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HYDROGEN EXTRACTION FROM A GAS MIXTURE

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HYDROGEN EXTRACTION FROM A GAS MIXTURE

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ABSTRACT

Hydrogen extraction from the gaseous mixture CH_4, H_2, N_2, NH_3, O_2, H_2O,CO_2, occuring as impurities has been performed by chemical reaction with uranium metal - Thermodynamical and kinetical investigations have confirmed hydrogen could be purified by this process, but experiments performed at 973 K point ou the importance of the interferences that can occur in the system uranium - gases mixture.

1.- INTRODUCTION.

Burned gases exhausted from the plasma chamber of a fusion device contain impurities linked with hydrogen atoms - After being separated from the main hydrogen stream, these impurities must be decomposed to recover their tritium content. The aim of this work is to study the hydrogen extraction from the gaseous mixture, N_2, H_2, CH_4, NH_3, O_2, using chemical reactions with an appropriate metal. This consists in cracking hydrogenated molecules and in absorbing the impurities without holding back hydrogen. A bibliographic study as well as a thermodynamic one lead us to predict that uranium could satisfy these conditions.

2.- THERMODYNAMIC STUDY OF THE CHEMICAL REACTIONS.

For T > 423 K, the hybride formed is UH_3 (β) and respectively UD_3 (β) and UT_3 (β), with deuterium and tritium | 1 |. The equilibrium reaction between uranium and hydrogen, implies that, at T = 700 K if hydrogen pressure (respectively deuterium and tritium pressure) is lower than 1.31 10^5 Pa (respectively 1.99 10^5 and 2.66 10^5 Pa) no uranium hydride will be formed (Fig 1).

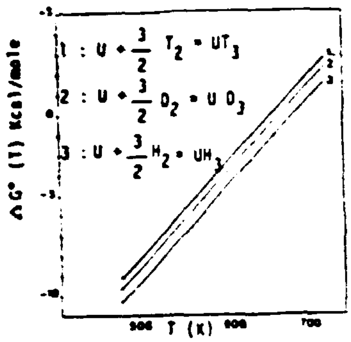

FIG 1 : URANIUM HYDRIDE FORMATION

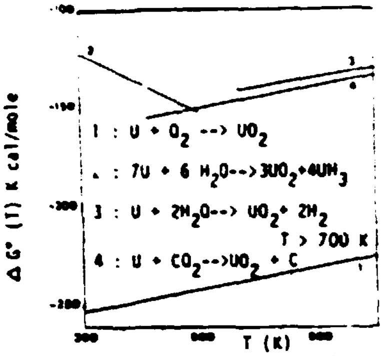

FIG 2 : URANIUM OXIDE FORMATION

The two stable forms of uranium oxide are UO_2 and $U_3 O_8$ |2|. The first step of uranium oxidation being UO_2 formation, we only take this reaction into account in the thermodynamic study. All the oxidation reactions are irreversible (Fig. 2).

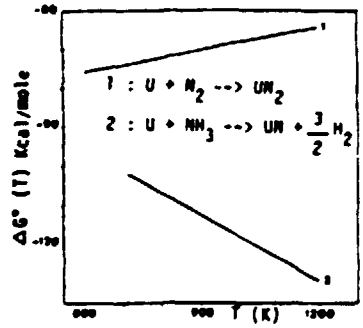

FIG 3 : URANIUM NITRIDE FORMATION

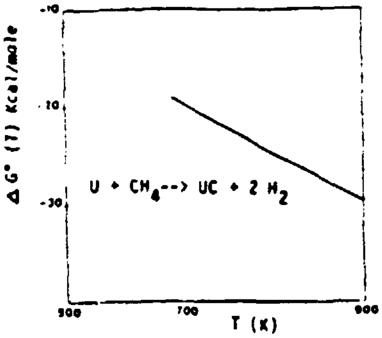

FIG 4 : URANIUM CARBIDE FORMATION

The three stable forms of uranium nitride being UN, $U_2 N_3$ and UN_2, the first step of the reaction is the formation of UN_2 for T < 1000 K and of UN for T > 1000 K |3, 4|. Only UN formation was considered since no thermodynamic values were found for UN_2. UN form is the most stable one. At 1473 K, at pressure lower than 10^{-4} Pa, it could be decomposed into uranium and gaseous nitrogen, when 0,25 Pa is sufficient to decompose $U_2 N_3$ or UN_2 as $U_2 N_3$ ---> 2UN + ½ N_2 |3,4|. The results gathered in figure 3, confirm that nitride formation is irreversible.
Like oxide and nitride productions, the reaction between uranium and methane is irreversible (Fig 4), the first step being the formation of the monocarbide UC |5|.

