Science and Technology

Solutions, Separation Techniques, and the PUREX Process for Reprocessing Nuclear Waste

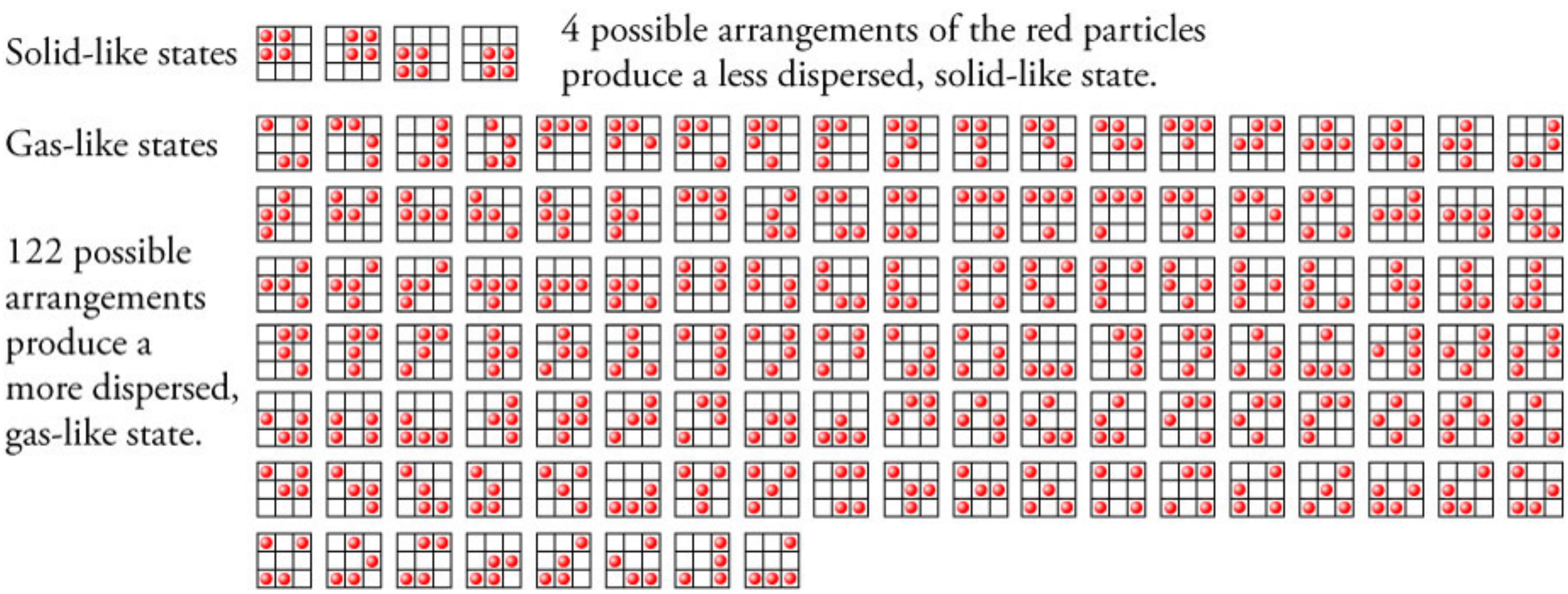
Why Changes Happen

- Consider a system that can switch freely between two states, A and B.
- Probability helps us to predict that the system will shift to state B if state B has its particles and energy more dispersed, leading to more ways to arrange the particles and energy in the system.

State A $\rightleftharpoons$ **State B**

State A	State B
Less probable	More probable
Fewer ways to arrange particles and energy	More ways to arrange particles and energy
Less dispersed (spread out)	More dispersed (spread out)

9-Point Universe



Probability of Gas

- In 9-point universe, 96% of the arrangements of 4 particles are gas-like.
- In 16-point universe, 99.5% of the arrangements of 4 particles are gas-like.
- Therefore, an increase in the number of possible positions leads to an increase in the probability that the system will be in the more dispersed, gas-like state.
- In real systems, there are huge numbers of particles in huge numbers of positions, so there is an extremely high probability that the systems will be in the more dispersed, gas-like state.

General Statement

- Changes tend to take place to shift from less probable, less dispersed arrangements that have fewer ways to arrange the particles to more probable, more dispersed states that have more ways to arrange the particles.

Solids shift spontaneously to gases.

