MARCHETTI-29_A1

Höhne

Paschal

Weyand

Franzen

Ziegler

Block

Teggers

Valette

Zimmer.

De Leone

Paris

Jeffroy

Gallone

Van Heek

Steeman

Chelle

Post

Kugeler

Siebker

Knoche

De Beni

Caprioglio

Marchetti

PROCEEDINGS ROUND TABLE on DIRECT HYDROGEN PRODUCTION

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 Director of this Center	Welcome and opening speech
9.25 h	Dr. C. Marchetti Head of Phys.Chem.Div.	The philosophy behind our effort towards a "direct" production of hydrogen
9.40 h	Prof. R. Schulten Prof. f. Reaktortechnik Direktor Institut für Reaktorentwicklung KFZ Jülich	Costs and temperatures for heat from HT reactors - Medium term trends (Read by Kugeler)
10.20 h	Prof. Knoche Prof. für Technische Thermodynamik TH Aachen	Thermodynamical considerations on "coupled" chemical reactions
10.50 h	Coffee break	
11.00 h	Dr. De Beni Physical Chem. Div.	MARK-1 as an example of a "direct" process for producing 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-Sidelor-Paris
Dr. Post	Staatsmijnen Centraal Lab.-Geleen
Dr. Steeman	Staatsmijnen Centraal Lab.-Geelen
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 Bovery, Mannheim

Euratom Ispra

Dr. P. Caprioglio	Director CCR Ispra
Dr. C. Marchetti	Head of Phys.-Chem. Division
Dr. G. De Beni	Phys.-Chem. Division

Euratom Bruxelles

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 Speach

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 impli-
cations, 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 membre   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 poten-
tial 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 apprecia-
te 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 rised
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, exclu-
ding 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 compli-
cated 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 technolo-
gical 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 los-
ses. 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 trans-
porting 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 de-
compose 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 breack 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 pratically 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 peopl: studying the use of hydrogen for produ-
cing food. Actually a certain kind of yeasts can
feed on hydrogen as the energy source and use CO_2
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 pro-
duce hydrogen, and hydrogen to feed the Hydrogeno-
monas 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 o-
peration that requires the use of a source of pri-
mary 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 pro-
fessor 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 pre-
sent there are three High Temperature Gas Reactors in
the world which are based on Helium, Graphite and coa-
ted 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 rea-
ched 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 col-
laborate 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 tem-
peratures 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 tecmperatures
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, irra-
diated by neutron doses in the same order of magni-
tude we can expect in normal operation, the rates of
fission product release do not increase in a unaccepta-
ble 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 tempe-
ratures 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 invest-
ment 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 specifi-
cations, the reactor could be designed for a tempe-
rature 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 concen-
trated. 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 outli-
ned, 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 up-
per 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 in-
cluding 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 ga-
ses 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 gasifica-
tion 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 pro-
cesses 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 coa-
tings of pyrolytic graphite. We have today a maximum
temperature of 1300°C; there are irradiation expe-
riments 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 essen-
tially 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 prac-
tical applications. This is the trend that Dr.Kugeler
is indicating, showing 950°C for the gas outlet tem-
perature in five years and going hopefully beyond
1000°C to 15 years; this is the trend based on the
present experience. Of course the phenomenum 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 there-
fore 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 tem-
perature 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 a-
round 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 con-
sidered 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 ha-
ve been developped essentially, and I should say
exclusively, for producing electricity, but it so
happens that they are also suitable for other ap-
plications, and since they are the only power reac-
tors that produce heat at such a high temperatures,
they have always been pointed as the most obvious
choice between reactor types (for all chemical ap-
plications).

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 de-
veloped 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 clas-
sical energy, you see, coal and gas, e.g. in Ger-
many, 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 mi-
nimum 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.

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M. Caprioglio

Sorry 60%. Still, anyway we will get into the discus-
sion 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 bet-
ween 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 other-
wise it would be difficult to ignite the process.

M. Marchetti

Perhaps I should say just another thing :
hydrogen is made from these fuels and, per calo-
rie 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 de-
> scribed 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 mine-
> ral sources of energy which is not really our
> purpose. We know that the problem is complex, in-
> tricated and it depends very much on local situa-
> tions, on taxation, on a number of things.

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

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 discus-
sion.

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 gi-
ven you, thanks to the kindness of the Jülich re-
presentative, the status of the art for high tempe-
rature 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 de-
composition 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 re-
servoir KK at a temperature T_0. A flow of steam
enters the system (state 1) and a flow of decompo-
sed steam leaves it with state 2.
We have to consider the energy conservation, the
first law of thermodynamics. Due to the second

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

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

$$\jmath_2 - \jmath_1 = \frac{q}{T} - \frac{q_0}{T_0} + \Delta \jmath_{irr} \qquad (2)$$

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.

$$q = \frac{T}{T - T_0} \left\{ h_2 - h_1 - T_0 \left(\vartheta_2 - \vartheta_1 \right) \right\} (1 + \nu)$$

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

$$\nu = \frac{T_0 \, \Delta \vartheta_{irr}}{h_2 - h_1 - T_0 \left(\vartheta_2 - \vartheta_1 \right)} \qquad (3)$$

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 complete-
ly 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 ful-
fill our general thermodynamic restrictions and to
see what the equilibrium conditions for such reactions
are.

