0.60

^a $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^bStandard deviation about the regression.

Table 2. Parameter Values for the Quadratic Equation of the Excess Molar Gibbs Energy Divided by T with Respect to the Temperature (eq 10 in the Text) for KCl Solutions Obtained by Using Parameterization PII

$(m/m^\circ)^a$	$u/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$10^3v/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-2}$	$10^6w/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-3}$	$10^3(s_G)^b/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
0.001	-0.38451	-0.52041	-3.086	0.028
0.002	-0.53740	-0.71455	-4.411	0.039
0.005	-0.83048	-1.06367	-7.128	0.059
0.01	-1.14546	-1.40113	-10.339	0.082
0.02	-1.56574	-1.78051	-15.17	0.119
0.05	-2.32387	-2.21101	-25.83	0.165
0.10	-3.07858	-2.21212	-39.72	0.22
0.15	-3.59958	-1.88370	-51.84	0.25
0.20	-4.00608	-1.39401	-63.09	0.28
0.30	-4.63164	-0.15031	-84.17	0.32
0.40	-5.11316	1.29602	-104.15	0.36
0.50	-5.50849	2.86401	-123.48	0.38
0.60	-5.84597	4.51467	-142.4	0.40
0.70	-6.14175	6.21994	-160.9	0.42
0.80	-6.40600	7.97524	-179.3	0.44
0.90	-6.64550	9.76093	-197.4	0.45
1.00	-6.86508	11.5767	-215.4	0.46

^a $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^bStandard deviation about the regression.

$$b_{1,\text{NaCl}} = 0.0077 + 3.1853 \times 10^{-3} \left(\frac{T - T_0}{\text{K}} \right) - 25.17 \times 10^{-6} \left(\frac{T - T_0}{\text{K}} \right)^2 \quad (8)$$

$$b_{1,\text{KCl}} = -0.048607 + 2.487 \times 10^{-3} \left(\frac{T - T_0}{\text{K}} \right) - 20.00 \times 10^{-6} \left(\frac{T - T_0}{\text{K}} \right)^2 \quad (9)$$

and it was determined in ref 20. As mentioned, the parametrization obtained through eqs 7 and 8 is denoted PI.

The main interest presently is the testing of parametrization PI against the existing calorimetric data for KCl solutions. However, we included in the tests the previous quadratic equation of parameter $b_{1,\text{KCl}}$ because in ref 19 it was shown that the equation applies sufficiently for practical purposes to KCl solutions up to a temperature of 343 K. It has the form

and the calculations associated with this parametrization are designated here as those of PII in the same way as in ref 20 for NaCl solutions.

RESULTS AND DISCUSSION

Determination of Quadratic Equation for $\Delta G_{\text{ex}}/(mT)$ with Respect to Temperature at Rounded Molalities from (0 to 1.0) $\text{mol}\cdot\text{kg}^{-1}$ for Calculation of the Relative Apparent Molar Enthalpies. As in the NaCl case,²⁰ KCl calculations were based on a simple quadratic equation for $\Delta G_{\text{ex}}/(mT)$ as a function of the temperature. The equations

Table 3. Values of Apparent Molar Enthalpy^a and Relative Apparent Molar Enthalpy of the Salt Obtained by Using Parametrization PI and PII for KCl Solutions at 298.15 K and the Errors When the Apparent Values Are Predicted by eq 12 with the Parameter Values Given in Tables 4 and 5

$(m/m^\circ)^b$	$(n_1/\text{mol})^c$	$H_{\text{app},2}^a$ J·mol ⁻¹	$\Delta H_{\text{app},\text{PI}}$ J·mol ⁻¹	$\epsilon_{\text{H,PI}}^d$ J·mol ⁻¹	$\Delta H_{\text{app},\text{PII}}$ J·mol ⁻¹	$\epsilon_{\text{H,PII}}^d$ J·mol ⁻¹
0.001		17301	59.9	4.0	60.0	4.3
0.002		17324	82.8	3.8	83.1	4.0
0.005	11100	17366	125.1	3.1	126.2	3.2
0.01	5551	17409	168.0	2.1	170.5	2.1
0.02	2775	17461	220.4	0.3	225.7	0.2
0.05	1110	17538	297.1	-3.1	311.4	-3.4
0.10	555.1	17585	343.9	-5.6	373.2	-5.9
0.15	370	17594	353.3	-6.0	397.9	-6.2
0.20	277.5	17586	344.5	-5.3	404.3	-5.5
0.30		17538	297.0	-2.5	387.5	-2.5
0.40		17468	226.5	0.7	347.7	0.8
0.50		17383	142.2	3.2	294.2	3.4
0.60		17290	48.7	4.7	231.6	4.9
0.70		17190	-51.4	4.6	162.2	4.7
0.80		17084	-156.6	2.9	88.0	3.0
0.90		16975	-265.7	-0.7	9.7	-0.8
1.00		16863	-378.0	-6.2	-71.7	-6.4

^aThe value of 17241 J·mol⁻¹ from Kilday²⁸ was used in eq 5 for the partial molar enthalpy of KCl at infinite dilution as well as the relative value obtained by parametrization PI. ^b $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^cThe amount of water giving the molality in question. ^dThe difference between the suggested and predicted value.

were determined at many rounded molalities from (0.001 to 1.0) mol·kg⁻¹ in the following way: First, after Hückel parameter b_1 was obtained from eq 7 or 9 for a certain temperature, the molar excess Gibbs energies ($\Delta G_{\text{ex}}/m$) were calculated for these series of different molalities from eqs 1, 2, and 3. These calculations were performed at all temperatures from (273.15 to 353.15) K in intervals of 5 K in the same way as in ref 20 for NaCl. To study ΔG_{ex} at different temperatures at a given molality, next, a quadratic equation of type

$$\frac{\Delta G_{\text{ex}}}{mT} = u + v(T - T_0) + w(T - T_0)^2 \quad (10)$$

where $T_0 = 273.15 \text{ K}$, was fitted to these results. The resulting values of parameters u , v , and w are given for parametrizations PI and PII at the different molalities in Tables 1 and 2, respectively. For PI, they have been determined using the temperature values from (273.15 to 353.15) K in intervals of 5 K and for PII the same intervals were used but for the range of (273.15 to 313.15) K. To describe the quality of the fit, the standard deviation about regression is included in both tables for each molality.

The relative apparent molar enthalpy of the salt can be calculated from the values of parameters u , v , and w given in Tables 1 and 2 using equation

$$\Delta H_{\text{app}} = -T^2 \frac{\partial \left(\frac{\Delta G_{\text{ex}}}{mT} \right)}{\partial T} = -T^2 [v + 2w(T - T_0)] \quad (11)$$

Sample enthalpies are presented in Table 3 for 298.15 K. The symbol for the relative apparent molar enthalpy obtained, for example, by parametrization PI is $\Delta H_{\text{app},\text{PI}}$ throughout this article. Table 3 also shows the absolute apparent molar enthalpies based on the relative values calculated using PI and

the value of 17241 J·mol⁻¹ presented by Kilday²⁸ for the partial molar enthalpy of KCl at infinite dilution. The relationship between the resulting ΔH_{app} values and the molality was then determined by fitting these points with a function of the following type

$$\Delta H_{\text{app}} = a_1 + \alpha_T \sqrt{\frac{m}{m^\circ}} + a_2 \left(\frac{m}{m^\circ} \right) + a_3 \left(\frac{m}{m^\circ} \right)^{3/2} \quad (12)$$

where a_1 , a_2 , and a_3 are the fitting parameters. The theoretical value based on the Debye–Hückel theory was used for the coefficient of the square root term (i.e., for α_T). These α_T values were taken from ref 27 and are given in Table 4. For parametrization PI, the parameter values of a_1 , a_2 , and a_3 for eq 12 at all considered temperatures are also collected in this table. For PII, these values are given in Table 5. The standard deviation about regression is provided for each fit in both tables. At 298.15 K, the relative apparent enthalpies calculated by PI and PII and those predicted by eq 12 with the parameter values in Table 4 and in Table 5, respectively, are also displayed as errors in Table 3. The quality parameters in Tables 3, 4, and 5 are all close to each other for PI and PII.

