THE EFFICIENCIES OF THEMORCHEMICAL ENERGY TRANSFER

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ABSTRACT

A general thermodynamic study of thermochemical energy transfer and work production processes is presented. Both gaseous systems in which the effluent of each reactor is not separated into the reactant and product species, and liquid/gas systems in which the effluent separarates spontaneously into liquid and gas phases, are treated. The study extends to consideration of non-isothermal reactors, to the individual roles of reactor and heat exchanger in the work production processes, and to the significance of the intrinsic work of phase separation. The overall system efficiency is derived as the product of two efficiencies: the energy storage efficiency which defines the fraction of the input energy passed in chemical form to storage

and the work recovery efficiency which defines the fraction of this stored energy available as output work. The fundamental thermodynamic processes underlying the derivation of these efficiencies is examined from the point of view of optimization of the design and operation of individual system components. In particular, it is shown that the available work from a thermochemical energy transfer system approaches the maximum value given by the Gibbs' free energy change when the temperature profile of the exothermic reactor is suitably tailored.

The work of separation has formed the basis of the analysis of specific system components and has given a useful insight into the understanding of energy storage efficiency. Work recovery efficiencies are calculated for the ammonia/hydrogen-nitrogen system and the paper concludes with a discussion of some practical considerations relating to the recovery of work and the performance that one might ultimately expect from this system.

1. INTRODUCTION

Considerable interest has developed recently into the use of reversible chemical reactions both for transporting energy from a solar collector array to a central power generating plant and for transporting high grade heat from nuclear power plants. A working fluid undergoes an endothermic reaction in absorbing thermal energy at the source or multiple sources and is reconstituted during the reverse exothermic reaction with regeneration of the reaction heat. Distances over which high grade heat must be transported are minimised by using a counterflow heat exchanger at each of the endothermic and exothermic reactors thus allowing the working fluid to be transported over the remaining distance through pipes at ambient temperature. Thermal lagging is unnecessary and furthermore, considerable potential exists for long term lossless storage of energy through storage of the fluid at ambient temperature.

In this paper we are particularly interested in those systems where the end use of the recovered heat is the production of work by means of a heat engine. A number of reversible reactions suitable for thermochemical energy transfer and work production have been proposed [1-5] and may be divided essentially into two classes: non-separating systems such as sulphur trioxide dissociation/synthesis (Chubb [1]) and two-phase separating systems such as ammonia dissociation/ synthesis (Carden [2]). In non-separating systems, the exothermic reactor is fed by the effluent of the endothermic reactor and conversely, the endothermic reactor is fed by the effluent of the exothermic

reactor. It is desirable from the point of view of achieving a high value of stored enthalpy per mole that both reactions proceed as close as possible to completion. This requirement favours those reactions which, because of their higher reactivity, progress easily towards equilibrium even at the lower temperature of the exothermic reactor. In addition to this restriction the choice of operating temperatures is restricted also, and indeed, the endothermic reactor must always operate at a higher temperature than the exothermic reactor.

On the other hand, liquid/gas separating systems offer greater flexibility in the choice of both reactions and temperatures. Reactions need not proceed to completion because the effluent of each reactor separates spontaneously into the basic reactants which may then be stored or recirculated to the reactors in any desired proportions. The storage of separate components instead of mixtures of the two enables the achievement of high values of stored enthalpy per mole without restricting other parameters such as the reaction temperatures.

In order to optimise the operation of a thermochemical energy transfer system it is necessary to gain a detailed insight into the inherent processes of energy transfer and work production. The thermodynamics of such systems have been examined in several earlier papers [5-9] but to date there has been no general study of the problem. Wentworth and Chen [5] have examined thermochemical energy transfer systems from the point of view of establishing criteria for selecting the best chemical systems. In particular, they have derived a 'turning' temperature T^* which characterises the operating temperature range of a

system. Their definition of T^* applies only to systems operated at ambient pressure but in a separate paper [6] we have extended the definition to all system pressures and further, have related T^* to the maximum thermodynamic efficiency. Expressions for thermodynamic efficiency have been derived by Cox et al [7], but apply only to non-separating systems operating with isothermal reactors and with fluids of equal specific heat flowing in each arm of the associated heat exchangers. Cox et al conclude that for such systems the maximum available work given by the Gibbs' free energy change at the engine sink temperature cannot be approached since the output heat is necessarily produced at a considerably lower temperature than the input heat.

In this paper, we present a general thermodynamic study of both separating and non-separating thermochemical energy transfer systems. The study extends to consideration of non-isothermal reactors, to the individual roles of reactor and heat exchanger in the work production processes, and to the significance of the intrinsic work of phase separation. Our purpose is twofold: we derive two basic system efficiencies, the energy storage efficiency and the work recovery efficiency; and we examine the fundamental thermodynamic processes underlying the derivation of these efficiencies from the point of view of optimization of the design and operation of individual system components. The energy storage efficiency defines the fraction of the input energy passed in chemical form to storage and the work recovery efficiency defines the fraction of this stored energy available as output work. These efficiencies are relevant whether or not storage of the fluids is actually implemented and our theoretical treatment

is correspondingly quite general. In contrast to the findings of Cox et al [7] for the special case of non-separating systems with isothermal reactors, we show that the available work from a general system may indeed approach the Gibbs' free energy change if the exothermic temperature profile is suitably tailored.

In examining the underlying mechanisms of energy transfer, our analysis gives new recognition of the significance of work of separation. In an earlier study [8], Soliman et al calculated the work of separation applied externally to the gaseous products of several specific thermochemical processes. They concluded that processes where spontaneous two-phase separation occurred were preferable, implying that the work of separation was comparatively small. Recently Funk [9] has derived a general expression for the work of separation of ideal gaseous products where the separation is carried out at the same temperature as the reaction. In the present study we draw attention to the fact that work of separation for ideal gases reduces with temperature and we show that the work of separation for spontaneous processes is essentially equivalent to the former when the separation occurs at the sink temperature of heat engines rather than at the reaction temperature. Thus we have elucidated the conclusion of Soliman et al referred to above.

In this paper, separation work refers to spontaneous separation into two phases and applies to separating systems only, although it has a more complex counterpart in non-separating systems. The work of separation has formed the basis of our analysis of specific system components and has given a useful insight into the understanding of energy storage efficiency. Work

recovery efficiencies are calculated for the ammonia/hydrogen-nitrogen system proposed by Carden [2] and the paper concludes with a discussion of some practical considerations relating to the recovery of work and the performance that one might ultimately expect from this system.

2. THERMOCHEMICAL ENERGY TRANSFER SYSTEMS

The basic elements of non-separating and liquid/gas separating thermochemical energy transfer systems are shown in Figure 1 where the endothermic reactor can represent either a single reactor as typical of a nuclear heat source, or a multitude of small reactors in parallel as typical of a distributed collector solar power plant. The corresponding temperature-enthalpy diagrams for the two systems are shown in Figure 2.

The operation of a non-separating system is straightforward: each reactor is fed by the product mixture of the other and counterflow heat exchangers ensure that energy transport between the reactors occurs at ambient temperature. The working fluids are generally gas mixtures throughout and there is no provision for separating the components.

Operation of a liquid/gas separating system is similar with the exception that the product mixtures, which are two-phase at ambient temperature, pass to gravitational settling tanks from which two separate component streams are drawn, one liquid and one gaseous. These components may pass to storage or be recirculated to the counterflow heat exchangers in any desired proportion. In the heat exchanger adjoining an endothermic reactor the mixture of

component fluids flows along the input channel towards the high temperature reactor and, as it is heated, the liquid vaporises. In the reactor, heat is absorbed and the product mixture then passes through the second channel of the heat exchanger towards ambient temperature, the liquid component condensing as the temperature is lowered. In a similar manner, the exothermic reactor is fed with a tailored mixture preheated by its adjoining heat exchanger. High grade reaction heat is generated within the exothermic reactor and may be converted into useful work.

Work may also be obtained from the counterflow heat exchangers which are treated in this study as additional heat sources (positive or negative) as well as devices which transfer heat from one fluid to another. Because the two fluid streams are liable to have significantly different specific heats at any given temperature, particularly the reactants in two-phase systems, and in order to maintain thermal equilibrium within any elemental length of the two adjacent heat exchanger passages, one or both of the following must occur:

(a) heat must flow to or from external components or elements
(b) the temperature gradients in the adjacent passages must differ widely.

The latter process acting alone is dealt with in standard texts where it is shown that as a consequence the temperature profiles along the passages become markedly non-linear and non-parallel resulting in localised high temperature differentials between the passages. Under these conditions, the processes occurring within the heat exchanger are considerably irreversible and are therefore not conducive to efficient conversion of heat to work.

On the other hand, if additional balancing heat flows are provided at the appropriate temperatures from a device external to the heat exchanger, an ideal reversible situation may be approached in which conductive temperature differentials become negligible. In this paper we will always consider a heat exchanger as a device which produces flows of heat (positive or negative) over a spectrum of temperatures as illustrated for example in Figure 3 and we will consider that any associated temperature differentials between adjacent fluid elements due to conduction are negligible. In a solar energy system one would wish to approach this ideal for the exothermic loop exchanger but not necessarily for the endothermic loop exchangers since for a practical system external work will neither be added nor extracted at these locations. (However, the reverse may be true for a nuclear power source supplying process heat to many remote consumers.)

Thus for solar energy applications, it is assumed that the exothermic exchanger is operated reversibly as part of a central plant. Excess heat from the exchanger is supplied to Carnot engines which operate as heat pumps when the excess heat is negative, and fluid friction throughout the system is regarded as negligible. The overall output work W is then regarded as originating from the combination of exothermic reactor and associated heat exchanger. We may define a work recovery efficiency η_R as the ratio of output work to chemical energy transferred from storage:

$$\eta_R = W/\Delta H(T_S) \tag{1}$$

Expressions for η_R are derived below in Section 3.

