

Freezing Point Depressions of Dilute Potassium Chloride Solutions

Jaakko Ilmari Partanen

Laboratory of Physical Chemistry, Department of Chemical Technology, Lappeenranta University of Technology, P. O. Box 20, SF-53851 Lappeenranta, Finland

Partanen, J. I., 1990. Freezing Point Depressions of Dilute Potassium Chloride Solutions. – *Acta Chem. Scand.* 44: 317–320.

Freezing point depressions of dilute KCl solutions were computed by means of the best activity coefficient equations. In the calculations the equations of Hückel, Hamer and Pitzer were used for the activity coefficients. All these equations have been determined from experimental data measured at the temperature of 298.15 K. It is confirmed in this paper that with any one of these three equations, the existing freezing point data available in the literature can be predicted within experimental error. The freezing point depressions tabulated in this paper at rounded molalities can be highly recommended, because the activity coefficient equations used in the evaluation also explain almost all electrochemical data at 298.15 K.

The determination of freezing point depressions of aqueous solutions has been highly developed since Roloff¹ in 1895 as the first investigator abandoned the original super-cooling method of Raoult.² Roloff determined by analysis the composition of solutions in equilibrium with a large amount of ice which had been frozen out of the solutions. The use of thermocouples instead of mercury thermometers by Hausrath³ and Osaka⁴ in 1902 is likewise an important improvement, especially in the cryoscopy of dilute electrolyte solutions. The difference between the freezing point of pure water and of a dilute aqueous solution can be measured using thermocouples with an uncertainty not greater than 0.0001 K. The experimental error with mercury thermometers has seldom been smaller than 0.001 K.

The most significant innovations in the determination of the freezing points of dilute solutions were made around the turn of the last century. Therefore old measurements contain reliable data of the cryoscopy of different substances. For example, in potassium chloride solutions the freezing point depressions reported by Jahn⁵ appear to be entirely reliable, although this set was measured as early as in 1904. After the first paper of Jahn several accurate studies of the cryoscopy of dilute KCl solutions have been published.^{6–12} In addition, there are papers containing cryoscopic results where at least some points have been determined in dilute KCl solutions.^{13–19} According to the literature cited above, a great deal of research has been concentrated on the cryoscopy of KCl solutions. For this reason, KCl solutions were chosen for the calculations of the present paper.

It is well known (see, for example, Spencer²⁰) that the activity coefficients of KCl (or of many other corresponding electrolytes) at 298.15 K can be calculated from the freezing point results in the case of very dilute solutions

(i.e. at molalities less than about 0.01 mol kg⁻¹) without making any temperature corrections. In less dilute solutions these corrections become more important, but they can be accurately made only when there are enough calorimetric data available about the solutions. At present the activity coefficients determined from the freezing point measurements cannot be changed with appropriate calorimetric data to correspond to the temperature of 298.15 K without losing some of the accuracy.

The most accurate activity coefficients of dilute KCl solutions can be obtained without question from the results of electromotive force measurements by galvanic cells with transference. At 298.15 K the most reliable study with this kind of cell is probably the one by Hornibrook *et al.*²¹ The author²² has shown that the activity coefficients obtained from that study can be predicted within experimental error by a two-parameter equation of the Hückel type. Moreover, the author has shown that the freezing point depressions of several of the abovementioned investigations can be predicted within experimental error with the Hückel equation determined from the EMF measurements of Hornibrook *et al.* No corrections due to differences in the temperatures were needed in those calculations.

The freezing point depressions of the dilute KCl solutions determined by the different authors introduced above do not agree with each other as well as desired (see for example Randall and White²³). Therefore some obscurity still exists as to the exact freezing point lowerings of dilute KCl solutions expressed as accurately as it is possible to verify experimentally. In this paper these values are presented at several rounded molalities. The freezing point depressions of this paper are based on the activity coefficient equations determined primarily for the temperature of 298.15 K. In addition to the Hückel equation mentioned

above, the equations of Pitzer²⁴ and of Hamer and Wu²⁵ are also used in the calculation of the freezing point depressions. Because all these three equations predict the experimental cryoscopic data equally well, and so that the errors appear to be random, it is very likely that the correct freezing point depressions for dilute KCl solutions can be calculated with these equations.

