

MARCHETTI-29_R.1

Höhne

Paschal

Weyand

Franzen

Ziegler

Block

Teggors

Valette

Zimmer.

**PROCEEDINGS
ROUND TABLE**

on

Paris

De Leone

**DIRECT
HYDROGEN
PRODUCTION**

Gallone

Jeffroy

Steeman

Van Heek

Post

Chelle

Siebker

Kugeler

De Beni

Knoche

Caprioglio

Marchetti

COMMISSION DES COMMUNAUTES EUROPEENNES
Etablissement d'Ispra du CCR
(EURATOM)

ROUND TABLE

on

DIRECT PRODUCTION OF HYDROGEN
WITH NUCLEAR HEAT

Ispra - December 12th, 1969

EUR/C-IS/1062/1/69 e

P R O G R A M M

ROUND TABLE ON DIRECT HYDROGEN PRODUCTION - Ispra Dec. 12th

- 9.00 h Pick-up at Hotel Europa
- 9.15 h Dr. P. Caprioglio Welcome and opening speech
Director of this Center
- 9.25 h Dr. C. Marchetti The philosophy behind our
Head of Phys.Chem.Div. effort towards a "direct"
production of hydrogen
- 9.40 h Prof. R. Schulten Costs and temperatures for
Prof. f. Reaktortechnik heat from HT reactors -
Direktor Institut für Medium term trends
Reaktorentwicklung (Read by Kugeler)
KFZ Jülich
- 10.20 h Prof. Knoche Thermodynamical considera-
Prof. für Technische tions on "coupled"
Thermodynamik chemical reactions
TH Aachen
- 10.50 h Coffee break
- 11.00 h Dr. De Beni MARK-1 as an example of a
Physical Chem. Div. "direct" process for produ-
cing hydrogen
- 11.20 h Discussion
- 13.30 h Lunch
- 14.30 h Round table : What to do next? A tentative Euratom
program is presented for discussion.
- 16.30 h Closure of the meeting

List of Participants Present at the Round Table

Prof. F.E. Block	Technische Hochschule Aachen
Dr. Chelle	A.P.C. Toulouse
Dr. R. De Leone	Com. Naz. Energia Nucleare, Roma
Dr. J. Franzen	Heinr. Koppers, Essen
Prof. S. Gallone	Agip Nucleare, Milano
Dr. R. Höhne	Lurgi Verwaltung, Frankfurt (M)
Dr. J.E. Jeffroy	Ugine Kuhlmann - Sèvres
Prof. K.F. Knoche	Technische Hochschule Aachen
Dr. K. Kugeler	Kernforschungsanlage Jülich
Ing. I. Paris	SNAM-Progetti-Milano
Dr. F. Paschal	Wendel-Sideler-Paris
Dr. Post	Staatsmijnen Centraal Lab.-Geleen
Dr. Steeman	Staatsmijnen Centraal Lab.-Geleen
Dr. H. Teggers	Union Kraftstoff, Wesseling
Dr. K.H. Van Heek	Bergbau-Forschung, Essen
Dr. Weyand	Regierungsdirektor Bundesministerium f. Wissenschaft, Bonn
Dr. A. Ziegler	Pechiney St. Gobain, Neuilly-s.-Seine
Dr. Zimmermann	Brown Boveri, Mannheim
<u>Euratom Ispra</u>	
Dr. P. Caprioglio	Director CCR Ispra
Dr. C. Marchetti	Head of Phys.-Chem. Division
Dr. G. De Beni	Phys.-Chem. Division
<u>Euratom Bruxelles</u>	
Dr. M. Siebker	Head of Div. 2 - Direct. C - DG XII
Dr. H. Martin	DG XII - C-2
Dr. L. Valette	High Temp. React. Project - DG XV

M. Caprioglio

Welcome and Opening Speech

I should like to say very briefly what is customary under similar circumstances, namely that we are very grateful that you could accept our invitation for this meeting which is somewhat unusual for us insofar this is the first time that we are confronted with a new and large problem, that we have some ideas on how to tackle it, but for whom we need to keep our feet on the ground. Therefore the main reason for asking you to be present at this meeting is to help us in keeping our feet on the ground.

We feel that the kind of activity you will be talking about today is something that fits rather well with our competence here in Ispra and with the things that we are supposed to do. It is a long term activity; it has rather deep and complex technological implications, it requires a multiplicity of competences in various fields and it has a large economic and even, I should say, politic prospect and implication. Therefore we feel that it is the sort of things that we should embark upon here in Ispra in the Joint Research Center.

Together with the positive qualities that I have just mentioned there is one negative quality which is also pointing towards us, and pushing us into doing this kind of work, and it is that this kind of activity is somehow risky in the sense that it's not yet clear how far it's going to be an economic proposition that has a real chance of becoming interesting for industry.

Therefore it's a sort of thing that is not really worth doing six times in our member countries.

This is the frame of mind in which we are : we feel that the thing is, generally speaking, interesting. We feel that it has a long term potential which is very serious. We feel that since the very beginning we should keep our feet on the ground and we should be in very close connection with industry who knows about these problems, and who can appreciate and evaluate the importance and implications of what we are supposed to do. We feel that we have the technical competence for tackling at least some of the preliminary problems that are going to be raised by this line of endeavour and after today's meeting we would like to be informed in a continuous way about what we are doing, without, of course, excluding other possible interests in the community. I would not like to go now into any detail of our work because this is what Mr. Marchetti and Mr. De Beni will tell you and I should only like to introduce ourselves. That has already been done in the paper that you have received but it is now perhaps useful for you to know ourselves.

(The presentation follows)

I should like now to ask Mr. Marchetti to go ahead with the meeting. So many thanks for coming and I hope that the meeting will be very useful for you, certainly it will be useful to us.

M. Marchetti

I should give a short account on how we came to the idea of using nuclear energy for making hydrogen without recourse to other raw materials apart from water. The development of this idea is quite complicated historically but I will try to make it rational shuffling a little the time scale.

The basic problem can be set as follows : energy from classical sources could be defined as mineral energy, in the sense that coal and oil are minerals just like nickel and iron; a particular price structure depending on mining costs and known reserves and on expanding markets tends to make their price soar. In the case of nuclear energy there is always a certain link to mineral because we need uranium but the incidence of its cost on that of energy is small now, and will be negligible with the advent of breeders. So we can say that the cost of nuclear energy is of technological character.

Now if we examine the trends in cost for technological operations we see that these costs tend to decrease as far as technology advances and they decrease in a more or less exponential way. This has a very simple consequence, that energy from classical sources is going to increase in price; energy from nuclear sources is going to decrease in price, in the long run. Then at a certain moment, and this moment has come, the costs will be more or less equal and in the future nuclear energy will be cheaper than other sources of energy.

So, we said, what has been done up to now, with nuclear energy? We made electricity. But electricity takes more or less 20% of the total market of primary energy, let me say between 15% and 25%

depending on the particular situation of a technological society. So we have another 80% of the market which could be penetrated in some way through nuclear energy, if we find the right way to penetrate it.

Now, nuclear energy is produced as heat but heat is not transportable very easily because it's diluted - if you have a gas or a liquid which is heated up, the energy density is very low -; and because the pipes leak, I mean energy is lost through heat losses. So we have to find a stable form for this energy.

Stable form means putting this heat into a chemical form. But what chemical? We made an analysis of all the possible chemicals that could be used for transporting nuclear energy, I mean, for putting nuclear heat into chemical energy and we found that, by far, hydrogen is the most convenient form, for various reasons.

The first one is that water is the primary source of hydrogen, water we can find everywhere; and because water is the final product of hydrogen combustion and water you can dispose of everywhere and the third point is that hydrogen has a market now which is quite large, and which is comparable in size to the market for electrical energy. I should say half of it if we exclude the possibility of reducing iron ore with hydrogen; or more or less the same size if we include this possibility. So we have, to start with, a fat market, of hydrogen as a chemical. That means, hydrogen that can be used for purposes for which people are ready to pay quite large prices.

Now, how to make hydrogen? We are informed that in Europe and in the US and in Japan people are thinking about nuclear heat to complement the processes for producing hydrogen using classical fuels, e.g. coal or oil. If we use coal or oil to make hydrogen by steam reforming the overall reaction is endothermic. So we could supply this extra heat needed from nuclear sources. But the amount of heat is relatively small, i.e. the endothermicity represents about 20% of the total energy that enters the process.

This means to start with, we can help relatively little, and second that we have to use reactors which cannot be very large, because the amount of heat needed is relatively small. Again this means, that we can't produce energy at the lowest cost, i.e. with very large reactors.

So we thought that the solution of the problem is in making hydrogen using only nuclear heat. Only in that way we can carry over the consumer all the benefits of a very low price for the primary energy, I mean the nuclear energy. Well, this is the general frame.

Now decomposing water with heat would be very simple if one could produce heat at 3000°C because water cracks at such a temperature. But reactors, now, produce heat at a max. temperature of, let me say, 750°C. So we looked for a process which could decompose water using only heat at temperatures lower than 750°C.

Now, when we say that this can be done people observe: well, but what about thermodynamics? It is very simple to answer this question of thermodynamics: instead of breaking water in a single stroke we break it in two.

Mr. De Beni is going to explain more in detail how things are working for our Mark-1, so I should go on talking a little more about hydrogen. For a couple of years I screened the literature looking for the possible uses of hydrogen and thinking about the possible means of penetrating the energy market. What I found is simple and striking : with hydrogen we can make practically everything in the sense that hydrogen could be only primary energy source for an advanced society. Just to give an example, a very little one, I pick in the bundle, there is at Battelle Institute in Columbus a group of people studying the use of hydrogen for producing food. Actually a certain kind of yeasts can feed on hydrogen as the energy source and use CO₂ as the carbon source. And they produce everything, I mean, they produce proteins, fats, vitamins and things like that. At Battelle they are studying this problem in view of long travels in space; e.g. if astronauts want to go to Mars, they have to stay out for a year or so; and it's more economical to produce food in loco than carrying a large weight of provisions. What comes out is very interesting: with something like two square meters of solar cells one can feed a man indefinitely using solar cells to produce electricity, electricity to produce hydrogen, and hydrogen to feed the Hydrogenomonas yeasts. Well, this is just an example, but you can see that even in the most exclusive field of energy input, that of food, hydrogen can penetrate. I could give examples for almost every kind of operation that requires the use of a source of primary energy.