It is particularly important to conserve heat at the endothermic loop and therefore we are concerned with those parts along the (ideal) heat exchanger where there is a net heat outflow. Generally a heat exchanger may be divided along the length of the passages into positive or negative zones depending on whether net heat flow is respectively to or from the heat exchanger. In practice, heat from a negative zone will be conserved provided there are positive zones of lower temperature to which it can all be conducted. However, if the negative flows exceed the positive flows or if the lowest temperature zone is negative, heat must necessarily be wasted to the environment. This waste heat is clearly the difference between the minimum solar energy input Q and the chemically stored enthalpy $\Delta H(T_S)$. Thus we define energy storage efficiency

$$\eta_{ST} = \Delta H(T_S)/Q \tag{2}$$

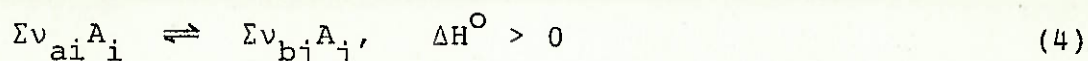The method for evaluating the magnitude of η_{ST} for a given system is discussed below in Section 5.

Clearly, the overall thermodynamic efficiency W/Q for the system is obtained as the product of (1) and (2):
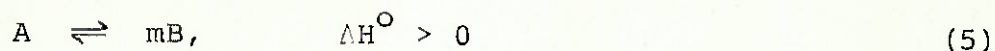
$$\eta_o = \eta_{ST}\eta_R \tag{3}$$

3.   WORK RECOVERY

3.1 Formulation

We consider the general reversible chemical reaction

$$\Sigma \nu_{ai} A_i \;\rightleftharpoons\; \Sigma \nu_{bj} A_j, \quad \Delta H^O > 0 \tag{4}$$

in which m moles of the B mixture are generated for each mole of the A mixture consumed. Stoichiometric proportions are assumed amongst the reaction components for both A and B mixtures, allowing the reaction to be written in the simplified form

$$A \;\rightleftharpoons\; mB, \quad \Delta H^O > 0 \tag{5}$$

The characteristics of any mixture of A and B may be defined in terms of the mole fraction x of B or the weight fraction δ of B which, by the reaction stoichiometry, are related according to

$$\delta = \frac{x}{m(1 - x) + x} \tag{6}$$

The extent of reaction $\Delta\delta$ between mole fractions x_1 and x_2 is given by

$$\Delta\delta = \delta(x_1) - \delta(x_2) \tag{7}$$

and will always be defined positive. Thermodynamic variables such as enthalpy change ΔH and Gibbs' free energy change ΔG are defined on the basis of constant system mass equal to the mass of one mole of A or m moles of B. On this basis, the number of moles in any mixture of A and B is given by

$$N(x) = \frac{m}{m(1 - x) + x} \tag{8}$$

It is convenient to scale the energy transfer and work production calculations described below to unit mass of A generated by chemical reaction. Thus the mole numbers for the two end points of a reaction of extent $\Delta\delta$ are scaled to the value

$$n(x) = N(x)/\Delta\delta \tag{9}$$

Both exothermic and endothermic reactions are assumed to occur within the ideal solution region and therefore mixing heats are zero at the reaction temperature T_f. Furthermore, in separating systems, the liquid and gas phases which form during cooling are assumed to comprise respectively pure A and pure B at the sink temperature T_S so that in this instance mixing heat is also zero. We are therefore able to relate system enthalpy changes scaled similarly to (9) to the enthalpy of reaction:

$$\Delta H(T_f)/\Delta\delta = \Delta H_o(T_f), \quad \text{both systems}$$

$$\tag{10}$$

$$\Delta H(T_S)/\Delta\delta = \Delta H_o(T_S), \quad \text{separating systems alone}$$

and system free energy changes to the Gibbs' free energy of reaction:

$$\Delta G(T_f)/\Delta\delta = \Delta G_o(T_f) - T_f[\Delta S_m(x_1) - \Delta S_m(x_2)]/\Delta\delta, \quad \text{both systems}$$

$$\tag{11}$$

$$\Delta G(T_S)/\Delta\delta = \Delta G_o(T_S), \quad \text{separating systems alone}$$

where $\Delta S_m(x)$ is the entropy of mixing.

In the present study it is assumed that the storage reservoirs and transport system are isobaric. However, the liquid phase may be stored more economically at ambient pressure as in the case of ammonia which is refrigerated to $-34°C$. The introduction of a separate reservoir temperature T_R distinct from T_S will be dealt with in a future paper together with the question of incomplete separation at T_S (mixtures of A and B in each phase). However, studies so far show that the errors introduced by our simplifying assumptions in this paper are small.

3.2 Energy Transfer and Work Production

For the purposes of the present study it is convenient to return to first principles in order to identify the fundamental processes occurring within the exothermic loop of a thermochemical energy transfer system. A schematic diagram of the energy transfer processes is shown in Figure 4 in which the recirculation components are omitted in the case of a non-separating system. Figure 4 models a reversible system capable of degeneration into a real reaction process. Components A and B are treated as single fluids, a simplification which can be readily validated, and the flow quantities are scaled according to (9) so that unit mass undergoes chemical conversion.

Three sources of available work are identified, the first being the heat exchanger where it is assumed that operation is reversible as described above with nett work generation equal to

$$W_H = \frac{1}{\Delta\delta} \int_{T_S}^{T_f} -d(\Delta H)\left(1 - \frac{T_S}{T}\right) \tag{12}$$

where the integrand represents the contribution from the infinitesimal Carnot engine at T.

We define

$$Q_H = \Delta H(T_S) - \Delta H(T_f) \tag{13}$$

which is recognised for separating systems as an effective latent heat of vaporisation of A. The factor $d(\Delta H)/T$ occurring in (12) is a differential entropy and it is thus convenient to define also a characteristic temperature T_H such that

$$T_H = \frac{Q_H}{\Delta S(T_S) - \Delta S(T_f)} \tag{14}$$

Equation (12) then reduces to the simplified form

$$W_H = \frac{Q_H}{\Delta\delta}\left(1 - \frac{T_S}{T_H}\right) \tag{15}$$

which is equivalent to the work output of a single Carnot engine operating between reservoirs T_H and T_S.

Equations (13), (14), and (15) also specify the quantities Q_{Ho}, T_{Ho} and W_{Ho} defined as the values of Q_H, T_H and W_H respectively when $\Delta\delta$ equals unity. These special case quantities depend only on the properties of A and B since they describe the situation when the heat exchanger passages contain respectively the two pure components. For separating systems we are able to write, from (10)

$$Q_{Ho} = Q_H/\Delta\delta = \Delta H_o(T_S) - \Delta H_o(T_f) \tag{16}$$

Two other sources of available work are located within the isothermal reactor of Figure 4. A total of $n(x_1)$ moles of reactant mixture leaving the heat exchanger is separated into the respective partial pressures (partial fugacities at high system pressure) of the components A and B by passage through a pair of semipermeable membranes. Neither energy transfer nor work production occurs at this stage. Each component is then expanded to its chemical equilibrium partial pressure by means of a reversible isothermal expansion engine. This process produces work and absorbs heat resulting respectively in a decrease of free energy and increase of entropy of the components passing through. In contrast, the enthalpy will be unchanged since the mixture is ideal.

A total of m moles of component B then passes through a membrane into a vessel containing a mixture in chemical equilibrium at the system pressure and at temperature T_f. In this vessel m moles of B are converted to 1 mole of A and heat ΔH_o is released. Constant mass and composition are maintained in the vessel by withdrawing at the same time through a second membrane the one mole of A which has been produced and this is added to the bypass A. Both A and B are then compressed isothermally to their final partial pressures (or fugacities), again by means of reversible engines, and finally the two components pass without energy transfer through a third pair of membranes to form the mixture returned to the heat exchanger. Since all processes in this reactor system are reversible and isothermal, it follows by definition that the net work output from the engines, our second source of available work, is in fact the total free energy change

$\Delta G/\Delta\delta$ between the input mixture and output mixture. Similarly, by definition, the net heat output is $T_f\Delta S/\Delta\delta$. Furthermore, because all processes outside the vessel are isenthalpic, the system enthalpy change $\Delta H/\Delta\delta$ equals the vessel enthalpy change ΔH_o. Thus, employing the standard relationship between enthalpy, free energy and entropy, the above heat output is expressed:

$$T_f\Delta S/\Delta\delta = \Delta H_o - \Delta G/\Delta\delta \qquad (17)$$

Part of this heat may be converted in a Carnot heat engine to form the third source of available work from the system. The total available work from the three sources is therefore

$$W_o^{rev} = \Delta G(T_f)/\Delta\delta + (\Delta H_o(T_f) - \Delta G(T_f)/\Delta\delta)\left(1 - \frac{T_S}{T_f}\right)$$

$$+ Q_H\left(1 - \frac{T_S}{T_H}\right)/\Delta\delta \qquad (18)$$

In practice, the free energy component represented by the first term of (18) is not fully available as work, being first irreversibly converted into heat within the reactor before being partially converted into work by the adjoining Carnot engine. The difference between the total reversible work available and W_o, the work available in practice, is therefore

$$\frac{T_S}{T_f}\Delta G(T_f)/\Delta\delta$$

and hence

$$W_o = \Delta H_o(T_f)\left(1 - \frac{T_S}{T_f}\right) + Q_H\left(1 - \frac{T_S}{T_H}\right)/\Delta\delta \qquad (19)$$

Moreover, the reversible work W_o^{rev} is identified as the stored

Gibbs' free energy $\Delta G(T_S)/\Delta\delta$ by substitution of equations (13) and (14) in (18) and by application of the standard relationship between thermodynamic quantities referred to above. This result is in accordance with established theory and confirms the validity of (18). We are therefore able to derive from (19)

$$W_O = \Delta G(T_S)/\Delta\delta - \frac{T_S}{T_f} \Delta G(T_f)/\Delta\delta \qquad (20)$$

3.3 Work Recovery Efficiency

Work recovery efficiency is expressed from (1) in terms of (20) and the corresponding stored enthalpy as

$$\eta_R = [\Delta G(T_S) - \frac{T_S}{T_f}\Delta G(T_f)]/\Delta H(T_S) \qquad (21)$$

which is the general result for isothermal reactions. Equation (21) may be extended to a general reaction temperature profile by development of an integral form for η_R, a convenient form being

$$\eta_R = \frac{\int \eta_R(T,\ x)d\delta}{\Delta\delta} \qquad (22)$$

where $\eta_R(T,x)$ is the limiting value of (21) as the reaction extent $\Delta\delta$ is reduced to zero

with $\Delta G(T)$ replaced by $\Delta\delta \left. \frac{\partial G}{\partial\delta} \right|_T$

and $\Delta H(T_S)$ by $\Delta\delta \left.\dfrac{\partial H}{\partial\delta}\right|_{T_S}$.

