A Temperature Swing Process for Hydrogen Isotope Separation

Experiments on the separation of hydrogen isotopes were conducted using vanadium hydride in a temperature swing process. Process behavior followed trends predicted by an equilibrium theory of process operation, but was modified by a kinetic isotope effect and by finite rates of hydrogen absorption and isotope exchange.

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SCOPE

Pressure and temperature swing adsorption processes are widely used industrially to separate gaseous mixtures. They function by inducing oscillatory motion of concentration wave fronts within adsorption columns with a drift toward one end of the apparatus. They are particularly effective in removing strongly adsorbing impurities from an inert carrier. For such high separation factor systems, virtually complete impurity removal can be accomplished with high recovery of purified carrier and low carrier losses in the waste stream. However, when the impurities are only slightly more strongly adsorbed than the carrier, i.e., when the separation factors are just slightly greater than unity, complete impurity removal is still possible but with low recovery of purified carrier and high carrier waste stream losses. This picture of cyclic adsorption process operation has been given quantitative expression in a theory in which separation is controlled by interphase equilibrium (Chan et al., 1980). Kinetic effects can drastically modify this picture, as shown for instance by wong et al. (1980).

In the present paper, a temperature swing technique similar to parametric pumping was applied to the separation of hydrogen isotopes, a low separation factor mixture. The mixture consisted of a trace of tritium in hydrogen. The solid phase was vanadium monohydride, a substance which takes up tritium preferentially in the presence of hydrogen. Experiments were performed to determine the behavior and effectiveness of the process in removing contaminating tritium from hydrogen. The experimental results were compared with an equilibrium theory of process operation to determine the mechanisms controlling the separations observed. The characteristics of the isotope separations obtained with the temperature swing process were compared with those of a pressure swing process (Wong et al., 1980).

CONCLUSIONS AND SIGNIFICANCE

The equilibrium theory of Chan et al. (1980) was adapted to apply to the temperature swing adsorption process. For given process temperature and pressure conditions, tritium removal from hydrogen was predicted to be independent of cycle time, to increase with purge-to-feed ratio, and to be complete at purge-to-feed ratios above a critical value.

In experiments conducted at approximately 700 kPa between temperatures of 333 and 423°K with cycle times of 600 s or longer, tritium removal was found to be in good quantitative agreement with equilibrium theory with certain exceptions. Tritium removal was independent of cycle time except at short cycle times (less than 600 s) and it increased with purge-to-feed ratio but did not become complete above the predicted critical value. Also process tritium concentration transients showed momentary increases at the beginning of each half-cycle rather than the expected uniform decrease. Several kinetic limitations were held to be responsible for these departures from equilibrium behavior: finite rates of hydrogen absorption and isotope exchange and a kinetic isotope effect in the rates of hydrogen absorption and desorption.

These kinetic limitations had also been found in a pressure swing adsorption hydrogen isotope separation process employing vanadium monohydride (Wong et al., 1980). The difference in the times required for pressure and temperature changes resulted in opposite behavior of the temperature and pressure cycling processes. Tritium was enriched in the product (high pressure) stream of the short transient pressure cycling process whereas in the long transient temperature cycling process tritium was removed from the corresponding (low temperature) stream.

The present work provides an understanding of the behavior of the temperature cycling process and, together with the work on the pressure cycling process, provides a general framework for appraisal of the potential of hydrogen isotope separation processes using metal hydrides.

INTRODUCTION

Hydrogen isotope separation is a topic of considerable interest in the nuclear industry. It is important in heavy water production, in tritium removal from fuel processing effluents, and in fusion reactor technology. A summary of recent work on hydrogen isotope separation was presented by Rae (1978).

Some research on this topic, motivated by technological interest and also by an interest in continuous chromatographic separations, was reported recently by Hill et al. (1979) and Wong et al. (1980). The particular separation studied in these papers was the removal of a trace quantity of tritium, present as HT, from gaseous hydrogen. A continuous chromatographic separation of this mixture conducted at moderate temperatures (300 to 500°K) and pressures (100 to 1000 kPa) required a solid phase with appreciable capacity for hydrogen and a significant isotopic preference at these conditions. Vanadium hydride was chosen for this purpose. This sub-

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stance has the required capacity and it has an equilibrium isotope effect such that a heavy isotope is taken up preferentially (Wiswall and Reilly, 1972). The separation process employed was the two-column pressure swing adsorption process known as heatless adsorption (Skarstrom, 1959). The separations obtained were found to be based not only on the known equilibrium isotope effect but also on an isotope effect in the rate of hydrogen absorption. Tritium was absorbed and released more slowly than hydrogen. Thus the kinetic isotope effect led, on a short time scale, to preferential hydrogen uptake, whereas preferential tritium uptake followed on a long time scale from the equilibrium effect.

