1. INTRODUCTION.

Like so many other branches of science, the field covered by the term "Luminescence", cannot be assigned to any one definite subject. Instead, it is a branch of science embracing both chemistry and physics, and yet not wholly within the accepted boundaries of physical chemistry. In general, the preparation of luminescent materials is a complex chemical process, and the investigation of what would appear to be properties of fundamental importance involves complicated physical measurements. Luminescence is, therefore, a subject which attracts both chemists and physicists alike, and in the present thesis it is from the chemical side that the subject has been approached.

The various subdivisions and types of luminescence have been described so frequently[1,2] that it is intended to define here only that terminology of the subject which will subsequently be used. The form of luminescence studied in the text is photo-luminescence. That is, the emission of visible or near visible radiation from a substance due to the absorption of electro-magnetic radiations. The electromagnetic radiation which is absorbed is called the "excitation" or "exciting energy", and in the present study is of such a wavelength that it falls within the ultra-violet regions of the spectrum. Inorganic compounds which are excited to luminescence in this way, are often referred to as "phosphors", and, generally, such phosphors result only after a suitable thermal treatment of non-luminescent inorganic materials. When a phosphor is excited by ultra-violet radiation,

the luminescence which is emitted is called "fluorescence", and any luminescent emission which occurs after the source of exciting energy is removed is referred to as "phosphorescence" or afterglow.

Inorganic phosphors are often divided into two types - (a) "pure" phosphors and (b) "impurity activated" phosphors. A "pure" phosphor is an inorganic compound free from all traces of impurities and which is luminescent after heating in such a manner that a certain crystalline form of the compound has been obtained. Calcium tungstate is an example of a "pure" phosphor, because the pure compound is luminescent after a suitable thermal treatment. An "impurity activated" phosphor is an inorganic compound which contains a small proportion of another element, known as the "activator", and which is only luminescent when such an activator is suitably incorporated in the matrix lattice. Calcium fluo-phosphate of the apatite structure is only luminescent when an activator such as antimony is suitably incorporated in the apatite lattice. Calcium fluophosphate antimony is, therefore, an example of an impurity activated phosphor in which antimony is the impurity which activates the luminescence.

Although there are a number of exceptions, such as aluminium oxide activated by chromium, the majority of phosphors are salts of the elements of Group II of the Periodic Classification. Moreover, these phosphors, when grouped together according to the acid radical which they contain show greater similarities to one another than when the various phosphors of any one metal are grouped together. The best known group of phosphors consists

of the sulphides of the Group II elements. More recently other large groups such as the silicates, tungstates and phosphates of these elements have been found to be phosphors, and other compounds of these elements, such as the oxides, fluorides and borates, are also sometimes luminescent. Of these various groups of phosphors the tungstates were selected for closer study for the reasons outlined below.

No phosphor is easy to prepare and to repeat the preparation and obtain an identical product each time, is generally extremely difficult. This is especially true of the sulphide, silicate, and borate phosphors; for example, close inspection of a freshly prepared sample of a zinc cadmium sulphide phosphor under ultraviolet light always reveals wide differences in luminescent properties throughout the mass. On the other hand, repeatable results can be obtained in the preparation of tungstate phosphors provided care is exercised during the preparation.

Sulphide phosphors have been the subject of an immense amount of study, and yet fundamentally they are a most complicated group of phosphors. Thus, they have outstanding phosphorescent properties, they are extremely sensitive to the presence of impurities, and show great variations in luminescent behaviour due to multiple activators and solid solution effects. An example of the influence of solid solution formation on luminescence is provided by zinc sulphide and cadmium sulphide. These sulphides together form a complete series of solid solutions. The luminescence shown by pure zinc sulphide gradually becomes of longer wavelength as zinc atoms of the matrix

are replaced by cadmium atoms. Tungstate phosphors, on the other hand, have no visible phosphorescence, and, therefore, the mechanism of luminescence would appear to be of a somewhat less complicated type. Moreover, variations in luminescent properties within any one sample or between successive preparations of a tungstate phosphor are at least restricted to differences in intensity of fluorescence and are not complicated by differences in fluorescent colour and afterglow.

The fluorescence of pure tungstates appears in the blue regions of the spectrum, and, therefore, from a spectroscopic aspect is more readily studied than if the fluorescence is in the red or even near infra-red regions as is the case with some silicates, borates, phosphates, and sulphides. Finally, although the tungstate phosphors played a most important part in proving the utility of fluorescent lighting before they were replaced by phosphate materials[2], as a group of phosphors, they have received comparatively little study.

The following thesis is, therefore, devoted to a study of the tungstate phosphors of the Group II elements. The most important members of this group are magnesium, calcium, zinc and cadmium tungstates. The conditions required for preparing these phosphors are described and discussed in relation to the crystal structure of the phosphors. The characteristics of the fluorescent emissions is considered next, and then follows a description of an investigation of the effects of certain impurities on the luminescent properties of these tungstates. These results are discussed from a theoretical

point of view.

A table of the properties of the samples prepared in this investigation is given in Appendix I, and the methods used for investigating the properties of the samples are described in Appendix II.