Another point is that hydrogen is a quite concentrated form of energy and pipelines designed for instance for transporting methane, with the same pressure profile can transport more or less the same amount of energy because hydrogen has less energy content per cubic meter, but it runs faster in a pipe and the two things nearly compensate. It means that in the long run, we can visualize a system in which hydrogen and electricity are the main energy carriers and nuclear energy is the main primary energy source.

This doesn't mean that carbon sources are going to lose their importance overnight.

You see, carbon is a very important chemical, and the need for chemicals increases with the increasing of human population and of pro capita consumption so that I don't think there is any problem from that point of view in the very long run. Well, that's what i wanted to say.

M. Caprioglio

I suppose we should go ahead in our program after this general introduction on why hydrogen and what is the potential of this mean for allowing nuclear energy to penetrate into the general energy market. Now we should hear something about the reactors that are supposed to produce energy at the temperatures needed for such a process of splitting water. This had to be presented by Prof. Schulten, who is professor of Reaktortechnik at the research center of Julich and who is well known for having spent most of his professional life in the HTGR reactors field.

Prof. Schulten, unfortunately, could not come and Dr. Kugeler is going to present Prof. Schulten's introduction on the costs and temperatures for heat from HTGR.

M. Kugeler (Translation)

I thank you for the invitation. You know that at present there are three High Temperature Gas Reactors in the world which are based on Helium, Graphite and coated particles as fuel. Two of three reactors, which work with prismatic fuel elements, can reach at present a maximum gas outlet temperature of 750°C; the third one, the AVR in Jülich, is designed for a gas outlet temperature of 850°C.

Now the question is : what potential is available in this development, i.e. what temperatures can be reached on the basis of present technology and what costs for the heat from these reactors are to be expected on the basis of this development.

You certainly know that two lines are followed : one to produce electricity using higher temperatures through the use of closed cycle gas turbines; we hope by this way to increase efficiency from 40% to 45%, and possibly to reduce capital investments by 10%. This means that by improving the process of making electricity, we hope at best to reduce its cost by 10%.

The second line, that we follow intensively, points at the utilization of nuclear heat for chemical processes. We have started some research in the last years limiting ourselves to the application of nuclear heat to the transformation of fossile fuels.

We are also ready, in the future, when the processes here presented will show they have a chance, to collaborate on these processes. Our primary interest lies finally and quite naturally, in the utilization of reactor heat for chemical processes.

From our investigations it came out that for the simplest process of gasification (steam reforming of Methane or Naphta), temperatures of 950°C are necessary and for coal gasification with steam temperatures are above 1000°C. This means that increasing temperatures in the aim of transforming fossile fuels we have basically two steps to reach : one medium term, with the reactor reaching 950°C and the other, long term, with perhaps 1100°C or 1200°C.

The question is now what is the development work we have to perform on the reactor side. I think you all know the principle of an HTR, in the form we are developing. The critical points for the high temperatures are actually : the fuel elements, the coated particles, the bottom of the core and the other components exposed to hot gas. All parts that are in the cooler part of the reactor can be made with present technology.

Let me say now a few words about the prospects about coated particles and fuel elements to be taken into consideration when we want to reach temperatures around 950°C.

It is known that the life of coated particles is limited by four effects: a) by build up of fission gases in the coating; b) by the swelling of the fuel due to the build up of fission products; c) by the change in dimensions of pyrolytic graphite due to

fast neutron irradiation; d) by the damage to the innermost coating layer due to the bombardment of fast fission fragments.

In the last times many irradiation experiments at elevated temperatures have been made, in particular Gulf General Atomics did experiment with temperatures between 1500°C and 1900°C and with burn-ups up to 25% FIMA, i.e. Fissions per Initial Metal Atom.

It did appear that from the coated particles, irradiated by neutron doses in the same order of magnitude we can expect in normal operation, the rates of fission product release do not increase in an unacceptable measure, i.e. from the point of view of fuel we are now convinced that we can reach higher temperatures.

The actual design of the coated particles for 1300°C is certainly a safe one. We believe, however, that in the near future 1400°C and in a further future resp. 1600°C will be certainly reached.

If such max. temperatures of, let's say 1400°C can be reached in the future, then fuel elements of six centimeters diameter will permit outlet temperatures of 1000°C.

An important specification which is actually made, a maximum fuel element surface temperature of 1000°C in the next future can probably be increased up to 1100°C. Then using present day fuel technology and fuel elements, mean gas temperatures of 1000°C will be possible. Another important question in the discussion on temperatures that could be reached is the operation of the reactor at reduced power.

It is known that Public Utility Companies insist on electric power generation plants being able to run between 40% and 100% of the nominal capacity. This requirements is obviously not pertinent to chemical processes because chemical plants tend to be run at nominal capacity because of high investment cost.

A safety margin of 100°C in case of reduced power operation, is foreseen for the fuel elements of the THTR i.e. dropping the reduced power specifications, the reactor could be designed for a temperature which is 100°C higher. The second critical point, in the construction of the reactor is the bottom of the core. It is one of the subjects where our most important development efforts are concentrated. We must take into account that for all the chemical processes proposed including the one which is proposed here now, process hydrogen will get into the cooling medium and into the core. Hydrogen reacts with formation of methane and corrodes the core.

It is known from thermodynamics that going to high temperatures the equilibrium is shifted toward the side of hydrogen on the other side the reaction rates increase exponentially with temperature and we must test under irradiation and in hydrogen, how much the corrosion of the graphite will really be and what corrosion will be tolerable.

For the case that graphite is not a suitable material for the core bottom, the use of alumina, zirconium carbide or silicon carbide has been envisaged. Those materials resist the attack of hydrocarbons.

But the behaviour of these materials under irradiation is not sufficiently known. Alumina has been irradiated up to neutron doses which lie about a factor of ten below the required values. Much development work has to be done here.

The next point is an improved channelling of the hot gases in the lower part of the reactor. We are not afraid of this problem because this part is not exposed to radiation damage.

Another point is that of a new design of the gas purification plant. If hydrogen diffuses in the expected amounts into the reactor circuit, the capacity of the gas purification plant must be increased. Solutions should be possible which would permit to run it economically.

These are the technical problems on the project. We shall concentrate our efforts towards reaching within the next five years temperatures between 950°C and 1000°C; pressures of 40 atm in the reactor and a thermal power of 3000 Mwth.

For this purpose extended irradiation tests and tests on materials for the core bottom and other reactor components will be carried on.

The economy which is clearly very important for all those processes can be evaluated at present only with a certain uncertainty. As I have already outlined, making use of the high temperature level in a gas turbine, an increase of efficiency and a decrease of investment costs of about 10% is to be expected.

In comparison with chemical processes where the upper temperature level can be used with an efficiency of perhaps 90-100% the electric power generation is not very attractive. We are particularly interested therefore, to find processes which use heat at high temperature, directly for gasification or chemical reactions.

The costs for a unit of 3000 Mw were estimated including steam generator, turbine, and electrical generator to be all together about DM 460/Kw.

If the plant runs 8000 hrs per year, which is the rule for chemical plants, fuel cycle cost will be DM 0.0015 per Mcal. It is then much cheaper than heat from fossile fuel, as we get it, e.g. by the combustion of coal, petrol or natural gases.

In a comparison for producing hydrogen, natural gases seem to be the most advantageous because they are more easy to reform, while for the combustion of coal or heavy oil for the production of hydrogen, oxygen must be added. This heat, if the oxygen plant is taken into account, costs four to five times more than the heat from the reactor.

Attention is to be given to that fact that reactor heat with costs of DM 0.0033 per Mcal, investment costs included, is directly available in gasification plants or in chemical reactions under pressure. Because of this high cost margin between heat from a reactor and heat from possible fuels, we believe that the application of the THTR for these chemical processes will have a great future.

M. Caprioglio

Dragon, Peach Bottom, AVR are three existing reactors of the HTGR type. Dragon has been built and it is actually operating in U.K. and it is the result of a joint work of various European countries; Peach Bottom has been built by the Gulf General Atomics Comp. in U.S.A. and AVR is a reactor that has been built by B.B.K. in Germany. These three reactors are actually operating now and have been working already at the temperatures indicated. The cooling gas is Helium, and the outlet temperatures are 750°C for the first two, actually for Dragon it went higher than that, and 850°C for AVR reactor.

M. Kugeler

We hope that the temperature of HTR reactors can reach the value of 950°C in five years and we hope the temperature will be 1100°C in 15 years. That's our feeling about the timing

M. Caprioglio

That is, the temperature is of course limited by the behaviour of the materials in the reactor, this is usually obvious.

M. Kugeler

The coated particles, the fuel in our reactors, are built in this way : a fuel core, then several coatings of pyrolytic graphite. We have today a maximum temperature of 1300°C; there are irradiation experiments at 1600°C to 1900°C, at General Atomic.

M. Caprioglio

I am explaining in a few words, now, the gas outlet temperature which has been indicated depends of course on the behaviour of the materials and essentially on the behaviour of the fuel and the graphite.

Now the fuel is in the form of coated particles: small particles of fuel covered by a pyrolytic carbon skin. These particles actually work at 1300°C. Experiments are now going on on irradiation at 1600°C-1900°C and there is a good hope that in five years time these experimental fuels will be ready for practical applications. This is the trend that Dr. Kugeler is indicating, showing 950°C for the gas outlet temperature in five years and going hopefully beyond 1000°C to 15 years; this is the trend based on the present experience. Of course the phenomenon that really determines the temperatures at which this fuel can be used, is the kinetics of the leaking out of the particle of the fission products which are produced in the fuel.