In the present work, the same separation employing the same solid phase was examined using a two-column temperature swing process similar to parametric pumping. The presence of the equilibrium and kinetic isotope effects led to considerably different results in the temperature cycling process than in the earlier pressure cycling process.

PROCESS DESCRIPTION

The temperature cycling process consists of four steps as shown in Figure 1. In the first step, feed consisting of a trace of HT in H_2 is introduced continuously into column 1 maintained at a low temperature T_L and a high pressure p_H. Part of the purified effluent is taken off as product. With negligible pressure drop across column 1 the product pressure is the same as that of the feed. The remainder of the effluent from column 1 is supplied to column 2 maintained at a high temperature T_H and a low pressure p_L where it serves to purge previously sorbed HT. Good heat exchange at the column entrance results in essentially instantaneous increase of the gas temperature to T_H. p_H is maintained greater than p_L to provide for pressure losses across metering and check valves. In the second step, column 2 is cooled to T_L while its pressure is raised to p_H. At the same time, the temperature and pressure levels in column 1 become T_H and p_L respectively. During this step, the product ends of the columns are closed. Feed is supplied to column 2 and the exhaust gas of column 1 exits through a vent. The third and the fourth steps are the same as the first and second respectively except that the points of feed introduction and exhaust are reversed with respect to columns 1 and 2.

A higher HT concentration front velocity must be possible in the hot column than in the cold column in order to be able to obtain, in principle, complete purge of HT from the hot column while at the same time taking off a portion of the cold column effluent as purified product. This higher velocity is possible because of the expansion of the gas as it moves from a low temperature, high pressure zone to a high temperature, low pressure zone, and because of decreased affinity of the solid phase towards HT at the higher temperature (Wong and Hill, 1979).

THEORY

The assumptions used in the development of an equilibrium theory of the temperature cycling process are as follows:

(1) The column is assumed to be one-dimensional and axial dispersion is absent.
(2) The gas and solid phase are always at equilibrium thermally and with respect to the distribution of isotopic species. Distribution occurs in accordance with the exchange reaction

$$HT(g) + H(VH_{\sim 0.7}) \rightleftarrows H_2(g) + T(VH_{\sim 0.7}) \qquad (1)$$

The separation factor for tritium with respect to hydrogen for this reaction is defined as

$$\alpha = \frac{2C_{H_2}C_T}{C_{HT}C_H} \qquad (2)$$

This definition is valid when tritium is present at trace levels. The separation factor decreases with temperature but is not a function of pressure (Wong and Hill, 1979).
(3) The temperature is assumed to be uniform throughout each column and to change instantaneously from one level to the other at the end of each half cycle.
(4) The perfect gas law is used to evaluate gas concentrations in terms of pressure and temperature.
(5) There are no axial pressure gradients.

Material balances for hydrogen and tritium in a column are

$$\epsilon \left[\frac{\partial C_{H_2}}{\partial t} + \frac{\partial (uC_{H_2})}{\partial z}\right] + \frac{1}{2}(1-\epsilon)\frac{\partial C_H}{\partial T} = 0 \qquad (3)$$

$$\epsilon \left[\frac{\partial C_{HT}}{\partial t} + \frac{\partial (uC_{HT})}{\partial z}\right] + (1-\epsilon)\frac{\partial C_T}{\partial t} = 0 \qquad (4)$$

By using Eq. 2 in Eq. 4 to eliminate C_T and evaluating C_{H_2} and C_{HT} in terms of the perfect gas law with the mole fraction of H_2 ≈ 1, Eqs. 3 and 4 can be written as

$$\left[\frac{\epsilon}{RT} + \frac{1}{2}(1-\epsilon)\frac{\partial C_H}{\partial p}\right]\frac{\partial p}{\partial t} + \left[\frac{1}{2}(1-\epsilon)\frac{\partial C_H}{\partial T} - \frac{\epsilon p}{RT^2}\right]\frac{\partial T}{\partial t} + \frac{\epsilon p}{RT}\frac{\partial u}{\partial z} = 0 \qquad (5)$$

$$\left[(1-\epsilon)\frac{y}{2}\left(C_H\frac{\partial \alpha}{\partial T} + \alpha\frac{\partial C_H}{\partial T}\right) - \frac{\epsilon p y}{RT^2}\right]\frac{\partial T}{\partial t} + \left[\frac{\epsilon y}{RT} + (1-\epsilon)\frac{\alpha y}{2}\frac{\partial C_H}{\partial p}\right]\frac{\partial p}{\partial t} + \left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_H\right]\frac{\partial y}{\partial t} + \frac{\epsilon u p}{RT}\frac{\partial y}{\partial z} + \frac{\epsilon p y}{RT}\frac{\partial u}{\partial z} = 0 \qquad (6)$$

