CONF-780802--5

LA-UR-78-938

TITLE: Irreversibility Analysis of Hydrogen Separation Schemes in Thermochemical Cycles.*

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SUBMITTED TO: To be presented at the 2nd World Hydrogen Energy Conference, 21-24 August 1978, Zurich, Switzerland, and to be published in the proceedings. (uncl.)

*Work completed under the auspices of the Division of Energy Storage Systems, United States Department of Energy.

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UNITED STATES
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DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

IRREVERSIBILITY ANALYSIS OF HYDROGEN SEPARATION SCHEMES IN THERMOCHEMICAL CYCLES*

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ABSTRACT

Six processes have been evaluated as regards irreversibility generation for hydrogen separation from binary gas mixtures. The results are presented as a series of plots of separation efficiency against the mol fraction hydrogen in the feed gas. Three processes, condensation, physical absorption and electrochemical separation indicate increasing efficiency with hydrogen content. The other processes, physical and thermal adsorption, and diffusion show maxima in efficiency at a hydrogen content of 50 mol percent.

Choice of separation process will also depend on such parameters as condition of feed, impurity content and capital investment. For thermochemical cycles, schemes based on low temperature heat availability are preferable to those requiring a work input.

INTRODUCTION

Currently there is wide apread interest in the development of a "hydrogen economy" as an eventual solution to many of the problems associated with the increasing energy crisis. Fossil fuel sources will become inadequate and eventually large-scale hydrogen production facilities will have to rely on nuclear fission, fusion and/or solar energy for the decomposition of water by electrolysis, or by thermochemical cycles, and perhaps, by hybrid combinations of these methods.

The potential higher efficiency and lower cost for thermochemical methods, versus the overall electrolysis path has been rather widely recognized. As a consequence, several laboratories throughout the world are conducting programs to develop thermochemical processes for water decomposition. A large number of thermochemical cycles have been conceived. Unfortunately, many have been published without experimental verification of the reactions or separation steps in the cycle. As a direct consequence, most evaluations and/or comparisons of thermochemical processes for process efficiency and cost have been based on assumed data or conditions that have not been achieved experimentally. Nevertheless, several cycles have now been published where all of the reactions have been demonstrated in the laboratory. As a result of this, the development of methods for engineering and cost analyses for this new technology can be based on the actual steps, both physical and chemical, involved in demonstrated cycles.

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In many of the demonstrated cycles for thermochemical production of hydrogen from water, hydrogen is produced in a reaction step in conjunction with other gaseous species. These gaseous species could either be other gaseous products or reactant gases or both in some instances. Separation of hydrogen from these gaseous species or impurities must therefore be performed to yield a pure product hydrogen. The energy expenditure involved in this separation may be of paramount importance in cycle selection and in the determination of the overall thermal efficiency of the cycle. Examples of thermochemical cycles that illustrate the above point are described briefly.

PROPOSED CYCLES

At the 1st World Hydrogen Energy Conference in March 1976, the General Atomic Co. presented a cycle based on sulfuric acid and iodine.[1] The cycle may be written simply as:

1. $2H_2O + SO_2 + x\ I_2 = H_2SO_4 + 2HI_x$ Aqueous — 300 K
2. $2HI_x = xI_2 + H_2$ — 350-650 K
3. $H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$ — 1100-1200 K

In the above cycle, hydrogen is obtained from the thermal decomposition of hydrogen iodide as seen in steps 4 and 5 which make up step 2.

4. $2HI_x = 2HI(g) + (x-1)I_2$
5. $2HI(g) = H_2 + I_2(g)$ — 360-625 K

Equilibrium conversion of HI varies from 8 percent at 360 K to 20 percent at 625 K; with actual data for HI decomposition over different catalysts showing lower than equilibrium conversion values.[2] Recycling of hydrogen iodide is thus required in step 5 due to its incomplete decomposition. In addition, hydrogen must be separated from the mixture of hydrogen iodide, iodine and hydrogen leaving the decomposition reactor.

Many cycles involving the iron-chlorine family employ the hydrolysis of iron (II) chloride for the hydrogen generation step as detailed.[3]:

6. $3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$ — 925 K

With an excess of water (steam) present, the product hydrogen must be removed from a gas stream containing steam, hydrogen chloride in addition to hydrogen. Condensation of the gas mixture yields a corrosive hydrochloric acid solution and product hydrogen. The difficulty with condensation as a practical method of hydrogen recovery in this case is that hydrogen chloride and water form an azeotrope from which both these species must be recovered for further use as a recycle stream. Also, the heat penalty in partly condensing a gas is significant. A suggested improvement in the separation

technique for this mixture involves the use of a dual step chemical sequence to isolate the gaseous products effectively as seen in 7 and 8.

7. $FeCl_2 + H_2O = FeO + 2HCl$ (red. atm.)

8. $FeO + H_2O = Fe_3O_4 + H_2$

Separation of hydrogen from the excess water is done in step 8 by condensation. Thus separation phenomena also play an important role in obtaining hydrogen from schemes such as these.

Gas separations are also important in the separation of oxygen from product gas streams; although this has not been emphasized nearly as much in thermochemical cycle literature it is still an important consideration bearing on cycle overall thermal efficiency. An example can be taken from the hybrid sulfuric acid cycle currently under intensive development at the Westinghouse Electric Corporation.[4] This cycle consists of two basic steps:

9. $2H_2O + SO_2 = H_2SO_4 + H_2$ (Electrolytic) 300-350 K

10. $H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$ 1100-1200 K

The hydrogen separation problem is overcome in this cycle by use of an electrolytic step, 9, however oxygen must be separated from the steam, oxygen, sulfur dioxide, and unreacted sulfur trioxide gas mixture leaving the sulfuric acid decomposer. In addition, sulfur dioxide must also be recovered for recycling to the elctrolyser.

The above examples serve to illustrate the importance of gas separation and the need for technology to perform these separations economically and efficiently in a thermochemical cycle.

The "ideal" or thermodynamic work of separation can easily be calculated given the compositions and physical conditions of the gas mixture and separated products. The actual work of separation and irreversibility produced in the separation process depends on the actual process used to effect the separation. Detailed calculation is necessary to obtain the separation work and the thermodynamic efficiency of the separation process.

The processes considered here for hydrogen separation from gas mixtures include conventional as well as novel technology. These processes include: condensation, diffusion and physical adsorption. Newer methods include an electrochemical separation method analogous to electrolysis that employs a solid polymer electrolyte. Adsorption of hydrogen on a metal substrate to form a metal hydride that can later be decomposed to yield hydrogen is an alternate method. Most of the methods involving a direct input of work, such as gas compression, are often highly-energy-intensive and show significant irreversibilities.

More efficient separation schemes such as the electrochemical scheme also involve work, however mechanical losses are avoided leading to less irreversibility.

The "ideal" and the actual work of separation as well as the irreversibility have been calculated for a variety of actual processes. The hydrogen concentration in the gas mixture was used as a parameter in the calculations. The plots obtained from these calculations may be of use to those concerned with the effect of separative work on the overall thermal efficiency of thermochemical cycles for hydrogen production by water-splitting.

THEORY

Separation processes are associated with each reaction step in the thermochemical process. Funk [5] has covered the work of separation for the chlorine-water Reverse Deacon reaction showing the variation of "ideal" work with the extent of reaction.

A short summary of the salient thermodynamics for separation processes taken largely from King [6] but also available in most thermodynamics texts is presented below.

Minimum Separation Work

The minimum isothermal work of separation of a binary gas mixture may be derived by postulating a continuous reversible process as seen in Figure 1.

For the case in which $P_1 \neq P_2$, it can readily be shown that:

$$11.\quad W_{min,T} = RT\left[x_F \ln \frac{P_2}{P_1 x_F} + (1-x_F)\ln \frac{P_2}{P_1(1-x_F)}\right]$$

This result is readily extended to that for a multicomponent mixture that is separated into a number of pure product streams.

$$12.\quad W_{min,T} = RT \sum_i x_{iF} \ln \frac{P_2}{P_1\, xi_F}$$

where W = Work per mole of inlet gas, (kJ/mol)

R = Gas Constant (8.314 J/mol.K)

T = Temperature (K), P - Pressure (Pa/atm)

x_F = Inlet hydrogen mol fraction

Note that the work requirements given by equations 11 and 12 above are reducible to equations 13 and 14, below, for products at the same pressure (and temperature) as the feed.

$$13.\quad W_{min,T} = -RT\,[x\ln x + (1-x)\ln(1-x)]$$

$$14.\quad W_{min,T} = -RT \sum_i x_{iF} \ln x_{iF}$$

If a binary gas stream is to be separated into product streams that are not completely pure but only enriched in a component, an analysis yields the following expression under isobaric and isothermal conditions.

$$15.\quad W_{min,T} = -\frac{RT}{x_1-x_2}\left\{(x_F-x_2)\left[x_1 \ln \frac{x_F}{x_1} + (1-x_1)\ln\frac{1-x_F}{1-x_1}\right] + (x_1-x_F)\left[x_2 \ln \frac{x_F}{x_1} + (1-x_2)\ln\frac{1-x_F}{1-x_2}\right]\right\}$$

These equations are more easily visualized in the form of a plot in which ($W_{min,T}/RT$) is plotted against x_F the inlet mol fraction of hydrogen.

A plot of Equation 13 is given in Figure 2 as the curve (1). Notice that an equimolal feed mixture has the maximum work of separation per mol of feed as compared to mixtures of any other composition. For a thermochemical cycle, the important quantity is the work of separation per mol of hydrogen separated from the feed. In this case, $W_{min,T}$ must be divided by the mol fraction of hydrogen in the feed mixture. A plot of this quantity, derived for conditions of 1 atmosphere and 300 K, is shown in Figure 3. Due to the necessity of having to process a larger quantity of feed to extract one mol of hydrogen from a lower as compared to a higher concentration feed, the minimum work requirement per mol of hydrogen will always be greater at the lower inlet concentration. This is clearly illustrated in Figure 3. Curve (2) in Figure 2 gives the minimum work of separation for the case of a binary feed where arbitrary product compositions, $x_1 = 0.95$ and $x_2 = 0.2$ are chosen. The important point to be made here is that the minimum work for separation into impure products is substantially less than that for separation into pure products. This was stated earlier by King.[6] The minimum work of separation, $W_{min,T}$, represents the lower bound on the energy consumed by a separation process. In actuality, the energy requirement may be many times greater than this minimum. It is also apparent that the term $W_{min,T}$ represents the increase in Gibbs free energy of the products over the input, thus:

$$16.\quad \Delta G_S = W_{min,T}$$

Quite often, the energy used to perform separations is in the form of heat rather than work. In cases such as these, a "net work consumption" of the process can readily be defined as the difference between the work attainable from that heat in a Carnot cycle and the work obtained from the reject heat also operating in a Carnot cycle. The sink of both Carnot engines is, of course, at ambient temperature, T_o, usually taken as 300 K. This net work consumption may be expressed simply as,

$$17.\quad W_n = QT_o\ (1/T_L - 1/T_H)$$

if no work is consumed in the process and if the enthalpy difference between the feed and products can be considered negligible.

