

M. De Beni

MARK-1 as an Example of a "Direct" Process for Producing Hydrogen

Introduction :

Hydrogen is produced today by reacting certain fuels (methane, oil, coal) with water. These fuels somehow reduce water, liberating its hydrogen, and a certain amount of heat is absorbed in the process.

Extra heat is necessary because the overall reaction is endothermic. It comes usually from the partial combustion of the fuels reacting with water, but it can be added through a heat exchanger, and the source can be a nuclear reactor.

In the last case, however, the amount of nuclear heat that can be sold as chemical energy can cover a quite limited fraction of the chemical energy in the products (10 + 15%), and, as a consequence, it can't have a large influence on the prices.

On the other side there is a great advantage in using reactors of very large size because heat cost is very size-sensitive.

As Mr. Marchetti said, this has been the driving force to find a process exclusively linked to nuclear energy. So our goal was clearly set: extract hydrogen from water using just heat without using fuels or electrolysis, that means finding a way to substitute completely the role played by the fuel. This with the obvious constraint that temperatures must be in tune with what reactors can give now or in the next future.

The Search for a "Direct" Process

As a general trend, with the remarkable exception of carbon monoxide, the free energy of formation of a certain oxide is continuously decreasing as the temperature increases. So, for each oxide, it will exist a certain temperature T_d at which the equilibrium oxygen pressure will reach, e.g. 1 atm.

The simplest way then to split water would be to heat it high enough to dissociate it and to separate in some way the dissociation products: hydrogen and oxygen (at the temperature of dissociation, e.g. by permeation or after a rapid quenching).

But to realize this process, heat at about 2500° - 3000°C would be necessary, and this is out of the possibilities offered today by nuclear reactors.

The free energy values for oxide formation at room temperature are quite spread from positive to very negative values, even higher than -100 Kcal/mole.

If the room temperature value of free energy for a certain oxide is lower than about 30 Kcal/mole there is a probability that its T_d will be lower than 1000°C. (Figure 1 : ΔF versus T for various oxides). We took 1000°C as reference maximum temperature that we could use in the process.

As it can be seen from the diagram, oxides lying in the upper left region will dissociate before reaching the temperature of 1000°C.

So, an indirect way to dissociate water could be the following : to transfer the oxygen from water to another element, whose T_d is lower than 1000°C. From the same diagram it is also possible to draw informations about the reaction that can take place

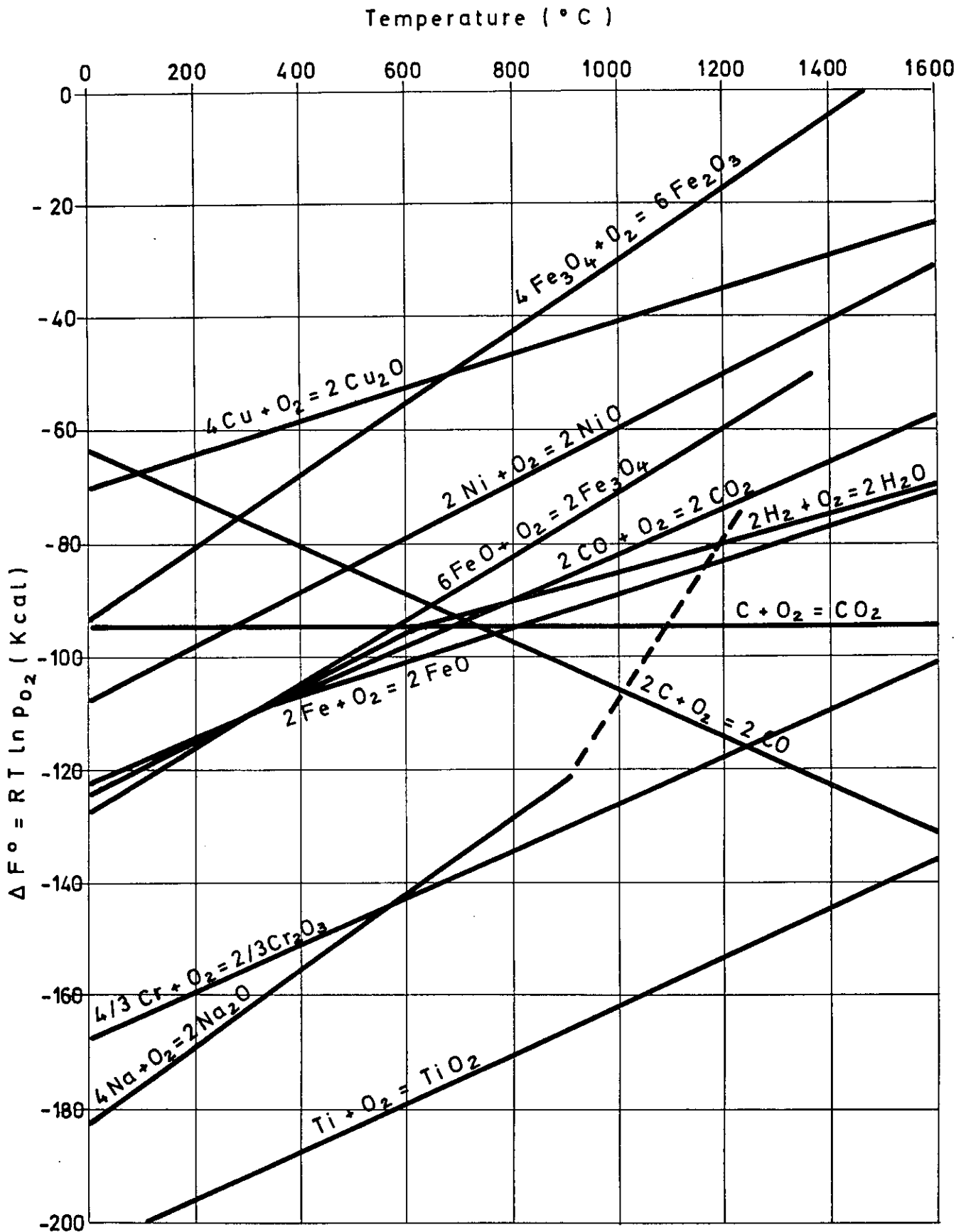


Fig 1 Standard free energy of formation of oxides as a function of temperature



between an element and an oxide. If we put together one element and one oxide or, and it is just the same, two elements with a deficiency of oxygen, the oxide will be formed that has the more negative free energy of formation. That is, in this diagram, the stabler oxide will be that in the lower position.