Tests of the New Equations for the Apparent Molar Enthalpy with the Heat-of-Dilution Data. The most extensive measurements for heats of dilution of aqueous KCl have been carried out by Lange and Leighton²⁹ at 285.65 and 298.15 K. Both of those sets contain more than 20 points in the molality range of (0.00025 to 0.5) mol·kg⁻¹. The details of these data are given in Table 6 and as can be seen, the data contain several repeat determinations. In these data, the molar heats of dilution ($=\Delta H_{\text{m,dil}}$) are reported for several initial concentrations (denoted here as $m_{\text{initial}} = m_i$) and final concentrations ($m_{\text{final}} = m_f$) of KCl. (To be precise, Lange and Leighton used molalities instead of molalities as the composition variable but the correction between these quantities is not important for the dilute solutions considered in the article.) These data are used here as the corresponding data of Robinson³⁰ in Table 6 of ref 20 for NaCl solutions and the experimental heats were predicted using parametrizations PI and PII. The molar heat of dilution can be calculated from the apparent molar enthalpies of the final and initial solutions by

$$\Delta H_{\text{m,dil}} = \Delta H_{\text{app}}(m_f) - \Delta H_{\text{app}}(m_i) \quad (13)$$

The apparent enthalpies are obtained using eq 12 with the parameters given either in Table 4 or in Table 5. The deviation between the experimental and predicted value is calculated from

$$\epsilon_{\text{H,PX}} = \Delta H_{\text{m,dil}} (\text{observed}) - \Delta H_{\text{m,dil}} (\text{predicted using PX}) \quad (14)$$

in which the predicted value is generally obtained by PX where PX is PI or PII. According to Table 6 where these errors are presented for PI and PII, the heat-of-dilution data from Lange and Leighton²⁹ can be predicted quite well using these parametrizations, but the former applies slightly better to these heats.

In more concentrated KCl solutions, calorimetric dilution experiments were carried out by Richards and Rowe,³¹ Wood et al.,³² Leung and Millero,³³ and Mayrath and Wood.³⁴ In the first³¹ of these studies four points were measured at 293.15 K with $m_i = 2.2204 \text{ mol}\cdot\text{kg}^{-1}$, and in the second,³² seven points were measured at 298.15 K. In those, m_i was either 1.0 or 3.0 mol·kg⁻¹. In the third,³³ the initial molality was 1.03081 mol·

Table 4. Parameter Values for the Equation of the Dependence of Relative Apparent Molar Enthalpy on the Molality (eq 12 in the Text) for KCl Solutions Obtained by Using Parametrization PI

T/K	$a_1/\text{J}\cdot\text{mol}^{-1}$	$(\alpha_T)^a/\text{J}\cdot\text{mol}^{-1}$	$a_2/\text{J}\cdot\text{mol}^{-1}$	$a_3/\text{J}\cdot\text{mol}^{-1}$	$(s_H)^b/\text{J}\cdot\text{mol}^{-1}$
273.15	-9.25	1363	-3088.79	488	5.2
278.15	-6.09	1449	-3009.12	466	4.1
283.15	-4.47	1560	-2967.00	472	3.7
285.65	-4.22	1625 ^c	-2960.50	486	3.7
288.15	-3.84	1690	-2948.73	498	3.6
291.15	-3.86	1776 ^c	-2945.92	521	3.8
293.15	-3.74	1833	-2938.74	534	3.8
296.65	-3.98	1941 ^c	-2937.44	566	4.0
298.15	-4.07	1988	-2934.75	579	4.1
301.35	-4.44	2093 ^c	-2934.21	612	4.4
303.15	-4.53	2152	-2929.74	629	4.5
308.15	-5.11	2324	-2919.53	681	4.9
313.15	-5.77	2505	-2907.57	738	5.4
318.15	-6.40	2693	-2887.78	796	5.9
323.15	-7.13	2890	-2864.54	858	6.4
328.15	-7.78	3094	-2832.74	921	6.9
333.15	-8.43	3306	-2793.90	986	7.5
338.15	-9.17	3527	-2749.57	1054	8.0
343.15	-9.97	3757	-2699.38	1125	8.6
348.15	-10.82	3996	-2642.95	1199	9.2
353.15	-11.74	4245	-2582.76	1278	9.9
358.15	-12.87	4505	-2519.44	1362	10.6
358.85	-13.01	4542 ^c	-2509.88	1374	10.8
360.15	-13.36	4612 ^c	-2493.06	1397	11.0
363.15	-14.08	4775	-2450.67	1450	11.4
368.15	-15.62	5058	-2382.75	1546	12.4
373.15	-17.41	5353	-2312.47	1648	13.4
373.15 ^d	-19.25	5353	-2312.19	1780	15.0

^aTheoretical Debye–Hückel parameter for enthalpy values, taken from ref 27. ^bStandard deviation about the regression. ^cObtained by interpolation from the other values. ^dNaCl parameters determined in the present study from the results of ref 20.

Table 5. Parameter Values for the Equation of the Dependence of Relative Apparent Molar Enthalpy on the Molality (eq 12 in the Text) for KCl Solutions Obtained by Using Parametrization PII^a

T/K	$a_1/\text{J}\cdot\text{mol}^{-1}$	$a_2/\text{J}\cdot\text{mol}^{-1}$	$a_3/\text{J}\cdot\text{mol}^{-1}$	$(s_H)^b/\text{J}\cdot\text{mol}^{-1}$
273.15	-7.13	-2670.68	457	4.4
278.15	-4.41	-2610.52	442	3.5
283.15	-3.24	-2590.57	456	3.3
285.65	-3.30	-2594.86	473	3.4
288.15	-3.23	-2594.36	488	3.4
293.15	-3.68	-2611.06	533	3.8
298.15	-4.61	-2635.66	587	4.3
303.15	-5.75	-2661.15	646	5.0
308.15	-7.03	-2684.38	708	5.6
313.15	-8.42	-2708.84	776	6.4

^aThe values of α_T are given in Table 4. ^bStandard deviation about the regression.

kg^{-1} , and eight points were measured at 303.15 K. The last study³⁴ reports dilution enthalpies for KCl solutions at the high temperatures of 373.15, 423.7, and 473.0 K, and the data at 373.15 K were used here in the testing of parametrization PI. These data contain eight points from (0.0310 to 4.5) $\text{mol}\cdot\text{kg}^{-1}$. The results of all of these calculations^{31–34} are shown in Table S1. This table is given in the Supporting Information of the present study, and the acronym used for each data set is explained in footnote *a* to this table. For the data of Richards and

Rowe,³¹ Table S1 also includes the NaCl results from these authors, and the symbol of this NaCl set is RiRo20NaCl. Also for the other NaCl sets in this table, the same notation logic is used. For the NaCl sets, the PI and PII parameters presented in ref 20 (taken there from Table 4 or 5) were used when possible.

The data from the two old data sets of ref 31 in Table S1 can be predicted well only using parametrization PII. As mentioned above and observed in ref 20, PII applies better than PI to less dilute solutions at or close to 298 K as also observed in this case for the sets containing not dilute solutions. The same is also true concerning the PI and PII predictions for the data of set WRB25 in this table. The heat-of-dilution data from Wood et al.³² at $m_i = 1.0 \text{ mol}\cdot\text{kg}^{-1}$ can be predicted well only using PII and the two points where $m_i = 3.0 \text{ mol}\cdot\text{kg}^{-1}$ are predicted relatively well with this parametrization. In the same way, the high-precision data of set LeMi30 support satisfactorily only PII because this set contains data from less dilute solutions only. The data from set MaWo100 support quite well the PI parameters up to $0.1244 \text{ mol}\cdot\text{kg}^{-1}$ but not above $0.25 \text{ mol}\cdot\text{kg}^{-1}$. In Table S1, we included the NaCl results of Mayrath and Wood³⁵ at higher temperatures (i.e., at 348.15 and 373.15 K), and these data correspond closely to the data of ref 34 at 373.15 K. The PI parameters for NaCl solutions at 348.15 K were taken from Table 4 of ref 20, and at 373.15 K they are given in Table 4 of the present study. At the former temperature, these heats support PI very satisfactorily up to $0.5 \text{ mol}\cdot\text{kg}^{-1}$. At the latter temperature, the agreement for these NaCl solutions is close to that of KCl solutions in this table.

Table 6. Heats of Dilution Reported by Lange and Leighton²⁹ for KCl Solutions at 298.15 and 285.65 K and the Resulting Errors (See eq 14) When These Values Are Predicted Using Parametrization PI or PII

