9. CHEMICAL PROPERTIES OF ALKALINE EARTHS AND HALOGENS

In the modern periodic table, the elements are arranged according to their electronic structures. As one progresses down a group (or family) the principal quantum number increases for electrons in the outermost shell, but the arrangement of electrons in that shell (the valence-shell configuration) is the same for all members of the family.

As might be expected, with identical electron arrangements in the valence shell the members of the same group will exhibit similar chemical properties. In fact, the early arrangements of the elements by Döbereiner (1846), Newlands (1866), and Meyer and Mendeleev (1869) were based upon similarities in chemical properties of the elements.

However, since the principal quantum number of the valence shell electrons changes by one for each successive member of a family, there are also regular trends in chemical behavior in descending a group. An example of such similarities and regular trends can be shown with the alkali metal family, Group 1. All members of the family react with water to produce hydrogen and a soluble ionic hydroxide (the similarity). The reaction becomes increasingly vigorous as the element becomes larger (the trend). An additional trend is the fact that the melting points of the metals vary smoothly from lithium (which melts at 180°C) to sodium (at 98°C), potassium (at 63°C), and rubidium (at 39°C). A discussion of the trends in chemical properties of the elements can be found in most general chemistry textbooks.

In this exercise the properties of two families will be studied-- Group 2 (II), the alkaline earth elements, and Group 17 (VII), the halogens. The alkaline earths are all active metals and include beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium compounds are often very poisonous and radium is highly radioactive, so we shall not include these two elements in the experiment. The elements in the halogen family are fluorine, chlorine, bromine, iodine, and astatine. We will study the uninegative anions of the three most common elements of this group, chlorine, bromine, and iodine.

The experiments with the alkaline earths involve determining the relative solubilities of the salts formed by the alkaline earth cations with the sulfate (SO$_4^{2-}$), carbonate (CO$_3^{2-}$), oxalate (C$_2$O$_4^{2-}$), and chromate (CrO$_4^{2-}$) anions. Solutions of each of the four cations will in turn be added to solutions of each of the four anions. In some cases an insoluble product (precipitate) will be formed.

We will also investigate the relative solubilities of the salts formed between the silver ion and the various halide ions. If a solution of silver nitrate, AgNO$_3$, is added to a solution of a halide NaX, the silver halide AgX will precipitate. This precipitate, although it is very insoluble in water, may dissolve in an ammonia solution by forming a complex ion:

\[
\text{AgX (s) + 2 NH}_3\text{(aq)} \rightarrow [\text{Ag(NH}_3)_2]^+\text{(aq)} + \text{X}^-\text{(aq)}
\]

where X represents any of the halogens. The solubilities of the silver salts of the halogens in ammonia solutions will allow you to arrange the halogens in order of reactivity.

Given the properties of the alkaline earths and halide ions as observed in this experiment, one can develop a systematic procedure for determining the presence of any Group 2 cation and any halide anion in a solution. In the last part of the experiment you will be asked to set up such a procedure and use it to establish the identity of an unknown solution containing a single alkaline earth halide.
PROCEDURE

Relative Solubilities Of Some Salts Of The Alkaline Earths

1. Add about 1 mL of 0.1 M solutions of the nitrate salts of barium, calcium, magnesium, and strontium to separate small test tubes. To each test tube add 1 mL of 1 M H₂SO₄ and mix by tapping sideways on the lower end of the test tube. Record your observations, noting whether a precipitate forms, as well as any characteristics that might distinguish the precipitate.

2. Repeat the same procedure but this time use 1 M Na₂CO₃ as the precipitating reagent and record your observations.

3. Repeat the experiment again, this time using the 0.25 M solution of ammonium oxalate, (NH₄)₂C₂O₄.

4. Finally determine the relative solubilities of the chromate salts. In this case the testing reagent is composed of 1 mL of 1 M K₂CrO₄ and 1 mL of acetic acid.

Solubilities Of The Silver Halide Salts

5. Add 1 mL of 0.1 M solutions of the three sodium halide solutions (NaCl, NaBr, and NaI) to separate test tubes. Add 1 mL of 0.1 M AgNO₃ to each test tube and mix. Note the color and appearance of each precipitate.

6. Centrifuge the mixture for 1 minute; be sure to balance the centrifuge rotor by placing test tubes in a symmetrical pattern. Decant and discard the liquid. To each of the precipitates add 7 M aqueous ammonia, NH₃ (often labeled incorrectly as “ammonium hydroxide”), dropwise with mixing, noting the effect that addition has upon the solubility of the precipitate in each case.

7. With any precipitates which do not dissolve after addition of about 2 mL of the 7 M ammonia, centrifuge and decant the supernatant solution and repeat step 6 with 15 M ammonia.

Identification Of Unknown Salt

8. On the basis of your observations devise a scheme by which you can establish which alkaline earth cation and which halide anion would be present in a solution containing a single alkaline earth halide. You must decide upon the number of tests required (you may not require all 22 reactions) and the best sequence of the tests in order to positively identify your two ions. Record your scheme as instructions (with justifications) or a flow chart in your notebook. Show the scheme to your instructor before proceeding to step 9.

9. Obtain a sample of an unknown salt from your laboratory instructor and record the identifying code. Carry out your procedure to identify the salt (one Group 2 ion and one Group 17 ion, e.g., CaBr₂). Follow the scheme you devised above exactly as written. Record all steps and observations. Discuss both the positive evidence and negative evidence that allowed you to make your conclusion.