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Fig. 1

isotherm – isobare reaction
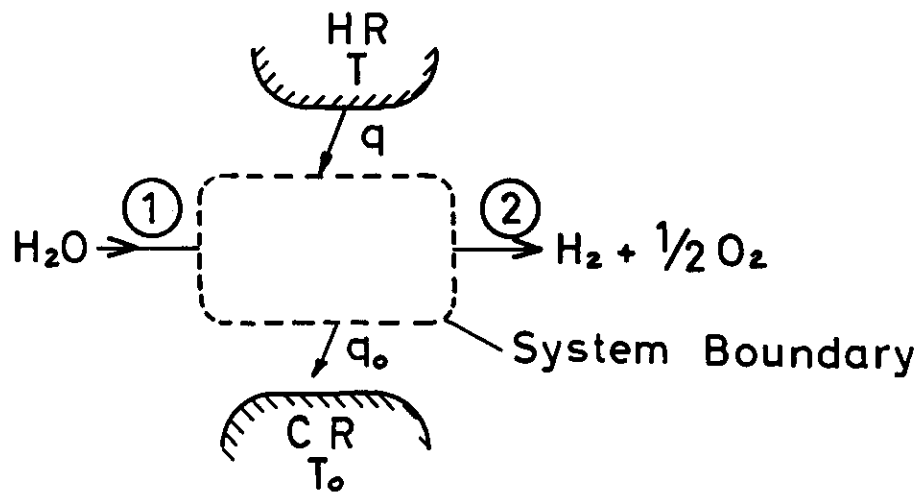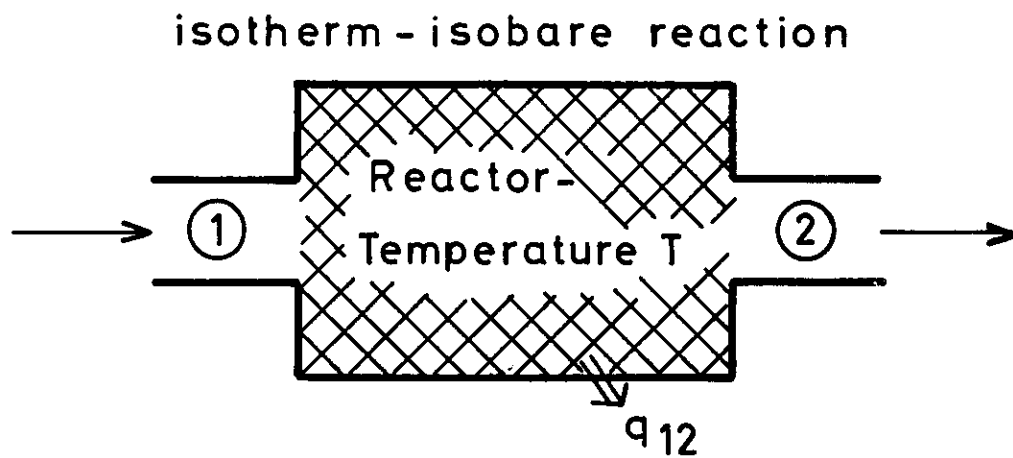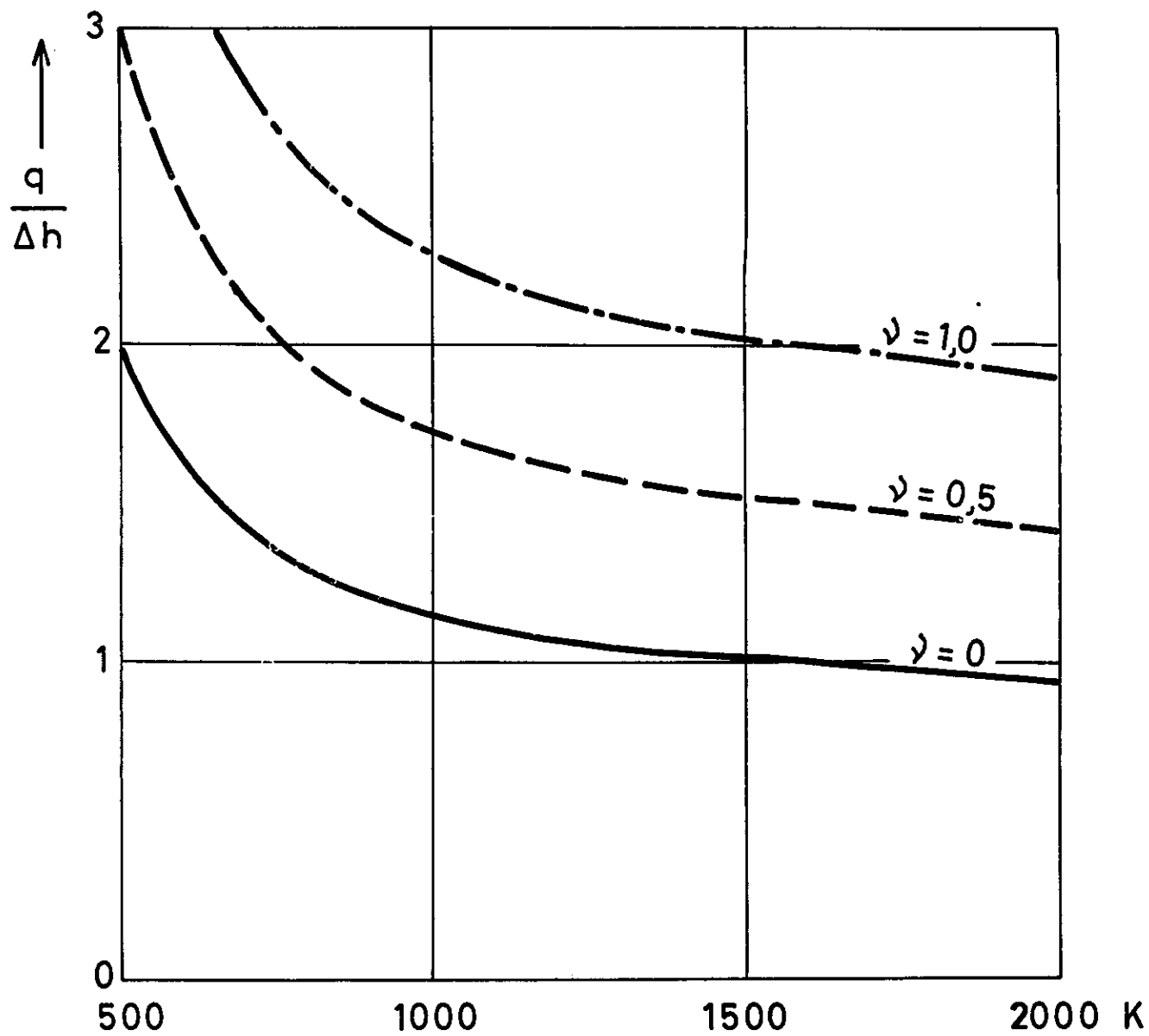
Fig. 3

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

$$ h_1 - h_2 = q_{12} \tag{4} $$

$$ \vartheta_2 - \vartheta_1 = \frac{q_{12}}{T} + \Delta\vartheta_{irr} \tag{5} $$

leads to the entropy production

$$ \Delta\vartheta_{irr} = \vartheta_2 - \vartheta_1 + \frac{h_1 - h_2}{T} > 0 \quad (T,p = const) \tag{6} $$

