# Influence of Temperature on Conversion of Values of Thermodynamic Functions for Acidity Constants from Molal to Molar Scale

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**The corrections to be added to the molal values of thermodynamic functions for acidity constants in aqueous solution to convert them to molar values have been calculated from values of the density of water and are tabulated for temperatures between 0° and 60° C.**

THE RELATION between the thermodynamic acidity constants on the molar, $K_c$, and molal, $K_m$, scales is (*1*, *4*)

$$K_c = K_m\rho,\ \mathrm{p}K_c = \mathrm{p}K_m - \log \rho \qquad (1)$$

where $\rho$ is the density of the solvent. The corrections to be added to the molal values of the thermodynamic functions for acidity constants to convert them to molar values can be calculated from expressions 2 to 5 (*1*).

$$\Delta\Delta G^\circ \ = \ \Delta G_c^\circ - \Delta G_m^\circ = -\mathbf{R}T \ln \rho \qquad (2)$$

$$\Delta\Delta H^\circ \ = \ \Delta H_c^\circ - \Delta H_m^\circ = \mathbf{R}T^2\, \partial \ln \rho/\partial T \qquad (3)$$

$$\Delta\Delta S^\circ \ = \ \Delta S_c^\circ - \Delta S_m^\circ = \mathbf{R}\ (\ln \rho + T\, \partial \ln \rho/\partial T) \qquad (4)$$

$$\Delta\Delta C_p^\circ \ = \ \Delta C_{p,c}^\circ - \Delta C_{p,m}^\circ = \ \mathbf{R}T\ (2\ \partial \ln \rho/\partial T + T\ \partial^2 \ln \rho/\partial T^2) \qquad (5)$$

Ashby *et al.* (*1*) have published a table of corrections for aqueous solutions at temperatures between 0° and 60° C. that were calculated by the aid of an equation of the form

$$\log K = -A/T + D - CT \qquad (6)$$

Unfortunately, the numerical values in their table are in error; the signs of the $\Delta\Delta G^\circ$ values and the values of $\Delta\Delta C_p^\circ$ are incorrect. For example, they give the value −8.8 cal. deg.$^{-1}$ mole$^{-1}$ for $\Delta\Delta C_p^\circ$ at 25° C., whereas the correct value is −2.0 cal. deg.$^{-1}$ mole$^{-1}$. Further, Equation 6 assumes a direct proportionality between $\Delta\Delta C_p^\circ$ and $T$ which does not seem to be true.

In Table I, corrections are listed for temperatures between 0° and 60° C., which is the temperature interval where most acidity constants are determined. They were calculated from smoothed values of water density (*3*, *5*) by the method of Clarke and Glew (*2*), employing an equation with seven parameters. The equation is actually of the form

$$\ln \rho = A + B/T + C \ln T + DT + ET^2 + FT^3 + GT^4 \qquad (7)$$

This number of parameters gives the best fit to the data, as deduced from the calculated variances. The 7th parameter is significant with a probability of 99.5% according to Student's *t*-test, as applied to the coefficients of the orthogonalized function set. The parameters $\Delta\Delta G^\circ$, $\Delta\Delta H^\circ$, $\Delta\Delta C_p^\circ$, $\partial\Delta\Delta C_p^\circ/\partial T$, $\partial^2\Delta\Delta C_p^\circ/\partial T^2$, $\partial^3\Delta\Delta C_p^\circ/\partial T^3$, and $\partial^4\Delta\Delta C_p^\circ/\partial T^4$ have the values 1.7354 ± 0.00018, −45.408 ± 0.0076, −2.0056 ± 0.0012, (6.5 ± 0.24) × $10^{-3}$, (−7.5 ± 0.41) × $10^{-4}$, (6.1 ± 0.57) × $10^{-5}$, and (−4.9 ± 1.1) × $10^{-6}$

Table I. Corrections to be Added to Molal Values of the Thermodynamic Functions for Thermodynamic Acidity Constants in Aqueous Solution to Convert Them to Molar Values

| Temp., ° C. | $\rho$, G. Ml.$^{-1}$ | $\Delta\Delta G^\circ$, Cal. Mole$^{-1}$ | $\Delta\Delta H^\circ$, Cal. Mole$^{-1}$ | $\Delta\Delta C_p^\circ$, Cal. Deg.$^{-1}$ Mole$^{-1}$ | $\Delta\Delta S^\circ$, Cal. Deg.$^{-1}$ Mole$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 0.9998676 | +0.0719 | +10.11 ± 0.047 | −2.640 ± 0.0166 | +0.03673 ± 0.00017 |
| 5 | 0.9999919 | 0.0045 | −2.46 ± 0.011 | −2.399 ± 0.0047 | −0.00885 ± 0.00004 |
| 10 | 0.9997281 | 0.1530 | −14.01 ± 0.012 | −2.232 ± 0.0018 | −0.05002 ± 0.00004 |
| 15 | 0.9991286 | 0.4992 | −24.87 ± 0.007 | −2.120 ± 0.0020 | −0.08805 ± 0.00002 |
| 20 | 0.9982336 | 1.0299 | −35.28 ± 0.008 | −2.049 ± 0.0012 | −0.12386 ± 0.00003 |
| 25 | 0.9970751 | 1.7354 | −45.41 ± 0.008 | −2.006 ± 0.0012 | −0.15811 ± 0.00003 |
| 30 | 0.9956783 | 2.6091 | −55.37 ± 0.007 | −1.981 ± 0.0015 | −0.19124 ± 0.00002 |
| 35 | 0.9940635 | 3.6461 | −65.24 ± 0.008 | −1.970 ± 0.0011 | −0.22354 ± 0.00003 |
| 40 | 0.9922473 | 4.8433 | −75.08 ± 0.008 | −1.968 ± 0.0015 | −0.25522 ± 0.00003 |
| 45 | 0.990244 | 6.1984 | −84.94 ± 0.009 | −1.977 ± 0.0023 | −0.28645 ± 0.00003 |
| 50 | 0.988070 | 7.7072 | −94.87 ± 0.014 | −1.998 ± 0.0019 | −0.31742 ± 0.00004 |
| 55 | 0.985731 | 9.3720 | −104.95 ± 0.013 | −2.040 ± 0.0061 | −0.34838 ± 0.00004 |
| 60 | 0.983237 | 11.1920 | −115.31 ± 0.061 | −2.110 ± 0.0198 | −0.37971 ± 0.00018 |

cal. per mole, respectively, at 25° C. The calculated values of the corrections are practically independent of the temperature range (0° to 60°, 0° to 42°, 0° to 100°, or 20° to 90° C.), the temperature interval (5° or 1°), and the equation used [Equation 6, the equation of Clarke and Glew (*2*), or the interpolation function for the density of water (*5*). The calculations were performed on an IBM 1130 computer at the Computing Center of the University of Turku.

The presented values can be used also when the temperature-dependence of kinetic data for reactions in which solvent participates is considered. The experimental first-order rate coefficient $k_1$ and the true $(n + 1)$th order rate coefficient $k_{n+1}$ for such a reaction in aqueous solution are related as follows.

$$k_1 = k_{n+1}[H_2O]^n = k_{n+1}(1000\rho/M_{H_2O})^n \qquad (8)$$

$$\ln k_{n+1} = \ln k_1 - n \ln (1000/M_{H_2O}) - n \ln \rho \qquad (9)$$

Consequently, the thermodynamic activation data contain terms closely related to those in Equations 2 to 5.

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