# Chemistry - PI 24

## ISOTOPIC SEPARATION - DEUTERIUM & HYDROGEN

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Objectives:

1. From memory, draw a simplified diagram of a Girdler-Sulphide, hot/cold tower system and note "relative" concentrations of deuterium on it for the gas and liquid streams. (Drawing will be similar to Figure 1, but exact numbers for concentrations are not required.)

2. Show how the equilibrium constant for the Girdler-Sulphide exchange reaction can be used to define the ratios of Deuterium/Hydrogen in the gas and liquid stream.

3. State whether the equilibrium constant is higher, lower, or the same at 30°C or 130°C.

4. Briefly explain how deuterium is "squeezed" to the centre of a Girdler-Sulphide tower due to the change in equilibrium constant.

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Suggested Reading:
- Course 438, Lesson 20-1
- Course 124, Lesson 30-2
- Course 424, Lesson 12-3

In Module 11-1, chemical exchange reactions were mentioned as viable paths for isotopic separation. In particular, the Girdler-sulphide process for enrichment of water in the deuterium isotope uses the reaction:

$$H_2O(l) + HDS(g) \rightleftharpoons HDO(l) + H_2S(g)$$

(l) = liquid (g) = gas

It should be noted that this is an equilibrium reaction, ie, molecules are constantly changing from one form to another, however there is, at dynamic equilibrium, a steady concentration of each species (at any one particular temperature). The concentrations are related by the equilibrium constant:

$$K = \frac{[HDO][H_2S]}{[H_2O][HDS]}$$

[ ] = concentration in molar units.

This expression can be rearranged as follows:

$$K = \frac{[HDO]/[H_2O]}{[HDS]/[H_2S]}$$

or more simply, the ratio of D/H in the two phases:

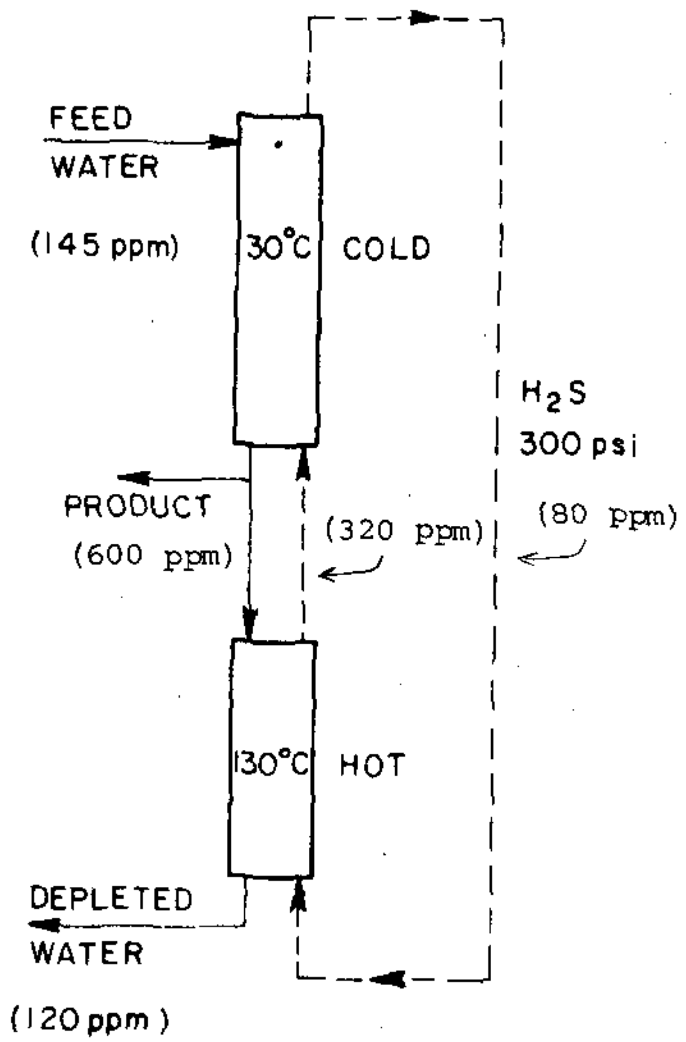
$\frac{[HDO]}{[H_2O]}$ is not exactly equal to $\frac{[D]}{[H]}$ for the water stream but is close enough for our purposes. Similarly:

$\frac{[HDS]}{[H_2S]} \approx \frac{[D]}{[H]}$ for the gas phase.

$$K = \frac{(D/H)_{\text{water stream}}}{(D/H)_{\text{gas stream}}}$$

At 30°C K = 2.35 which is to say the deuterium favours the water compared to the hydrogen sulphide by a factor of 2.35. In general terms, the deuterium favours the compound in which it is most strongly bonded. (The D-O bond is stronger than the D-S bond.)

The diagram, Figure 1, gives a simplified view of the Girdler-sulphide flow path. (For a detailed version of the system, the reader is referred to course PI-38.)




The values for the deuterium concentrations at Bruce are shown in parentheses. They are in ppm D/D+H.

Figure 1

Simplified GS Flowsheet

The equilibrium constants for the exchange reaction at plant operating temperatures are:

2.35 at 30°C
1.91 at 130°C

As both are greater than unity, the reaction always favours enrichment of water in deuterium and depletion of the hydrogen sulphide gas, although less so at the higher temperature.

In the cold tower as the water descends, enrichment in deuterium occurs. Then, when the water enters the hot tower due to the change in equilibrium constant at the new temperature, the enrichment of water is less favoured and the deuterium migrates to the gas phase to achieve the new equilibrium distribution. In achieving this new equilibrium, the water phase gives up so much deuterium to the gas phase that the waste water from the hot tower actually contains less deuterium than the feedwater to the cold tower.

We can now make two very important observations:

1. The towers "squeeze" the deuterium into the interface: both the gas and the water there are richer than they were at time zero. We have the choice of tapping either enriched water or gas off from the interface to send to stage 2 (and thence to stage 3) for further enrichment.

2. The depleted water leaving the hot section contains less deuterium than natural water, ie, some lake water deuterium has remained in the tower! - we have a process for which the separation factor is greater than unity.

## Practice Exercises

1. Draw a simplified Girdler-Sulphide hot/cold tower system and mark on it the relative deuterium concentrations in both the gas and the liquid stream at the top, middle and bottom.

2. Write the expression for the equilibrium constant for the Girdler-Sulphide reaction:

$$H_2O(l) + HDS(g) \rightleftharpoons HDO(l) + H_2S(g)$$

and explain how the variation in constant with temperature promotes a buildup of deuterium at the centre of the tower, between the hot and cold sections.

For question #1 compare your answer to the data in Figure #1. For question #2 check with a colleague to see if your explanation is satisfactory.

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