The "Correct" Value of ΔH_{dis} for Acetic Acid

After performing the exercise in which this quantity is determined calorimetrically, some students may be interested in whether or not the value they have determined agrees with the "accepted" value for this interesting thermodynamic quantity.

The answer is far from simple. A thermodynamic study of the dissociation of acetic acid in the range from 0 °C to 60 °C was conducted and published in the 1930's (Harned & Ehlers *J. Am. Chem. Soc.*, 1933, *55* (2), pp 652–656). The acid dissociation constant of acetic acid was measured electrochemically over the above temperature range. ΔH_{dis} was determined through the thermodynamic relationship

$$d \ln K / dT = \Delta H / RT^2$$

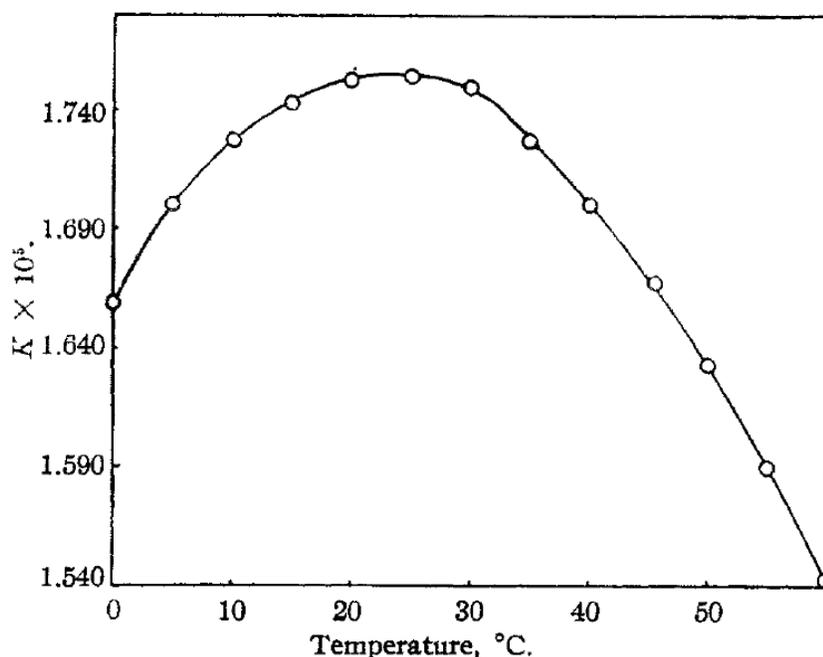Their graphical result for the temperature dependence of the dissociation constant, K, is reproduced below.

Fig. 1.—The dissociation constant of acetic acid as a function of the temperature.

K clearly experiences a maximum at ~23 $^{\circ}$C. Consequently, ΔH_{dis} is 0 at that temperature, positive at temperatures below and negative at temperatures above ~23 $^{\circ}$C.

They report that the values of ΔH_{dis} fit the following dependence on the absolute temperature:

$$\Delta H_{dis} = 6871.0 - 12.9436\ T - 0.035161\ T^2$$

While the paper does not specify units, it is assumed that their results are in cal/mol which was the common thermochemical convention at the time. In terms of SI units (kJ/mol) and converting from Kelvins to Centigrade degrees, we can re-write their equation as:

$$\Delta H_{dis} = 2.9793 - 0.1345\ T - 0.0001471\ T^2 \quad \text{kJ/mol, T in } ^{\circ}\text{C}$$

The enthalpy of dissociation changes sign just in the range of temperatures characteristic of room temperature. It is small (3.0 kJ /mol at 0 $^{\circ}$C and -3.3 kJ/mol at 50 $^{\circ}$C) near those temperatures.   This suggests that the results of this exercise – both with respect to magnitude and sign - can depend on small environmental variations in the laboratory.

An interesting secondary question is what chemical conclusions follow from the very small value the enthalpy of dissociation.   We might expect based on the enthalpy change alone that acetic acid would dissociate extensively.   But it is a weak acid (pK_a = 4.75 at 298 K).   Since ΔG = - RT ln K, we can estimate the free energy of ionization to be about - 27 kJ/mol.

The Free Energy of the reaction provides a clue ($\Delta G = \Delta H - T\ \Delta S$). ΔH is near 0 so bond making and breaking must not dominate the energetics of the process. The principal contribution to ΔG must be from the entropy term.   At 298 K, we can estimate the ΔS_{dis} to be about + 90 J/mol.   This large positive value for the entropy change suggest that the ionization process has a large impact on the structure of the solvent, water.

Ionization of substances in polar solvents like water is not a simple process. While we write a simple chemical equation for the process, it is much more complex at the molecular level.