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PRODUCTION OF METAL HYDRIDES

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Fig. 1.

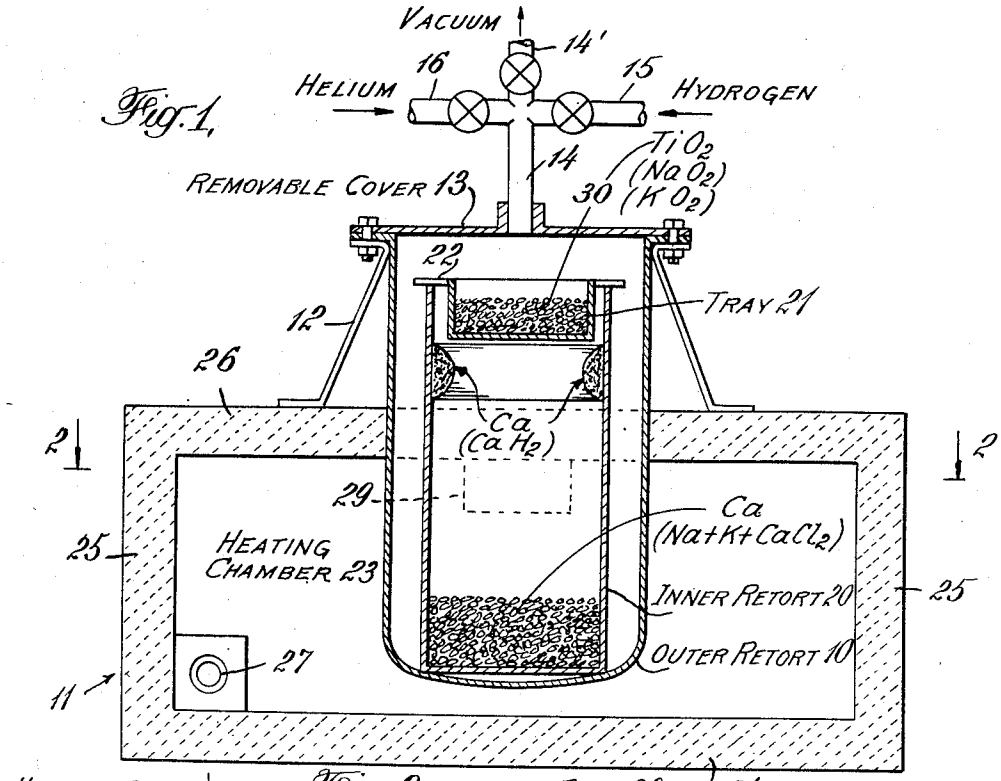
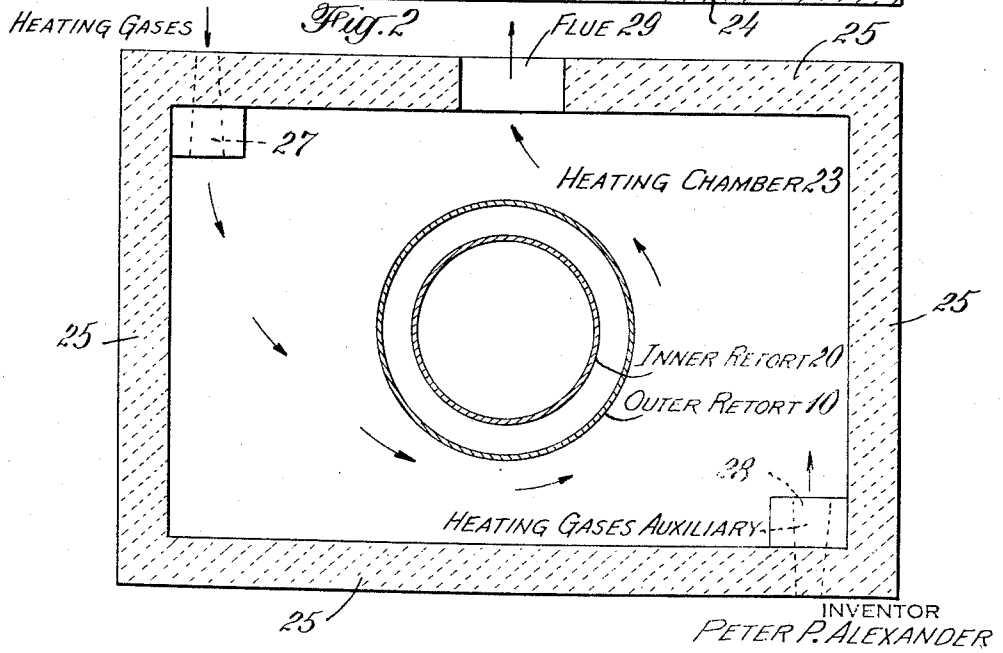