Results

The following dependence can be derived for the freezing point depression (ΔT_f) of a solution of a uni-univalent electrolyte on the molality (m) of the electrolyte.

$$\Delta T_f = T_f^* - T_f = \frac{2 RT_f^* M_1 (m + I)}{2RM_1 (m + I) + \Delta H_{\text{fus}}/T_f^*} + \frac{\Delta C_p \Delta T_f + \Delta C_p (T_f^* - \Delta T_f) \ln[(T_f^* - \Delta T_f)/T_f^*]}{2RM_1 (m + I) + \Delta H_{\text{fus}}/T_f^*} \quad (1)$$

where

$$I = \int_0^{\ln \gamma_{\pm}} m \, d \ln \gamma_{\pm} \quad (2)$$

In eqn. (1) T_f^* is the freezing point of pure water (i.e. 273.15 K) and T_f that of the solution, ΔH_{fus} is the molar enthalpy of fusion of water at T_f^* (6008 J mol⁻¹), ΔC_p is the difference between the molar heat capacities of water as liquid and as solid at the pressure of 101.3 kPa (this difference is 38.07 J K⁻¹ mol⁻¹ and it is assumed to be independent of the temperature), M_1 is the molar mass of water (= 0.018015 kg mol⁻¹) and R is the gas constant (= 8.31451 J K⁻¹ mol⁻¹). In eqn. (2), γ_{\pm} is the mean activity coefficient of the electrolyte on the molality scale, and it can be calculated from the molality with any of the activity coefficient equations studied in this paper. When the values of ΔT_f are computed from eqn. (1), iterative calculations are needed because the second term on the right-hand side contains this quantity.

In the beginning of the calculations of this paper the experimental ΔT_f values of dilute KCl solutions will be compared with the values obtained from eqn. (1). Three sorts of values of ΔT_f are calculated for these comparisons. These differ from each other in the formula used for the activity coefficients in the calculations. As mentioned above, these formulae have been determined on the basis of the experimental data measured at 298 K. Of these equations the simplest one is the Hückel equation, and it takes the form of eqn. (3) for uni-univalent electrolytes, in which $m^\circ = 1 \text{ mol kg}^{-1}$ and α and β are the constants of Debye and Hückel [at 298.15 K $\alpha = 1.1762 \text{ (kg mol}^{-1})^{1/2}$

$$\ln \gamma_{\pm} = -\frac{\alpha m^{1/2}}{1 + \beta \alpha^* m^{1/2}} - \ln(1 + 2M_1 m) + b_1 m/m^\circ \quad (3)$$

and $\beta = 3.287 \text{ (kg mol}^{-1})^{1/2} \text{ nm}^{-1}$] and where for KCl solutions the author²² has determined the following values for the other parameters: $a^* = 0.37 \text{ nm}$ and $b_1 = 0.097$.

The second equation used in the calculations has been presented by Hamer and Wu.²⁵ In the case of KCl solutions it can be expressed in the form of eqn. (4) where $A =$

$$\lg \gamma_{\pm} = {}^{10}\log \gamma_{\pm} = -\frac{Am^{1/2}}{1 + Bm^{1/2}} + C(m/m^\circ) + D(m/m^\circ)^2 + E(m/m^\circ)^3 \quad (4)$$

0.5108 (kg mol⁻¹)^{1/2} (= $\alpha/\ln 10$), $B = 1.295 \text{ (kg mol}^{-1})^{1/2}$, $C = 0.00007$, $D = 0.003599$ and $E = -0.00019540$. The third equation has been presented by Pitzer.²⁴ It has the form of eqn. (5) for uni-univalent electrolytes.

$$\ln \gamma_{\pm} = f^y + B^y(m/m^\circ) + C^y(m/m^\circ)^2 \quad (5)$$

where

$$f^y = -A\Phi \left(\frac{m^{1/2}}{1 + bm^{1/2}} + \frac{2}{b} \ln(1 + bm^{1/2}) \right) \quad (6)$$

$$B^y = 2\beta^0 + \frac{2\beta^1}{\alpha^2 m} \left[1 - e^{-\alpha m^{1/2}} \left(1 + \alpha m^{1/2} - \frac{\alpha^2}{2} m \right) \right] \quad (7)$$

and

$$C^y = (3/2) C^\psi \quad (8)$$

The parameters A_ψ , b and α in these equations do not depend on the electrolyte, and Pitzer has presented the following values for them: $A_\psi = 0.392 \text{ (kg mol}^{-1})^{1/2}$, $b = 1.2 \text{ (kg mol}^{-1})^{1/2}$ and $\alpha = 2.0 \text{ (kg mol}^{-1})^{1/2}$. Parameters β^0 , β^1 and C^ψ depend on the electrolyte, and Pitzer and Mayorga²⁶ have tabulated the following values of them for KCl: $\beta^0 = 0.04835$, $\beta^1 = 0.2122$, and $C^\psi = -0.00084$.