The entropy production $\Delta\vartheta_{irr}$ 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 pro-
duction can be represented by the horizontal distan-
ce 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 easi-
ly be shown that the vertical distance of those
tangents represents the change in free enthalpy.
With the help of such Mollier-charts it is possi-
ble, 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 de-
composed steam. A tangent is included at a tempera-
ture 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 pres-
sures of the decomposition products H_2 and O_2 ;
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 wa-
ter - 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 :

$$Cu + H_2O + J_2 = CuO + 2HJ$$

Fig. 4

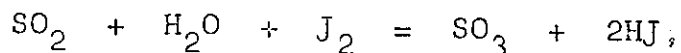$$\Delta S_{irr} = S_2 - S_1 + \frac{h_1 - h_2}{T}$$
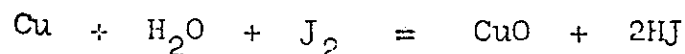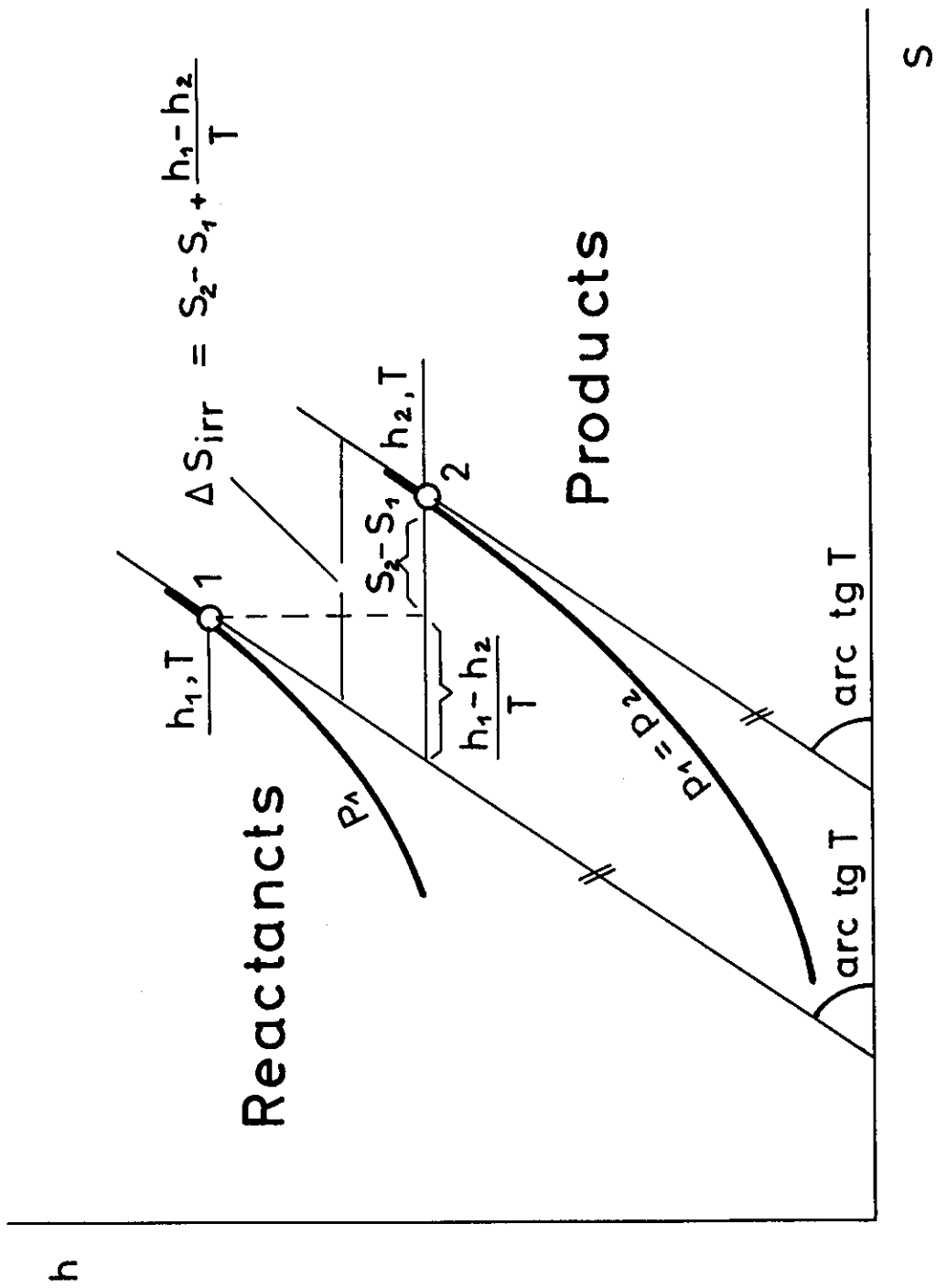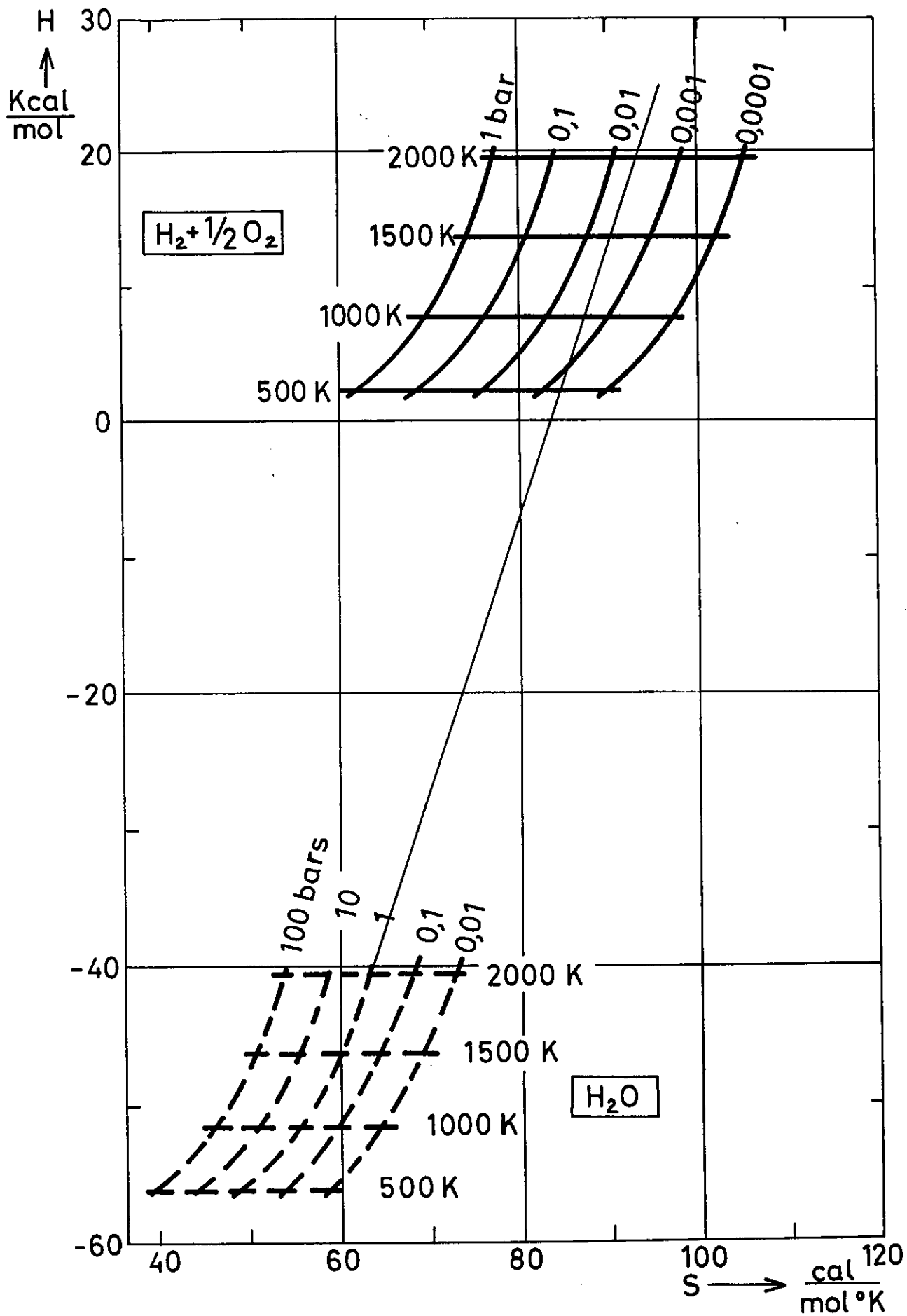
Fig. 5