Lastly, it is possible to define the "thermodynamic efficiency" of separation as the ratio of:

$$18.\quad \eta_S = W_{min,T}/W_n$$

The difference between W_n and $W_{min,T}$ is a measure of the irreversibility of the separation process, thus:

$$19.\quad I_S = W_n - W_{min,T},\ \text{or}\ I_s = W_n\ (1-\eta_s)$$

Examples illustrating these principles and exploring the energy requirements for single-stage processes in actual large-scale use for hydrogen purification (from methane) have been detailed by King.[6]

PROCESS EVALUATION

Six processes were selected for evaluation of irreversibility loss in separation of hydrogen from gas mixtures. The processes chosen included some that may be classed as known technology, e.g., condensation, physical absorption and diffusion; and others that are less well known and might be classed as newer technology. In this category are included physical and thermal adsorption, and electrochemical separation.

Input feed to the processes was a binary gas mixture at 1 atmosphere pressure, 300 K temperature containing hydrogen with a concentration varying from 0.1 to 0.9 mol fraction. The contaminant gas was assumed to be a substance such as hydrogen iodide, although other gases or mixtures of gases could just as easily have been chosen for the evaluation.

The separation process was assumed to be perfect in that pure components, hydrogen and hydrogen iodide, were the final product species. Commercially, less stringent conditions of purity are often specified depending on the end-use of the products, however in a thermochemical cycle, hydrogen product purity must remain high due to the necessity of recycling all intermediate chemicals.

Short descriptions and a brief explanation of the computational procedure follow for each of the processes selected for hydrogen separation. Numerical results for the process evaluation are presented in Table I.

1. Condensation

This process in which the total gas mixture is chilled in order to condense out hydrogen iodide leaving the non-condensable hydrogen in the gas phase is illustrated in Figure 4. Refrigeration is necessary to cool the feed gas mixture to the point at which the desired separation takes place between the hydrogen gas and the hydrogen iodide liquid that is condensed out. The cold products are used to recuperatively chill as much of the feed gas as possible.

Properties of hydrogen iodide used in the calculations include:

a. Normal boiling point: -35.38 C (237.74 K)

b. Melting point: -50.8 C (222.3 K)

c. Heat of Vaporization: 18.83 kJ/mol (4.5 kcal/mol) (estimated)

The calculation assumes cooling to a low enough temperature so that the vapor pressure of the hydrogen iodide in the product hydrogen is negligible, and that the refrigeration duty covers the heat of vaporization of the hydrogen iodide, the incoming feed is assumed to be cooled by the departing product gases. Thus if the refrigeration circuit is a reversible heat pump, its net work consumption corresponding to the refrigeration duty is,

$$20. \quad W_n = Q_r \cdot (T_o - T_r)/T_r$$

where Q_r refers to the refrigeration duty and T_r, the cool temperature has been taken as 235 K in this case. In an actual situation, the refrigeration cycle is irreversible and its thermodynamic efficiency is taken nominally as 0.35. The results are shown in Figure 5. The separation efficiency for this process clearly depends on the refrigeration duty which, in turn, depends on the amount of hydrogen iodide in the feed mixture. Thus, the separation efficiency increases with the purity of the feed mixture, expressed from the hydrogen viewpoint.

2. Physical Absorption

The second process envisions one in which the contaminant gas is absorbed in a liquid absorbent. The heat of absorption is assumed negligible and the absorbent for hydrogen iodide is left unidentified. Reclamation of the hydrogen iodide is done in a stripping column in which the loaded absorbent is heated by steam coils to a temperature high enough to lower the solubility of hydrogen iodide thus effecting its recovery. The regenerated

absorbent liquid is then recycled to the absorber for contact with the feed gas. A schematic of this process is shown in Figure 6.

Assumed quantities are:

a. 400 kg absorbent/kg mol of hydrogen iodide

b. Absorber temperature: 300 K

c. Stripper temperature: 400 K

The heat duty in the stripper column is simply a linear function of the hydrogen iodide content of the entering gas mixture. The net work is obtained by multiplying the heat duty by a Carnot factor based on the temperatures of the stripper and the absorber. The results of the evaluation for this process are shown in Figure 7. As in the previous case with the condensation process, the separation efficiency is seen to rise with the hydrogen content of the feed gas. The result is intuitively obvious as the heat duty for separation increases with the amount of material that has to be absorbed, or inversely with the feed's hydrogen content.

3. Diffusion

Diffusional separation processes have long been recognized as ones capable of performing gaseous separations by application of the correct membrane. Palladium metal has the unique property of allowing hydrogen to diffuse through it at significant rates and at the same time not transmitting other gases to any appreciable amount. A schematic diagram of a diffusion process for hydrogen separation is shown in Figure 8. To achieve significant rates and to prevent adsorption of the hydrogen iodide species on the palladium surface, the diffusion vessel is operated at 615 K. The feed gas is heated by the effluent gases and by a furnace. A partial pressure difference must be maintained in order to provide a concentration gradient for the diffusion process. The inlet gas mixture is compressed 30 atmospheres pressure, the hydrogen product being released at atmospheric pressure. The hydrogen iodide product is expanded through an expansion engine to recover some of the work of compression. The net work for this process is supplied in two parts, the larger portion is due to the actual work of compression, the lesser part is the net work supplied by the heat input to the furnace.

Assumptions made were that the compression efficiency (isothermal work/actual work) was 0.7. This efficiency was also used for the expander.

The results for the diffusion process are illustrated in Figure 9. It may be noted that the separation efficiency initially rises as hydrogen content increases and reaches a plateau at a hydrogen concentration from 0.3 to 0.5 mol fraction. At concentrations of hydrogen greater than 0.5 mol fraction, the separation effiency decreases. At first sight, it appears that this behavior is anomalous from that of the two previous cases, condensation and physical absorption, that were discussed earlier.

The reason for the curve exhibiting a maximum point is that initially at low hydrogen levels, work is recovered from the effluent hydrogen iodide stream. At moderate (0.3-0.5 mol fraction) hydrogen concentrations, the net work increases however the theoretical work also increases, leading to a higher value of the separation efficiency. As the hydrogen content of the feed gas is further increased, the net work increases but the theoretical work decreases leading to lower efficiency.

This result is somewhat similar to what is expected from examination of the theoretical work requirement graph shown earlier in Figure 2.

4. Physical Adsorption

A physical adsorption process based on molecular sieves was developed at Linde [7] to provide a high purity hydrogen product containing small amounts of impurity in the parts-per-million range. Figure 10 illustrates the principle of both presssure swing and thermal swing adsorption. The two curves are isotherms that show how the loading of a given adsorbate increases with the partial pressure of the adsorbate at two different temperatures. A pressure swing cycle operates between two pressures at the same temperature, adsorbing at the higher pressure and desorbing at the lower. A thermal swing cycle, on the other hand, operates between two different temperatures, but at the same pressure.

In practice, a characteristic of pressure swing cycles is a loss caused by blowdown and purging of the adsorbent bed. By judicious operation, these losses may b minimized by increased pressure, with recoveries in the 99 percent range. Basically then, the energy requirements for pressure swing adsorption come from compression of the feed gas to allow the adsorption to take place. As the impurity is the species adsorbed, the hydrogen passes through essentially unreduced in pressure. In these calculations, the hydrogen is allowed to expand to atmospheric pressure to recover some of the work of compression. The adsorption is assumed to take place at a pressure of 30 atmospheres.

Results for this process of gas separation are shown in Figure 11. There is a striking similarity of the shape of the curve obtained for physical adsorption to that of the diffusion process presented earlier. Both processes depend on compression work rather than on thermal energy. Thus the characteristics of the processes as regards separation efficiency are bound to be similar in nature.

5. Thermal Adsorption

This process has been described above and is illustrated in Figure 10. The feed gas must be introduced to the adsorber at ambient temperature. On loading of the bed, heating brings about desorption. Both pressure and thermal swing adsorption processes are by their very nature, batch processes, and as such possess certain disadvantages as compared to the alternate processes discussed that are continuous in operation.

A desorption temperature of 600 K was chosen with no thermal recuperation of the adsorbed gas species. Again, no heats of adsorption or of desorption were assumed, thus the thermal requirement was provided as sensible heat to the adsorbed species. The results seen in Figure 12 show a similarity to those for physical adsorption as well as for the diffusion process. The relative high value of the separation efficiency maximum at 50 mol percent hydrogen is due to the relatively small heat load caused by raising the temperature of only half the feed (on a molar basis) to 600 K.

6. Electrochemical Separation

Hydrogen may be separated from an inert (to the membrane) gas by an electrochemical scheme such as shown in the schematic of Figure 13. The gas mixture is fed to the anode where hydrogen contacts the solid polymer electrolyte (SPE) - electrode interface.[8] Upon application of external work (electricity), hydrogen is transformed into protons, releasing electrons to the edternal circuit. The protons move across the SPE to the cathode where they recombine to form pure molecular hydrogen, leaving behind the impurity gas species in the anode compartment. The hydrogen can also be "pumped" electrochemically to high pressures in this scheme.

The applied voltage to sustain current density is that required to overcome resistive losses plus that required by the Nernst equation to raise hydrogen from its partial pressure (P_1) on the anode to the cathode partial pressure (P_o). The relationship is given below.

$$21. \quad E = IR + \frac{0.059}{2} \log (P_o/P_1)$$

Corrections can be made to this equation to take into account the variation of hydrogen partial pressure through the anode compartment as the effluent gas will be depleted in hydrogen.