Equation (22) is useful if charts of constant $\eta_R(T, x)$ are available such as Figure 5 for the ammonia/nitrogen hydrogen system. Such charts may be prepared by calculating $\eta_R(T, x)$ in the ideal solution region using the limiting value of (21) to give

$$\eta_R(T, x) = \frac{\left.\dfrac{\partial G}{\partial\delta}\right|_{T_S} - RT_S \ln\left[\dfrac{(1 - x_e)x^m}{(1 - x)x_e^m}\right]}{\left.\dfrac{\partial H}{\partial\delta}\right|_{T_S}} \tag{23}$$

where x_e describes the equilibrium mixture at T. Equation (30) is derived by taking the limit of equation (15) after substitution of standard logarithmic expressions for the thermodynamic quantities

$$\Delta S_m(x) = -RN(x)[x\ln x + (1 - x)\ln(1 - x)] \tag{24}$$

and

$$\Delta G_o(T) = -RT\ln\left(\frac{x_e^m}{1 - x_e}\right) \tag{25}$$

The partial derivatives in (23) equal respectively $\Delta G_o(T_S)$ and $\Delta H_o(T_S)$ for separating systems according to (11) and (10), and for non-separating systems may be taken equal to $\Delta G(T_S)/\Delta\delta$ and $\Delta H(T_S)/\Delta\delta$. These results verify that η_R reaches a maximum value $\Delta G(T_S)/\Delta H(T_S)$, or specifically $\Delta G_o(T_S)/\Delta H_o(T_S)$ for separating systems when the reaction path follows the equilibrium line, and that reaction paths running closely parallel to the equilibrium line will yield recovery efficiencies approaching this maximum value. Thus we may determine from the reactor temperature profile the maximum work available from both reactor and heat exchanger

without specific or detailed knowledge of the contribution of either.

The maximum work recovery efficiency η_R^{max} is related to the effective temperature T_c^* by the Carnot equation

$$\eta_R^{max} = 1 - \frac{T_S}{T_c^*} \tag{26}$$

We have shown elsewhere [6] that T_c^* is related to the turning temperature T^* introduced by Wentworth and Chen [5] as the temperature at which neither the forward nor the reverse reaction in a thermochemical energy transfer system is favoured. T_c^* is related to the variables in the present study according to

$$T_c^* = \Delta H(T_S)/\Delta S(T_S) \tag{27}$$

Thus for systems where T_f exceeds T_c^* it is possible under certain circumstances for the available work from the reactor heat to exceed the available work W from the system in which case the available work from the heat exchanger must be negative.

4. SEPARATION WORK

4.1 Identification of Loop Work

Our study so far has been generally applicable to all thermochemical energy transfer systems and we have obtained results related to overall system performance. We now direct attention to the performance of individual components, particularly the exothermic reactor and heat exchanger, and to the

manner in which the available work contributions from both add to give the known output W_O. Because the treatment depends on separation work it is strictly applicable only to two-phase separating systems. However, similar but more complex mechanisms proceed in non-separating systems so an insight into their behaviour may be gained also.

We begin by rewriting the output work equation (20) for an isothermal reactor using the standard relationship between Gibbs' free energy, entropy and enthalpy, together with equations (11), (13), (14) and (16)

$$W_O = \Delta H_O(T_f)\left[1 - \frac{T_S}{T_f}\right] + Q_{Ho}\left[1 - \frac{T_S}{T_{HO}}\right]$$
$$- T_S[\Delta S_m(x_2) - \Delta S_m(x_1)]/\Delta\delta \qquad (28)$$

The first two terms may be identified respectively with the Carnot work available from an irreversible isothermal reactor and the maximum possible value W_{HO} of heat exchanger work. We now identify the third term as the work required for spontaneous separation into A and B in the general case when the fluids are mixtures of the two. Our analysis is based on the well understood process of separation of ideal gases by application of external work and we consider initially the thermodynamic cycle shown in Figure 6(a) in which a two component ideal solution of A and B characterised by mole fraction x of B is cooled from a source temperature T_f to sink temperature T_S. At T_S the components of the ideal solution are separated reversibly by input of external work W_S (for example by selective compression of the individual components to the system pressure) and rejection of an equal

amount of heat. The unmixed components are then heated to T_f and mixed reversibly to complete the cycle. Since mixing heats are zero throughout, the heating and cooling arms of the cycle are indistinguishable on the T-H diagram.

The entire loop comprises a single heat source Q_f at T_f, heat rejection Q_S at T_S and nett work production $W_f - W_S$. The cycle therefore constitutes a single Carnot engine with output work given by

$$W_f - W_S = Q_f \left(1 - \frac{T_S}{T_f} \right) \tag{29}$$

Since zero enthalpy change occurs at T_f, both Q_f and W_f assume the same value $T_f \Delta S_m(x)$ equal to the reversible isothermal work of mixing. By substitution of this value into (29) we obtain an expression for the externally applied work of separation

$$W_S = T_S \Delta S_m(x) \tag{30}$$

We now turn our attention to the case of interest where the separation proceeds spontaneously. The equivalent thermodynamic cycle is shown in Figure 6(b). In this case, the excess heat of mixing defined by

$$\Delta H^E(x, T) = H(x, T) - (1 - \delta)H(0, T) - \delta H(1, T) \tag{31}$$

is not zero except at T_S where the system components are fully separated and also within the ideal solution region at high temperatures. We may again reduce the system to a single Carnot engine operating with the same heat input Q_f as before, but with nett work output given by $W_f - W_L$ where W_L is the loop work associated with traversing the complete cycle. That is,

$$W_L(x) = \int_{T_S}^{T_f} d[\Delta H^E(x, T)] \left(1 - \frac{T_S}{T}\right) \tag{32}$$

By following the same argument as before, we determine that the magnitude of $W_L(x)$ is given by $T_S \Delta S_m(x)$ and that an equal value of heat is rejected at the sink. Since, in traversing the cycle the components successively mix and separate as in the first case, and by drawing analogy with (30), we obtain the important result that the loop work $W_L(x)$ is the work of separation $W_S(x)$.

Thus by analogy with the case for ideal solutions, any mixture being cooled from the ideal solution region may be regarded as undergoing physical separation at T_S by application of external work W_S provided the mixture is considered to be virtual in the sense that it possesses the thermal properties of the unmixed components. This result provides the link between W_H (dependent on a specific mixture of components) and W_{Ho} (dependent on the properties of the unmixed components), a link which will be derived formally and expressed in equation (34) below.

4.2 Thermodynamic Significance

The separation work is a function of the composition of the mixture and is proportional to T_S provided that T_f occurs within the ideal solution region. Furthermore, with this proviso, the separation work is independent of the nature of the process by which the components are separated. Identification of the loop work given by (32) forms the basis of the calculation of energy storage efficiencies described in the following section and in the accompanying paper (Williams and Carden [9]). The separation work

for Figure 6(b) may also be expressed in terms of an equivalent temperature and enthalpy change for each branch according to the concepts described for the derivation of (14) and (15). Thus for positive W_S, the equivalent temperature of the mixed branch must always be less than the equivalent temperature of the unmixed branch.

We are now in a position to identify the last terms of the available work equation (28). The separation work associated with the exothermic reaction loop of the thermochemical energy transfer cycle shown in Figure 2 may be calculated simply from the difference between the values of loop work at x_1 and x_2. We obtain for the separation work

$$\Delta W_S = T_S [\Delta S_m(x_2) - \Delta S_m(x_1)]/\Delta \delta \qquad (33)$$

which is the same as the last terms in equation (28). Comparison of (19) and (28) using (15) and (16) gives the further result that

$$\Delta W_S = Q_{Ho} T_S \left(\frac{1}{T_H} - \frac{1}{T_{Ho}} \right) = W_{Ho} - W_H \qquad (34)$$

and, as we have anticipated above, ΔW_S may be of either sign.

The nature of the origin of the separation work associated with exothermic reaction loops has therefore been identified. The work is externally applied in the sense that the full work W_{Ho} which would have been available from the heat exchanger had the components been unmixed is reduced by the quantity ΔW_S.

In the case of the endothermic reaction loop, where the heat source normally supplies net heat to the heat exchanger, the separation work is related to the ability of the source to do

Carnot work and to the heating and subsequent cooling of that part of the liquid feed that remains unconverted to B in the reactor. The net effect of these two latter processes is the transfer of heat from the source at one effective temperature and the return of an equal quantity at another temperature. The consequent change in available Carnot work from the source is the quantity ΔW_S.

What happens to the returned heat depends on the magnitude of the heat exchanger input Q_{Ho} and its temperature spectrum $d[\Delta H_o(T)]/dT$ (illustrated in Figure 3), for clearly if it is possible to choose a temperature T_A such that the returned heat in the range $T_S < T < T_A$ exceeds

$$\int_{T_S}^{T_A} d[\Delta H_o(T)]$$

then the difference will not be effectively absorbed by the source and must therefore be wasted. This is the origin of the inefficiency discussed in the next section.

5. ENERGY STORAGE EFFICIENCY

5.1 Limiting Efficiency

The loss mechanisms associated with energy storage may be explained partly by means of general thermodynamic arguments and partly in terms of specific molecular models. We have already pointed to a link between energy loss and separation work, the evidence for which is based on thermodynamic arguments, but it is not possible to develop this link further without a specific

molecular model. Nevertheless, a limiting value to energy storage efficiency may be established from the thermodynamic argument which we now present. Proceeding from equation (2), and considering only the case $T_f < T_c^*$ where T_f is the maximum temperature of the endothermic reactor, we obtain for the maximum work available from the source

$$W_{max} \leq \frac{\Delta H(T_S)}{\eta_{ST}} \left[1 - \frac{T_S}{T_f} \right]$$

Since the recovered work cannot exceed W_{max} nor $\Delta H(T_S)(1 - T_S/T_c^*)$ it follows that

$$\eta_{ST} < \frac{1 - \dfrac{T_S}{T_f}}{1 - \dfrac{T_S}{T_c^*}} \quad , \qquad T_f < T_c^* \tag{35}$$

In the range $T_f \geq T_c^*$ molecular effects continue to operate and it does not necessarily follow that here η_{ST} is unity.