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 :

$$SO_2 + H_2O + J_2 = SO_3 + 2HJ,$$

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.

$$CO + 2H_2O + 3Cd = CH_4 + 3CdO$$
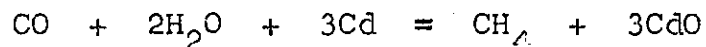
This reaction which under atmospheric pressure is
known to run the opposite way, may be performed
under high pressures, fig. 10. In a next step one
could think of the following reaction :

$$CH_4 + H_2O + N_2 = 2NH_3 + CO,$$
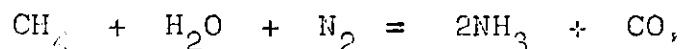
where high pressure has to be applied in order to
avoid the decomposition of ammonia, fig. 11.
The maximum equilibrium concentrations of ammonia
are in the range of about 10%.

The direct formation of ammonia from nitrogen and
steam in the presence of Cadmium, fig. 12, would
theoretically be possible only at very high pres-
sures 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.

Fig. 6

Fig. 7

Fig. 8

$$\boxed{CaBr_2 + H_2O \longrightarrow CaO + 2HBr}$$
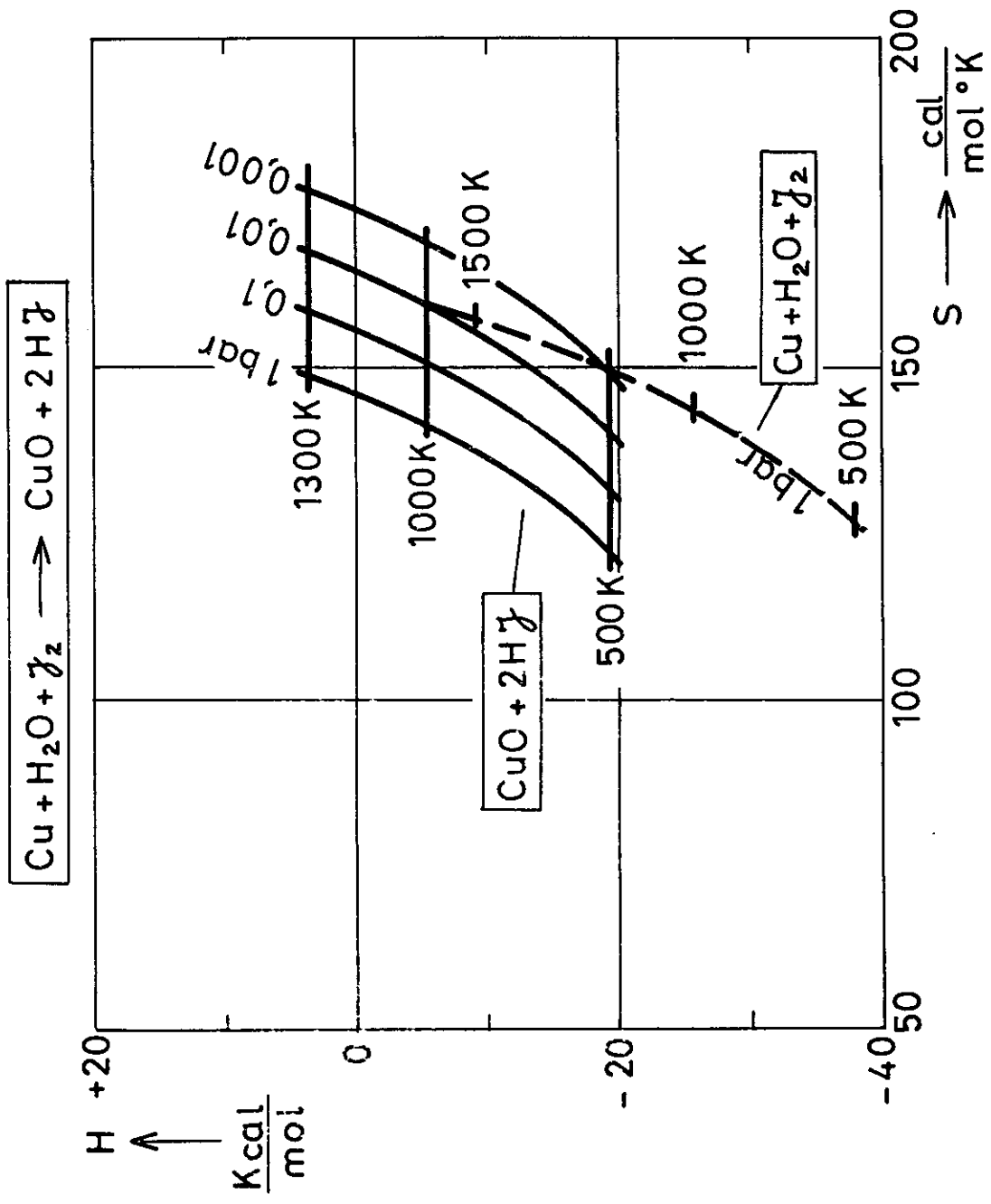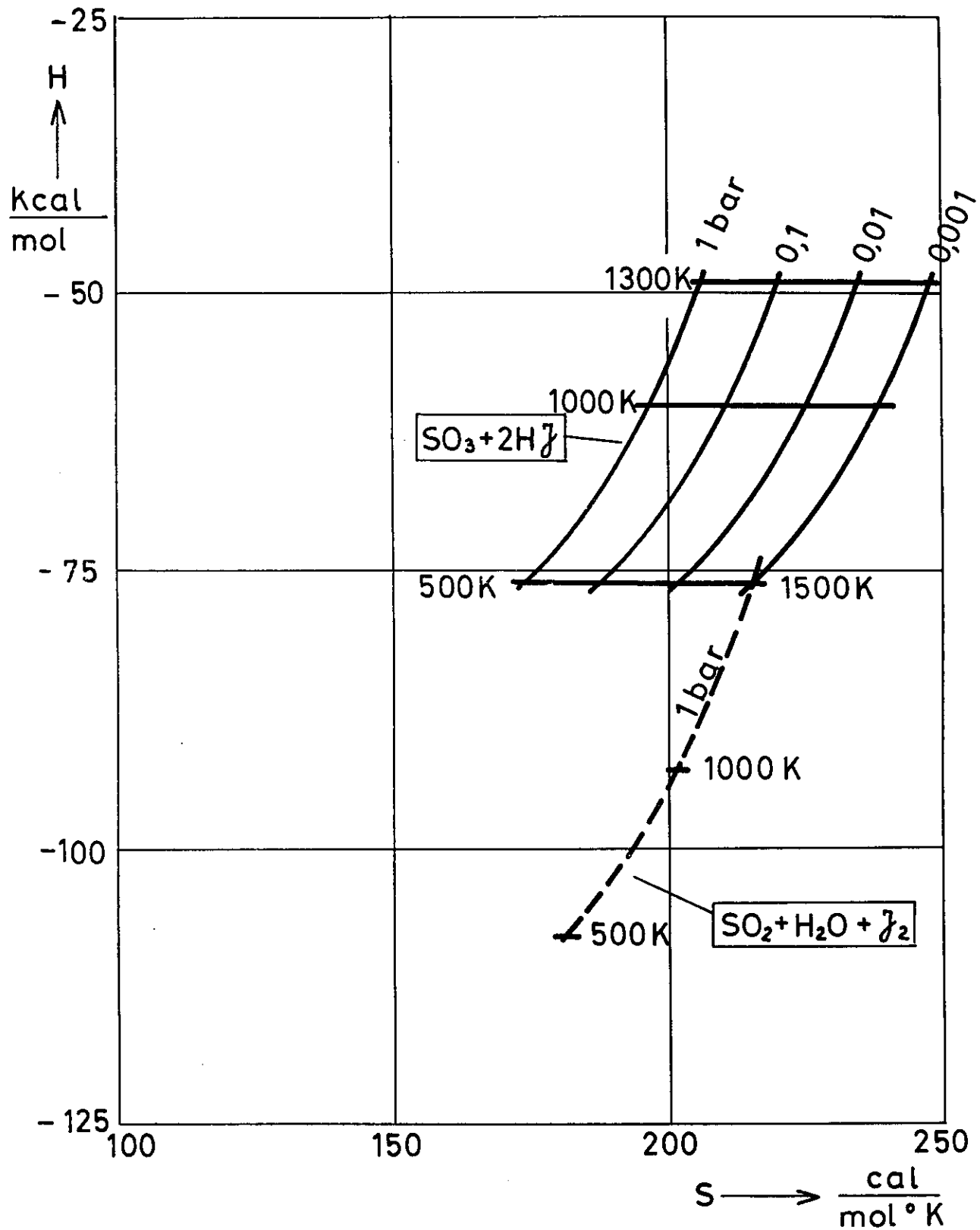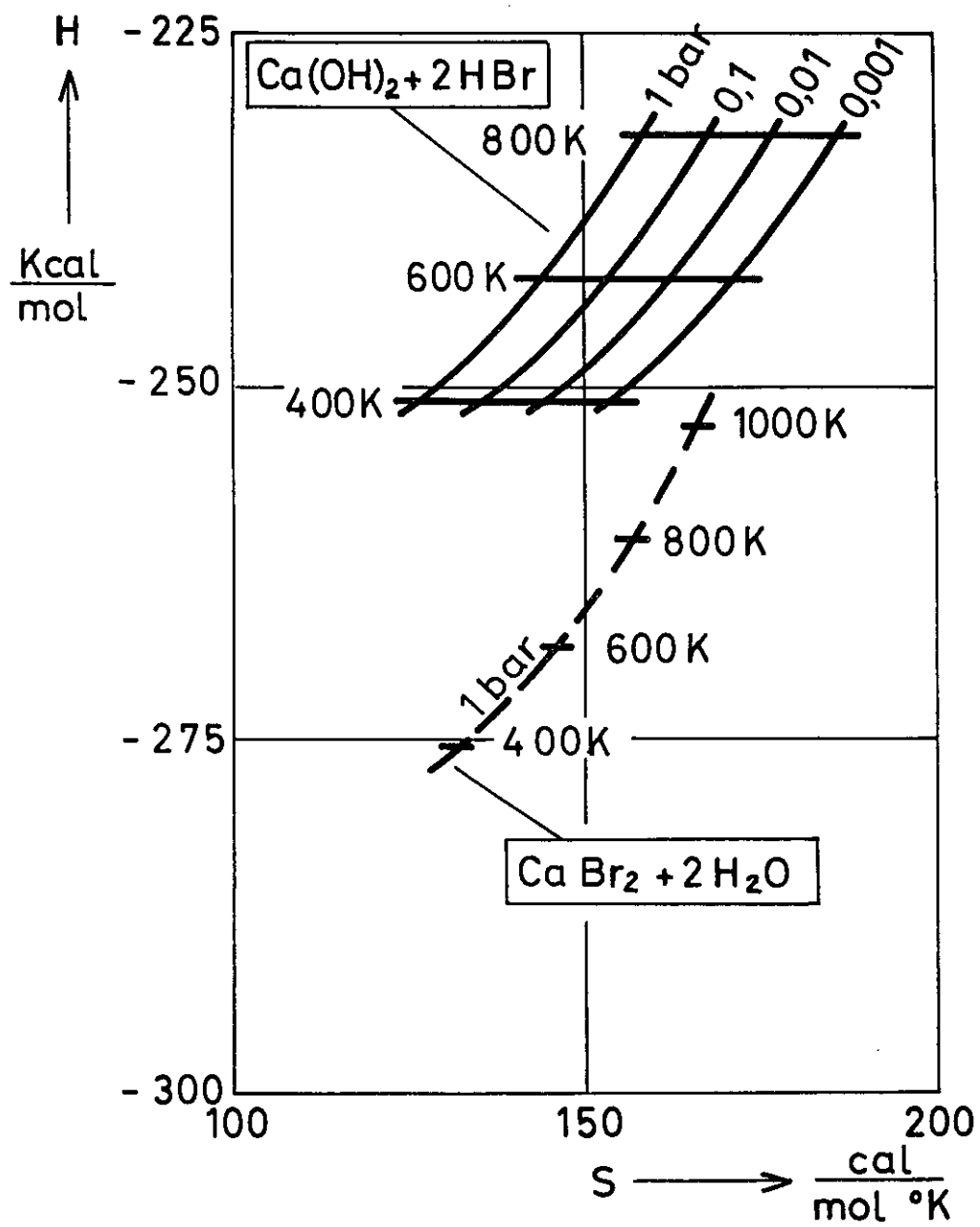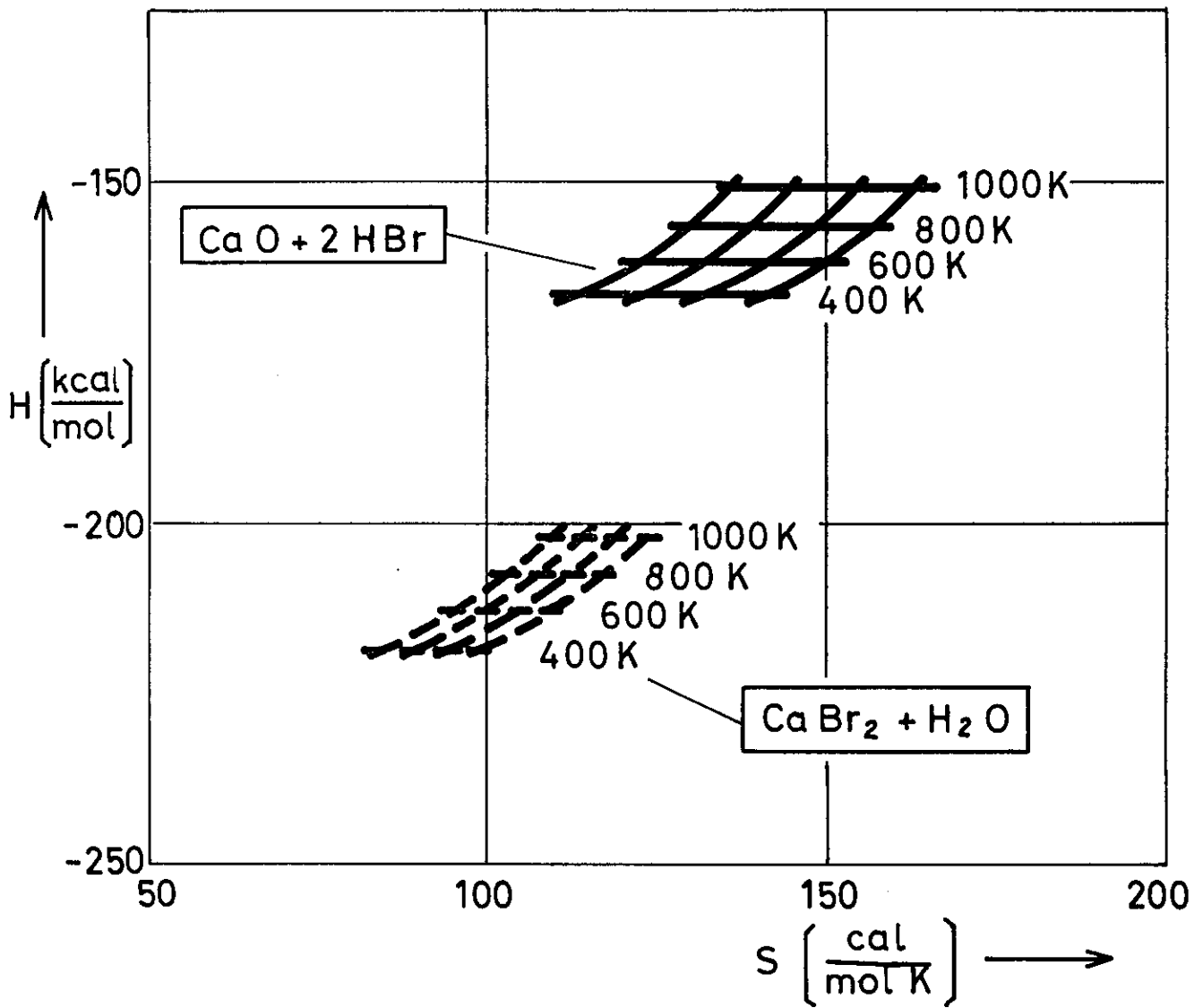
$p = 1\,atm$