Uranium burns in the particle; the fission products diffuse through the coating, and the temperature at which the fuel works determines of course the speed at which these products leak out, and therefore together with a development of the coating, so that less fission products are leaking out and higher temperatures are achievable, together with this, there is of course also the aspect of what is the maximum amount of fission products one can accept in the primary circuit.

So far one has been extremely conservative about this for this first reactor, but specifications could be relaxed in the future.

So, on both these grounds one hopes that during the course of the next 10 to 15 years necessary to these gentlemen here to develop their thing, that the reactor will in fact give heat at a temperature that is high enough, by far, for what is needed.

M. Kugeler

And now the costs of the heat you are interested in. We hope to reach an investment cost of 460 DM pro Kwe in reactors of 3000 Mwth and we think that heat from such reactors will have a price of around 0,33 Dpf per Mcal.

M. Caprioglio

Well, this cost usually is 100 and something in dollars : 460 DM/Kwe means 125 dollars.

This is the capital investment which is now considered to be generally accepted as the investment for a large power station of 3000 Mw thermal.

The cost of the Mcal that goes together with this size of plant, is a third of a Dpf or 0,9 mills.

This of course was based on the new ratio between DM and Dollars. This is really a sort of picture of where these reactors stand. These reactors have been developed essentially, and I should say exclusively, for producing electricity, but it so happens that they are also suitable for other applications, and since they are the only power reactors that produce heat at such a high temperatures, they have always been pointed as the most obvious choice between reactor types (for all chemical applications).

Many thanks, Dr. Krugeler. We got really the point that the source of heat at the temperatures that would be needed is already there, having been developed for other purposes, and it is not a main problem in our work.

M. Marchetti

We would like to ask what is the cost of the classical energy, you see, coal and gas, e.g. in Germany, to have a reference.

(Dr. Kugeler writes down some figures on the black board).

M. Caprioglio

This really gives a picture. We range from a minimum of half a pfenning more or less for braunkohle and heavy oil to a maximum of around one pfenning for coal, hard-coal, and light oil (All the variation is more or less in this range of one half to one pfenning).

So in fact the ratio, let me say the advantage of the nuclear source for producing thermal energy is of an order of two to three.

This is really the starting point. I suppose that in Holland natural gas should be cheaper than those

M. Steeman

Prices in Holland are 60 - 65% of the prices written down on the blackboard.

M. Caprioglio

Sorry 60%. Still, anyway we will get into the discussion all these questions, but apart from obviously privileged sources of energy, which still are in the same order of magnitude or may be even higher than what nuclear reactor of sufficiently large size, this is the key point, of sufficiently large size can do, this means that we are not out of the economic framework.

The real point I should like to stress is that in order to get those costs for the calorie, one has to go to very large sizes, and we feel that hydrogen, and this is one of the reasons why we have picked hydrogen, because hydrogen already now has a market for such a very large size, and can be relatively easily transported. So this is the connection between what Dr. Marchetti has just said before and what Dr. Kugeler has said now: the source of heat exists, it is large enough, it has to be very large, and therefore we must produce chemicals which have already a sufficiently large market. Because otherwise it would be difficult to ignite the process.

M. Marchetti

Perhaps I should say just another thing :
hydrogen is made from those fuels and, per calorie it costs about the double. So a calorie in form of hydrogen has a price 5 or 6 times larger than the nuclear calorie.

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M. Weyand

We go starting now with the discussion and I think it might be useful that we can get some figures from the Dutch representatives about the natural gas in Holland, only this one figure I propose

M. Höhne

The topic is not the gasification of fossile fuels today. The topic is quite different. So I suggest we first have all the contributions and after that we can discuss and we should try to stay to the topic and the topic which is a process to be described by Dr. De Beni.

M. Caprioglio

Yes, I agree with you completely. My point is this: we will have a large amount of time to discuss about anything you wish. We may have chosen the wrong method in the sense of piling up all the discussions at the end, it could perhaps be more wise to have discussions after each paper, but I think it worthwhile to stick to our program, because in fact we run the risk now into getting a long discussion between specialists on costs of mineral sources of energy which is not really our purpose. We know that the problem is complex, intricate and it depends very much on local situations, on taxation, on a number of things.

The real point we wanted to stress is that with these nuclear reactors developed for making electricity, we have a margin with respect to fossile fuel that we can exploit.

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How big is this margin, is a question that can be endlessly discussed. What we want really to stress is that we do have a margin and that this margin we would like to exploit. So we will come back to Dr. Weyand's suggestion and after the discussion I'm sure that we will get interventions from the representatives of the Staatsmijnen on the point of how this large amount of natural gas, that has been found in Holland in the Northsea and so forth, can represent a challenge, long term, to nuclear energy. I think it will be a very interesting discussion.

So I suggest that we proceed with our work a step further. We have given you the general philosophy why we went into this type of reserach. We have given you, thanks to the kindness of the Jülich representative, the status of the art for high temperature reactors, that could be used for producing heat, at a certain price and in a certain range of temperatures. We would like now to go a step further and ask Prof. Knoche to explain the thermodynamics of the splitting of water with heat and why it can be possible to split water and get hydrogen out of it, using temperatures lower than 3000°C that are usually considered necessary to do the job and so I would like now to ask Prof. Knoche to present his paper.

M. Knoche

Thermodynamic Aspects of Coupled Chemical Reactions

Discussing chemical processes for the thermal decomposition of water into hydrogen and oxygen at low temperatures, our first question should be : What are the requirements of the first and second law of thermodynamics for such a reaction?

Fig. 1 shows the necessary elements of such a process. It consists of a thermodynamic system which exchanges heat with a heating reservoir HK at a temperature T and also with a cooling reservoir KK at a temperature T_0 . A flow of steam enters the system (state 1) and a flow of decomposed steam leaves it with state 2.

We have to consider the energy conservation, the first law of thermodynamics. Due to the second

$$q - q_0 = h_2 - h_1 = \Delta h \quad (1)$$

law of thermodynamics the entropy increase of the material flow consists of the entropy exchange with the heating and cooling reservoirs and the entropy production due to the irreversibilities of the process

$$\sigma_2 - \sigma_1 = \frac{q}{T} - \frac{q_0}{T_0} + \Delta \sigma_{\text{irr}} \quad (2)$$

From these two equations we obtain an equation for the necessary amount of heat from the heating reservoir which is essentially a function of the temperature of the heating reservoir.

$$q = \frac{T}{T - T_0} \left\{ h_2 - h_1 - T_0 (\Delta_2 - \Delta_1) \right\} (1 + \nu)$$

In these equations we have besides the thermal properties of the material flow the degree of loss due to the irreversibility of the process which is defined by

$$\nu = \frac{T_0 \Delta \Delta_{irr}}{h_2 - h_1 - T_0 (\Delta_2 - \Delta_1)} \quad (3)$$

In Fig. 2 the ratio $q / \Delta h$ is plotted versus the temperature T for different values of ν . Even at a temperature T of the heating reservoir as low as 500 K the necessary amount of heat in a completely reversible process would not be more than twice the enthalpy difference of the material flow. Due to the irreversibilities of the process this necessary amount of heat will be considerably increased.

The next step in our considerations would be to look for special chemical reactions which promise to fulfill our general thermodynamic restrictions and to see what the equilibrium conditions for such reactions are.

