CORRADIATION USING THE REVERSIBLE AMMONIA REACTION

by

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ABSTRACT

A system is described for the large scale generation of power
from solar energy in which energy is transferred by means of the
reversible chemical reaction $2\,NH_3 \rightleftharpoons N_2 + 3H_2$. An array of pressed
steel paraboloidal mirrors is employed each having a focal absorber in
which the endothermic forward reaction proceeds. The exothermic reverse
reaction occurs at a common central plant and the heat energy recovered
operates a thermodynamic power plant. The reactants are transferred in
small diameter steel piping at ambient temperature. Storage of energy
may be catered for by providing storage for the reactants.

The results so far of design studies are used to assess both the
technical and economic viability of the complete scheme.

INTRODUCTION

The Minneapolis-Honeywell group (Honeywell 1974) has made a comparative study of several large scale solar energy systems. The results of this study indicate that (a) systems relying solely on absorptive surfaces are not competitive, and (b) systems in which the corradiation of energy from the collectors to a central station is by means of the heat content of a hot circulating fluid are not competitive unless the fluid temperature is below 300°C. One system which avoids these two constraints is the power tower in which all the corradiation is performed optically except for the energy transferred down the tower. The power tower concept has been most fully developed by the Houston-Mcdonnell-Douglas group (Houston 1974).

This paper describes an alternative scheme in which corradiation is accomplished partly by optical means using paraboloidal mirrors and partly by a closed loop chemical method which involves the marginal development of an intrinsic component of all optical systems viz. the umbilical system of power and control cables and/or pipes necessary for steering the mirrors. Being therefore a more balanced development of essential components it should possess an economic advantage over the power tower. Furthermore the system described here has inherent in it a potential for lossless storage of energy which no other system in the Minneapolis-Honeywell study possesses.

The present system employs the dissociation and resynthesis of ammonia for absorbing heat at the foci of the mirrors and recovering it at a common regeneration plant. As shown in fig. 1 an essential element in this process is the separator whose duty is to regroup the components of the mixtures emanating from the dissociation and synthesising reactors into the two appropriate feedstocks. By providing a separator one avoids the need for the reaction to proceed to substantial completion in either reactor and thus removes some of the constraint that would otherwise be imposed on the reactor temperatures. Indeed there is no barrier, in principle, against the two reactor temperatures being equal, or even against the synthesis temperature being greater than the dissociation temperature.

However the energy requirements of the separator prevent any overall advantage accruing from the latter situation, at least from the point of view of efficient energy transmission.

Chubb (1974, 1975) describes a thermo chemical corradiation system using sulphur trioxide dissociating into sulphur dioxide and oxygen. Chubb does not however use a separator relying instead on the existence of two temperatures T_{end} and T_{ex} at which the reaction has proceeded substantially completely in either the endothermic or exothermic direction. Thus by operating the dissociation reactor at T_{end} and the synthesis reactor at T_{ex} the need for separation is avoided. However, because T_{ex} is always substantially less than T_{end} this method provides lower thermodynamic efficiency than the present concept is able to provide. In addition because the present concept allows operation of both reactors at a temperature between T_{ex} and T_{end}, it is possible to avoid extreme temperatures in the dissociation reactor.

On the other hand the present concept relies on efficient separation processes. Unfortunately the simplest method viz. condensation of a liquid phase is not very efficient but there is good reason to believe that other separating processes can be developed with much less associated loss.

Both Chubb and Hildebrandt (1975) list a number of candidate reactions for thermo-chemical energy transfer all of which are given in Table I. The need for low cost energy transfer components appears to favour reactions with high reaction energy per gram (listed) and high fluid densities (dependent on pressure). The last two reactions in Table 1 follow existing commercial synthesising processes which are carried out at high pressures typically 300 atm. In the present system it is proposed that the pressure throughout be essentially constant and at about 300 atm. The effect of system pressure on performance and on the size and mass of several components is discussed in sections 10, 11 and 12.

In comparing the present system with the one proposed by Chubb it is felt that the former offers the following advantages:

(a)   less hazardous since any ammonia which might accidentally escape is lighter

than air whereas both sulphur dioxide and sulphur trioxide are heavier than

air and at the same time are extremely toxic and form corrosive products;

(b)   more energy transferred per unit volume (approximately 50 times

more);

(c)   pipes and some other components are smaller and less massive;

(d)   less potential difficulties with materials since the operating temperatures

are lower and there is more flexibility in their final choice;

(e)   the catalyst is likely to be less expensive.

Table 1

Reaction		Kcal/gram
$SO_3 \rightleftharpoons SO_2 + \frac{1}{2} O_2$	$+$ 24 Kcal[1]	.29
$\frac{1}{2} H_2O + \frac{1}{2} CH_4 \rightleftharpoons \frac{1}{2} CO + \frac{3}{2} H_2$	$+$ 24.5 Kcal[2]	1.44
$COCl_2 \rightleftharpoons CO + Cl_2$	$+$ 26 Kcal[1]	.26
$2NF_3 \rightleftharpoons N_2 + 3F_2$	$+$ 31 Kcal[1]	.43
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	$+$ 59 Kcal[2]	.98
$CH_3 OH \rightleftharpoons 2H_2 + CO$	$+$ 25 Kcal[2]	.78
$NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2$	$+$ 13.5 Kcal	.79

1.   from Chubb (1975)

2.   from Hildebrandt (1975)

2.   GENERAL DESCRIPTION

The principles of the present system have been described by Carden (1974. 1).

Solar energy is collected by means of a large number of paraboloidal pressed steel

mirrors notionally of 10 m^2 aperture area each (refer to Fig. 1). At the focus of

each mirror is an absorber in which high pressure ammonia gas undergoes chemical

dissociation into hydrogen and nitrogen. This reaction is endothermic the heat of

reaction being provided by the absorbed solar energy. The temperature of the absorber

is maintained constant at about 700°C by means of a temperature sensitive automatic flow control valve acting on the supply of ammonia. The incoming ammonia and out-going hydrogen and nitrogen pass through a counter-flow heat exchanger mounted on the mirror and by this means it is possible for the nitrogen and hydrogen emerging from the heat exchanger to be practically at ambient temperature the same as the incoming ammonia. Thus through the flow of gases into and out of the mirror assembly energy may be transferred from it in simple pipes having no thermal insulation.

Within a central plant the nitrogen and hydrogen from a large number of mirror-absorbers is collected and passed through a large common counter-flow heat exchanger in which the temperature is raised to approximately 450°C. The gases then pass through a catalyst chamber where partial recombination to ammonia takes place. This reaction is exothermic the heat produced from it being approximately equal to all the solar energy originally collected by the mirrors. The gases emerging from the catalyst chamber pass through the heat-exchanger and are consequently

cooled to approximately ambient temperature. As a result ammonia liquefies and is easily separated from the uncombined nitrogen and hydrogen which is recycled through the heat-exchanger and catalyst chamber.

The heat exchanger and catalyst chamber are thermally coupled to the working fluid of a heat engine (for example a Rankine steam cycle or a Stirling hydrogen cycle) whereby mechanical or subsequently electrical power may be extracted. Since the whole system is virtually at constant pressure, the only compressor needed is a small one for initial charging and for making up gas leakage. One or two circulating pumps are required for the synthesis loop and the corradiation system.

The system described above and the various parameter values given represent what is believed to be achievable with present knowledge. It does not closely approach the ideal concept described in section 1, in as much as the two reactor temperatures are far from being equal and the mechanism of separation chosen is apparently well below maximum theoretical efficiency. There is, therefore, much room for development but even so it is felt that the presently described system may stand competitively in its own right.

3.   THE THERMOCHEMISTRY OF THE AMMONIA CYCLE

The reversible reaction under consideration is: $N_2 + 3H_2 = 2NH_3 + \triangle H$ in which $\triangle H$, the heat of formation is a function of temperature and pressure and has the values given in Table II (Mellor 1964. 1). These values appear in the temperature enthalpy diagram prepared by Revie (1975) , Fig. 2, as the horizontal distances between the enthalpy curves of ammonia and the nitrogen-hydrogen mixture. In Fig. 2 is traced the complete dissociation of ammonia at 300 atm pressure beginning from an ambient temperature of $25^{\circ}C$ and returning after dissociation to the same temperature. The total heat absorbed by 2 mols of dissociating ammonia is given as 31. 5 Kcal and it will be seen that this is independent of the temperature at which the actual dissociation reaction occurs.

The complete recombination of nitrogen and hydrogen is also traced on Fig. 2 and it will be seen that at $450^{\circ}C$ 2 mols of recombined ammonia will provide 25 Kcal of heat or 79% of the heat originally absorbed. The part of the trace showing the cooling of the ammonia follows the 50 atm line instead of the 300 atm line because recombination in the catalyst chamber is incomplete and 50 atm represents the partial pressure of the emergent ammonia. This pressure is such that upon cooling, ammonia condenses thus enabling it to be separated from the uncombined nitrogen and hydrogen.

The heating and cooling segments of the dissociating trace show varying slopes which indicate varying specific heats and this is relevant to the performance of the mirror

heat-exchanger as explained in section 5. A mismatch in specific heats is also evident on the recombination trace. This mismatch could be corrected by means of numerous heat leaks from the catalyst chamber to a succession of points along the heat exchanger membrane, but it would be more efficient to turn these leaks, effectively, into heat engines using the membrane as a sink. The section on heat engines suggests how this might be achieved.

The reversible reaction under study here always tends to an equilibrium condition, characterised by the percentage of ammonia in the mixture, which is a function of temperature and pressure. High pressures and low temperatures favour increased fractions of ammonia in the equilibrium condition. Fig. 3 shows the equilibrium conditions for a range of temperatures and pressures.

The rate of reaction depends on three factors: how close the mixture is to the equilibrium mixture for the particular temperature and pressure of the mixture; the temperature; and the presence of a catalyst. Catalysts, high temperatures, and large departures from equilibrium favour high reaction rates. It will be seen that at least one set of conflicting requirements emerges: for the production of ammonia a high temperature favours a fast reaction rate but a low temperature favours a higher equilibrium yield of ammonia. Clearly a compromise in temperature must be reached and in practice there will never be sufficient time to achieve complete equilibrium. Fig. 4 adapted from information about a commercially available catalyst and reaction chamber, shows a typical interrelationship between percentage ammonia, temperature and reaction rate.