Fig. 8 bis
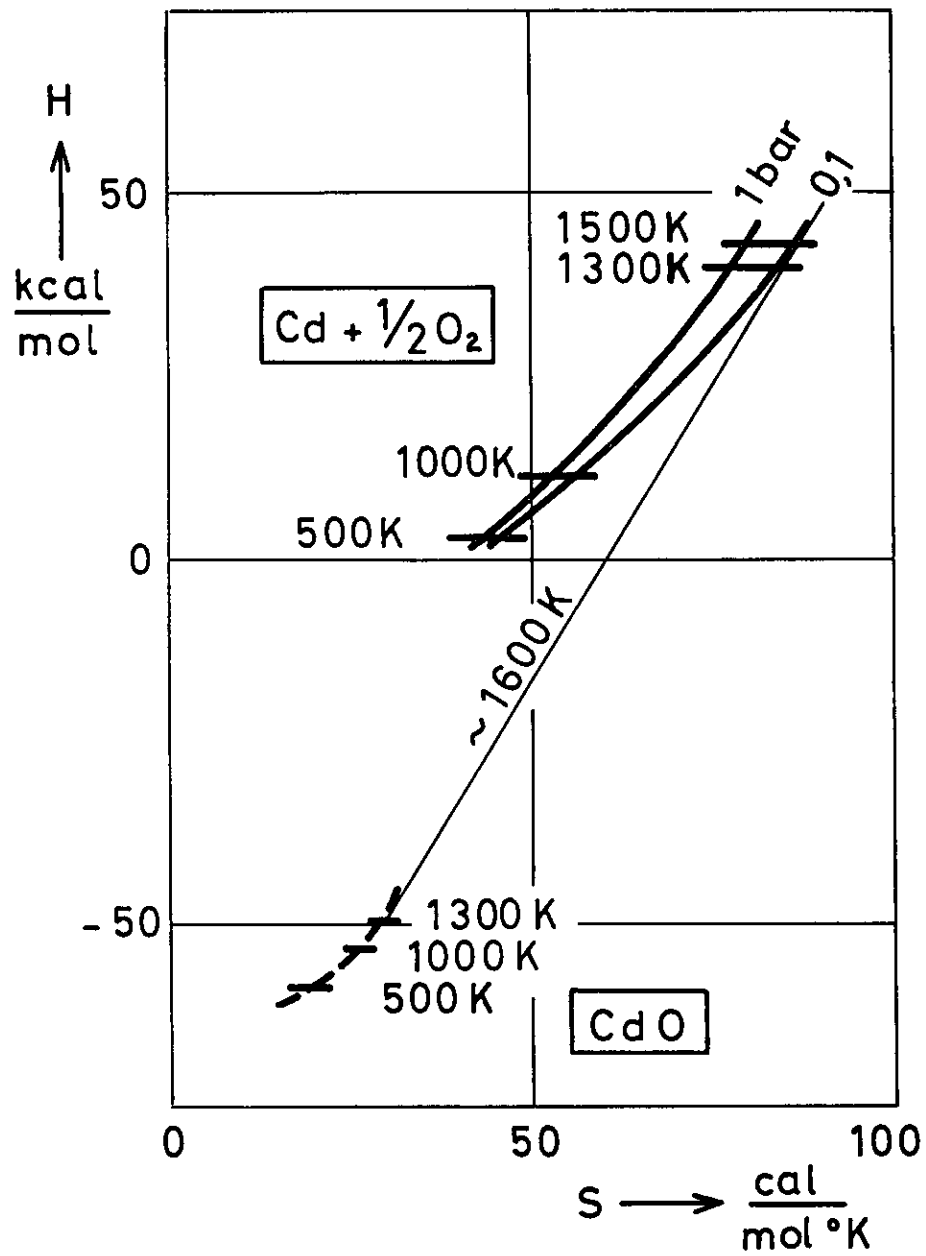
Fig. 9
