CHAPTER 1

INTRODUCTION

Substances may be classified into three main divisions according to states of matter: gases, liquids and solids by considerations of the relative ease of motion of the atoms or the molecules in each of these states (1). Solid molecules may have a greater to lesser tendency to cohere or stick together. Generally, the stronger the cohesive forces of a substances, the greater are the density, hardness, strength, and ability to resist the effects heating. The weaker the cohesive forces, the greater is the tendency of a substance to spread out in space (2). A part of space bounded on all sides does not perceptibly flow. Between typical solids and liquids are many gradations designated by terms such as viscous solid, semi-solid, viscous liquid, and etc (3).

Some materials that are physically rigid, such as glasses, are regarded as highly viscous liquids because they lack crytalline structure. All solids can be melted (i, e., the attractive forces acting between the crystals are disrupted) by heat, and are thus converted to liquids. For ice, this occur at 32^{o}F, for some metals the melting point may be as high as 6,000^{o}F (4).

Solid, in general, comprise both metallic and nonmetallic, crystalline as well as noncrystalline materials. It is a state of matter in its most highly concentrated form, i.e., the atoms or molecules are much more closely packed than in gases or liquids, and thus more resistant to deformation. It appears to be a substance of definite shape, relatively great density, low internal heat content, and great cohesion of its molecules. It may be homogeneous (as crystals and solid solutions), or heterogeneous (as amorphous and colloidal substance) (5). The normal condition of the solid state is crystalline structure, the orderly arrangement of the constituent atoms of a substance in a framework is called a lattice. Crystals are of many types, and normally have defects and impurities that profoundly affect their applications, as in semiconductors. The geometric structure of solids is determined by X - rays, which are reflected at characteristic angles from the crystal lattices, which act as diffraction gratings. It is the science of crystallography.

During the last years of the nineteenth century Robert Austen[(6)] had shown that gold and lead could form alloys at temperatures where no liquid phase could be presented. Masing (7) had discovered that a compound Mg_3Sb_2 began to form far below the eutectic temperature of the system and similar observations had also been made by Tammann (8) Spring (9) and Cobb (10) got result from some experiments with non - metallic powder mixtures. But there was seemingly some hesitation about accepting the results as facts then the experiments were not pursued. The reason for this are not known - possibly, but the opposition in academic circles was too strong, perhaps there was too little interest in these matters at the time, or may be the explicit significance of the evidence was not appreciated. (11)

This field of research was started in 1910,at that time the very little was known about the structure of crystals (7). This was only changed in 1912 through Max von Laue's discovery of x-ray diffraction for studying crystal structure. In 1920, J. Arvid Hedvall (11) employed X - ray methods to prove the possible occurrence of solid - solid reactions.

The first result of powder compound reactions in non-metallic systems was the formation of Rinman's Green from compounds of black Co_3O_4 and white ZnO. The very small green crystals, which was produced after mixing the two oxides, was examined by microscope at 1000 times magnification (12).

Frenkel's theory of disorder was presented in 1926 (13), Schottky and Wagner presented statistical thermodynamic theory of disorder in 1931 (14). In 1941, R.M. Barrer introduced the theory of diffusion within and through solids. From that time, the mechanism of solid - solid reactions was believed to be a diffusion of electronic and ionic species within solid crystals (15).

When investigations began in this virtually untouched field of research, there were three main questions to be answered. Firstly, could reactions occur between solely solid phases in general, secondly, what factors influenced the reactivity of solid - solid interaction, and thirdly, could the atmospheric moisture affect the process of reactions.

How can name material a solid ?

Solid, in contrast to gas and liquid, is generally considered its obvious hardness and definite shape. It is now interesting to consider about wood whether it is a solid or solution. The large quantities of water in wood do lead no one to name it a wood solution, but care nothing about its liquid portion and it is still classified as a solid, corresponds with its definite shape. Such as potashalum, $Al_2(SO_4)_3.K_2SO_4.24H_2O$, the assemblage of twenty four moles of water in each complex crystal is chemically said to be a solid substance. When the 24 moles of water are compared to the amount of water from atmospheric moisture which may be absorbed by anhydrous solid sample. The later is sometimes less than the number of the moles of water existed in potashalum crystal. However, potashalum is classified as a solid because of the obvious hardness and definite shape neglecting its water crystallization. Then the association of anhydrous solid with atmospheric moisture is also considered as a solid in the same manner unless the state was changed.

What is reaction ?

In general, with very few exceptions, reaction is concerned with the change of type and quantity of the components, in particular, it involves the change of bond, state, structure, colour and etc. of the components (16). Sometimes there are some problems about the later three, the change of state, structure and colour of the components, when they are used to indicate the occurrence of reactions.