In order to get the oxygen transferred, as mentioned before, we must have an element whose free energy of formation is higher, in absolute value, than that of water at room temperature, and become 0 below 1000°C. On the usual diagram the line of the free energy of formation of this ideal element (or component in general) would lie in the upper left region and would have a slope high enough to intersect the line of water at the lower temperature and the line of zero ΔF before 1000°C. Unfortunately we didn't find such compound (and probably it doesn't exist).

In absence of this ideal compound we must look for another trick, and this will be more easily found the higher the maximal temperature available. Originally our maximum allowable temperature had been tentatively fixed at 1000°C, with an incentive for process using heat at less than 800°C.

Due to these limitations we thought that the way to dissociate water would be more easily found if the process could be splitted in two branches; that is if water can be transformed in one acid and one base; then using the acid to attack some metal, and the base to generate some hydroxide that could be dissociated in the temperature range we had allocated.

Once these points established, the choice among the various possibilities has been quite restricted; for the oxides we thought, for ex., of mercury, silver, higher oxides of uranium, manganese, indium, lead.

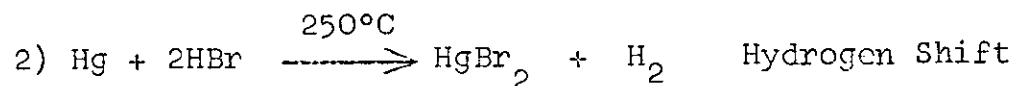
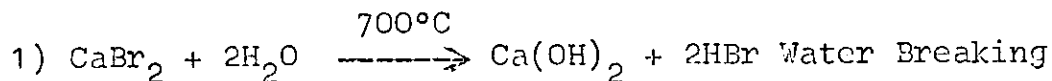
The choice of the metal restricts the fields of possible acids to react conveniently, and so on for the following steps.

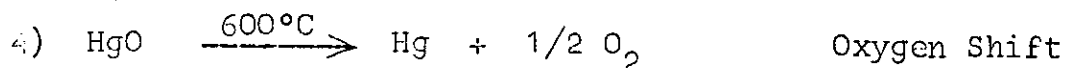
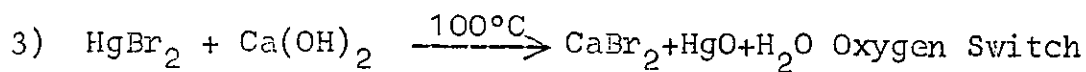
As the result of this type of iteration process, we have found a set of chemical compounds through which it is possible to realize the dissociation of water by a closed chemical cycle.

It is quite evident that there exist other possible cycles, that will be, as we already said, more and more simple as higher and higher is the maximum allowable temperature.

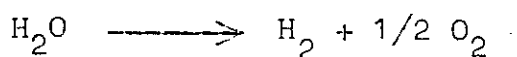
The MARK-1 Cycle

The chemical elements on which our cycle, named MARK-1, is constructed are : mercury, bromine and calcium. The set of reactions in the cycle is the following :





The sum of the four reactions is :



For each reaction we have a certain enthalpy change ΔH , and their sum will be equal to the enthalpy change for the dissociation of water, taking naturally into account not only the ΔH of the reactions, but also the heats involved in heating and cooling the various products, and in the concentration (i.e. compression) of HBr and CaBr_2 . In fact HBr is produced in reaction (1) at a certain partial pressure in an excess of steam and must be concentrated, and CaBr_2 is produced in a water solution containing more than the two molecules of water necessary for its hydrolysis.

Now, if we add the enthalpies of the four reactions, the heat for heating, cooling and compression of the various fluids and materials and the enthalpy for the formation of water from the elements we find that $\Delta H = 0$. It must be clearly so because the cycle must respect the first law of thermodynamics. But the second law imposes other constraints we are going now to analyse.

Thermodynamical considerations

One of the first reactions we had to face when presenting the process is that the fact that we can

extract the heat by reacting hydrogen and oxygen at a temperature quite higher than the maximum temperature at which heat has been consumed in the chemical reactions appears as a contradiction to the second law. This is not the case because the reactions in the cycle are such that we have also a release of degraded heat at low temperature.

Stated in a different way : the lack in entropy coming from the high temperature combustion of hydrogen is compensated by an excess of entropy coming from the enthalpy of exothermic reactions at low temperature; as a result the sum of the entropies of all the steps will be zero, respecting the second law of thermodynamics. I don't write here the values of all entropy changes connected with the various steps of the cycle, because they are not reliable enough, in particular the values for high temperature are lacking, so the balance loses real meaning. We must say, however, that all the reactions have been tested in our laboratory and they run in the proper direction. But I can give an example of a much simpler cycle where the mechanism is precisely verified (Fig. No. 2, F of sulfides versus T).

This is a diagram in which are reported the free energies of formation of sulfides (the first one did refer to the oxides) vs. temperature. The same type of information can be extracted from this second diagram, and I refer to the following three lines : the line of zero free energy of sulfur, the line of the equilibrium $FoS-FoS_2$ and the line of formation of hydrogen sulfide.