The results of the comparison of the theoretical freezing point depressions with the experimental values are shown in Figs. 1 and 2. The theoretical depressions have been consequently calculated from eqn. (1) by means of eqns. (3), (4) or (5). In both figures the differences between the experimental and theoretical values are presented as a function of the molality. This difference (or error) $\varepsilon(\Delta T_f)$ is therefore defined by eqn. (9).

$$\varepsilon(\Delta T_f) = \Delta T_f(\text{observed}) - \Delta T_f(\text{predicted}) \quad (9)$$

The results of the dilute solutions are included in Fig. 1. In the graphs of the figure the errors of the predicted values of the different activity coefficient models are denoted by different symbols.

The results for stronger solutions are shown in Fig. 2.

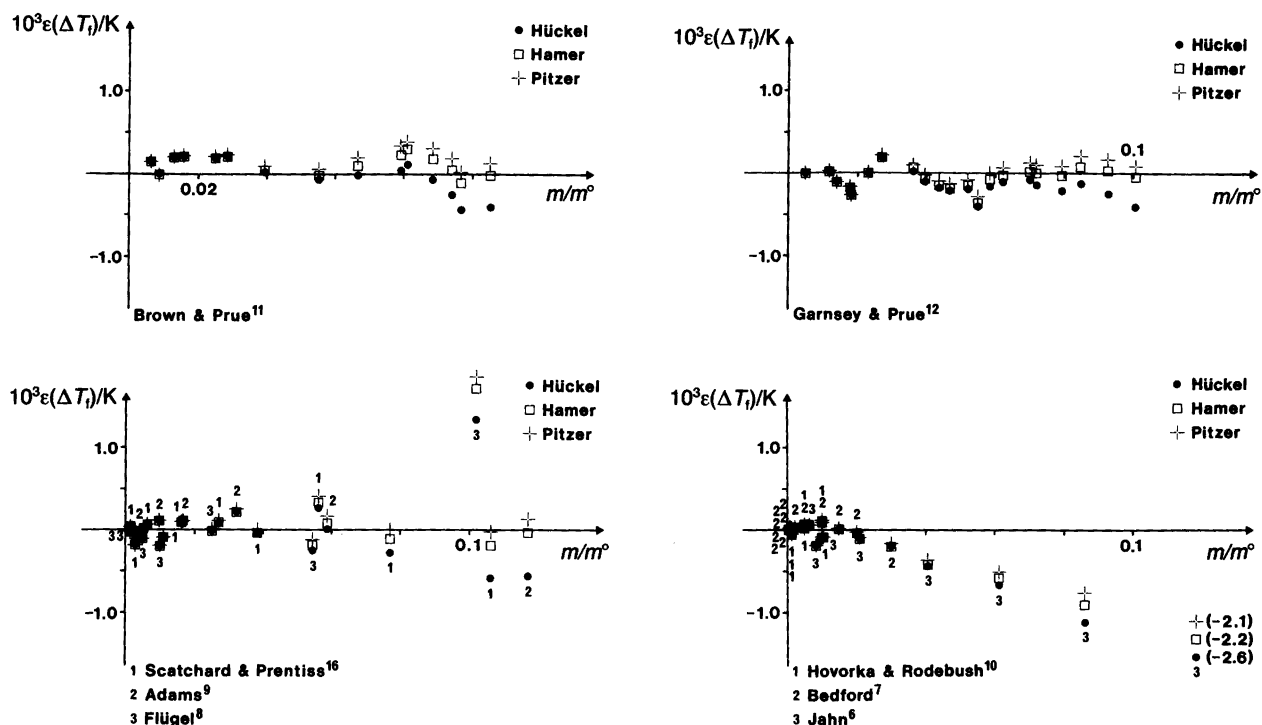


Fig. 1. Differences between the measured and predicted freezing point depressions as a function of the molality in the sets containing dilute KCl solutions. The errors of the different activity coefficient equations are denoted by the symbols shown in the graphs. Each graph contains the results of the measured sets noted in the graphs. In the fourth graph a point in the Jahn's set (3) is outside the ranges of the scale of $\epsilon(\Delta T_f)$ axis; the errors of this point are denoted numerically using the same scale as on the $\epsilon(\Delta T_f)$ axis.