For example, red-violet crystal of hexaaquo cobalt choloride, $CoCl_2.6H_2O$, its pale pink solution was used as a colourless ink at room temperature. The colourless letter that was written with this ink was changed to navy blue when such a written paper was heated but could turn back to colourless again when cooled. A mechanism of the colour change process was completely reversible.

$$\underset{\text{red}}{CoCl_2(s)} \longrightarrow \underset{\text{pink}}{[Co(H_2O)_n]^{2+}} \rightleftharpoons \underset{\text{blue}}{[CoCl_4]^{2-}}$$

By the chemical sense in general, the process was not accepted to be a chemical reaction because of its reversible deformation. But when the saturated solution of $CoCl_2.6H_2O$, red solution, was used the pinkish blue colour occurred maintainly after heated and the pinkish blue colour which was different shade from the navy blue was still maintained forever.

It might come to the conclusion that this irreversible phenomena was depend on the concentration. Now, can this irreversible change be accepted to be a chemical reaction ? In fact the above equation readily manifested how chemical reaction took place in view point of coordination chemistry. Another example of colour change when heating was also tried with silver tetraiodo mercurate (II), yellow crystal Ag_2HgI_4, the colour changed from yellow to orange when heated and turned to yellow again when cooled. After the certain time of heating, the irreversible change was appeared and the orange colour was maintained. It was said to be a process of structural deformation but process of chemical change or reaction was better left unsaid. Then the transformation of graphite to diamond might be incredible to be a chemical reaction for someone who never expressed the chemical properties of atom or ion with respect to number and nature of coordinating neighbour atom or ion. If that was so, then the process of an aqueous solution of salt was undoubtedly a chemical reaction. It was described in the sense of coordination chemist.

However, another point was also intended to display, apart from how chemical reaction took place, that theoretical explanation might not enough or sometimes could not cover every phenomena. Experiment result often showed new and convincing information.

What is solid reaction ?

In general, chemical reaction can always be divided into two types which rather seems to depend on what criteria are considered about. If the phase of the system is concerned then they are heterogeneous and homogeneous reactions (17). Reactions in liquid, which are homogeneous, differ markly from reactions in the solid phase because of the role of solvation. Reactions of solid with gas, such as the reaction of iron with oxygen gas which is called the corrosion of iron, and reactions between solid and liquid, such as the reaction of zinc metal with sulphuric acid, is heterogeneous and the progression of reactions depends on the ease of the diffusion of gas or liquid into such solids, or in the otherhand, the area of contact surface of solid. These two types of reactions, solid with gas and solid with liquid, sometimes are accepted as solid reaction. But when reactions of solid with solid, which are obviously heterogeneous, are refused to be solid reactions. Then, what type of reaction between two solids, if anyone can name or classify them more suitably.

The solid - solid reactions occur at the contact area and nucleate new phase (s) which are products. The growth of the products is result from the diffusion of some species through different phases.

It could be said that it was the first time in Thailand where the study of solid - solid reaction happened to chemist's sight. Therefore, at first sight it seemed to be the incredible task for the others. But the objection criticism never cause any obstacle to the progressing of this research work at all.

However, the application of these reactions related to the natural solid - solid interaction was the most important criterion of this job. For this reason the experimental condition was set up nearly the same as in the natural state. The atmospheric moisture which is the strong point of objection was not the strong aversion for this work. The effect of the atmospheric moisture was considered to be the factor which could also reduce or increase the reaction rate. Most of solid reactions seemed to occur rather frequently at high temperature.

In some cases, solvent molecules as water could reduce the ease of reaction occurring and tended to reduce reaction rate. The reaction between two insoluble compounds, red mercury iodide HgI_2 and pale yellow silver iodide AgI, never took place in water media. But in contrast to the reaction in solid state, the yellow product of Ag_2HgI_4 was immediately formed at the contact area.

Solid reactions introduced a new and rather strange evidence for the information of chemical processes. The chemists right now should open and make up their mind widely and readily to use academic consideration toward problem eventhough it completely opposed to theoretical discipline which usually was chemical familiar to them. It might be awkward to realize that, apart from salty property, no one really knew another properties of solid sodium chloride or any simple solid salt. All they had been concerned, were phenomena deriving from $[Na(H_2O)_n]^+$, aquo sodium species, which behaved differently from solid sodium chloride. That was why this research work was trying to study chemistry of simple compound in solid state.

This research work was intended to show the possibility of solid - solid reaction in non - metallic system at room temperature, normal pressure and then collected products for further study. The occurrence and quantity of products from both solution and solid state of the same system were carried out in parallel and studied what difference between two types of reaction. For some interesting reactions, the possible experimental methods were set up to get much more detail of these reactions. The colour change was used to indicate whether the powder solid - solid reactions in non - metallic system took place at room temperature.

The interesting reactions were selected to search for the chemistry information such as mechanism, the composition of products, the structural change between products and reactants, and the conductivity during the chemical change. The composition of product was analysed by X - ray fluorescence techniques and other possible ways. The structural change was compared between reactants and products by the infrared pattern and X - ray powder pattern. The conductivity of compounds and reactions were observed before and during the progressive period.