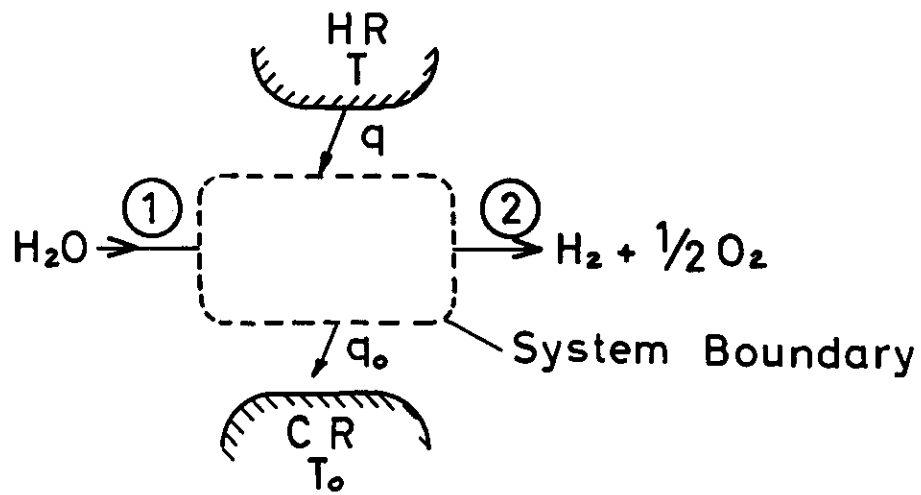


Fig. 1

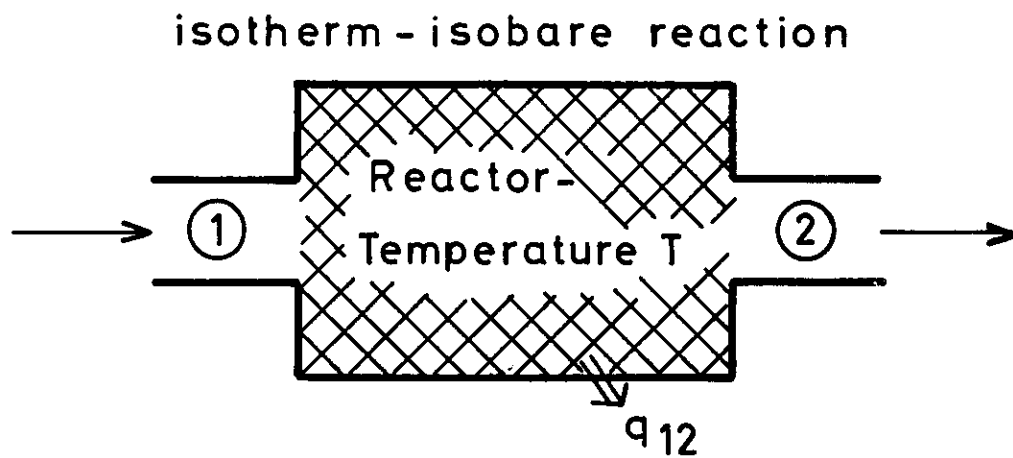


Fig. 3

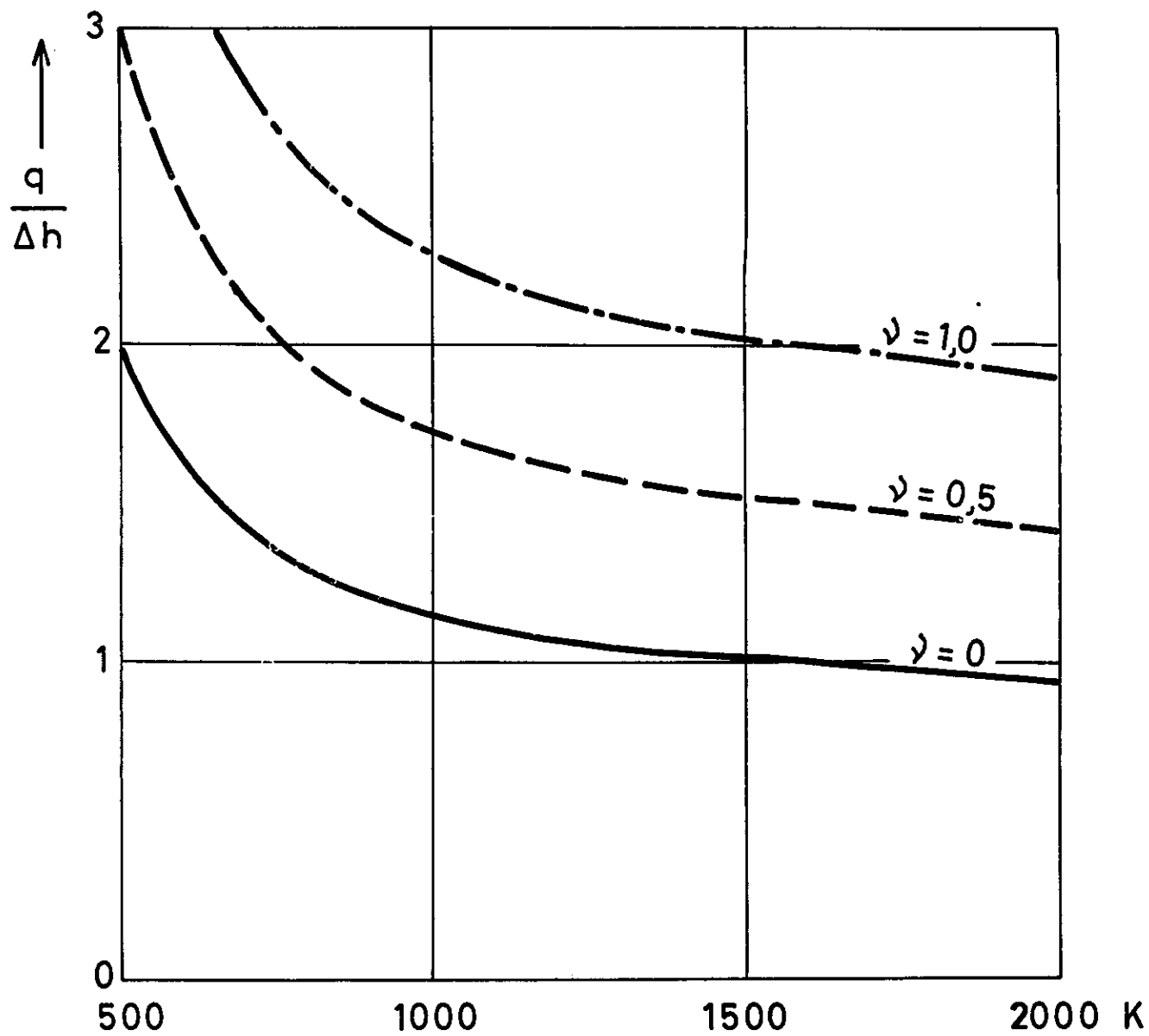


Fig. 2

If we consider only reactions at constant pressure and constant temperature, fig. 3, the application of the first and second law of thermodynamics

$$h_1 - h_2 = q_{12} \quad (4)$$

$$\Delta \mathcal{S}_2 - \Delta \mathcal{S}_1 = \frac{q_{12}}{T} + \Delta \mathcal{S}_{\text{irr}} \quad (5)$$

leads to the entropy production

$$\Delta \mathcal{S}_{\text{irr}} = \Delta \mathcal{S}_2 - \Delta \mathcal{S}_1 + \frac{h_1 - h_2}{T} > 0 \quad (T, p = \text{const}) \quad (6)$$

The entropy production $\Delta \mathcal{S}_{\text{irr}}$ in a process at constant p and T can be represented very easily in a Mollier enthalpy-entropy chart of the reactants and the products, fig. 4.

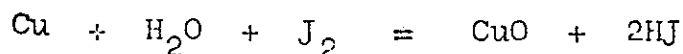
The thermodynamic properties of the reactants are represented on the upper line and the thermodynamic properties of the product on the lower line, both valid for the same pressure $p_1 = p_2$.

The inclination of the lines of constant pressure depends on the temperature only, so that the tangents in two points 1 and 2 having the same temperature $T_1 = T_2$ are parallel. The entropy production can be represented by the horizontal distance of these two tangents.

Because the entropy production has to be always positive, the reaction can proceed only from left to right with respect to the tangents. In case of reversible reactions in thermodynamic equilibrium the entropy production approaches zero. It can easily be shown that the vertical distance of those tangents represents the change in free enthalpy. With the help of such Mollier-charts it is possible, to get a fairly good idea about the equilibrium concentrations of the substances involved.

Fig. 5 shows such a Mollier-chart for a rather well-known reaction - the thermal decomposition of steam at very high temperatures. The lower part of the diagram shows the thermodynamic properties of steam for different values of temperature and pressure and the upper diagram the thermal properties of decomposed steam. A tangent is included at a temperature of 2000°K and a pressure of 1 bar, which shows that the steam and its products of decomposition are in equilibrium only at very small partial pressures of the decomposition, products H₂ and O₂ ; that means, at very low concentrations of those products.

As a next step I would like to discuss some coupled chemical reactions with the help of the same method. One coupled reaction for the decomposition of water - proposed by Schulten and co-workers [1] - is the oxidation of metals (like copper) by steam, which can be performed in the presence of jodine vapour :