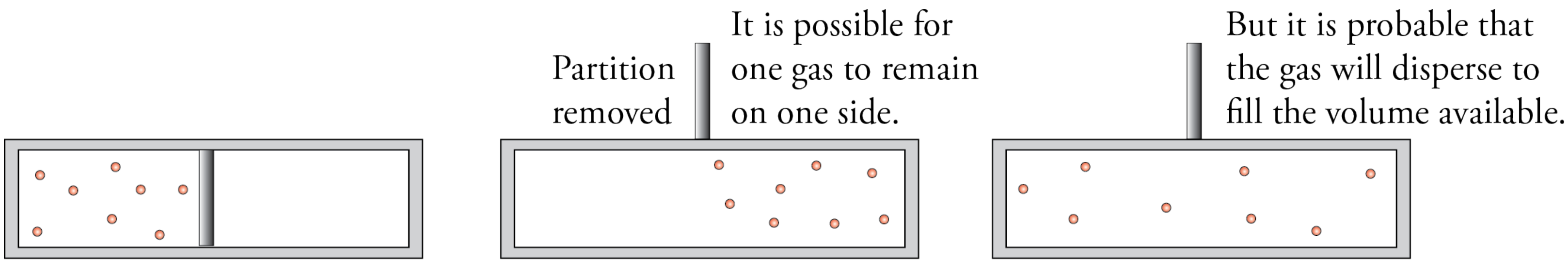
- Why does dry ice, $CO_2(s)$, sublime? Why does the change favor the gas?
  - Internal kinetic energy is associated with the random movement of particles in a system.
  - Internal kinetic energy makes it possible for CO_2 molecules to move back and forth between solid and gas.
  - If the particles can move freely back and forth between solid and gas, they are more likely to be found in the more dispersed gas state, which has more equivalent ways to arrange the particles.

Solid to Gases

$$CO_2(s) \longrightarrow CO_2(g)$$

Less dispersed	More dispersed
Fewer ways to arrange particles	More ways to arrange particles
Less probable	More probable

Gases Expand



(a) System before partition is removed

(b) Gas in one chamber
Less dispersed
Fewer ways to arrange particles
Less probable

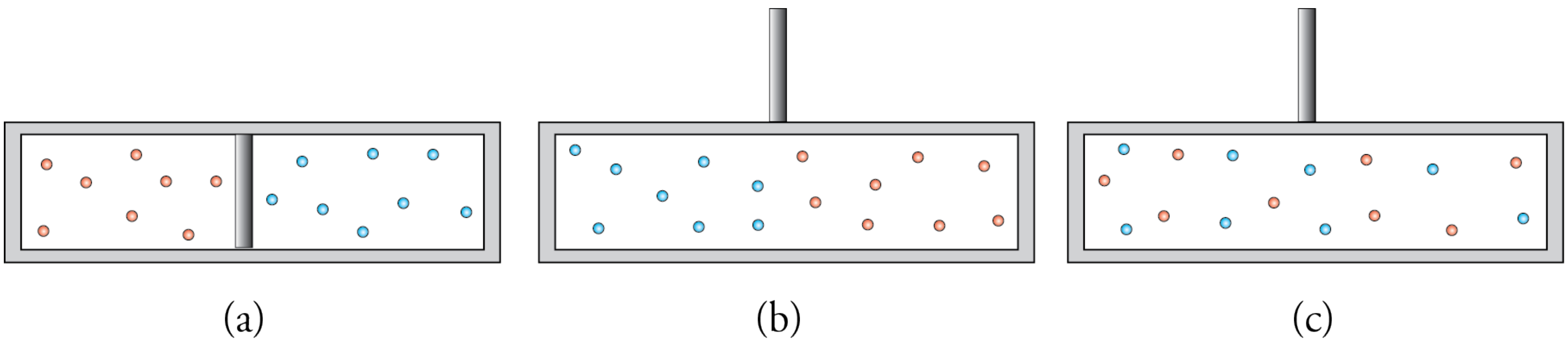
(c) Gas in both chambers
More dispersed
More ways to arrange particles
More probable

When the barrier between the two chambers in the container shown in (a) is raised, it is possible that the gas will end up in one chamber, like in (b), but it is much more likely that it will expand to fill the total volume available to it, like in (c).

Matter gets dispersed (spread out).