The relationship between reaction rate and temperature is of vital importance to the operation of the focal absorber because if equilibrium should be attained instantaneously then there can be no difference between the mixture entering the mirror heat-exchanger and that leaving it. However, as indicated in section 4, work so far indicates that recombination without a catalyst will be comparatively slow so that the products of

dissociation upon leaving the catalyst chamber will remain practically constant in composition.

4. REACTION KINETICS

According to Temkin and Pyzhev (1940) the synthesis reaction rate is given by

$$w = k_2 \left[K_p \ P_{N_2} \left(\frac{P^3_{H_2}}{P^2_{NH_3}} \right)^{\propto} - \left(\frac{P^2_{NH_3}}{P^3_{H_2}} \right)^{1-\propto} \right] \qquad 3.1$$

in which k_p is the equilibrium constant.

Vancini (1971) gives evidence that this equation is also applicable to the de-composition of ammonia (strictly fugacities should replace the partial pressures employed in eqn. 3.1). Various authors (Vancini 1971) give values of $\propto$ ranging from .5 to .724. Taking $\propto = .5$ and known equilibrium constants, the expression in square brackets in eqn. 3.1 has been evaluated and is plotted in fig. 5. against m, the ammonia mole fraction. The two curves shown are for $700^{\circ}C$ and $450^{\circ}C$ and, in each case the total pressure is 300 atm.

The parameter k_2 varies with temperature T compared with base temperature T_o (Bridger, et al.) according to:

$$k_2 = k_{2(o)} \ \exp \left\{ - \left[\frac{\triangle E}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \right\} \qquad 3.2$$

where $\triangle E$, the activation energy, is 38 Kcal/mole.

It follows that the effect on k_2 in raising the temperature from $450^{\circ}C$ to $700^{\circ}C$ is an increase by 854.

Point A on curve (a) corresponds to common commercial synthesis practice whereas point B represents the dissociation of ammonia to approximately 50% by mass. The ratio of the two reaction rates when the effect of temperature is included is:

Rate B/Rate A = 569.

The effects of a change in rate w upon the quantity of catalyst required V and also the time t that the reactants are required to be in contact with the catalyst are explained

by Vancini (1971, 1). Thus to the first order of approximation:

$$t \propto V \propto 1/w$$

It follows that approximately 569 times less catalyst should be required for the conditions of point B compared to those of point A. Since commercial synthesis plants employ V of about 4 tonnes/MW$_{thermal}$ we might therefore expect approximately 7 gms/kw of similar catalyst to be required in the dissociation chamber.

As explained in section 8, the consideration of granule size may permit a reduction in this quantity to still lower values.

5. COUNTERFLOW HEAT EXCHANGER

An essential device upon which this system relies is the counter-flow heat exchanger. In principle it consists of two flow passages which are thermally joined side by side throughout their length by means of a common membrane of high thermal conductance. In contrast the thermal conductance longitudinally along the length of the membrane should be very low. Ideally heat should flow laterally from one flow passage through the membrane to the other flow passage with a negligible temperature difference. Thus by maintaining one end of the membrane and flow passages at a lower temperature say T_1 and the other end at a higher temperature T_2 it is possible to make a fluid at temperature T_1 enter one passage at the T_1 end of the heat exchanger, increase in temperature as it passes through the passage finally emerging at T_2, make it then enter the T_2 end of the other passage and finally emerge at T_1. This may be accomplished without any continuous supply of heat and is made possible by the simultaneous heating and cooling of elements of fluid in the passages either side of each element of the membrane. In similar fashion the (ideal) heat exchanger may be employed to lower the temperature of a fluid without the need for continuous refrigeration.

An essential factor in the ideal performance of a counterflow heat-exchanger is that the specific heats of the fluids in the two passages be identical for each temperature. When the same fluid flows in both there is no difficulty here. But when the fluids are different, e. g. ammonia in one passage and a mixture of nitrogen and hydrogen in the other, there may be a difference in specific heats which will result in either the heated fluid not reaching the maximum temperature or the cooled fluid not reaching the minimum temperature. The former is the case with ammonia and nitrogen/hydrogen in the focal heat exchanger because the average specific heat of ammonia is greater than the average specific heat of the nitrogen/hydrogen. Edwards (1975) has calculated the temperature profile along a focal heat exchanger, and his results are shown in Fig. 6. This particular heat exchanger consists essentially of two interwound helical passages the separating walls between the passages being 0.5 mm. Each passage has a cross section 1 mm x 10 mm the former being a measurement in the axial direction of the helix and the latter being in the radial direction. The outer diameter of the helices is 3 cm and the overall length 30 cm. Such a heat exchanger may be made by screw threading a rod which is then shrunk fitted into a tube.

The deficiency in exit temperature of the ammonia, evident in fig. 6, is made up by means of a small focal heater appended to the focal reaction chamber.

6.   OUTPUT THERMODYNAMICS

The maximum work that it is possible to extract thermodynamically from the system may be calculated by considering the heat flows and temperatures in the reaction chamber and synthesis heat exchanger. The latter must be included because the heat extracted from one side of the heat exchanger is less than that required by the other side due to the differing specific heats.

The thermodynamic process is most easily followed on a temperature-entropy (T-S) diagram of a circulating working fluid considered to be successively in perfect thermal contact with the reaction chamber and the deficit side of the heat exchanger (fig. 7(a)). Entropy is derived from $dS = dQ/T$ where dQ is the heat transferred to the working fluid

at temperature T. The T-S diagram of fig. 7b represents a modified Carnot cycle and has been derived in this way using the data of the synthesis path in fig. 2. but omitting the anomalous behaviour following the onset of condensation. Referring to fig. 7(b), stage 3 - 0 represents adiabatic compression, 0 - 1 isothermal expansion, 1 - 2 controlled expansion (during which 1.5 Kilo cals is extracted from the working fluid) and, finally, stage 2 - 3 isothermal compression during which heat is rejected to a sink.

The controlled expansion stage may be calculated assuming the difference in enthalpies between the fluids in the heat exchanger has the linear form $\triangle H = aT$. The maximum work obtainable from the cycle is then

$$W_{max} = a \, T_2 \ln\!\left(T_1/T_2\right) + (T_1 - T_2)(S_1 - S_3 - a)$$

The numerical values applicable to the case under consideration are

$$a = 1.5 \text{ Kcal}/420^{\circ}\text{K} = .00357$$

$$(S_1 - S_3) = \frac{\text{Heat of reaction}}{T_1} = .0346$$

Hence it follows that $W_{max} = 14.0 \text{ Kcal}/2 \text{ mol } NH_3$

Comparing this value with the minimum required solar energy of 31.5 Kcal/2 mol NH_3 the maximum possible overall thermodynamic efficiency is 44%. The choice of a suitable practical heat engine cycle is discussed in section B.

7. THE SEPARATION OF AMMONIA FROM THE SYNTHESIS PRODUCTS

The most practical method of separation appears to be by liquefaction. The ammonia in the emergent mixture will always at least partially liquefy provided a low enough temperature can be reached. As the mixture is cooled (in the counter-flow heat exchanger) it will reach the dew point determined by the partial pressure, and ammonia liquid will begin to condense. Provided there is no undue longitudinal mixing in the flow passage of the heat exchanger, this condensation will result in lowering the partial pressure of ammonia in the gas phase and thus will allow the progressive lowering of

the gas phase temperature as more and more of the ammonia liquefies and less is present as gas. Finally the liquid ammonia is separated from the gas phase in a standard liquid level controlled chamber.

The efficiency of separation can therefore be gauged by comparing the vapour pressure corresponding to the lowest temperature achieved in the cooling process with the original "emergent" partial pressure of ammonia. (Since the whole process is isobaric, the partial pressure of the residual ammonia after separation will be approximately independent of temperature and remain approximately equal to the ammonia vapour pressure in the separator). Fig. 8 shows the vapour pressure-temperature characteristic of ammonia and to one side is also shown the minimum synthesis pressures that are necessary in order to achieve emergent partial pressures equal to the vapour pressures indicated on the ordinate. Thus, for example, a system pressure of 300 atm can achieve a maximum ammonia partial pressure of 111 atm in the catalyst chamber emergent mixture. As this mixture is cooled, condensation will begin, according to the graph, at about 103°C. If the lowest temperature achieved were 20°C the residual partial pressure would be about 9 atm so the estimated efficiency of separation would be (111-9)/111 or about 92%. In practice separation efficiencies are less than values calculated in this way. Table III, giving maximum achievable recovery percentages, is reproduced from Comings (1956).

Table III

Pressure, atm	NH_3 in gas from Converter %	Condenser temp. $^{\circ}$C	Ammonia recovered %	Ammonia in gas from condenser %
1000	25	20	86	4.4
600	25	20	84	5.0
300	15	20	80	6.3
300	15	-5	91	2.8

Note: all % are molar

Commercial ammonia synthesis plants operating at around 150 atm usually employ refrigeration to about -30°C in order to induce more efficient separation and this means may be considered here also. Provided an efficient heat exchanger is employed which allows most of the heat extracted during cooling to be used in reheating the separated components, it appears that the refrigeration work required between 30°C and -40°C would be approximately 0.2 Kcal/2 mol NH_3. This is relatively small and thus may afford an advantage in raising the synthesis reactor temperature, a move which would improve the heat engine efficiency at the expense of reducing the equilibrium percentage of ammonia emerging from the reactor. However the simplest method of achieving satisfactory separation appears to be through the adoption of a sufficiently high pressure. Some of the consequences of using higher pressures will be discussed in later sections. One obvious consequence is indicated by the curves of fig. 3 which show that equilibrium conditions are slightly less favourable for the dissociation process going on in the mirror absorbers, so evidently a nice compromise is required between a number of contrary factors.

8. CATALYSTS

Iron is practically the only catalyst used commercially for ammonia production (Mellor 1964. 2. Bridger et al. 1970) presumably because it is abundant, inexpensive and effective. It is, however, rarely used without the addition of a few percent of a promoter, e.g. 0.8% potash and 2.5% alumina (Bridger 1970). A commonly used commercial catalyst (I. C. I. 35-4) consists essentially of porous granules about 1 cm in size which are generally supplied to the manufacturer as Fe_2O_3. The manufacturer reduces the material in his plant by passing hot hydrogen through it.

The life of a catalyst in commercial use is generally about five years limited by the action of impurities in the synthesis gas. In the present system catalyst lives of 10 to 20 years are expected* because the same gas will be continuously circulated.

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*Advice from chemical engineer operating ammonia synthesis plant.

Drawing parallels with commercial practice it is estimated that 4 tonnes of catalyst will be required in the synthesis plant per thermal MW.

