

## **Thermodynamics of the Four Micro-Reactions for 4-Aminobenzoic Acid from 25 to 125 °C**

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There are two proton ionizable groups on 4-aminobenzoic acid, the carboxylate group and the amino group. The numerical values for the equilibrium constants for protonation of these two groups are very close. This gives rise to four equilibrium constants: two for the carboxylate group (one when amino group is protonated and one when the amino group is not protonated) and two for the amino group (one when the carboxylate group is protonated and one when the carboxylate is not protonated). Potentiometric titrations yield values for two macro-constants, which are a combination of the four micro-constants. Similarly, titration calorimetry yields two macro-values for  $\Delta H$  which are a combination of the four micro-values of  $\Delta H$ . NMR measurements allow the calculation of the micro-constants. The combination of NMR, potentiometric, and calorimetric measurements has allowed us to calculate the  $\log K$ ,  $\Delta H$ , and  $\Delta S$  values for the four micro-reactions from 25 to 125 °C. The values of the macro- and mirco-  $\log K$ ,  $\Delta H$ , and  $\Delta S$  and the mathematical relationships among the values are reported. The trends of the thermodynamic quantities with temperature for the micro-reactions follow the trends generally observed in ionic reactions, while those for the macroscopic reactions do not. Hence, the trends with temperature of the thermodynamic quantities that are measured using potentiometry or calorimetry (macro-values) cannot be explained without using knowledge of the micro-reactions.