T/K	$(m_i/m^\circ)^a$	m_i/m°	$\Delta H_{m,dil}$	$\epsilon_{H,PI}$	$\epsilon_{H,PII}$
			J·mol ⁻¹	J·mol ⁻¹	J·mol ⁻¹
298.15	0.00303	0.000326	-59.4	6.3	7.1
	0.00303	0.000326	-62.3	3.4	4.2
	0.00606	0.000653	-79.5	8.9	10.5
	0.00606	0.000653	-89.5	-1.2	0.4
	0.0101	0.00109	-105	2.8	5.5
	0.0101	0.00109	-109	-0.9	1.8
	0.0202	0.00218	-129	9.2	14.6
	0.0202	0.00218	-126	12.1	17.5
	0.0354	0.00382	-146	16.6	26.1
	0.0354	0.00382	-144	18.7	28.2
	0.0600	0.00648	-159	19.1	35.2
	0.0600	0.00648	-160	18.2	34.4
	0.0600	0.00648	-161	17.4	33.5
	0.0600	0.00648	-158	19.9	36.0
	0.1010	0.00275	-234	23.4	53.0
	0.1010	0.00279	-233	24.0	53.6
	0.2000	0.00545	-216	7.0	65.9
	0.2000	0.00550	-214	8.1	67.0
	0.3600	0.0098	-122	-29.4	77.0
	0.3600	0.0099	-121	-29.3	77.1
0.5000	0.0136	-7.5	-57.3	91.0	
0.5000	0.0138	-7.5	-58.4	89.8	
285.65	0.0024	0.000259	-38.5	8.7	9.5
	0.0024	0.000259	-41.8	5.3	6.1
	0.0024	0.000259	-40.2	7.0	7.8
	0.0048	0.000517	-58.6	4.5	6.1
	0.0048	0.000517	-54.4	8.7	10.3
	0.0048	0.000517	-54.4	8.7	10.3
	0.0048	0.000517	-62.8	0.4	1.9
	0.0096	0.001035	-81.6	0.4	3.6
	0.0096	0.001035	-79.5	2.5	5.6
	0.0096	0.001035	-77.4	4.6	7.7
	0.0192	0.002070	-90.0	11.8	18.0
	0.0192	0.002070	-91.2	10.6	16.8
	0.0192	0.002070	-90.0	11.8	18.0
	0.0202	0.002180	-93.3	9.8	16.3
	0.0336	0.003620	-94.6	19.7	30.6
	0.0354	0.003820	-92.5	22.5	33.9
	0.0480	0.00518	-100	16.8	32.3
	0.0506	0.00545	-94.1	23.1	39.5
	0.0506	0.00545	-93.7	23.5	39.9
	0.0708	0.00763	-80.8	31.5	54.4
0.0708	0.00763	-80.8	31.5	54.4	
0.125	0.00340	-103	37.8	81.7	
0.125	0.00344	-102	38.6	82.5	
0.250	0.06800	11.7	-86.2	-21.1	
0.250	0.06880	10.0	-88.2	-23.3	

^a $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$.

Tests of the New PI Equations for the Apparent Molar Enthalpy with the Heat-of-Solution Data. The dissolution of crystalline KCl into water has been used for many years as an important reference reaction for endothermic solution calorimetry. In 1980, the National Bureau of Standards published an article²⁸ in which Kilday recommends that the enthalpy of solution of the reference material of SRM 1655 of crystalline

KCl at 298.15 K is $(17584 \pm 17) \text{ J}$ for the solution that contains an amount of 1 mol of KCl and that of 500 mol of water. The dilution ratio is thus 1/500 and the molality of such solution is $0.11102 \text{ mol}\cdot\text{kg}^{-1}$. In the paper of Kilday, extensive studies were performed to obtain the molar enthalpy for this solution and for other corresponding reference values in the temperature range of (296 to 358) K. Many data sets from this research were used here in the testing of parametrization PI. At temperatures close to 298.15 K, Kilday measured 26 points using different experimental methods to treat the crystalline reference material. All of these points were used in the present tests without any correction. It is a general definition in thermodynamics that the molar solution enthalpy is the same as the apparent molar enthalpy for the solute (i.e., $H_{app,2}$ in eq 4). The test results are shown as an error plot in graph A of Figure 1. In this plot, the error defined by

$$\epsilon_{H,app} = \Delta H_{app}(\text{observed}) - \Delta H_{app}(\text{predicted}) \quad (15)$$

is presented as a function of the molality. In the calculation of the relative values required in eq 15, we used the value for the partial molar enthalpy of KCl at infinite dilution (i.e., for $H_{m,2}^\infty$) that gives the best fit in the error plot. This value is $17177 \text{ J}\cdot\text{mol}^{-1}$. The value suggested by Kilday for this quantity is $17241 \text{ J}\cdot\text{mol}^{-1}$. The latter was based on the recommended NBS-solution-enthalpy at $m = 0.11102 \text{ mol}\cdot\text{kg}^{-1}$ and some additional calorimetric information from more concentrated KCl solutions. While this value is close to ours, we think that ours is superior as it utilizes (in addition to the high precision data measured by Kilday) all thermodynamic data for dilute KCl solutions reported in the literature for this temperature.

The new value determined here is also presented in Table S2 in the same way as all $H_{m,2}^\infty$ values employed now in the calculations of the heat-of-solution data. This table is given in the Supporting Information of the present study. The error plot for this data set in graph A of Figure 1 is completely random and thus supports parametrization PI excellently. It is interesting to observe that the largest absolute errors in graph A are an order of about $150 \text{ J}\cdot\text{mol}^{-1}$. These errors are clearly larger than the errors obtained using the heat-of-dilution data (for example, see Table 6). Indicating that the heats of dilution can be measured more accurately than the heats of solution.

Sanahuja and Cesari³⁶ have also reported heats for dissolution of small amounts of solid KCl into water in experiments that lead to dilute aqueous solutions at 298.15 K. In the prediction of these experimental ΔH_{app} values, the value of $H_{m,2}^\infty$ was taken to be $17206 \text{ J}\cdot\text{mol}^{-1}$ following their paper. Our fitted PI value for this quantity agrees closely to this original value. The resulting error plot for this set is shown in graph A of Figure 1. Evidently, the data from this set support PI as well as the data of Kilday in this graph.

At 298.15 K, Zverev and Krestov,³⁷ Abrosimov and Krestov,³⁸ Dadgar and Taherian,³⁹ and Bazlova et al.,⁴⁰ have additionally reported heats of solution for dilute KCl(aq). These data were predicted here using parametrization PI. The $H_{m,2}^\infty$ values for these data are given in Table S2, and the resulting error plots are in graphs B and C of Figure 1. Graph B shows the results from refs 37 and 38. In refs 39 and 40, NaCl solutions were also considered, and the resulting calorimetric data are included in these graphs. The NaCl errors of ref 39 are presented in graph B, and the KCl errors are in graph C. The errors for both electrolytes from ref 40 are illustrated in graph C. This graph also shows the errors from the high-precision data by Benjamin⁴¹ in less dilute NaCl solutions. For this NaCl set, the dilute-solution

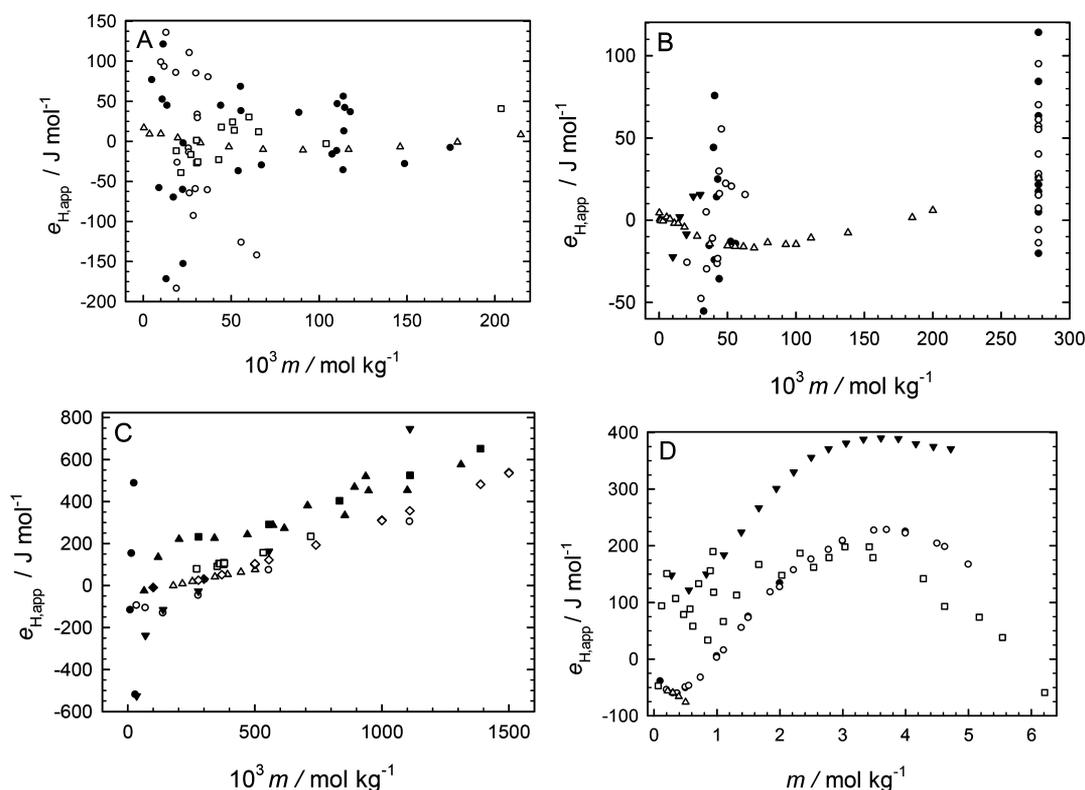


Figure 1. Plot of $e_{H,app}$ (eq 15), the deviation between the suggested relative apparent molar enthalpy for KCl or NaCl solutions and that predicted using parametrization PI or PII of the present study (see text) at 298.15 K as a function of molality m . The suggested values have been calculated from the heats of solution or dilution by Kilday,²⁸ Sanahuja and Cesari,³⁶ Zverev and Krestov,³⁷ Abrosimov and Krestov,³⁸ Dadgar and Taherian,³⁹ Lange and Monheim,⁴³ Bazlova et al.,⁴⁰ Benjamin,⁴¹ Wüst and Lange,⁴⁴ and Hubert et al.⁴² Also the smoothed values from Parker⁴⁵ and Pabalan and Pitzer⁴⁶ were used in the testing. Details of the calculation are given in the text. Symbols for graph A where only parametrization PI was used: ●, ref 28, KCl; ○, ref 36, KCl; △, ref 43, KCl; □, ref 41, NaCl. Symbols for graph B where only parametrization PI was used: ●, ref 37, KCl; ○, ref 38, KCl; ▼, ref 39, NaCl; △, ref 45, KCl. Symbols for graph C where only parametrization PI was used: ●, ref 39, KCl; ○, ref 40, KCl; ▼, ref 40, NaCl; △, ref 43, KCl; ■, ref 44, KCl; □, ref 41, NaCl; ◆, ref 46, KCl; ◇, ref 45, KCl; ▲, ref 42, NaCl. Symbols for graph D where only parametrization PII was used: ●, ref 46, KCl; ○, ref 45, KCl; ▼, ref 44, KCl; △, ref 43, KCl; □, ref 42, NaCl. The KCl point where $m = 0.02 \text{ mol}\cdot\text{kg}^{-1}$ from ref 39 was omitted in graph C as an outlier. In graph D, some points of the set from ref 43 were omitted because of clarity.