It is expected that the same type of catalyst will be suitable in the dissociation process. However as previously mentioned, quantities are expected to be considerably smaller than for synthesis. One other favourable factor is that the granules may be much smaller than for synthesis since the small flows and quantities of catalyst will result in a greatly reduced pressure drop across the catalyst bed. According to Bridger (1970, 1972) , a reduction in granule size from 8 mm to 1 mm will increase reaction rate by a factor of five.

Other possible catalysts suitable for dissociation are ICI 27.1 and 47.1 both of which are composed of nickel oxide and alumina (in the unreduced state).

9. GAS FLOW RATES TO AND FROM THE MIRRORS

Assuming a maximum solar energy intensity of 1 kW/m^2 it may be established that a flow rate of .27 g/s of ammonia is required for each m^2 of mirror aperture. For our notional mirror of 10 m^2 aperture, the required flow can easily be supplied by means of a steel tube with 4 mm bore diameter. The friction power losses are negligible even for tube lengths of a few kilometers as is shown by the specific example set out in Table IV. The conclusions to be drawn from this Table are: w' is insignificant in comparison with the ideal system output previously stated as 14 kcal/2mol; and the tubing is quite small and amenable to routing by simply laying on the unprepared ground.

An important factor in the cost of the tubes is the quantity of material they contain. It is therefore instructive to compare the weight of the tube material with the weight of the pressed steel mirror which the tube serves. In both cases the material is steel although the qualities may differ slightly. Assuming that the mirror steel is 2 mm thick and the wall thickness of the tubing is a very conservative 1 mm it follows that 1 km of the tubing weighs about three quarters as much as a mirror. Furthermo)

dimensional analysis establishes that the pipe weight varies only as $p^{1/5}$ if the frictional losses are kept constant (and assuming f constant) i. e. even if the pressure were doubled the pipe weight would increase by a factor of only 1. 15.

The tubing may also serve as the means of supplying electric power and control signals to the mirror actuators. Thus, when allowance is made for the cost of the cable that would otherwise be essential to provide, the cost of the tubing may be expected to be a comparatively inexpensive item.

Table IV relates to ammonia only. Information is also required about the other gas components viz. nitrogen and hydrogen. The friction loss is expected to be greater for these gases by a factor of about 5 because of their lower density. Even so the total friction loss per kilometer of dual tubing will be only a fraction of a percent of the useful output of the system.

10. THE RELATION BETWEEN SYSTEM PRESSURE AND THE SIZE OF CONNECTING PIPES

The effect of system pressure on the size of tubing may be explored to an approximate degree by assuming that (a) perfect gas laws hold, (b) the Darcy formula (Lewitt, 1947) for friction pressure drop holds true i. e. $P_f = f \left(\frac{1}{2} \rho V^2\right) 1/d$, (c) the friction factor f in the Darcy formula is independent of Reynolds number and tube diameter (i. e. tube roughness scales with diameter), (d) the tube wall thickness t is kept proportional to tube internal diameter d and system pressure P, i. e. constant average stress in tube wall, and (e) the mass of the tube M is proportional to td.

By adopting these assumptions and considering mass flow, tube length and friction power loss to be constant, analysis reveals the following relationships:

$$d \ \infty \ P^{-2/5}$$
$$M \ \infty \ P^{1/5}$$
$$t \ \infty \ P^{3/5}$$

Fig. 9 is a graph of these relationships based on a system pressure P = 300 atm for which d = .4 cm, t = 0. 05 cm, and M = 1, which implies a maximum allowable average stress in the tube wall of about 17. 5 K p. s. i.

The chief significance of these relationships is that an increase in P will lead to only a very slow increase in the mass of steel required for the tubes.

However the reverse is not necessarily true for a decrease in P because this leads to a reduction in t to impracticably small sizes. If we consider it impractical to reduce t below .05 cms then the above relationships are only valid down to P = 300 atm, and below this pressure assumption (d) is no longer valid and we have

$$M \propto P^{-2/5}$$

This relationship also graphed in fig. 9, is clearly unfavourable towards low pressures.

An improvement in M may always be achieved by coalescing the flows of a number of mirrors into a common trunk line. In order to keep the friction energy loss a constant proportion of the chemical energy transferred, this procedure must not affect the friction pressure drop. Consequently we find the following relationships, derived directly from the Darcy equation:

$$d \propto n^{2/5}$$
$$M_n \propto n^{-3/5} t$$

where n is the number of tubes commoned and M_n is the mass of the trunk line normalised with respect to the mass of the n tubes it replaces (or the mass of trunk per unit of chemical energy transferred).

In the high pressure regime, where $t \propto d$, (above R, fig. 9) we therefore have

$$M_n \propto n^{-1/5}$$

which represents a very slow gain with increasing n. On the other hand in the low pressure regime, when t = .05 cm, we have $M_n \propto n^{-3/5}$ which provides considerably greater incentive to coalesce the flows of as many mirrors as possible. However in so doing another limit may be reached — that of the ratio d/t which will depend on either the strength of the tube at the system pressure or upon other considerations of a practical nature. Once a limit is placed on the magnitude of this ratio (e.g. $d/t \leq 200$) we find M_n reverting to the less dependent function of n viz. $M_n \propto n^{-1/5}$.

The conclusions of this study are therefore:

(a)   the mass of tubes connected directly to the mirrors is at a minimum around

300 atm. Below this pressure there is a rapid increase in mass but above it only a slow

increase e. g. from 300 atm to 1000 atm an increase in mass of only 27%.

(b)   for pressures below 300 atm there is a strong incentive, from the point of view

of reducing mass, to join mirror flows together in a common pipe-line of increasing

diameter until the ratio d/t reaches a limit imposed by the consideration of either pressure

rating or practicalities in manufacture and handling.

(c)   both in the case of (a) and of (b) once the d/t limit is reached, there is only a weak

incentive to coalesce tubes or for further coalescence of trunk lines.

(d)   by increasing pressure - at least up to 300 atm - one may achieve a marked

reduction in the volume occupied by the tubes or pipes.

All these factors are relevant to the selection of a system configuration and to

other cost factors such as the cost of installation and transportation of the tubes and pipes.

For example 6 mm   o. d.   tubes may be simply reeled out onto the ground and connected

with standard hydraulic screw couplings whereas larger diameter pipes may require level

foundations and more frequent and costly joints.

11.   THE RELATION BETWEEN SYSTEM PRESSURE AND THE SIZE OF
        HEAT EXCHANGERS

The effect of increasing pressure on the size and cost of heat exchangers in ammonia

synthesis plant has been noted by Brown (1974) who states that an increase from 240 atm

to 330 atm results in a reduction of 40% in heat exchanger surface area (the thermal duty

remaining constant) and a reduction in cost of 10% to 25%.

Using two concentric tubes as a model heat exchanger, the effect may be simply

explored assuming the following:

(a)   frictional pressure drop $\propto \rho v^2 l/d$

(b)   friction power loss maintained constant;

(c)   fluid boundary layer heat transfer coefficient $h \propto d^{-1.8}$;

(d)   temperature drop across fluid boundary layer $\triangle T$ maintained independent

of pressure;

(e)   total heat transferred in heat exchanger H and mass flow m maintained

constant.

Assumption (a) is derived from the   Darcy   equation with f constant. The

equation is applicable to compressible fluids provided the ratio (friction pressure drop)/

(system pressure) is small.

Assumption (b), taken with constant mass flow implies constant frictional pressure

drop.

Assumption (c) is derived from the standard heat transfer formula (e.g. H.

Schenck 1960)

$$Nu = .023 \, (Re)^{.8} \, (Pr)^{n}$$

in which Nu, Re and Pr are the Nusselt, Reynolds and Prandtl numbers respectively and

n is between 0.3 and 0.4.

From (a) and (b) one may derive

$$d^{5} \propto 1 \, P^{-2} \quad \text{where} \quad d = \text{heat exchanger tube diameter}$$
$$1 = \text{tube length}$$
$$P = \text{system pressure.}$$

Combining this with (c) yields

$$h \propto 1^{-.36} \, P^{.72}$$

The calculation of total heat transferred H, with $\triangle T$ constant, gives

$$H \propto d^{4.2} \, P^{2}$$

Thus, with H constant, we have:

$$d \propto P^{-.48}$$
$$1 \propto P^{-.38}$$
$$h \propto P^{.86}$$

The material weight of the heat exchanger M is proportional to $P \, d^{2} \, 1$ which, with

appropriate substitutions, gives:

$$M \propto P^{-.33}$$

This relationship reveals a six-fold reduction in mass resulting from an increase in pressure from one atmosphere to 300 atm.

The factor is much larger if limits on tube wall thinness due to practical considerations are considered as they were in section 10.

12. THE RELATION BETWEEN SYSTEM PRESSURE, MIRROR SIZE AND FOCAL ABSORBER PARAMETERS

The focal reaction chamber may be considered as one side of a heat exchanger. Therefore the analysis given in section 11 holds for it also.

Consider the focal absorber as a cylindrical cavity having walls constructed of layers of tubes, (fig. 10). The shape of this cavity may well be determined by both optical considerations and the heat flux into the wall of the cavity, which two factors are independent of mirror diameter D_m.

We might initially assume then that the shape of the cavity should be independent of mirror diameter D_m. Therefore, during a change of scale, the volume of the cavity will be proportional to $D_m{}^3$. Of interest is the fraction of this volume that must be taken up by the tubes in the cavity wall and the variation of this fraction with system pressure and mirror diameter.

The analysis of section 11, if repeated with the inclusion of m, the mass flow through the heat exchanger or focal absorber gives:

$$d \propto P^{-.48} \, m^{0.52}$$
$$l \propto P^{-.38} \, m^{-0.62}$$
$$h \propto P^{.86} \, m^{-0.14}$$

The mass of the focal absorber tubes is then

$$M \propto P^{-.33} \, m^{1.67}$$

and volume $d^2 l \propto P^{-1.33} \, m^{1.67}$

In this analysis both the friction power loss and the heat transferred into the focal absorber tubes are made proportional to m while ΔT is kept constant.

These results for the mass and volume of the focal absorber tubes clearly favour the use of a high system pressure.

Returning to the question of the fraction: $\dfrac{\text{volume of tubes in absorber}}{\text{volume of cavity}}$ $(= S)$

we note that, substituting $D_m{}^2$ for m,

$$\text{tube volume} \propto P^{-1.33} D_m{}^{3.34}$$

Hence the required fraction is:

$$S \propto P^{-1.33} D_m{}^{0.34}$$

from which it will be evident that a low system pressure and large mirror diameter may lead to awkwardly large values of this fraction. If now we place a practical limit on the size of S, e.g. 0.2, we may determine how the mirror diameter can be varied to compensate for the deleterious effect of a further reduction in system pressure. Hence by making S constant we have:

$$D_m \propto P^4$$

a somewhat surprising result perhaps for it shows that to compensate for a reduction in P, a comparatively large reduction in mirror diameter is required, so large in fact as to rule out the practical possibility of compensation at all.

