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UNITED STATES PATENT OFFICE.

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PURIFICATION OF GASES.

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To all whom it may concern:

Be it known that I, ROY GRIFFITH JONES, a citizen of the United States, and a resident of Bloomfield, in the county of Essex and State of New Jersey, have invented a new and useful Improvement in Purification of Gases, of which the following is a specification.

This invention relates to the purification of gases, and more particularly it relates to the separation of monatomic from diatomic gases.

An object of the invention is the provision of a simple, economical and rapid method for the separation of rare or monatomic gases from common or diatomic gases.

Another object of the invention is the provision of a process for obtaining rare or noble gases in a very high state of purity.

A further object of this invention is the provision of a process for controlling the degree of purity of monatomic or elastic gases.

Other objects will be apparent from a reading of the specification.

It is well known that the rare gases, which exist mostly in the atmosphere, constitute such a very small percentage of the same that it is difficult to obtain large quantities in a very pure condition. It is now possible to obtain the rare gases in a comparatively high state of purity, say about 98%, by the liquefaction of air and subsequent fractional separation of the constituents. It is also possible to separate the monatomic from the diatomic gases and obtain a purity of about 98% of the former by passing a mixture over heated calcium carbide. For many purposes, however, such as for use in gas-filled electrical-discharge devices, it is necessary for the successful operation of the same that only monatomic gases be used and that these be practically 100% pure. This is especially true in an electrical-discharge device which it is necessary to operate at a low voltage, since the ionization potentials of some of the rare gases are lower than those of the common gases.

The use of pure monatomic gases is also valuable and necessary when it is desired to pass an electrical discharge through a gas at a potential less than the ionizing potential of the same; this is due to the fact that conduction may take place through a monatomic gas at the resonance potential, which is lower than the ionization potential, whereas conduction does not occur in diatomic gases below the ionization potential. Very small amounts, however, of common gases, when inter-mixed with the noble gases, raise the discharge potential greatly and result in ionization when conduction begins.

A hot-cathode gas-filled rectifier is an example of a device which it is necessary to operate below the ionization potential of the gas because, if operated at or above this potential, positive ions bombard the hot cathode and destroy it. This would be the case if a very small percentage of a diatomic gas were present, since this gas would be ionized. However, by using a substantially pure monatomic gas, the discharge can take place without substantial ionization and, consequently, without deterioration of the cathode.

For the separation of the monatomic from the diatomic gases, I employ reagents which are capable of combining with the diatomic or common gases and which form therewith reaction products having a negligibly low vapor pressure. According to my invention, the reagent employed to combine with the gaseous impurities is raised to the highest temperature necessary, and the gas to be purified is preferably repeatedly circulated over or through the heated reagent and in contact therewith. While it is necessary for rapid purification to heat the reagent to a comparatively high temperature to activate it, complete purification cannot be obtained by keeping the reagent at this temperature. I have found, however, that rapid and complete purification may be effected by reducing the temperature of the reagent while continuing the circulation of the gases in contact therewith. I have found also that there is a definite relation between the temperature to which the reagent is cooled while circulating the gas and the purity of the latter, the purity increasing as the temperature of the reagent decreases. One cause for this may be that the dissociation of the reaction products is less at low than at high temperatures, so that there is less re-contamination of the gas at the low temperature.

The reagent used to purify a monatomic gas may be any solid which requires heating above room temperature to activate it and which will react with the impurity to be eliminated to form solid compounds of low vapor pressure at reduced temperatures.

Since it is frequently necessary to eliminate several impurities from a monatomic gas, any required number of purifying agents may be used, either simultaneously or in succession, each agent being selected as the best eliminant of a given impurity. I have found it convenient, however, to use metals, such as barium, strontium, magnesium and calcium, which combine with and fix all the diatomic gases commonly found in the rare gases. Calcium is especially valuable in this way as it reacts rapidly with every gas having valency, that is, with all gases except those of the zero group of the periodic table, to form solid compounds. For the purpose of simplicity and illustration, therefore, discussion of the purifying agent will be restricted to calcium.

In the separation of nitrogen, for example, from a monatomic gas, such as argon, it is found that it is necessary to heat the calcium to a temperature in the neighborhood of 700° in order to start the reaction with nitrogen, but it is also found that the argon cannot be obtained in its highest state of purity if repeatedly passed over calcium at its reaction temperature. The reason for this is probably due to the fact that, while the calcium combines with impurities at this temperature, the reaction is reversible, or, in other words, the reaction products are partially dissociated at the activation temperature so that there is always present in the gas small amounts of impurities which are released by association. This may be illustrated by the equation:

$$3Ca_2+2N_2=2\,Ca_3N_2.$$

The nature of the reaction between calcium and nitrogen is such that it does not proceed completely to the right at high temperatures, the calcium nitride slightly decomposing which causes the reaction to go to the left.

