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Kinetics of a Square Cascade of Close-Separation Stages under Total Reflux

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Abstract

To facilitate the determination of the separation factor and the number of theoretical stages of a square cascade of close-separation stages from measurements of its long-time kinetics under total reflux, extensive tables of kinetics parameters have been produced in accordance with K. Cohen's theory. Cohen's treatment has been extended in several ways. The kinetics parameters of the first transient term have been finely mapped, and the ranges of various parameters have been extended to include large overall separations as well as the stripping section. The second transient term of the long-time kinetics has been evaluated, and a possible application of this correction term has been suggested in relation to the experimental determination of the column parameters. Under comparable conditions a steady concentration profile, along the column, is attained faster in the stripping section than in the enriching section. A distinction between the enriching and stripping section is important in using the transient theory for the evaluation of the cascade characteristics under ordinary laboratory conditions.

The transient behavior of a square, countercurrent cascade of close-separation stages during start-up period was theoretically analyzed by Cohen (*1*) in relation to the fractionation of uranium-235. A consideration of the material balance of desired substance between the product stage and the s-th stage under conditions of constant flows leads (*1*) to a partial differential equation:

$$\lambda\frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial s^2} - \varepsilon\frac{\partial}{\partial s}[\Psi N + N(1 - N)] \tag{1}$$

where $N = N(s, t)$ is the average mole fraction of the desired substance in the input streams for the s-th stage (cf. Fig. 1), counted toward the product end starting from the feed point in the cascade, at time t from the start-up of the cascade. Other quantities used in Eq. (1), all being dimensionless, are:

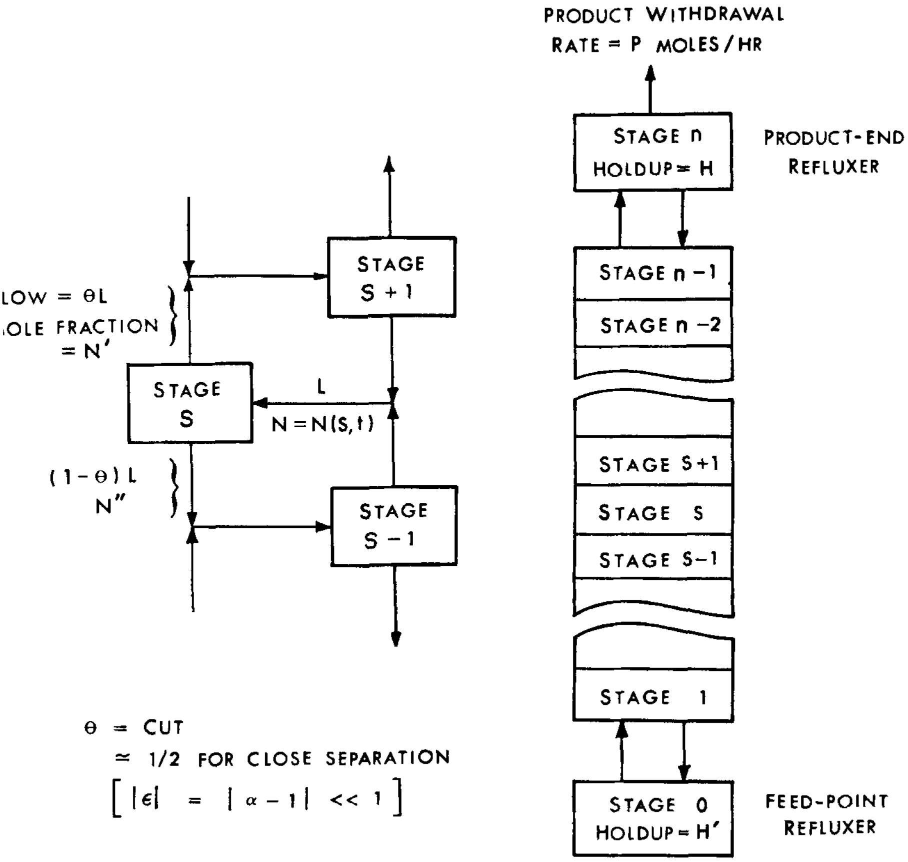

FIG. 1. Cascade notation.