Work so far with the present system at $P = 300$ atm indicates that $S = 0.2$ can be comfortably achieved for a mirror of 4 m diameter and a cavity 20 cm diameter x 5 cm. lined with a single layer of tubing. The estimated friction pressure drop is 3.5 atm. The relationships derived above indicate that this simple design type cannot be used for pressures much below 300 atm but that pressures higher than this figure will allow even simpler designs.

13. MATERIALS COMPATIBLE WITH AMMONIA

A wide range of experience in the ammonia synthesis industry indicates that there is no difficulty in using carbon steel for all parts in contact with ammonia. The materials to be particularly avoided are copper and brass. One alloy which is suitable for ammonia, nitrogen and hydrogen at the high temperatures envisaged contains 32% Ni and 21% Cr (incoloy 800).

14.   THE HEAT ENGINE

The obvious cycle to investigate first is the Rankine cycle, e.g. water-steam since it offers the chance of easy isothermal extraction of heat from the catalyst bed. However it may be difficult to provide superheating which is necessary if the engine cannot stand a two-phase mixture for its working fluid. There is also the problem of feed water heating. In conventional power stations the flue gas provides a ready source at virtually any desired temperature for heating the feed water economically. This source is not however available in the present system and it is difficult to see an alternative method of heating the feed water without resorting to the degradation of a high temperature source. There is also the problem of the discrepancy in specific heats of the fluids in the two passages of the counterflow heat exchanger mentioned previously and a problem whose solution should, if possible, be included in the overall solution. For these reasons the present author is inclined to discard the Rankine cycle in favour of a modified Stirling cycle which will now be described.

Ideally the Stirling Cycle is as efficient as the Carnot cycle. Essentially the working fluid is heated at constant volume, expanded isothermally, cooled (again at constant volume), isothermally compressed and so on. The heating and cooling is achieved by means of a counterflow heat exchanger in the continuous flow version of the cycle, or else the heat is stored in the cooling phase and transferred back in the heating phase in the reciprocating version using a device that is essentially a counterflow heat exchanger with built-in storage (usually called a "regenerator").

The isothermal expansion phase of the Stirling Cycle matches the isothermal generation of heat in the synthesis reaction chamber and the heating and cooling phases could at least partially be matched to the heating and cooling of the reactants as they circulate between reaction chamber and separator. This could be achieved by integrating the synthesis heat exchanger and engine working fluid heat exchanger, the advantage

being that the anomalies caused by the mismatch in specific heats referred to in section 5 could then be catered for. This might be accomplished, for example, by slightly modifying the heating phases of the Stirling Cycle in order to effectively reduce its specific heat and so compensate for the excessive specific heat of the nitrogen-hydrogen mixture being heated prior to entry into the reaction chamber. The specific heat of the working fluid would be effectively reduced if, while undergoing heating, it were slightly compressed (i. e. its volume diminished).

Further analysis of such an engine has not yet been attempted. In any case the ideal performance will never be achieved but one might hope that perhaps 6 Kcals may ultimately be salvaged from the ideally available 14 (after allowing for other system losses as well). Such a performance would be quite creditable as it would represent an overall efficiency of 20 percent.

15. MIRROR ABSORBER THEORY

According to Whyte (1974) one of the best mirror-absorber combinations is a hemispherical absorber capped with an insulating disc combined with a mirror whose aperture radius is twice the focal length. The radius of the absorber should be 0.02 to 0.05 times the focal length. The radiation loss of such a combination, considering a black absorber and an operating temperature of $700^{\circ}C$ is 0.8% to 12% of the collected energy.

Since virtually 100% of the energy entering the mirror aperture reaches the absorber (assuming no reflection loss) the net absorption efficiency of this combination is between 99% and 88%.

The same author gives data for disc absorbers which indicate that a cylindrical cavity with aperture radius between .05 and .1 times the focal length when combined with the same mirror will give maximum net absorption efficiencies of 85% to 82%. Some improvement on this can be gained by reducing the mirror radius to 1.5 focal lengths and combining this with a cavity of aperture radius .05 focal length. The net absorption efficiency in this case is 96%. No preferred absorber configuration has emerged from

studies so far although it is clear that simple cavity designs are practicable.

16.   MIRRORS

The mirrors are paraboloidal in shape with a peripheral flange and a central location hole. According to engineers at a motor factory (G.M.H. 1974) these could be pressed economically and accurately although specially large presses would probably have to be developed to accommodate the notional size of 10 m^2. The determination of the optimum size awaits further studies of the various factors involved but it is believed that an overriding consideration will be compatibility with available modes of transport.

A suitable reflective surface has not yet been developed or selected. It is hoped that the versatility of the control system as described in a later section will enable protective manoeuvres to be accomplished in inclement weather and so help to prolong the life of the reflective surface.

The accuracy of the surface, defined by the angular deviation of the normal of an element from the focal direction, should be about 5 to 20 mrads depending on the absorber size and, according to the motor engineers, this can be achieved fairly easily.

17.   SUN-SENSOR

To enable automatic tracking of the sun it is necessary to have mounted on the mirror a sun sensor from which tracking errors may be derived. An inexpensive and accurate device has been developed which contains no lenses, mirrors (other than a portion of the main mirror), or windows. It consists simply of three photo-sensitive elements which are normally located in the penumbra of a shadow disc. The error information is derived from the gradation of intensity across the penumbra.

18.   FOCAL ABSORBER ASSEMBLY

The hemispherical absorber already referred to may be   made from a number of hollow fins which form cavities into which the radiation is directed. The cavities are necessary in order to reduce the radiation intensity on the absorber

surface to an acceptable level and it is thought that the fin structure may enable a labyrinth of narrow, and therefore pressure resistant, channels to be press-formed into complementary pairs of thin steel sheets which are subsequently resistance welded together along the seams between the channels.

The mirror heat exchanger may be of the form described in section 5 or it may consist simply of three concentric tubes the middle one having a thin wall (the "membrane") and the other two a thick wall for withstanding the system pressure and to serve as a support for the absorber mounted on it. In this design there would be two spiral elements between the tubes serving to elongate the flow paths.

The absorber, heat exchanger and sun-sensor can be designed to form a composite structure as depicted in fig. 7. The insulating cap on the absorber also forms the shadow disc of the sensor whose photo detectors are mounted on the heat exchanger in such a position as to be self-compensating with regard to errors in the position of the absorber. The temperature-sensitive automatic valve has been omitted from fig. 7.

19.   MIRROR SUPPORT STRUCTURE

A suitable mounting arrangement has not yet been decided upon. However it is thought that mounting in pairs may be an advantage since the mirrors could then be brought together to provide mutual protection in adverse environmental conditions.

Rotating joints in the high pressure gas lines are not necessary since flexible couplings can easily be formed by coiling the tubing. If thought necessary, the diameter of the tubing may be reduced over short lengths in order to improve the flexibility.

20.   ACTUATORS

At least two actuators are necessary in order to accommodate the two degrees of freedom required to point the mirror. It is thought that printed motors offer the most promise but there is the problem of providing a high ratio reduction drive for them.

The possibility of using pneumatic actuators based on the readily available supply of high pressure gas has not been ruled out.

21. MIRROR CONTROL

Methods generally used to control mirrors employ a separate automatic sun tracking unit for each mirror (Trombe et al, 1973, Houston 1974). The present system differs in that all the mirrors share a common computer-based control unit. Thus the sun sensor on each mirror is periodically sampled and the speeds of the actuators of each mirror periodically adjusted according to decisions made by the computer. The advantages of this method have been described by Carden (1974.2). Briefly they are related to the ability of the computer to provide more comprehensive control functions and the ability of the computer to monitor performance and diagnose faults. The control functions not usually provided by individual automatic control units are: the mirrors may track the path of the sun when the sun is hidden by cloud; the position of sun-rise may be anticipated; protective manoeuvres may be implemented in potentially damaging weather conditions; other manoeuvres may be performed which are designed to provide performance or diagnostic data. Important savings in cost are believed to arise from: more efficient maintenance; less weather damage; the minimising of components on each mirror; more efficient tracking especially during intermittent cloud cover; and a number of less significant factors which arise from the enhanced versatility of the method.

22. INSOLATION AND SITING

In order to proceed with a discussion of costs it is necessary to assume values of solar radiation throughout a period of time certainly not less than a year. It is also useful to have a site in mind so that transport and power distribution costs may be assigned. Unfortunately there is a dearth of information about the intensity of direct radiation for all areas of interest in Australia. Estimates may be made from sunshine hours records and observations of cloud cover. In some instances calculations may be made from continuous measurements of global and diffuse radiation on a horizontal surface but these calculations tend to be inaccurate when the sun is at a low elevation e. g. early morning, late afternoon and winter. Nevertheless this last method

is likely to be more reliable than the method based on cloud cover observations.

Carden (1974. 2) reports that calculations based on radiation measurements taken at

Griffith in western N. S. W. give an annual average intensity of direct radiation for the

years 1972 and 1973 of 6.17kw.hrs/m^2 day. This figure is not inconsistent with the 70%

of maximum sunlight hours given by the "World Survey of Climatology" (1971). Hence

this figure will be adopted as being representative of western N. S. W., northern S. A.,

Central Australia and the mid-west coast of W. A.

23. COST CONSTRAINTS FOR COLLECTION AND CORRADIATION

Evidently the salient difference between a conventional fossil fuelled power

plant and a solar power plant is that the former uses a costly fuel whereas the latter

uses a costly collection and corradiation system. For the latter plant to be competitive

with the former, it is therefore necessary for the annual running costs and capital

service charges of the collection and corradiation system to be about equal to the annual

fuel bill of the conventional plant. On the basis of costs and charges being 15 percent

of capital cost, an average solar derived heat output (after making an allowance for

losses) of 3.8 kW/m^2. day. and a fuel oil price of *$10/bbl, the allowable capital cost

of the collection and corradiation system per square metre of collector area is $50.

This is a difficult constraint to meet and is the main reason why pressed steel mirrors

are being advocated here.

