CHAPTER 5

EXPERIMENTAL

5.1 Materials

The starting materials used for study the solid reaction in this research work were reagent grade, while analytical grade were used in the preparation of standard reagents for analysis. Hygroscopic compounds were kept in a desiccator over the anhydrous silica gel.

5.2 Preliminary investigation of solid reaction at various temperatures

5.2. I The investigation of the solid reaction at room temperature

Compounds of the first transition metals such as chromium, iron, cobalt and copper were used as ones of the reactants to react with every other 170 compounds. Two solid reactants were placed in contact with each other on a plastic plate in circular form as shown in figure 5.1

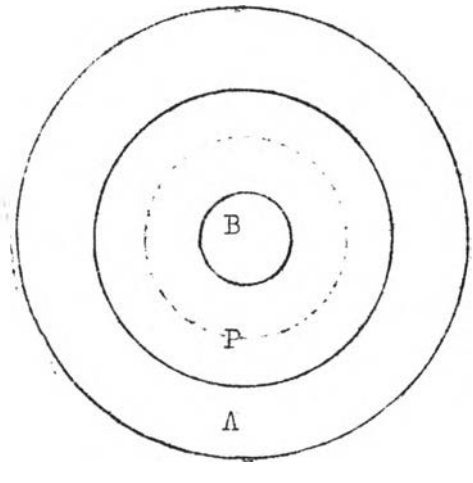

Fig 5.1 Reaction of solids A and B to give product P

Observing each pair of reactions by the colour change at the contact area was the criterion. The product P was found when its colour was different from solid reactants A and B. Solid A, which was supposed to be compound of the first-transition element, was maintained at each time while B, one of the other 170 compounds was changed in turn.

5.2. 2 Investigation of solid reaction at higher temperature

From experiment 5.2. 1, unreaction pair of compounds at room temperature, were selected to study at higher temperature from 50-200 ^{o}C. Solid A and B were filled in a pyrex semi-micro test-tube separately in two layers with their steadily contacting surfaces. The experimental temperature was varied and increased by ten degree Celcius, then the reaction was observed at each temperature for ten, thirty and sixty minutes respectively.

5.2.3 The comparison between reactions in solid state and aqueous solution at room temperature

From experimental 5.2.1, solid-solid reaction was studied simultaneously with its reaction in aqueous solution at room temperature. The concentration of each reactant was twenty percents by weight.

5.3 Study on kinetic and mechanism of interesting reactions at various temperatures (25^{o}C -150^{o}C)

The selecting reactions for mechanism study were carried out in pyrex semi-micro test tubes at room temperature up to 150^{o}C. The length of each changeable species was measured at various time. The reaction mechanism at the higher temperature, of interesting reactions was carried out at the temperature from 40-150^{o}C and

arranged at intervals of every increment of five degree Celcius. The length measurement compared between reactants and product was observed in a period of 10, 30, 60 minutes respectively.

5.4 Taking photographs of the colour change during the progression of interesting reactions by microscope at 100-400 times magnification

Among the reactions studied, it was possible to divide them into two broad classes depended on the rate of reaction. First, the solid-state reaction occurred immediatly when the two reactants were brought into contact together. Second, they occurred after contact for a long period of time.

The progressive process of the reaction in the first class was capable to follow. Olympus microscope model BHC and camera PM-6 were used to take a photograph consecutively, but it was impossible for the latter, when the problem was due to the long range of reacting time.

5.5 The study of solid reactions by instrument methods

5.5.1 Infrared spectroscopic technique

Infrared spectra were obtained with a Pye Unicam sp 200 G Grating Infracord Spectrophotometer. Two methods of preparing solid samples, the KBr-pellet and mull techniques, have to be considered in case the sample reacts with KBr (such as copper compounds). In the first method, the dried mixture of KBr and any entity, reactant or product, was mixed well and ground thoroughly to achieve homogeneous mixture which was transferred evenly into

a standard Pye unicam dic(13 mm.). The Blackhawk Enerpac model P-39, 10,000 Psi,was used in making pellet of the mixture under a pressure of 3,000 Psi. For mull technique, the sample (product or reactant) was ground very finely with paraffin in an agate mortar. The suspension is then placed on NaCl plate. The optimum wave number of infrared spectrophotometer was scanned between the range of 4,000 cm^{-1} to 667 $cm.^{-1}$

5.5.2 X-ray Powder diffraction technique

It is possible unambiguously to identify a material from its X-ray diffraction pattern, since the diffraction pattern given by a substances is unique as the positions of the reflections are determined by the spacing between the layers of atoms in a crystal and the intensity of these reflections is dependent on the arrangement of the atoms in the crystal lattice. The simplest way to identify a substance is to compare its diffraction photograph visually with those of known materials taken under identical conditions. The X-ray powder photographs were recorded at $26^{o}C$ with the Guinier-Hagg XDC-700 focusing powder camera using CuK_{α_1}-radiation (λ = 1.54051 ^{o}A), 34 Kv, 21 MA exposed for two hours, and silica was used as the internal calibration standard.

5.6 Determination the composition of the product from the interesting reaction

The products were collected to analyse quantitatively both in solid state by X-ray fluorescence technique and in solution by atomic absorption technique, following together with gravimetric and volumetric analyses.

5.6.1 X-ray fluorescence analysis

The quantity of heavy atoms was analyzed by X-ray fluorescence technique with a gamma ray source (Pm^{147}/Al isotope) and a Si(Li) detector.