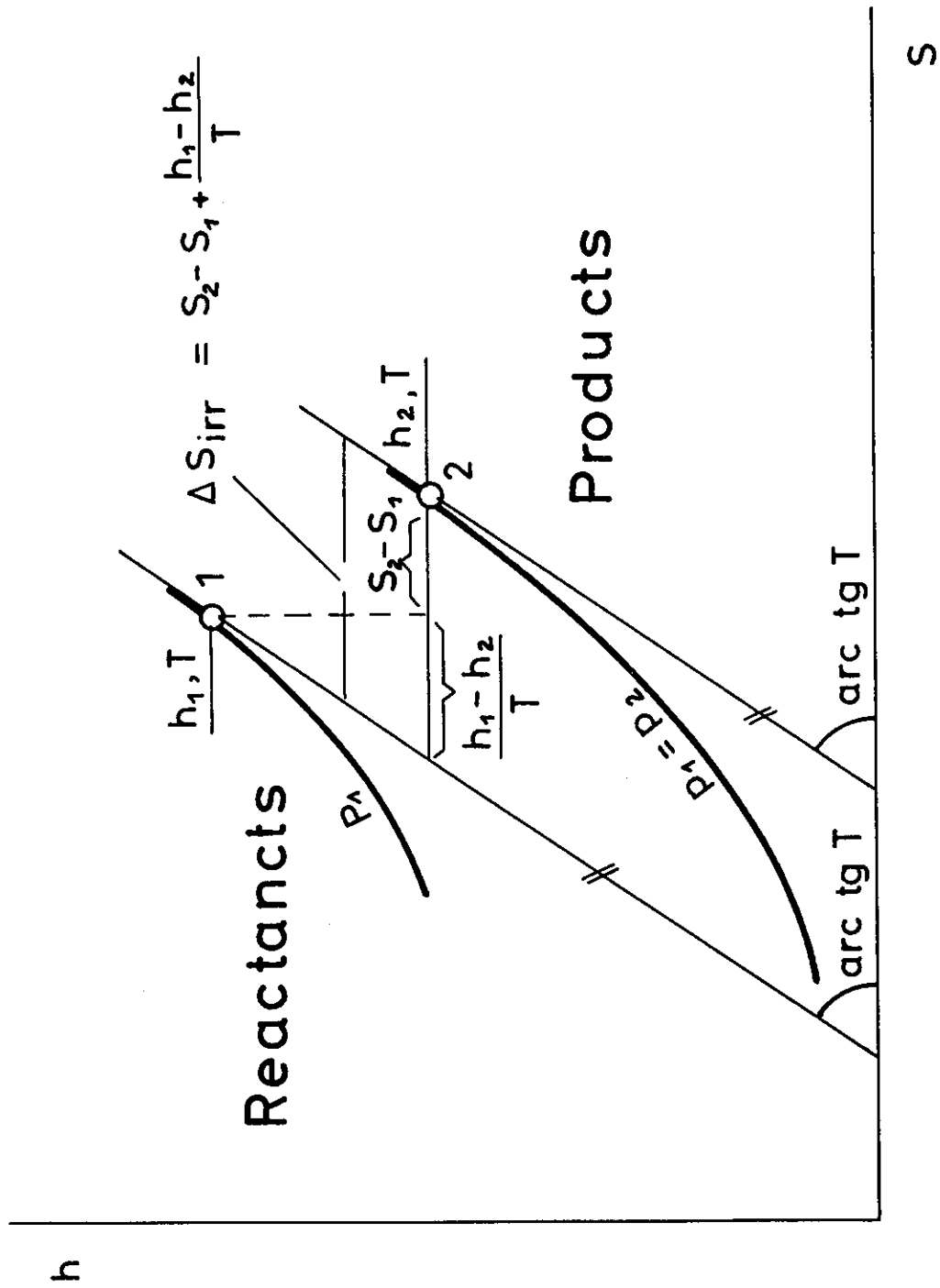


Fig. 4

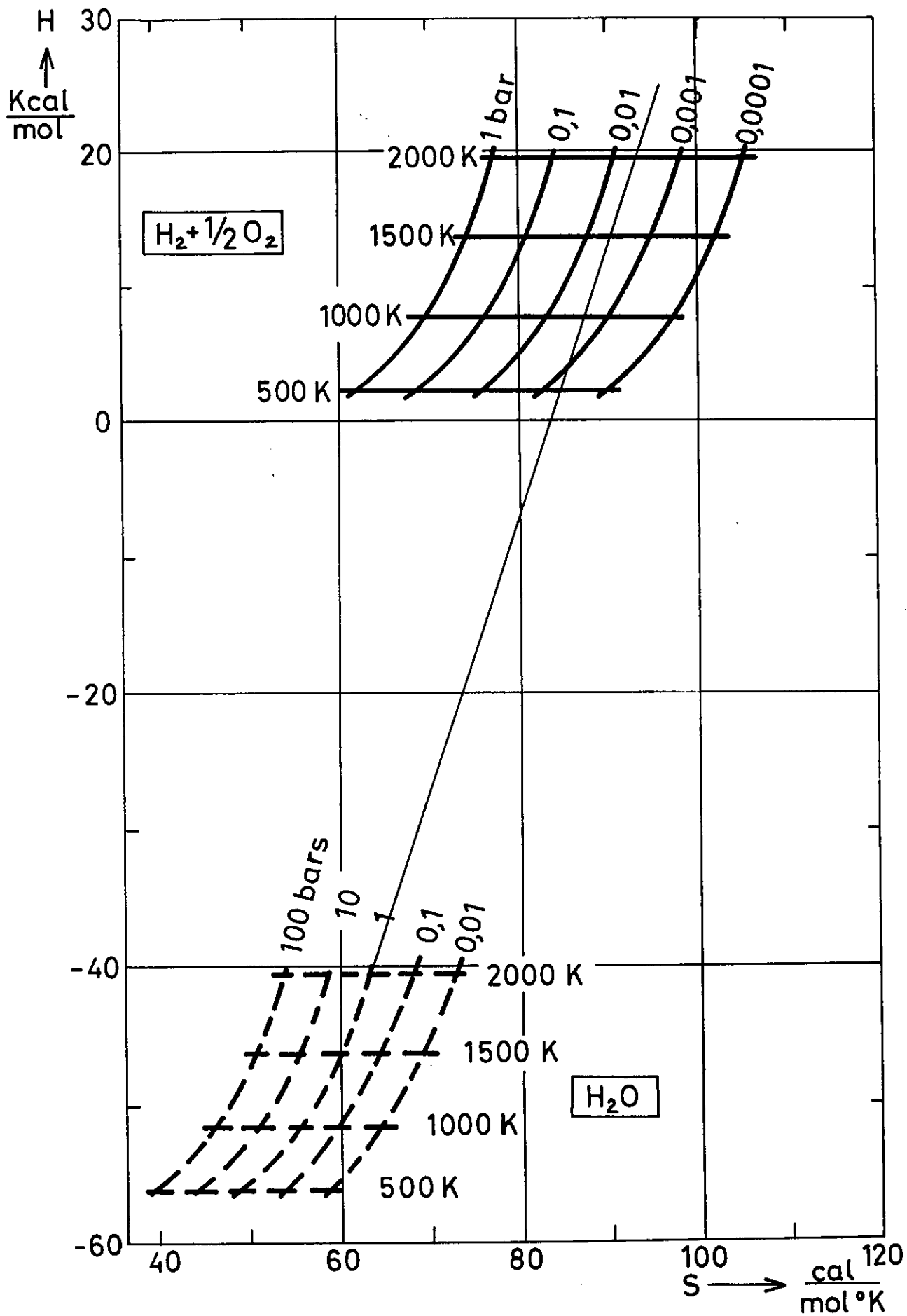
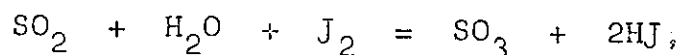


Fig. 5

Copper oxide can be dissociated at high temperatures ; the same is true for HJ. However, at equilibrium the partial pressure of HJ is very small resulting in equilibrium concentrations of HJ in the range of a few per cent, fig. 6. The same would be true for the oxidation of the sulfur dioxide, fig. 7 :



a reaction also proposed by Schulten and his group [1].

The hydrolysis of Calcium bromide by steam (fig. 8), which is one essential step in a process by De Beni [2], results in low equilibrium concentrations of the desired product.

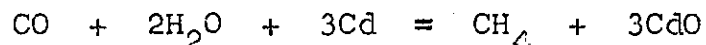
Another material, which seems to be quite interesting for such coupled chemical reactions is Cadmium and its oxides.

The direct oxidation of Cadmium by water vapour is possible at higher temperatures with resulting hydrogen-concentrations of a few per cent. Theoretically Cadmium-oxide can be dissociated by thermal dissociation at high temperatures, fig. 9.

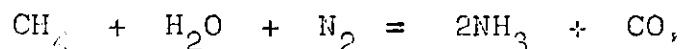
In reality the thermal dissociation of Cadmium Oxide is not so easy to perform because at high temperatures Cadmium metal and its oxide form rather stable compounds in the solid state.

The same will be true for copper and its different oxides. Though the thermal dissociation of Cadmium oxide would possibly be difficult to perform in an

industrial application, it might be meaningful to discuss some more complex reactions of Cadmium with steam, e.g.



This reaction which under atmospheric pressure is known to run the opposite way, may be performed under high pressures, fig. 10. In a next step one could think of the following reaction :



where high pressure has to be applied in order to avoid the decomposition of ammonia, fig. 11.

The maximum equilibrium concentrations of ammonia are in the range of about 10%.

The direct formation of ammonia from nitrogen and steam in the presence of Cadmium, fig. 12, would theoretically be possible only at very high pressures and low temperatures and - even under these conditions - with rather poor ammonia concentrations.

Summary

With respect to possible chemical processes for the thermal decomposition of steam at low temperatures, equilibrium conditions have been examined for some coupled chemical reactions.

Chemical kinetics has been completely excluded from these first considerations.

Acknowledgements : The thermodynamic properties have been taken from a recent compilation by Knacke and Barin [3]. The diagrams have been calculated by D. Minke. I would like to thank for their help.

