CHEM 355
EXPERIMENT 3

The Solubility of Silver Chloride

The concentrations of ions in equilibrium with its sparingly soluble salt are sufficiently low therefore, their direct determination can be quite difficult. A far simpler and common procedure is to set up a cell in which one of the electrode reactions involves the insoluble salt, and whose net cell reaction corresponds to the dissolution of the salt. For example, to determine the solubility product constant, $\mathrm{K_{sp}}$ for silver chloride, one can use the following cell;

$$\mathrm{Ag}(s) \mid \mathrm{Ag^+}(aq) \parallel \mathrm{Ag^+, Cl^-} \mid \mathrm{AgCl}(s) \mid \mathrm{Ag}(s)$$

whose net equation corresponds to the dissolution of silver chloride:

$$\textit{anode: } \mathrm{Ag}(s) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s) + e^-$$

$$\textit{cathode: } \mathrm{Ag^+}(aq) + e^- \rightarrow \mathrm{Ag}(s)$$

$$\textit{net: } \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s)$$

The potential of an electrode is determined by the activities (or concentrations) of these species that participate in the electrode reaction; as a consequence; measurement of a half cell potential is often a convenient method for the determination of the concentration of a saturated solution of sparingly soluble salt as illustrated in Figure 1. A galvanic cell does electrical work as the reaction drives electrons through an external circuit. The work done by a given transfer of electrons depends on the cell potential, the potential difference between the two electrodes. Cell potential is measured in volts (V, where $1\mathrm{V} = 1\mathrm{J.C^{-1}}$) . A cell in which the reaction is at equilibrium can not produce electrical work and its potential is zero.

One important aspect of such measurements is that the determination can be made without affecting appreciably any equilibria that may exist in the solution. For example, the potential of a silver electrode in a solution containing silver chloride depends only upon the silver ion activity;with a suitable equipment this potential can be measured with a negligible passage of current. Since the concentration of silver ions in the solution is not sensibly altered under these conditions, the position of the following equilibrium at a constant temperature is not disturbed by the rneasurement process. Equilibrium of a slightly soluble salt such as silver chloride in its saturated solution can be shown as;

$$\mathrm{AgCl}(s) \rightleftarrows \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

$$K_{sp} = (a_{Ag^+}) \times (a_{Cl^-})$$

In this expression, a refers to activity which means effective concentration used for real or dilute solutions.

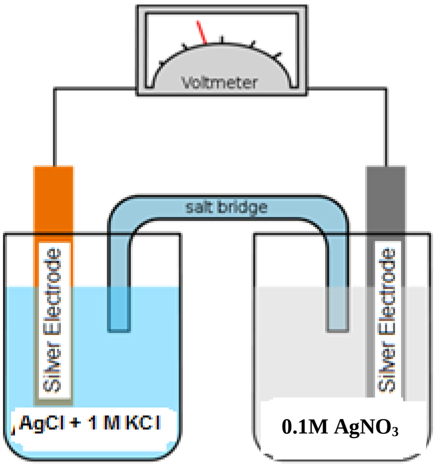


Figure 1. Experimental Set-up for Determination of Solubility of AgCl.

Figure 1 shows the experimental setup that will be used in the determination of solubility of AgCl. If the potentials of the left *(anode)* and right hand side (cathode) electrodes are E_a, and E_c, respectively; the electromotive force (e.m.f.) of the cell is given by:

$$E_{cell} = E_c - E_a \tag{1}$$

The potentials $E_a$and E_c can be given by the following equations:

$$E_a = E^o_{Ag/AgCl} - \frac{RT}{F}\ln(a_{Cl^-})_a \tag{2}$$

$$E_a = E^o_{Ag/AgCl} - \frac{RT}{F}\ln\frac{K_{sp}}{(a_{Ag^+})_a} \tag{3}$$

$$E_c = E^o{}_{Ag^+/Ag} + \frac{RT}{F}\ln(a_{Ag^+})_c \tag{4}$$

$$E^o_{Ag/AgCl} = E^o{}_{Ag^+/Ag} + \frac{RT}{F}\ln(K_{AgCl}) \tag{5}$$

From eqns. 1, 2, 3 and 4

$$E_{cell} = \frac{RT}{F}\ln\frac{(a_{Ag^+})_c}{(a_{Ag^+})_a} \qquad (6)$$

If we assume that activity coefficients of Cl^- and Ag^+ ions are equal to unity, then one can replace activities with molar concentrations, then eq.(6) becomes:

$$E_{cell} = \frac{RT}{F}\ln\frac{[Ag^+]_c}{[Ag^+]_a} \qquad (7)$$

$[Ag^+]_a$ equals to the solubility of AgCl(s) in 1M KCl

$[Ag^+]_c$ is the concentration of Ag^+ ion in the *cathode* half-cell, R is the gas constant, T is the absolute temperature and F is the charge of 1 mol electron and is equal to 96500 coulombs.

Thus, by having E_{cell} and $[Ag^+]_c$ at a definite temperature, one is able to calculate the solubility of AgCl in 1M KCl and finally in water.

The relationship between the free energy change of a cell reaction, ΔG, and the e.m.f., of the cell, *E,* is given by the following equation

$$\Delta G = -nFE \qquad (8)$$

where, n is the number of electrons participating in cell reaction.