Table 7. Partial Molar Enthalpies of Potassium Chloride (Symbol 2) at Infinite Dilution Obtained Using Parameterization PI from the KCl Data of Kilday,²⁸ Vasilj'ev and Lobanov,⁴⁹ and Olofsson et al.⁵⁰

T/K	$H_{m,2}^{\infty}/\text{J}\cdot\text{mol}^{-1}$
291.15	18322 ⁴⁹
296.65	17489 ²⁸
298.15	17177; ^a 17241; ^b 17235; ^c 17223; ²⁸ 17195; ⁴⁹ 17194 ⁵⁰
298.55	17165 ²⁸
301.35	16725 ²⁸
303.15	16381 ²⁸
308.15	15575; ²⁸ 15666 ⁴⁹
313.15	14762; ²⁸ 14803; ⁴⁹ 14885 ⁵⁰
323.15	13221 ²⁸
328.15	12525; ⁴⁹ 12524 ⁵⁰
333.15	11735; ²⁸ 11817 ⁵⁰
343.15	10126; ²⁸ 10280 ⁴⁹
353.15	8613 ²⁸
358.15	7914 ⁴⁹
358.85	7755 ²⁸
360.15	7710 ⁵⁰

^aPresented in Table S2 (see Supporting Information) for ref 28.

^bGiven by Kilday in ref 28. ^cGiven by Lange and Monheim in ref 43.

errors up to $0.21 \text{ mol}\cdot\text{kg}^{-1}$ are reported in graph A. The data of Benjamin⁴¹ were not considered in our previous calorimetric article²⁰ for NaCl solutions. All calculations for the NaCl solutions were performed using parametrization PI determined in ref 20.

In graph B of Figure 1, the dilute-solution data from the group of Krestov^{37,38} support parametrization PI very well for KCl solutions as also the results of numerous determinations at $m = 0.27755 \text{ mol}\cdot\text{kg}^{-1}$. This molality corresponds to the dilution ratio of 1/200. On the other hand, all four KCl points from Dadgar and Taherian³⁹ do not agree in graph C with the predictions obtained by using PI. These points are probably not reliable. In contrast, the NaCl data of this group seem to be accurate in graph B and the $H_{m,2}^{\infty}$ value estimated from these points (i.e., the value of $3833 \text{ J}\cdot\text{mol}^{-1}$ in Table S2) is very close to the value recommended in ref 20 for this quantity (i.e., close to $3824 \text{ J}\cdot\text{mol}^{-1}$ in Table 7 of that reference). Bazlova et al.⁴⁰ have determined heats of solution in more concentrated NaCl and KCl solutions than those considered above, and the results are shown in graph C for both cases. Their KCl data can be predicted quite satisfactorily using parametrization PI but the $H_{m,2}^{\infty}$ value presented for this set in Table S2 (i.e., $17349 \text{ J}\cdot\text{mol}^{-1}$) is not very close to the value obtained from the more accurate sets. The NaCl data of this group do not agree well with the predictions obtained by PI and are thus probably not reliable.

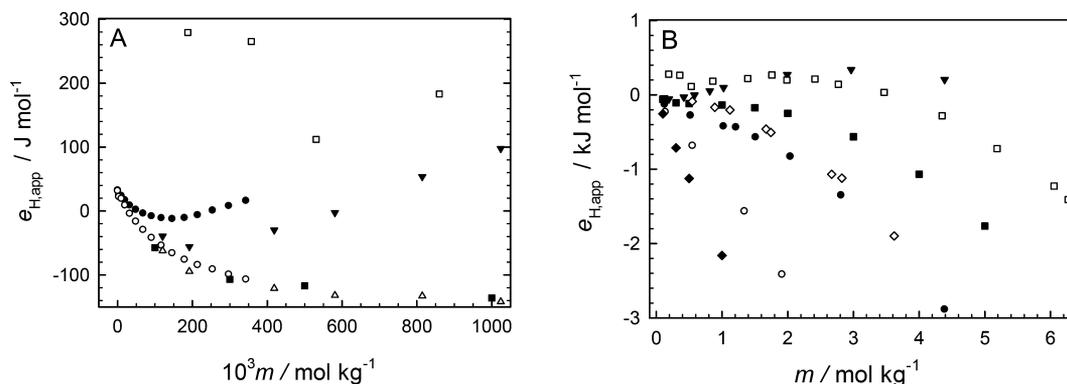


Figure 2. Plot of $e_{H,app}$ (eq 15), the deviation between the suggested relative apparent molar enthalpy for KCl or NaCl solutions and that predicted using parametrization PI or PII of the present study (see text) at temperatures other than 298.15 K as a function of molality m . The suggested values have been given by Lange and Monheim⁴³ and Snipes et al.⁴⁸ on the basis of the heat-of-dilution measurements in KCl solutions and by Hubert et al.⁴² on the basis of heat-of-solution measurements in NaCl solutions. Also the smoothed values from Pabalan and Pitzer⁴⁶ for KCl solutions were used in the testing. Details of the calculations are given in the text. Symbols for graph A: ●, ref 43, $T = 285.65$ K, parametrization PI, KCl; ○, ref 43, 285.65 K, PII, KCl; ▼, ref 48, 313.15 K, PI, KCl; △, ref 48, 313.15 K, PII, KCl; □, ref 42, 318.15 K, PI, NaCl; ■, ref 46, 323.15 K, PI, KCl. Symbols for graph B where only parametrization PI was used: ●, ref 48, $T = 333.15$ K, KCl; ○, ref 48, 353.15 K, KCl; ▼, ref 48, 313.15 K, KCl; ■, ref 46, 323.15 K, KCl; □, ref 42, 318.15 K, NaCl; ◆, ref 46, 373.15 K, KCl; ◇, ref 42, 333.15 K, NaCl. In graph B, the errors of the strongest points are outside the scale of graph at 333.15, 353.15, and 373.15 K.

