Chemistry - PI 24

COVER GAS PURITY

Objectives

1. Very briefly using chemical reactions or written description, describe how deuterium and oxygen are produced in the moderator and cover gas systems.

2. State two reasons why D_2 and O_2 in the systems are undesirable. (Corrosion/Explosion).

3. Briefly describe the removal of D_2 and O_2 by recombination units and cover gas purging.

4. State the reason for having an oxygen addition facility on a recombination unit.

5. Briefly describe how Nitric and Nitrous acids are formed in the cover gas and how they are removed.

In Module 22-2 we noted that radiolysis of heavy water had the net reaction,

$$D_2O \xrightarrow{\sim} D_2 + O_2 + D_2O_2$$

This module will outline a possible mechanism for this reaction and discuss some of the consequences due to the presence of the products in the moderator and cover gas system.

In the moderator system the water molecules are continuously bombarded by gamma radiation and fast neutrons. These radiations deposit energy in the water molecules causing them to split up into D_2O^+ and a free electron (a form of ionization).

$$D_2O \longrightarrow D_2O^+ + e^-$$

The two products being of the opposite charge attract each other and gain energy as they accelerate towards each other. They meet and neutralize each other to form a neutral excited (ie, high energy) water molecule.

$$D_2O^+ + e^- \longrightarrow D_2O^*$$

This excited water molecule will lose energy by splitting up to form D and OD **radicals.**

You will recall from your high school chemistry that if water ionizes, two ions, one positive and one negative are formed.

$$D_2O \longrightarrow D^+ + OD^-$$

The significant thing to remember in ionization of water is that the deuterium which ends up as the positive ion has given up its electron to the OD^- ion.

Now in the split up of the excited water molecule formed above the deuterium does not give up its electron but retains it and becomes a neutral radical. By the same token the OD radical also has no charge.

$$D_2O^* \longrightarrow D^O + OD^O$$

(I have written in the "O" charge although this is not normally done).

The radicals will attempt to combine to form stable products.

$$D + OD \longrightarrow D_2O$$

$$D + D \longrightarrow D_2$$

$$OD + OD \longrightarrow D_2O_2$$

Water will also be reduced by the solvated electrons, formed in the initial radiation induced split.

$$2D_2O + 2e^- \longrightarrow D_2 + 2OD^-$$

Thus, as a result of radical combination and the reducing action of solvated electrons we have produced D_2 gas and deuterium peroxide, D_2O_2.

The deuterium gas will tend to "bubble off" into the cover gas. As the concentration of D_2O_2 rises, it will tend to react with OD radicals.

$$4OD + D_2O_2 \longrightarrow D_2O_2 + O_2 + 2D_2O$$

(This is actually a two-step process with regeneration of D_2O_2 in the second step. For further details consult lesson 124.20-2).

The D_2O_2 will tend to reach an equilibrium concentration as using up OD radicals as above inhibits the initial production of D_2O_2. The O_2 gas produced will "bubble off" into the cover gas.

The slight amount of D_2O_2 left in the moderator poses two problems:

(a) It is very reactive, corrosion of system metals is favoured.

(b) If it gets to the ion exchange resins in the purification system it may break these resins down, releasing organics into the system. The other half of the radiolysis problem is an accumulation of D_2 and O_2 in the cover gas which is an explosion hazard.

Oxygen, in the moderator and cover gas will corrode system components. (It should be noted here that not all the D_2O_2 is used up to produce O_2. Therefore there is a slight stoichiometric deficiency of O_2 vs D_2 in the cover gas, ie, $D_2:O_2 < 2:1$).

To remove D_2 and O_2 from the cover gas the gas is continuously circulated over a catalytic recombination unit (see Lesson 233.20-3 for system detail). The RCU contains a catalyst:

(a) to allow recombination to take place at all $D_2 + 1/2O_2 \longrightarrow D_2O$.

(b) to ensure that this recombination is peaceful rather than explosive. (In any case RCU's are fitted with flame arrestors to prevent the propogation of any explosion that may occur). The catalyst used by NGD is palladium coated on to clay or alumina pellets. Heaters are installed on the RCU's as the catalyst will not work if it is wet.

Cover gas is monitored for D_2 and O_2 and should the O_2 concentration be too low, O_2 may be added before the RCU to achieve the appropriate ratio for recombination.

If D_2 in cover gas rises above station limits, purging of the cover gas with fresh helium may be required to bring the concentration down.

Before we leave radiolysis, we should consider the effect of air leakage into the cover gas system. Although the system is pressurized and thus should exclude air, from time to time, some air does enter.

Air is for all practical purposes a mixture of NITROGEN and OXYGEN, plus a few trace elements.

Without going into detail on mechanisms, if there is N_2 and O_2 in the cover gas, exposed to radiation, NITRIC and NITROUS oxides are formed, these dissolve in the moderator water to form acids. Naturally these acids are corrosive. Removal of these acids is via the ion exchange resins in the purification system.

Trace elements in the air, notably, Argon, tend to be come activated, posing radiation hazards.

Practice Exercises

1. Review the objectives at the front of Module 22-2, 22-3 and 22-4. Satisfy yourself that you have the data straight by jotting down the points and checking with a colleague on the notes.

2. Try the following AECB questions. The course instructor will lend you a book of "standard" answers - (after! you have tried the questions).

   (NOTE: You may find some overlap in the questions. Also you may have to draw on other knowledge and courses for complete answers).

TYPICAL AECB QUESTIONS:

MODERATOR AND COVER GAS

1. Discuss two reasons for using a catalyst in the recombination units.

2. Why are RCU's fitted with flame arrestors?

3. Why are RCU's fitted with heaters?

4. Discuss five reasons for maintaining cover gas and moderator chemistry.

5. List and discuss the main chemicals and impurities concerned with MODERATOR AND COVER GAS Chemistry.

6. How is moderator and cover gas chemistry maintained?

7. What components are most likely to be damaged by:

Cl^-	(chloride)
F^-	(fluoride)
O_2	(oxygen)
N_2	(NITROGEN)

What are the sources; problems; counteractions for each of the above?

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