Assuming the actual work requirement to be twice that of the reversible work obtained from Nernst's equation, the results shown plotted in Figure 14 are obtained.

It can be seen that the separation efficiency rises monotonically in this process for hydrogen separation. The efficiency rises to a maximum as the hydrogen concentration reaches unity as expected. This is due to the fact that the electrochemical work tends to the value of the theoretical work of separation as the mol fraction of hydrogen in the gas mixture rises to unity.

DISCUSSION

Several processes have been evaluated for the purpose of determining the separation efficiency or irreversibility generation on separating hydrogen from a hypothetical binary gas mixture. Three processess, condensation, physical gas absorption and electrochemical separation show separation efficiencies increasing monotonically with increasing inlet hydrogen concentration.

These processes essentially expend energy in proportion to the amount of impurity that has to be removed and hence as the hydrogen concentration is increased, less energy is used and the separation efficiency rises. A different type of separation efficiency behavior with respect to the inlet mol fraction hydrogen is observed in the three other processes studied, diffusion, physical and thermal adsorption. In these latter cases, the separation efficiency rises initially with mol fraction hydrogen reaching a maximum at 50 mol fraction, the efficiency then drops as the inlet mol fraction of hydrogen is further increased. This effect is due to work that has to be provided to the total mixture that is not recovered as the hydrogen content of the feed gas increases.

The above results should serve as a guide in selection of alternate processes for gas purification in thermochemical cycles. Actual dictation of the process to be employed for such separation must depend on intimate knowledge of the conditions and actual concentrations of gaseous species in the hydrogen-containing stream. Chosen in the above examples was a feed stream at 1 atmosphere pressure and 300 K temperature. In many cases, feeds will be pressurized and at higher temperatures. The higher pressure will be of definite economic benefit to any thermochemical process as hydrogen at 1 atmosphere pressure requires compression for transport by pipeline or for use in further chemical syntheses. An economic calculation was done illustrating this point and the results are presented in Figure 15. Chosen as parameters for this calculation were compression ratio as well as the cost of electricity (work) in mil/kWh. (1 mil = 10^{-3}\$). The results were expressed in additional cost that would have to be added to a thermochemical or any type of hydrogen production process if additional gas compression were required. The right hand ordinate indicates the initial pressure of the hydrogen for a final delivery pressure of 50 atmospheres. As an example of use, assume an initial pressure of 1 atmosphere, a final pressure of 50 atmospheres (compression ratio = 50) and a work (electricity) cost of 5 mil/kWh. The cost of hydrogen compression is then seen to be equivalent to \$1/10^6 BTU or approximately equal to \$1/gJ hydrogen equivalent energy.

In addition to the above considerations, the choice of separation process will also be dictated by capital investment. Diffusional processes that depend on palladium, an expensive metal, probably require a greater investment than do condensation processes. Also, of critical importance in thermochemical cycles is the availability of energy. Processes that can use low temperature thermal energy such as physical absorption or thermal adsorption are probably favored over processes that require work for separation, such as diffusion or electrochemical separation. Many thermochemical cycles indicate exothermic low temperature reactions that would possibly yield energy to perform the desired gas separations.

REFERENCES

1. J. L. Russell, et al., "Water Splitting - A Progress Report," Proc. First World Hydrogen Energy Conference, Vol. I., 1A-105, March 1-3, 1976, Miami Beach, Florida.

2. J. H. Norman, et al., "Water Splitting - The Chemistry of the I_2-SO_2-H_2O Reaction and the Processing of H_2SO_4 and HI Products," Report GA-A14746, General Atomic Co , San Diego, California, December 1977.

3. K. F. Knoche, et al., "Feasibility Studies of Chemical Reactions for Thermochemical Water Splitting Cycles of the Iron-Chlorine, Iron-Sulfur and Manganese-Sulfur Families," Int. Journ. of Hydrogen Energy, Vol. 2, 269-289, 1977.

4. G. H. Farbman, "Hydrogen Generation Process," Report FE-2262-15, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania, June 1977.

5. J. E. Funk, "Thermochemical and Electrolytic Production of Hydrogen from Water," Proc. USA-Japan Joint Seminar on Key Technologies for the Hydrogen Energy System, Tokyo, Japan, July 1975.

6. C. J. King, "Separation Processes," McGraw-Hill, New York, 1971.

7. H. A. Stewart and J. L. Heck, "Pressure Swing Adsorption," Chem. Eng. Progr., 65(9), 78-83, 1969.

8. J. McElroy, "Solid Polymer Electrolyte Hydrogen Separator/Pump," Private Communication, General Electric Co., Wilmington, Massachusetts, August 1977.

TABLE I

RESULTS OF PROCESS EVALUATION

Process		1. Condensation		2. Phys. Absorp.		3. Diffusion		4. Phys. Adsorp.		5. Therm. Ads.		6. Elect. Sept.	
x_{H_2} Mol Fract.	W_{min} (T=300K) kJ/mol	W_{net} kJ/mol	η_S	W_{net} kJ/mol	η_S	W_{net} kJ/mol	η_S	W_{net} kJ/mol	η_S	W_{net} kJ/mol	η_S	W_{net} kJ/mol	η_S
0.1	0.82	13.6	0.06	18.8	0.04	6.53	0.13	11.0	0.07	4.39	0.19	22.8	0.04
0.2	1.25	12.0	0.11	16.7	0.07	7.20	0.17	10.4	0.12	4.39	0.28	16.0	0.08
0.3	1.50	10.5	0.14	14.6	0.10	7.82	0.19	9.71	0.15	4.39	0.34	12.0	0.13
0.4	1.64	9.04	0.18	12.6	0.13	8.49	0.19	9.05	0.18	4.39	0.37	9.08	0.18
0.5	1.74	7.53	0.23	10.5	0.17	9.16	0.19	8.40	0.21	4.39	0.40	6.86	0.25
0.6	1.64	6.02	0.27	8.37	0.20	9.79	0.17	7.74	0.21	4.39	0.37	5.06	0.32
0.7	1.50	4.52	0.33	6.28	0.24	10.5	0.14	7.08	0.21	4.39	0.34	3.54	0.42
0.8	1.25	3.01	0.41	4.18	0.30	11.1	0.11	6.43	0.19	4.39	0.28	2.21	0.56
0.9	0.82	1.51	0.55	2.09	0.39	11.8	0.07	5.77	0.14	4.39	0.19	1.05	0.78