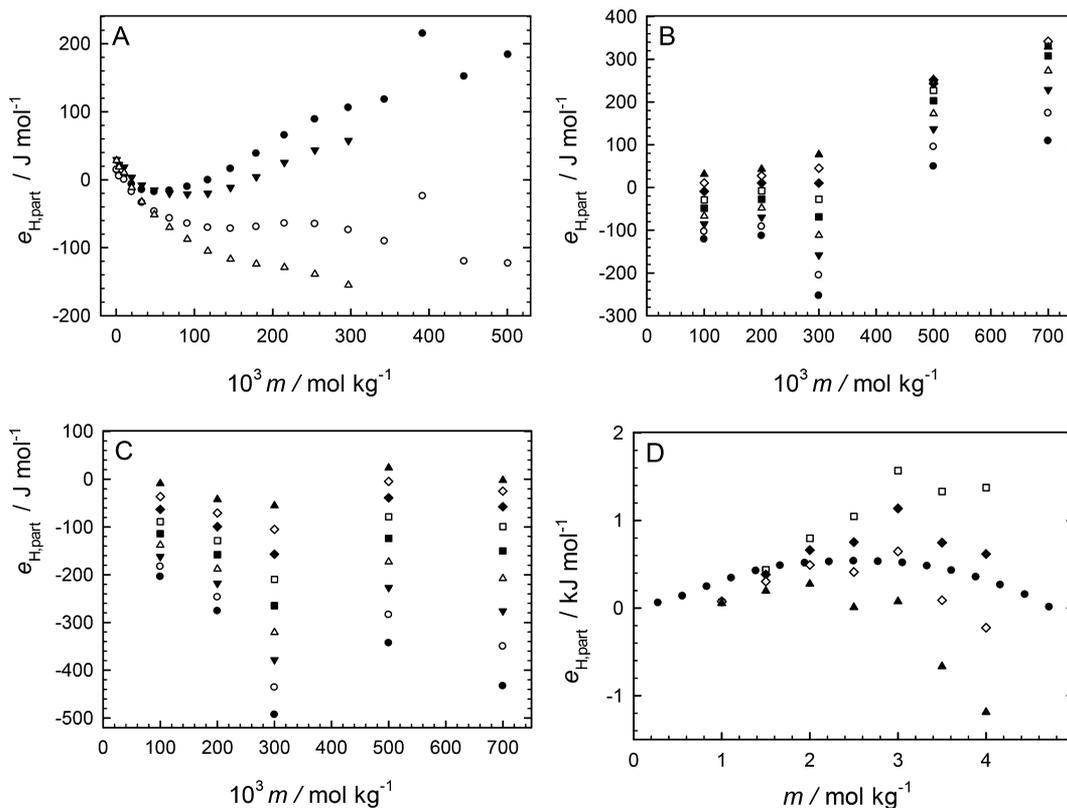


Figure 3. Plot of $e_{H,part}$ (eq 16), the deviation between the suggested relative partial molar enthalpy for KCl solutions obtained from the heats of dilution measured by Monheim and Lange⁴³ and Wüst and Lange⁴⁴ and from the cell-potential differences measured by Harned and Cook²⁶ and that predicted using parametrization PI or PII of the present study (see text) as a function of molality m at various temperatures. Symbols for graph A for which only the results from ref 43 were used: ●, $T = 298.15$ K, PI; ○, 298.15 K, PII; ▼, 285.65 K, PI; △, 285.65 K, PII. Symbols for the graphs B and C for which only the data from ref 26 was used; in graph B only parametrization PI was used and in graph C only PII: ●, $T = 273.15$ K; ○, 278.15 K; ▼, 283.15 K; △, 288.15 K; ■, 293.15 K; □, 298.15 K; ◆, 303.15 K; ◇, 308.15 K; ▲, 313.15 K. Symbols for the graph D where only parametrization PII was used: ●, ref 44; $T = 298.15$ K; □, ref 26; 298.15 K; ◆, ref 26; 303.15 K; ◇, ref 26; 308.15 K; ▲, ref 26; 313.15 K. In graphs B and C, the results of the point where $m = 0.05$ mol·kg⁻¹ have been omitted because of clarity. All of these errors are small.

The 23 experimental points from Benjamin⁴¹ for NaCl solutions belong to a high-precision set up to a molality of 0.72 mol·kg⁻¹. As mentioned, the less dilute solutions from this set are considered in graph C, and they can be predicted very well using

PI. Also the absolute errors for this set in the dilute solutions of graph A are very small. The errors in graph A were used in the determination of the $H_{m,2}^{\infty}$ value for Table S2, and the resulting value is 3866 J·mol⁻¹. It is thus quite close to $H_{m,2}^{\infty} = 3824$ J·

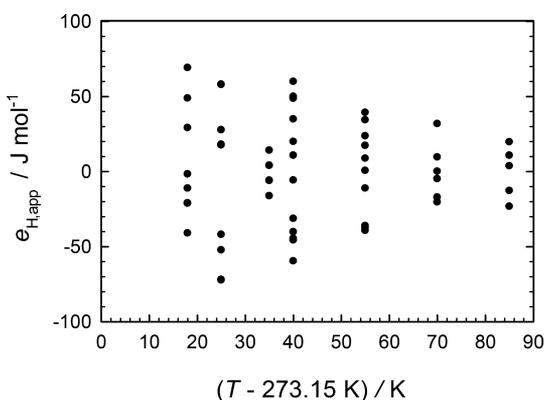


Figure 4. Plot of $e_{H,app}$ (eq 15), the deviation between the suggested relative apparent molar enthalpy for KCl solutions from the data of Vasil'ev and Lobanov⁴⁹ and that predicted using parametrization PI of the present study (see text) at a molality of about $0.123 \text{ mol}\cdot\text{kg}^{-1}$ as a function of temperature T . Exact molalities given in ref 49 were used in the calculations as well as the values of $H_{m,2}^{\infty}$ given in Table 7 for these data.

mol^{-1} given in ref 20. For many other NaCl sets considered in ref 20, PI did not work so far at 298.15 K as it applies to this set⁴¹ in graph C.

At 298.15 K and also at 318.15 and 333.15 K, Hubert et al.⁴² have determined heats of solution mainly for less dilute NaCl solutions. (Actually, the measurement temperatures were 297.6, 317.5, and 332.4 K but these data can be predicted using the activity models at these rounded Celsius temperatures of 25, 45, and 60 °C because the enthalpy data are not very precise.) The data for less concentrated solutions were predicted using parametrization PI for NaCl solutions, and the parameters for eq 12 are given in Table 4 of ref 20 together with the values of $H_{m,2}^{\infty}$ shown in Table S2. The resulting error plots for 298 K are presented here in graph C of Figure 1. All data at 298 K were predicted using PII with the parameters given in Table 5 of ref 20 and the results are shown in graph D of this figure. The data for

the other two temperatures of 318 and 333 K were predicted here using only PI. The results at 318 K from dilute solutions are given in graph A of Figure 2, and all results containing also those from less dilute solutions at this temperature are given in graph B of this figure in addition to the results obtained at 333 K. All the data from this source except the most concentrated points at 333 K in graph B support at least very satisfactorily the PI parameters of NaCl determined in ref 20.

Tests of the New Values for Relative Apparent Molar Enthalpy with Those Presented in the Literature. Lange and Monheim⁴³ and Wüst and Lange⁴⁴ have reported apparent molar enthalpies for KCl solutions at 298.15 K on the basis of their heat-of-dilution experiments. We predicted these data using parametrizations PI and PII. The results obtained using PI for the dilute solutions at 298.15 K from the set of Lange and Monheim⁴³ are given as an error plot in graph A of Figure 1. These results support the parametrization excellently. More concentrated solutions from this set are treated with PI in graph C and all solutions from this set using PII in graph D of this figure. In both of these graphs, the agreement is good throughout. The set of Wüst and Lange⁴⁴ consists of ΔH_{app} values for more concentrated solutions than those given in ref 43 starting at a molality of $0.28 \text{ mol}\cdot\text{kg}^{-1}$ and extending up to $4.7 \text{ mol}\cdot\text{kg}^{-1}$. The PI errors for this set in the five most dilute points are shown in graph C, whereas all PII errors are given in graph D of Figure 1. Graph C shows that PI applies satisfactorily to these data up to $0.6 \text{ mol}\cdot\text{kg}^{-1}$ as well as graph D shows that PII applies to the data of all molalities reported in refs 43 and 44. The most likely cause of the quite large systematic error in the plot for the latter data⁴⁴ in graph D is the fact that the value of $H_{m,2}^{\infty}$ obtained here from ref 43 (see Table S2) was used in the calculations instead of the fitted value. Most of the dilute-solution points from ref 43 were omitted from graph D because of clarity, and the omitted errors are all close to those in graph C for PI.

PI and PII at 298.15 K were also tested against the ΔH_{app} values reported by Parker.⁴⁵ The errors of the former parametrization are shown in graphs B and C and those of the

Table 8. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (273.15 to 298.15) K as a Function of Molality m ^b

$(m/m^{\circ})^c$	$\Delta H_{app}(0)^d$	$\Delta H_{app}(5)^d$	$\Delta H_{app}(10)^d$	$\Delta H_{app}(15)^d$	$\Delta H_{app}(20)^d$	$\Delta H_{app}(25)^d$
0.005	72	81	91	101	111	122
0.01	97	109	122	136	151	166
0.02	123	140	158	178	198	220
0.03	137	157	179	203	228	255
0.04	144	167	193	220	250	281
0.05	147	173	201	232	265	300
0.06	146	175	207	241	277	315
0.07	144	175	209	246	285	327
0.08	140	174	210	250	292	337
0.09	135	170	209	251	296	344
0.1	128	166	207	251	299	349
0.12	113	154	200	248	301	356
0.14	94	139	189	242	299	359
0.15	84	131	182	237	296	359
0.16	73	122	175	232	293	359
0.18	50	103	159	220	286	355
0.20	26	82	142	207	276	350

^aDefined by equation $\Delta H_{app} = H_{app,2} - H_{m,2}^{\infty}$, and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^{\circ} = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

Table 9. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (303.15 to 328.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(30)^d$	$\Delta H_{\text{app}}(35)^d$	$\Delta H_{\text{app}}(40)^d$	$\Delta H_{\text{app}}(45)^d$	$\Delta H_{\text{app}}(50)^d$	$\Delta H_{\text{app}}(55)^d$
0.005	133	145	157	170	183	197
0.01	182	199	216	235	254	274
0.02	243	267	292	319	347	376
0.03	284	313	345	378	412	448
0.04	314	348	385	423	463	505
0.05	337	376	417	460	505	553
0.06	356	399	444	492	542	594
0.07	371	418	467	519	573	630
0.08	384	434	487	542	601	662
0.09	394	448	504	563	625	690
0.1	403	459	519	582	647	716
0.12	416	478	544	613	686	762
0.14	423	491	563	639	718	802
0.15	426	497	571	650	732	819
0.16	428	501	578	660	745	836
0.18	429	507	590	677	769	865
0.20	428	511	599	692	789	892