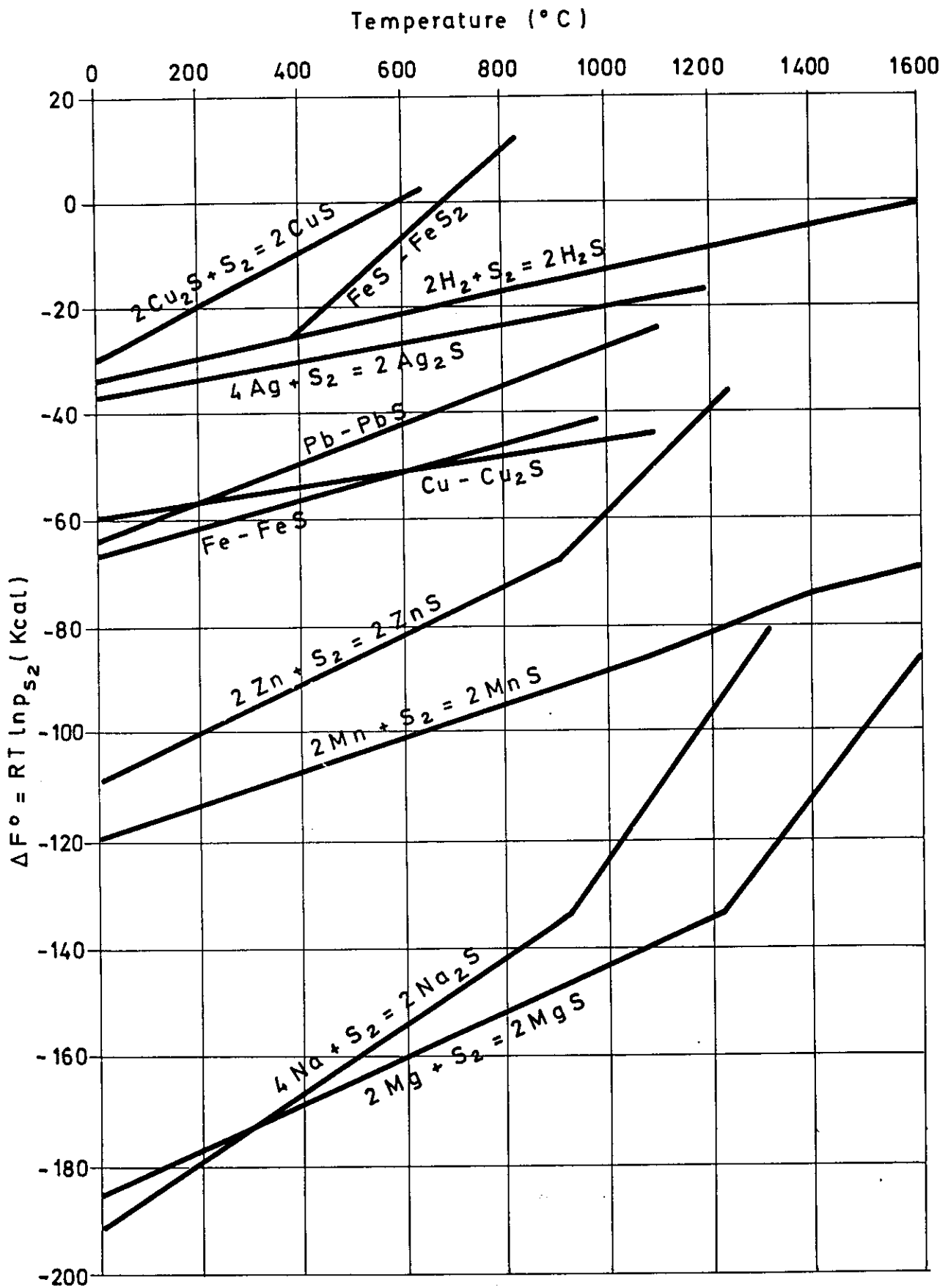
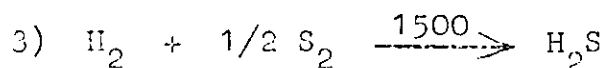
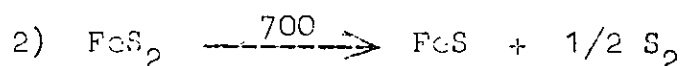
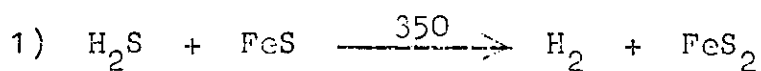


Fig. 2 Standard free energy of formation of sulfides as a function of temperature

By the same rules already mentioned, we know that the three following reactions go in the direction marked at the temperature indicated:



Here we have again a closed chemical cycle with a transfer of heat to higher temperatures, a kind of heat pump, but without consumption of chemicals.

Let us look now at the thermodynamics of the cycle. The enthalpy changes roughly calculated for the reactions are the following :

$$\text{reaction 1 : } \Delta H = - 16 \text{ Kcal}$$

$$\text{reaction 2 : } \Delta H = + 44 \text{ "}$$

$$\text{reaction 3 : } \Delta H = - 28 \text{ "}$$

The sum of the enthalpy change (with the assumption that heats for heating and cooling are balanced) is zero, according to the first law of thermodynamics. The values of the entropy associated with the reactions are the following : -26, 45 and -16 and their sum is again nearly zero, so the second law of thermodynamic is respected. The small discrepancies come from uncertainties in the state of association of gaseous sulfur : S_2 or S_6 .

(By the way, if we had a source of hydrogen sulfide this could be a mean to dissociate it in hydrogen and sulfur, something perhaps interesting refineries who now liberate sulphur by partial oxidation of H_2S).

This cycle could also be seen as a mean of disproportionating heat : the heat that goes in this black box at $700^\circ C$ comes out part at $350^\circ C$ and part at $1600^\circ C$. The three amounts are such that the entropy balance is always zero (in conditions of reversibility).

In general we can say that if the release temperature of the high temperature heat is continuously increasing, the entropy associated with this energy is diminishing and the entropy balance must be finally supported by the heat released at low temperature, actually we find the relation $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ and this is just the well known relation determining the efficiency of a Carnot cycle, for producing e.g. mechanical energy from heat.

More details on MARK-1

In fig. 3 we show how the various steps of the cycle are interconnected. The real layout may be quite different, but in this diagram the primary connections linking the different steps are already present. The lines refer just to chemical products, and there are no indications for the heat flows.

Being a closed cycle we can start at any point.

In step 1) (where reaction 1 runs) calcium bromide and water vapor are going in, and, after reaction, hydrobromic acid with excess steam and calcium hydroxide are coming out.