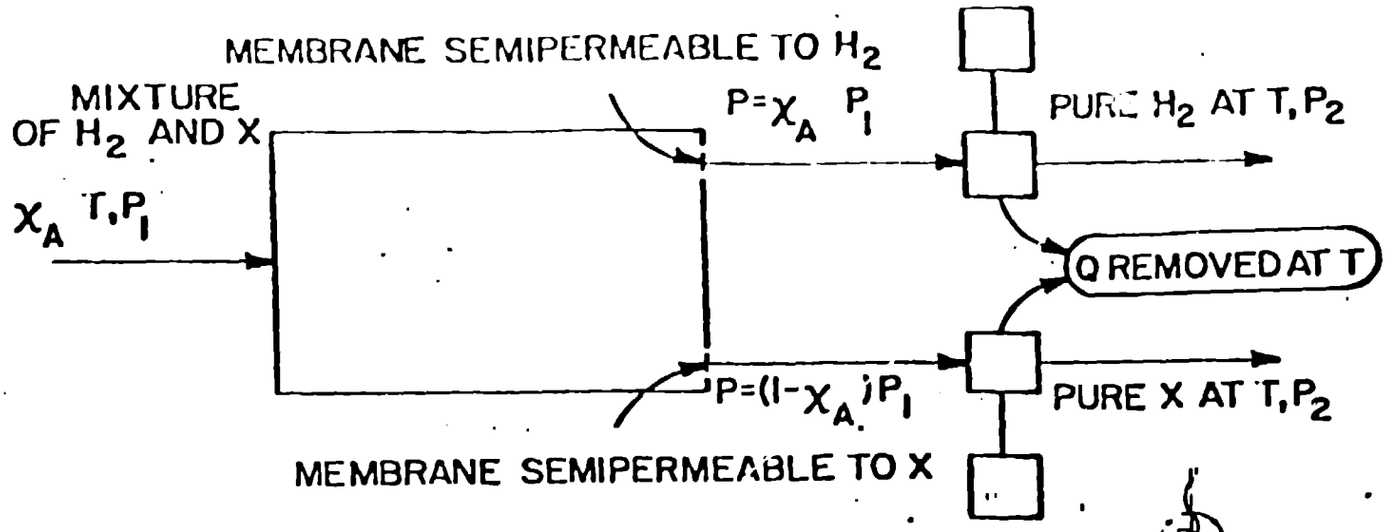

FIGURE 1 REVERSIBLE SEPARATION OF A BINARY GAS MIXTURE INTO PURE COMPONENTS

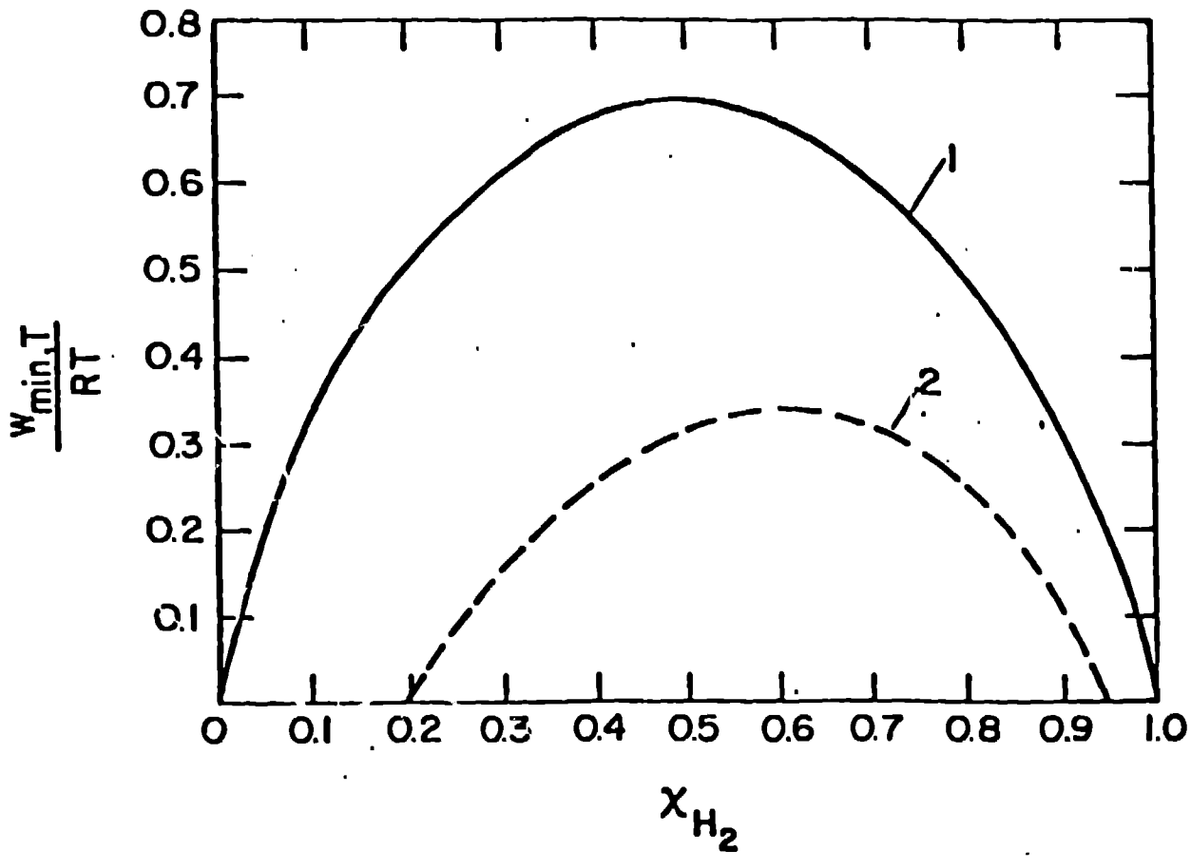

FIGURE 2 MINIMUM (THEORETICAL) WORK OF SEPARATION FOR A BINARY GAS MIXTURE

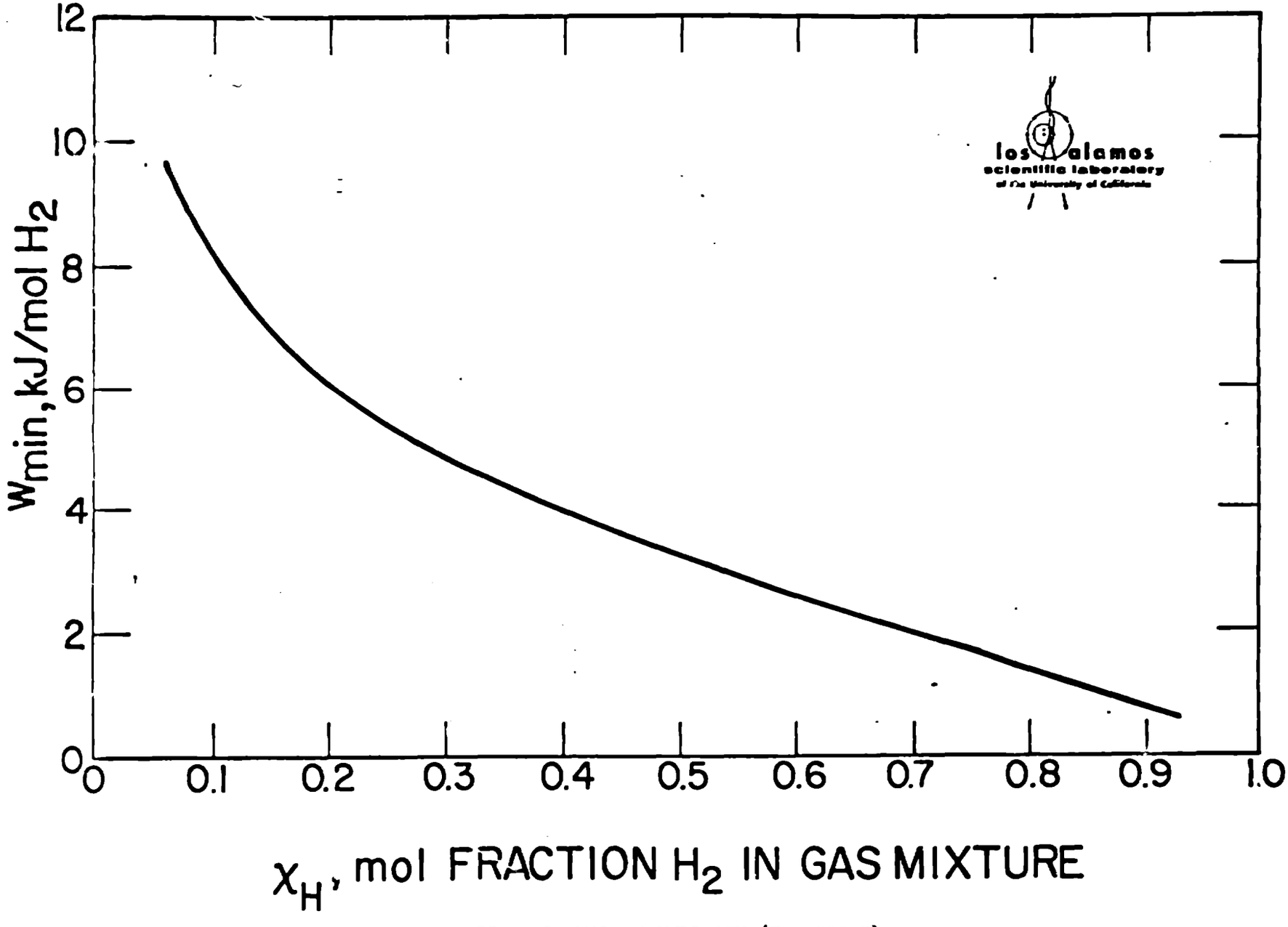

FIGURE 3 MINIMUM WORK OF SEPARATION PER MOL OF HYDROGEN (T = 300 K)

KEC

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scientific laboratory
of the University of California