Fig. 2.



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PRODUCTION OF METAL HYDRIDES

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28 Claims. (Cl. 23—204)

This invention relates to the production of substantially pure metal hydrides and has for its object more particularly the production of substantially pure metal hydrides from hydride-forming metals of comparatively low boiling point which are contaminated with metal impurities of lower boiling point.

It is known that a number of metals react directly with hydrogen at a sufficiently high temperature to form corresponding metal hydrides. The purity of the metal hydride conforms to that of the metal used to make the hydride. If a standard grade of electrolytic calcium, for example, which has an average purity of about 90%, is used, the resulting calcium hydride will also have a purity of about 90%; because, during the formation of a hydride, hydrogen is merely added and adsorbed by the metal until the metal hydride is formed. To produce a metal hydride of high purity, it is therefore necessary to use a metal of high purity.

In some cases, however, high purity metals are difficult to handle safely. This is especially true of the alkaline earth metals contaminated with alkali metals. The alkaline earth metals, calcium, strontium and barium, are usually made by subjecting their fused chlorides to electrolysis. Since the salts of the alkali metals, sodium and potassium, are usually present in these chlorides, the resulting alkaline earth metal is usually contaminated with a small amount of alkali metal, as well as of the chloride of the alkaline earth metal itself. To purify the alkaline earth metal, it has been proposed to subject the metal to distillation in a closed retort that has been evacuated to remove objectionable air. The distilled metal is permitted to condense in a cooler part of the retort, usually in the form of a more or less spongy deposit. After cooling the retort, air is admitted, the retort is opened and the condensed metal is removed. The resulting product is so reactive that it frequently oxidizes rapidly on the surface and produces heat in sufficient amount to ignite the whole mass, with the result that fires are quite common. This objectionable result is all the more apt to occur because of the presence of the more highly reactive alkali metals, sodium and potassium. These alkali metals are also distilled and condense in a cooler part of the retort. The small deposits of sodium and potassium are so reactive that they almost invariably catch fire when the retort is opened and they come in contact with the oxygen of air. If by skillful manipulation the condensed calcium is removed successfully from the retort, it is then placed in another retort; the retort is closed, filled with hydrogen and heated until the hydrogen reacts with the calcium to form substantially pure calcium hydride. These operations are dangerous and require considerable time.

As a result of my investigations, I have discovered that these disadvantages may be overcome for the most part. The alkali metals, sodium and potassium, may be distilled and segregated from the alkaline earth metals in a form to make them non-inflammable on exposure to the oxidizing influence of air. The alkaline earth metal likewise may be distilled and separately collected and at the same time be substantially freed of its chloride. The alkaline earth metal is preferably retained in the retort in which it is distilled and converted into calcium hydride in situ.

In accordance with the invention, a hydride-forming metal contaminated with metal impurity of lower boiling point is heated in the absence of air to a temperature at which the metal impurity is distilled. The resulting metal impurity vapor is selectively oxidized by bringing it into reactive contact with a metallic oxide located away from the main body of the hydride-forming metal. The oxidized metal impurity is collected as a solid separate from the hydride-forming metal. The hydride-forming metal is itself distilled and condensed as a solid separate from the oxidized metal impurity and hydride-forming metal residues. The condensed hydride-forming metal is brought to a temperature at which it reacts with hydrogen, after which it is brought into reactive contact with hydrogen until it is converted to metal hydride. The substantially pure metal hydride is then suitably recovered.