24. MIRROR COSTS

According to the motor body engineers interviewed by the author (G. M. H. 1974)

mirrors 2 m in diameter could be produced in quantity using existing presses for a

cost of $6/m^2 (early 1974). The mirrors would be made from 1.5 mm thick steel and

the estimate includes polishing the reflector side and priming the back side. The cost

of applying the reflecting coating is not included. This figure is a very encouraging

beginning and leaves a fair margin for the remaining cost factors which have to be

taken into account.

*U. S. currency used throughout this paper

25.   AMMONIA SYNTHESIS COSTS

The author's interviews with ammonia manufacturers indicate that the 1972 cost of a 1,200 tonne/day plant using natural gas feedstock is approximately $35M. The synthesis component of this plant defined as the catalyst reactor and heat exchanger and excluding compressors and refrigerator represents approximately 5 percent of total plant capital. The synthesis components represent approximately 50 percent of the combined cost of synthesis components and compressor. Becker et al (1971) give the total plant cost as approximately $28M (1971) and the cost of the synthesiser and compressor as $3.7M. Mundo (1974) gives the (1972) component of production cost attributable to capital charges of 24 percent as $20/t. which projects a plant capital of $35M. All these figures indicate that the 1972 cost of a 1200 t/d synthesiser is close to $1.75 M. Now a 1200 t/d ammonia output can easily be equated to a thermal output of 43 MW or an electrical output of perhaps 13 MW. We therefore arrive at an estimate of approximately $135/kW for the ammonia synthesis component of the present solar power system. This estimate is based on costs of existing plant whose power capacity is two orders of magnitude smaller than what is required. Some further reduction in cost might therefore be expected eventually resulting from an economy of scale.

However, even as it stands, this figure compares favourably with the capital cost of a nuclear plant given as $400/kW (Zener 1973). The synthesiser can in fact be roughly equated, in cost and function, to the steam generator of a conventional power plant including handling equipment for fuel, ash and flue gas.

26.   THE POSSIBILITY OF A SOLAR BASED FERTILIZER PLANT

Ammonia is the feedstock for the production of nitrogenous fertilizer such as ammonium nitrate. In principle some ammonia is oxidised to form nitrogen peroxide which when further reacted with water and more ammonia yields ammonium nitrate. Often liquid or hydrous ammonia is used directly as a fertilizer. Advantage

could be taken in the present system of the fact that an ammonia synthesis plant already exists so that it might be economical to arrange for a net output of ammonia instead of electrical energy. If this were done almost the entire power output would be required for the electrolysis of water to produce hydrogen. A small proportion would be needed to liquefy air in order to separate nitrogen. It will be noted in passing that oxygen is a significant by-product of both of these processes and should be considered in an economic assessment.

In order to arrive at a cost of producing ammonia in this way it is instructive to examine the production cost components of conventional plant. Mundo (1974) shows that a large proportion of the present production cost is attributable to the cost of feedstock e.g. natural gas and it is evident that this proportion might be 90 percent nowadays. The purpose of the feedstock is of course simply to dissociate water which is a very energy intensive process. Hence it can be said that most of the production cost is the cost of energy involved. Therefore if the energy were supplied as electricity derived from burning the feedstock in a powerplant, the cost of ammonia would rise by at least a factor of three resulting from the inefficiency of energy conversion of heat to electricity. It follows that, given that the present solar energy system yields electricity at a cost equal to conventional plant, the production cost of ammonia produced by it would be somewhat higher than that of conventionally produced ammonia despite the fact that the component due to servicing capital would be undoubtedly lower.

Roughly similar comments apply to a version of the present system designed to produce only hydrogen.

27.   STORAGE AND TRANSMISSION

Storage of energy, for example, for night-time use, would involve storage of nitrogen and hydrogen and the provision of adequate space for storing the ammonia resulting from power production. The present study has not been extended yet to include these factors.

The transmission of energy over long distances by piping ammonia in one direction and a nitrogen hydrogen mixture in the other is unfavourable when compared to piping hydrogen alone. However pipelines may be an economical means of storage so that economical transmission might arise incidentally from this.

28. COMPARISON WITH POWER TOWER

Since the power tower has been favourably regarded in comparative studies (Honeywell 1974) it is a useful yardstick against which the possible improvements of the present system may be gauged. There follows a list of five factors regarded here as improvements.

(1) The present system uses paraboloidal mirrors whereas the power tower uses flat mirrors. The latter are inherently unrigid whereas the former have in comparison a greatly enhanced natural rigidity. Flat mirrors need a rigid supporting structure, e.g. a dimpled pressed steel frame comparable in itself in cost to a paraboloid. Flat mirrors a¹ likely then to be at least twice the cost of paraboloidal mirrors and this is a very important consideration in view of the need to keep costs down in this area (see section on costs). It turns out upon analysis that equal mirror distortions in both cases have approximately equal effects.

(2) The tracking problem is much simpler in the present system than in the power-tower. In the present system tracking consists simply of facing the sun and can be achieved through the use of a simple on-board sun sensor. On the other hand the power-tower mirrors must be made to face half way between the sun and the common focus. This usually requires a sun sensor firmly attached to the ground in front of the mirror and accurately aligned with the common focus (although Carden[*] has described a method not requiring this). In order to achieve the same degree of focus the pointing accuracy of the power-tower must be twice that of the present system.

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* 1974. 2

(3)   The present system does not require a high tower.

(4)   For a power-tower to operate at maximum efficiency the mirrors must be carefully located in relation to one another in order to fully utilize the limited area of effectiveness around the tower. This means careful site selection and surveying and each power tower complex is predetermined in size by the height of the tower. The present system on the other hand is much more flexible: suitable land areas for placing the mirrors may be of any shape and any one complex may be easily extended or combined with a neighbouring complex. No precise interrelationship of position is required of the mirrors of the present system.

(5)   For the power-tower, the effective aperture area of the collectors (mirrors) is generally less than their actual aperture because they generally do not face the sun squarely. On the other hand with the present system the effective aperture is always equal to the actual aperture.

29.   CONCLUSION

The foregoing has provided basic information for further studies of a system which on the surface appears to have a number of advantages over alternatives. There is scope for a great deal of further research. For example, according to an observation of Baur (1901) it may be possible to construct a fuel cell which converts nitrogen and hydrogen to ammonia at ambient temperature and generates electricity. Such a development would of course revolutionise the system proposed here.

The most encouraging aspect of the study so far is that the costs do not appear prohibitive. This is due, to a large extent, to the avoidance of extremes. No exotic materials are required - simply iron and steel, no extreme operating conditions are called for - temperatures are not unreasonably high and the pressure is well within commercial experience, the working fluid is made from abundant components and is comparatively free from hazards. In short, there is every reason for further study and development.

ACKNOWLEDGEMENTS

TABLE II

Heat of Formation of Ammonia kcal/mol

Temperature $^{\circ}$C	0	300	500	600	700
Pressure atm					
1	10.63*	11.99	12.66	12.89	13.04
100	–	12.43	12.92	–	13.23
300	–	13.32	13.45	–	13.61
600	–	14.66	14.24	–	14.19

* Ammonia in the gaseous phase

TABLE IV

ρ	density	0.595 g/cm^3	300 atm , 50°C, From Mellor (1964.3)
μ	viscosity	1427 x 10^{-6} poise	100°F, 4000 p.s.i. Mellor (1964.4)
d	internal tube diameter	0.4 cm	
l	tube length	1000 m	
m'	mass flow rate	2.7 g/s	
V	mean fluid velocity	36.1	
R	Reynolds Number	6,022	
r	tube roughness	0.001	
f	friction factor	0.03	
P_f	friction pressure drop	2.9 atm	$P_f = f(\tfrac{1}{2}\rho V^2)l/d$
P	system pressure	300 atm	
P_f/P		0.0095	
w'	friction work for 2 mols of ammonia circulated	0.010 kcal/km	

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Fig. 1

Schematic diagram of present system.

1. Sun's rays.

2. One of many paraboloidal mirrors.

3. Focal Absorber.

4. Mirror unit counter-flow heat-exchanger.

5. Gas carrying tubes from other mirror units.

6. Central plant catalytic synthesiser.

7. Central plant counter-flow heat-exchanger.

8. Central plant ammonia separator.

9. Gas circulating pump for synthesis loop.

10. System compressor.

11. Gas circulating pump for corradiation.

12. Gas corradiation tubing.

13. Heat output to engine.

Fig. 2

Basic temperature-enthalpy diagram. On the left is the temperature-enthalpy diagram of ammonia and on the right is shown the (idealised) temperature-enthalpy diagram of the stoichiometric mixture of nitrogen and hydrogen. The horizontal separation of the two sets of curves represents the heat of reaction which is a function of both temperature and pressure. The shaded area represents the region of two phase equilibrium for ammonia. The dashed lines show the track taken during dissociation (commencing from the left and for a pressure of 300 atm) and during synthesis (commencing from the right and for an ammonia partial pressure of about 50 atm). The diagram has been constructed by Revie (1975) from available data on enthalpy, heats of reaction and specific heats.

Fig. 3

Equilibrium percentages of ammonia in stoichiometric mixtures of nitrogen, hydrogen and ammonia at various temperatures and pressures.

Fig. 4

The rate of the ammonia synthesis reaction for various temperatures and percentages of ammonia for a pressure of 220 atm. The curves shown are constant rate curves and the numbers are relative reaction rates.

Fig. 5

Reaction rate parameter vs ammonia fraction. The parameter excludes temperature effects.

The ammonia fraction scale is given both as mole fraction m and fraction by weight f.

(a) curve based on equilibrium point appropriate for 450°C and 300 atm;

(b) curve based on equilibrium point appropriate for 700°C and 300 atm.

A end point for typical synthesis process.

B end point for a typical dissociation process.

Fig. 6

Temperature profile along a helical dissociation heat exchanger assuming pure ammonia incoming and pure nitrogen and hydrogen outgoing.

The heating side ranges from 25°C to 522°C and the cooling side from 700°C to 27°C. The difference between these two ranges is determined only by the differences in specific heat between ammonia and its constituent elements.

Mass flow rate 5 gm/sec.

Smooth surfaces assumed.

Total pressure drop approximately 2 atm.

<u>Fig. 7</u> (a)

The thermal interconnections between the synthesis loop and the working fluid of a modified Carnot engine. The figures are the number of Kcal transferred per 2 moles of NH_3 synthesised. The fig. of 56 is on the basis of 20% of the incoming N_2 and H_2 to the reaction chamber being converted to NH_3).

<u>Fig. 7</u> (b)

Temperature entropy diagrams for modified Carnot cycle.