We have been interested by the chemical reactions between the reactions products : oxides (UO_2, $U_3 O_8$), nitrides (UN_2, $U_2 N_3$) and uranium carbides (UC, UC_2) and a fresh gaseous mixture of H_2, O_2, NH_3, CH_4, N_2. A bibliographic investigation suggests that hydrogen reduction as well as oxidation of the solid products are the two important effects |7|.

All the products formed with pure uranium may be oxidized, giving off impurities such as CO_2, O_2or N_2, even with oxygen traces, as soon as Kp is lower than $K_{p_{eq}}$ (Table 1).

TABLE 1 : OXIDATION OF THE SOLID PRODUCTS AT $T = 600$ K

Reaction	$G°$ (600K) k cal/mol	ln K_{peq}
$3\,UO_2 + O_2 \dashrightarrow U_3O_8$	- 64.73	54
$3\,UN + 4\,O_2 \dashrightarrow U_3O_8 + \frac{3}{2}N_2$	- 527	439
$3\,U_2N_3 + 8\,O_2 \dashrightarrow 2\,U_3O_8 + \frac{9}{2}N_2$	- 1070	892
$3\,UC + 7\,O_2 \dashrightarrow U_3O_8 + 3\,CO_2$	-811	676

The hydrogenated molecules being cracked, the reactions products will be in contact with great quantity of free hydrogen, giving rise to new chemical reactions (Fig 5).

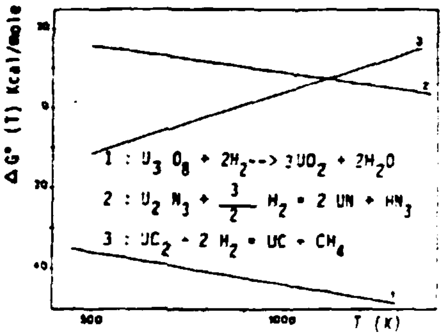

FIG 5 : REDUCTION OF THE SOLID PRODUCTS BY H_2

Hydrogen completely reduces U_3O_8 from the low temperatures giving off H_2O. The equilibrium reactions of U_2N_3 and UC_2 reductions prove that temperature and pressure conditions have to be judiciously choosen, in order to avoid any ammonia either methane releasing, this occuring respectively at the highest temperature and at the lowest one. For example, with an hydrogen pressure of 10^5 Pa, the releasing of ammonia can reach 1.29 10^4Pa at 1300 K and 3.11 10^4 Pa pressure of CH_4 at 900K, at the equilibrium.

The reactions between the solid compounds imply that oxygen, nitrogen and carbon have to be dissolved in the same uranium lattice, to give U (C, O, N). This occurs at $T > 1473$ K and $P < 7\ 10^{-3}$ Pa, and no significant gaseous releasing will be observed |6|.

These thermodynamic considerations suggest us that uranium could be used for the extraction of free hydrogen from the gaseous mixture H_2, N_2 NH_3, CH_4, O_2, but under appropriate operating conditions of temperature and pressure.

At temperature higher than 700 K and hydrogen pressure lower than 1.31 10^5 Pa, hydrogen will not react chemically. On the contrary, the remaining gases will form solid uranium products. They could however be oxidized giving off N_2 or CO_2.A solution might be to favour oxidation of pure uranium in order to eliminate any oxygen trace. They could also be reduced by hydrogen giving off H_2O, CH_4 or NH_3, this occuring preferably at $T < 900$ K and $T > 1200$ K for carbides and nitrides respectively, and as soon as K_p is lower than the equilibrium constant $K_{p_{eq}}$.

The practical use of uranium under these conditions depends however on the kinetics of the reactions : the initial solid attack, representative of surface phenomena, the kinetics at high conversion rate of the solid, that will give the usable mass of solid, and the likely interferences that should be taken into account to obtain a good representation of the system uranium-gases mixture.The two first points were previously described in litterature |2,5,8,9|.In order to define the resistance of uranium to gases such as oxygen, ammonia, nitrogen or methane, the authors carried out their investigations at constant pressure. Solid attacks are generally linear and produce porous layers that can also undergo desquamation. The results agree with the possible formation of a compact film of product, laying on the uranium surface (2, 3, 5).Diffusion of gas through this compact layer could be the limiting step of each chemical reaction and will be related to the evolution of composition and compacity of the reaction products with temperature.

