

Preparation of Zinc Cyanide and Elimination of Free Alkali in Cyanide

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Abstract. Zinc cyanide can be prepared by double decomposition reaction of sodium cyanide or potassium cyanide with zinc chloride. Before the preparation of zinc cyanide, it is necessary to remove the free alkali in the raw material sodium cyanide or potassium cyanide. Magnesium chloride is used to remove the free alkali in sodium cyanide or potassium cyanide. The concentration of cyanide ion in potassium cyanide solution under different conditions is measured. The results show that magnesium chloride can not only remove the original free alkali in potassium cyanide, but also promote the hydrolysis of potassium cyanide to produce new free alkali and react with it to form new precipitate. By analyzing the components of the precipitate, it is determined that the main components in the precipitation are Mg(OH)₂ and MgCO₃. The final conclusion: after the free alkali in cyanide is removed by magnesium chloride, the solution must be quickly put into the double decomposition reaction to reduce the further loss of cyanide ion; In the preparation of zinc cyanide, the adding order needs to be noted: the cyanide aqueous solution must be added into the zinc chloride solution to ensure the excess of zinc chloride.

1 INTRODUCTION

Zinc cyanide is a raw material needed in many chemical production. Zinc cyanide, potassium cyanide or sodium cyanide solid can be used to replace hydrocyanic acid for chemical reaction in some chemical production [1-3], which can reduce the harm of hydrogen cyanide poisonous gas to human body and environmental pollution to a certain extent. Zinc cyanide is usually prepared by double decomposition reaction of sodium cyanide or potassium cyanide with zinc chloride[4,5]. The preparation process is shown in the following figure:

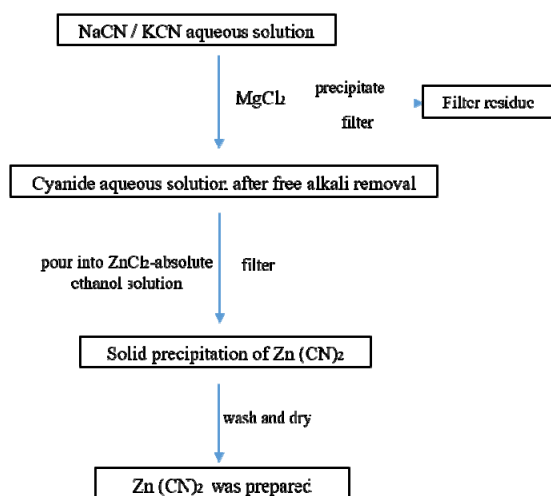


Fig.1 preparation process of zinc cyanide

Cyanide such as potassium cyanide and sodium cyanide are often used as raw materials for chemical experiments or industrial synthesis. They are easily soluble in water and ethanol, and are highly toxic dangerous chemicals. Their aqueous solutions are strongly alkaline and hydrolyzed. At low temperature, the hydrolysis of cyanide is reversible; at high temperature, part of hydrogen cyanide volatilizes, resulting in the acceleration of hydrolysis rate.

Based on the above characteristics, it can be preliminarily inferred that solid potassium cyanide and sodium cyanide are easy to deteriorate in humid air[6]. Therefore, it is inevitable to produce free alkali during the storage of this kind of cyanide. Taking potassium cyanide as an example, the equation is as follows:

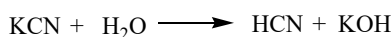
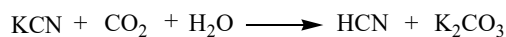


Fig. 2 deterioration of potassium cyanide in air

A small amount of alkali is often added to some industrial cyanide to reduce its hydrolysis degree. However, these free alkali sometimes bring some troubles to its subsequent synthesis and chemical production.

In the synthesis experiment of zinc cyanide, the free alkali in potassium cyanide or sodium cyanide will be removed before the reaction of potassium cyanide or sodium cyanide with zinc chloride to reduce the interference of subsequent reaction[4]. In theory, a small

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amount of magnesium chloride can be used to eliminate free alkali in cyanide solution by precipitation reaction:

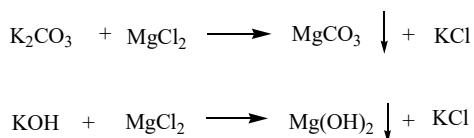


Fig. 3 precipitation reaction of free alkali

2 Free alkali removal experiment

Potassium cyanide (or sodium cyanide) solid was completely dissolved in 100 mL of water (the content of free alkali K_2CO_3 was calculated as 8% of cyanide mass used). Anhydrous magnesium chloride powder was slowly dissolved in 10 mL water and prevent overheating splash. Magnesium chloride solution is added into potassium cyanide (or sodium cyanide) aqueous solution, precipitation reaction occurs, filtration, the filtrate is cyanide aqueous solution after free alkali is removed.