These and other features of the invention may be better understood by referring to the accompanying drawing, taken in conjunction with the following description, in which:

Fig. 1 is a diagrammmatic representation, being a side elevation in section, of an apparatus with which the method of the invention may be practiced; and

Fig. 2 is a horizontal section on the line 2—2 of Fig. 1.

The apparatus shown comprises an outer retort 10 supported within a heating furnace 11, the retort being held in position by means of two or more supports 12 resting on top of the heating furnace. The retort preferably consists of heat-resistant steel. It is fitted with a removable cover 13 having attached thereto a vertical pipe 14, provided with lateral valved branches 15 and 16, connectable with a source of hydrogen, and

helium, respectively, and a vertical valved branch 14', connectable with a source of vacuum. A removable inner retort 20, having an open top, fits within the outer retort. A removable tray 21 rests over the open top of the retort, being supported thereon by means of three or more lugs 22 extending over the wall of the inner retort. The heating furnace 11 consists essentially of a rectangular chamber 23 having a refractory bottom 24, side and end walls 25, and a top 26 having an opening of a size adapted to receive the outer retort. An expanding opening 27 is provided at or near a lower corner of one of the side walls of the chamber, for the introduction of heating gases into the chamber. A similar opening 28 is preferably provided at or near an opposite corner, as a spare or auxiliary means for introducing heating, or cooling, gases into the chamber. When not in use, the opening 28 is closed. A flue opening 29 extends through the same wall as the opening 27, preferably at a higher level, so that heating gases passed into the chamber through the opening 27 tend to pass almost completely around the retort before leaving the chamber through the flue opening 29.

The apparatus may be used as follows: A charge of calcium, for example, contaminated with sodium, potassium, and calcium chloride, is placed in the bottom of the inner retort 20. The inner retort is then placed in the outer retort 10. A layer of titanium oxide 30 is placed in the tray 21, which is in turn placed across the open top of the inner retort. The removable cover 13 is placed on the outer retort 10 and locked thereon to provide a sealed joint. The vertical branch 14' is then connected to a source of vacuum. With the valve of this vertical branch open, and the valve of the lateral branches 15 and 16, closed, the outer and inner retorts are placed under vacuum to remove objectionable air.

Heating gases are passed through opening 27 into the heating chamber, where they circulate almost completely around the retort and then pass through the flue opening 29 to the outside atmosphere. As the lower portion of the outer retort 10 is heated, the lower portion of the inner retort 20 is also heated. As the temperature rises, a point is reached where the sodium and potassium present in the calcium are distilled. The resulting sodium and potassium vapors rise to the upper and cooler portion of the retort where they come in contact with the titanium oxide 30 in the tray 21. Due to their great affinity for oxygen, the sodium and potassium are promptly oxidized and the titanium dioxide is reduced to titanium and a sub-oxide of titanium according to reactions which may be indicated as follows:

$$Na+TiO_2 \rightarrow NaO_2+Ti$$
$$Na+4TiO_2 \rightarrow NaO_2+2Ti_2O_3$$
$$K+TiO_2 \rightarrow KO_2+Ti$$
$$K+4TiO_2 \rightarrow KO_2+2Ti_2O_3$$

As the temperature at the bottom of the inner retort continues to rise, a point is reached where the calcium is distilled and its resulting vapor tends to condense and settle out against the wall of the inner retort immediately below the tray 16. Some calcium vapor may of course rise sufficiently to come in contact with titanium dioxide in the tray and react with it in a manner similar to sodium or potassium vapor. The bulk of the distilled calcium may, however, be separately condensed and collected, as shown. A residue consisting essentially of calcium chloride, admixed perhaps with a small amount of sodium chloride or potassium chloride, or both, remains as a residue in the bottom of the inner retort.

