

1

3,419,348

SEPARATION OF METALS

Clarence James Hardy, Wantage, and Brian Orlando Field, Abingdon, England, assignors to United Kingdom Atomic Energy Authority, London, England
 No Drawing. Filed Apr. 16, 1964, Ser. No. 360,440
 Claims priority, application Great Britain, Apr. 22, 1963, 15,726/63
 4 Claims. (Cl. 23—102)

ABSTRACT OF THE DISCLOSURE

A process for the separation of certain metal compounds of a required metal from a mixture containing several metals or compounds comprises forming a volatile nitrate, nitrite, nitrate- or nitrosyl-compound of the required metal and separating it from non-volatile compounds of other metals by a distillation process.

The present invention relates to the separation of metals.

Many workers have recently reported that under certain circumstances some metal nitrates, nitrites and nitrosyl-complexes are volatile, although other workers have reported that the same compounds of the same metals are not volatile or decompose. However we have now shown definite volatility under precisely defined conditions of certain of these compounds and equally definite non-volatility of the same compounds of other metals under the same conditions. In this connection it should be explained that the term "non-volatility" is used herein to include compounds which decompose (usually to the oxide) provided that the oxide is not volatile.

With this information in our possession, we have therefore developed a process for the separation of certain metal compounds and, according to the present invention, there is provided a process for the separation of a compound of a required metal from a mixture containing several metals or compounds comprising forming a volatile nitrate, nitrite, nitrate- or nitrosyl-compound or the required metal and separating it from non-volatile compounds of other metals by a distillation process.

The term "nitrate" is used to indicate a compound which is believed to contain the nitrate ion, and the term "nitrate" complex to indicate a compound in which the NO₃ group is covalently bonded to a metal by one or more of its oxygen atoms.

The term "distillation" should be understood to include "sublimation" in all relevant instances.

In some cases a fractional distillation process can be carried out as described in more detail hereinafter.

The precise compounds which may be used and the temperatures at which the distillation process may be effected will of course differ from metal to metal.

Specifically in the case of the alkali metals lithium, sodium, potassium, rubidium caesium and also possibly thallium, the preferred compounds are the ionic nitrate or nitrite which are normally anhydrous and which may be distilled without decomposition at a temperature in the range 350 to 500° C., at a pressure of 0.005 millimetre of mercury. In general, the other metal nitrates decompose at this temperature.

However, in the case of the metals beryllium, copper, gold, hafnium, indium, mercury, palladium, tin, titanium, vanadium, zinc and zirconium, the anhydrous nitrate complexes and, in the case of iron, the nitrosyl nitrate complex, are volatile, provided that they are prepared by the reaction with either liquid dinitrogen pentoxide (N₂O₅) or in some cases a solution of dinitrogen tetroxide (N₂O₄) in a suitable solvent, e.g., ethyl acetate. In some cases this treatment with oxides of nitrogen gives an anhydrous nitrate and in other cases a nitrate or nitrosyl complex.

2

It is also important to list the metals which do not form volatile compounds under these conditions and we have confirmed this non-volatility in the case of the metals aluminum, barium, cadmium, cobalt, manganese, neodymium, molybdenum, nickel, niobium, silver, thorium and uranium. We have reason to believe that the following metals will probably not be volatile under the conditions in question: bismuth, calcium, iridium, lead, magnesium, osmium, plutonium, rhodium, strontium. In general, we have found, as will be observed from the above lists, that the nitrates and nitrites of Group 1A metals (together with metals which behave similarly, e.g., thallium) are volatile whilst the nitrate complexes of several metals having a stable 4 valency are also volatile; thus we predict that germanium should have a volatile complex if it can be prepared. It is clearly difficult to predict which metals are not volatile under the conditions in question as (for example) the case of ruthenium will show, where the evidence is that the nitro, nitrate and nitrosyl compounds are not volatile but decompose to give the highly volatile oxide.

The temperature at which the nitrate and nitrosyl complexes distil freely is of the order of 100 to 200° C. at a pressure of the order of 0.05 millimetre of mercury.

In order that the invention may more readily be understood certain examples will now be given by way of explanation.

