Experiment 2

The Change of Solubility with Temperature

Purpose :

The determination of solubility and the calculation of the heat of solution at saturation are illustrated in this experiment.

Principle :

Since the solubility of a solid, i.e. the concentration in a saturated solution, is a special case of the equilibrium constant. The **van't Hoff** equation is applicable.

$$\frac{d \ln S}{dT} = \frac{\Delta \overline{H}}{RT^2} \qquad (1)$$

The above equation may be integrated as an indefinite integral:

$$\log S = -\frac{\Delta \overline{H}}{2.303RT} + constant \qquad (2)$$

where R is gas constant, S is the solubility in *moles* per *1000g* of solvent at temperature T, and $\Delta \overline{H}$ is the average heat of solution per *mole* over the temperature range used. It is the heat of solution at the saturation concentration.

In this experiment, $\Delta \overline{H}$ is the heat absorbed when *1 mole* of the solid is dissolved in a solution that is already practically saturated. It differs from the heat of solution at infinite dilution, which is the heat of solution usually given in tables, by an amount equivalent to the heat of dilution from saturation to infinite dilution.

Apparatus and Chemicals :

Thermostat; ten *125-ml* Erlenmeyer flasks; *250-ml* beaker; *100-ml* graduated cylinder; *5-ml* pipette; *50-ml* burette; *100℃* thermometer; funnel; safety bulb; spatula; glass bar; a piece of glass tube with rubber tube.

Oxalic acid; *1N* NaOH; KHP; phenolphthalein.

Procedures :

(1) A saturated solution of oxalic acid is prepared at about *50℃* (add about *50 g* oxalic acid into *100 ml* distilled water) and is placed in a thermostat at *45℃* .

(2) As the solution cools to the studied temperature, crystallization takes place. After stir frequently for *20 minutes*, a *5 ml* of solution is removed using a pipette, drained into an Erlenmeyer flask, and weighed to *0.001 g*. Remember to weigh the Erlenmeyer flasks before experiment. To prevent drawing small crystals into the pipette along with the solution, you can heat the pipette previously using a hair dryer.

(3) Add about *20 ml* of distilled water and titrate with *1N* NaOH solution, using phenolphthalein as an indicator.

(4) Carry out the determination in duplicate.

(5) Repeat **steps (1)-(4)** for four more temperatures with *45℃* being replaced by *42*, *39*, *36*, and *33℃* for respectively.

(6) Standardize *1N* NaOH solution: Add accurately *2 g* KHP into distilled water and titrate with NaOH, using phenolphthalein as an indicator.

Calculations :

(1) Calculate the solubility in *moles* per *1000 g* of solvent at each of the temperatures.

(2) Plot $\log S$ vs. $1/T$ and calculate the heat of solution of oxalic acid in water.

References :

(1) P. W. Atkins and J. de Paula, "*Physical Chemistry*," 9th ed., pp. 172-173, Oxford University Press, U.S.A (2010).

(2) F. Daniels and others, "*Experimental Physical Chemistry*," 6th ed., pp. 124-128, Europe-Asia book company, Taiwan (1956).

(3) O. F. Steinbach and **C. V. King**, "*Experiments in Physical Chemistry*," pp. 89-93, American book company, U.S.A. (1950).