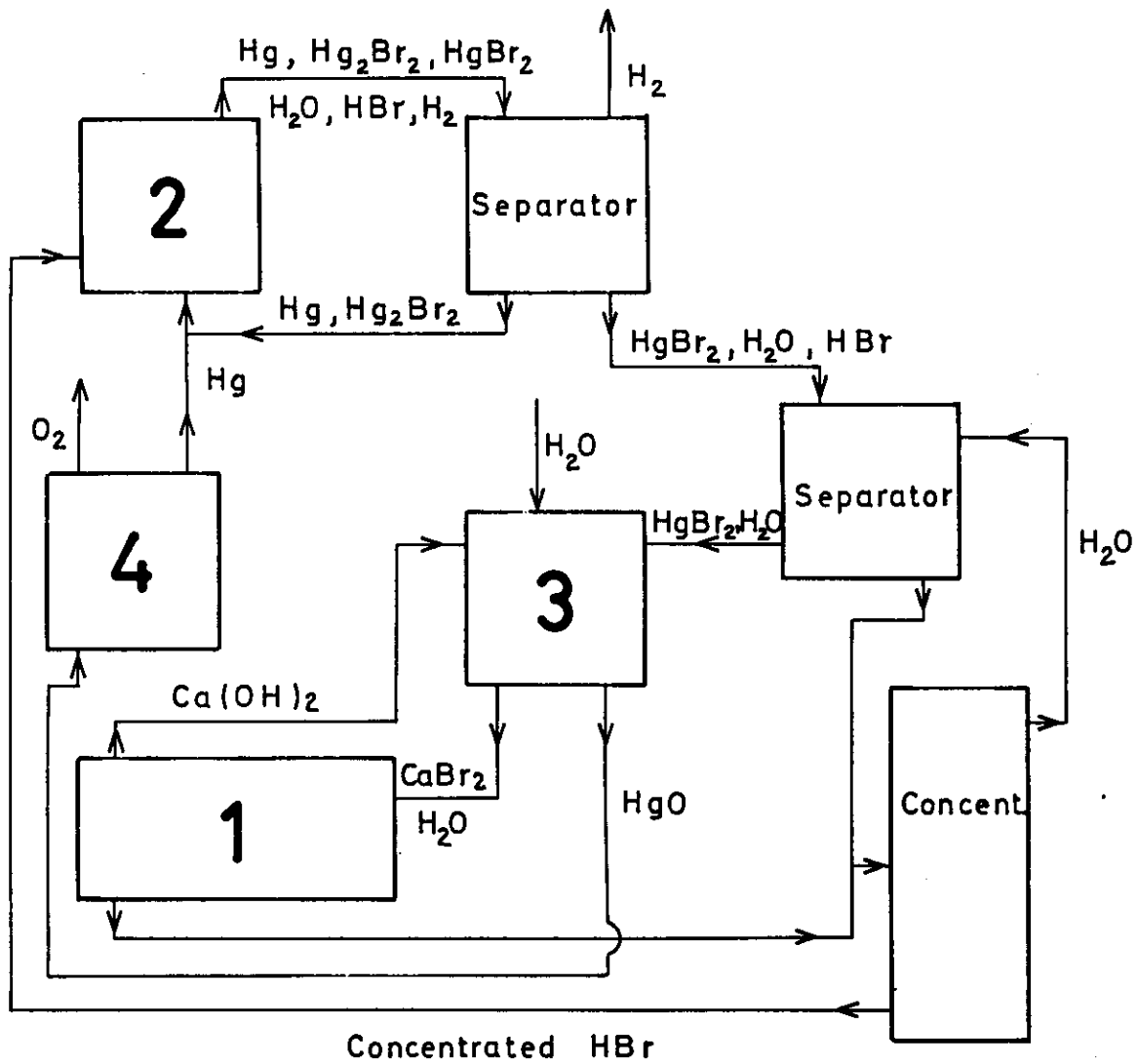


Fig.3 Block diagram.

Hydrobromic acid goes to a distillation column in this scheme, whose outputs are water at the top and concentrated hydrobromic acid at the bottom. The concentrated hydrobromic acid is fed into the step 2), with mercury, to perform reaction No. 2. The products of this reaction are : hydrobromic acid, water, mercury, mercurous bromide, mercuric bromide and hydrogen. In a first separator, gases are separated from the liquid, and here we produce hydrogen (that must then be washed with some calcium hydroxide before leaving the plant); in the same separator mercury and mercurous bromide (quite insoluble) are separated. Mercury and mercurous bromide are fed again in step 2); the remaining solution is stripped to separate most of the hydrobromic acid it contains; the stripped hydrobromic acid goes in the distillation column at the proper level; the remaining solution of mercuric bromide is fed into step 3) with the water and the calcium hydroxide coming from step 1).

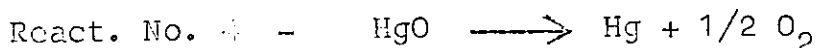
After this step we have a solution of calcium bromide which is easily separated from the mercuric oxide precipitate. The solution of calcium bromide is concentrated before going to hydrolysis in step 1).

Mercuric oxide is fed in step 4) where we have its thermal dissociation.

The separation of the products of dissociation can be realized for example by quenching the vapors and so condensing the mercury, avoiding in this way a backward reaction with oxygen. This quenching could also be realized, e.g. by expanding the vapors in a turbine. Mercury coming out from this step goes into step 2) to react with hydrobromic acid. At this point the cycle is completed and an input of water and an output of hydrogen and oxygen is the global result.

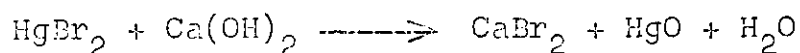
The knowledge we have now for some of the reactions is not sufficiently good for evaluating yields, not to speak about costs.

Chemical Consideration about the Reactions (1) - (4)



Only the dissociation of mercuric oxide is well known; dissociation rate is not a problem and there are catalysts able to increase this rate if necessary; dissociation pressure vs. temperature is well known, too. A better knowledge is needed for the rate of recombination because this rate defines the cooling rate for the vapors.

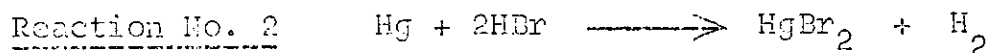
React. No. 3



We didn't find any information in the literature for the precipitation of mercuric bromide with calcium hydroxide. From some experiments performed in our laboratory, we found that the precipitation can be realized in a boiling solution at atmospheric pressure with a certain excess (10--20%) of calcium hydroxide, boiling the solution for a few minutes.

We are running other tests in order to verify if some mercuric bromide is held in solution as a complex with calcium bromide already formed. A similar possibility of complex formation exists when the precipitation is made with sodium or potassium hydroxide, but there are no data for calcium hydroxide. Another parameter we are going to study is the time required for the proper precipitation of mercuric oxide. We must reduce this time at a minimum in order to reduce the hold up of chemicals, particularly in those steps where mercury is present.