Terms involving $\partial p/\partial z$ and $\partial T/\partial z$ do not appear in these equations because of the assumptions of uniformity with respect to axial position. Also $\partial \alpha/\partial p$ is taken as zero. These equations can be solved by the method of characteristics to give two ordinary differential equations:

$$\frac{dz}{dt} = \frac{up\epsilon/RT}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_H\right]} \qquad (7)$$

$$\frac{dy}{dt} = \frac{-(1-\epsilon)\frac{y}{2}\left[C_H\frac{\partial \alpha}{\partial t} + (\alpha-1)\frac{\partial C_H}{\partial T}\right]\frac{\partial T}{\partial t} - (1-\epsilon)\frac{y}{2}(\alpha-1)\frac{\partial C_H}{\partial p}\frac{\partial p}{\partial t}}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_H\right]} \qquad (8)$$

Integration of Eq. 7 over a half cycle of process operation yields the distance of penetration of a tritium concentration front during that step. Thus expressions for the feed and purge step penetration distances are

$$L_F = \frac{\epsilon p_H/RT_L}{\epsilon p_H/RT_L + \frac{1}{2}(1-\epsilon)\alpha(T_L)C_H(T_L,p_H)}\, u_F \qquad (9)$$

$$L_{PG} = \frac{\epsilon p_L/RT_H}{\epsilon p_L/RT_H + \frac{1}{2}(1-\epsilon)\alpha(T_H)C_H(T_H,p_L)}\, u_{PG} \qquad (10)$$

To compute the characteristic position shift resulting from the temperature and pressure transitions, the approach of Shendalman and Mitchell (1972) is followed. The resulting expression is

$$\frac{dz}{dt} = \frac{-z\left[\frac{1}{2}(1-\epsilon)\frac{\partial C_{\mathrm{H}}}{\partial T} - \frac{\epsilon p}{RT^2}\right]\frac{\partial T}{\partial t} - z\left[\frac{\epsilon}{Rt} + \frac{1}{2}(1-\epsilon)\frac{\partial C_{\mathrm{H}}}{\partial p}\right]\frac{\partial p}{\partial t}}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]} \tag{11}$$

Since $y = y(p,T)$, $z = z(p,T)$ and $p = p(t)$, $T = T(t)$, one can write,

$$\frac{dz}{dt} = \frac{\partial z}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial z}{\partial p}\frac{\partial p}{\partial t} \tag{12}$$

$$\frac{dy}{dt} = \frac{\partial y}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial y}{\partial p}\frac{\partial p}{\partial t} \tag{13}$$

Comparing Eqs. 12 and 11, one can identify

$$\frac{\partial z}{\partial p} = -\frac{\left[\frac{\epsilon}{RT} + \frac{1}{2}(1-\epsilon)\frac{\partial C_{\mathrm{H}}}{\partial p}\right]z}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]} \tag{14}$$

and

$$\frac{\partial z}{\partial T} = -\frac{\left[\frac{1}{2}(1-\epsilon)\frac{\partial C_{\mathrm{H}}}{\partial T} - \frac{\epsilon p}{RT^2}\right]z}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]} \tag{15}$$

Similarly between Eqs. 13 and 8, one has

$$\frac{\partial y}{\partial p} = -\frac{(1-\epsilon)\frac{y}{2}(\alpha-1)\frac{\partial C_{\mathrm{H}}}{\partial p}}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]} \tag{16}$$

and

$$\frac{\partial y}{\partial T} = -\frac{(1-\epsilon)\frac{y}{2}\left[C_{\mathrm{H}}\frac{\partial \alpha}{\partial T} + (\alpha-1)\frac{\partial C_{\mathrm{H}}}{\partial T}\right]}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]} \tag{17}$$