3.- EVOLUTION OF THE NATURE OF THE PRODUCTS WITH TEMPERATURE.

At $573 < T < 973$ K, the formation of U_3O_8 favours uranium oxidation by fissuring the product layer, so that the compact film UO_2 is no more protective |2| - At $T > 1073$ K, U_3O_8 sintered and oxidation rates slow down |7|.

At $T < 1023$ K, UN_2 is the main product in the compact film and in the out-layer solid. From 1023 K to 1173 K, there would be a film of UN and an out-layer of U_2N_3 -UN_2 |3,4|, and the solid is as more pulverulent as the temperature is growing up |8,9|.

At $T < 973$ K, uranium methane reaction mainly provides UC, while at $T > 1173$ K, pure UC_2 may be formed, the reaction rate increasing with temperature |5|.

These thermodynamic and kinetic results let us suggest the existence of a temperature range $873 \text{ K} < T < 1173$ K, where impurities consumption as well as products stability under various conditions should be the most efficient.

4.- PRELIMINARY EXPERIMENTS.

In order to check and extend the experimental results established in litterature and more precisely to define the interferences that may occur in uranium-gases mixture system, we have built an apparatus (Fig 6).

Gases mixture, prepared in a first loop, is flowing in the reactor loop, which volume is 2.5 liters, at rates set at about 5 l/mn. Thermocouples (type K) measure solid and gas temperature respectively at T_1 and $T_{2-->5}$, capacity transmitters of pressure provide gas pressure at P_1 and ΔP_1, and a gas chromatograph define gas composition as function of time. We utilize small cylinders, cut in impoverished uranium of 99,5 % purity, that we first clean with pure nitric acid and then polish with abrasive paper.

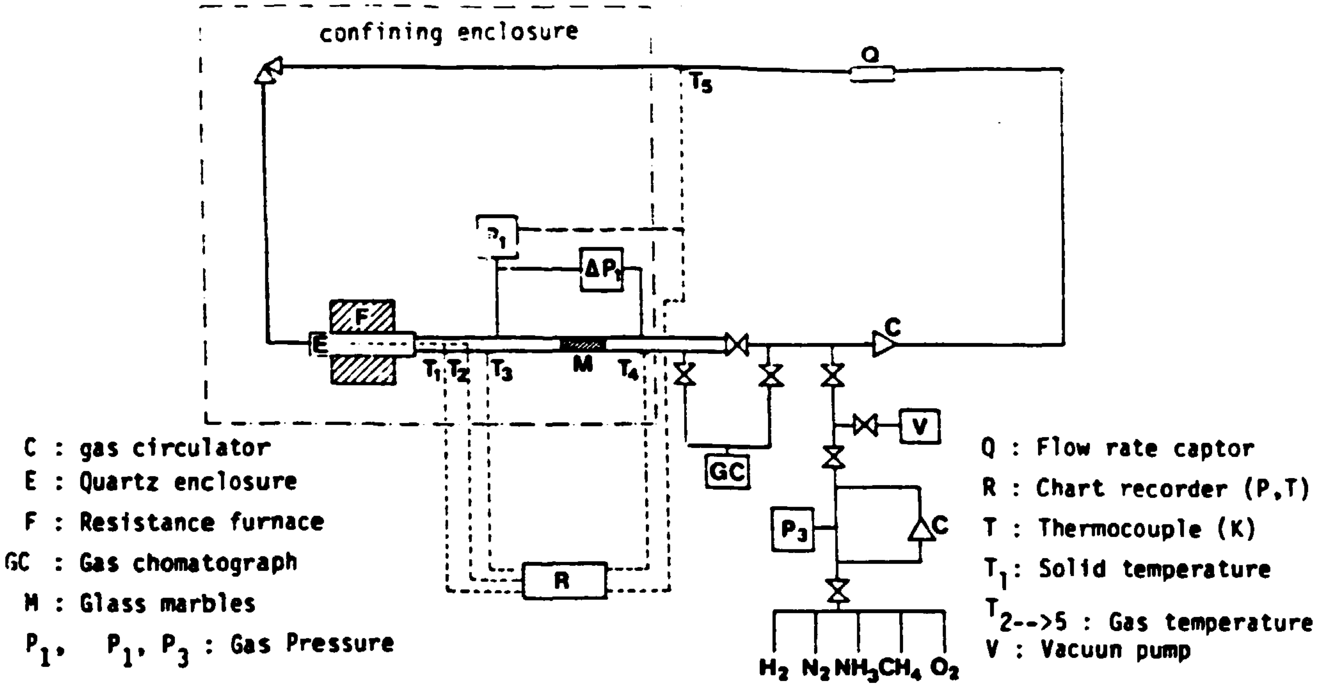

FIG 6 : APPARATUS DIAGRAM

Two qualitative experiments were performed at 973 K. The present gas mixture was O_2, H_2, NH_3, CH_4, N_2 in the first experiment, while there was no oxygen in the second one. The initial ratios of gas moles number to uranium surface were respectively 60 moles/m^2 and 100 moles/m^2.