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{\text{m},2}^\infty$, and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

Table 10. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (333.15 to 353.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(60)^d$	$\Delta H_{\text{app}}(65)^d$	$\Delta H_{\text{app}}(70)^d$	$\Delta H_{\text{app}}(75)^d$	$\Delta H_{\text{app}}(80)^d$
0.005	212	227	243	259	276
0.01	295	317	340	364	388
0.02	406	438	471	505	541
0.03	485	525	566	608	653
0.04	549	595	642	692	744
0.05	602	654	708	764	823
0.06	648	705	765	827	892
0.07	689	751	816	884	954
0.08	725	792	862	935	1011
0.09	759	830	905	982	1064
0.1	789	865	944	1026	1113
0.12	843	926	1014	1106	1202
0.14	889	981	1077	1177	1282
0.15	910	1006	1106	1210	1319
0.16	930	1029	1133	1241	1355
0.18	967	1073	1184	1300	1422
0.20	999	1113	1231	1355	1484

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{\text{m},2}^\infty$, and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

latter in graph D of Figure 1. These errors were obtained from the heats of dilution estimated by Parker after evaluating all calorimetric data available for KCl solutions at around 298.15 K until the publication of his article. The publication year was 1965. The errors in graphs B and C validate the use of PI in these relatively dilute solutions while the errors in graph D justify the applicability of PII also in more concentrated solutions.

Finally, we compared predictions from PI and PII to the ΔH_{app} data that can be obtained from the Pitzer equations determined by Pabalan and Pitzer⁴⁶ for KCl solutions at rounded molalities at 298.15 K. In the determination of these Pitzer equations, thermodynamic data apart from calorimetric data was also employed, as usually for these multiparameter treatments. The multiparameter equations determined by

Archer⁴⁷ are also available in the literature for KCl solutions, and these equations were considered previously in ref 19. As before, the errors from dilute solutions up to $1.5 \text{ mol}\cdot\text{kg}^{-1}$ for ref 46 are presented for PI in graph C and the errors from all data for PII in graph D of Figure 1. Because the Pitzer equation follows exactly the enthalpies of Parker,⁴⁵ also these smoothed values agree quite well with the predicted ones in the graphs. All symbols for ref 46 are not discernible from those of ref 45 in these graphs.

As the data of Herbert et al.⁴² above show, relative apparent molar enthalpies have also been presented in the literature for temperatures other than the normal reference temperature of 298.15 K. The study of Lange and Monheim⁴³ contains values for 285.65 K and the study of Snipes et al.⁴⁸ contains values for

Table 11. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (358.15 to 373.15) K and Those of Sodium Chloride at 373.15 K in Aqueous NaCl Solutions as Functions of Molality m^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(85)^d$	$\Delta H_{\text{app}}(90)^d$	$\Delta H_{\text{app}}(95)^d$	$\Delta H_{\text{app}}(100)^d$	$\Delta H_{\text{app}}(\text{NaCl},100)^{d,e}$
0.005	294	312	331	350	348
0.01	414	440	468	496	495
0.02	578	616	656	698	697
0.03	699	747	797	849	848
0.04	798	854	913	974	973
0.05	884	947	1014	1082	1082
0.06	959	1030	1103	1179	1179
0.07	1028	1105	1184	1268	1268
0.08	1091	1173	1259	1349	1350
0.09	1149	1237	1329	1425	1427
0.1	1203	1297	1394	1496	1499
0.12	1302	1406	1515	1628	1632
0.14	1391	1505	1624	1748	1753
0.15	1433	1552	1676	1805	1811
0.16	1473	1597	1725	1859	1866
0.18	1549	1681	1819	1963	1972
0.20	1620	1761	1908	2061	2071

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{\text{m},2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). $c_m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$. ^eThe value is given for NaCl solutions.

Table 12. Recommended Values of Relative Partial Molar Enthalpies ($\Delta H_{\text{m},2}$)^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (273.15 to 298.15) K as a Function of Molality m^b

$(m/m^\circ)^c$	$\Delta H_{\text{m},2}(0)^d$	$\Delta H_{\text{m},2}(5)^d$	$\Delta H_{\text{m},2}(10)^d$	$\Delta H_{\text{m},2}(15)^d$	$\Delta H_{\text{m},2}(20)^d$	$\Delta H_{\text{m},2}(25)^d$
0.005	105	118	132	146	162	178
0.01	135	152	171	192	214	237
0.02	160	184	211	240	271	304
0.03	166	196	229	265	303	344
0.04	162	197	236	277	322	369
0.05	153	192	235	282	332	385
0.06	139	182	230	282	337	395
0.07	122	169	221	277	337	401
0.08	102	154	209	270	334	403
0.09	81	136	195	260	328	401
0.1	58	116	179	247	320	398
0.12	8.4	73	143	218	299	385
0.14	-45	26	102	184	272	366
0.15	-73	0.6	80	166	257	355
0.16	-102	-25	58	146	241	342
0.18	-161	-78	10	105	207	315
0.20	-221	-134	-39	62	170	285

^aDefined by equation $\Delta H_{\text{m},2} = H_{\text{m},2} - H_{\text{m},2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). $c_m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T-273.15)/\text{K}$.

313.15, 333.15, and 353.15 K. Similarly as Lange and Monheim, Snipes et al. determined these values using dilution experiments. Smoothed values have been presented by Pabalan and Pitzer⁴⁶ for 323.15 and 373.15 K in the same way as for 298.15 K. Here, all of these data were predicted using parametrization PI and the results are collected as error plots of graphs A and B in Figure 2. Parametrization PII was only used for the set of Lange and Monheim at 285.65 K and that of Snipes et al. at 313.15 K. The results of these two sets for both PI and PII are shown in graph A. Graph B contains additionally the results of the latter set in less dilute solutions but only PI was used in the calculations. The fourth set used in graph A is the one suggested by Pabalan and Pitzer⁴⁶ at 323.15 K. All results in graph A at 285.65, 313.15, and

323.15 K can be predicted well using PI but PII is not as good for the results at 285.65 and at 313.15 K. In graph B, the set of Snipes et al. at 323.15 K can be well predicted using PI while the set at 333.15 K is only satisfactorily reproduced with this parametrization. These sets contain points where the molality extends up to about $4 \text{ mol}\cdot\text{kg}^{-1}$. Also the Pitzer values⁴⁶ at 323.15 K agree quite well with the PI predictions up to this molality. The points of Snipes' group⁴⁸ at 353.15 K and those of Pabalan and Pitzer at 373.15 K agree with the PI predictions only in dilute solutions.

Tests of the New Values for Relative Partial Molar Enthalpy with Those Presented in the Literature. In thermal literature, the heat-of-dilution or heat-of-solution values

Table 13. Recommended Values of Relative Partial Molar Enthalpies ($\Delta H_{m,2}$)^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (303.15 to 328.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{m,2}(30)^d$	$\Delta H_{m,2}(35)^d$	$\Delta H_{m,2}(40)^d$	$\Delta H_{m,2}(45)^d$	$\Delta H_{m,2}(50)^d$	$\Delta H_{m,2}(55)^d$
0.005	195	213	232	251	272	293
0.01	261	287	314	342	371	402
0.02	339	376	415	455	497	542
0.03	387	432	480	530	583	638
0.04	419	472	528	586	648	712
0.05	442	501	564	630	700	772
0.06	458	523	593	666	743	823
0.07	468	540	615	695	778	866
0.08	475	552	634	719	809	904
0.09	479	561	648	739	836	937
0.1	480	567	659	756	859	966
0.12	476	573	675	783	896	1016
0.14	465	571	683	801	925	1056
0.15	458	568	684	807	937	1074
0.16	450	564	685	813	947	1090
0.18	430	553	683	820	965	1117
0.20	408	538	677	823	978	1141

^aDefined by equation $\Delta H_{m,2} = H_{m,2} - H_{m,2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T-273.15)/\text{K}$.