The relation (35) holds for both separating and non-separating systems and explains why non-separating systems, which necessarily operate endothermically well above T_c^*, tend to have higher storage efficiencies than separating systems. Thus, although separating systems possess slightly lower storage efficiencies, this may now be placed in proper perspective in relationship to their advantage of being able to operate at lower temperatures.

5.2 Energy Storage Efficiency

The value of energy storage efficiency defined by equation (2) may be determined for a given endothermic energy transfer loop directly from the temperature-enthalpy characteristics of the system as shown in Figure 7 for a liquid/gas separating system. The enthalpy requirements of the endothermic loop are shown in Figure 7(b). Clearly, sufficient heat Q must be drawn from the source to develop the maximum value ΔH_{max} of enthalpy requirement. The heat may be supplied to the heat exchanger at the different temperatures required or, in a practical solar absorber, perhaps at significantly higher temperatures with irreversible degradation of the heat by conduction along the heat exchanger.

Since heat rejected from the endothermic loop cannot be utilized in a practical distributed solar power plant, we obtain the result that

$$\eta_{ST} = \Delta H(T_S)/\Delta H_{max} \tag{36}$$

Clearly, the storage efficiency equals unity for any system in which ΔH_{max} equals $\Delta H(T_S)$, a condition which often occurs in non-separating systems. The maximum enthalpy difference for a liquid/gas separating system is generally coincident with the dew point temperature of the output fluid, as seen from Figure 7. Actual values of η_{ST} for a given system can only be determined if the temperature-enthalpy characteristic curves are known for all mixtures of reactants over a wide temperature range. Such information is not generally available within the chemical engineering literature. It has therefore been necessary in the

case of ammonia/nitrogen-hydrogen to generate the required data from available phase equilibrium measurements, and from the requirement that a given system be thermodynamically consistent. In particular, the shapes of the characteristic curves must be consistent with the criterion that the loop work calculated by means of (6), (31) and (32) for a given mixture equals the separation work for the mixture. A full description of the method as applied to the ammonia/hydrogen-nitrogen system is given in the accompanying paper [10]. The results show that the energy storage efficiency approaches the maximum value of unity as the endothermic reaction approaches completion, and values exceeding 0.90 are obtained providing that the reaction extent exceeds 60%. This result is encouraging for the potential use of liquid/gas separating thermochemical systems in solar power plants.

6. PRACTICAL CONSIDERATIONS

We have explored the maximum work potential of an energy recovery system comprising an exothermic reactor and associated heat exchanger and our results imply that although the average temperature of the reactor may be increased to the point where the available work recoverable from that component approaches $\Delta H_o(T_f)$, the countering effect of the heat exchanger work $Q_H(1 - T_S/T_H)$, which may be of either sign, limits the total available work to $\Delta G_o(T_S)$. From a practical point of view it may be difficult to extract the available exchanger work involving as it generally does the utilization of relatively low grade heat. However, it is possible to choose conditions enabling the heat exchanger work to

be zero or negligible, and the exothermic loop of Figure 7(a) has been specifically chosen to illustrate this situation. The available heat from this loop is shown in Figure 7(c) and may be divided into four broad zones. Zone A is that encompassing the reactor, B the heat exchanger above the condensation zone C, and D the evaporation zone. The mean temperatures of the zones, the corresponding values of difference in ΔH across the zones and the available nett work

$$\Delta W = \int d(\Delta H) \left(1 - \frac{T_S}{T} \right)$$

for a sink temperature of 300 K are listed in Table 1 together with the percentage available work from each zone. It is clear that most of the available work is produced in the reactor zone A and the available work values from zones B, C and D almost cancel. However, it is unlikely that work could be derived practically from zone C for the purpose of pumping heat to zone B and one must therefore consider other solutions to the problem of supplying the deficit zones B and D. An obvious alternative is to supply these zones by conduction from A and C respectively. A second alternative is to employ some of the waste heat from the heat engine which inevitably occurs as a result of mechanical inefficiencies, thermodynamic irreversibilities and direct thermal losses. This waste heat, possibly amounting to 40% of the available work, is unlike the thermodynamic sink heat in that it is available at temperatures above the sink temperature, some even at the high temperature of zone B. This heat may be tapped by providing suitable jackets around the turbine. It seems preferable to adopt the second alternative for supplying zone B

rather than degrade the source A. The first alternative, however, seems adequate for zone D.

Thus, with appropriate engineering design and choice of reactor temperature it seems possible to cope with the unorthodox features of this new heat source and at the same time achieve engine working fluid temperatures comparable with modern power generation practice. It is therefore expected that the predicted work recovery efficiency achievable for thermochemical fluids will be comparable to that now achieved by the combustion of fossil fuels.

7. CONCLUSIONS

In this paper we have introduced the fundamental thermodynamic theory underlying the operation of separating and non-separating thermochemical energy transfer systems proposed for use in both nuclear and solar power plants. The maximum efficiency for work production is essentially limited only by the constraints imposed by the second law of thermodynamics and is fixed for each thermochemical system. On the other hand, the division of work production among the individual system components is governed by a different mechanism identified in the case of separating systems as the generation of work of separation. It has been shown that the separation work is provided by the degradation of mixing heat within the system and that this is partly responsible for small losses at the thermal absorbers of a distributed collector solar power plant.

In comparing separating and non-separating systems, we find that the former possess an advantage of increased flexibility in choice of operating systems and conditions. The storage of separated gas and liquid components provide a high stored enthalpy per mole and further, the reaction temperatures may be chosen independently of one another and of the required extent of reaction. Practical energy storage efficiencies exceeding 0.90 and work recovery efficiencies of approximtely 0.5 can be achieved realistically for the ammonia/hydrogen nitrogen system. It would be expected that practical efficiencies for work production would be approximately 60% of the theoretical values, giving an overall efficiency for the thermochemical energy transfer-work production system of about 27%. This is an encouraging result and should prompt further development of thermochemical energy transfer systems.

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NOMENCLATURE

A, A_i	Reactant species.
B, B_j	Product species.
$\Delta G(T)$	Gibbs' free energy change per unit mass of A.
$\Delta G_o(T)$	Gibbs' free energy of reaction at pressure P and temperature T, including reactant and product mixing terms.
$H(x,T)$	System enthalpy at T and mole fraction x.
$\Delta H(T)$	Enthalpy change per unit mass of A.
$\Delta H_o(T)$	Enthalpy of reaction at P and T.
ΔH_{max}	Maximum value of ΔH for endothermic loop.
$\Delta H^E(x, T)$	Excess heat of mixing.
m	Moles of B produced per mole of A consumed.
$n(x)$	Mole number at x defined by (9).
$N(x)$	Mole number at x per unit mass of A.
P	System pressure.
Q	Heat absorbed from source.
Q_H	Nett heat transferred across heat exchanger.
Q_{HO}	Nett heat transferred across heat exchanger for complete reaction.
Q_S	Mixing heat absorbed at T_S.
Q_f	Mixing heat rejected at T_f.
R	Gas constant.
$\Delta S(T)$	Entropy change per unit mass of A.
$\Delta S_o(T)$	Entropy of reaction at P and T.
$\Delta S_m(x)$	Entropy of mixing at x.
T	Absolute temperature.

|	
T_S	Sink temperature.
T_f	Reaction temperature.
T^*	Turning temperature.
T_c^*	System characteristic Carnot temperature.
T_H	Heat exchanger characteristic temperature.
T_{HO}	Heat exchanger characteristic temperature for complete reaction.
W	Output work.
W_f	Work of mixing at T_f.
W_H	Heat exchanger work.
W_{HO}	Heat exchanger work for complete reaction.
$W_L(x)$	Loop work at x.
W_o	Available work.
W_o^{rev}	Reversible available work.
$W_S(x)$	Separation work at x.
ΔW_S	Separation work for endothermic or exothermic reaction loop.
x	Mole fraction of B in mixture.
x_e	Equilibrium mole fraction of B.
δ	Weight fraction of B.
$\Delta\delta$	Extent of reaction.
η_R	Work recovery efficiency.
η_R^{max}	Maximum work recovery efficiency.
$\eta_R(T, x)$	Limiting value of η_R at T and x.
η_{ST}	Energy storage efficiency.
η_o	Overall thermochemical efficiency.
ν_{ai}, ν_{bj}	Stoichiometric coefficients.

FIGURE CAPTIONS

Figure 1   (a) Non-separating thermochemical energy transfer system.

       (b) Liquid/gas separating thermochemical energy transfer system.

Figure 2   (a) Temperature-enthalpy diagram for a non-separating thermochemical energy transfer system with isothermal reactors.

       (b) Temperature-enthalpy diagram for a liquid/gas separating thermochemical energy transfer system with isothermal reactors.

Figure 3   (a) Extreme curves of the T-H diagram for a liquid/gas separating system.

       (b) Temperature spectrum of the external heat Q_{Ho} required by a reversible counterflow heat exchanger in which A is heated and B is cooled.

Figure 4   Energy transfer and work production from a reversible exothermic reactor and associated reversible counterflow heat exchanger.

      --- Semipermeable membrane.

      C Carnot engine.

      E Reversible isothermal expansion engine at T_f.

      === Work.

      ███ Heat.

Figure 5   Curves of constant work recovery efficiency for
                the ammonia/ 3:1 hydrogen-nitrogen system at
                300 atmospheres with $T_S = 300°K$. The curves
                are dashed outside of the ideal solution region.

Figure 6   Origins of separation work shown by T=H diagram
                and equivalent single Carnot engine.

                (a) Ideal solution with external separation.

                (b) Liquid/gas phase separation.

Figure 7   (a) Temperature-enthalpy diagram for a Thermo-
                     chemical energy transfer system. The diagram
                     represents the ammonia/hydrogen-nitrogen
                     system at 300 atmospheres with $T_S = 300$ K.

                (b) Temperature profile of enthalpy changes
                     occurring in the endothermic loop of
                     Figure 7(a).