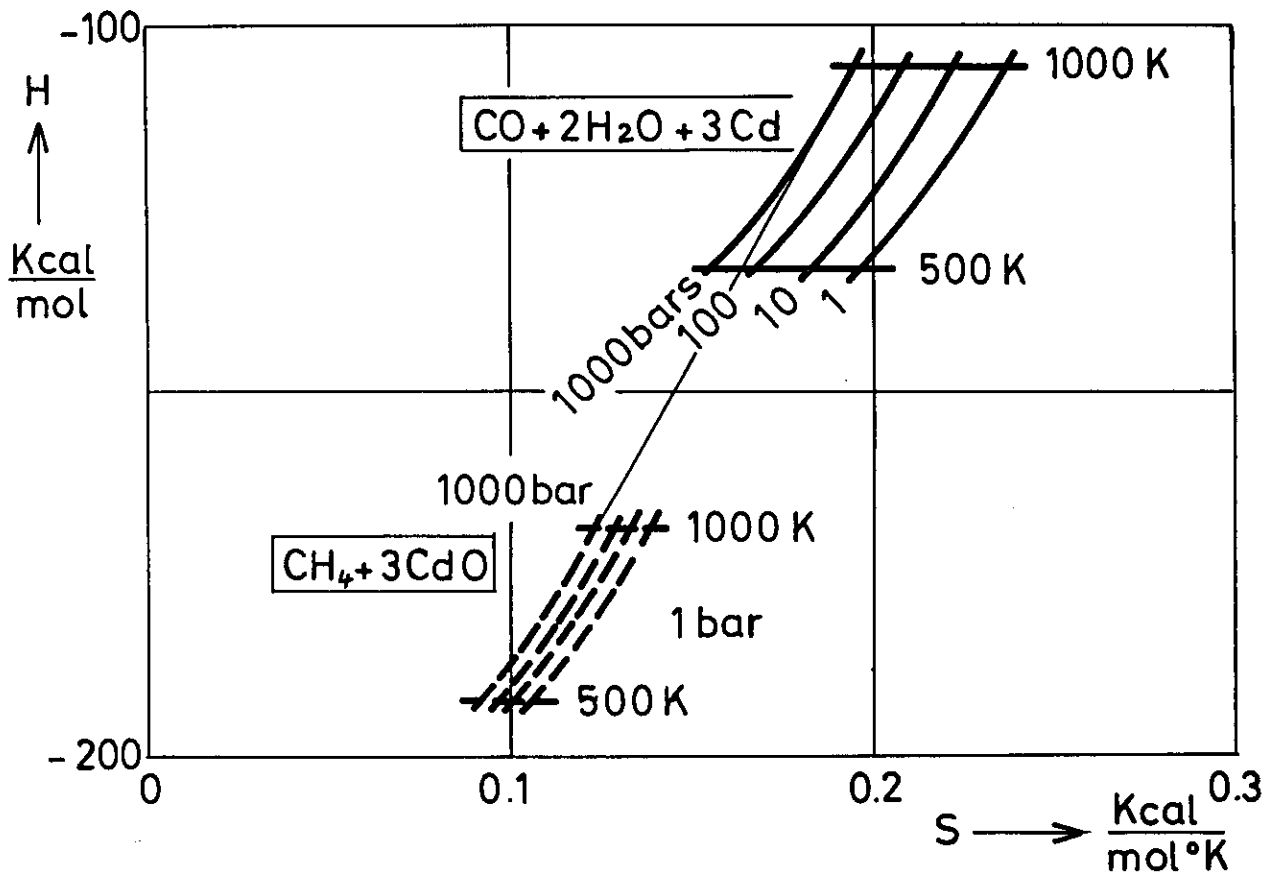
Fig. 10
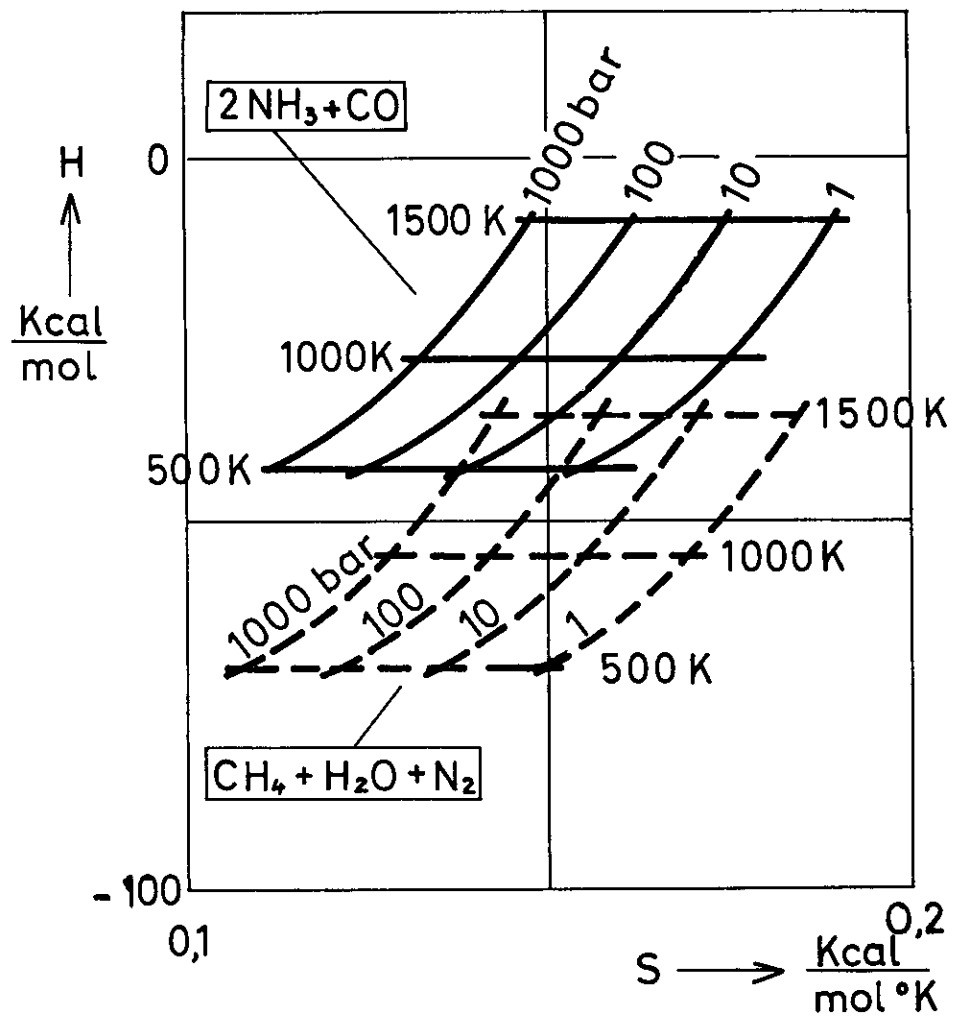
Fig. 11