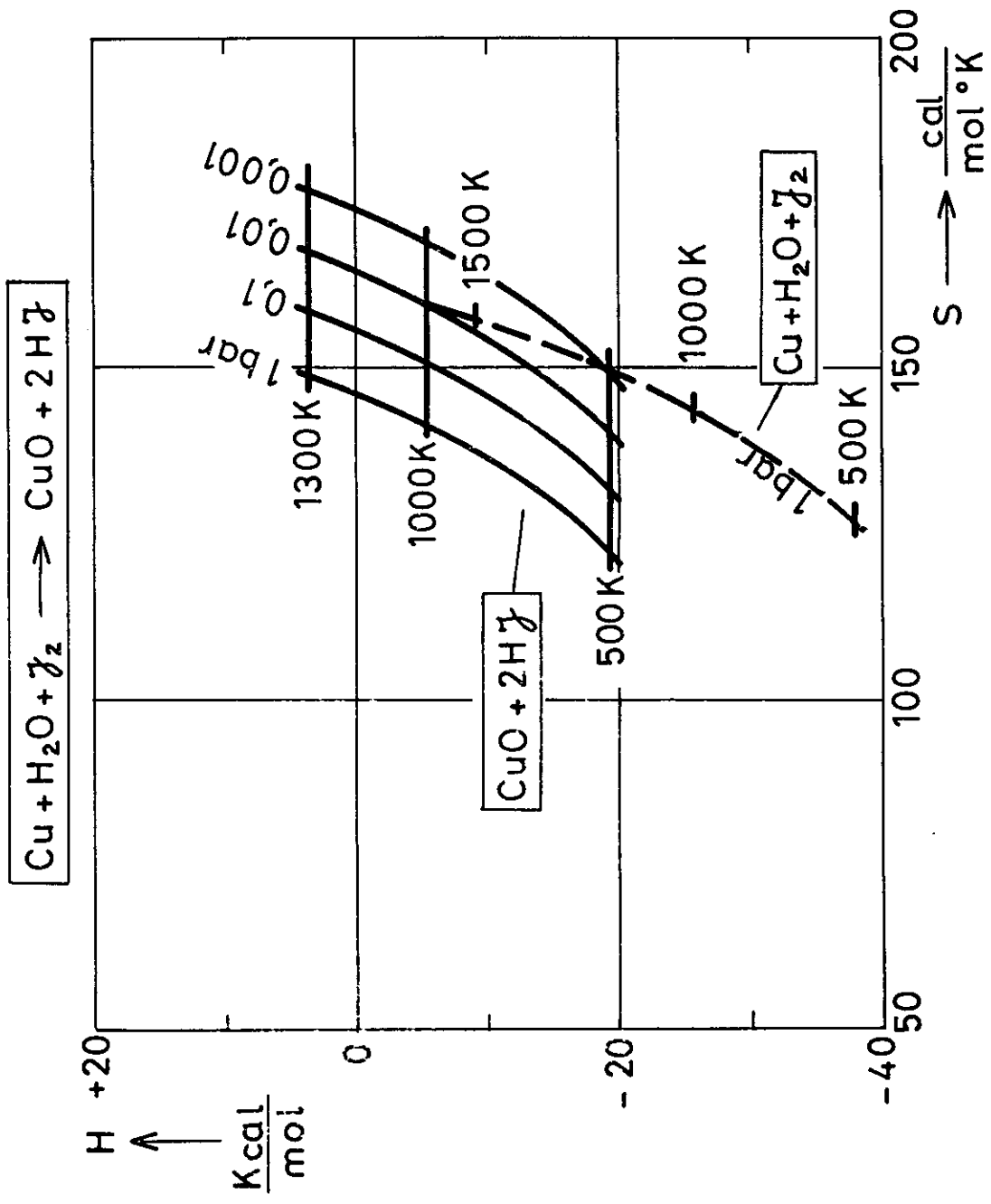


Fig. 6

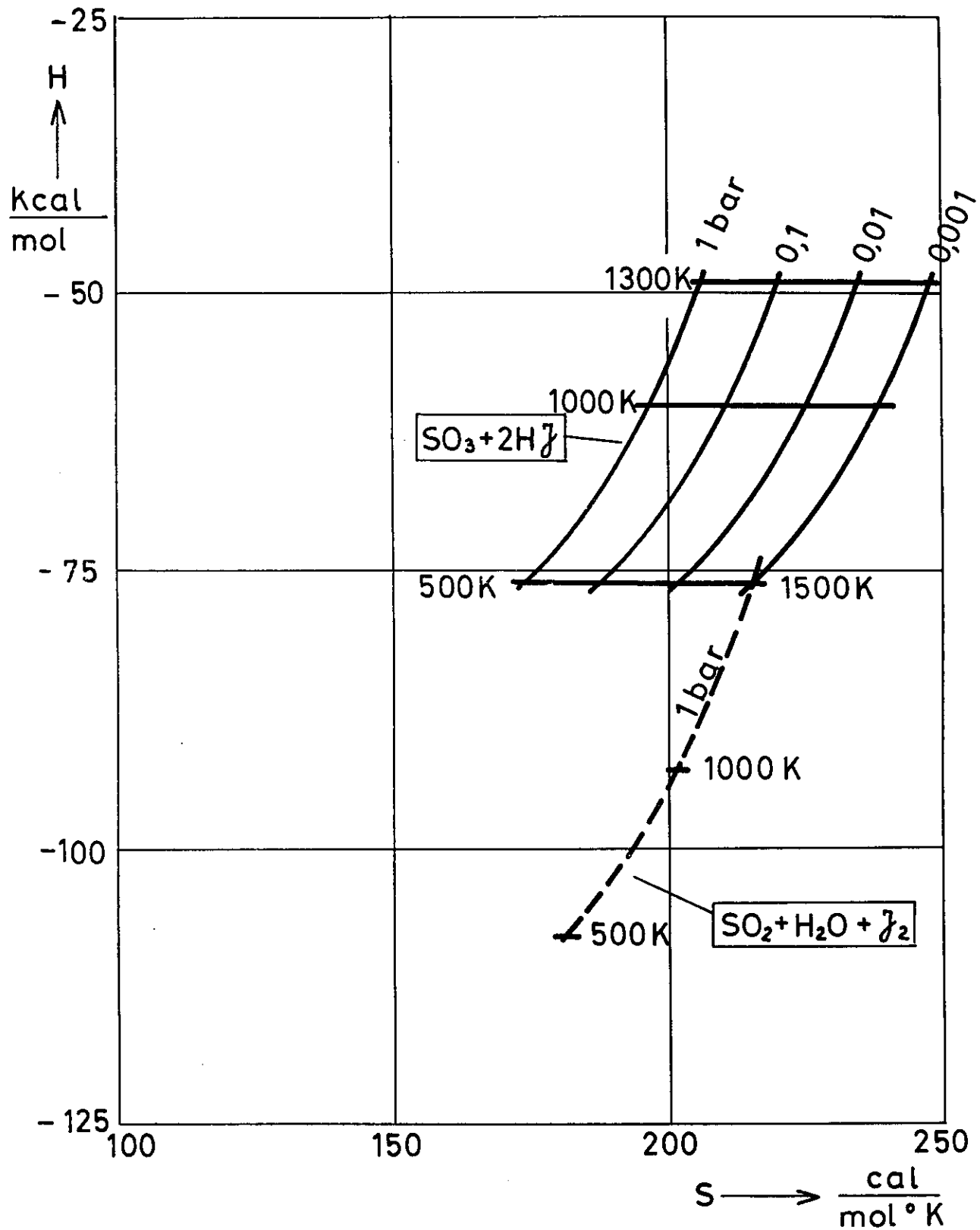


Fig. 7

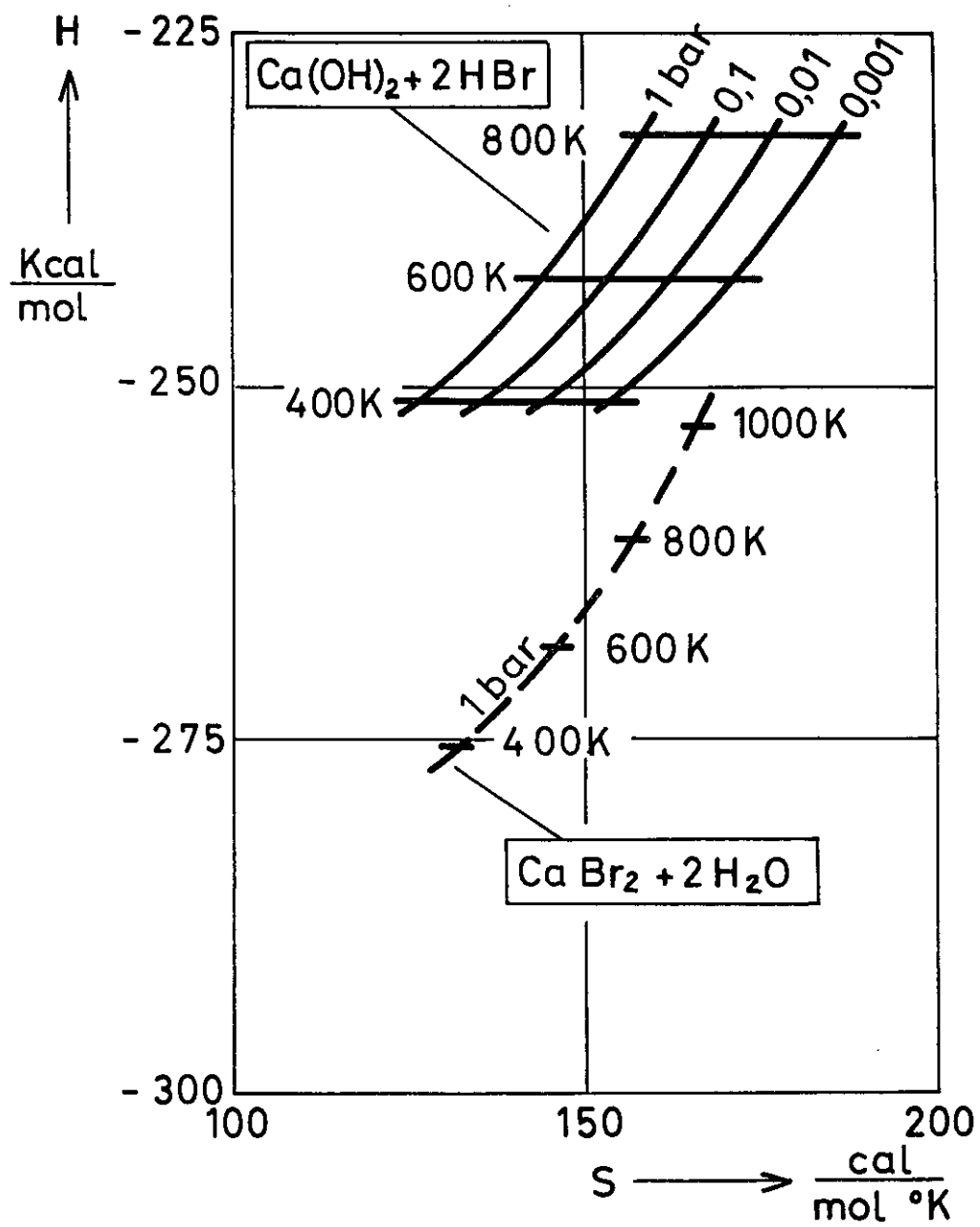


Fig. 8



$p = 1 \text{ atm}$

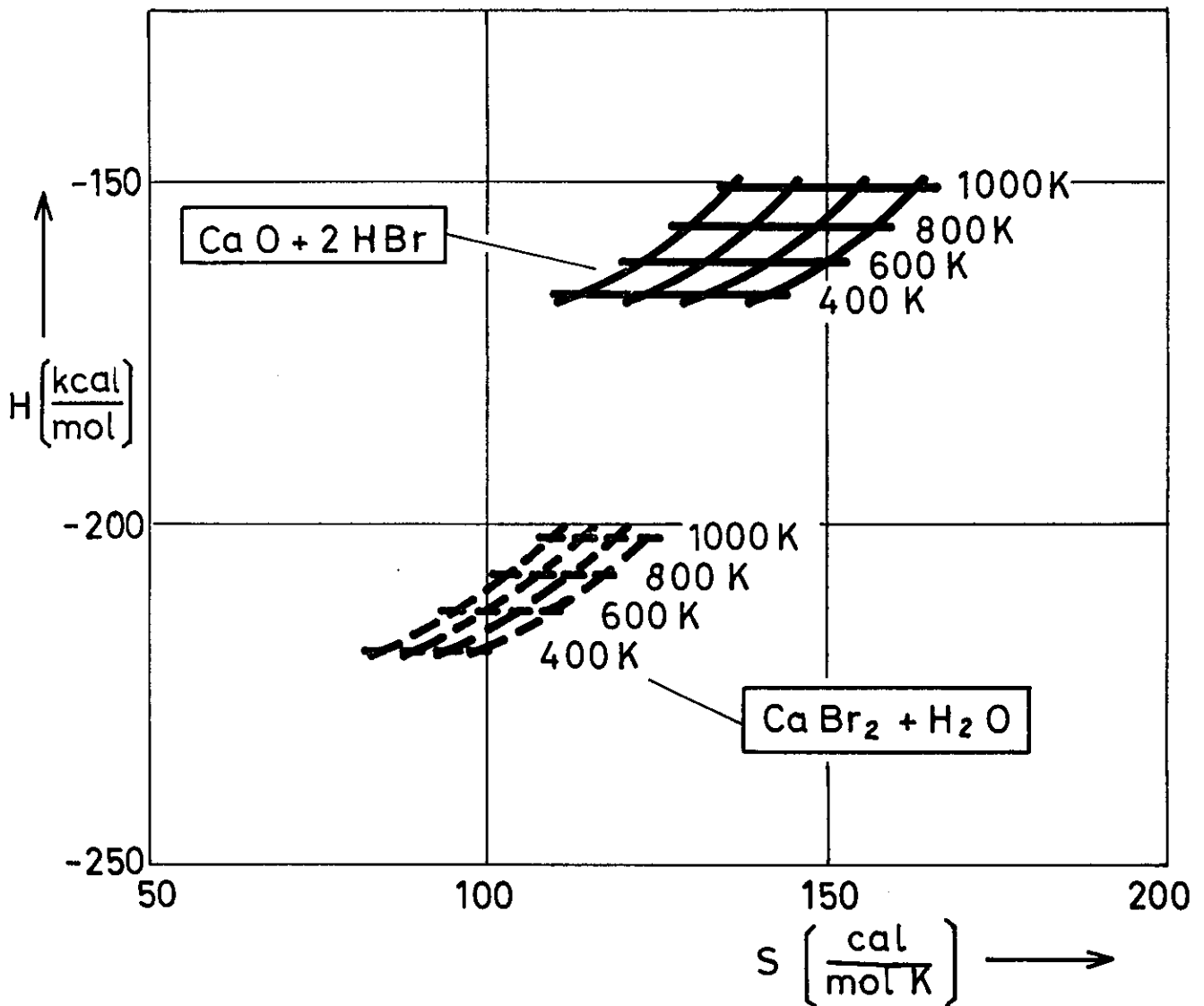


Fig. 8 bis

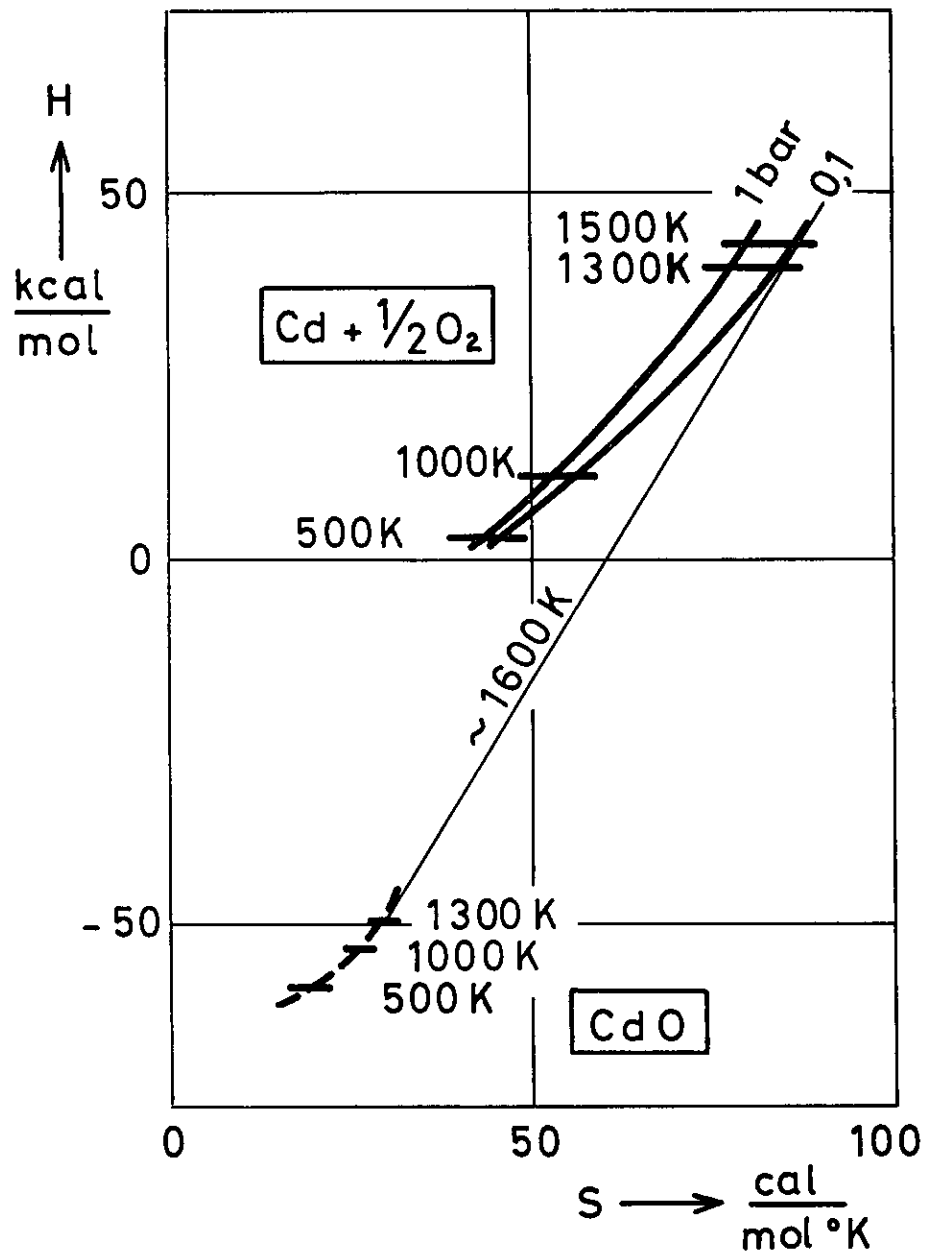


Fig. 9

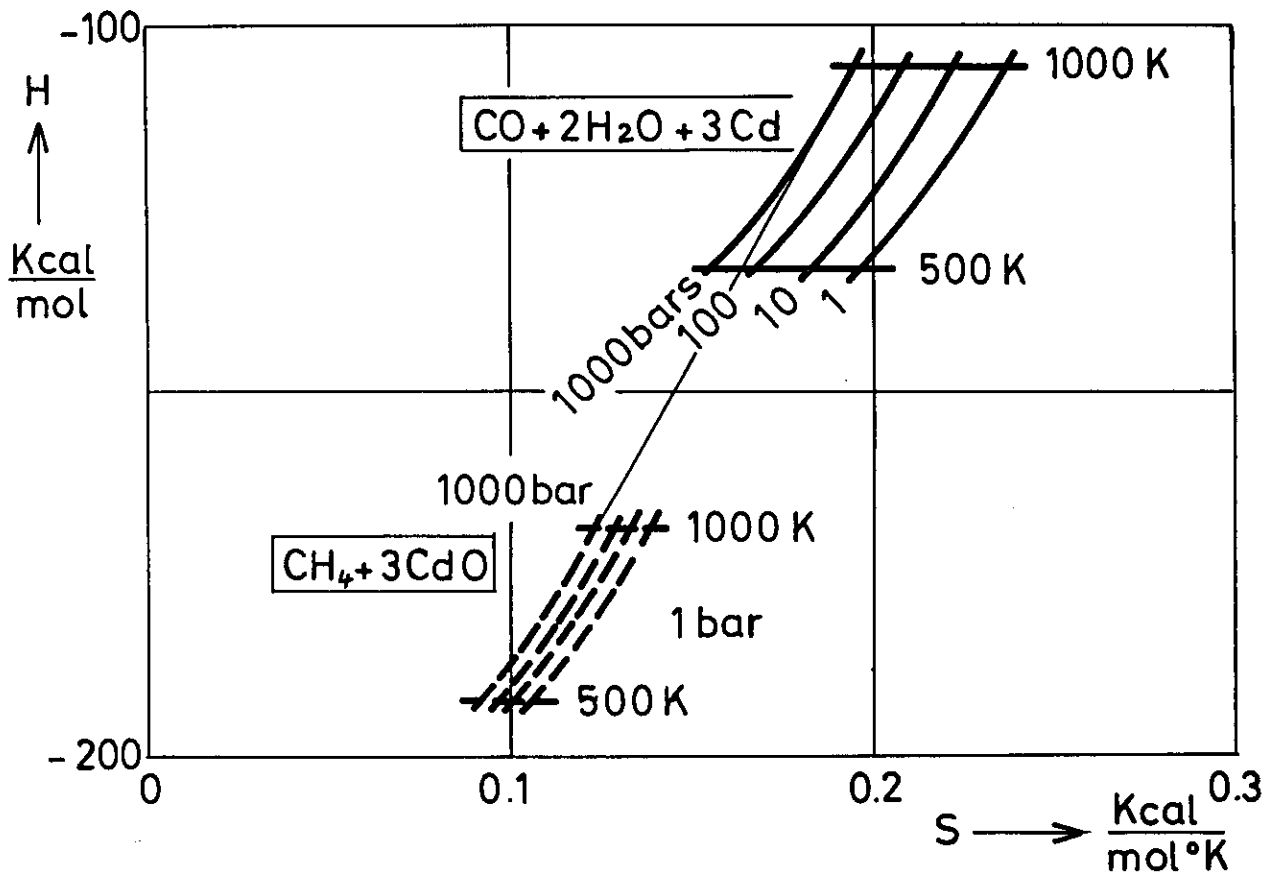


Fig. 10

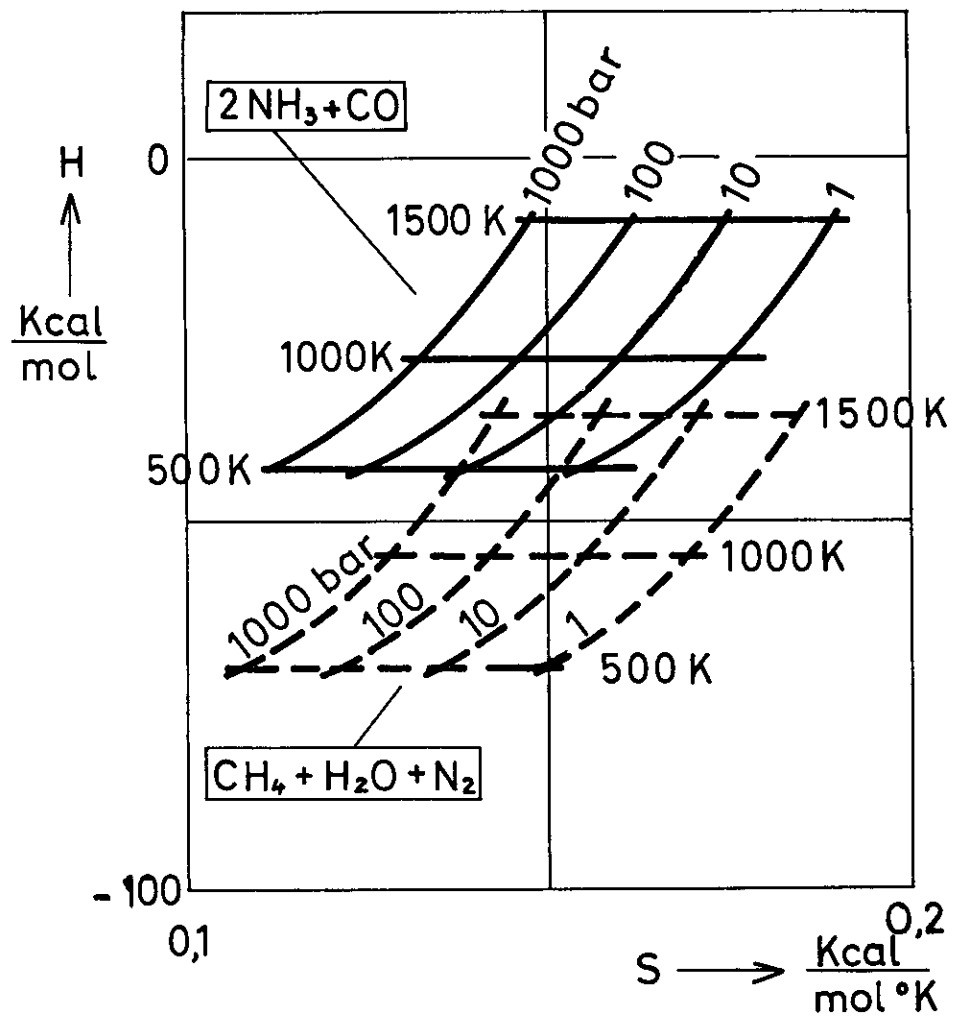


Fig. 11

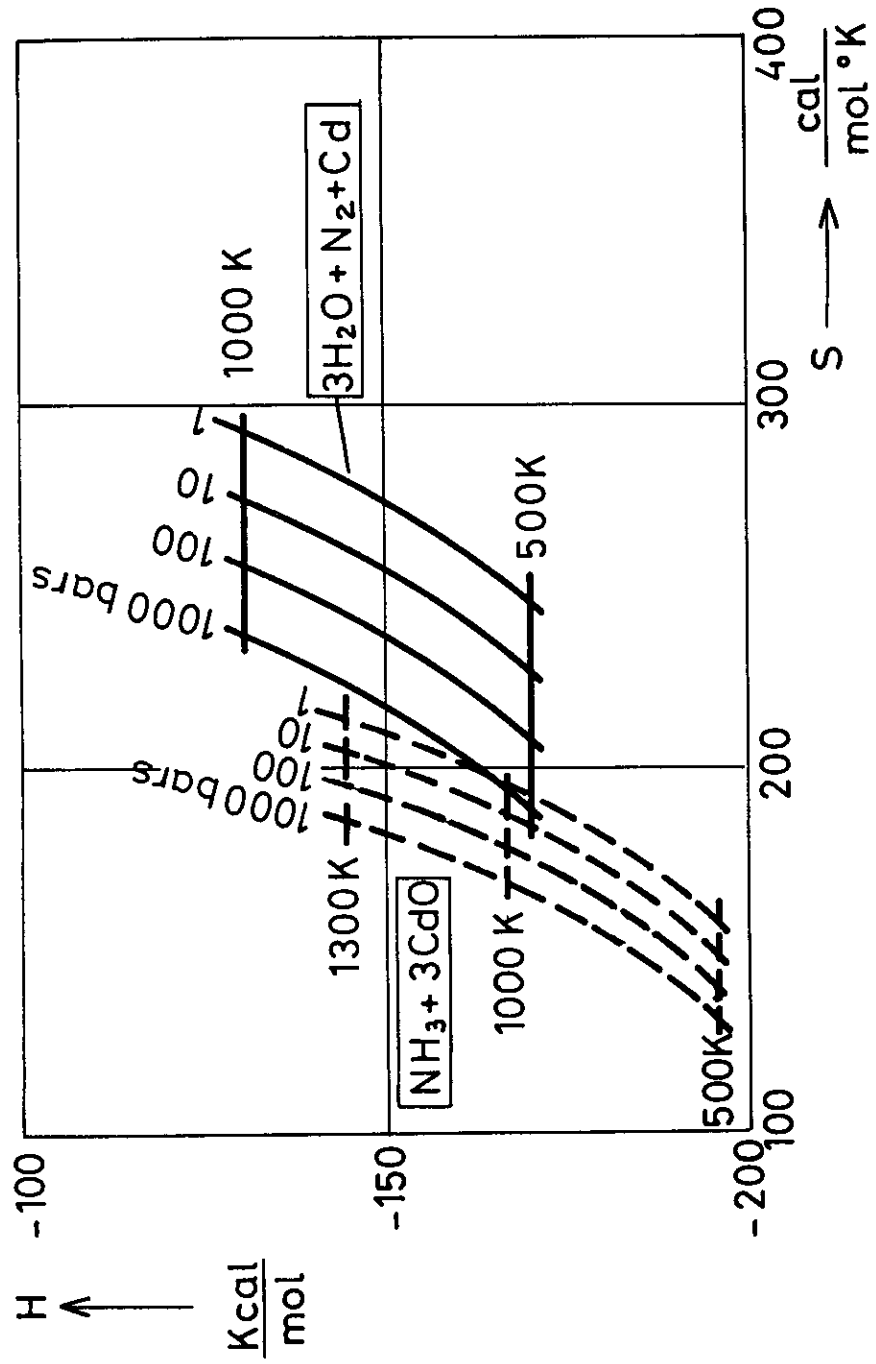


Fig. 12

References

- [1] R. Schulten : private communication, 1969
- [2] G. De Beni : private communication, 1969
- [3] O. Knacke and Barin : unpublished values, 1969

M. Marchetti

I would like to thank prof. Knoche for the very clear and the very imaginative paper. As you see there are many arrows to be thrown against the target of direct production of hydrogen. Well, the future will tell which is the best. Perhaps there is not a single best, perhaps a similar process could be developed to produce for instance ammonia, instead of hydrogen, using nuclear heat and water and some nitrogen.

Well, I think that we have still 10 min. before the coffee break. So if you have some questions to ask we can introduce a little discussion here. No questions? Perhaps Mr. De Beni?

M. De Beni