Equations 14 and 16 are equivalent to the expressions developed for the pressure swing process (Wong et al., 1980) to account for the changes in characteristic position and composition during the pressurization and blowdown steps. Calculations with Eqs. (14–17) showed that for the experiments reported here the changes in characteristic position and HT mole fraction due to the pressure change were a few percent of the changes due to the temperature change. Hence, to a good approximation, the characteristic position shift and composition change can be calculated solely by Eqs. 15 and 17). The results are,

$$\frac{z_2}{z_1} = J = \exp\left(-\int_{T_1}^{T_2}\frac{\left[\frac{1}{2}(1-\epsilon)\frac{\partial C_{\mathrm{H}}}{\partial T} - \frac{\epsilon p}{RT^2}\right]}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]}dT\right) \tag{18}$$

and

$$\frac{y_2}{y_1} = K = \exp\left(-\int_{T_1}^{T_2}\frac{\frac{(1-\epsilon)}{2}\left[(\alpha-1)\frac{\partial C_{\mathrm{H}}}{\partial T} + C_{\mathrm{H}}\frac{\partial \alpha}{\partial T}\right]}{\left[\frac{\epsilon p}{RT} + (1-\epsilon)\frac{\alpha}{2}C_{\mathrm{H}}\right]}dT\right) \tag{19}$$

Complete removal of tritium from the cold column effluent at steady state will be obtained if $L_F \leq hJ$ and $L_{PG} \geq L_F/J$. The minimum fraction of the feed which must be used as purge in order to obtain complete removal is equal to the ratio of the purge to the feed on a molar basis when there are no net characteristic movements in a complete cycle of operation; i.e.,

$$G_{\mathrm{crit}} = \frac{1}{J}\frac{\left[\epsilon/RT_{\mathrm{H}} + \frac{1}{2}(1-\epsilon)\alpha(T_{\mathrm{H}})C_{\mathrm{H}}(T_{\mathrm{H}},p_L)/p_L\right]}{\left[\epsilon/RT_L + \frac{1}{2}(1-\epsilon)\alpha(T_L)C_{\mathrm{H}}(T_L,p_{\mathrm{H}})/p_{\mathrm{H}}\right]} \tag{20}$$

Since in practice the amount of hydrogen in the gas phase is much less than that in the solid phase, to a good approximation,

$$G_{\mathrm{crit}} = \frac{1}{J}\frac{\alpha(T_{\mathrm{H}})C_{\mathrm{H}}(T_{\mathrm{H}},p_L)p_{\mathrm{H}}}{\alpha(T_L)C_{\mathrm{H}}(T_L,p_{\mathrm{H}})p_L} \tag{21}$$

Expressions for the mole fraction transient of HT in the cold column effluent are derived in the same manner as those of the companion pressure swing work (Wong et al., 1980). For the case in which $G > G_{\mathrm{crit}}$ and $L_F \leq hJ$, the product mole fraction for a given half cycle is equal to the product mole fraction for the previous half cycle multiplied by the factor K. Since for the present work K is less than unity, then the product mole fraction will decrease with the number of cycles of operation and approach zero as a theoretical limit. For the case in which $G < G_{\mathrm{crit}}$, the product mole fraction will consist of contributions from a number of concentration fronts which, after a certain number of half cycle operations, will also include that of the feed which breaks through into the product stream. In this case an average non-zero mole fraction based on the weighted sum of all the contributions will be attained at steady state. Detailed derivations of the expressions for this average mole fraction can be found in the companion pressure swing work (Wong et al., 1980).

In evaluating any of the theoretical expressions above, α, $\partial\alpha/\partial T$, C_{H}, $\partial C_{\mathrm{H}}/\partial p$, and $\partial C_{\mathrm{H}}/\partial T$ were obtained from the data of Wong and Hill (1979).

EXPERIMENTAL

Apparatus and Materials

These were basically the same as in the companion pressure cycling study. Details for that study are given by Wong et al. (1980). The apparatus consisted of two jacketed stainless steel columns in series as in Figure 1 with

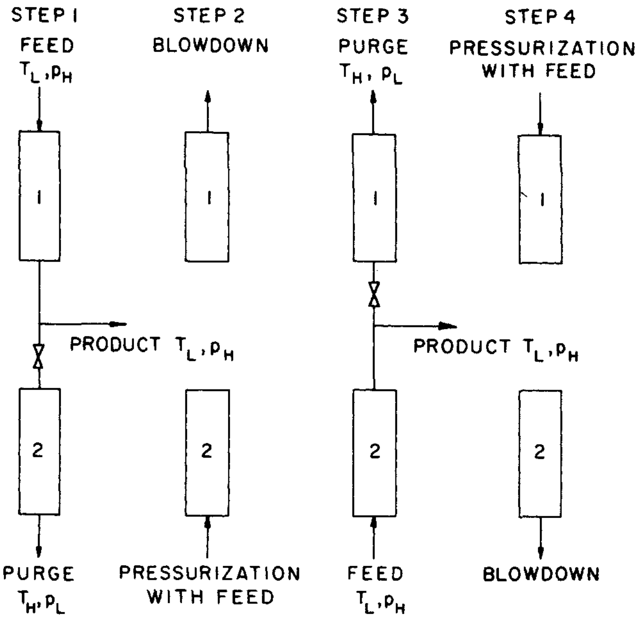

Figure 1. Steps in the temperature cycling process. $T_F < T_{PG}$, $p_F > P_{PG}$.

