Summary and Notes for Exam Preparation: Nitrogen and Sulfur

1. Introduction to Nitrogen and Sulfur Family

Nitrogen Family (Group 15/VA)

- Elements: N, P, As, Sb, Bi
- Electronic configuration: ns^2np^3
- Key characteristics:
    - 5 valence electrons
    - Can form -3 to +5 oxidation states
    - Forms covalent compounds primarily
    - Shows diagonal relationship with carbon

Example: NH_3 vs PH_3

- NH_3 forms hydrogen bonds (more soluble in water)
- PH_3 doesn't form hydrogen bonds (less soluble)
- NH_3 is more basic than PH_3

2. Nitrogen Gas (N_2)

Physical Properties

- Colorless, odorless gas
- Low boiling point (-196°C)
- Inert at room temperature
- Triple covalent bond (N≡N)

Chemical Properties

- Very stable due to strong triple bond
- Bond energy = 946 kJ/mol
- Low reactivity at room temperature
- Needs high temperature/pressure or catalyst for reactions

3. Thunderstorms and Nitrogen Fixation

Process

1. Lightning provides energy to break N_2 and O_2 bonds

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2. Reaction occurs at ~2000°C
3. Chemical equation: $N_2 + O_2 \rightarrow 2NO$
4. Further oxidation: $2NO + O_2 \rightarrow 2NO_2$
5. Dissolution in rainwater: $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$

Example calculation: If lightning produces 8.0g of NO, calculate the mass of N_2 used:

- Equation: $N_2 + O_2 \rightarrow 2NO$
- Molar mass NO = 30g/mol, N_2 = 28g/mol
- 8.0g NO = (8.0/30) = 0.267 mol NO
- N_2 required = 0.267/2 = 0.133 mol
- Mass N_2 = 0.133 × 28 = 3.73g N_2

4. Ammonia and Ammonium Compounds

Properties of Ammonia

- Molecular formula: NH_3
- Pyramidal shape
- Bond angle: 107°
- Highly soluble in water
- Forms hydrogen bonds
- Basic in nature

Ammonium Ion (NH_4^+)

- Tetrahedral shape
- Forms when NH_3 accepts H^+
- Present in many fertilizers
- Stable in aqueous solution

5. Haber Process

Conditions

- Temperature: 450°C
- Pressure: 200-300 atm
- Catalyst: Iron
- Equation: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Optimization Factors

1. Temperature effects:
    - Forward reaction is exothermic

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- Lower temperature favors NH_3 formation
- Higher temperature increases reaction rate
- 450°C is optimum compromise

2. Pressure effects:
   - Higher pressure favors NH_3 formation
   - 4 volumes → 2 volumes
   - Limited by equipment costs
3. Catalyst role:
   - Iron with Al_2O_3 and K_2O promoters
   - Lowers activation energy
   - Doesn't affect equilibrium position

Example calculation: Calculate % yield if 10.0g NH_3 is produced from 5.0g N_2:

- Theoretical yield from equation:
  - $N_2 + 3H_2 \rightarrow 2NH_3$
  - 28g N_2 yields 34g NH_3
  - 5.0g N_2 should yield (5.0 × 34/28) = 6.07g NH_3
- Actual yield = 10.0g
- % yield = (actual/theoretical) × 100
- % yield = (10.0/6.07) × 100 = 164.7%

6. Ammonium Compounds as Fertilizers

Common Fertilizers

1. Ammonium nitrate (NH_4NO_3)
   - 34% nitrogen content
   - Highly soluble
   - Risk of explosion
2. Ammonium sulfate ($(NH_4)_2SO_4$)
   - 21% nitrogen content
   - More stable than nitrate
   - Acidifies soil

Advantages

- High nitrogen content
- Water-soluble
- Quick nitrogen release
- Cost-effective

7. Laboratory Preparation of Ammonia

Method

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1. Heat ammonium salt with strong base
2. Equation: $NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$

Apparatus Setup

1. Round-bottom flask
2. Delivery tube
3. Gas collection by downward delivery
4. Drying tower (optional)

Test for NH_3:

- Red litmus turns blue
- White fumes with HCl
- Turns Cu^{2+} solution deep blue

8. Uses of Ammonia and Compounds

Industrial Applications

1. Fertilizer production
2. Nitric acid manufacture (Ostwald process)
3. Explosives
4. Plastics
5. Cleaning products

Nitric Acid Production

1. Oxidation: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
2. Further oxidation: $2NO + O_2 \rightarrow 2NO_2$
3. Absorption: $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

9. Nitrate Fertilizers

Types

1. Sodium nitrate ($NaNO_3$)
2. Potassium nitrate (KNO_3)
3. Ammonium nitrate (NH_4NO_3)

Environmental Impact

- Eutrophication
- Groundwater contamination
- Soil acidification

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- N_2O emissions

10. Nitrogen Oxides in Atmosphere

Sources

1. Natural
   - Lightning
   - Bacterial action
   - Forest fires
2. Anthropogenic
   - Vehicle emissions
   - Power plants
   - Industrial processes