The predicted values obtained with either Hamer's or Pitzer's equation are identical within experimental error and so the errors of any set in the figure can be described by one symbol. The results of the Hückel equation are not included in Fig. 2, because the upper limit of applicability of that equation is about 0.1 mol kg^{-1} , and so it is not interesting to use this equation in higher molalities than this value.

Discussion

It can be seen in Fig. 1 that almost all experimental data can be explained with the activity coefficient eqns. (3), (4) or (5) within 0.0005 K . Only the three points of the most concentrated solutions of Jahn's newer set and the strongest point of Flügel's set lay outside these ranges. Usually the freezing point depressions in dilute electrolyte solutions are not expressed in the literature more accurately than with four digits. So with any one of the three activity coefficient equations almost all observed ΔT_f values can be predicted so accurately that the last significant digit in the predicted value is not more erroneous than by five units. At molalities of about 0.1 mol kg^{-1} the Hückel equation predicts values that are slightly but systematically too high for the freezing point depressions; the error is approximately -0.0004 K .

From the results of the stronger solutions it can be first

concluded that the measured values of ΔT_f are not known as accurately as the freezing point depressions in the dilute solutions. In most of the sets of the experimental data in Fig. 2 the precision of the freezing point determination has not been much better than 0.001 K . Probably only the sets of Scatchard and Prentiss¹⁶ and of Damköhler and Weinzierl¹⁷ are exceptions, but unfortunately the results of these sets do not agree well with each other. According to Fig. 2 it can be seen that the values of ΔT_f for KCl solutions can

Table 1. Recommended freezing point depressions of KCl solutions at several rounded molalities.

m/m°	$\Delta T_f/K$	m/m°	$\Delta T_f/K$
0.005	0.0181 ₅	0.07	0.2432
0.01	0.0360	0.075	0.2601
0.015	0.08	0.2771	0.0536 ₅
0.02	0.0712	0.085	0.2940
0.025	0.0886 ₅	0.09	0.3109
0.03	0.1060	0.095	0.3278
0.035	0.1233	0.10	0.3447
0.04	0.1406	0.11	0.378 ₃
0.045	0.1578	0.12	0.411 ₉
0.05	0.1749	0.13	0.445 ₅
0.055	0.1921	0.14	0.479 ₀
0.06	0.2092	0.15	0.512 ₅
0.065	0.2262		

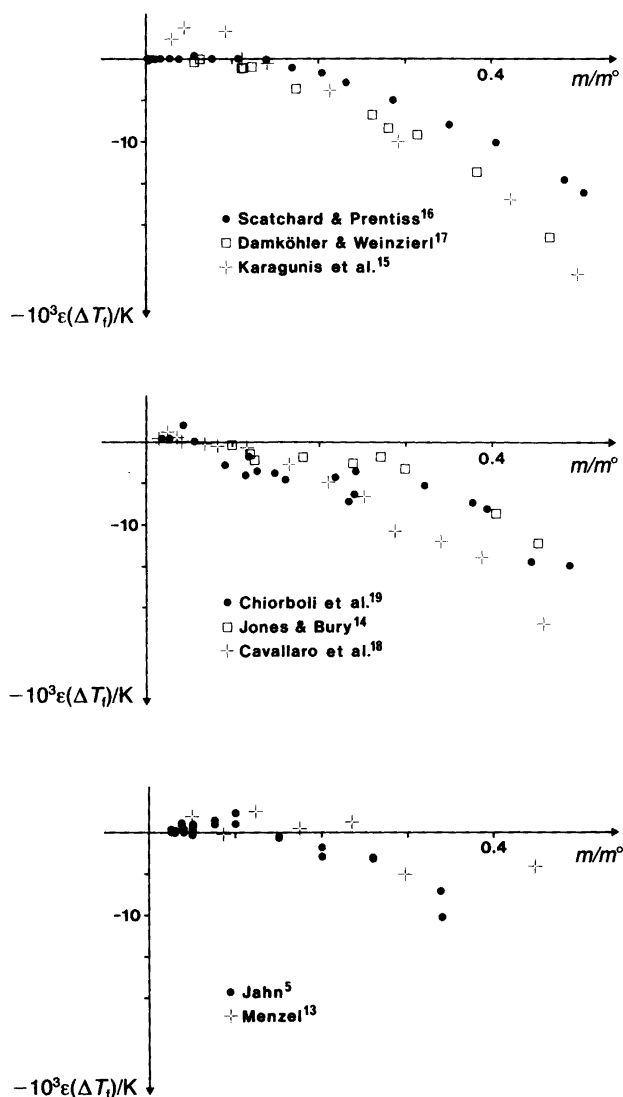


Fig. 2. Differences between the measured and predicted freezing point depressions as a function of the molality in the sets containing less dilute KCl solutions. The predicted ΔT_f values have been calculated by means of Hamer's (or Pitzer's) equation for the activity coefficients (see text). Each graph contains the results of the measured sets denoted by the different symbols in the graphs.

be plausibly estimated within 0.001 K up to the molality of 0.15 mol kg⁻¹ using either Pitzer's or Hamer's equation.

