Summary and Notes for Exam Preparation: Group 17 Elements

1. Physical Properties of Group 17 Elements

Key Elements

- Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), Astatine (At)

Trends in Physical Properties

a) Atomic and Ionic Size

- **Trend**: Increases down the group
- **Explanation**: More electron shells are added as atomic number increases
- **Example**: F^- (133 pm) < Cl^- (181 pm) < Br^- (196 pm) < I^- (220 pm)

b) Melting and Boiling Points

- **Trend**: Increases down the group
- **Explanation**: Stronger instantaneous dipole-induced dipole (dispersion) forces between larger atoms
- **Values**:
  - Cl_2: mp -101°C, bp -34°C
  - Br_2: mp -7°C, bp 59°C
  - I_2: mp 114°C, bp 184°C

c) Electronegativity

- **Trend**: Decreases down the group
- **Explanation**: Outer electrons are further from the nucleus and more shielded

d) Reactivity

- **Trend**: Decreases down the group
- **Explanation**: Decreasing electronegativity and increasing atomic/ionic size

2. Reactions of Group 17 Elements

A. Displacement Reactions

General Equation:

$2X + 2Y^- \rightarrow 2X^- + Y_2$ [where X and Y are halogens]

Examples:

1. **Chlorine and Bromide Ion**:
    - $2Cl + 2Br^- \rightarrow 2Cl^- + Br_2$
    - Cl_2 is more reactive than Br^-, displacing Br_2
2. **Bromine and Iodide Ion**:
    - $2Br + 2I^- \rightarrow 2Br^- + I_2$
    - Br_2 is more reactive than I^-, displacing I_2

B. Reactions with Hydrogen

General Equation:

$H_2 + X_2 \rightarrow 2HX$ [where X = halogen]

Examples:

1. **Hydrogen and Chlorine**:
    - $H_2 + Cl_2 \rightarrow 2HCl$
    - Highly exothermic reaction, requires careful control
2. **Hydrogen and Bromine**:
    - $H_2 + Br_2 \rightarrow 2HBr$
    - Slower reaction, requires UV light or high temp

C. Reactions of Halide Ions

1. With Silver Nitrate:

- $X^- + AgNO_3 \rightarrow AgX + NO_3^-$
- Forms insoluble silver halide precipitates

2. With Concentrated Sulfuric Acid:

- $2X^- + 2H^+ + H_2SO_4 \rightarrow X_2 + SO_2 + 2H_2O$
- Evolves gaseous halogen

D. Disproportionation of Chlorine

Disproportionation of Chlorine in Alkaline Conditions

Cold Alkali (15°C)

Equation: $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO^- + 3H_2O$

Explanation:

- In cold, dilute alkaline conditions (around 15°C), chlorine gas (Cl_2) undergoes disproportionation.

- The chlorine is simultaneously oxidized and reduced, forming both chloride (Cl^-) and hypochlorite (ClO^-) ions.
- This reaction is important for the use of chlorine in water purification and disinfection.

Reaction Mechanism:

1. $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$
   - Chlorine reacts with hydroxide ions to form hypochlorite and chloride.
2. $Cl_2 + Cl^- \rightarrow Cl_3^-$
   - Chlorine also reacts with chloride ions to form the trichloride ion (Cl_3^-).
3. $Cl_3^- + 3OH^- \rightarrow ClO^- + 2Cl^- + 3H_2O$
   - The trichloride ion then reacts further with hydroxide, producing hypochlorite and chloride.

Hot Alkali (70°C)

Equation: $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

Explanation:

- In hot, concentrated alkaline conditions (around 70°C), the disproportionation of chlorine produces chlorate (ClO_3^-) instead of hypochlorite.
- The higher temperature and more concentrated hydroxide solution favor the formation of the more stable chlorate ion.

Reaction Mechanism:

1. $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$
   - Chlorine initially reacts with hydroxide to form hypochlorite and chloride, as in the cold alkali reaction.
2. $3ClO^- + 3OH^- \rightarrow 2Cl^- + ClO_3^- + 3H_2O$
   - The hypochlorite ions then undergo further reaction with hydroxide to produce chlorate and chloride.