Example 1

The fission products obtained during the treatment of irradiated uranium contain, inter alia, caesium, strontium, zirconium, niobium, ruthenium and, in the case of the magnox reactors, aluminium and iron. A simple treatment with dilute nitric acid will prepare these fission products as hydrated nitrates and, by distillation at a temperature in the range 400 to 500° C. and a pressure of 0.005 millimetre of mercury, caesium nitrate alone will be recovered, this being a relatively simple and cheap route for the preparation of caesium-137.

If ruthenium volatilises as the oxide, it should do so at a lower temperature, and can therefore be separated by fractional distillation.

Example 2

Lithium nitrate is normally only available as the trihydrate and is difficult to obtain or prepare in the anhydrous state. However, the present invention shows that lithium nitrate can be distilled, and consequently, if the tri-hydrate is heated to a temperature of 90–100° C., at a pressure of 0.005 millimetre of mercury and the water removed and thereafter the anhydrous nitrate distilled at 350 to 500° C. whilst maintaining a pressure of 0.005 millimetre of mercury, pure anhydrous lithium nitrate is obtained.

Example 3

Potassium nitrite is not readily available in the pure state and the commercially available material is usually slightly yellow and is only about 96 percent pure. By treatment in accordance with the present invention, pure potassium nitrite is obtained at a temperature and pressure similar to that used in Example 2.

Example 4

In the preparation of pure beryllium, for example either as the metal or as the oxide, it is necessary to separate the beryllium content of the ore from relatively large amounts of aluminium and iron. If the ore is leached with dilute nitric acid a solution of metal nitrate will be obtained and this solution can be evaporated to dryness to obtain a mixture of the solid nitrates. As explained above, the beryllium nitrate in its normal form will not distil in accordance with the present invention and it must first be converted to the anhydrous form by treatment with di-

nitrogen pentoxide. Alternatively, it may be possible to obtain the anhydrous form directly by leaching the ore with liquid dinitrogen pentoxide or dinitrogen tetroxide in an organic solvent.

The mixture of complexes may be heated in vacuo (0.05 millimetre of mercury) to remove and recover the excess oxides of nitrogen, and the beryllium complex $\text{Be}_4\text{O}(\text{NO}_3)_6$, can then be distilled from the non-volatile aluminium complex at 100°C . If iron is present it will form a volatile nitrosyl complex under the above conditions and iron must be separated from the beryllium either in a previous stage, in a subsequent stage, or, as a third alternative, by fractional distillation. The resultant beryllium will not contain any alkaline earth metals or unwanted anions such as a chloride or sulphate and, moreover, will be free from alkali metal nitrates as these do not distil at the temperatures involved.

Example 5

Beryllia and beryllium are also both possible materials for nuclear reactors and may be separated from uranium in accordance with the process of this invention. Thus a mixture of beryllium and uranium nitrates may be treated to form a beryllium complex as described with reference to Example 4, which complex will distil as in that example. Uranium does not form a volatile compound under these conditions but some fission product complexes may be distilled.

Example 6

Zirconium forms a volatile nitrate complex $\text{Zr}(\text{NO}_3)_4$ which may be prepared by the reaction of dinitrogen pentoxide with zirconium chloride or hydrated zirconium nitrate, this complex distilling at 100°C . at a pressure of 0.05 millimetre of mercury. The process of the present invention may therefore be applied in order to separate zirconium contaminating uranium or uranium dioxide fuel elements either in the recovery of unirradiated scrap or, for example as a head-end treatment to remove the zirconium prior to processing the uranium.

Example 7

The volatile zirconium complex described above may also be used to separate zirconium from its niobium daughter products when preparing zirconium-95 by the n,γ reaction, as the niobium nitrate complex $\text{NbO}(\text{NO}_3)_3$ is not volatile.