Environmental Effects

1. Acid rain formation
   - $NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
   - Damages buildings
   - Affects aquatic life
2. Photochemical smog
   - NO_2 + sunlight $\rightarrow NO + O$
   - $O + O_2 \rightarrow O_3$ (ozone)
   - Respiratory problems

Example calculation: Calculate volume of NO_2 produced from 2.5L of NO: $2NO + O_2 \rightarrow 2NO_2$

- From equation, volumes are equal
- Therefore, 2.5L NO produces 2.5L NO_2

Practice Questions

1. Explain why NH_3 is more basic than PH_3.
2. Calculate the equilibrium constant for the Haber process at 450°C.
3. Describe the environmental impact of excess nitrate fertilizers.
4. Compare the nitrogen content in different fertilizers.
5. Explain the role of iron catalyst in the Haber process

1. Sulfur and its Properties

Physical Properties

- Yellow solid at room temperature
- Several allotropes (different forms)

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- Low melting point (119°C)
- Insoluble in water
- Soluble in organic solvents

Allotropes of Sulfur

1. **Rhombic Sulfur (α-sulfur)**
   - Stable below 95.5°C
   - Yellow, octahedral crystals
   - S_8 rings in crystal structure
2. **Monoclinic Sulfur (β-sulfur)**
   - Stable between 95.5°C and 119°C
   - Needle-like crystals
   - Also S_8 rings, different arrangement

Example: Transition Temperature Calculation

- If 2.0g of rhombic sulfur absorbs 0.38 kJ when converting to monoclinic sulfur at 95.5°C
- Calculate the enthalpy change per mole:
   - Moles of S_8 = 2.0/(32 × 8) = 0.00781 mol
   - ΔH = 0.38/0.00781 = 48.7 kJ/mol

2. Sulfur Oxides

Sulfur Dioxide (SO_2)

1. **Physical Properties**
   - Colorless gas
   - Pungent smell
   - Highly soluble in water
   - Dense than air
2. **Chemical Properties**
   - Acidic oxide
   - Reducing agent
   - Forms sulfurous acid in water
   - Can be oxidized to SO_3
3. **Preparation Methods**

$S + O_2 \rightarrow SO_2$

$2H_2SO_3 \rightarrow SO_2 + H_2O + SO_2$

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

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Sulfur Trioxide (SO_3)

1. **Properties**
   - White fumes
   - Reacts violently with water
   - Forms H_2SO_4
2. **Formation**

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (V_2O_5 catalyst)

Example Calculation: Calculate the volume of SO_2 produced when 5.0g of sulfur is burned in excess oxygen:

- Equation: $S + O_2 \rightarrow SO_2$
- Moles of S = 5.0/32 = 0.156 mol
- Moles of SO_2 = 0.156 mol
- Volume at RTP = 0.156 × 24 = 3.74 L

3. Acid Rain Formation and Effects

Formation Process

1. **Primary Pollutants**
   - SO_2 from fossil fuels
   - NO_2 from vehicles/industry
   - CO_2 from combustion
2. **Chemical Reactions**

$SO_2 + H_2O \rightarrow H_2SO_3$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

Environmental Effects

1. **Aquatic Ecosystems**
   - Lowers pH of water bodies
   - Affects fish populations
   - Disrupts food chains
   - Releases toxic metals
2. **Terrestrial Effects**
   - Soil acidification
   - Reduced crop yields

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- Forest damage
- Building/monument erosion

3. **Economic Impact**
    - Agricultural losses
    - Infrastructure damage
    - Health care costs
    - Tourism reduction

Example: pH Calculations If rain water has $[H^+] = 1.0 \times 10^{-4}$ mol/dm³:

- $pH = -\log[H^+]$
- $pH = -\log(1.0 \times 10^{-4})$
- pH = 4.0 (acidic rain)

4. Sulfuric Acid (H_2SO_4)

Industrial Production (Contact Process)

1. **Stage 1: SO_2 Production**

$S + O_2 \rightarrow SO_2$

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

2. **Stage 2: SO_2 to SO_3**

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

Conditions:

- Temperature: 450°C
- Pressure: 1-2 atm
- Catalyst: V_2O_5

3. **Stage 3: H_2SO_4 Formation**

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum)

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Properties of H_2SO_4

1. **Physical Properties**
    - Dense, oily liquid

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    - Colorless
    - High boiling point
    - Miscible with water
2. **Chemical Properties**
    - Strong diprotic acid
    - Dehydrating agent
    - Oxidizing agent
    - Forms two series of salts
3. **Reactions**

With metals: $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

With bases: $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Dehydration: $C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$

Example: Concentration Calculations Calculate the mass of H_2SO_4 in $250cm^3$ of 0.5M solution:

- Moles = concentration × volume
- Moles = 0.5 × 0.250 = 0.125 mol
- Mass = moles × Mr
- Mass = 0.125 × 98 = 12.25g

Practice Questions

1. Explain the conditions required for the Contact Process and their importance.
2. Calculate the pH of rainwater samples and explain their environmental impact.
3. Write balanced equations for the reactions of concentrated H_2SO_4 with: a) Copper b) Sodium hydroxide c) Sugar (dehydration)
4. Describe the industrial production of H_2SO_4 using flow diagrams.
5. Compare the properties of rhombic and monoclinic sulfur.

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