5.6.1.1 Preparation of standard sample

Internal standard method was used to prepare standard sample by varying weight of reactants with fixed weight of calcium carbonate to give totally of 5 grams and then mixed thoroughly in order to get a homogeneous mixture.

5.6.1.2 Percentage determination

The measuring solid was transferred into a plastic container of 15 mm. diameter and 20 mm. in depth, where the sample thickness of 10 mm. was the optimum one for eleminating the absorption enhancement effect. The container was placed at a fixed position on the Si(Li) detector and irradiated with Pm^{147}/Al isotope gamma source about 5 minutes long then the multichannal pulse height analyzer was switched on and the printer was used. Each heavy element has its characteristic energy of K_α and L_α -band which displays a maximum peak refered to a maximum yield of scattering , so each element was observed at the different range of channel.

5.6.2 Atomic Absorption Analysis

This technique is based on flame absorption and depends upon the fact that metal atom absorbs strongly at discrete characteristic wavelength which coincides with the emission spectra

lines of the particular metal. All metals in the reaction product were analyzed by this method. Varian Techtron Atomic Absorption Spectrophotometer Model AA-5 was used.

5.6.3 Gravimetric and Volumetric Analysis

Non-metal ions such as NH_4^+, SO_4^{2-}, Cl^-, CrO_4^{2-}, etc., were analyzed by gravimetric and volumetric method.

The water of hydration process was used to determine the percentage of water.

5.7 Conductivity measurement

5.7.1 Preparation of sample

The two millimeters thickness pellet of the dried solid compound of reactant or product was made under a pressure of 3,000 Psi by the Blackhawk Enerpac, for the measurement of conductivity. However, the pellet thickness was changed to one millimeter when the progressive reaction was studies through the conductivity measurement.

5.7.2 Apparatus

The Yew microammeter, milliammeter with scale 0-3, 0-30, 0-100, the Yew Voltmeter with scale 0-30, 0-100, 0-1000, and unicam power supply with 0-100 volt were connected together with two carbon electrodes of 1 cm diameter and 10 cm length with one of their ends was tipped with copper plate which joined with copper wire.

Both electrode and sample were hold together within the 15 cm. long glass-tube as in the Figure 5.2.

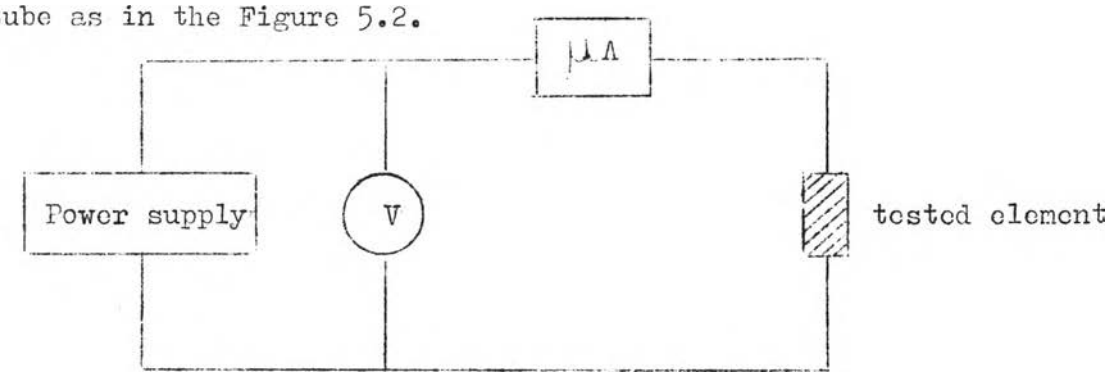

Fig. 5.2 The electric circuit for conductivity measurement in solid state

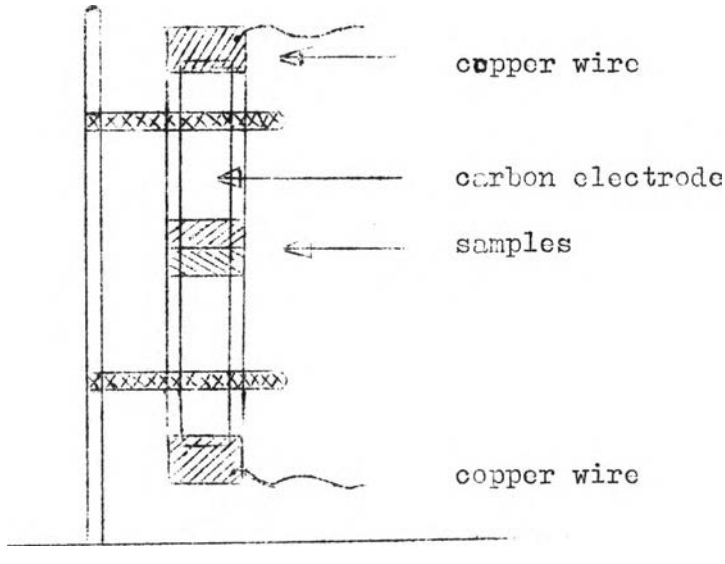

Fig 5.3 The enlargement of tested element part

5.7.3 The comparison of the conductivity measurement between product and reactants

To compare the characteristic conductivity between product and reactants, pellet sample was kept to dryness in a desiccator before use. Each pellet was placed between two carbon electrode, while the voltage power supply was varied from 0-300 volts, then the electric current was measured.

5.7.4 Conductivity measurement of reaction during the progressive period

Two pellet reactants of interesting reactions were assembled between carbon electrodes the optimum voltage power supply was selected and kept constant during the measurement . The electeic current at given time was noted.