$\varepsilon = \alpha - 1$, where α is the "head-to-tail" separation factor. This use of α is different from Cohen's in that the latter is the "head" or "tail" separation factor. This α is twice Cohen's α (*2*, *3*).

$\lambda = 2h$, where h is the holdup per stage per unit flow, or the average process time per stage.

$\Psi = \dfrac{2P}{\varepsilon L}$, where P is the production rate, or the rate of withdrawal of product at the product-end of the column, and L is the total interstage flow rate at the stage s. In a square cascade, L is independent of s. In a square distillation cascade under total reflux, L is also equal to twice the boil-up rate.

When the mole fraction of the desired substance is negligibly small compared to unity, Eq. (1) becomes linear:

$$\lambda \frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial s^2} - \varepsilon(1 + \Psi)\frac{\partial N}{\partial s} \tag{2}$$

This would be the case in preliminary fractionation processes of isotopes, such as ^{235}U, D, ^{13}C, and ^{15}N. Cohen solved the equation under the following initial and boundary conditions:

At $t = 0$;

$$N(s, t = 0) = N_0, \qquad \text{at all } s$$

At $s = 0$ (feed point);

$$N(0, t) = N_0, \qquad \text{at all } t$$

At $s = n$ (product end);

$$P = 0, \qquad \text{at all } t$$

Holdup in refluxer $= H$

Such a solution is of general interest for two reasons. First, in large-scale production, one seeks to minimize the initial start-up period during which the system is operated under total reflux. Second, observations of the transient behavior can be used for evaluating such separation system constants as the number of theoretical plates and the separation factor (*1*).

The theory of transient column behavior is of primary importance in both applications. The present study is a part of our effort to extend limits of the validity of Cohen's theory.

The solution, at $t > \lambda n^2/10$, is of the form (*1*)

$$\frac{N(n, t)}{N_0} = e^{\varepsilon n} - (e^{\varepsilon n} - 1)A(\varepsilon n, K/\lambda n)\exp\left[-\frac{B(\varepsilon n, K/\lambda n)t}{\lambda n^2}\right] \qquad (3)$$

where A and B are related to the smallest root of a transcendental equation, which will be discussed later. Cohen gave tables of A and B for $K/\lambda n$ between 0.0 and 0.5 in steps of 0.1 and for εn between 0.0 and 1.2 in steps of 0.1. It is highly desirable to extend and refine Cohen's table beyond the limits for εn in both the positive and negative directions. We also feel that it is useful to extend the time limit to the region below $t = \lambda n^2/10$ by adding a higher term of expansion to Eq. (3).

MATHEMATICAL PROCEDURE

Cohen's solution can be transformed into

$$\frac{N - N_0}{N_\infty - N_0} = 1 - A_1 e^{-B_1\tau} - A_2 e^{-B_2\tau} \qquad (4)$$

where $N_\infty = e^{\varepsilon n}$ is the overall separation at steady state, and $\tau = t/\lambda n^2$ is the reduced time, or the time measured in the unit of average process time divided by the number of stages. A_1 and B_1 are Cohen's A and B, respectively. The last term in Eq. (4) represents the next higher term in the approximation.

Both B_1 and B_2 are defined as

$$B \equiv a^2 + x^2 \qquad (5)$$

where $a \equiv \varepsilon n$, and x is either the smallest positive root x_1 or the second smallest positive root x_2 of the equation

$$\tan x = \frac{x}{c + bx^2} \qquad (6)$$

in which $b \equiv K/\lambda n = H/Lhn$, $K \equiv 2H/L$, and $c \equiv a^2 b + a$. In the special case of $c > 1$, an imaginary root exists, in which case $B_1 = a^2 - x_0{}^2$, where x_0 is the only root of the equation,

$$\tanh x = \frac{x}{c - bx^2} \qquad (7)$$

All the cases have been summarized in Table 1. It is to be noted that the case of $c < 1$ includes all negative values of c. Cohen's table covers the cases of $0 \leq c \leq 1.92$ for B_1. The case of $a = b = 0$ represents a singular point, where $B_1 = (\pi/2)^2$, although this has no physical meaning. The ranges of x_1 and x_2 for all conceivable cases have been tabulated in Table 2.

