

Freezing-Point Depression

The experiment involves two substances: a strong acid (HCl) and a weak acid (monochloroacetic). The goal of the measurements on the first is the determination of the practical osmotic coefficient ϕ , the solvent activity a_A , and the solvent activity coefficient γ_A . The goal of the latter is the determination of the acid dissociation constant. In both cases the measured quantities are the freezing point T_f and the molality of acid m_B . T_f is measured directly with a thermistor, except that the raw data must be corrected in accord with calibration data. The acid molality is determined by titrating known masses of solution (meaning it is necessary to measure the mass of solution extracted for each titration analysis). The processing of the data in the two cases, however, proceeds in different directions.

Strong Acid.

Strong acids are fully dissociated into ions in solution, resulting in activities and activity coefficients that are far from the ideal values. This means that strong acids will not follow very closely the simple expression given in eq 2 in the writeup. Accordingly, we must analyze the data using the more comprehensive approach of eqns 3-9. In particular:

- (1) ϕ is determined from T_f (after correction) and m_B using eq 7. (k_f and ΔH_{fus} are known).
- (2) The solvent activity a_A is then calculated using eq 6. (Again, all other quantities are known.)
- (3) Alternatively, a_A can be determined directly from eq 3 (with T_f^* and ΔH_{fus} known); then ϕ can be obtained from eq 6 (with γ_A known).
- (4) The mole fraction x_A of solvent is calculated using eq 5. n_B and n_A can be computed from the measured molalities m_B , using the definition of molality.
- (5) Finally γ_A is calculated using eq 4.

The error propagation computations start with the uncertainties in T_f (from your fit of the T_f vs. time data, along with consideration of uncertainties related to your calibration data), and in m_B (which you can estimate from the statistics of your triplicate standardization of your NaOH solution). The error in ϕ is readily computed using the concept of relative error propagation explored in Problem Set 2. In estimating the error in a_A , note that in eq 6 $\ln a_A$ is proportional to the product of ϕ and m_B , which is in turn just proportional to T_f . Thus the relative error in $\ln a_A$ is the same as that in T_f . This can also be seen clearly in eq 3. Use the error propagation formula to obtain the error in y ($= e^z$) from the error in $z = \ln y$, to complete the calculation.

For these dilute solutions, you should be able to show that the uncertainty in x_A is very much smaller than that in a_A . [It is easier to propagate the error in $1/x_A$; then note that the relative error in x_A is the same as in its reciprocal.] Thus the error in γ_A is dominated by that in a_A . Or in other words, since $x_A \ll 1$, the error in γ_A is very nearly the same as that in a_A .

Weak Acid.

The goal of the weak acid measurements is determination of K_a° . Here we use the approximate relation of eq 2 (with $\gamma = 1$) to obtain the apparent molality m' . The actual molality m (the same as m_B for the strong acid) is again obtained by titration. m and m' yield an estimate of K_m for each analyzed solution. These estimates are extrapolated to zero molality via eq 14 to obtain K_a° . This extrapolation also corrects for the approximate nature of eq 2.

The error propagation calculations outlined on p. 64 of the writeup are not exact but should be more than adequate. They are based on the recognition that the error in K_m (eq 12) is dominated by the uncertainty in ϕ ; and the error in ϕ is the same as that in $r = m'/m$ (defined on p 62). [Note that ϕ is typically a small number, around 0.1.]