Example 8

Palladium also forms a highly volatile nitrate complex unlike the other platinum group metals. Thus a group of these metals may be dissolved in aqua regia, precipitated as the hydroxides and treated with liquid dinitrogen pentoxide. The mixture may then be heated at reduced pressure and pure dinitrato palladium (II) distilled off. This palladium complex, $\text{Pd}(\text{NO}_3)_2$, is thought to be the only thermally stable volatile compound of palladium prepared to date and has not previously been disclosed. The present invention therefore includes within its scope this compound per se. The complex is believed to be a suitable material for the use in the electromagnetic separation of the palladium isotopes.

Example 9

Iron forms a volatile nitrosyl complex $\text{FeNO}(\text{NO}_3)_4$ as previously described and this complex, which can be produced by the treatment of the hydrated nitrate or the metal with dinitrogen pentoxide, or the metal with dinitrogen tetroxide in an organic solvent can be distilled at 100°C . under a pressure of 0.05 millimetre of mercury. The complex can be used in the purification of aluminium by the removal of traces of iron as the aluminium complex is not volatile. The process may also be used to prepare carrier free iron, e.g., Fe^{59} , for tracer applications.

Example 10

Titanium forms a volatile nitrate complex $\text{Ti}(\text{NO}_3)_4$

by treatment of the metal with dinitrogen pentoxide and can be distilled at a temperature as low as 20°C . and a pressure of 0.03 millimetre of mercury, distillation being rapid at 100°C . and a pressure of 0.02 millimetre of mercury. The product is substantially pure as shown by its sharp melting point $58\pm 0.5^\circ\text{C}$. and thus the present invention provides a route for the preparation of pure titanium from its ores, particularly rutile. The complex may readily be prepared by the treatment of the hydrated nitrate with liquid dinitrogen pentoxide or by treatment of the tetrachloride with the same compound. The complex appears to be extremely reactive and may be used to nitrate and oxidise saturated paraffin hydrocarbons such as n-dodecane.

Example 11

Copper also forms a volatile complex having the formula $\text{Cu}(\text{NO}_3)_2$ and this complex may be used to separate carrier-free copper-64 from zinc-64 from which it is made by an n,p reaction, by dissolving the zinc contaminated copper product in dinitrogen pentoxide and distilling off of the pure carrier-free copper complex at a temperature of about 150°C . The zinc complex is not volatile under these conditions, but is volatile at a higher temperature.

We claim:

1. A process for the separation of a compound of an alkali metal from a mixture, such process comprising the sequential steps of

(a) treating the mixture to form a volatile nitrogen-containing compound of said alkali metal and selected from the group consisting of alkali metal nitrates and alkali metal nitrites, and

(b) effecting a distillation process at a temperature in the range $350\text{--}500^\circ\text{C}$. and at a pressure of the order of 0.005 millimetre of mercury to separate such volatile nitrogen-containing compound.

2. A process for the separation of a caesium compound from fission products comprising the sequential steps of

(a) treating the fission products with dilute nitric acid to obtain a mixture of nitrates, and

(b) effecting a distillation process to separate caesium nitrate at a temperature in the range $400\text{--}500^\circ\text{C}$. and at a pressure of the order of 0.005 millimetre of mercury.

3. A process for the separation of anhydrous lithium nitrate comprising the steps of

(a) heating hydrated lithium nitrate to a temperature of the order of $90\text{--}100^\circ\text{C}$. at a pressure of 0.005 millimetre of mercury to obtain anhydrous lithium nitrate, and

(b) effecting a distillation process at a temperature of $350\text{--}500^\circ\text{C}$. and a pressure of the order of 0.005 millimetre of mercury to separate the anhydrous lithium nitrate.

4. A process for the separation of pure potassium nitrite which comprises distilling impure potassium nitrite at a temperature of $350\text{--}500^\circ\text{C}$. and at a pressure of the order of 0.005 millimetre of mercury to effect the separation of pure potassium nitrite.

References Cited

UNITED STATES PATENTS

2,874,039 2/1959 Pruvot ----- 23—17 X

OTHER REFERENCES

Addison et al.: "Chem. Soc. Journ." (London), pp. 3099—3106 relied on (1958).

OSCAR R. VERTIZ, *Primary Examiner*.

A. GRIEF, *Assistant Examiner*.

U.S. Cl. X.R.

75—62, 66