TABLE 1

Summary of Formula for B_1 and B_2

$c = a^2b + a$	B_1	B_2
< 1	$a^2 + x_1{}^2$	$a^2 + x_2{}^2$
$= 1$	a^2	$a^2 + x_1{}^2$
> 1	$a^2 - x_0{}^2$	$a^2 + x_1{}^2$

TABLE 2

Ranges of Roots of Eq. (6)

c	b	γ[a]	x for $B_1 = a^2 + x^2$[b]	x for $B_2 = a^2 + x^2$	Remarks
$c > 1$	$b = 0$		$< \infty$	$(\pi, 3\pi)$	
	$b \neq 0$		$< \sqrt{\frac{c}{b}}$	2	
$c = 1$			$= 0$	$\left(\pi, \frac{3\pi}{2}\right)$	
$0 < c < 1$			$\left(0, \frac{\pi}{2}\right)$	$\left(\pi, \frac{3\pi}{2}\right)$	
$c = 0$	$b = 0$		$= 0$	None	$B_1 = \left(\frac{\pi}{2}\right)^2$
	$b \neq 0$		$\left(0, \frac{\pi}{2}\right)$	$\left(\pi, \frac{3\pi}{2}\right)$	$c < 0$
$c < 0$	$b = 0$		$\left(\frac{\pi}{2}, \pi\right)$	$\left(\frac{3\pi}{2}, 2\pi\right)$	$a < 0$
	$b \neq 0$	$\gamma < \frac{\pi}{2}$	$\left(\gamma, \frac{\pi}{2}\right)$	$\left(\pi, \frac{3\pi}{2}\right)$	
		$\frac{\pi}{2} < \gamma < \frac{3\pi}{2}$	$\left(\frac{\pi}{2}, \gamma\right)$	$\left(\pi, \frac{3\pi}{2}\right)$	
		$\frac{3\pi}{2} < \gamma$	$\left(\frac{\pi}{2}, \pi\right)$	$\left(\frac{3\pi}{2}, \gamma \text{ or } 2\pi\right)$[c]	

[a] $\gamma \equiv \sqrt{-c/b}$.

[b] When $c > 1$, $B_1 = a^2 - x^2$, where x is the magnitude of the imaginary root.

[c] γ or 2π, whichever is smaller.

The preexponential coefficients A_1 and A_2 are both related to B_1 and B_2, respectively, by

$$A_i = \frac{2a}{B_i(e^{2a} - 1)\left[b + \frac{1}{2} + \frac{C_i(C_i + 1)}{2(B_i - a^2)}\right]} \tag{8}$$

where

$$C_i \equiv -bB_i - a^2$$

Singularities exist as follows: When $c = a^2b + a = 1$,

$$A_1 = \frac{2}{a(e^{2a} - 1)(b + \frac{1}{3})} \tag{9}$$

while A_2 is nonsingular. When $a = 0$,

$$A_i = \frac{1}{B_i\left[b + \frac{1}{2} + \frac{C_i(C_i + 1)}{2B_i}\right]} \tag{10}$$

A pair of computer subroutine programs were written, one for calculations of A_1 and B_1, and the other for A_2 and B_2. Each subroutine takes a and b as input from a calling program, and returns a pair of numbers A_i and B_i. The root of the transcendental Eq. (6) is obtained by using Newton's linear iterative algorithm. All precautions were taken to avoid accidental crossover to an undesired branch of the function during the iterative process.