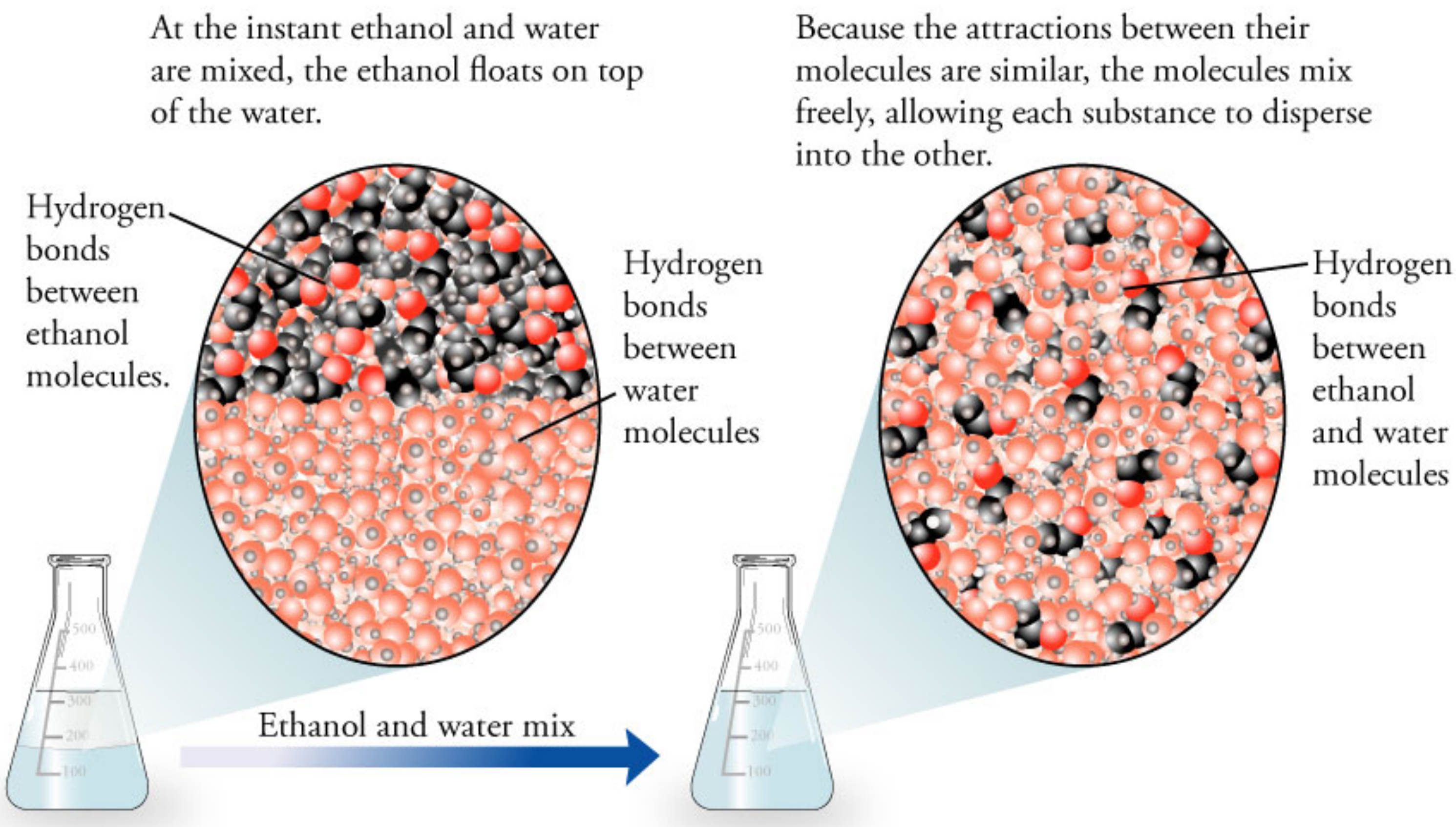
Gas in one chamber	→	Gas in both chambers
Fewer ways to arrange particles		More ways to arrange particles
Less probable		More probable
Less dispersed		More dispersed

Substances tend to mix.