For the reactions of precipitation and dissociation it seems that there are no serious problems concerning yield, rate of reaction and materials of construction. Difficulties arise when hydrobromic acid is present. This is the case of the distillation column, and the equipments for the separation and stripping processes after the reaction 2. In such cases we have an acidic solution at temperatures between 100° and 200°C; and only few metals or alloys are expected to withstand these environmental conditions. In particular we think of the Hastelloys (or Tantalum and Niobium). The other two reactions run at more drastic conditions and construction materials become the key problem.



The reaction of mercury with hydrobromid acid is not described in the literature; there are just some indications that a reaction can take place with formation of hydrogen.

Let us examine it in detail: as is written reactants are mercury and hydrobromic acid, but in our case the last one is not the pure acid, it is an azeotropic solution coming from the distillation column.

For the economy of the reactions, things would probably go better if we could use anhydrous hydrobromic acid, but this would mean an additional operation on the hydrobromic acid solution after it has been concentrated to the azeotropic level. The choice between the two possibilities will be the result of a more detailed study on the relative economies.

Our experiments have shown that the reaction runs well in liquid phase (this should not rule out the possibility of running it in the gas phase). The pressure

was the vapor pressure of the solution of hydrobromic acid, that has been evaluated to be 6-7 atm at 200°C. Containing such a pressure clearly is not a problem, and indeed our tests at 200°C have been performed using glass capsules. But some tests, also in glass capsules, have shown a quite faster reaction rate at 250°C, and we expect again higher reaction rates at higher temperatures; however, thermodynamical calculation shows a less favourable equilibrium constant as the temperature increases (the reaction is exothermic).

It became evident at this point, however, that we couldn't use glass capsules as the temperature increases because the vapour pressure of solution becomes too high and furthermore there is the build-up of hydrogen, so we are studying devices, e.g. a reflux cooler, allowing the extraction of part of the hydrogen from the reaction vessel while the reaction is running. However, right now and for our laboratory experiments we are assessing the already mentioned materials: Hastelloy, Tantalum, Niobium, keeping in mind that also mercury is present, and Monel 400, a useful alloy for acidic environment, suffers stress corrosion cracking in presence of mercury or mercury salts. Other possible solutions could be based on enamels and impervious graphites.

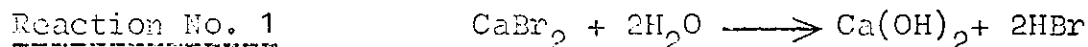
As we already said we must look for conditions where reaction rates are high when expensive mercury is present.

In this reaction we have also a negative effect due to the overvoltage for the formation of hydrogen on mercury surfaces. This overvoltage results in a slow-down of the reaction rate and in an unfavourable displacement of equilibrium. We don't know yet how hydrogen

overtoltage will play a role in those conditions of temperature and pH, but in any case we have planned to do a certain set of tests with the addition of proper materials (graphite grit or platinum) in order to reduce the effects of overtoltage.

Among the reaction products there is also Hg_2Br_2 ; we don't know the kinetics of formation of the two mercury bromides, and due to the higher free energy of formation for the Hg_2Br_2 (by respect to HgBr_2) it could be that this product is an intermediate in the formation of HgBr_2 .

In any case at the end of our tests (of a duration from 1 to 10 hours) we always find a certain amount of Hg_2Br_2 . This product can easily be separated and a study is necessary to find if it can be disproportionated in HgBr_2 and mercury, to be recycled, or if it must be recycled as it is.



For the hydrolysis of calcium bromide there is also very little information in literature, and, in spite of the good intentions of the authors, they are only qualitative.

We tried some experiments of hydrolysis and we were faced immediately with the difficult problem of materials. Thermodynamical calculation, and some experiments we did, show that the equilibrium concentration of hydrobromic acid is more favourable as the temperature increases. But as the temperature increases there are also problems which rapidly grow. To give an idea of the temperature range of interest, we can say that under 500°C there is practically no hydrolysis. Over 700°C calcium bromide begins to be too volatile and may distill away to the cooler parts of the vessel.

The products of hydrolysis are hydrobromic acid and calcium hydroxide. We try to obtain this last product instead of calcium oxide because the enthalpy of the overall reaction, that is strongly endothermic, is diminished by about 15 Kcal/mole. But calcium hydroxide is in equilibrium with water vapor at one atmosphere already at 547°C and the equilibrium pressure is doubling about every 40°C. For that reason we must work under pressure if we wish to profit of the heat of hydration of calcium oxide.

Tentative reaction conditions finally are :

- 1) Max. temperature near 700°C;
- 2) Pressure high enough to form $\text{Ca}(\text{OH})_2$ (it will probably be around 50 atm);
- 3) High HBr concentration in the gas phase : we expect some percent in partial pressure.

Due to the presence of an alkali on the wall we must find a material able to withstand all these conditions and with a not too bad thermal conductivity. It might be that this reaction could be performed with another scheme requiring less stringent material conditions, for example with a spray tower, where hydrolysis is being performed "in flight" , or with a fluidized bed where heat is carried by circulating steam, but to assess these possibilities a better knowledge of the kinetics is needed.

Some elements of economics

Thermodynamical calculations show that the theoretical efficiency of the process is around 75% (it depends a little from the temperatures at which reactions are actually run). This means that a minimum amount of heat, $3000/75 = 4000 \text{ Kcal/Nm}^3\text{H}_2$ is needed for the process.

The actual amount of heat consumed/ Nm^3 of hydrogen

produced depends clearly on the practical efficiency of the process that can be calculated only at a quite advanced stage of plant design. We assume for our considerations that this efficiency is 50%, this brings the heat necessary for making 1 Nm³ of H₂ to 6000 Kcal. If we take electrolysis as a reference process and we examine it only from the point of view of energy consumption, we see that we need 5 Kwh/Nm³ H₂; this means at least 15 thermal Kwh at the level of the power plant heat exchanger or about 13.000 Kcal/Nm³H₂ (apart from the plant efficiency, transformation and transportation losses have to be taken into account). Electrolysis has some value as a reference, because it also uses only heat to decompose water and because it has been proposed as a mean to use nuclear energy to produce (relatively) cheap chemicals.