The introduction of heating gases to the heating chamber is stopped and the retort is permitted to cool. When the condensed calcium has reached a temperature at which calcium hydride can be formed without dissociation, the vacuum is broken by opening the valve of lateral branch 15 to admit hydrogen to the interior of the retort. Sufficient hydrogen is thus introduced to permit complete conversion of the condensed calcium to calcium hydride. For this purpose, under the conditions I have operated, the retort has been allowed to cool down to about 400° C., after which the hydrogen was admitted.

If the reaction proceeds too rapidly, the hydrogen is advantageously diluted with an inert or neutral gas, such as helium. As dilution slows down the reaction, it may be carried on to completion under complete control. Instead of diluting the hydrogen with such a gas, the hydrogen may be admitted at a slower rate than that at which it is capable of being absorbed by the calcium. A vacuum is then automatically maintained in the retort and the speed of reaction may be slowed down as desired.

The end of the reaction is indicated when a sufficient amount of hydrogen has been absorbed by a corresponding weight of calcium. The retort is then cooled to room temperature, hydrogen is displaced by air, and the retort is opened. Since all the sodium has been absorbed by the reaction with titanium oxide and all the distilled calcium has been converted into far less reactive calcium hydride, the danger of spontaneous combustion is eliminated. The substantially pure calcium hydride is then scraped out of the retort with comparative safety.

It will be clear to those skilled in this art that the invention lends itself to numerous modifications. Strontium and barium may be similarly treated to remove sodium and potassium, and to convert these explosive alkali metals into harmless compounds. Instead of titanium oxide, other suitable refractory metallic oxides, such as zirconium oxide and chromium oxide, may be employed, either separately or admixed.

In the practice of the invention, advantage is taken of the relative boiling points of the metals. The boiling points of sodium and potassium are substantially below those of calcium, strontium and barium. The temperature of the metal to be purified is therefore gradually elevated to a point where the metal impurity of lower boiling point is distilled. The retort is caused to yield a graduated temperature range. This is effected by heating the bottom of the retort, and permitting the upper portion of the retort to extend above the heating chamber into the open atmosphere. Since sodium and potassium have the lower boiling points, their vapors tend selectively to rise highest in the retort. Since calcium, strontium and barium have the higher boiling points, their vapors tend not to rise as high in the retort. They soon meet a temperature environment conducive to condensation. In other words, the alkaline earth metals may be made to condense in an intermediate section of the retort where the temperature is high enough to keep the alkali metals in vapor form. The alkali metal vapors, on the other hand, tend to rise to a cooler portion of the retort, where they were heretofore condensed, but where they are now converted into harmless compounds in accordance with the present invention.

This application is a continuation-in-part of my application Serial No. 434,052, filed March 10, 1942.

I claim:

1. In the method of producing substantially pure calcium hydride, the improvement which comprises heating calcium contaminated with a metal impurity of lower boiling point in the absence of air to a temperature at which the metal impurity but not the calcium is distilled, selectively oxidizing the resulting metal impurity vapor by bringing it in reactive contact with a refractory metallic oxide removed from the main body of calcium, collecting the oxidized metal impurity as a solid separate from the calcium, distilling the calcium, condensing the resulting calcium vapor as a solid separate from the oxidized metal impurity and calcium residues; cooling the condensed calcium to a temperature at which it reacts with hydrogen, bringing hydrogen into reactive contact with the calcium until it is converted to calcium hydride, and recovering the resulting substantially pure calcium hydride.

2. Method according to claim 1, in which the calcium is heated while under vacuum, and breaking the vacuum after the calcium vapor has condensed.

3. Method according to claim 1, in which the refractory metallic oxide is selected from the group: titanium oxide, zirconium oxide and chromium oxide.

4. Method according to claim 1, in which the metal impurity is at least one of the group: sodium and potassium.

5. Method according to claim 1, in which the hydrogen is diluted with an inert gas to slow down the speed of reaction between the hydrogen and the condensed calcium.