The enthalpy change for a reaction may also be deduced from e.m.f. measurements. The Gibbs - Helmholtz equation given:

$$\Delta H = \Delta G + T\ [\frac{\partial(\Delta G)}{\partial(\Delta T)}]_p \qquad (9)$$

Substituting for ΔG from eq. (8)

$$\Delta H = -nFE + nFT(\frac{\partial E}{\partial T})_p \qquad (10)$$

Entropy changes for the cell reactions may also be determined from the temperature coefficients of the cell e.m.f.

$$\Delta S = nF(\frac{\partial E}{\partial T})_p \qquad (11)$$

Apparatus and Chemicals

Apparatus: Silver electrodes and thermometer.
Chemicals: 0.1 M $AgNO_3$, 1 M KCl, 1 M NH_4NO_3, saturated KNO_3 as salt bridge, solid AgCl, crushed ice.

Procedure

1. Construct the apparatus shown in the Figure 1 with great care when installing the salt bridge (Utube).
2. Take 40 mL 0.1 M $AgNO_3$ in a beaker.
3. Take 40 mL 1 M KCl.
4. Add few drops of AgNO3 solution to the the KCl solution. Mix the solutiongently. Due to the reaction $AgNO_3 + KCl \rightarrow AgCl + KNO_3$, a low soluble AgCl is formed and a turbidity of the solution is observed. Clean two Ag electrodes by briefly sanding them with abrasive paper. Then wash them with alcohol and dry.
5. Then connect them with a salt bridge.
6. Use the crocodile clips to connect the terminals of the multimeter to the metal electrodes.
7. Experiment will be proceeded at five different temperatures; 20°C, 25°C, 30°C, 35°C, 40°C.
8. Record the voltage and temperature of each cell on your data sheet.

(Waste container of experiment: silver waste container)

Treatment of Data

1. Use Eq. 6 to calculate the concentration of Ag^+ in 1 M KCl solution i.e. the solubility of AgCl in 1 M KCl.
2. Using the following equation, calculate the solubility of AgCl in pure water.

$$S^2 = (a_{Ag^+})_a \times (a_{Cl^-})_a \qquad (1)$$

S : the solubility in pure water

a_{Cl^-}: the activity of Cl^- ions in 1M KCl (Take a_{Cl^-}= 0.60 in 1M KCl).

Calculate solubility of AgCl for each temperature.

3. Solubility is temperature dependent so Arrhenius equation becomes as following;

$$S(T) = S_0 \, e^{-\Delta H_{sol}/RT} \qquad (2)$$

$S(T)$: solubility as function of temperature
S_0 : solubility when the temperature goes to infinitity
ΔH_{sol} : enthalpy change of solution
R: 8.314 J/mol.K
T: temperature

$$lnS_0 = A - \frac{\Delta H_{sol}}{RT} \qquad (14)$$

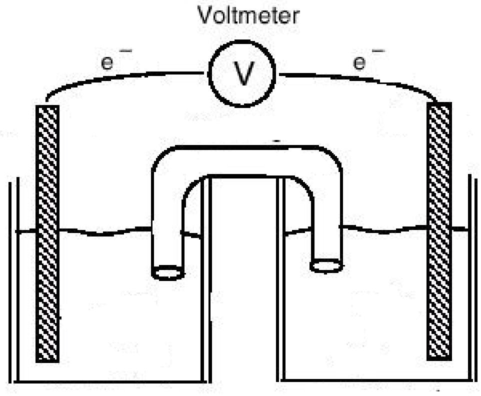
With the equation**Error! Reference source not found.**, plot lnS_0 vs. 1/T graph, enthalpy of solution (ΔH_{sol}) is found and compared with the one that is obtained from Gibbs - Helmholtz equation.

4. Plot E_{cell} vs. T graph and find the equation of the plot firstly and find ($\partial E/\partial T$) and use it in Eq. (10) and Eq.(11) to find ΔH and ΔS values for the cell for various temperatures that you performed. The plot should be polynomial and should be 5th in order to be able to calculate ($\partial E/\partial T$) for various temperatures. (if you have a linear equation, you will have only one value for ($\partial E/\partial T$).)

5. Discuss all of your findings, E_{cell}, ΔG, ΔH, ΔS, solubility of AgCl that you calculated, in the discussion part. Compare your results with theoretical ones and discuss whether your results make sense or not, along with mentioning your reasoning.

Questions

1. Discuss your results with the theoretical values and support your reasoning.
2. How does salt bridge affect this type of systems? Explain by using ions in the system.
3. On the figure, indicate:
- **a.** The signs of the electrodes
- **b.** The cathode and the anode
- **c.** The direction that the ions move
- **d.** The direction in which the electrons move
- **e.** The half-cell reactions



4. Define the followings: Faraday`s constant, salt bridge, coulomb, voltaic cell and electrolytic cell.

DATA SHEET Experiment 3. The Solubility of Silver Chloride

Group Number:………Group Members:……………………………………………………………
Date:……...................Assistant name and Signature:…………………………………………..

Temperature (^{o}C)	e.m.f (V)