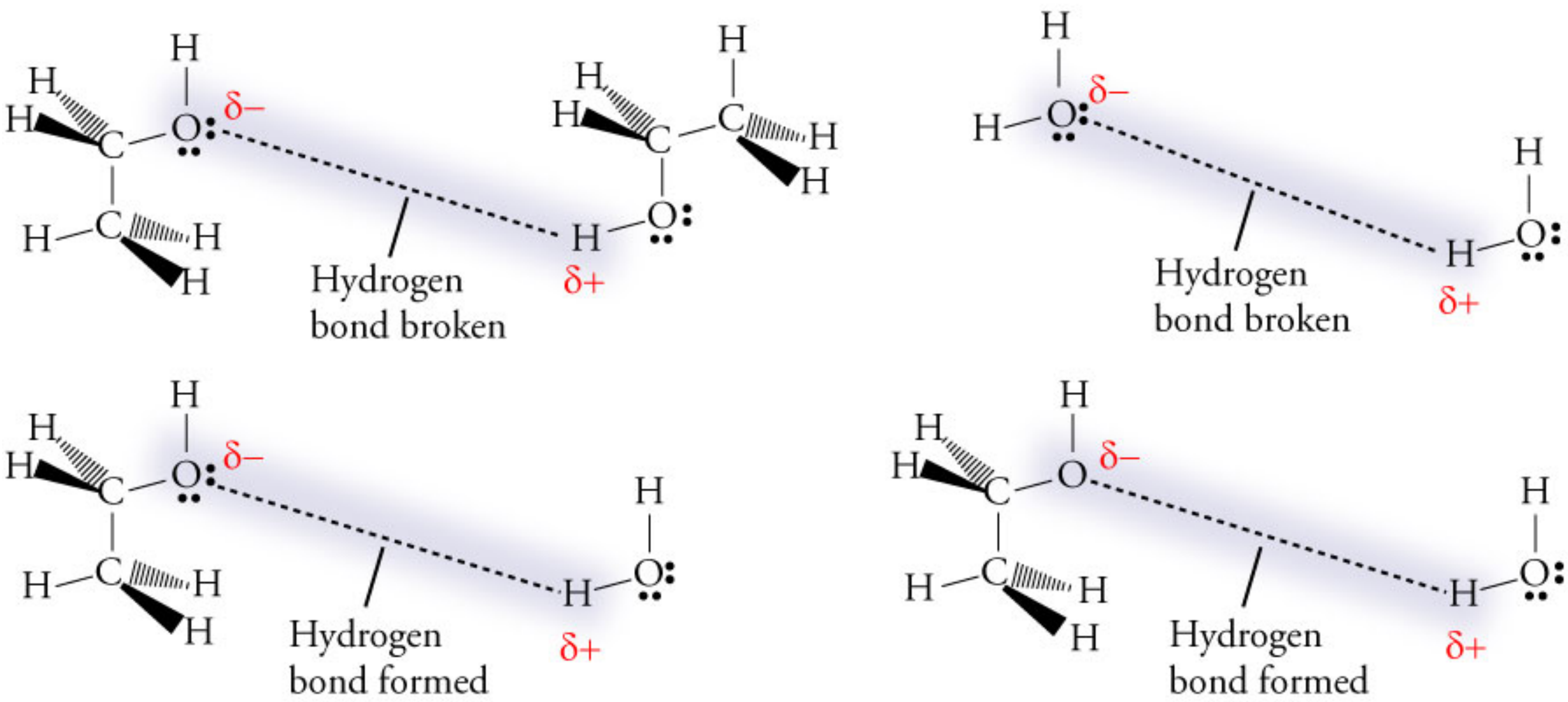


When the barrier between the two gases in the container shown in (a) is raised, it is possible that the gases will stay separated, like in (b), but it is much more likely that they will mix, like in (c).

Ethanol and Water Mixing



Attractions Broken and Made



Solubility

- If less than one gram of the substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered ***insoluble***.
- If more than ten grams of substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered ***soluble***.
- If between one and ten grams of a substance will dissolve in 100 grams (or 100 mL) of solvent, the substance is considered ***moderately soluble***.

“Like Dissolves Like”

- Polar substances are expected to dissolve in polar solvents.
  - For example, ionic compounds, which are very polar, are often soluble in the polar solvent water.
- Nonpolar substances are expected to dissolve in nonpolar solvents.
  - For example, nonpolar molecular substances are expected to dissolve in hexane, a common nonpolar solvent.

“Like Does Not Dissolve Unlike”

- Nonpolar substances are not expected to dissolve to a significant degree in polar solvents.
  - For example, nonpolar molecular substances are expected to be insoluble in water.
- Polar substances are not expected to dissolve to a significant degree in nonpolar solvents.
  - For example, ionic compounds are insoluble in hexane.

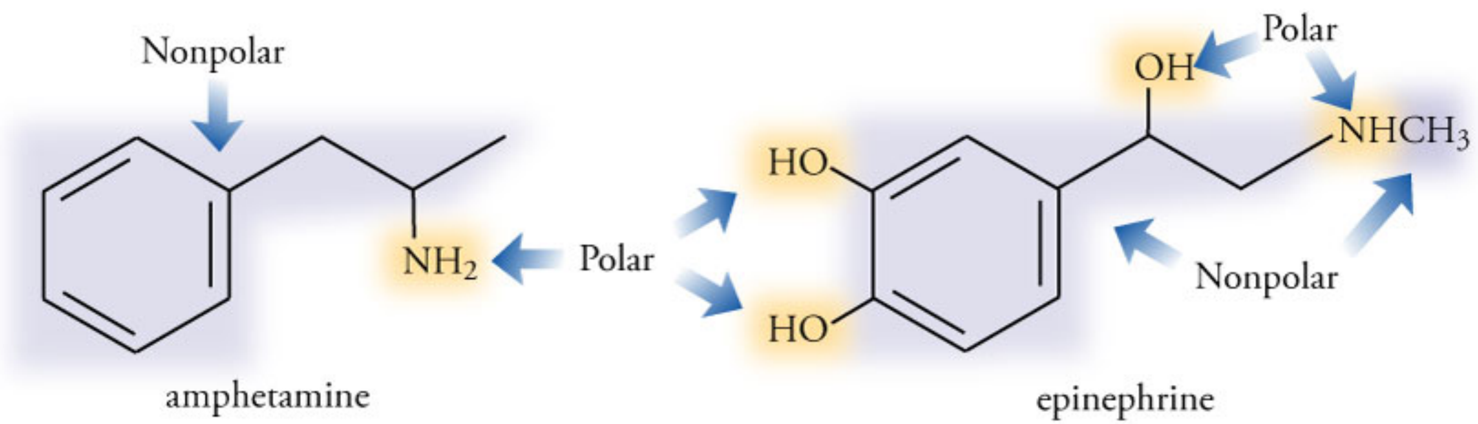
Summary of Solubility Guidelines

- Ionic Compounds
  - Often soluble in water
  - Insoluble in hexane
- Molecular compounds with nonpolar molecules
  - Insoluble in water
  - Soluble in hexane
- Molecular Compounds with small polar molecules
  - Usually soluble in water
  - Often soluble in hexane