6. Method according to claim 1, in which the hydrogen is diluted with helium to slow down the speed of reaction between the hydrogen and condensed calcium.

7. In the method of producing substantially pure metal hydride, the improvement which comprises heating a hydride-forming metal contaminated with a metal impurity of lower boiling point in the absence of air to a temperature at which the metal impurity but not the hydride-forming metal is distilled, selectively oxidizing the resulting metal impurity vapor by bringing it in reactive contact with a refractory metallic oxide removed from the main body of the hydride-forming metal, collecting the oxidized metal impurity as a solid separate from the hydride-forming metal, distilling the hydride-forming metal, condensing the resulting hydride-forming metal vapor as a solid separate from the oxidized metal impurity and hydride-forming metal residues, cooling the condensed hydride-forming metal to a temperature at which it reacts with hydrogen, bringing hydrogen into reactive contact with the hydride-forming metal until it is converted to metal hydride, and recovering the resulting substantially pure metal hydride.

8. Method according to claim 7, in which the hydride-forming metal is selected from the group: calcium, strontium and barium.

9. Method according to claim 7, in which the metal impurity is at least one of the group: sodium and potassium.

10. Method according to claim 7, in which the refractory metallic oxide is selected from the group: titanium oxide, zirconium oxide and chromium oxide.

11. Method according to claim 7, in which the hydride-forming metal is heated while under vacuum, and breaking the vacuum after the hydride-forming metal vapor has condensed.

12. Method according to claim 7, in which the hydrogen is diluted with an inert gas to slow down the speed of reaction between the hydrogen and the condensed hydride-forming metal.

13. Method according to claim 7, in which the hydrogen is diluted with helium to slow down the speed of reaction between the hydrogen and the condensed hydride-forming metal.

14. Method according to claim 7, in which the hydride-forming metal is selected from the group: calcium, strontium and barium; and the metal impurity is at least one of the group: sodium and potassium.

15. Method according to claim 7, in which the hydride-forming metal is selected from the group: calcium, strontium and barium; and the metal impurity is at least one of the group: sodium and potassium; and the refractory metallic oxide is selected from the group: titanium oxide, zirconium oxide and chromium oxide.

16. Method according to claim 1, in which the refractory metallic oxide is selected from the group: titanium oxide, zirconium oxide and chromium oxide; and the metal impurity is at least one of the group: sodium and potassium.

17. In the method of producing substantially pure metal hydride from impure hydride-forming metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure metal in a retort, evacuating the retort to remove objectionable air, heating the metal-containing part of the retort above the melting point of said metal, distilling the metal impurity but not the metal to be purified, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of metal to be purified, collecting the oxidized metal impurity as a solid separate from the main body of metal to be purified, distilling and condensing the metal thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed metal is converted into the corresponding metal hydride.

18. In the method of producing substantially pure metal hydride from impure hydride-forming metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure metal in a retort, evacuating the retort to remove objectionable air, heating the metal-containing part of the retort above the melting point of said metal, distilling the metal impurity but not the metal to be purified, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of metal to be purified, collecting the oxidized metal impurity as a solid separate from the main body of metal to be purified, distilling and condensing the metal thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting an inert gas and hydrogen gas into the retort, and continuing to supply hydrogen gas to the retort until the distilled and condensed metal is converted into the corresponding metal hydride.

19. In the method of producing substantially pure metal hydride from impure hydride-forming metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure metal in a retort containing in its upper part a body of reducible metal oxide, evacuating the retort to remove objectionable air, heating the metal-containing part of the retort above the melting point of said metal, distilling the more volatile metal impurity but not the metal to be purified and absorbing the more volatile metal impurity by reaction with the metal oxide, distilling and condensing the less volatile metal thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed metal is converted into the corresponding metal hydride.

20. In the method of producing substantially pure calcium hydride from impure calcium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure calcium metal in a retort, evacuating the retort to remove objectionable air, heating the calcium-containing part of the retort above the melting point of said calcium, distilling the metal impurity but not the calcium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of calcium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of calcium to be purified, distilling and condensing the calcium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed calcium is converted into the corresponding calcium hydride.