arrangements for reversing the feed entry and purge removal at the column ends. The columns were 46 cm long × 0.77 cm diameter and were packed with 60 g of vanadium monohydride with particle sizes in the range 0.71 to 0.86 mm. The hydride was made from a commercial grade vanadium with a purity of 99.5%. The feed consisted of approximately 4 ppb HT in 99.999% H_2. The mole fraction of HT in the cold product stream was monitored through continuous measurement of its count rate.

For the present study two constant temperature baths were used, one maintained at the high temperature and the other at the low temperature. The baths contained a high temperature fluid which permitted operation at temperatures up to 475°K. The temperature of each bath was regulated to within 1°K. Residence time of the fluid in a column jacket was 0.7 s.

Valves and a valve switching arrangement permitted reversal of introduction of the bath fluids between the jackets of the two columns. Valves to switch feed entry and purge removal points were operated simultaneously.

Also for the present study stainless steel sheathed chromel-alumel thermocouples 1.6 mm in diameter were installed along the centerline of the columns with hot junctions located approximately 1.3 cm from the product ends. The response time of these thermocouples (time to achieve 63% of a step change in surface temperature) was 1.2 s.

Procedure

The procedure for activation of the hydride material was the same as that of Wong et al. (1980).

Prior to a temperature cycling run, the columns were saturated with feed gas at the desired pressure and temperature levels. The pressure of the cold column was maintained about 70 kPa above that of the hot column. Following column saturation, the flow rates were adjusted to the desired values and the experiment was started by turning on timers which directed the cyclic operation of the valve systems referred to above. The experiments were conducted wholly in the monohydride region of the pressure-composition diagram of the vanadium-hydrogen system. Within this region the HT-H_2 separation was studied as a function of cycle time, purge-to-feed ratio, temperature level, and temperature difference.

RESULTS AND DISCUSSION

Conditions generally used for the experiments are shown in Table 1.

TABLE 1. EXPERIMENTAL CONDITIONS

Feed $F = 3.67$ std cm^3 s^{-1}
$T_L = 333$°K
$p_H = 689$ kPa
Purge GF std cm^3 s^{-1}
$T_H = 423$°K
$p_L = 620$ kPa

Variation with Cycle Time

Variation of this quantity (actually the half-cycle time, Δt) is equivalent to varying the ratio L_F/h at constant feed rate and constant column temperature. In terms of equilibrium theory, the average product mole fraction depends on L_F/L_{PG} and K but not on L_F/h or, equivalently, Δt. Thus cold product mole fraction transients should not vary with Δt.

Cold product mole fraction transients for a series of runs in which Δt was the only variable are depicted in Figure 2. A single transient for which $\Delta t = 300$ s yielded a high steady state value, different from that of four other runs with longer half-cycle times. Also the detailed shapes of the transients for the latter four runs are all very similar and different from that of the 300 s half-cycle time run. The reason for the difference of the short cycle time run is apparent in Figure 3. This figure shows the temperature variation in a column for a few cycles of several of these runs. It is seen that for the run for which $\Delta t = 300$ s thermal equilibrium was never achieved during a cycle whereas for a longer cycle time thermal equilibrium was achieved over a major portion of each cycle. For these latter runs, lack of dependence of the transients on Δt is consistent with predictions of equilibrium theory as discussed above.

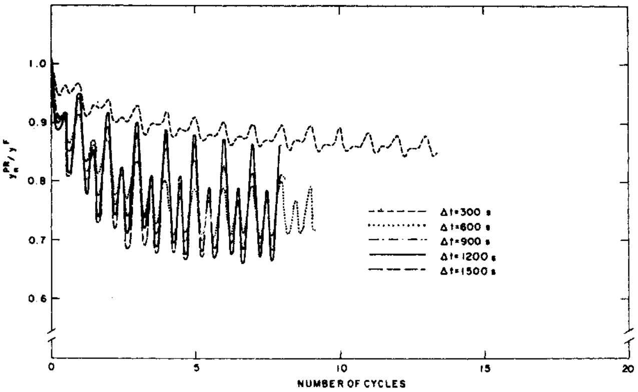

Figure 2. Cold product mole fraction transients as a function of half-cycle time. $G = 0.75$.