RESULTS AND DISCUSSION

Numerical results for A_1 and B_1 have been tabulated in Table 3 for $K/\lambda n$ from 0.00 to 0.50 and for εn from -1.2 to $+1.2$ (*4*). Similar tabulation is presented for A_2 and B_2 in Table 4 (*4*). It is seen that the present values of A_1 and B_1 are in complete agreement with Cohen's wherever the comparison is possible.

In Figs. 2 and 3, values of A_1 and B_1, respectively, have been plotted against εn, at various values of $K/\lambda n$, the ratio of the holdup in the product refluxer to the total holdup in the column. The negative εn represents the stripping section. In reference to Eq. (4), the contribution of the first transient term, $A_1 e^{-B_1 \tau}$, to the fractional equilibrium attainment, $(N - N_0)/(N_\infty - N_0)$, has been plotted in Fig. 4 as a function of the reduced time τ

TABLE 3

Functions for the First Transient Term

εn		A_1 and B_1 at holdup ratio $K/\lambda n$ of							
		0.00	0.05	0.10	0.15	0.20	0.30	0.40	0.50
−1.20	$A =$	0.6936	0.7429	0.7844	0.8187	0.8467	0.8883	0.9163	0.9355
	$B =$	3.8935	3.6001	3.3330	3.0923	2.8765	2.5110	2.2188	1.9810
−1.00	$A =$	0.7144	0.7616	0.8008	0.8328	0.8589	0.8972	0.9229	0.9405
	$B =$	3.6231	3.3405	3.0858	2.8580	2.6550	2.3136	2.0416	1.8224
−0.80	$A =$	0.7348	0.7798	0.8167	0.8465	0.8706	0.9059	0.9293	0.9454
	$B =$	3.3662	3.0944	2.8518	2.6365	2.4458	2.1273	1.8751	1.6726
−0.60	$A =$	0.7547	0.7975	0.8320	0.8598	0.8820	0.9143	0.9356	0.9502
	$B =$	3.1225	2.8615	2.6307	2.4275	2.2487	1.9519	1.7184	1.5317
−0.50	$A =$	0.7645	0.8061	0.8395	0.8662	0.8875	0.9183	0.9387	0.9526
	$B =$	3.0055	2.7499	2.5249	2.3276	2.1545	1.8682	1.6436	1.4644
−0.40	$A =$	0.7740	0.8145	0.8468	0.8725	0.8929	0.9223	0.1416	0.9549
	$B =$	2.8916	2.6414	2.4222	2.2307	2.0632	1.7871	1.5713	1.3993
−0.30	$A =$	0.7834	0.8228	0.8540	0.8786	0.8981	0.9262	0.9446	0.9571
	$B =$	2.7810	2.5361	2.3226	2.1368	1.9748	1.7086	1.5012	1.3363
−0.20	$A =$	0.7927	0.8309	0.8609	0.8846	0.9032	0.9299	0.9474	0.9593
	$B =$	2.6734	2.4338	2.2260	2.0458	1.8892	1.6327	1.4334	1.2754
−0.10	$A =$	0.8017	0.8387	0.8677	0.8904	0.9082	0.9336	0.9502	0.9614
	$B =$	2.5689	2.3346	2.1324	1.9577	1.8063	1.5592	1.3679	1.2165
0.00	$A =$	0.8106	0.8464	0.8743	0.8960	0.9130	0.9372	0.9529	0.9635
	$B =$	2.4674	2.2384	2.0417	1.8724	1.7262	1.4883	1.3047	1.1597
0.10	$A =$	0.8192	0.8539	0.8807	0.9015	0.9177	0.9406	0.9555	0.9656
	$B =$	2.3689	2.1451	1.9539	1.7899	1.6487	1.4198	112436	1.1048
0.20	$A =$	0.8276	0.8612	0.8869	0.9068	0.9222	0.9439	0.9580	0.9675
	$B =$	2.2733	2.0548	1.8689	1.7101	1.5739	1.3536	1.1847	1.0518
0.30	$A =$	0.8359	0.8683	0.8930	0.9119	0.9266	0.9472	0.9605	0.9694
	$B =$	2.1806	1.9673	1.7867	1.6331	1.5016	1.2898	1.1279	1.0008
0.40	$A =$	0.8438	0.8751	0.8988	0.9168	0.9308	0.9503	0.9628	0.9712
	$B =$	2.0907	1.8826	1.7072	1.5586	1.4318	1.2283	1.0732	1.9517
0.50	$A =$	0.8516	0.8818	0.9044	0.9216	0.9348	0.9533	0.9651	0.9730
	$B =$	2.0036	1.8006	1.6304	1.4868	1.3646	1.1691	1.0205	0.9044
0.60	$A =$	0.8591	0.8882	0.9098	0.9262	0.9387	0.9561	0.9672	0.9747
	$B =$	1.9193	1.7214	1.5563	1.4175	1.2998	1.1120	0.9698	0.8590
0.80	$A =$	0.8735	0.9003	0.9200	0.9348	0.9560	0.9615	0.9713	0.9779
	$B =$	1.7587	1.5709	1.4158	1.2863	1.1772	1.0044	0.8743	0.7733
1.00	$A =$	0.8868	0.9115	0.9294	0.9427	0.9527	0.9664	0.9750	0.9808
	$B =$	1.6085	1.4306	1.2852	1.1647	1.0638	0.9050	0.7863	0.6945
1.20	$A =$	0.8992	0.9218	0.9380	0.9499	0.9588	0.9708	0.9784	0.9834
	$B =$	1.4684	1.3002	1.1641	1.0523	0.9591	0.8135	0.7054	0.6221