                (b) Temperature profile of enthalpy changes
                     occurring in the exothermic loop of
                     Figure 7(b) with the zones referred to in
                     the text labelled A-D.

ZONE	T (°K)	$\Delta(\Delta H)$ (Kcal/Mole NH_3)	ΔW	% WORK
A	725	2.02	1.184	100.5
B	500	−0.21	−0.084	−7.1
C	336	0.75	0.080	6.8
D	313	−0.05	−0.002	−0.2

Table 1   Characteristics of the four temperature
           zones of the exothermic loop shown in
           Figure 7(c) for ammonia/ 3:1 hydrogen
           -nitrogen.

(a)
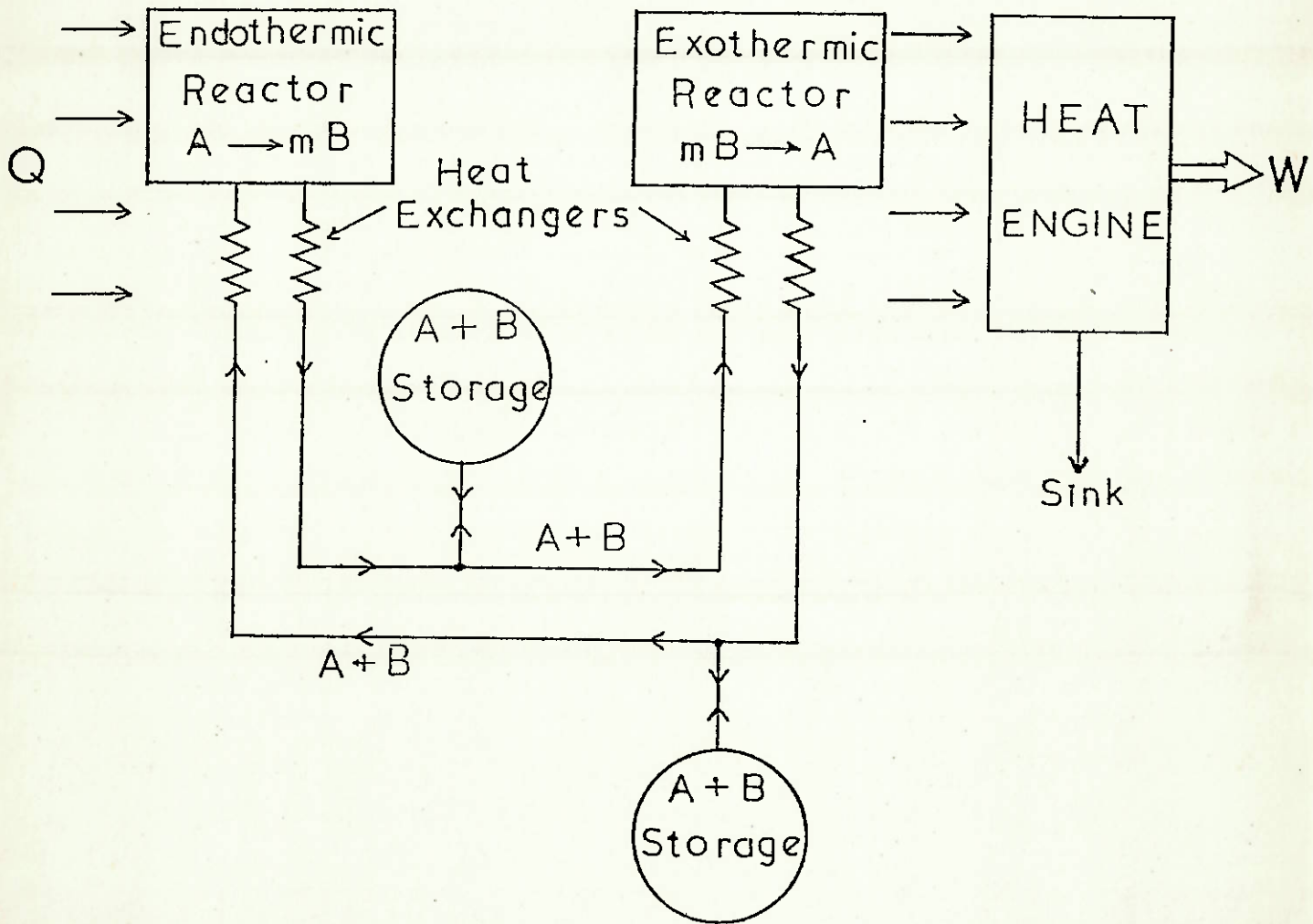
FIGURE 1(a): Non-separating thermochemical
energy transfer system.

(b)
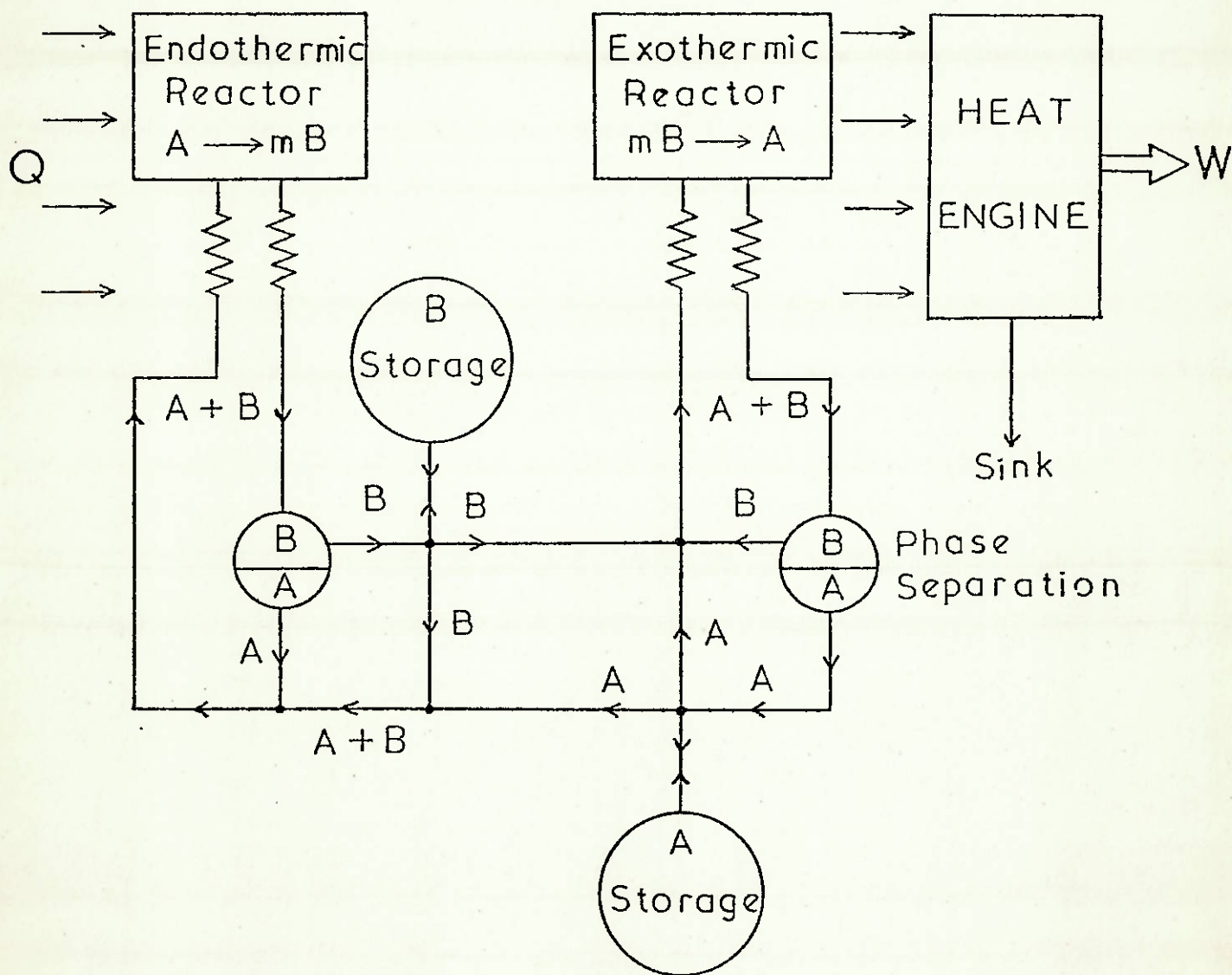
FIGURE 1(b):   Liquid/gas separating thermochemical
energy transfer system.
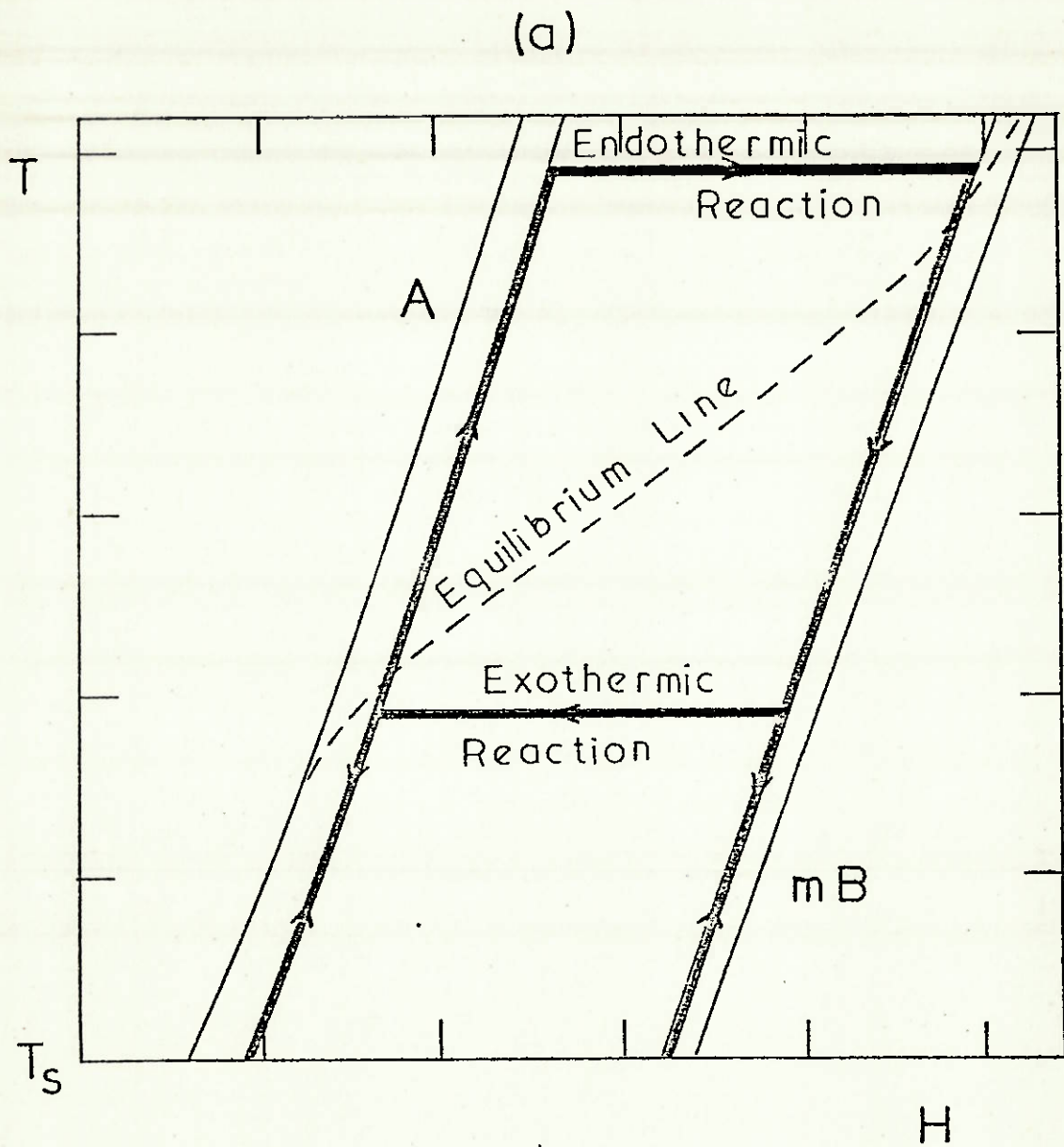
(a)