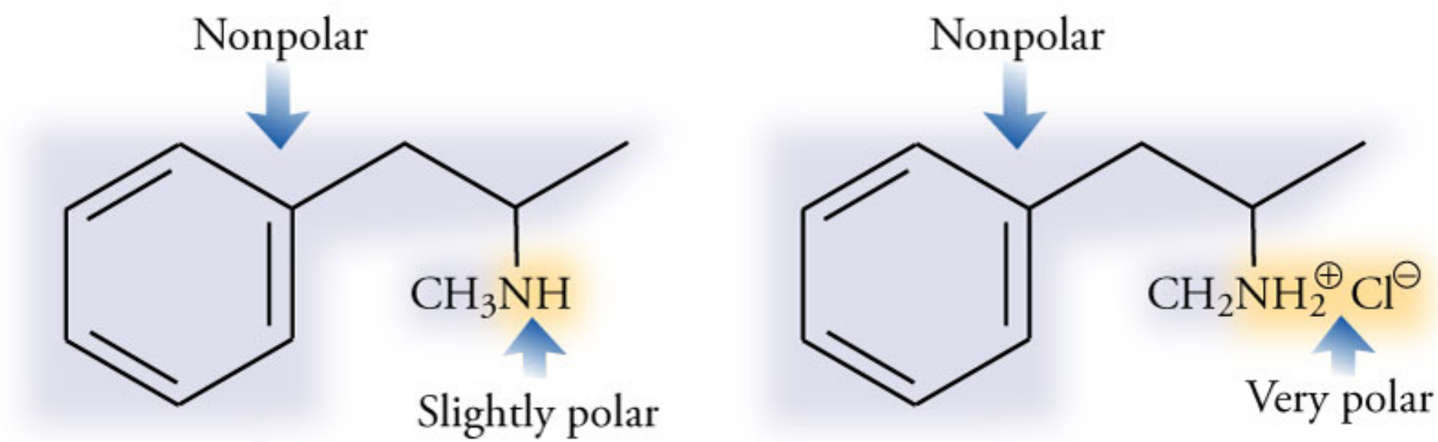
Water Solubility

- If we are comparing the water solubility of two similar molecules, the one with the higher percentage of the molecule that is polar (***hydrophilic***) is expected to have higher water solubility.
- We predict that the molecule with the higher percentage of its structure that is nonpolar (***hydrophobic***) to be less soluble in water.