I have a question, it refers to the diagram you have shown before on the hydrolysis of calcium bromide, where it appears that the pressure of hydrogen bromide in equilibrium is very very low, even at high temperature. I did some calculations, and also some experiments, and the results I will show during my exposition are quite different. Our partial pressure is much higher than that appearing on your diagram.

M. Knoche

Yes, maybe later we will see.

M. De Beni

An explanation could be that above a certain temperature the stable phase is not calcium hydroxide any more because calcium hydroxide tends to lose water and become calcium oxide. But in principle this should not change the equilibrium because the free energy is the same.

M. Knoche

Well, I should mention that the data are those of INF Tables and for this reaction we have also the data of Prof. Knacke, which are unpublished.

M. De Beni

Just a curiosity, you did consider the hydrolysis of calcium bromide independently of our process or just in relation ...

M. Knoche

No, no, just in relation.

M. Marchetti

One point is that the results are very dependent on the exact value of thermodynamical data and in general they come out as a difference between large numbers. So small errors in the data become large errors in the result. This points to the need of doing laboratory measurements on all the reactions under consideration of sometimes unusual reactions, as in our case. Very unusual.

M. Knoche

Maybe I should mention the method I applied. It seems to be a rather simple method. One can think of many

variations and very easily decide how the equilibrium conditions are, just by plotting the thermodynamical data.

M. De Beni

There is the danger of giving too much confidence to data we find in literature.

M. Marchetti

I want to present now a process for decomposing water, using heat at temperatures below 750°C, which is the maximum temperature available now from HTR. I would say that it is just an example, we don't claim that this process will be finally the best and we don't claim that the work we have done on it is sufficient to make a judgement about it.

The very important point, in my opinion, is that this process breaks the prejudice that to decompose water a chemical reductant is necessary. And it shows that heat can be kind of a reductant. It is the first process and it is clear why : the classical sources of energy are also reductants and it was very easy, very natural, to use them as reductants. Mr. De Beni is going to tell you in detail all the steps of this process for water decomposition, "direct" water decomposition.