Table 14. Recommended Values of Relative Partial Molar Enthalpies ($\Delta H_{m,2}$)^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (333.15 to 353.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{m,2}(60)^d$	$\Delta H_{m,2}(65)^d$	$\Delta H_{m,2}(70)^d$	$\Delta H_{m,2}(75)^d$	$\Delta H_{m,2}(80)^d$
0.005	315	338	363	388	414
0.01	434	468	502	539	577
0.02	588	636	687	740	794
0.03	696	756	819	884	953
0.04	780	850	924	1001	1081
0.05	849	928	1012	1099	1190
0.06	907	996	1088	1184	1285
0.07	958	1054	1155	1261	1371
0.08	1003	1107	1216	1329	1448
0.09	1043	1154	1271	1393	1520
0.1	1079	1197	1321	1451	1586
0.12	1141	1273	1411	1556	1707
0.14	1194	1339	1490	1649	1815
0.15	1217	1368	1526	1692	1865
0.16	1239	1396	1560	1733	1913
0.18	1278	1447	1624	1810	2004
0.20	1312	1493	1682	1881	2089

^aDefined by equation $\Delta H_{m,2} = H_{m,2} - H_{m,2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

are often expressed as the partial molar enthalpies of the solute. These partial enthalpies can be easily calculated using eq 6 from the polynomials given in eq 12 with the parameter values given in Tables 4 and 5. Both PI and PII were tested here against the relative partial molar enthalpies suggested in the literature. In these tests, the reported $\Delta H_{m,2}$ values are compared to the predicted ones, and the resulting errors are defined by

$$\epsilon_{H,\text{part}} = \Delta H_{m,2} (\text{observed}) - \Delta H_{m,2} (\text{predicted}) \quad (16)$$

are presented as a function of the molality. As mentioned above, Lange and Monheim⁴³ reported apparent molar enthalpies for KCl solutions at 285.65 and 298.15 K on the basis of their heat-of-dilution experiments. In addition, they provide the partial

molar enthalpies for all solutions considered in their study. Also these partial enthalpies were used here in the testing of both parametrizations PI and PII with the values of $H_{m,2}^\infty = 19422 \text{ J}\cdot\text{mol}^{-1}$ and $H_{m,2}^\infty = 17216 \text{ J}\cdot\text{mol}^{-1}$ (see Table S2 in the Supporting Information) for 285.65 and 298.15 K, respectively. The results of these tests are given as error plots in graph A of Figure 3. According to this graph, both parametrizations apply well to all of these data. At 285.65 K, however, PI seems to apply slightly better.

Harned and Cook²⁶ thermodynamically determined partial molar enthalpies from their results of the amalgam-cell measurements at temperatures from (273 to 313) K using intervals of 5 K. Up to a molality of $1.0 \text{ mol}\cdot\text{kg}^{-1}$, these data are considered in graphs B and C of Figure 3. Graph B shows the

Table 15. Recommended Values of Relative Partial Molar Enthalpies ($\Delta H_{m,2}$)^a of Potassium Chloride (Symbol 2) in Aqueous KCl Solutions at Temperatures from (358.15 to 373.15) K and Those of Sodium Chloride at 373.15 K in Aqueous NaCl Solutions as Functions of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{m,2}(85)^d$	$\Delta H_{m,2}(90)^d$	$\Delta H_{m,2}(95)^d$	$\Delta H_{m,2}(100)^d$	$\Delta H_{m,2}(\text{NaCl},100)^{d,e}$
0.005	441	469	498	529	527
0.01	616	657	699	743	742
0.02	852	911	973	1037	1036
0.03	1024	1098	1176	1256	1256
0.04	1164	1251	1342	1436	1437
0.05	1284	1383	1485	1593	1595
0.06	1390	1500	1614	1732	1736
0.07	1485	1605	1730	1860	1864
0.08	1572	1702	1837	1977	1983
0.09	1653	1791	1936	2086	2094
0.1	1728	1875	2029	2190	2198
0.12	1865	2030	2201	2380	2392
0.14	1988	2170	2358	2555	2571
0.15	2046	2235	2433	2638	2655
0.16	2102	2299	2504	2718	2737
0.18	2207	2419	2641	2871	2895
0.20	2306	2533	2770	3017	3045

^aDefined by equation $\Delta H_{m,2} = H_{m,2} - H_{m,2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI (see text). ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T-273.15)/\text{K}$. ^eThe value is given for NaCl solutions.

Table 16. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Less Dilute Aqueous KCl Solutions at Temperatures from (273.15 to 293.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(0)^d$	$\Delta H_{\text{app}}(5)^d$	$\Delta H_{\text{app}}(10)^d$	$\Delta H_{\text{app}}(15)^d$	$\Delta H_{\text{app}}(20)^d$
0.2	26	82	142	207	276
0.3	-110	-40	40	120	210
0.4	-260	-180	-85	10	120
0.5	-420	-320	-220	-110	10
0.6	-580	-470	-360	-230	-100
0.7	-750	-630	-500	-360	-210
0.8	-910	-780	-650	-490	-330
0.9	-1100	-940	-790	-630	-450
1.0	-1250	-1100	-940	-760	-580

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{m,2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI. ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

results for parametrization PI, and graph C shows those for PII at all investigated temperatures. The errors support at least satisfactorily both of these parametrizations at all temperatures but PI applies in general slightly better to the data. In graph D, the more concentrated solutions of Harned and Cook have been used in the testing of parametrization PII up to $4 \text{ mol}\cdot\text{kg}^{-1}$. Only the results at temperatures 298, 303, 308, and 313 K were included in the graph, because those at the lower temperatures do not show even a satisfactory agreement that can be observed at these four temperatures. Like the two sets of Monheim and Lange,⁴³ the set of Wüst and Lange⁴⁴ at 298.15 K similarly consists of both apparent and partial molar enthalpies. This set reports values mainly for the less dilute solutions and the partial enthalpies were used here in the testing of PII at these higher concentrations with a value of $H_{m,2}^\infty = 17216 \text{ J}\cdot\text{mol}^{-1}$ (see Table S2). These results are displayed in graph D of Figure 3, and are seen there to support PII better than the amalgam-cell results.

Determination of the Partial Molar Enthalpy for KCl at Infinite Dilution at Various Temperatures from the Heats of Solution Measured using Dilute KCl Solutions. Vasil'ev

and Lobanov⁴⁹ have determined many values for the heat of solution for KCl(aq) where the molality of the salt was close to a value of $0.12335 \text{ mol}\cdot\text{kg}^{-1}$ at 291.15, 298.15, 308.15, 313.15, 328.15, 343.15, and 358.15 K. This molality corresponds to the dilution ratio of 1/450. These data were used here with parametrization PI to determine the partial molar enthalpies of KCl at infinite dilution at the seven temperatures. The experimental heats were predicted using PI together with the value of $H_{m,2}^\infty$ that gives the best fit at each temperature. The errors are shown in Figure 4 as a function of the temperature. The exact molalities used in our calculations are provided by the original paper.⁴⁹ They are all, however, very close to $0.12335 \text{ mol}\cdot\text{kg}^{-1}$. The resulting values for $H_{m,2}^\infty$ are reported in Table 7. The error plot in Figure 4 verifies that the agreement between the measured and predicted heats of solution is very good throughout.

For determination of $H_{m,2}^\infty$ values at various temperatures, the apparent molar enthalpies given by Kilday²⁸ can also be used. In addition to wide heat-of-solution data reported in her study at 298.15 K (see Figure 1A), she also determined one ΔH_{app} value

Table 17. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Less Dilute Aqueous KCl Solutions at Temperatures from (298.15 to 313.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(25)^d$	$\Delta H_{\text{app}}(30)^d$	$\Delta H_{\text{app}}(35)^d$	$\Delta H_{\text{app}}(40)^d$
0.2	350	428	511	599
0.3	300	400	500	615
0.4	230	340	470	600
0.5	150	275	420	570
0.6	50	200	360	530
0.7	0	100	290	490
0.8	0 ^e	0	230	440
0.9	0 ^e	0	150	380
1.0	-50 ^e	0 ^e	80	330
1.2	-220 ^e	0 ^e	-70	220
1.4	-370 ^e	-100 ^e	-210	110
1.5	-440 ^e	-180 ^e	-290	60
1.6	-520 ^e	-230 ^e	-360	0
1.8	-660 ^e	-350 ^e	-500	-100
2.0	-800 ^e	-460 ^e	-630	-190
2.5	-1100 ^e	-700 ^e	-940	-400
3.0	-1400 ^e	-900 ^e	-1200	-550
4.0	-1900 ^e	-1200 ^e		-720
5.0	-2200 ^e	-1300 ^e		-690

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{\text{m},2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI if not otherwise stated. ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$. ^eParametrization PII was used.