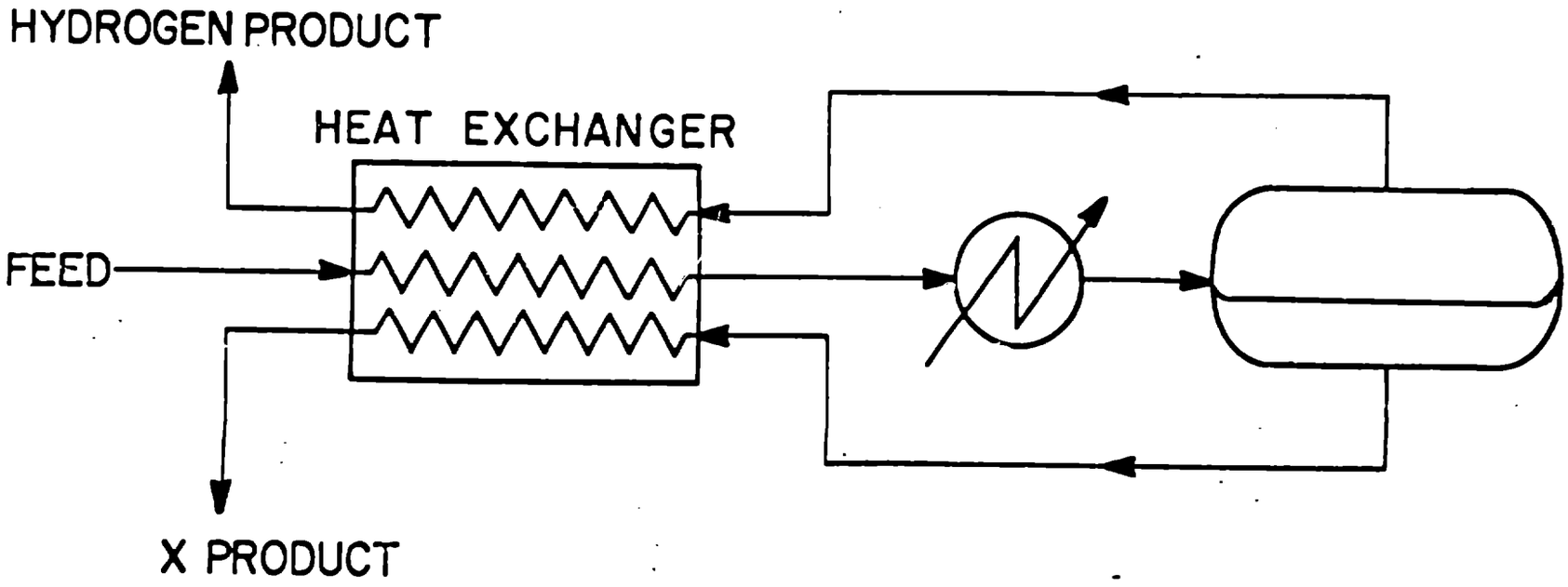

FIGURE 4 CONDENSATION PROCESS FOR SEPARATION OF HYDROGEN

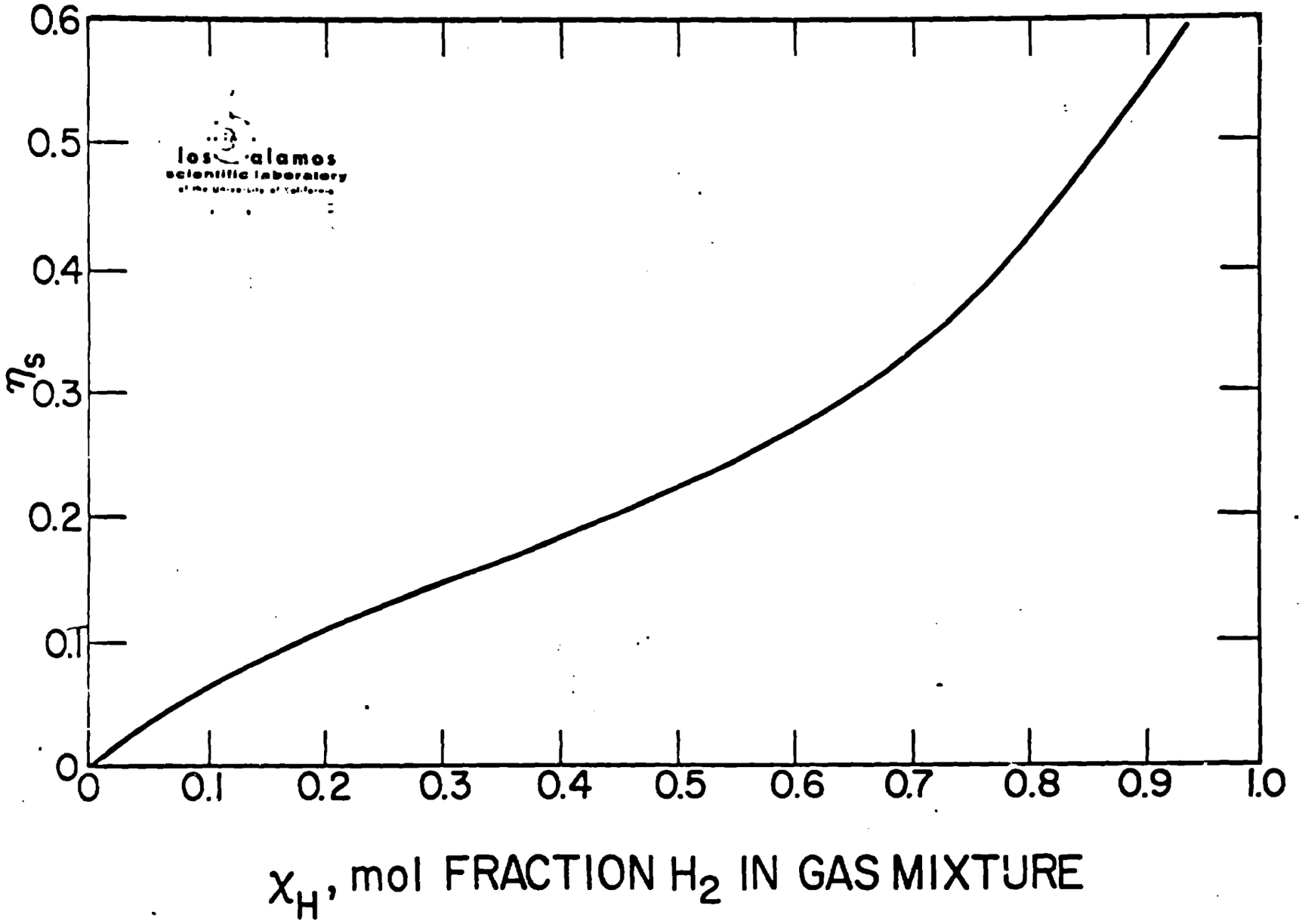

FIGURE 5 SEPARATION EFFICIENCY - CO. 'NSATION PROCESS

KEC

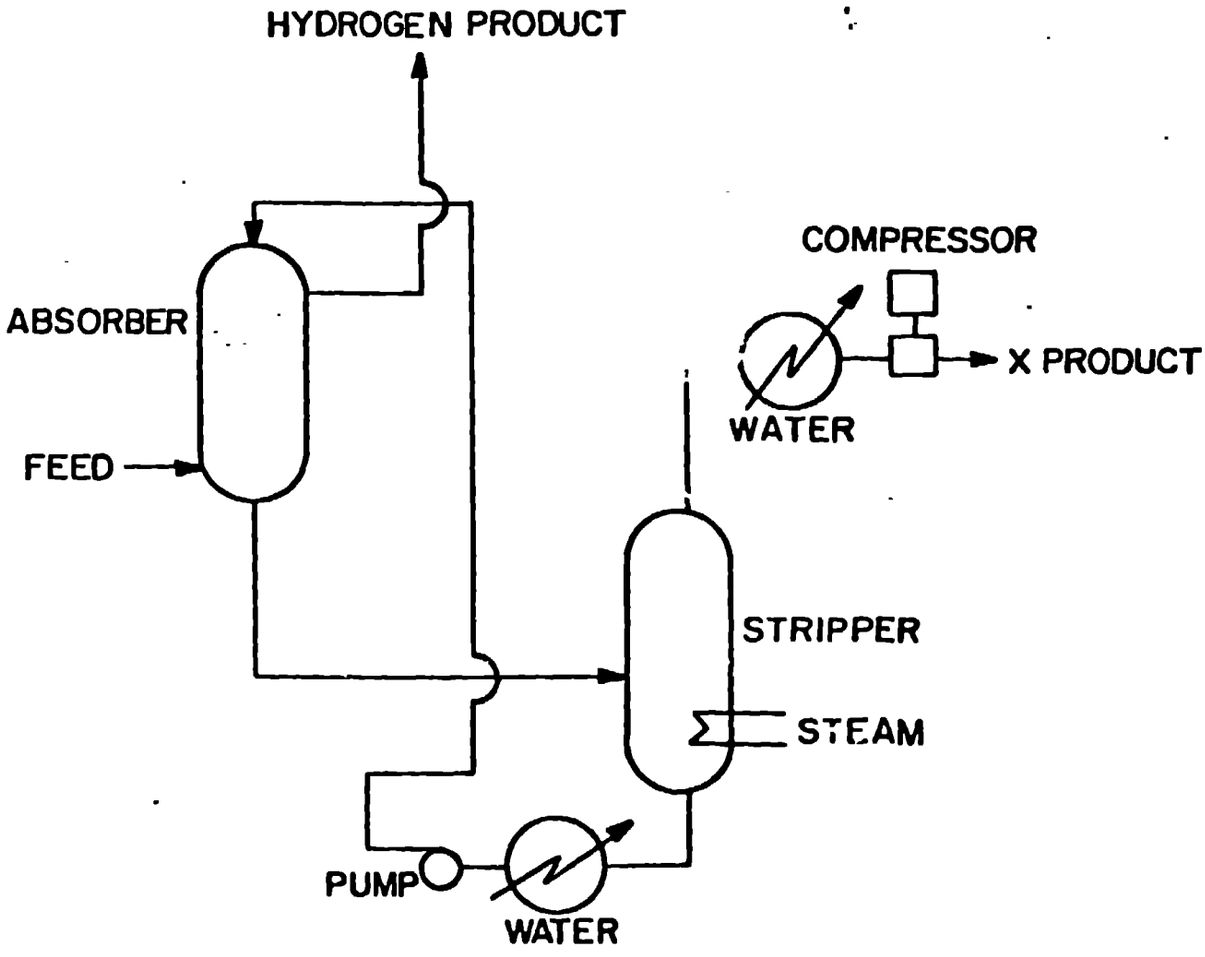

FIGURE 6 PHYSICAL ABSORPTION PROCESS FOR SEPARATION OF HYDROGEN