21. In the method of producing substantially pure calcium hydride from impure calcium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure calcium metal in a retort, evacuating the retort to remove objectionable air, heating the calcium-containing part of the retort above the melting point of said calcium, distilling the metal impurity but not the calcium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of calcium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of calcium to be purified, distilling and condensing the calcium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting an inert gas and hydrogen gas into the retort, and continuing to supply hydrogen gas to the retort until the distilled and condensed calcium is converted into the corresponding calcium hydride.

22. In the method of producing substantially pure calcium hydride from impure calcium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure calcium metal in a retort containing in its upper part a body of reducible metal oxide, evacuating the retort to remove objectionable air, heating the calcium-containing part of the retort above the melting point of said calcium, distilling the more volatile metal impurity but not the calcium to be purified and absorbing the more volatile metal impurity by reaction with the metal oxide, distilling and condensing the less volatile calcium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed calcium is converted into the corresponding calcium hydride.

23. In the method of producing substantially pure barium hydride from impure barium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure barium metal in a retort, evacuating the retort to remove objectionable air, heating the barium-containing part of the retort above the melting point of said barium, distilling the metal impurity but not the barium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of barium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of barium to be purified, distilling and condensing the barium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed barium is converted into the corresponding barium hydride.

24. In the method of producing substantially pure barium hydride from impure barium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure barium metal in a retort, evacuating the retort to remove objectionable air, heating the barium-containing part of the retort above the melting point of said barium, distilling the metal impurity but not the barium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of barium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of barium to be purified, distilling and condensing the barium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting an inert gas and hydrogen gas into the retort, and continuing to supply hydrogen gas to the retort until the distilled and condensed barium is converted into the corresponding barium hydride.

25. In the method of producing substantially pure barium hydride from impure barium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure barium metal in a retort containing in its upper part a body of reducible metal oxide, evacuating the retort to remove objectionable air, heating the barium-containing part of the retort above the melting point of said barium, distilling the more volatile metal impurity but not the barium to be purified and absorbing the more volatile metal impurity by reaction with the metal oxide, distilling and condensing the less volatile barium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed barium is converted into the corresponding barium hydride.

26. In the method of producing substantially pure strontium hydride from impure strontium

metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure strontium metal in a retort, evacuating the retort to remove objectionable air, heating the strontium-containing part of the retort above the melting point of said strontium, distilling the metal impurity but not the strontium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of strontium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of strontium to be purified, distilling and condensing the strontium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed strontium is converted into the corresponding strontium hydride.

27. In the method of producing substantially pure strontium hydride from impure strontium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure strontium metal in a retort, evacuating the retort to remove objectionable air, heating the strontium-containing part of the retort above the melting point of said strontium, distilling the metal impurity but not the strontium, selectively oxidizing the resulting metal impurity vapor by bringing it into reactive contact with a reducible metal oxide removed from the main body of strontium to be purified, collecting the oxidized metal impurity as a solid separate from the main body of strontium to be purified, distilling and condensing the strontium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting an inert gas and hydrogen gas into the retort, and continuing to supply hydrogen gas to the retort until the distilled and condensed strontium is converted into the corresponding strontium hydride.

28. In the method of producing substantially pure strontium hydride from impure strontium metal contaminated with a metal impurity of lower boiling point, the improvement which comprises placing the impure strontium metal in a retort containing in its upper part a body of reducible metal oxide, evacuating the retort to remove objectionable air, heating the strontium-containing part of the retort above the melting point of said strontium, distilling the more volatile metal impurity but not the strontium to be purified and absorbing the more volatile metal impurity by reaction with the metal oxide, distilling and condensing the less volatile strontium thus purified in a cooler part of the retort removed from the oxidized metal impurity, admitting hydrogen gas into the retort and continuing to supply hydrogen gas to the retort until the distilled and condensed strontium is converted into the corresponding strontium hydride.

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