Table 18. Recommended Values of Relative Apparent Molar Enthalpy (ΔH_{app})^a of Potassium Chloride (Symbol 2) in Less Dilute Aqueous KCl Solutions at Temperatures from (318.15 to 333.15) K as a Function of Molality m ^b

$(m/m^\circ)^c$	$\Delta H_{\text{app}}(45)^d$	$\Delta H_{\text{app}}(50)^d$	$\Delta H_{\text{app}}(55)^d$	$\Delta H_{\text{app}}(60)^d$
0.2	692	789	892	999
0.3	730	860	990	1130
0.4	740	890	1050	1210
0.5	740	910	1090	1280
0.6	720	910	1120	1330
0.7	690	910	1140	1380
0.8	660	900	1150	1420
0.9	630	890	1160	1460
1.0	590	880	1170	1490
1.2	520	850	1190	1560
1.4	460	820	1210	1630
1.5	420	810	1220	
1.6	390	800	1240	
1.8	330	790	1270	
2.0	280	780	1310	
2.5	180	790	1440	
3.0	130	860	1640	

^aDefined by equation $\Delta H_{\text{app}} = H_{\text{app},2} - H_{\text{m},2}^\infty$ and some partial molar enthalpies of the salt at infinite dilution are given in Table 7. ^bThe values have been calculated using parametrization PI. ^c $m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$. ^dUnit is $\text{J}\cdot\text{mol}^{-1}$ and the value is given at temperature T expressed in parentheses as $(T - 273.15)/\text{K}$.

at the molality of about $0.111 \text{ mol}\cdot\text{kg}^{-1}$ at the 13 temperatures starting from 296.58 K and extending up to 358.85 K, see Table 7. Using parametrization PI, we solved $H_{\text{m},2}^\infty$ from these values,

and the results are reported in this table. At temperatures very close to 296.65 K, a unified value is presented in Table 7. In the calculations of the results at various temperatures, only the PI parameters given in Table 4 were used. This means, for example, in the determination of $H_{\text{m},2}^\infty$ for 298.54 K, the PI parameters for 298.15 K in Table 4 were used. The determination of $H_{\text{m},2}^\infty$ at various temperatures, was also based here on the apparent molar enthalpies determined by Olofsson et al.⁵⁰ for the KCl solution where the molality of KCl was $0.123 \text{ mol}\cdot\text{kg}^{-1}$. This group reports the enthalpy values of this solution at 298.15, 313.15, 328.15, 333.15, and 360.15 K. We determined using parametrization PI from these enthalpies the $H_{\text{m},2}^\infty$ values that are presented in Table 7.

The agreement between the $H_{\text{m},2}^\infty$ values from different sources in Table S2 and Table 7 is quite good at 298.15 K but not at the higher temperatures. The largest discrepancy between the analogous values in Table 7 is observed at 343.15 K where the absolute difference is over $150 \text{ J}\cdot\text{mol}^{-1}$. This implies that only two digits in the limiting value are reliable. According to the present study, for example, the relative enthalpy values are known in dilute solutions to a much higher accuracy. Therefore, it is not reasonable to tabulate absolute enthalpies as recommended values but instead to tabulate those of the relative enthalpies.

The use of parametrization PI enables us to suggest a new calibration method for calorimetric heat measurements at 298.15 K and possibly also at other temperatures. For this purpose, Table 1 shows at 298.15 K the molar solution enthalpies and the amounts of water for the solutions where the dilution ratio is close to the calorimetric calibration value of 1/500 suggested by Kilday²⁸ based on Kilday's value for $H_{\text{m},2}^\infty$ ($=17241 \text{ J}\cdot\text{mol}^{-1}$). All of these solution enthalpies are, in our opinion, as reliable as the value of $17584 \text{ J}\cdot\text{mol}^{-1}$ recommended by Kilday for the dilution ratio of 1/500 (i.e., at molality $m = 0.11102 \text{ mol}\cdot\text{kg}^{-1}$).

Recommended Values for the Relative Apparent Molar Enthalpy and Relative Partial Molar Enthalpy of Salt in KCl Solutions from (273.15 to 373.15 K) and Those in Dilute NaCl Solutions at 373.15 K. On the basis of the abundant evidence provided by the test results given in refs 19 and 22 and here (see Figures 1–4 and Tables 6 and 7 in the text and Table S1 in the Supporting Information), the experimental data available in the literature for dilute KCl solutions from (273 to 333) K can often be predicted within experimental error using the new Hückel equations at least up to a molality of $1 \text{ mol}\cdot\text{kg}^{-1}$. In the upcoming Part 2 of this study, it will be shown that this conclusion applies also to the heat capacities in dilute KCl solutions. Completely traceable thermodynamic quantities can be obtained using parametrization PI at least up to $0.2 \text{ mol}\cdot\text{kg}^{-1}$ in the temperature range of (273 to 373) K. Recommended traceable activity coefficients and osmotic coefficients in KCl solutions up to 383 K have already been tabulated in ref 22. To supplement the tables with the calorimetric properties, we present here new values for the relative apparent and partial molar enthalpies (i.e., for ΔH_{app} and $\Delta H_{\text{m},2}$) in the dilute KCl solutions at rounded molalities on the basis of the used model. We have collected the values for apparent molar enthalpies (ΔH_{app}) in Tables 8, 9, 10, and 11 at the temperatures in ranges (273.15 to 298.15) K, (303.15 to 328.15) K, (333.15 to 353.15) K, and (358.15 to 373.15) K, respectively. We also report accordingly the corresponding partial molar enthalpies ($\Delta H_{\text{m},2}$) in Tables 12–15. For dilute NaCl solutions at 373.15 K, the values of ΔH_{app} and $\Delta H_{\text{m},2}$ are given in Tables 11 and 15,

respectively. For other temperatures for these NaCl solutions, the values are given in Figures 8 and 9 of ref 20. Without question, the values presented at these rounded molalities are the most reliable ones determined so far for NaCl and KCl solutions and no high-quality experimental data in the literature contradict these values.

We have also examined these enthalpies for more concentrated solutions than those considered in Tables 8–15. Up to 333.15 K and at least up to 1.0 mol·kg⁻¹, the relative apparent molar enthalpies are reported in Tables 16–18 on the basis of parametrization PI. The reported values for these less dilute solutions are not as accurate as those in Tables 8–11. For concentrated solutions above 1 mol·kg⁻¹, parametrization PII gives a better agreement than PI in the interpretation of the existing calorimetric data in the temperature range of (298 to 303) K. These ΔH_{app} values based on PII are reported in Table 17 for temperatures 298.15 and 303.15 K up a molality of 5 mol·kg⁻¹. At these two temperatures and in the molality range of about (0.7 to 1.2) mol·kg⁻¹, the ΔH_{app} values are close to zero and parametrizations PI and PII suggest slightly different values. At the moment, it is not possible to recommend convincingly either of those, and so the relative values at the rounded molalities have been set in Table 17 simply to be zero.

CONCLUSIONS

On the basis of the extensive testing against the existing high-quality enthalpy data presented in this communication, against heat-capacity data presented in a future communication (Part 2 of this study), and against the other thermodynamic data presented in our previous studies,^{19,20,22} we conclude that the experimental data for dilute KCl solutions can often be predicted within experimental error up to 1.0 mol·kg⁻¹ in the temperature range of (273 to 373) K with a simple reparametrization of the Hückel equation. Completely traceable thermodynamic quantities can be obtained using the new Hückel parametrization at least up to 0.2 mol·kg⁻¹ in all of these temperatures. These main results for KCl solutions are analogous to those obtained in refs 20–22 for NaCl solutions. In the present part (Part 1) of the calorimetric KCl study, new values of the relative apparent and partial molar enthalpies, that is, of ΔH_{app} and $\Delta H_{\text{m},2}$ for which 2 refers to the solute, have been tabulated for dilute solutions on the basis of our simple model. The corresponding values for the activity coefficient of KCl and osmotic coefficient of water in KCl solutions have been tabulated in ref 22. In the second part (Part 2) of this study, we will give in the near future, accordingly, the values for the relative apparent and partial molar heat capacities, that is, for ΔC_{app} and $\Delta C_{\text{m},2}$ in these solutions. The tabulated values are congruent with all the available high-quality experimental data, and represent the most accurate values determined for this system up to date.

For molalities larger than 1 mol·kg⁻¹ in the temperature range from (298 to 303) K, a previously suggested alternative parametrization yields better agreement with experiments than the parametrization that resulted to completely traceable values of these thermodynamic quantities. Concurrently, this alternative parametrization was employed in the prediction of enthalpy values of KCl solutions at these higher molalities in the tables for 298.15 and 303.15 K. Even though this parametrization lacks traceability and the values it predicts are generally less reliable than the ones recommended for more dilute solutions, they are still useful for applications because the existing experimental data are often well reproduced.

The dissolution of crystalline KCl into water has been used for many years an important reference reaction for endothermic solution calorimetry. In 1980, the NBS published a paper²⁸ where Kilday recommends that the enthalpy of solution of the reference material of SRM 1655 of crystalline KCl at 298.15 K is (17584 ± 17) J for a solution that contains an amount of 1 mol of KCl and that of 500 mol of water. Table 1 in the present study shows alternative suggestions for dilution ratios of this standard enthalpy at 298.15 K. In this table, we give the molar solution enthalpies and the amounts of water for the solutions where the amount of KCl is 1 mol and the dilution ratio is close to the calorimetric calibration value of 1/500 suggested by Kilday.²⁸ These enthalpies have been calculated using our traceable parametrization (PI) with the Kilday's value for $H_{\text{m},2}^{\infty}$ (=17241 J·mol⁻¹). Each of these solution enthalpies is, according to our understanding, as reliable as the value recommended by Kilday for the dilution ratio of 1/500. The values in Table 3 (as well as the corresponding values calculated using PI for other reasonable dilution ratios than those shown in the table) apply probably to the use as the reliable calorimetric standards at 298.15 K.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.9b00031.

Heat-of-dilution data existing in the literature for KCl solutions at various temperatures and the results obtained with these data using the thermodynamic parametrization considered in the present study; partial molar enthalpies of KCl at infinite dilution determined from the existing heats of solution (PDF)

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Notes

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