If we take methane as the primary energy source for hydrogen production, we find that the overall thermal efficiency of the process (steam reforming) is about 50% and that assuming the cost of the Mcal being equal to one, for methane, in arbitrary units, the price of the Mcal of hydrogen is about 2.5 (see data in the paper of Prof. Schulten).

Now, if we can have the primary Mcal at a cost of 0.5 in the same units, as the HT Reactors seem to promise, the energy cost for producing H₂ will be 1/Mcal (in the same units) and we have a difference of 1.5 to accomodate capital costs and profits. This sounds quite reasonable, in the light of chemical industrial practice, for very large plants and it is at the base of the justification for the effort of research we are proposing.

It should also be taken into account the fact that when making hydrogen with coal or methane, oxygen comes out in bound form, as practically valueless CO₂. But a process of "direct" reduction produces it as a valuable chemical : pure O₂.

M. Marchetti

I would like to thank Dr. De Beni, after all he did invent this process, and I ask you to start raising questions about the process itself. If I could resume: the economic driving force for going into this kind of process of producing hydrogen is that heat from the reactor costs 1 and the energy in hydrogen costs 5. In this factor of 5 we should have the room for accommodating the efficiency, the cost of the process and, we hope, some benefits.

I open the discussion, if you have any question...

M. Kugeler

Can you give me the enthalpy values for the several reactions, for each reaction as a value per cubic meter of Hydrogen. You said 6.7 Mcal for the whole process?

M. De Beni

Yes, I have them all. You wish to have the enthalpies for the reactions?

For reaction of hydrolysis is 25 Kcal/mole;

for reaction No.2 we have - 22 Kcal/mole, it is exothermic;

for reaction No.3 it is very low: 6 Kcal/mole;

for the last one, the dissociation of mercuric oxide is 33 Kcal/mole,

This is not all because we must take into account the amount of heat necessary for concentrating hydrobromic acid and calcium bromide. It is 40 Kcal for the concentration of hydrobromic acid and 26 Kcal for the calcium bromide. Also heats of cooling and heating have to be balanced.

M. Steeman

Does the figure 6700 Kcal/m³ also contain the energy

needed to run plant e.g. to run pumps, pressurise vessels, etc. ?

M. Höhne

You said the first reaction gives + 25 Kcal, the next - 22, the next +6, the next +33. So if you add this together, you have +42 kcal. Now in order to split water you theoretically need 57.8 kcal. What is the reason for the difference?

M. De Beni

As I said before to Mr. Kugeler the extra calories are spent in concentrating hydrobromic acid and dehydrating calcium bromide.

M. Höhne

But we are talking now in theoretical terms. You need the theoretical heat in any case and in practice even more.

M. De Beni

Concentration of hydrobromic acid means compression because here in this reaction we have this enthalpy change, but we have at the end an hydrobromic acid at low pressure, that means that we have this in an excess of steam. Practically this is equivalent to have hydrobromic acid at low pressure. It must react then as concentrated acid. That means, we must compress hydrobromic acid.

M. Höhne

That means you need actually more energy somewhere...

M. De Beni

We still have two steps more ...

M. Höhne

So at least we come up to the required amount.

M. Marchetti

I may say that theoretical efficiency is 75% more or less; thermodynamical efficiency, yes, that means you need; 1.3 calories of input heat to get one calorie in hydrogen. This is the result of the calculations made in more detailed form.

M. Knoche

Now is the question what is the concentration of hydrobromic acid in the first step.

M. De Beni

Experimental results for the hydrolysis reaction at atmospheric pressure:



Temperature °C	Concentration g.HBr/Liter condensated steam
300	2,43
400	4,45
500	10,9
600	34,4
650	68,8 ; 73,0
700	278
727(1000°K)	433
750	408

The last value probably is not correct, because at this temperature calcium bromide melts and so the surface of contact was not large enough to reach the equilibrium value during hydrolysis. In any case you have these concentration values: the highest value is from the 1000°K experiment and given a density of 1.29 corresponding to 5.35 mols/liter with a mole fraction of 0.1 that is 10% in mols at 1000°K.

M. Valette

The amount of heat which was given to produce hydrogen from electrolysis it was given 5Kwh for the production of one Ncubic meter and it was assumed an effeciency of 30%. This is why you reached 15 Kwh for Ncubic meter the equivalent being 13000 Kcal and this is for normal electrolysis. Now if you take your process, if I understood well, the figure was 8000 Kcal.

M. De Beni

No, it was 6700.

H. Valette

I understood 8000 was your required energy. In any case I wanted to say that nuclear reactors in particular HTR, are aiming at producing electricity with 50% efficiency with gas turbines. So there instead of 13000 Kcal for the equivalent of 5 Kwh you would have something like 8600 if you have 50% efficiency. So you have 8600 Kcal, so the margin will be smaller than the one given there.

M. Marchetti

I just want to give a little answer to Mr. Valette. Another point which is very important is that capital costs for electricity production is quite high. I mean you have a long process. You go from to mechanical energy and then to electrical energy and then rectify it then you make electrolysis. And at every step you have machinery handling all the energy down to the step of electrolysis. In our case we have a single step.

M. Valette

But I don't know what would be the capital investment for such a plant neither, so this is ...

M. Marchetti

You see, general trends say that chemical plants for the same amount of energy handled are much cheaper than electromechanical plants. I can't demonstrate such a statement for our process, in general it is so.

H. Van Heek

I have some question about some of these reactions. The first one is that a solid-gas reaction and the next one is liquid-solid?

M. De Beni

Liquid-liquid

M. Franzen

Yes, it must be so, because mercury is liquid.

H. Van Heek

And reaction three what ...

H. De Beni

We have a solution of mercury bromide. Mercury bromide is quite soluble, and to the solution we add a suspension of calcium hydroxide, a slurry. Calcium hydroxide is quite insoluble but it goes in solution as it reacts with mercury bromide.

M. Höhn

We need at least two fluidized beds for the reaction between solid state and gas and you will have at least two liquid reactors which are actually not too expensive. So this process appears feasible from the technical point of view.