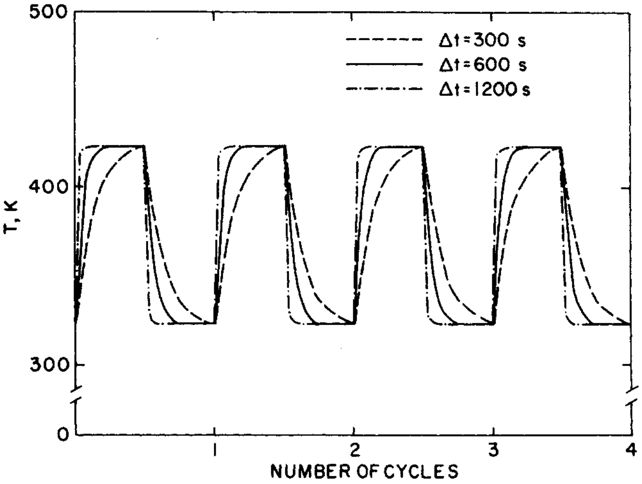

Figure 3. Temperature transients in a column undergoing temperature cycling. $G = 0.75$.

Variation with G

A series of experiments was performed in which G was the only variable. Dimensionless cold product mole fraction transients are shown in Figures 4 and 5. A half cycle time of 900 s was used, insuring that over a major portion of each half-cycle thermal equilibrium was achieved. In general HT depletion increases with G, in agreement with equilibrium theory expectations. An interesting structure is seen in the detailed mole fraction ratio variation over a cycle. This structure changes with G. For $G = 0$, as shown in Figure 4, each odd half-cycle begins with a spike with values exceeding unity. This spike is followed by a drop in mole fraction

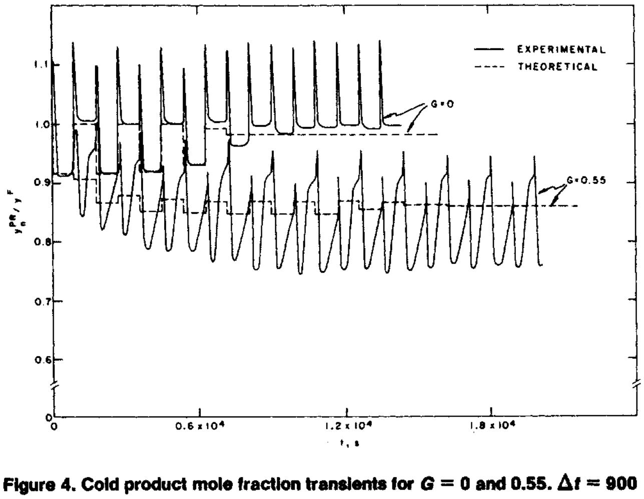

Figure 4. Cold product mole fraction transients for $G = 0$ and 0.55. $\Delta t = 900$ s.

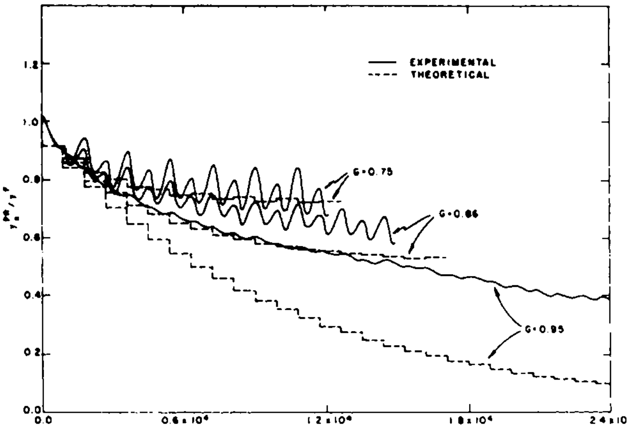

Figure 5. Cold product mole fraction transients for G = 0.75, 0.86 and 0.95. Δt = 900 s.