0 - 1	isothermal expansion
1 - 2	controlled expansion
2 - 3	isothermal compression
3 - 0	adiabatic compression

fig. 7(a)

4 - 5	heat exchanger (heating side)
5 - 6	synthesis reactor
6 - 7	heat exchanger (cooling side)

<u>Fig. 8</u>

Vapour pressure-temperature diagram for ammonia. The bar graph on the right shows the partial pressure P_p of the ammonia which emerges from the catalytic synthesiser (under chemical equilibrium conditions) for the corresponding system pressures P indicated and at 450°C. P_p is drawn to the same scale as the partial pressures.

<u>Fig. 9</u>

Curves showing the relation between system pressure P and the mass M of the pipes connected to the mirrors (for a fixed length and a fixed number of mirrors). All curves are on the basis of internal diameter $d \propto P^{-.4}$.

(a)   wall thickness of pipe t is the minimum required for strength;

(b)   ratio of d/t limited to 200.

(c)   t limited to 0.05 cms.   All curves are based on the point R at which M = 1,

        P = 300, d = 0.4 cms and t = .05 cms.

Fig. 10

        Simple cylindrical focal cavity absorber.

(a)   radiation reflected from paraboloidal mirror

(b)   cavity volume

(c)   volume occupied by reactor tubes.

Fig. 11

        Diagram showing the absorber heat-exchanger sensor mirror assembly.