TABLE 4

Functions for the Second Transient Term

		A_2 and B_2 at holdup ratio $K/\lambda n$ of							
εn		0.00	0.05	0.10	0.15	0.20	0.30	0.40	0.50
−1.20	$A =$	0.1389	0.1461	0.1414	0.1301	0.1165	0.0907	0.0704	0.0554
	$B =$	23.7453	21.5994	19.7998	18.3597	17.2238	15.6073	14.5483	13.8165
−1.00	$A =$	0.1307	0.1364	0.1312	0.1202	0.1074	0.0836	0.0649	0.0511
	$B =$	23.4423	21.3157	19.5452	18.1341	17.0231	15.4424	14.4050	13.6865
−0.80	$A =$	0.1225	0.1267	0.1211	0.1106	0.0986	0.0765	0.0595	0.0469
	$B =$	23.1578	21.0502	19.3082	17.9255	16.8389	15.2932	14.2774	13.5723
−0.60	$A =$	0.1142	0.1172	0.1113	0.1012	0.0900	0.0697	0.0542	0.0428
	$B =$	22.8919	20.8032	19.0890	17.7340	16.6712	15.1600	14.1656	13.4740
−0.50	$A =$	0.1101	0.1125	0.1065	0.0966	0.0859	0.0064	0.0516	0.0408
	$B =$	22.7659	20.6865	18.9862	17.6448	16.5936	15.0994	14.1156	13.4308
−0.40	$A =$	0.1060	0.1079	0.1018	0.0922	0.0818	0.0632	0.0491	0.0388
	$B =$	22.6446	20.5746	18.8878	17.5599	16.5203	15.0429	14.0697	13.3917
−0.30	$A =$	0.1020	0.1033	0.0972	0.0878	0.0778	0.0600	0.0466	0.0368
	$B =$	22.5280	20.4672	18.7940	17.4794	16.4512	14.9904	14.0278	13.3566
−0.20	$A =$	0.0980	0.0988	0.0927	0.0835	0.0739	0.0570	0.0442	0.0349
	$B =$	22.4161	20.3646	18.7047	17.4033	16.3864	14.9421	13.9900	13.3255
−0.10	$A =$	0.0940	0.0944	0.0882	0.0794	0.0701	0.0540	0.0419	0.0331