FIGURE 2(a):   Temperature-enthalpy diagram for a non-separating thermochemical energy transfer system with isothermal reactors.

(b)
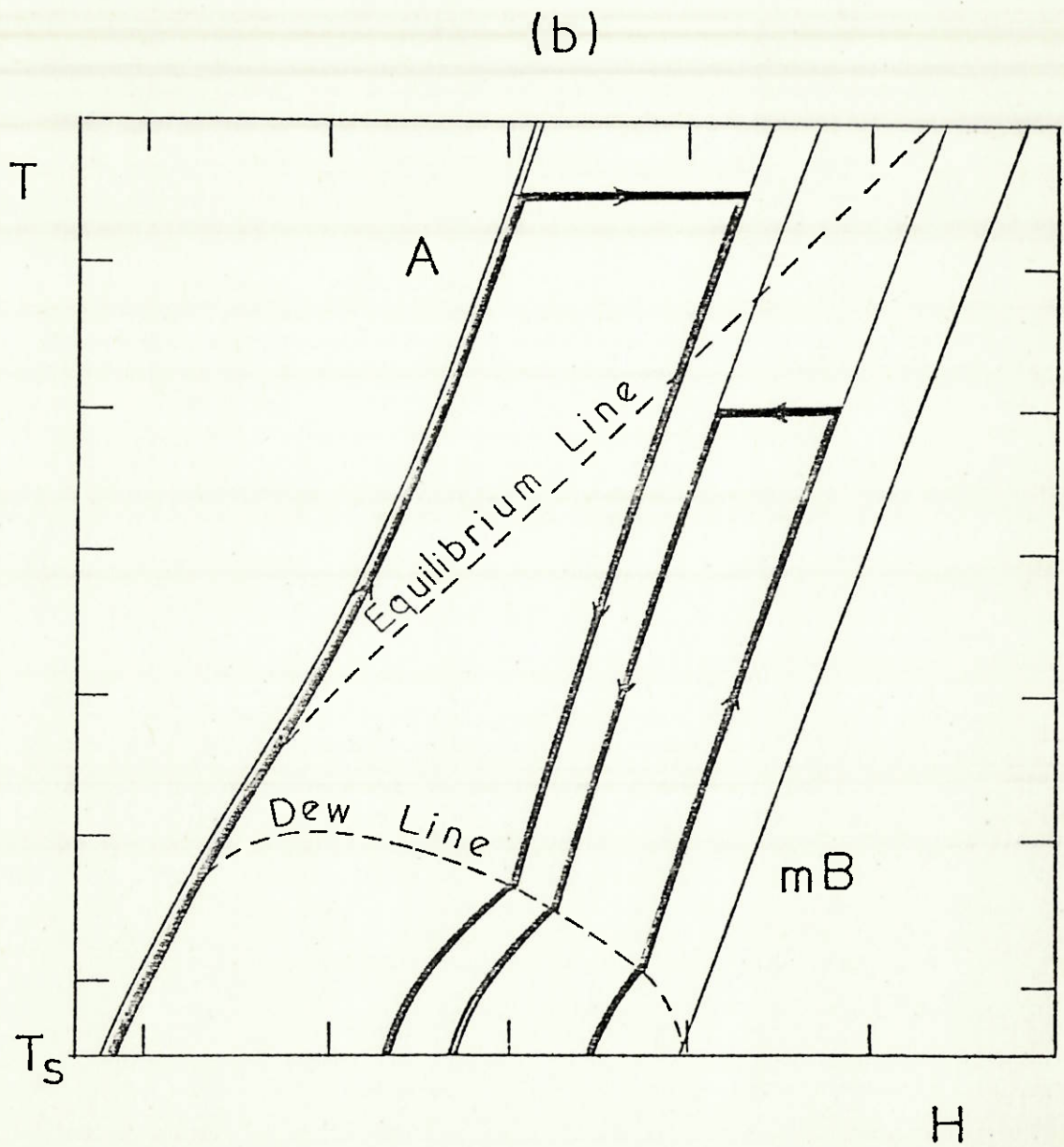
FIGURE 2(b): Temperature-enthalpy diagram for a liquid/
gas separating thermochemical energy transfer
system with isothermal reactors.
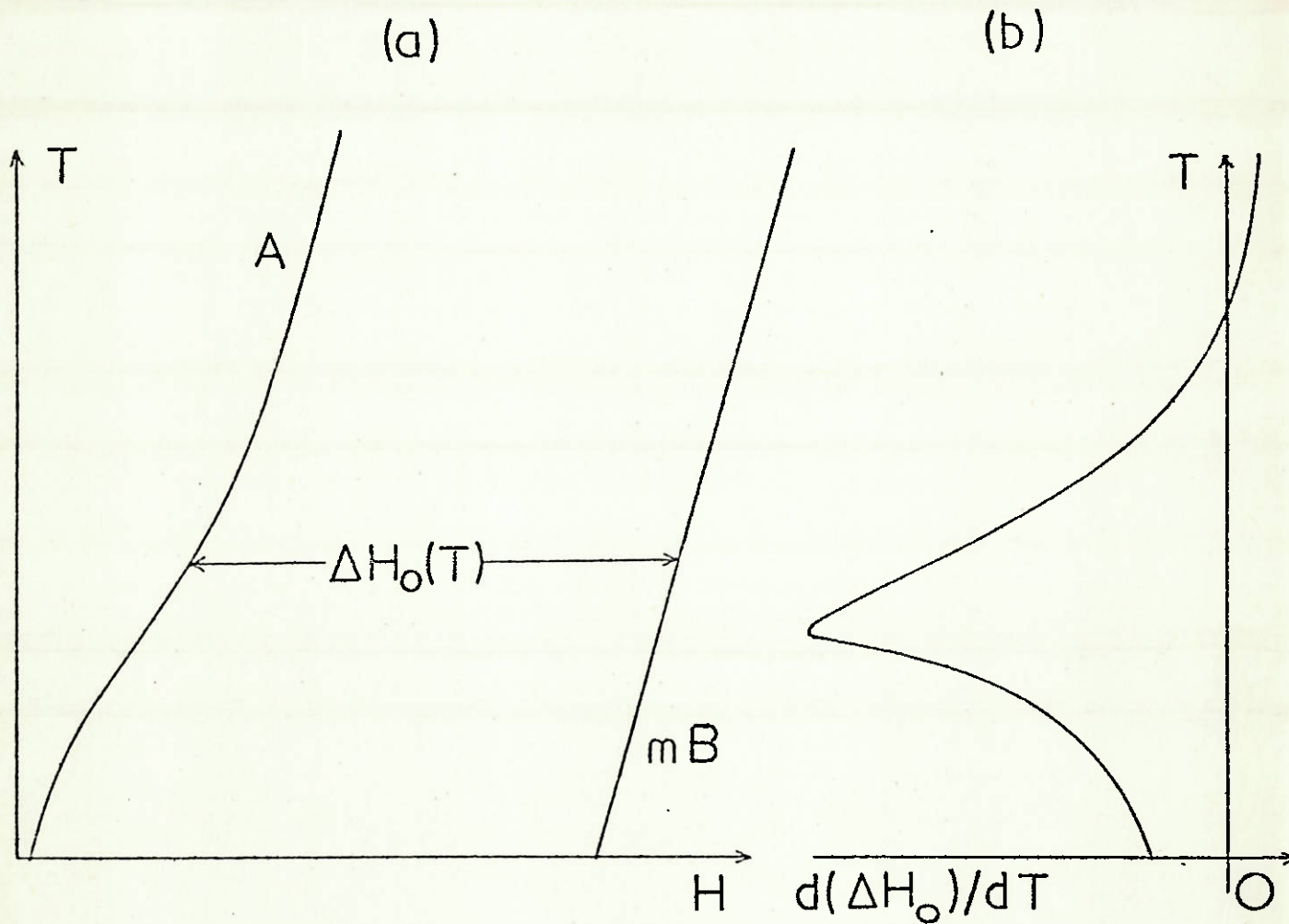
FIGURE 3(a): Extreme curves of the T-H diagram for a liquid/gas separating system.