Results : Oxygen was immediately consumed. Then a first part of ammonia reacted with uranium giving a nitride (Fig 7), the other part being decomposed into gaseous nitrogen and hydrogen. We also observed methane and nitrogen reactions with uranium (Fig 8), that are much slower than the first ones. Initially present hydrogen did not react chemically, and ammonia and methane crackings provided the predicted hydrogen amounts.

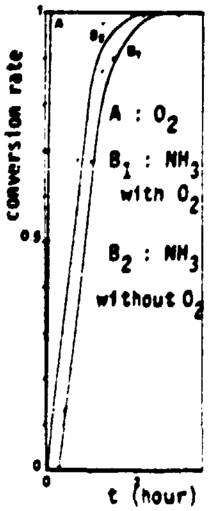

FIG 7 : CONVERSION RATES OF O_2 (A) NH_3 (B_1, B_2), O_2 BEING PRESENT (B_1) AND WITHOUT O_2 (B_2)

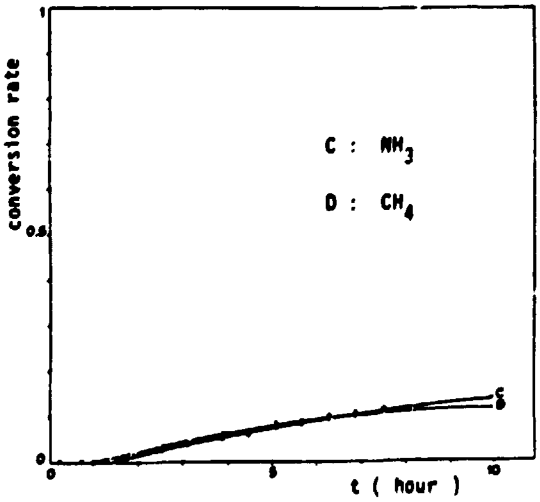

FIG 8 : CONVERSION RATES OF NH_3 AND CH_4

The obvious selectivity of the chemical reactions between uranium and the gaseous mixture, oxygen reactivity being higher than ammonia then nitrogen and methane ones, leads to interferences into the system. Oxygen delays ammonia reaction (Fig.7) as well as ammonia delays methane reaction (Fig.8), while ammonia decomposition into gaseous nitrogen maskes initial nitrogen conversion rate (Fig. 8). In order to define the influence of the different product layers progressively formed at uranium surface, on the gas reactivity, we aim to first study each chemical reaction at 973 K, and then to compare the rate constants to their values when in gaseous mixture.

5.- CONCLUSION.

Qualitative experiments seem to confirm that uranium could be used for hydrogen purification, at 973 K. Our aim is now to study each chemical reaction at different pressures, to predict the reactivity of the gaseous mixture on uranium as function of its composition. This will let to predict the uranium amount required for the treatment of various composition gaseous mixtures.

REFERENCES :

| 1 | The Chemical Thermodynamics of actinide elements and compounds - International Atomic Energy Agency - VIENNA, 1984.

| 2 | Fundamental Aspects of Nuclear Reactor Fuel Elements - D. OLANDER - National Technical Information Service Ed (1976).

| 3 | Compounds of interest in nuclear reactor Technology - I M D Special report N° 13.

| 4 | R.N. ALIRE and J.H Mc CRARY, J. Chem. Phys. 45,11,3958, (1966)

| 5 | F.A. ROUGH and W. CHUBB-Report N° BMI 1488 (1960)

| 6 | F.ANSELIN - G. DEAN - R. LORENZELLI - Carbides in Nuclear Energy Mc Millan and coll London - Vol 1 - 113 - 1964.

| 7 | R. DARRAS, Corrosion des combustibles à base d'uranium, in PASCAL, Nouveau traité de chimie minérale, Tome XV, 4ème fascicule - Masson et Cie, Ed (1967), pp 944 - 1012

| 8 | Y. ADDA - Rapport C.E.A. N° 757

| 9 | M. W. MALLET and A.F. GERDS, J. Electrochem. Soc. 102,292 (1955).