Let me mention still another point. We should not link the chemical problems with the energy problems, because you said that for the high temperature reactor you need a development time of 10 to 15 years and you don't know

yet which process will be economical in 15 years, using higher temperatures. In order to reach the aim, one should always take the conditions as they are now. For the water splitting process under discussion it should already now be economical to use fossile fuels in order to obtain marketable hydrogen. We should not look now at a nuclear source of heat, we just should use fossile fuels to make this process work; and if this is the case it will be even more economical at a later time if nuclear energy is used. In other terms: at present we should not link the development of the chemical process with the development of nuclear plants.

M. Franzen

What I want to say is: the development of the special techniques to combine these four steps can be done independently of what type of heat you have to introduce into it; where the heat is coming from, whether from a nuclear reactor or from a simple combustion of existing fuels, of course, this development can be done, You cannot see from the what source it comes from.

M. Höhne

And it has to be economic at this time already with fossil heat sources.

M. Franzen

So this brings me to a question I want to ask you. Did you ever just calculate, assuming a certain cost for the heat to put into the various steps, what would be the price of one cubic meter of hydrogen, say at a purity of 99%;not higher? The economics for using hydrogen for various processes are so that the market at this time and in the next years will accept hydrogen only at certain cost conditions. This is for instance what the hydrocracking people say: hydrogen can be used in enormous quantities for the hydrogenation of high

boiling residues; if you can dispose hydrogen at a price, say below 4, make it 3,5 to 4 Dpf for one Ncubic meter with a concentration higher than 90%, that would cause an enormous consumption of hydrogen. This is my question.

M. Marchetti

I can try to give an answer. We started with a certain price of heat. That is in mills 0.8 mills. The theoretical efficiency of the process is 75%, let me say, that the practical one is 50%, a figure like another. That means that just from the heat balance the cost of hydrogen will be 1.6 mills per Mcal of energy in hydrogen.

M. Kugeler

May I do a little calculation, you need 6.7 Mcal for Ncubic meter hydrogen and if you take a price for the Mcal in fossile fuels like in the Netherlands, 0.52 Dpf/Mcal, you get without any capital costs a hydrogen price of 3.5 Dpf pro Ncubic meter.

M. Marchetti

But we are talking only of the heat balance not the capital cost for the moment.

M. Kugeler

Yes, without any capital cost.

M. Franzen

This production cost would be 3.5 Dpf for 1 Cubic meter, well, capital cost add a certain amount to that production price; this depends on what depreciation one could have for the capital, and on the size of the plant of course. If the size on the plant is big, the first condition and if you can say, well, we have a writing-off-time of 15 years or even more, then I think that the

addition to this production price on behalf of capital costs is only nominal, maybe 20% or 10, I don't know, but very nominal. So this would lead to the situation that, based on the energy cost of normal fuels we have on hand now, 0.52 for natural gas for instance, the hydrogen can be produced with the new processes at a price which is comparable with the price now on the market.

M. Höhne

Could I give it in a diagram?

M. Marchetti

Yes, yes, thank you.

M. Franzen

Yes, but this involves more equipment, because to convert heat from one level to another needs in practice more equipment.

M. Höhne

It may be easier to explain it with a piece of chalk.

Today hydrogen is produced by gasification processes. The price of this hydrogen is composed of two almost equal factors. One factor is the price of gas or coal required for gasification and the second factor is the depreciation.

To make the gasification process work you have to burn about 25% of the total fuel, in order to enable the other 75% to react with water to produce H_2 and CO_2 . The 25% of the total fuel amount, which is needed as heat source for gasification may be replaced by nuclear heat. The remaining 75% of fuel can, however, not be replaced if the process described by Dr. Kugeler is applied.

Now for the water splitting process described by Dr. De Beni the plant costs will be certainly higher.

I feel they may be almost twice as high as for the usual gasification process. This would mean that for the fixed cost alone you will reach a cost level equal to the total cost of hydrogen produced by usual methods.

Consequently hydrogen produced by the new process will in any case be more expensive than usually produced hydrogen, irrespective of the heat source involved.

However, the new process will also yield oxygen, and in all cases in which oxygen can be sold the new process may right now be economic.

If the price of the coal required for the usual process will, as expected, in future more intensely rise than the fixed plant costs, the relationship between the cost of the usual process and that of the new process will improve in favour of the new process, in particular if the price of the nuclear heat required for the new process decreases.

As a result, the chances of the new process will no doubt be more favourable than those of the usual method.

M. Marchetti

We agree with you, certainly.

M. Stecman

Well, the point is this. One of the main constraints in this process is the highest temperature that can be allowed: the 700° nowadays. Now when Dr. Kugeler is right you should keep in mind that in 5 or 10 years the highest temperature could be somewhere around 900° or something like that. Would that change your choice

of type of reactions you are to use to produce hydrogen?

M. Marchetti

A very good question. Well, perhaps the answer is now ready.

M. De Beni

Well, the field is open, the higher is the temperature we can dispose of, we can in principle find simpler cycles, with a higher efficiency.

M. Steeman

No, I was thinking nothing of a higher efficiency, but I have some experience in chemical industry and in handling things like chlorine, bromine and so on; especially at those high temperatures you are up for a quite a lot of corrosion problems. You spoke already about that.

Now suppose for a minute that when you reach an upper limit of about 900 or 1000° and you could devise a process not using halogens, or for instance, not using mercury. This would surely be much better, and one could fear then when you have developed a process like this in five years at least, it could become obsolete before it is introduced in industry.

M. Marchetti

You are perfectly right and in fact this afternoon we are going to discuss what to do next. We are very aware of this situation, and for that reason we think that in spite of the fact that our basic ideas are very probably sound, at present all this set of processes constitutes a field too risky for industry, in the sense that new processes can come out three years from now, for instance, or that we have a very rapid increase in the output temperature of reactors, because someone somewhere invents something. This is the main

reason in my opinion, for such kind of work should not be repeated in 20 places in Europe, but is done by a single European organisation. Our general objective after all is to work on problems which are very important, at medium-long term, and so risky that industry is not ready now to take them.

M. De Beni

I have a supplementary answer to you. Let us look again at slide No. 1. On this slide we can find another cycle, using higher temperatures. (M. Marchetti : A hidden in cycle). The first cycle I found with this diagram, is this one. Here we have the line of the water that intersects the line of the carbon. It means that at this temperature, that is at 700°C, we can react water with carbon to give carbon monoxide and hydrogen. At this temperature the pressures of all components are the same.