ratio to a value of about 0.915 for the first and the next two odd half-cycles. Another spike follows at the beginning of each even half-cycle. This spike is followed by a drop in mole fraction ratio to a value of approximately 1 for the initial four even half-cycles and approximately 0.99 thereafter. The feed appears to break through at the seventh half-cycle where the mole fraction ratio increases from 0.915 to 0.93. This structure is compared in the figure with the predictions of equilibrium theory. The composition change factor, K, for the experimental conditions was 0.917. Thus, the theory predicts that before feed breakthrough the mole fraction ratio should drop to 0.917 during an odd half-cycle and increase to 1 during the following even half-cycle. It also predicts that feed will break through at the seventh half-cycle and reach a constant ratio of 0.98 after the eighth half-cycle. It can be seen that, except for the spikes, the experimental non-steady state portion of the transient is in excellent agreement with the theoretical one. The reason that the steady state average mole fraction ratio of the theoretical transient is 0.98 instead of 1 is due to the fact that the breakthrough consists of feed introduced during the constant low temperature feed step and that introduced during the temperature transition step. As explained by Wong et al. (1980) in the case of the pressure cycling process, such a transition will create a concentration distribution along the column with mole fraction ratio distribution which is equal to 1 at the feed end of the column and falls to the value K at the end of front penetration. The average mole fraction ratio representing the portion of the breakthrough which was derived from this distribution is thus less than 1.

The duration of the spikes is about 100 s. The time to cool a column from T_H to T_L is about 150 s. During this cooling interval the solid phase in the column is absorbing hydrogen. It is postulated that protium is absorbed faster than tritium, leading to the spikes which exhibit mole fraction ratios higher than unity which corresponds to the feed concentration. (Note that in comparing the features of Figures 3 and 4 it should be remembered that the mole fraction ratio transients in Figure 4 are always associated with a column undergoing cooling.)

Spikes are also evident in the transient for G = 0.55. They are missing in the transients for larger values of G as shown in Figure 5. Their gradual disappearance is assumed to result from increasing axial dispersion as the hydrogen residence time in the product line leading from the two beds to the in-line counter is lengthened. (The flow rate in this line decreases with increasing G.)

An isotope effect on absorption rate was also indicated in the pressure cycling study of Wong et al. (1980). In that study the same HT-H_2-vanadium monohydride system was used in the same apparatus but with pressure cycling experiments conducted under isothermal conditions. In contrast to the present results HT enrichment rather than depletion was found in the product stream. Cycle times used were of the order of one hundred seconds or less and the time scale for a pressure change was of the order of 1 s. It is postulated that a slow rate of absorption of HT relative to H_2 is the pressurization step led to enrichment of HT in the product end of the column. Persistence of HT in the gas phase, as indicated by net enrichment of HT in the product stream, is thought to have been caused by the relatively short cycle time.

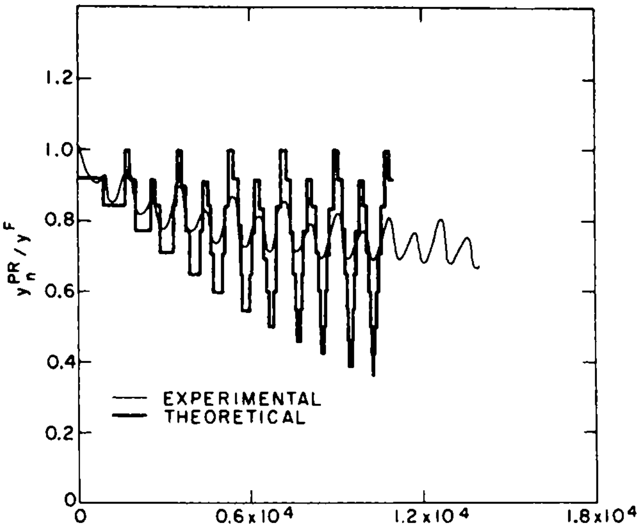

Figure 6. Comparison of an experimental transient with the exact profile predicted by equilibrium theory. G = 0.75, Δt = 900 s.

The agreement between experimental results and theory is good for runs with G ranging from 0 to 0.75 (Figures 4 and 5). For the run with G = 0.86 (Figure 5) the experimental steady state level is about 20% higher than that predicted by the theory. The critical value of G for the nominal onset of complete removal of HT from the product stream, calculated using Eq. 21, was 0.94. Thus, the experiment with G = 0.95 would have been expected in principle to result in a steady state mole fraction ratio of zero. The fact that it did not may have resulted from two causes. First, the rate of the exchange reaction (Eq. 1) has been measured and has been found to occur on a time scale of some 60 s at the temperatures and pressures of interest (Wong and Hill, 1979). Thus it is far from instantaneous as is assumed in equilibrium theory. Second, introduction of high mole fraction spikes into the product end of a column undergoing purge is counter to the ideal manner in which temperature swing processes are conceived to work. Both effects would tend to prevent obtaining complete cleanup. It should be noted that a staircase type of transient is predicted by equilibrium theory for experiments for which $G \geq G_{crit}$. This appears to have been found for G = 0.95.