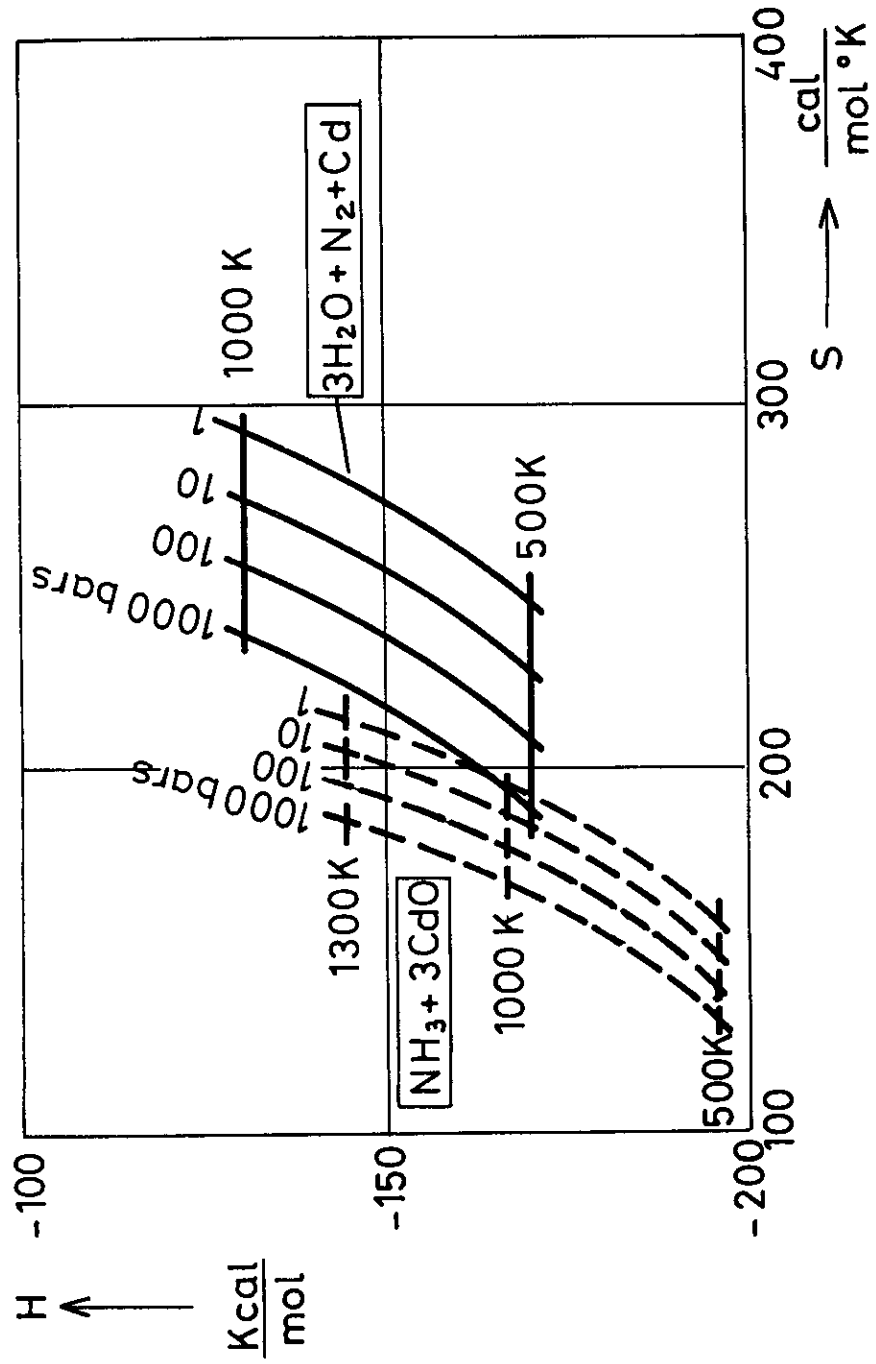Fig. 12

References

$\diagup 1 \diagup$ R. Schulten   : private communication,1969

$\diagup 2 \diagup$ G. De Beni   : private communication,1969

$\diagup 3 \diagup$ 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 ha-
ve shown before on the hydrolysis of calcium bro-
mide, where it appears that the pressure of hydro-
gen 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 ap-
pearing on your diagram.

M. Knoche

Yes, maybe later we will see.

M. De Beni
_____

An explanation could be that above a certain tempe-
rature 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 indipendently 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 gene-
ral 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 labora-
tory measurements on all the reactions under conside-
ration 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 decompo-
se 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 classi-
cal 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.