Hydrophobic and Hydrophilic

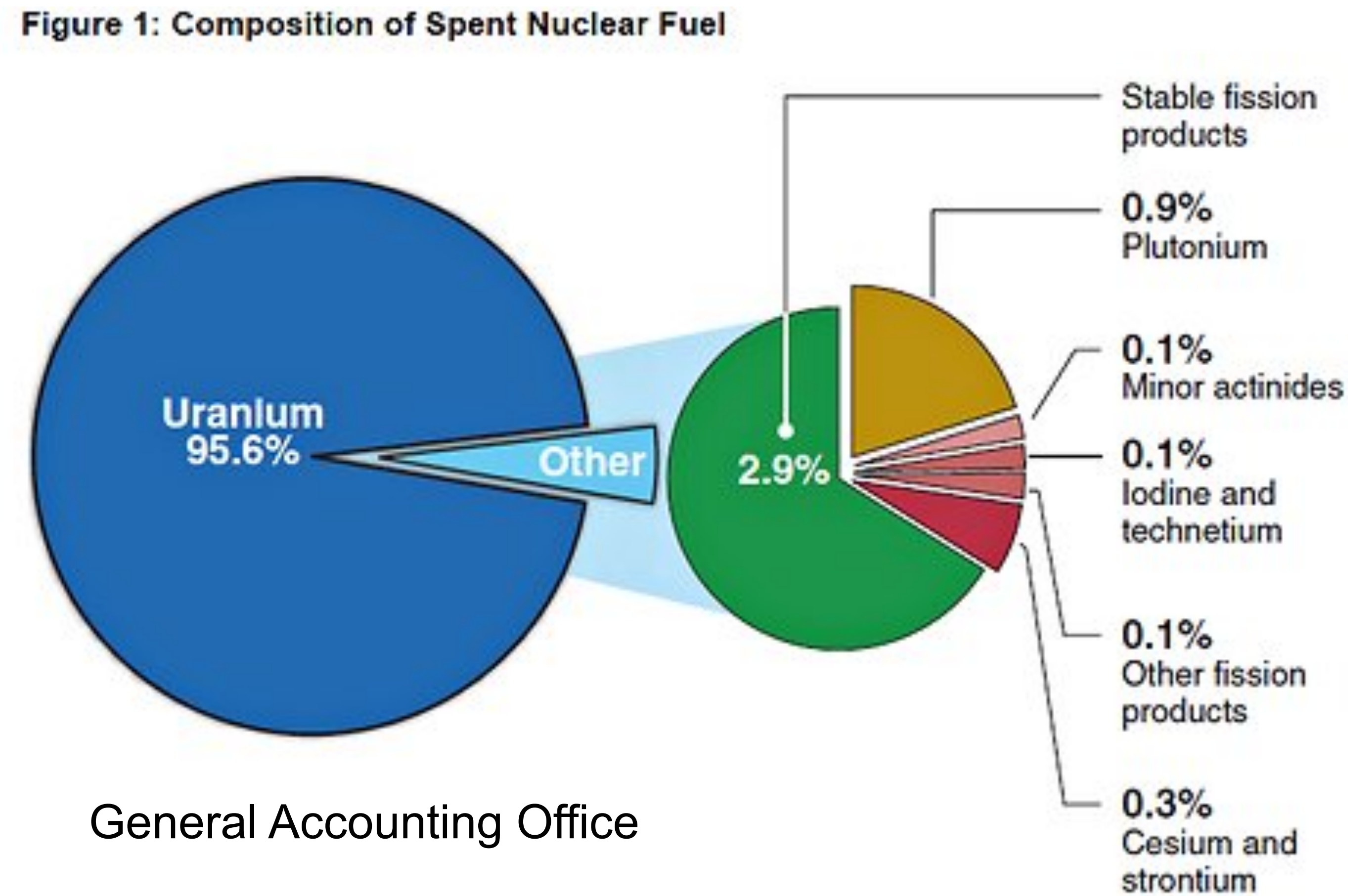


Methamphetamine



methamphetamine   methamphetamine hydrochloride

Spent Fuel Rods



General Accounting Office

- Fission products that emit beta and gamma radiation
- Some fissionable U-235 and Pu-239
- Alpha emitters, such as uranium-234, neptunium-237, plutonium-238 and americium-241
- Sometimes some neutron emitters such as californium (Cf).

Nuclear Reprocessing

- Process to chemically separate and recover fissionable plutonium and uranium from irradiated nuclear fuel.
- Purposes
  - Originally reprocessing was used solely to extract plutonium for producing nuclear weapons.
  - The reprocessed plutonium can be recycled back into fuel for nuclear reactors.
  - The reprocessed uranium, which constitutes the bulk of the spent fuel material, can in principle also be re-used as fuel, but that is only economic when uranium prices are high.
- Nuclear reprocessing reduces the volume of high-level waste, but by itself does not reduce radioactivity or heat generation and therefore does not eliminate the need for a geological waste repository.

http://en.wikipedia.org/wiki/Nuclear_reprocessing

Nuclear Reprocessing

- Reprocessing of civilian fuel has long been employed in France, the United Kingdom, Russia, Japan, and India
- Briefly done at the West Valley Reprocessing Plant in the United States.
- In October 1976, concerned about nuclear weapons proliferation, President Gerald Ford indefinitely suspended the commercial reprocessing and recycling of plutonium in the U.S.
- In March 1999, the U.S. Department of Energy (DOE) reversed its policy and signed a contract with a consortium to design and operate a mixed oxide (MOX) fuel fabrication facility. There are no customers yet.