	B =	22.3090	20.2666	18.6200	17.3316	16.3259	14.8979	13.9562	13.2986
0.00	A =	—	0.0901	0.0839	0.0753	0.0664	0.0510	0.0396	0.0313
	B =	—	20.1734	18.5399	17.2644	16.2697	14.8579	13.9266	13.2758
0.10	A =	0.0862	0.0859	0.0797	0.0714	0.0628	0.0482	0.0374	0.0295
	B =	22.1090	20.0849	18.4644	17.2016	16.2178	14.8221	13.9011	13.2571
0.20	A =	0.0824	0.0817	0.0756	0.0675	0.0594	0.0455	0.0352	0.0278
	B =	22.0162	20.0011	18.3936	17.1434	16.1703	14.7905	13.8798	13.2426
0.30	A =	0.0787	0.0777	0.0716	0.0638	0.0560	0.0428	0.0331	0.0262
	B =	21.9282	19.9222	18.3274	17.0896	16.1273	14.7632	13.8627	13.2323
0.40	A =	0.0750	0.0737	0.0678	0.0602	0.0528	0.0403	0.0312	0.0246
	B =	21.8450	19.8480	18.2659	17.0405	16.0887	14.7401	13.8498	13.2262
0.50	A =	0.0714	0.0699	0.0640	0.0568	0.0497	0.0378	0.0292	0.0231
	B =	21.7667	19.7787	18.2091	16.9959	16.0545	14.7214	13.8412	13.2243
0.60	A =	0.0679	0.0662	0.0604	0.0534	0.0467	0.0355	0.0274	0.0216
	B =	21.6933	19.7142	18.1571	16.9559	16.0248	14.7070	13.8368	13.2268
0.80	A =	0.0612	0.0591	0.0536	0.0472	0.0411	0.0311	0.0239	0.0188
	B =	21.5612	19.5998	18.0674	16.8899	15.9791	14.6915	13.8411	13.2445
1.00	A =	0.0549	0.0525	0.0473	0.0414	0.0359	0.0271	0.0208	0.0163
	B =	21.4488	19.5051	17.9969	16.8426	15.9517	14.6937	13.8630	13.2798
1.20	A =	0.0490	0.0464	0.0415	0.0361	0.0312	0.0234	0.0179	0.0141
	B =	21.3564	19.4303	17.9459	16.8144	15.9430	14.7140	13.9026	13.3328

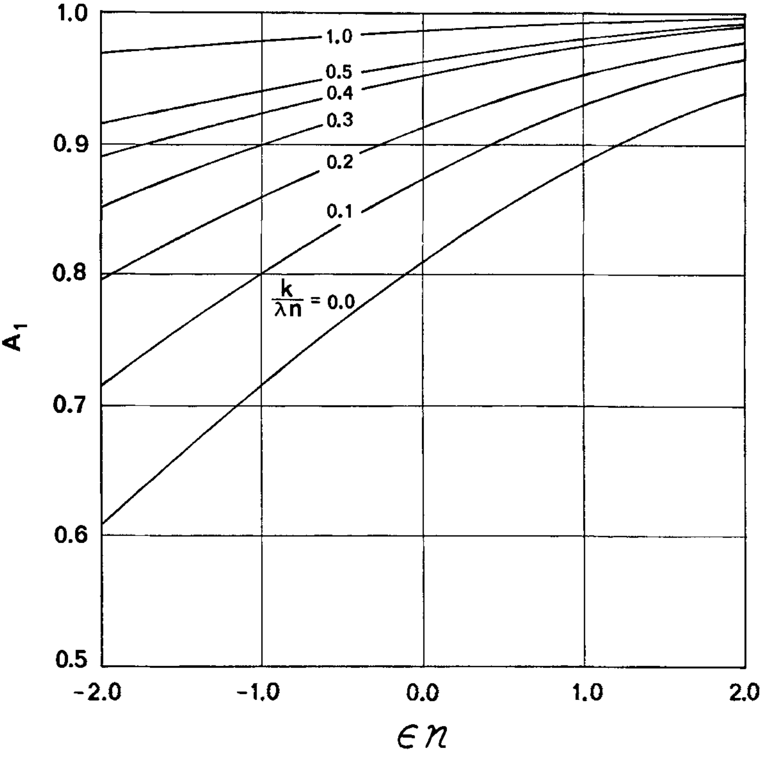

FIG. 2. Preexponential factor A_1 of first transient term.