Once this reaction performed, we can separate the carbon monoxide and cool it at a lower temperature e.g. 250°C and react it with magnetite, Fe_3O_4 . Thermodynamics is such that at this point, at a temperature lower than 250° we must have a reaction between carbon monoxide and Fe_3O_4 to give Fe_2O_3 and carbon. Once separated the products, carbon and Fe_2O_3 , we can heat Fe_2O_3 at 1400°C and have a dissociation of this product into oxygen and Fe_3O_4 . (M. Marchetti : The pressure of oxygen is one atmosphere).

This is just an example of another cycle that can work, in principle, with a maximum temperature of 1400°C.

The reactions are :

- water plus carbon gives carbon monoxide plus hydrogen at 700°C;
- carbon monoxide plus magnetite give carbon and hematite, yes, and this must go at 250° in principle;
- hematite will go to magnetite plus oxygen at 1400°C.

This is another possible cycle with a maximum temperature of 1400°C. Theoretically possible because there are complications e.g. there are separation problems, because the low temperature reaction yields two solid products that must be separated. It is not so easy. But this is just an example for another cycle which we could have using an higher value for the maximum temperature.

M. Gallone

The trouble is that this second temperature looks a little bit too high.

M. Marchetti

It is not the only trouble! But you see, this was just an answer to the question if it is possible when increasing temperatures ... it is possible thermodynamically.

M. Höhne

But you know you should first get accustomed with this type of reactions at all. So if one starts with mercury, it is quite right. Subsequently one can go over to the other systems, and one will use experience from the one process for the others.

So I don't think that this procedure is wrong.

M. Marchetti

That we will discuss this afternoon: What to do next? We have a scheme for answering all these questions about the **research** program.

M. Knoche

I would like to point out that all the reactions in your scheme are reactions with two constituents on

the left side. Only two different materials on the left side. One could think also of let me say, three or more reactants on the left side and this gives quite a much more variety, and I think the reactions proposed by Prof. Schulten are of that type. Are reactions with metal, steam and for instance iodine. So the choice of affinities are quite different and gives quite a possibility of varieties of combinations, and I think it may be quite fruitful to go to different reactions.

M. Höhne

What we are really interested in is to find a process as simple as possible. If you could use only one chemical, e.g. selenium which may alone be sufficient as a splitting agent, this would be the best solution.

M. Knoche

More constituents doesn't mean more steps, necessarily!

M. De Beni

Yes but more possibilities of reaction between them, e.g. putting together copper, water and iodine, the main products are CuI and water; not copper oxide and hydrogen iodide.

M. Knoche

Of course, of course.

M. Marchetti

I would like to hear our French guests which come from chemical firms and keep silent. If you have any problems in speaking English I could maybe help in translating, you can speak French.

M. Jeffrey

Ce sont des problèmes très très attachés au problème de chaleur et dans le fond nous pensons que c'est très nouveau pour pouvoir être comme ça décidé, on peut difficilement avancer des idées sans lancer des prix d'installations, et nous avons l'habitude, lorsque nous étudions des procédés nouveaux comme ceci, de lancer simultanément des prix d'installation. Et je pense qu'il est nécessaire pour nous d'avoir une idée du coût de l'investissement pour pouvoir exprimer une opinion sérieuse sur ce genre de choses.

M. Marchetti

You see, my point of view is that a process is economical when somebody is making profit out of it so at a quite large stage and we have to start somewhere, I would say that the frame into which we are trying to fit our process gives a certain room for economy but to give a fixed price we have to wait at least a pilot plant, a prototype plant and then some years later we will have a fixed price. So you see, we are at the very preliminary stage from the point of view of the utilisation and in fact my personal guess is that we are not going to see a pilot plant before 5 or 10 years, from now. Is that a good answer?

M. Höhne

I feel we will not get very much further if we discuss the technical details of this process because we do not know all relevant details. We just learned this process from your description and raised some questions. But in my opinion it would certainly be interesting at this moment if we could see your laboratory which would be more inspiring than theoretical discussions.

M. Marchetti

Well, in my opinion these discussions are of help to us at least and we come back to the reason why we invited you here. It's to have a reaction from people in industry about something which up to now has not been our vocational purpose.

M. Höhne

But this is a point of discussion for this afternoon. Now we are talking, as far as I understood, about your equations and the possibilities which arise out of these equations. We heard there are different possibilities, different ways; one using mercury, one using iron, one using this or that, e.g. cadmium, but we have no real impression of the difficulties occurring in practical operation.

M. Marchetti

We have been too clear, essentially.

M. Höhne

Well, I thought that we really are now at a point where we cannot discuss any further about the equations. I feel it would be preferable to use the time to see the laboratories, until lunch and after lunch we could talk about the further work.

M. Marchetti

Well, to see chemical laboratories, you don't see anything, after all. All you see is the same thing, furnaces and beakers and things like that. Our laboratory in particular is a laboratory devoted to developing of materials. Materials are very important questions about ... a chemical process, however, you don't see

anything which is precisely geared to the development of this process because the work we are doing now is chemical in character or theoretical and there is no special apparatus for doing that.

M. Höhne

Well, I thought you checked these steps in laboratory equipment, which will give an idea how simple the design of a pilot plant will be.

M. Marchetti

I don't think so, ... I give you an example. The reaction of hydrobromic acid with mercury. That's a quite tricky reaction because people think that, well ... If you ask a chemist, so straight, he says that hydrobromic acid does not react with mercury. Well, in fact it reacts under certain special conditions and we are studying the equilibrium values and the rate of reaction. But experimental apparatus are glass capsules which are inserted into a furnace. That's all and I can show you the glass capsules.

M. Höhne

I see it's not a continuous flow.

M. Marchetti

Now a continuous flow is made, in the case e.g. of the reaction of calcium bromide with water, with steam let me say, but also in that case the apparatus is very simple, it's a furnace with a tube and with some material in and with a condenser on one side and with an evaporator at the other. It's very simple. However, we may show you very shortly our laboratory, just so to give an idea.

Perhaps a certain number of persons are here for the first time and we can show what kind of laboratory we have and give a direct impression of our **strength**.

M. Höhne

Because after all we do not want to stay with the theory, we need an impression of practical operation.

M. Marchetti

So we have 1/2 h before going to lunch, if there is no opposition to this proposal, we can go to see our laboratories. You think so? O.K.