Effect of Cryogenic Distillation and Chemical Absorption on the Argon Concentration in Krypton Purification

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Abstract. Cryogenic distillation and chemical absorption are two important means of inert gas purification. Experiments show that the order of the two methods has an effect on the final purification result. In order to verify the relationship between the retention of argon and the order of the two methods, experimental verification was designed. At the same time, the numerical simulation was carried out by using the principle of low temperature distillation, and the influence results of the two methods on the argon content after gas purification was obtained.

1. Introduction
Gas cryogenic distillation refers to the enrichment and separation of one or more components of the mixed gas in the conditions of different low temperature by using different saturated vapor pressures of different gases. During the distillation process under low temperatures, the following to meet the relationship is met all the time1:

\[ n_i = P_i X_i \frac{V_g}{RT} + LX_i \]

\[ V_{tot} = \frac{(\Sigma n_i - L)RT}{\Sigma P_i X_i} + \Sigma LX_i \frac{m_i}{d_i} \]

The relevant parameters are shown as the table below.

| Gas | Volume fraction (%) | Moore quality (g/mol) | Gas liquid density (g/mL) | Saturated vapor pressure (77K, Pa) |
|-----|---------------------|-----------------------|---------------------------|----------------------------------|
| N₂  | 78.1                | 28.01                 | 0.808                     | 97056                            |
| O₂  | 21                  | 32.00                 | 1.141                     | 19632                            |
| Ar  | 0.93                | 39.94                 | 1.400                     | 25750                            |
| Kr  | 1.14 × 10⁻⁴         | 83.80                 | 2.740                     | 220                              |

In order to understand the principle of low temperature distillation and master the relevant parameters of the final degree of low temperature distillation, the following simulation is carried out:
Assuming a closed container volumed of 100 mL, 10 L of the sample was compressed into the vessel and the vessel was immersed in liquid nitrogen. Under such condition the sealed container had both liquid and gas phases. The continuous low-temperature distillation process is carried out. Assuming that the low-temperature distillation process is an infinite vapor phase extraction process, it is assumed that 10% volume of the gas phase in the vessel is extracted and the gas phase is immediately added in after each extraction, after a large number of iterations has been carried out, the relationship between the ratio of the retention value (the ratio of the remaining amount to the total amount of the component in the original sample) and the number of iterations of the various components in the container is shown in the Figure 1.

Figure 1. Numerical Simulation of Air Low Temperature Distillation

The use of sponge titanium to remove nitrogen and oxygen in gas samples is one of the most commonly used methods in the inert gases purification. Sponge titanium lump is composed of numerous small sponge titanium stacking accumulated macro body. Loose porous structure gives it a large specific surface area. It's conducive to its chemical reaction with the gas. Titanium sponge is covered with a layer of oxide, mainly titanium dioxide, under room temperature, it hinders the chemical reaction between different gases and titanium. So the performance of the titanium is stable and room temperature. However, the protective layer will rupture when the temperature gradually increased. With the temperature rising, the reaction rate of the gases with the titanium sponge was accelerated. So the reaction of titanium with gases and temperature are directly related. Under different temperatures, titanium can produce stable, irreversible titanium compounded with gases like oxygen and nitrogen, other than inert gases. Under atmospheric pressure of about 500 °C, sponge titanium begin to produce titanium dioxide and titanium oxide with oxygen. Titanium dioxide and carbon are produced with carbon dioxide. React with water to produce titanium dioxide with hydrogen released. Under 800 to 900 °C sponge titanium react to form titanium nitride with nitrogen.

2. Experimental Methods
Two experiments were designed as a comparison. Each controls 1L gas into the system. The total volume of the system is measured as 815mL. In the first group of experiments, the first step is to freeze the gas in the liquid nitrogen temperature, and extract air with a mechanical pump, next perform the operation of low-temperature distillation, then put the remaining gas into the sponge heating furnace to heat, and finally the total pressure inside the system is measured to reflect the effectiveness of argon removal.

In the second group of experiments, gas will be put into the titanium sponge firstly to make, gas and the hot sponge titanium completely react, and then pass the remaining gas through the cold trap of activated carbon under liquid nitrogen temperature, next, perform the operation of low temperature
distillation. In the meantime, record the final gas pressure in the system. Compared with the first set of experiments.

3. Results and Discussion

3.1. Results

After two sets of experiments, the results were as follows:

|                            | Start pressure value (Pa) | Final pressure (Pa) | Pressure difference (Pa) | Argon residual rate |
|---------------------------|---------------------------|---------------------|--------------------------|---------------------|
| The first group of experiments | 53Pa                      | 128Pa               | 75Pa                     | 8.06%               |
| The second group of experiments | 50Pa                      | 301Pa               | 261Pa                    | 27.9%               |

3.2. Simulation

The effect on the argon content of the order of adsorptive distillation and sponge titanium determines the concentration of argon the process of adsorptive distillation. When the adsorptive distillation is carried out firstly, the concentration of argon is the same as in the atmosphere, the value is 0.934%. If the sponge titanium reaction is performed in the first place, argon concentration will greatly increase.

In the first group of experiments, the concentration of the gas component was consistent with the concentration of air components. In order to know the concentration of argon in the second group of experiments, the composition of the gas subjected to the sponge titanium absorption operation was first analyzed and the following conclusions were obtained as Figure 2.

![Figure 2. Air component after sponge titanium reaction](image)

It can be said that after the sponge titanium reaction of the gas, nitrogen, oxygen content is minimal, the main component turns into argon, and the volume is also reduced by one hundred times. Therefore, assume that the simulation conditions are as follows: After the sponge titanium reaction, the sample gas is 10mL and the volume of the activated carbon cold trap is 5mL. The volume fraction of each component of the sample gas is shown as the Table 3:
Table 3. Sample component volume fraction of the adsorption Distillation Simulation assumption

| Ingredient | Ar  | N₂  | O₂   | Kr  |
|------------|-----|-----|------|-----|
| Volume fraction | 0.95 | 0.04 | 0.01 | $10^{-4}$ |

Using the related data in formula 1 and Table 1, for the result of numerical simulation calculation shows, the relationship between constituent retention rate and the total distillation time between the relationships as below.

![Figure 3. Comparison of low temperature distillation processes of different air content.](image)

As shown, in order to ensure the recovery rate of krypton unchanged, argon needs to be surplus. By analyzing the results of the simulation data, the conclusion is reached that the concentration of krypton began to decrease rapidly at 92%, in the first group of experiments, the residual rate of argon was 1.7% when the total amount of krypton was 92%. In the he second group of experiments, the residual rate of argon was 9.1% when the total amount of krypton was 92%. The experimental results are in good agreement with the simulation results.

4. Conclusion
1. Low temperature distillation has a strong effect on the separation and purification of krypton gas. After this process, the concentration of krypton in the gas can be improved by one hundred times.
2. Sponge Titanium has a strong gas absorption capacity, and through the sponge titanium reaction nitrogen and oxygen gas is almost absorbed completely.
3. The sequence of low temperature distillation and sponge titanium adsorption has an effect on the removal of argon in the gas. The first low-temperature distillation operation can lower the proportion of argon in the gas.

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