2.1 Experimental phenomena

If magnesium chloride solution is added to the above filtrate again, it is found that there is still precipitation. Repeated filtration and adding magnesium chloride solution to the filtrate will always produce sediment. It was also found that the clarified aqueous solution of potassium cyanide (or sodium cyanide) after removal of free alkali could spontaneously produce flocculent precipitation after a period of time, which affected the subsequent steps; while the original cyanide aqueous solution without free alkali removal has no obvious change after being placed.

2.2 Determination of cyanide ion concentration

In order to further explore the causes of the above phenomena, the concentration of cyanide ion in potassium cyanide aqueous solution under different conditions was measured with a micro cyanide ion detector (T-CN).

The determination steps of cyanide ion concentration are as follows:

-Dissolve the solid potassium cyanide in water, and take a small amount of potassium cyanide aqueous solution as sample 1;

-Sample 1 was diluted by a certain multiple and detected immediately. The concentration of cyanide ion in sample 1 after dilution was measured to be $C_{(CN^-)_1}$;

-When the theoretical amount of magnesium chloride solution is added into the potassium cyanide aqueous solution, the white precipitate appears and the filter is carried out immediately. A small amount of filtrate is marked as sample 2;

-Sample 2 was diluted in the same way as sample 1, and the concentration of cyanide ion in Sample 2 after dilution was measured to be C_1 ;

-After several hours of storage, sample 1 did not change significantly, then, it was diluted by the same method, the concentration of cyanide ion in the diluted sample: $C_{(CN^-)_2}$;

-After several hours, it was found that the filter residue turned yellow, and the filtrate sample 2 changed from transparent to turbid, resulting in flocculent precipitate. The color of the precipitate and the solution gradually became darker. The sample 2 was diluted with the same method, and the concentration of cyanide ion was measured again as C_2 .

Repeat the above steps several times to reduce the error. All dilution methods and multiples are the same. The concentration refers to the concentration of cyanide ion, unit: mg / L. The results are shown in Table 1.

Table 1 Concentration change of CN^-

Number	Temperature (°C)	$C_{(CN^-)_1}$ (mg/L)	Storage Time (h)	$C_{(CN^-)_2}$ (mg/L)	C_1 (mg/L)	Storage Time (h)	C_2 (mg/L)
1	10	0.335	5	0.334	0.234	20	0.222
2	13	0.334	5.5	0.331	0.249	5.5	0.235
3	9	0.314	22.5	0.316	0.271	23	0.207
4	18	0.597	21	0.539	—	—	—
5	15	0.078	—	—	0.064	6	0.032

The values of $C_{(CN^-)_1}$ and $C_{(CN^-)_2}$ was compared: the concentration of cyanide ion did not change significantly after the potassium cyanide solution was placed, which shows that cyanide aqueous solution is stable; $C_{(CN^-)_1}$ compared with the C_1 and C_2 : It was found that the concentration of cyanide ion decreased significantly after magnesium chloride was added and filtered, the cyanide ion was still consumed after the filtrate was placed.

2.3 Component analysis of filter residue

In the reaction of removing free alkali, if the cyanide solution added with magnesium chloride is precipitated and not filtered immediately, the color of the precipitate will gradually darken from milky white to black, and the cyanide solution will also be dyed to a dark color, and the color of zinc cyanide synthesized with cyanide will also turn dark. In the precipitation reaction of removing free alkali by adding magnesium chloride, the precipitate (filter residue) produced by the old cyanide which has

been stored for a long time is darker than that of the new cyanide.

When the filter residue reacts with a small amount of dilute hydrochloric acid, it can dissolve a lot and release bubbles, but there is a small amount of black powder insoluble substance in the aqueous solution. In reaction, the bubbles released by the filter residue with darker color are often more than those of light color.

Through the analysis of the deterioration of cyanide, combined with the above phenomena, it is determined that, the main components in the filter residue are $Mg(OH)_2$ and $MgCO_3$, which react with dilute hydrochloric acid to release heat and produce CO_2 . The darker the color is, the more gas is released, that is, the more CO_3^{2-} . Therefore, it can be inferred that the color deepening of the precipitation reaction is directly related to the content of CO_3^{2-} in the cyanide. The longer the cyanide is placed, the more it reacts with CO_2 in the air, and the cyanide itself will gradually turn brown from white, and the precipitate (filter residue) after the removal of free alkali will become darker due to the presence of more CO_3^{2-} . A small amount of black powder insoluble substance remained in the solution after reaction with hydrochloric acid may be a small amount of insoluble impurities contained in cyanide and magnesium chloride itself, which is dyed to a dark color after precipitation reaction.