The difference in products between the cold and hot alkali conditions is due to the kinetics and thermodynamics of the disproportionation reactions. The higher temperature and more concentrated hydroxide favor the formation of the more stable chlorate ion in the hot alkali case.

3. Testing for Halide Ions

1. With Silver Nitrate

- Forms insoluble silver halide precipitates
- Cl^-: White ppt
- Br^-: Pale yellow ppt
- I^-: Yellow ppt

2. With Concentrated Sulfuric Acid

- Cl^-: Evolves colorless Cl_2 gas
- Br^-: Evolves reddish-brown Br_2 gas
- I^-: Evolves violet I_2 vapor

3. With Dilute Ammonia

- Cl^-, Br^-, I^-: No reaction, halides remain as aqueous ions

4. With Concentrated Ammonia

- Cl^-, Br^-, I^-: Forms soluble diammine silver(I) complex ions
- Equations:
  - $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$
  - $AgBr + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Br^-$
  - $AgI + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + I^-$

The key differences in these halide ion tests are:

1. With dilute ammonia, the halide ions remain unchanged in solution.
2. With concentrated ammonia, the silver halide precipitates dissolve to form the soluble diammine silver(I) complex ion.

This distinction is important, as the solubility of the silver halides in concentrated ammonia can be used to differentiate between the halide ions. The formation of the colorless $[Ag(NH_3)_2]^+$ complex confirms the presence of a halide ion, without indicating which specific halide is present.

4. Uses of the Halogens and Their Compounds

A. Chlorine

1. **Water Purification**:
   - Kills bacteria and algae
   - Forms hypochlorous acid (HOCl)
2. **Bleaching and Disinfection**:
   - Sodium hypochlorite (NaClO) - household bleach
   - Calcium hypochlorite $[Ca(ClO)_2]$ - swimming pool treatment

B. Bromine

1. **Fire Retardants**:
   - Used in plastics, fabrics, and electronic components
2. **Photographic Film**:
   - Silver bromide (AgBr) in photographic emulsions

C. Iodine

1. **Antiseptic**:
   - Povidone-iodine (PVP-I) used to treat skin infections
2. **Nutritional Supplement**:
   - Potassium iodide (KI) added to table salt to prevent goiter

D. Fluorine

1. **Dental Care**:
   - Sodium fluoride (NaF) in toothpaste and mouthwash
   - Fluoride ions strengthen tooth enamel
2. **Refrigerants**:
   - Chlorofluorocarbons (CFCs) - now banned due to ozone depletion
   - Hydrofluorocarbons (HFCs) - alternative refrigerants

Exam Tips and Common Questions

1. Trend Questions

- Link trends to atomic/ionic size and electronegativity
- Explain increasing/decreasing reactivity down the group
- Use correct terminology for intermolecular forces

2. Displacement Reactions

- Predict the direction of reaction using reactivity series
- Write balanced equations
- Explain the role of redox in displacement

3. Disproportionation of Chlorine

- Understand the difference between cold and hot alkali conditions
- Write balanced equations for both cases
- Explain the formation of hypochlorite vs chlorate

4. Halide Ion Tests

- Recognize the characteristic precipitates and gas colors
- Write ionic equations for the reactions
- Explain the principles behind the tests

5. Real-World Applications

- Describe the use of halogens in water purification, disinfection, and medical/consumer products
- Understand the environmental concerns with some halogen compounds

- Explain the chemistry behind the applications

Sample Exam Question:

Q: Explain the trends in physical properties of the halogens (Group 17 elements) and how these relate to their reactivity.

Model Answer:

1. Atomic and ionic size increase down the group (F < Cl < Br < I)
2. Larger atoms have more electron shells, leading to weaker nuclear charge and less effective electron shielding
3. Melting and boiling points increase down the group due to stronger instantaneous dipole-induced dipole (dispersion) forces between larger atoms
4. Electronegativity decreases down the group as outer electrons are further from the nucleus and more shielded
5. Reactivity decreases down the group due to the combined effects of increasing atomic/ionic size and decreasing electronegativity
6. Larger halogens have lower ionization energies, making them less reactive as they are less eager to gain an electron