FIGURE 3(b): Temperature spectrum of the external heat Q_{Ho} required by a reversible counterflow heat exchanger in which A is heated and B is cooled.
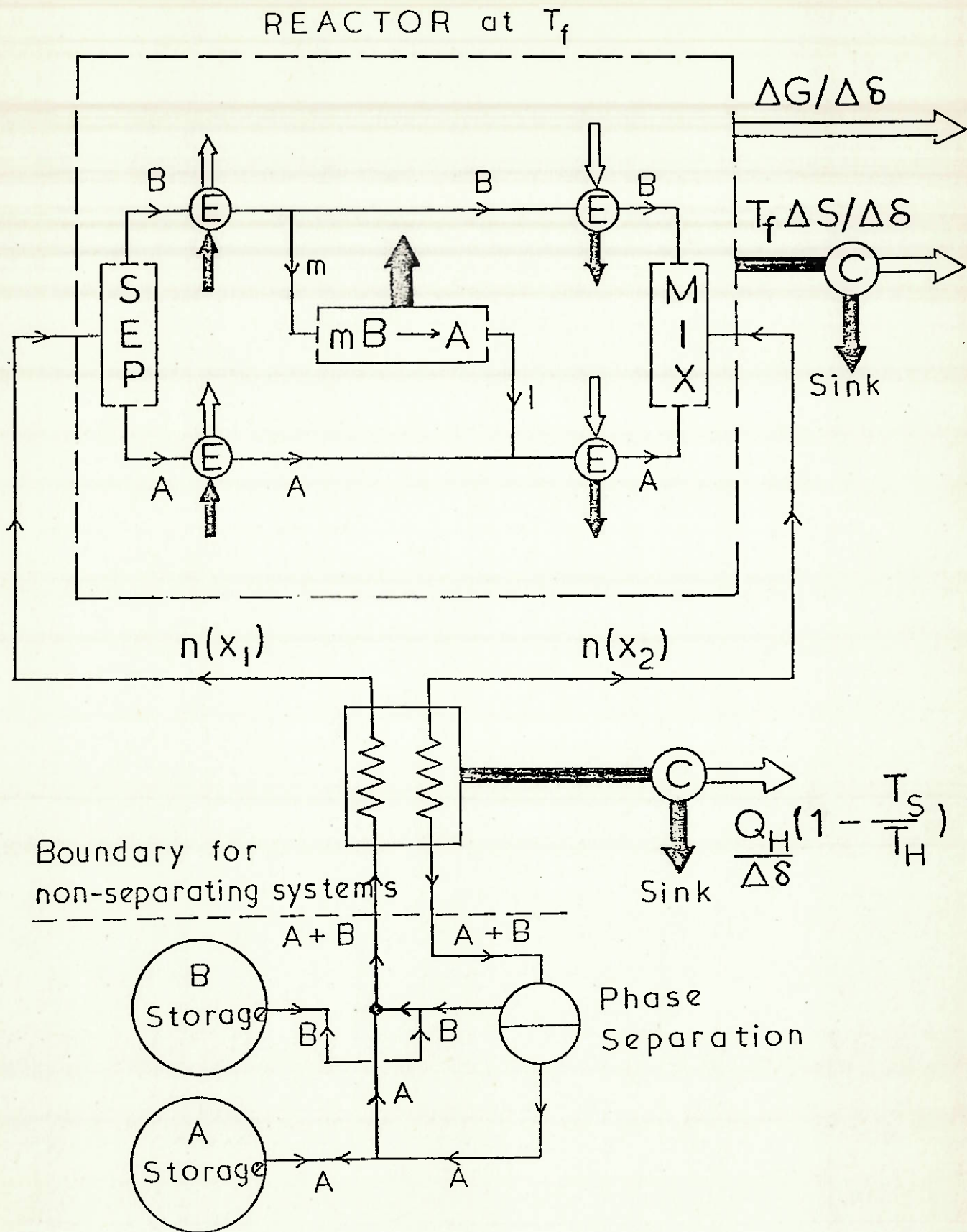
FIGURE 4: Energy transfer and work production from a reversible exothermic reactor and associated reversible counterflow heat exchanger

- - - - Semipermeable membrane
C   Carnot Engine
E   Reversible isothermal expansion engine at T_f.
══ Work
▬▬ Heat
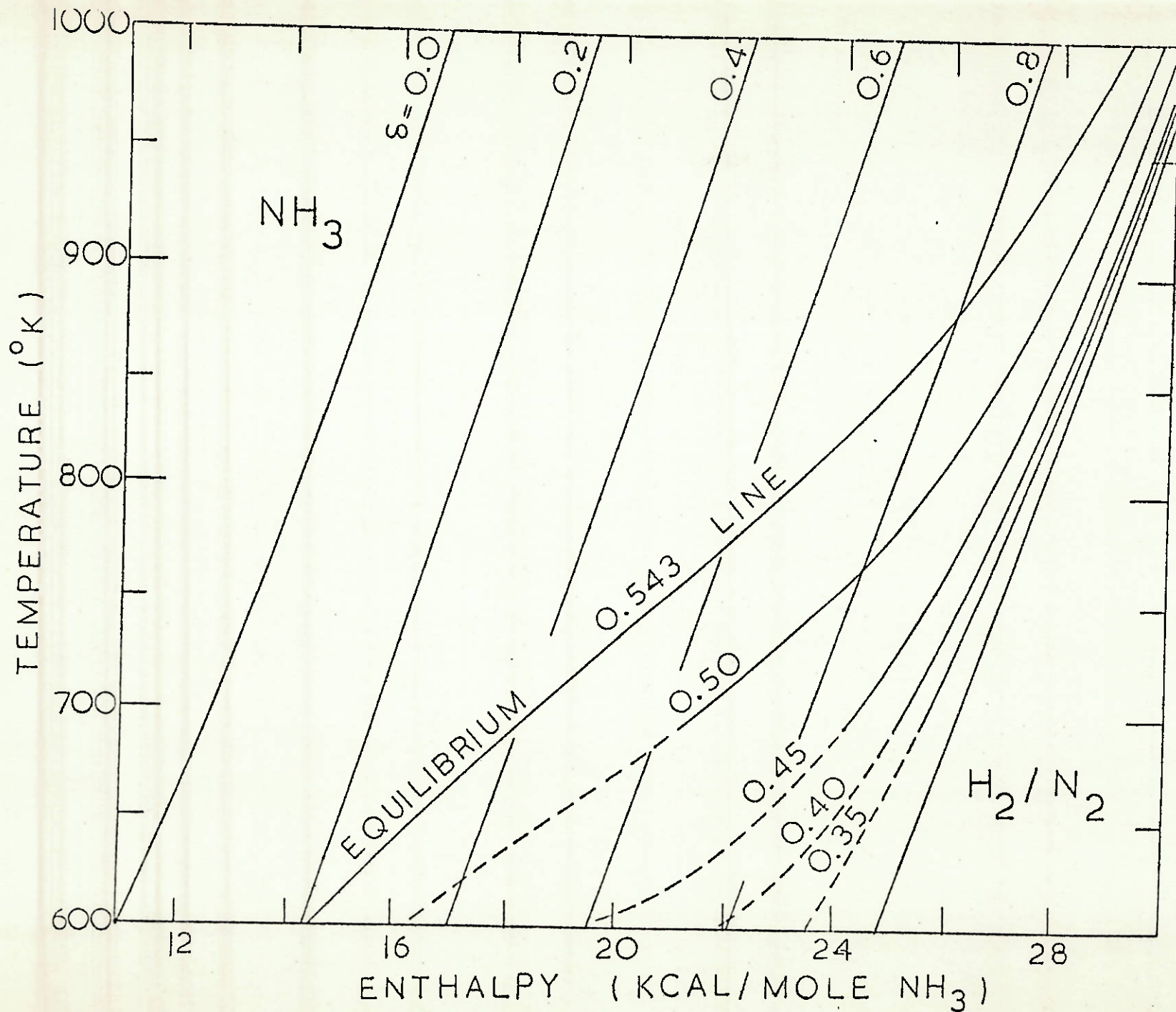
FIGURE 5: Curves of constant work recovery efficiency for the ammonia/3:1 hydrogen-nitrogen system at 300 atmospheres with $T_c = 300°K$. The ...ve ...re ...he ...uts... o...he ...al ...lution region.
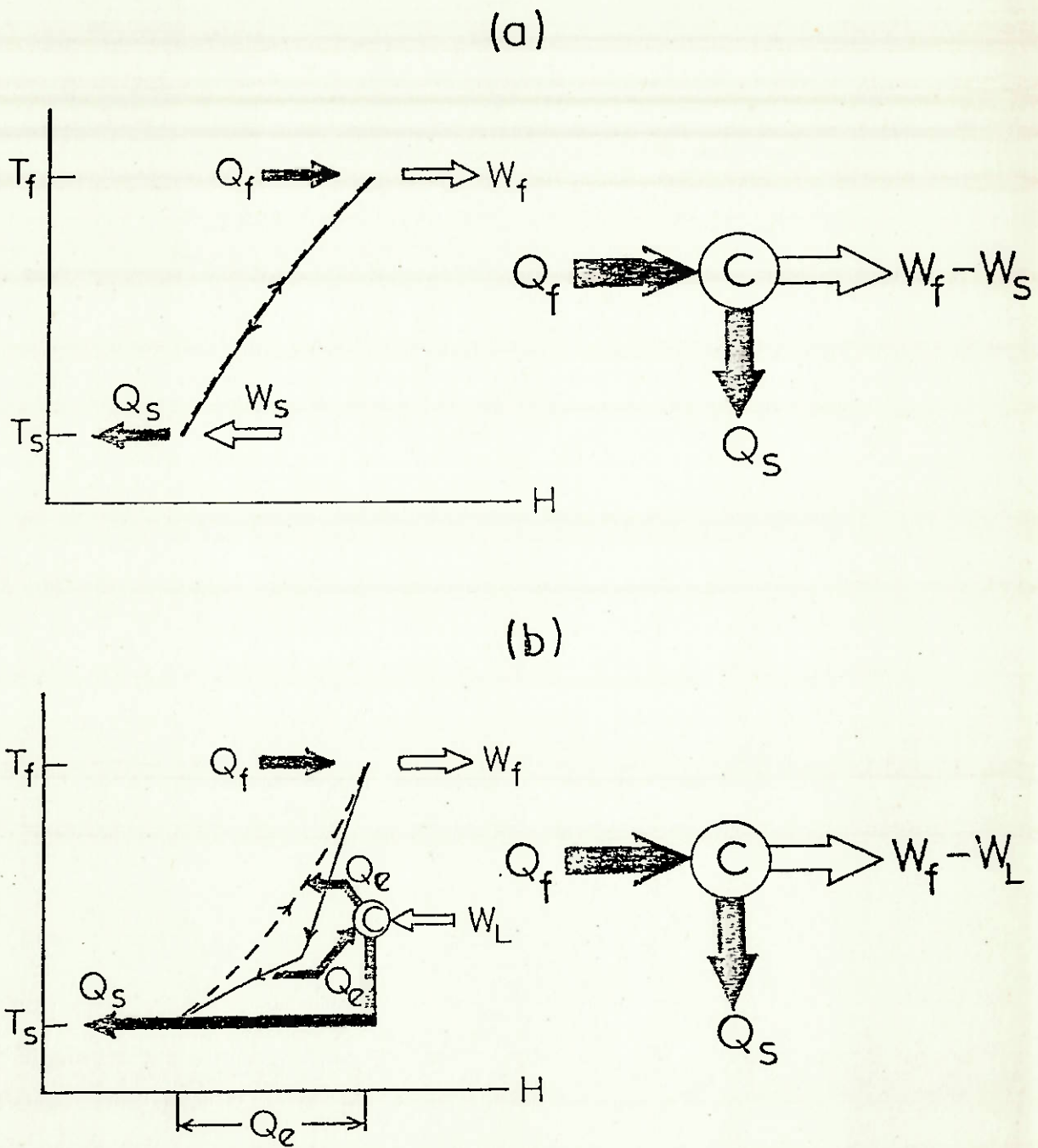
FIGURE 6: Origins of separation work shown by T-H diagram and equivalent single Carnot engine.