2.4 Conclusion

It can be concluded that cyanide aqueous solution is relatively stable at low temperature and will be hydrolyzed for a long time. The reason may be that the solid of cyanide contains free alkali such as OH^- , which can inhibit the hydrolysis of cyanide when dissolved in water.

After magnesium chloride was added into the solution, the free alkali was eliminated, and the concentration of cyanide ion in the filtrate decreased obviously. It can be concluded that magnesium chloride can not only remove the original free alkali in cyanide (caused by storage deterioration or industrial processing), but also promote the hydrolysis of cyanide to produce new free alkali, and react with it to produce new precipitation, which also explains the phenomenon of flocculent precipitation after the clarified filtrate is standing. Therefore, when magnesium chloride is used to remove the free alkali in cyanide, the precipitate must be filtered as soon as possible to prevent the color deepening of the system, and the cyanide solution should be quickly put into the next reaction to avoid further hydrolysis.

In addition, in order to remove the free alkali from cyanide solution, if barium chloride is used to remove CO_3^{2-} , the free OH^- can inhibit the further hydrolysis and consumption of cyanide ion to a certain extent, but excessive OH^- may still have certain impact on the subsequent reaction. Therefore, magnesium chloride should be used to remove CO_3^{2-} and OH^- as much as possible.

3 Preparation of zinc cyanide

Potassium cyanide or sodium cyanide were used as raw materials, react with zinc chloride to get zinc cyanide solid through filtration.

3.1 Preparation steps

Anhydrous zinc chloride solid (20% more than the theoretical amount) was dissolved in about 50 mL of absolute ethanol. The reaction was exothermic and the dissolution was promoted by stirring. Zinc chloride-absolute ethanol solution was filtered to obtain clear solution. After the removal of free alkali, the clarified aqueous solution of sodium cyanide (or potassium cyanide) was slowly added into the clear solution of zinc chloride-absolute ethanol. The double decomposition reaction occurred, and the system exothermic, and the temperature increased by $22^\circ C$. The pure white precipitate just started to float on the surface. With the addition of sodium cyanide (or potassium cyanide) aqueous solution, the white substance gradually diffused to the surface until a large amount of precipitate was produced in the reaction bottle. After 30 minutes, when the temperature drops and the precipitation reaction is finished, the solid is repeatedly washed with water and 95% ethanol, and dried. The pure white powdered zinc cyanide is 16.73g, and the yield is 91.33%. The concentration of cyanide ion in the solution before and after the double decomposition reaction was measured by the method of concentration difference. The purity of zinc cyanide was 94.79%. The concentration of cyanide ion in the filtrate was 0 mg/L, indicating that CN^- reaction was complete.

3.2 Effect of adding order of raw materials on yield

It was found that the different adding order of sodium cyanide (or potassium cyanide) and zinc chloride would affect the yield of zinc cyanide. When cyanide aqueous solution is slowly added into zinc chloride solution, the white precipitate produced floats on the surface and does not dissolve, and the final yield is generally above 90%; if the zinc chloride solution is slowly added to the cyanide aqueous solution, the white precipitate will sink into the bottom of the solution at the beginning, and the precipitate will disappear after shaking, and the final yield of zinc cyanide will be less than 90%.

3.3 Conclusion

In the preparation of zinc cyanide, in order to prevent the zinc cyanide obtained by reaction from dissolving in excess cyanide to form compound salt such as $Na_2Zn(CN)_4$ (showing white precipitate disappearing), affecting the yield, so the order of adding raw materials must be adding cyanide aqueous solution into zinc chloride solution, and the amount of zinc chloride is more than cyanide.

4 Summary

The preparation of zinc cyanide mainly consists of two parts, one is the removal of free alkali in cyanide, the other is the double decomposition reaction of cyanide and zinc chloride.

-Since cyanide aqueous solution has the characteristics of hydrolysis, when removing free alkali, after the precipitation reaction is stable, the filtration is carried out quickly, then, the filtrate is quickly put into the next step of double decomposition reaction to prevent further loss of cyanide ion.

-Zinc chloride is easy to hydrolyze in water, so water should be avoided as far as possible when preparing zinc chloride solution, and a small amount of absolute ethanol should be used to dissolve zinc chloride solid.

-In the double decomposition reaction, in order to prevent the product zinc cyanide from dissolving in the cyanide aqueous solution to form compound salt, it is necessary to add the cyanide aqueous solution into the zinc chloride solution slowly and keep the excess zinc chloride all the time.

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