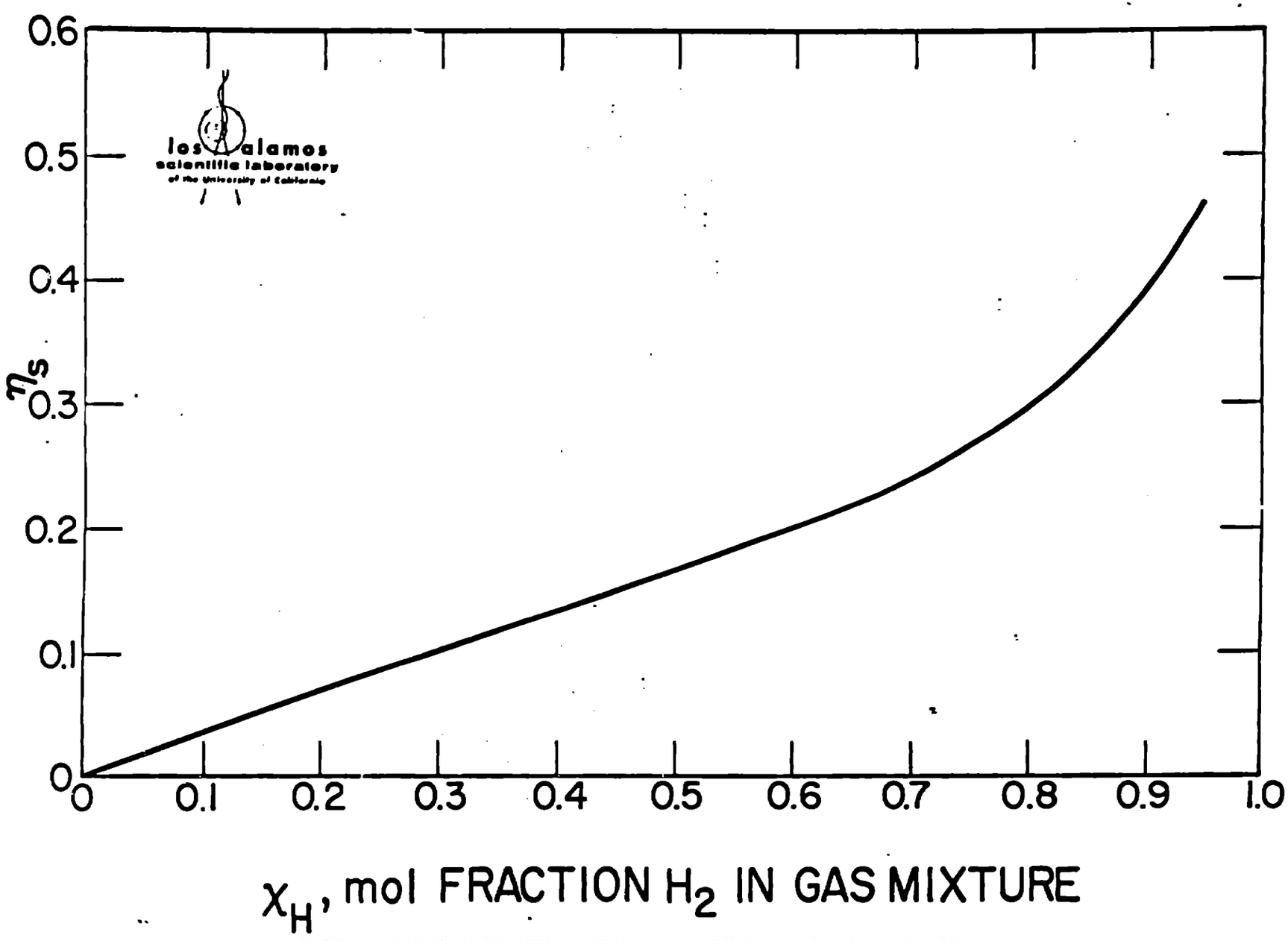

FIGURE 7 SEPARATION EFFICIENCY - PHYSICAL ABSORPTION PROCESS

KEC

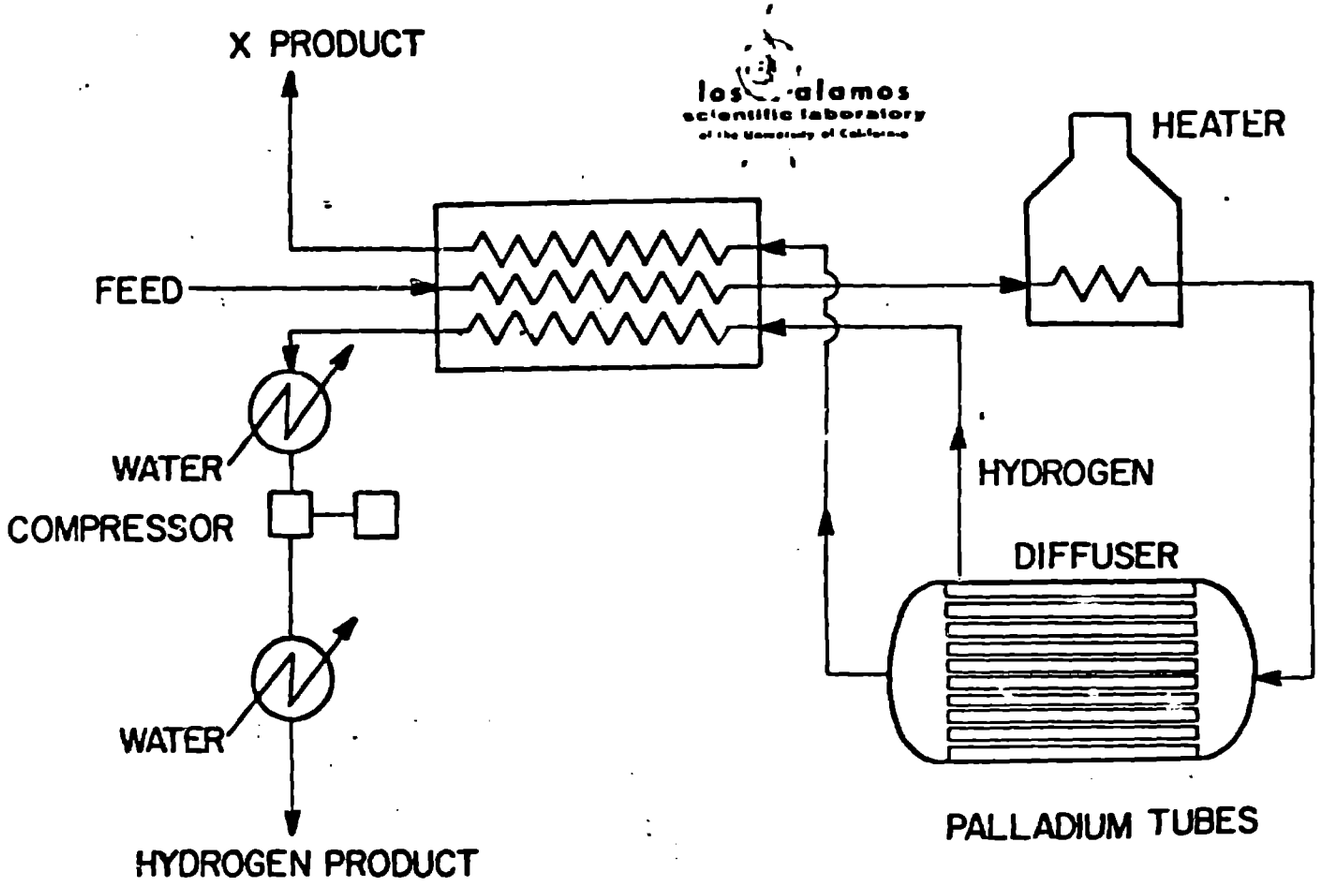

FIGURE 8 DIFFUSION PROCESS FOR SEPARATION OF HYDROGEN

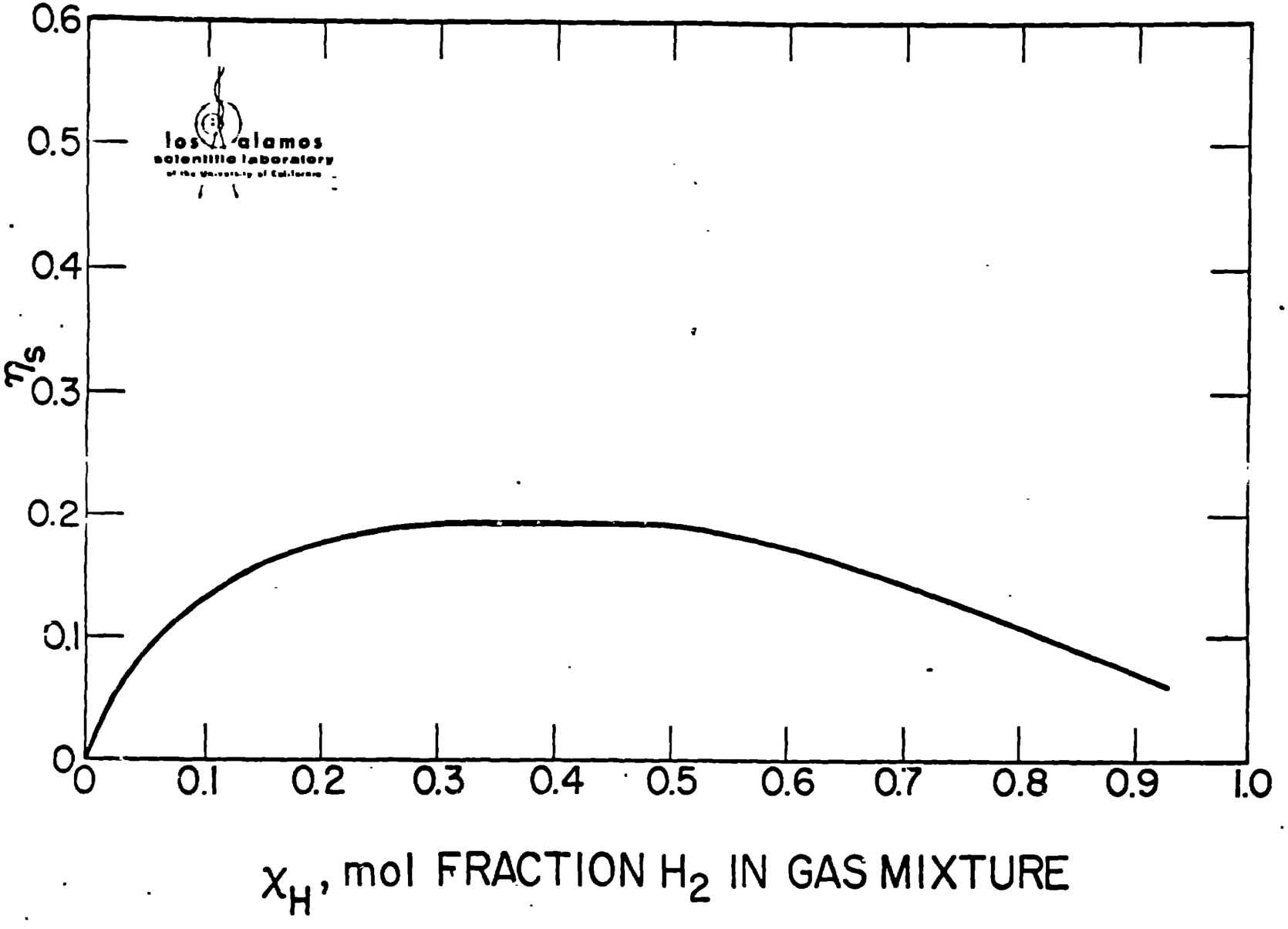

FIGURE 9 SEPARATION EFFICIENCY - DIFFUSION PROCESS

KEC