(a) Ideal solution with external separation.

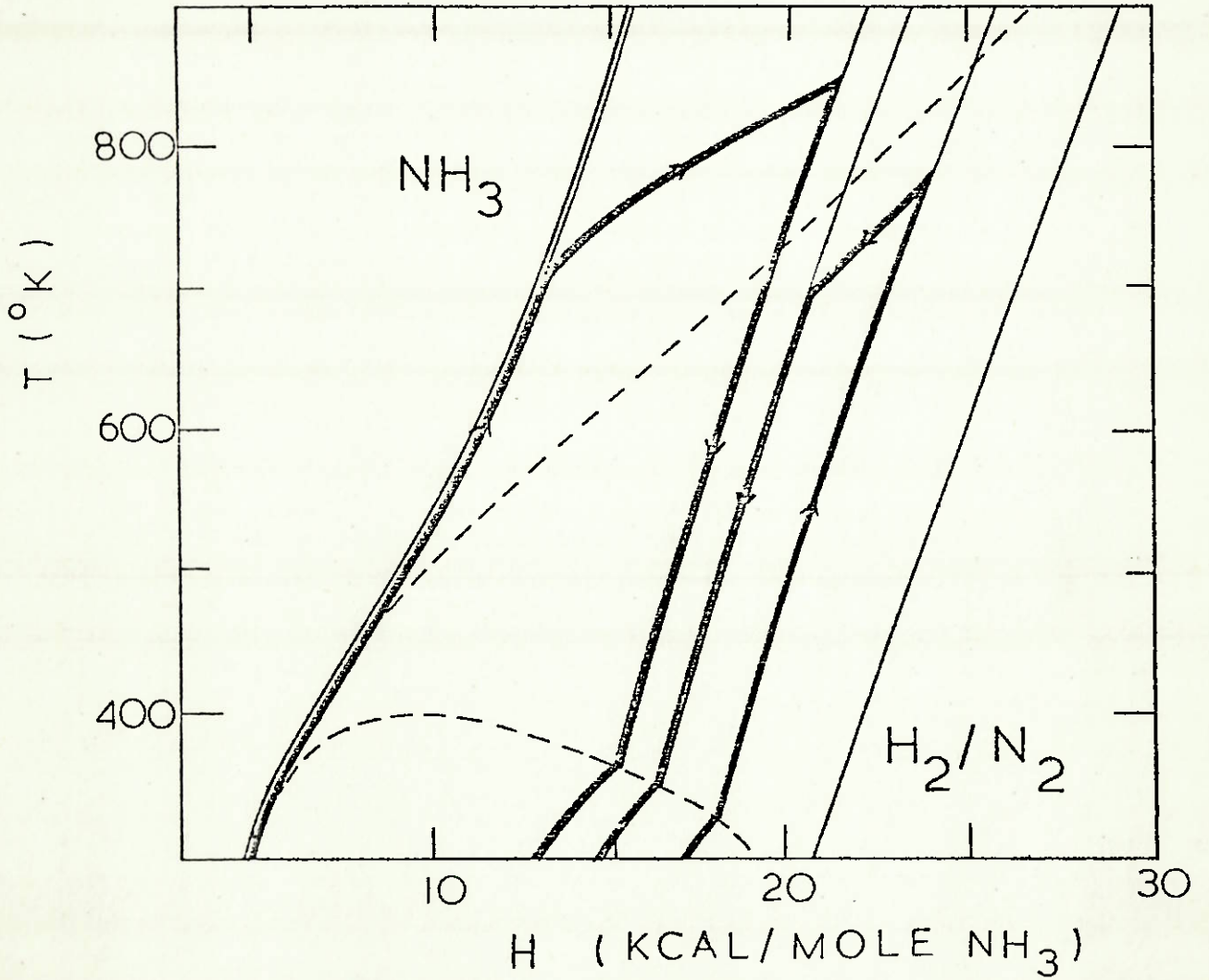(b) Liquid/gas phase separation.

(a)

FIGURE 7(a): Temperature-enthalpy diagram for a
thermochemical energy transfer system.
The diagram represents the ammonia/
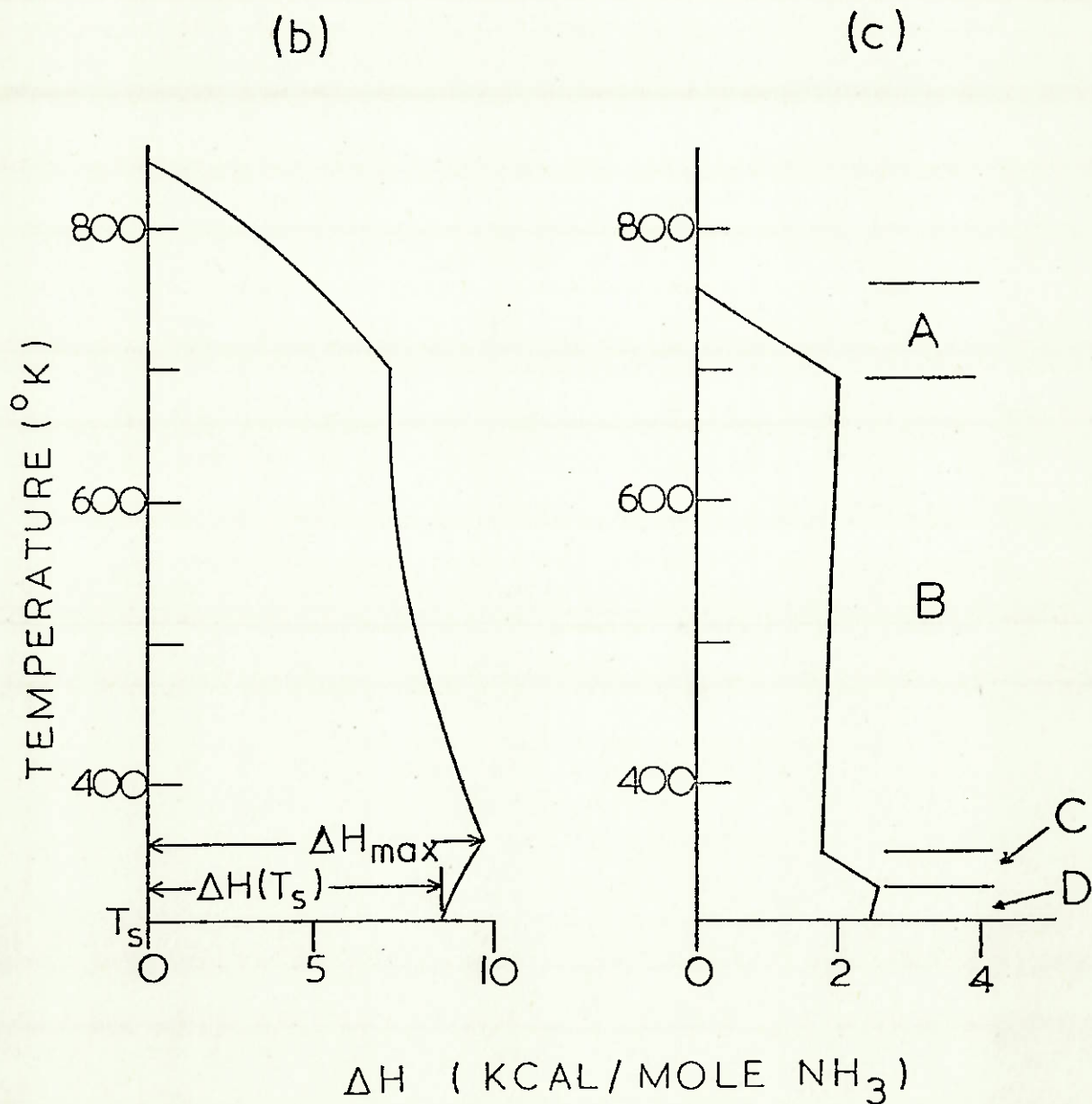hydrogen-nitrogen system at 300
atmospheres with $T_S = 300°K$.

FIGURE 7(b): Temperature profile of enthalpy changes occurring in the endothermic loop of Figure 7(a).

FIGURE 7(c): Temperature profile of enthalpy changes occurring in the exothermic loop of Figure 7(b) with the zones referred to in the text labelled A-D.