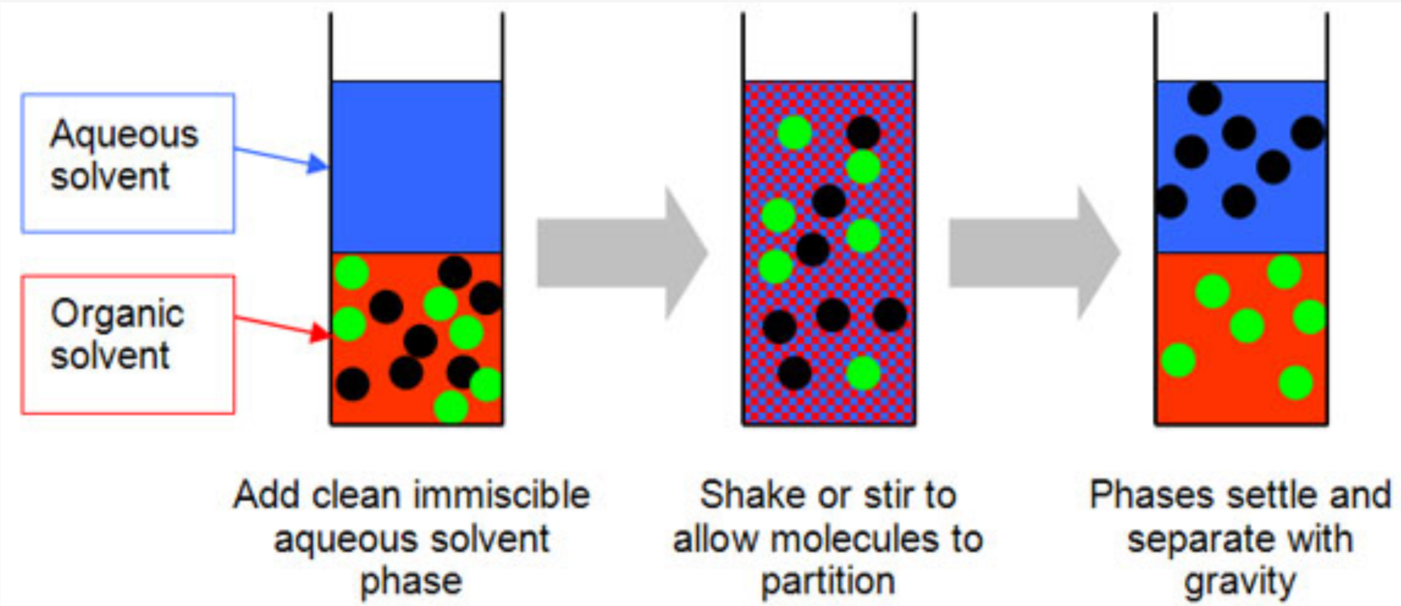
http://en.wikipedia.org/wiki/Nuclear_reprocessing

PUREX Process

- **PUREX** is a chemical method used to purify fuel for nuclear reactors or nuclear weapons.
- It is an acronym standing for **P**lutonium **U**ranium **R**edox by **Ex**traction or **P**lutonium **U**ranium **R**ecovery by **Ex**traction.

http://en.wikipedia.org/wiki/PUREX

Liquid-Liquid Extraction



Polar compounds will congregate in “aqueous” layer

Non-polar compounds will congregate in “organic” layer

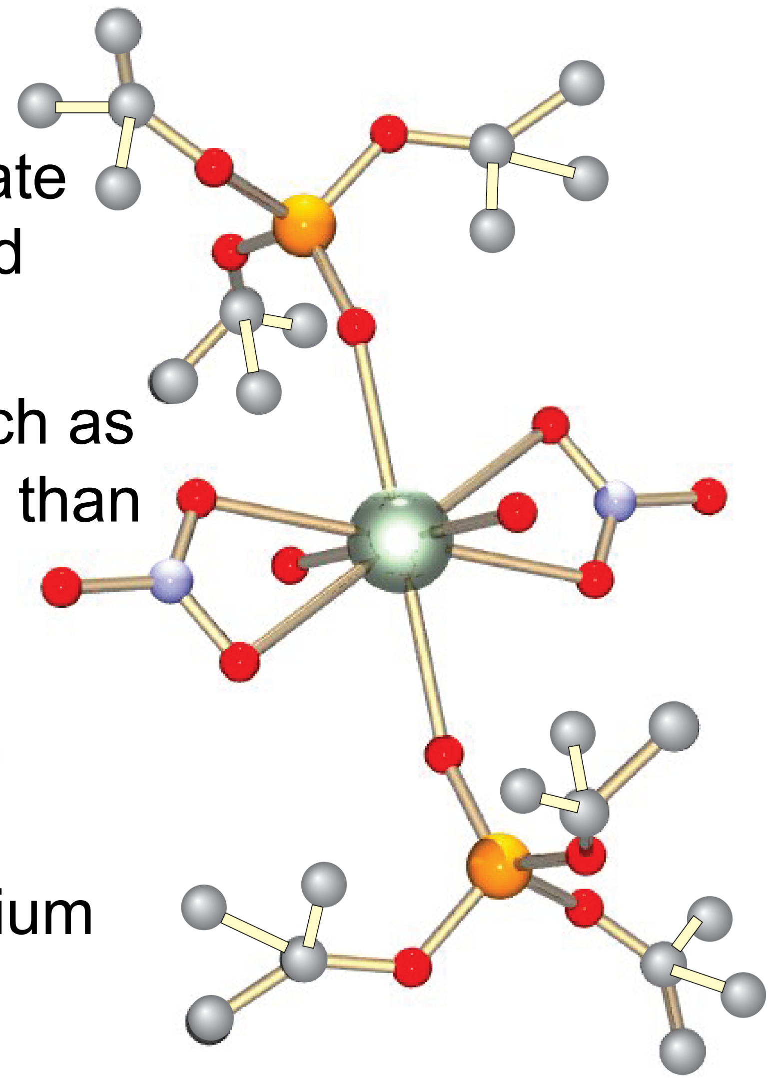
Typically performed in a separatory funnel:

Aqueous layer (polar things)

Organic layer (non-polar things)

PUREX Process

- Dissolve in 7 M HNO_3.
- Filter out solids
- Combine with 30% tributyl phosphate (TBP) to form $UO_2(NO_3)_2 \cdot 2TBP$ and $PuO_2(NO_3)_2 \cdot 2TBP$ complexes.
- Extract with an organic solvent, such as kerosene. (It is normal to use more than one extraction cycle.)
  - $UO_2(NO_3)_2 \cdot 2TBP$ and $PuO_2(NO_3)_2 \cdot 2TBP$ complexes in nonpolar organic solvent
  - Fission products, and transuranium elements americium and curium remain in the aqueous phase.



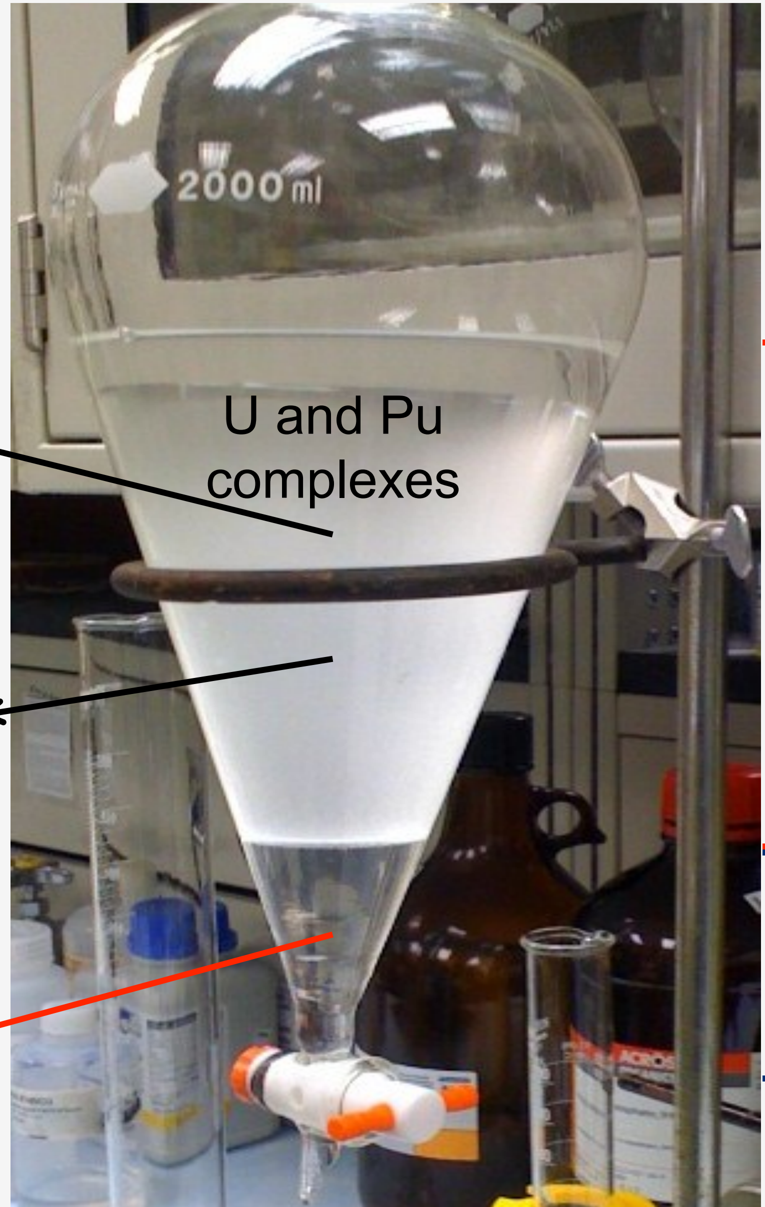
http://en.wikipedia.org/wiki/PUREX

Separation of U, Pu, and Fission Products

On to Uranium purification

On to Plutonium purification

Fission products, minor actinides: discarded as "high level waste"



Nonpolar solvent Layer

Aqueous Layer

PUREX Process

- Plutonium is separated from uranium in a separate extraction by treating the kerosene solution with aqueous iron(II) sulfamate, $Fe(SO_3NH_2)_2$, which reduces the plutonium to the +3 oxidation state. The plutonium passes into the aqueous phase.
- Variations on the PUREX process have been developed.

http://en.wikipedia.org/wiki/PUREX

One Sign of Reprocessing of Nuclear Wastes

- 2002 – China shipped about 20 tons of tributyl phosphate (TBP) to North Korea.
- Considered to be sufficient to extract enough material for three to five nuclear weapons