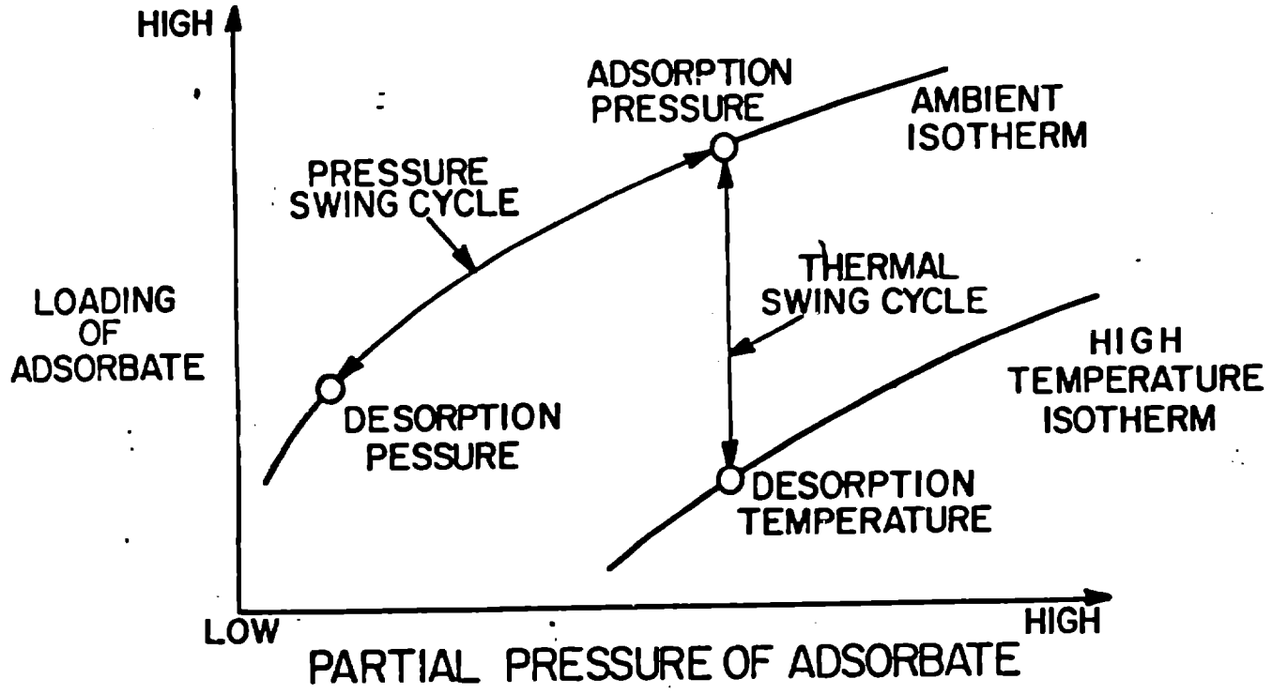

FIGURE 10 PRINCIPLE OF PHYSICAL AND THERMAL ADSORPTION PROCESSES

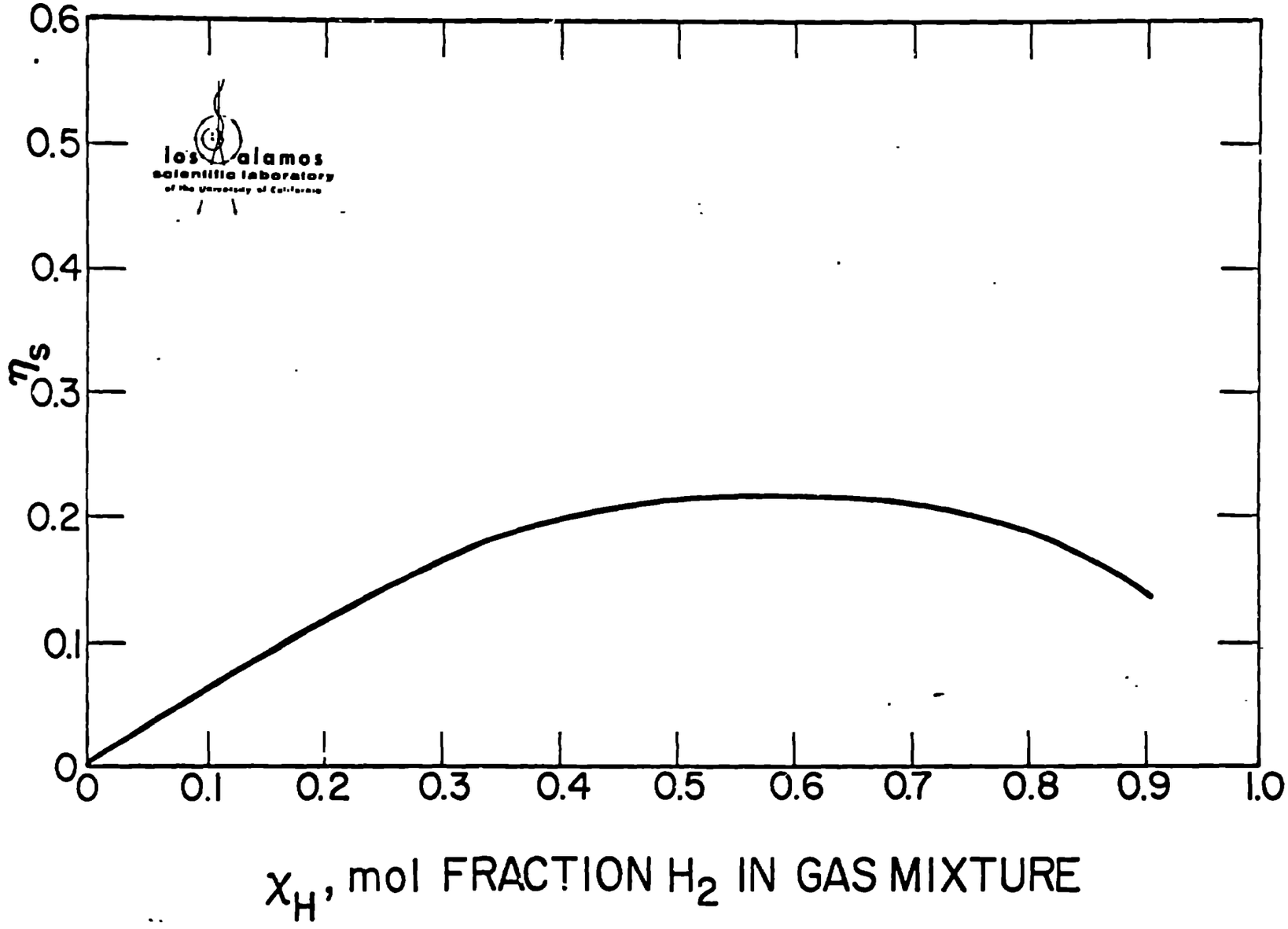

FIGURE 11 SEPARATION EFFICIENCY - PHYSICAL ADSORPTION (PRESSURE) PROCESS

KEC

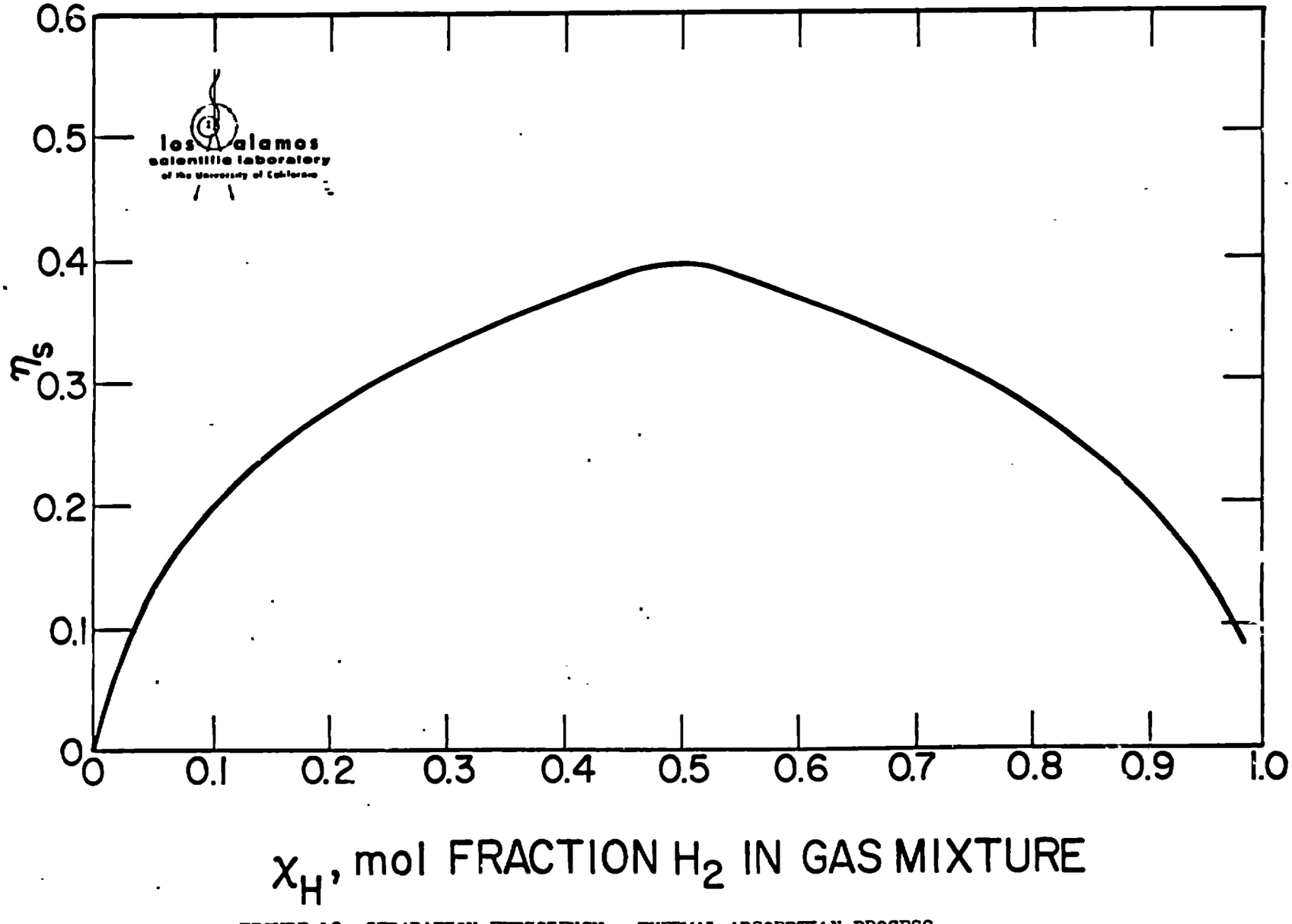

FIGURE 12 SEPARATION EFFICIENCY - THERMAL ADSORPTION PROCESS