The theoretical transients shown in Figures 4 and 5 are composed of the average values of the transients for each half-cycle. As has been mentioned in the theory section, an averaged transient is not found in detail in the two-bed temperature cycling process. This is because the monitored product is actually made up of a succession of mole fraction fronts as discussed earlier. Figure 6 illustrates the agreement between an experimental mole fraction ratio transient and a theoretical one in which all the mole fraction fronts are shown.

Variation with Temperature Level and Temperature Difference

In addition to the experiments described above with cold and hot temperatures of 333 and 423°K experiments were also conducted between 313 and 373°K and between 313 and 473°K. The dependencies on Δt and G were similar to those described here. However at the same values of Δt and G the steady state depletion of HT was greater for the experiments between 313 and 473°K and less between 313 and 373°K. Larger temperature differences would be expected to lead to greater depletion because of the larger variation of both separation factor and hydrogen content of solid phase. Higher temperatures would be expected to lead to more rapid exchange rates and hence less broadening of concentration fronts.

TABLE 2. STEADY-STATE STAGE CUTS AND SEPARATION FACTORS

Temperature Cycling Process (present work): $F = 3.67$ std cm^3 s^{-1}, $p_H = 689$ kPa, $T_L = 333$°K, $p_L = 620$ kPa, $T_H = 423$°K, $\Delta t = 900$ s. $G_{crit} = 0.94$.

G	y_∞^{PR}/y^F	y_∞^{PG}/y^F	θ	α_s
0.50	0.85	1.18	0.62	1.29
0.75	0.75	1.06	0.81	1.41
0.86	0.60	1.05	0.88	1.75
0.95	0.40	1.02	0.96	2.56

Pressure Cycling Process (Wong et al., 1980): $F = 3.58$ std cm^3 s^{-1}, $p_H = 1034$ kPa, $P_L = 103.4$ kPa, $T = 373$°K, $\Delta t = 60$ s. $G_{crit} = 1.00$.

G	y_∞^{PR}/y^F	y_∞^{BDPG}/y^F	θ	α_s
0.50	1.42	0.92	0.16	1.54
0.88	1.64	0.98	0.04	1.68

The maximum steady state HT depletion observed occurred in an experiment conducted between 333 and 423°K at a flow rate of 3.37 std cm^3 s^{-1}, with $G = 0.96$ ($>G_{crit}$), and a half-cycle time of 900 s. For this run y_∞^{PR}/y^F was approximately 0.2.

Stage Cuts and Separation Factors

Complete characterization of the temperature cycling process operating at steady state requires statement not only of the product mole fraction ratio but also of the cut or portion of the feed taken off as enriched product. A derived quantity of interest is the stage separation factor. This is the enriched product mole fraction divided by the depleted product mole fraction. Representative values of these quantities as well as product mole fractions are shown in Table 2 for the temperature and pressure cycling processes. G and y_∞^{PR} were determined experimentally. The other quantities were calculated from tritium or hydrogen balances. For both processes the stage separation factor increases with G but at the same time the cut approaches either zero (pressure cycling) or unity (temperature cycling). Cuts near 0.5 can be obtained but only with modest enrichment or depletion. If a multistage countercurrent cascade were to be based on these processes, it is conceivable that the temperature cycling process would be used in the enriching section, where cuts greater than 0.5 are desired and the pressure cycling process would be used in the stripping section where cuts less than 0.5 are desired.

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NOTATION

C_i = concentration of species i, mole m^{-3}
C_H, C_T = concentration of hydrogen or tritium atoms in hydride particle, mole m^{-3}
F = feed flow rate, std m^3 s^{-1}
G = purge-to-feed ratio
h = height of packed column, m
J = characteristic position shift factor defined by Eq. 18
K = composition change factor defined by Eq. 19
L = penetration distance of tritium front, m
n = half-cycle number
p = hydrogen pressure, kPa
R = gas constant, kPa – m^3/mole – °K
t = time, s
Δt = half-cycle time, s
T = temperature, °K
u = interstitial gas velocity ms^{-1}
y = mole fraction of HT in hydrogen stream
z = axial distance coordinate, m

Greek Letters

α = tritium-protium separation factor
ϵ = bed void fraction

Superscripts

BDPG = combined blowdown and purge
F = feed
PG = purge
PR = product

Subscripts

crit = critical
F = feed
H = pertains to high value of temperature or pressure
L = pertains to low value of temperature or pressure
n = pertains to n-th half-cycle
PG = purge

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