        1   focal absorber

        2   counter-flow heat exchanger

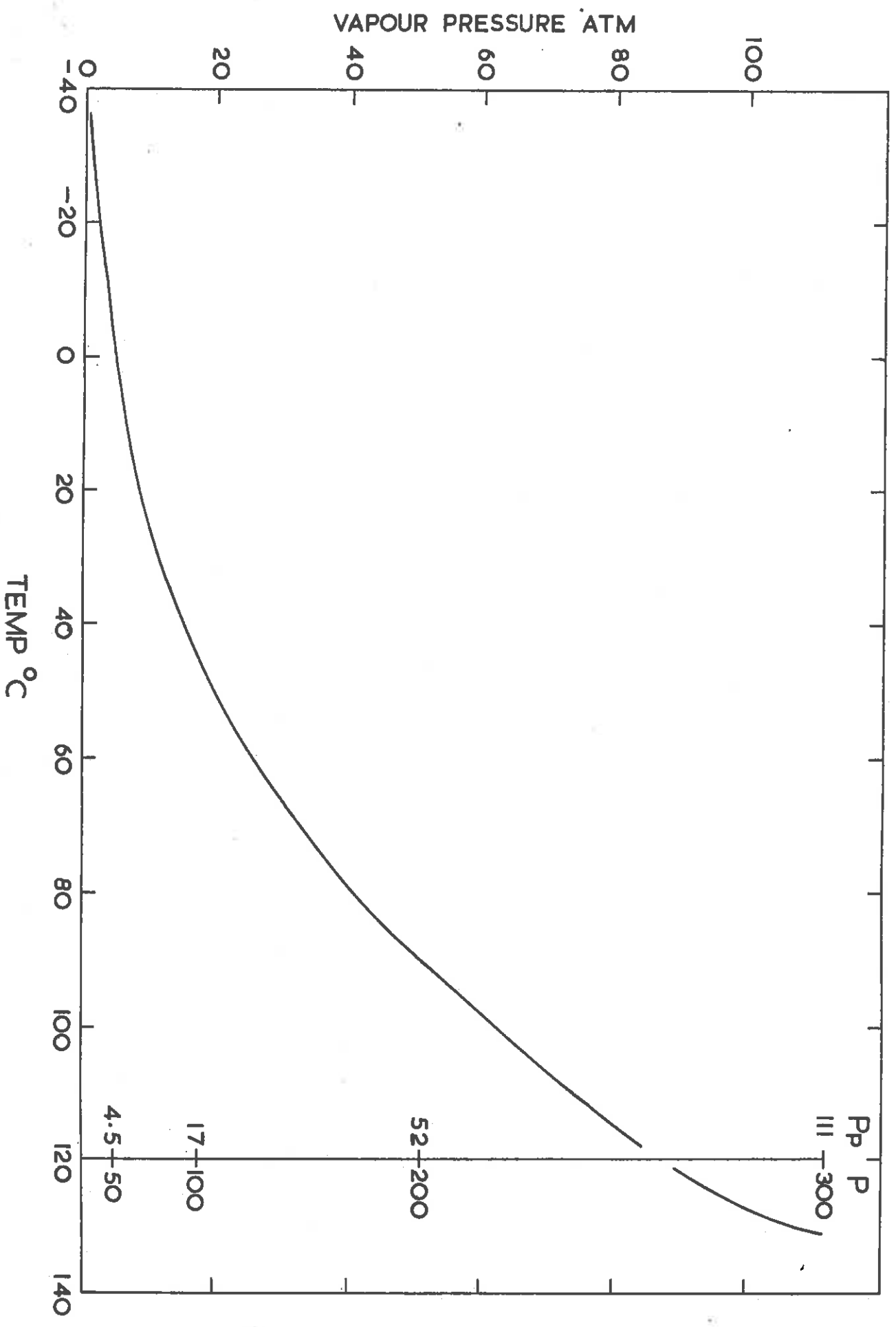   3   paraboloidal mirror

        4   sun-sensor.
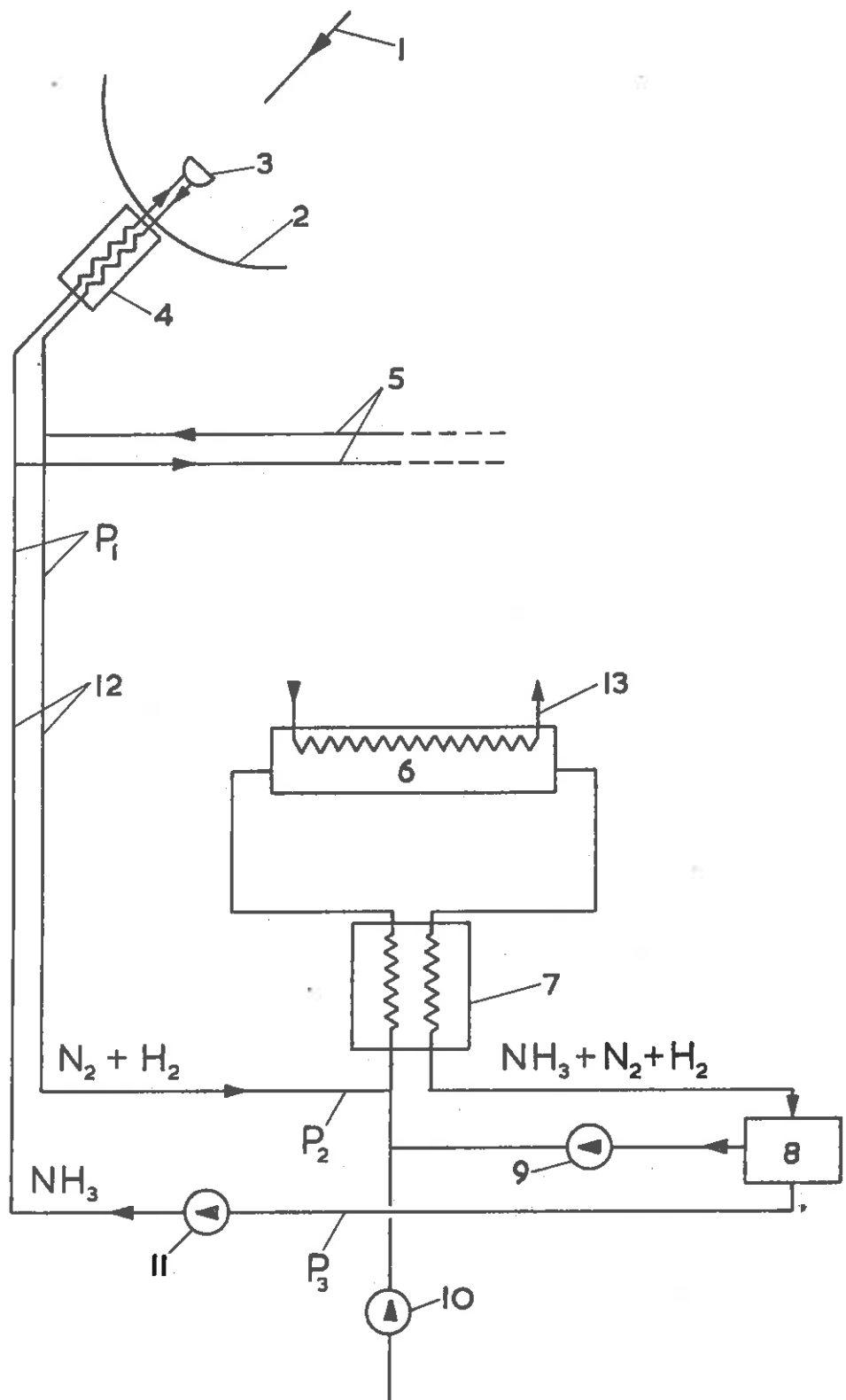
FIG I
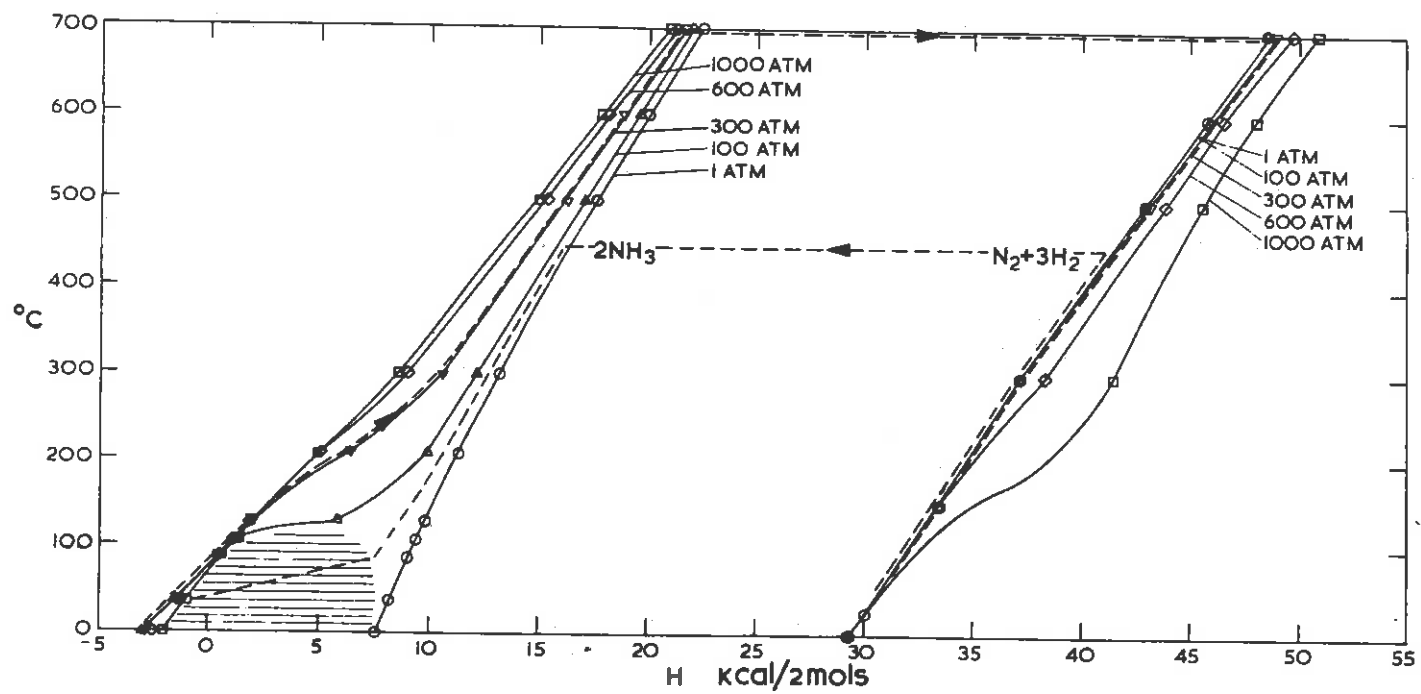
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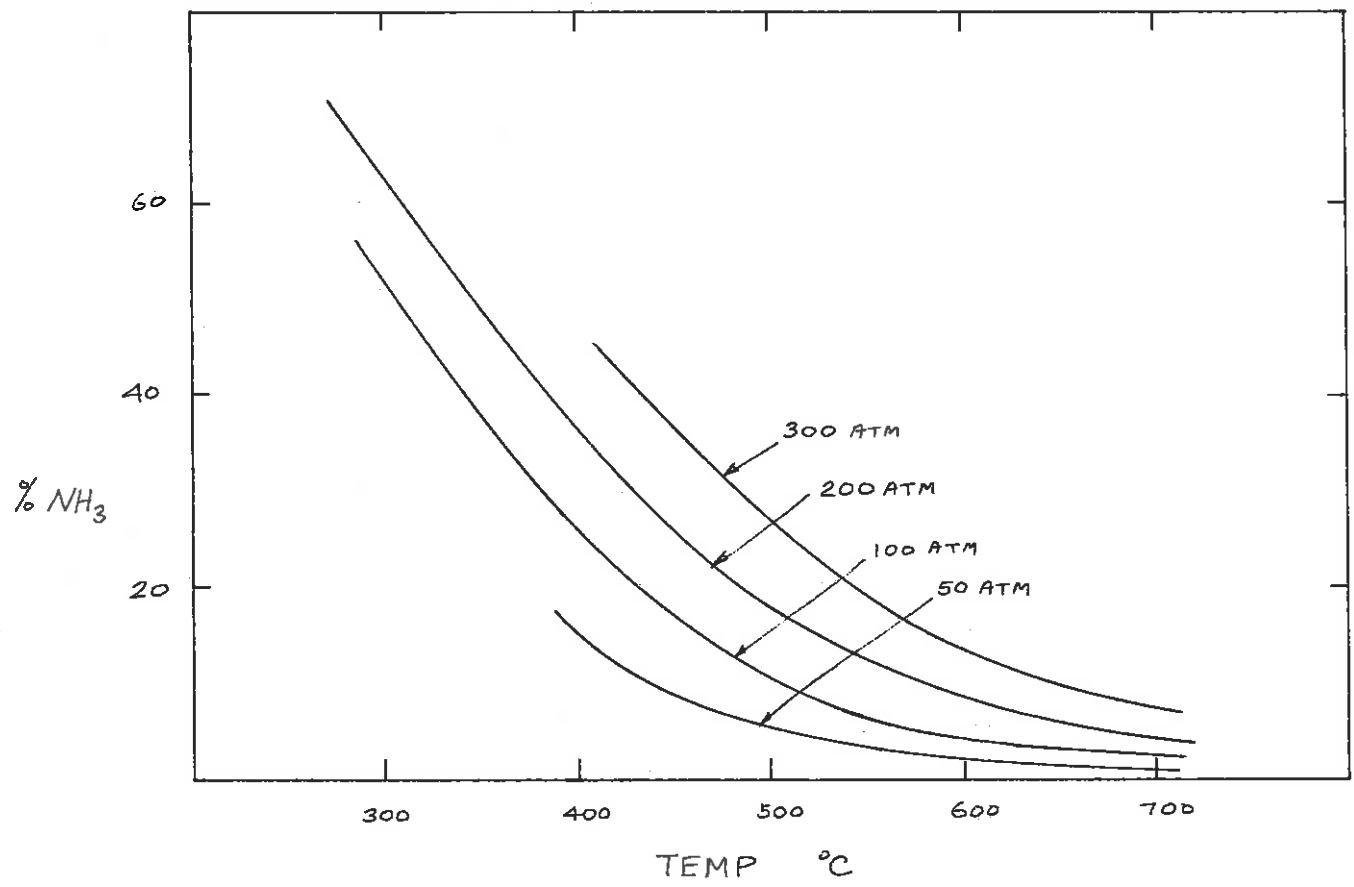
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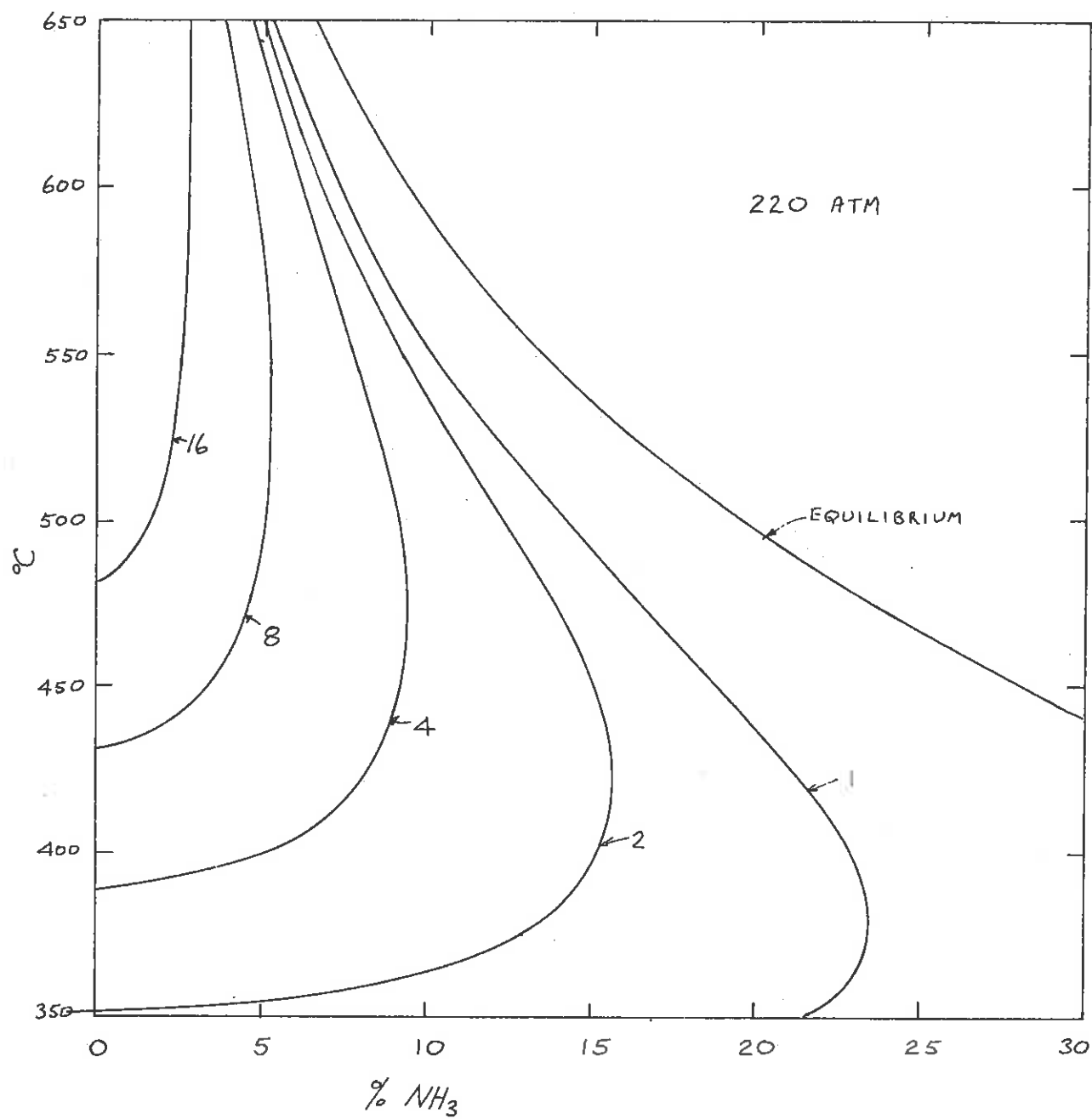
FIG 4