According to the calculations presented above, the experimental freezing point depressions can be evaluated within experimental error in dilute solutions of KCl with the best activity coefficient equations available for the temperature of 298 K. Therefore the values of ΔT_f for any dilute molality of KCl can be reliably calculated from eqn. (1) by means of eqns. (3), (4) or (5). In Table 1 these values are presented at several rounded molalities.

The ΔT_f values of Table 1 have been calculated for the molalities below 0.07 mol kg⁻¹ using the Hückel equation [eqn. (3)]. The predicted values of ΔT_f which were calculated using the other two activity coefficient equations differ from the values of Table 1 at the most by two units in the last digit. Above the molality of 0.07 mol kg⁻¹ the freezing point depressions of Table 1 have been calculated by using Hamer and Wu's equation [eqn. (4)] for the activity coefficients. The results obtained with Pitzer's equation [eqn. (5)] differ from the values of Table 1 by no more than two units in the last digit.

The freezing point depressions of Table 1 can be highly recommended because they have been based on the activity coefficient equations which explain, in addition to the experimental values of ΔT_f , almost all existing electrochemical data measured at 298.15 K. (See for example Ref. 22.)

References

1. Roloff, M. *Z. Phys. Chem.* 18 (1895) 572.
2. Raoult, F. M. *Ann. Chim. Phys.* 20 (1880) 217.
3. Hausrath, H. *Ann. Phys.* 9 (1902) 522.
4. Osaka, Y. *Z. Phys. Chem.* 41 (1902) 560.
5. Jahn, H. *Z. Phys. Chem.* 50 (1904) 129.
6. Jahn, H. *Z. Phys. Chem.* 59 (1907) 31.
7. Bedford, T. G. *Proc. R. Soc. London, Ser. A* 83 (1910) 454.
8. Flügel, F. *Z. Phys. Chem.* 79 (1912) 577.
9. Adams, L. H. *J. Am. Chem. Soc.* 37 (1915) 481.
10. Hovorka, F. and Rodebush, W. H. *J. Am. Chem. Soc.* 47 (1925) 1614.
11. Brown, P. G. M. and Prue, J. E. *Proc. R. Soc. London, Ser. A* 232 (1955) 320.
12. Garnsey, R. and Prue, J. E. *Trans. Faraday Soc.* 62 (1966) 1265.
13. Menzel, H. *Z. Elektrochem.* 33 (1927) 63.
14. Jones, E. R. and Bury, C. R. *Philos. Mag.* 3 (1927) 1032.
15. Karagunis, G., Hawkinson, A. and Damköhler, G. *Z. Phys. Chem.* 151 (1930) 433.
16. Scatchard, G. and Prentiss, S. S. *J. Am. Chem. Soc.* 55 (1933) 4355.
17. Damköhler, G. and Weinzierl, J. *Z. Phys. Chem.* 167 (1934) 71.
18. Cavallaro, L., Indelli, A. and Pancaldi, G. *Ric. Sci.* 23 (1953) 2237.
19. Chiorboli, P., Momicchioli, F. and Grandi, G. *Boll. Sci. Fac. Chim. Ind. Bologna* 24 (1966) 133.
20. Spencer, H. M. *J. Am. Chem. Soc.* 54 (1932) 4490.
21. Hornibrook, W. J., Janz, G. J. and Gordon, A. R. *J. Am. Chem. Soc.* 64 (1942) 513.
22. Partanen, J. I. *Acta Polytech. Scand.* 188 (1989) 1.
23. Randall, M. and McLaren White, A. *J. Am. Chem. Soc.* 48 (1926) 2514.
24. Pitzer, K. A. *J. Phys. Chem.* 77 (1973) 268.
25. Hamer, W. J. and Wu, Y.-C. *J. Phys. Chem. Ref. Data* 1 (1972) 1047.
26. Pitzer, K. S. and Mayorga, G. *J. Phys. Chem.* 77 (1973) 2300.

Received August 14, 1989.