When water vapor, for example, as well as nitrogen, is to be separated from the monatomic gases, the maintenance of the calcium at the temperature necessary for it to combine with the nitrogen is very probably so high that the reaction products resulting from the combination of calcium and water vapor are decomposed. It is found, however, that by circulating the mixture of a monatomic and a common gas repeatedly over calcium at its reaction temperature and continuing to circulate the gases while the calcium is slowly cooled, a very pure monatomic gas is obtained.

If a monatomic gas containing a definite amount of a diatomic gas is desired, the temperature of the calcium can be brought down to the temperature corresponding to the degree of purity desired. As an illustration of the beneficial action of the gradual cooling of the calcium, the following table is submitted showing the relation of temperature to purity.

Temperature of furnace.	Arc drop in argon.
700° C.	13.0
600	11.5
500	11.0
400	9.0
300	8.0
250	7.0
185	6.0
35	4.0

The percentage purity of the gas, however, (argon in this case), is not stated directly in this table, but a function of the purity is shown. This function is the voltage drop in the arc of a hot-cathode device in which the discharge passes through a monatomic gas combined with small amounts of impurities. It is found that the arc drop in such a device is a function of the purity of the gas through which the discharge passes, the arc drop becoming less the purer the monatomic gas through which the discharge passes. For example, an arc drop of 7 volts will indicate a purer gas than an arc drop of 13 volts measured under the same conditions of gas pressure, cathode temperature, distance of the anode from the cathode, current through the device, materials of the electrodes, etc.

It will be noted from the table that the gas becomes purer and lower the temperature to which the calcium is brought while passing the gas to be purified continuously over it. By cooling the calcium below room temperature, it is possible that such action may lead to a still further increase in purity, although it is found that a monatomic gas, practically 100% pure, as shown by the spectroscope, can be obtained by cooling the calcium to room temperature.

In practicing this invention, the calcium is preferably placed in a divided condition in nickel tubes or boats, which are placed inside closed steel tubes which, in turn, are placed in a furnace and heated to the required temperature. It is found that this method for separating the common from the rare gases enables me to purify a large quantity of gas in a very short period of time and to effect a complete separation of the monatomic from the diatomic gases.

Minor modifications may readily be made in the process as above described to attain the same results, but it is to be understood that such modifications come within the scope of this invention, as embraced in the appended claims.

What is claimed is:

1. The step in the process of separating a monatomic from a diatomic gas which consists in gradually reducing the temperature of a heated purifying agent.

2. The process of separating a monatomic

from a diatomic gas comprising gradually reducing the temperature of a heated purifying agent, while circulating a monatomic and a diatomic gas in contact therewith.

3. The method of controlling the purity of a monatomic gas which consists in circulating a mixture of a monatomic and a diatomic gas in contact with a purifying agent heated to its reaction temperature and subsequently reducing the temperature of said agent to a point corresponding to the desired degree of purity of the monatomic gas while continuing the circulation of said mixture in contact with said agent.

4. The process of separating a monatomic from a diatomic gas which consists in circulating a mixture of these gases in contact with a purifying agent heated to its reaction temperature and subsequently reducing the temperature of said agent while continuing the circulation of said gases in contact therewith.

5. The process of separating a monatomic from a diatomic gas which consists in circulating a mixture of these gases over a purifying agent heated to its reaction temperature and subsequently cooling said agent to a point at which the dissociation of the reaction products is negligible.

6. The process of separating a monatomic from a diatomic gas which consists in circulating a mixture of these gases in contact with calcium heated to its reaction temperature and subsequently reducing the temperature of the calcium while continuing the circulation of said gases in contact therewith.

7. The method of controlling the purity of a monatomic gas which consists in circulating a mixture of a monatomic and a diatomic gas in contact with calcium heated to its reaction temperature and subsequently reducing the temperature of said calcium to a point corresponding to the desired degree of purity of the monatomic gas while continuing the circulation of said mixture in contact with the calcium.

8. The method of obtaining pure argon from a mixture with diatomic gases which consists in circulating a mixture of said gases over calcium heated to its reaction temperature and subsequently reducing the temperature of the calcium to a point at which the dissociation of the reaction products is negligible.

9. The method of obtaining pure argon from a mixture of argon, oxygen, nitrogen and water vapor which consists in circulating a mixture of said gases over an alkaline earth metal heated to its reaction temperature and subsequently reducing the temperature of said metal to a point at which the dissociation of the reaction products is negligible.

In testimony whereof, I have hereunto subscribed my name this 31st day of December, 1921.

ROY GRIFFITH JONES.