FIG 5
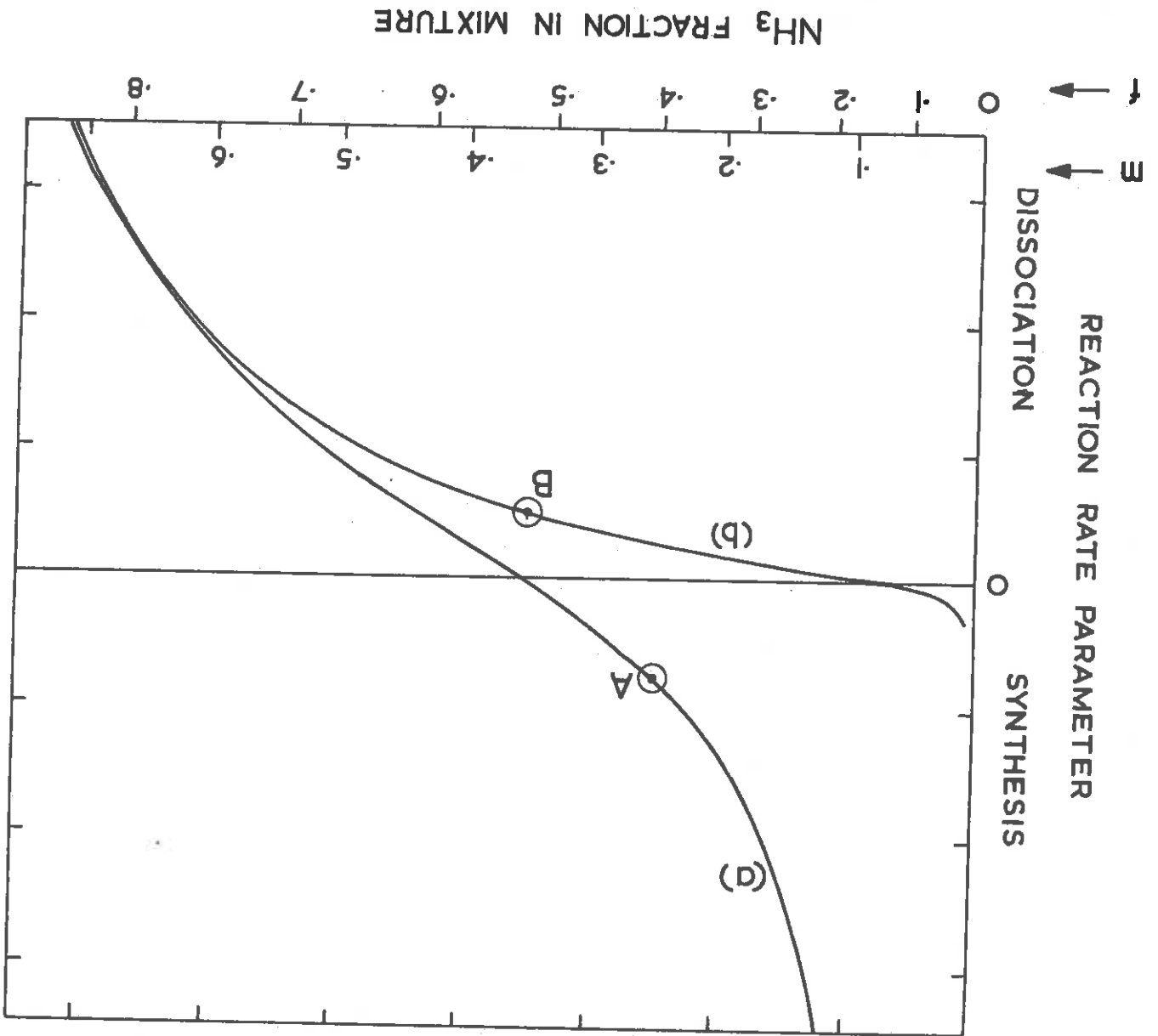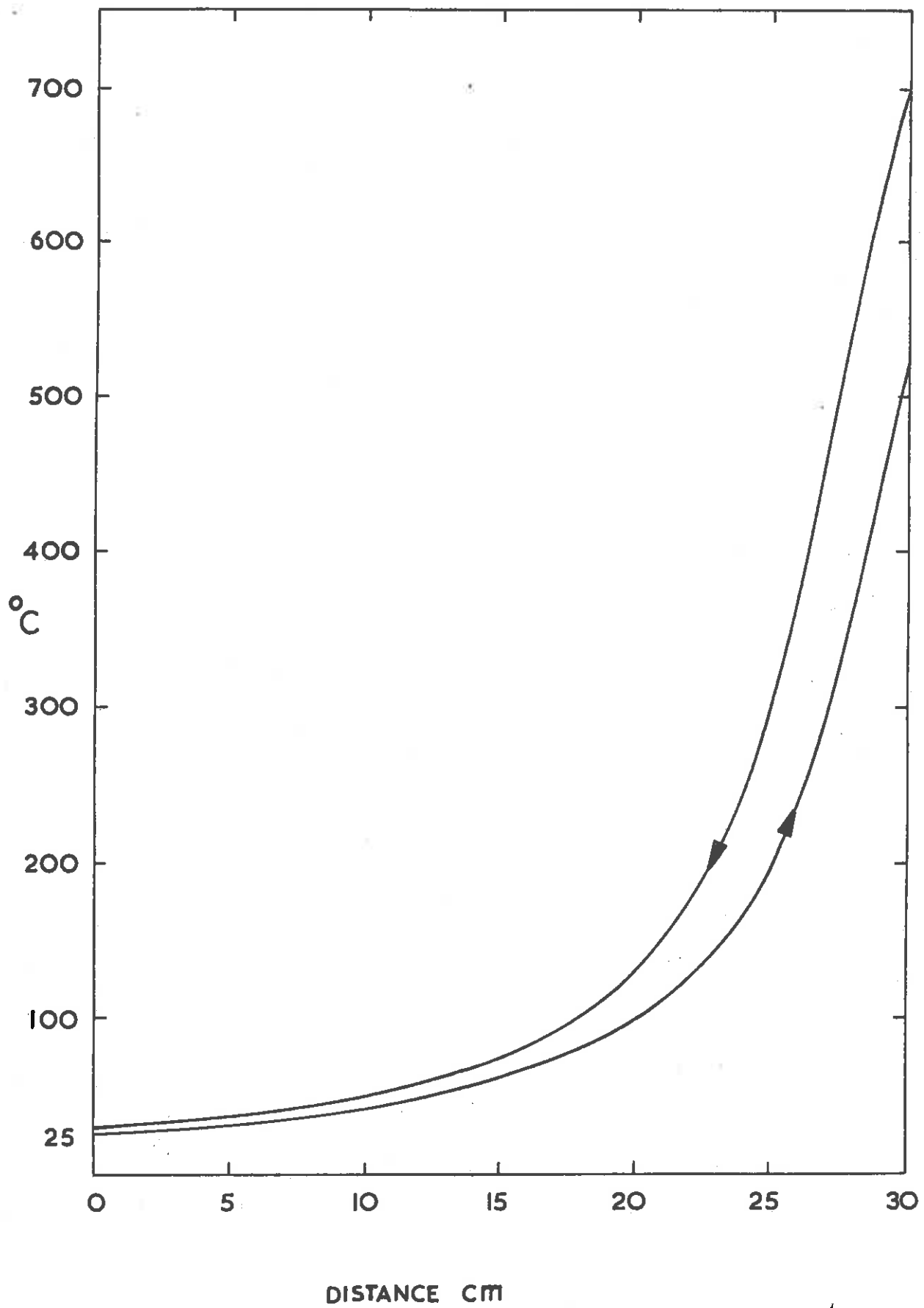
FIG 6
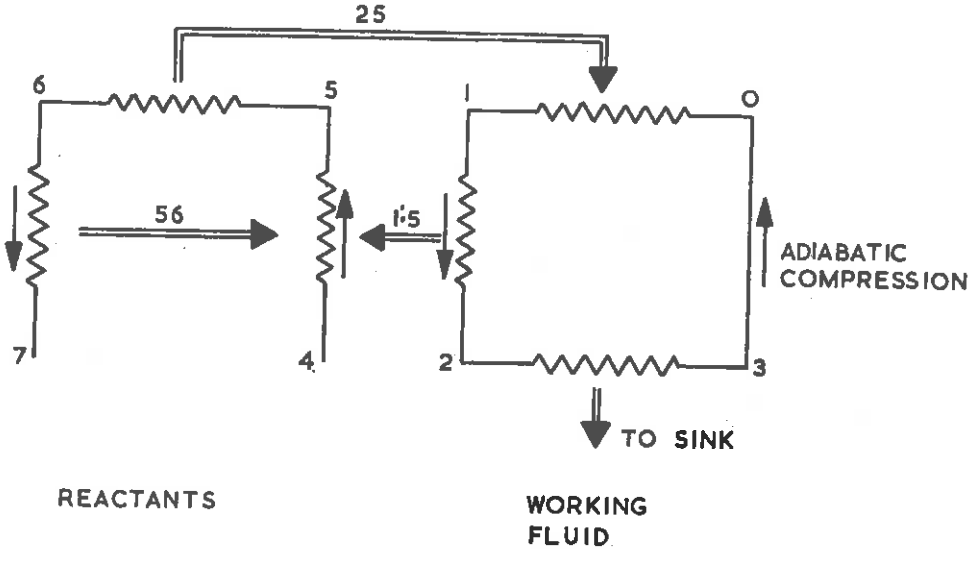
FIG 7(a)
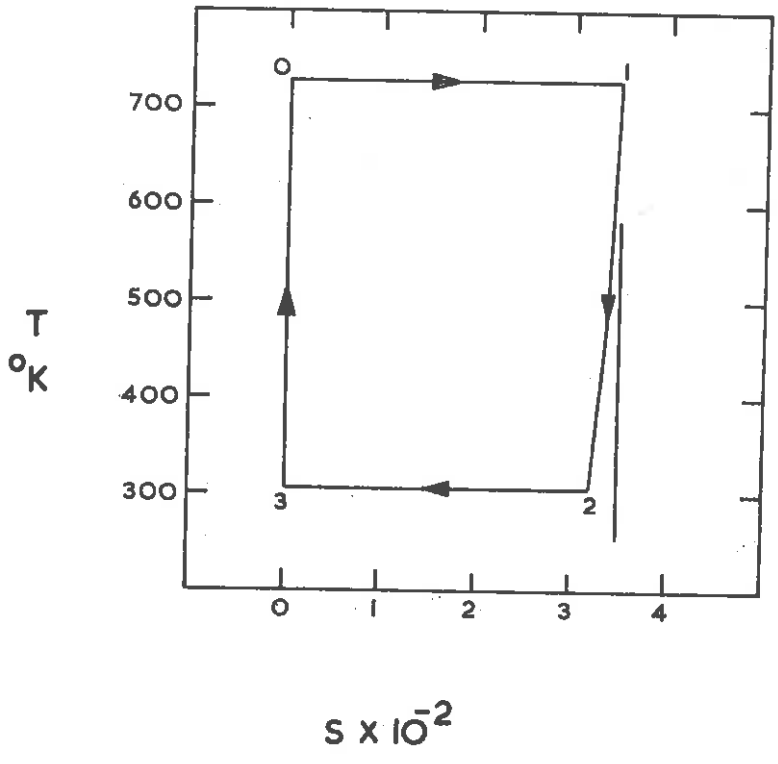
FIG 7(b)

FIG 8

FIG 9

FIG 10

FIG 11