KEC

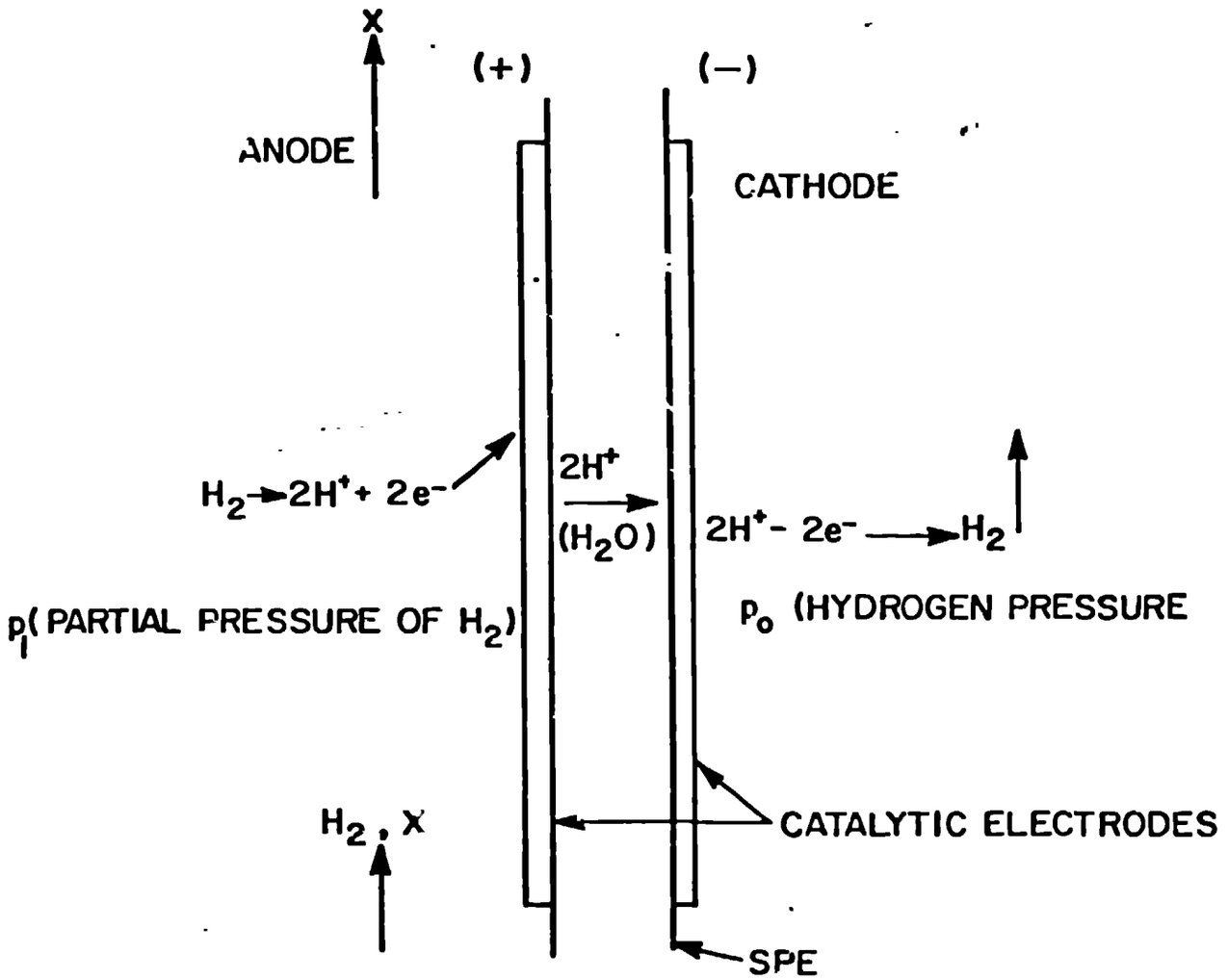

FIGURE 13 ELECTROCHEMICAL SEPARATION PROCESS FOR HYDROGEN

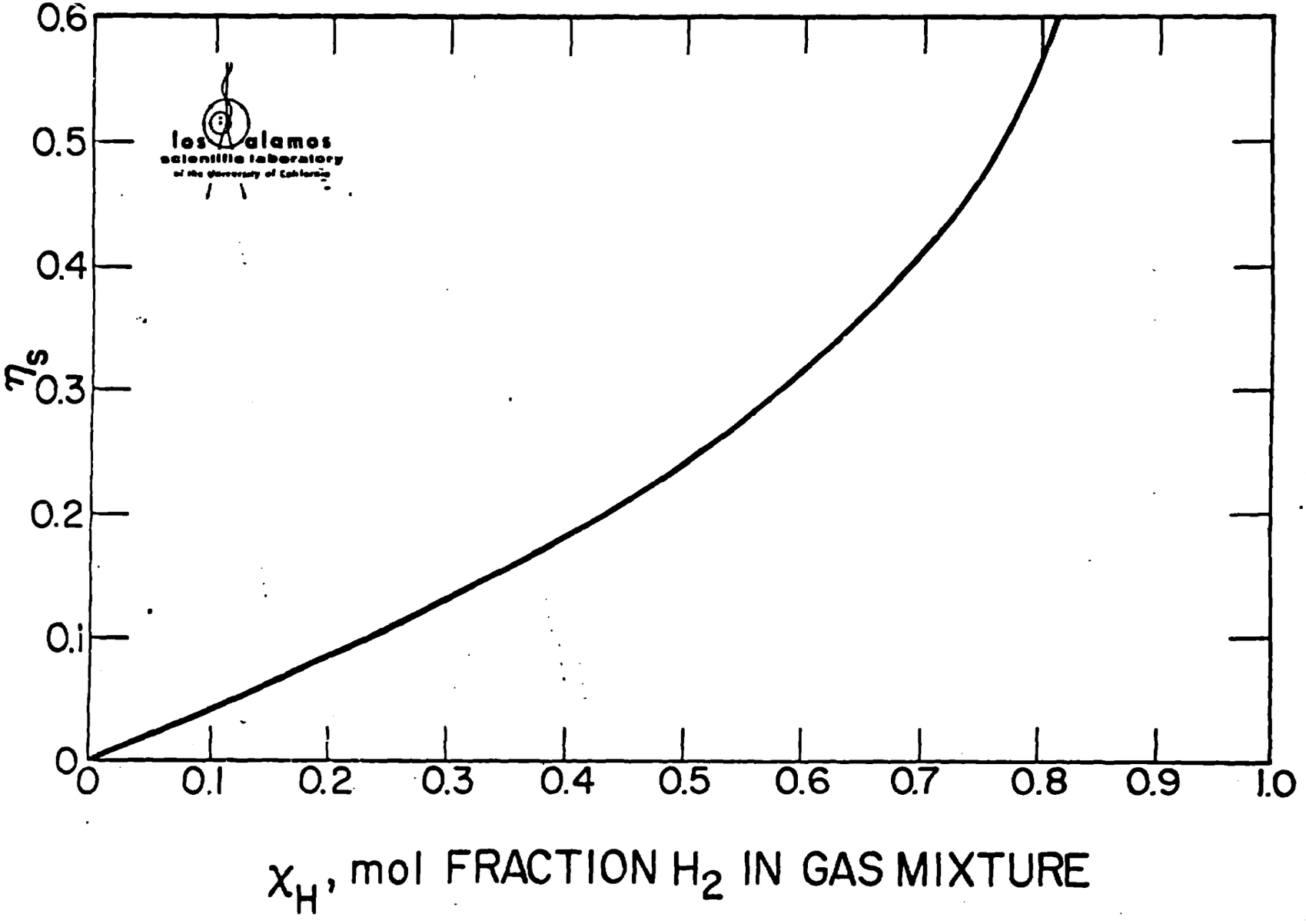

FIGURE 14 SEPARATION EFFICIENCY - ELECTROCHEMICAL SEPARATION PROCESS

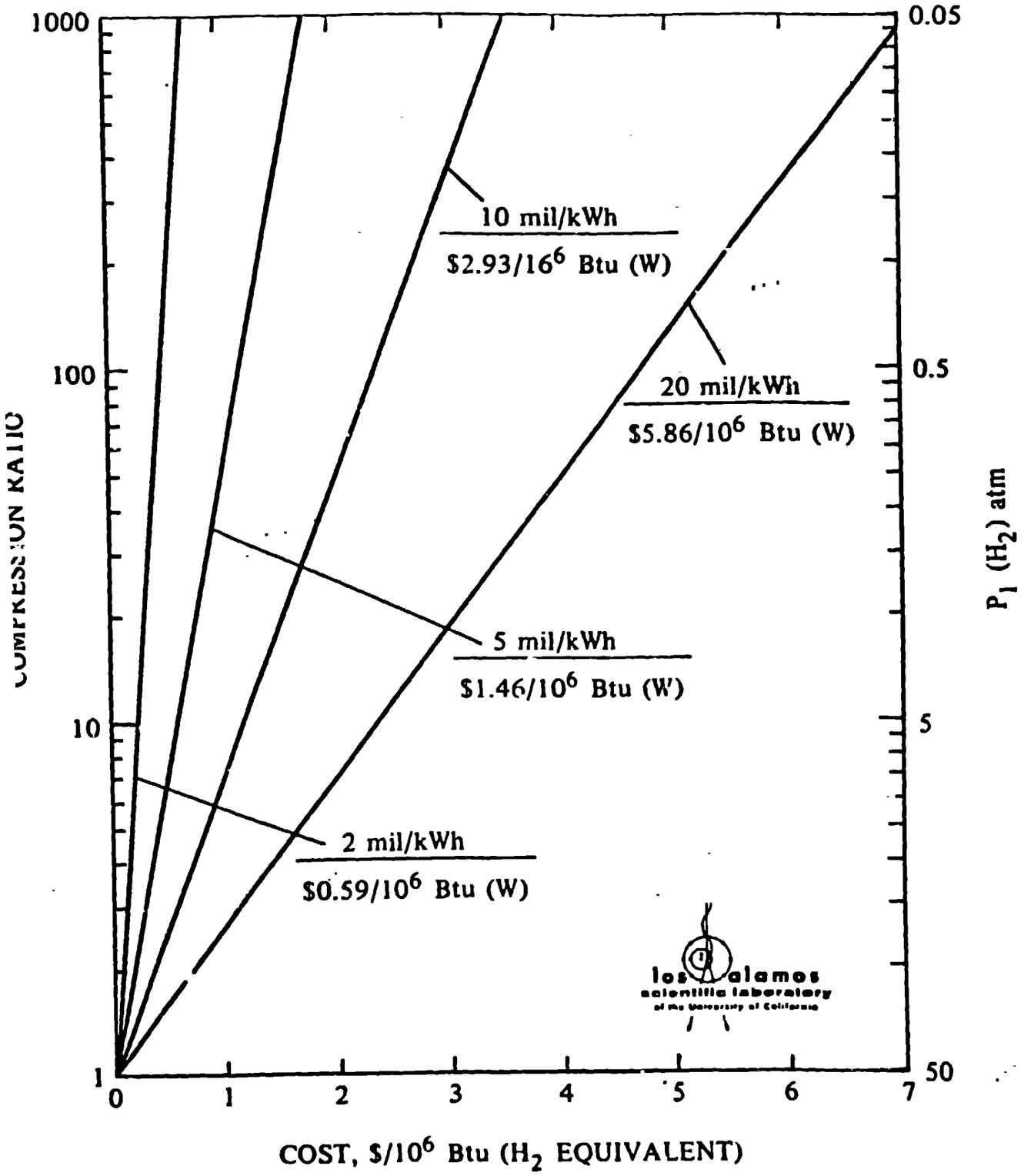

FIGURE 15 COMPRESSION COST FOR HYDROGEN