for the case of no refluxer holdup. The line for $\varepsilon n = 0$ has been included only for reference purposes. For the same reduced time, the stripping section attains its steady state much faster than the enriching section. However, the graph does not by any means imply that, within the stripping section, the equilibrium time in the longer column is shorter. The equilibrium time in the stripping section does in fact increase with the number of plates since $t = \lambda n^2 \tau$, although the rate of increase is much slower than that in the enriching section.

Plots of A_2, B_2, and $A_2 e^{-B_2 \tau}$ are presented in Figs. 5, 6, and 7, respectively. The most striking difference from the previous graphs is the complete reversal of trends of A as a function of εn and of $K/\lambda n$. Not only does A_2 decrease with increasing εn, but it also decreases with increasing holdup

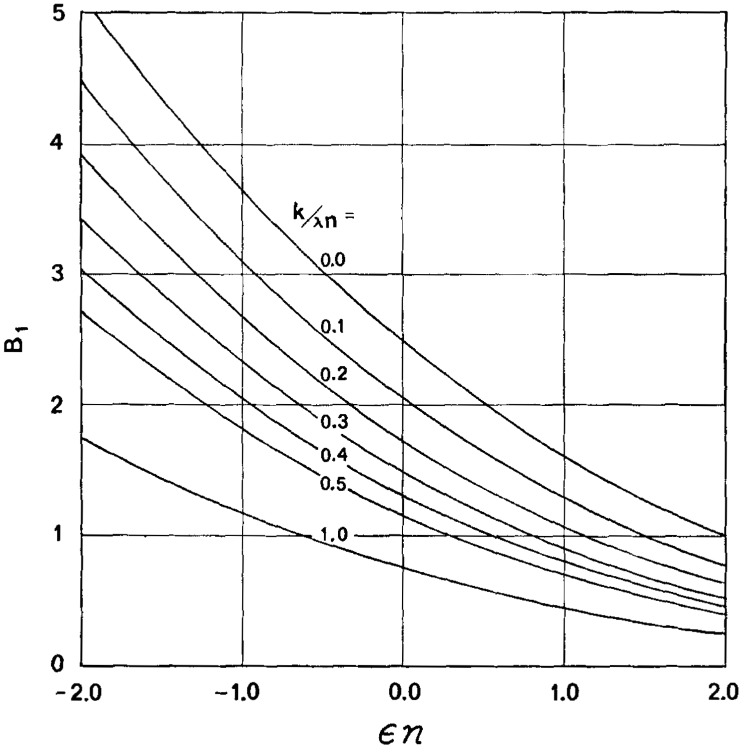

FIG. 3. Exponent factor B_1 of first transient term.

ratio, while A_1 increases with increasing εn and $K/\lambda n$. Although the magnitude of A_2 is smaller than A_1, it is evident that the second transient term becomes relatively significant at smaller values of εn and $K/\lambda n$. It is noted from Fig. 6 that, compared to the first transient term, the second term is damped much faster, so that the second term in general is important at small values of enrichment, holdup ratio, and time. Figure 7 verifies this for $K/\lambda n = 0$. The crossing over of lines in the stripping section of Fig. 7 is a result of interaction of the opposite trends of A_2 and B_2 against varying εn.

Finally, the relative importance of two transient terms is shown in Fig. 8. It must be noted that the comparison is made at $K/\lambda n = 0$, the smallest possible value, at which the second transient term is most sig-

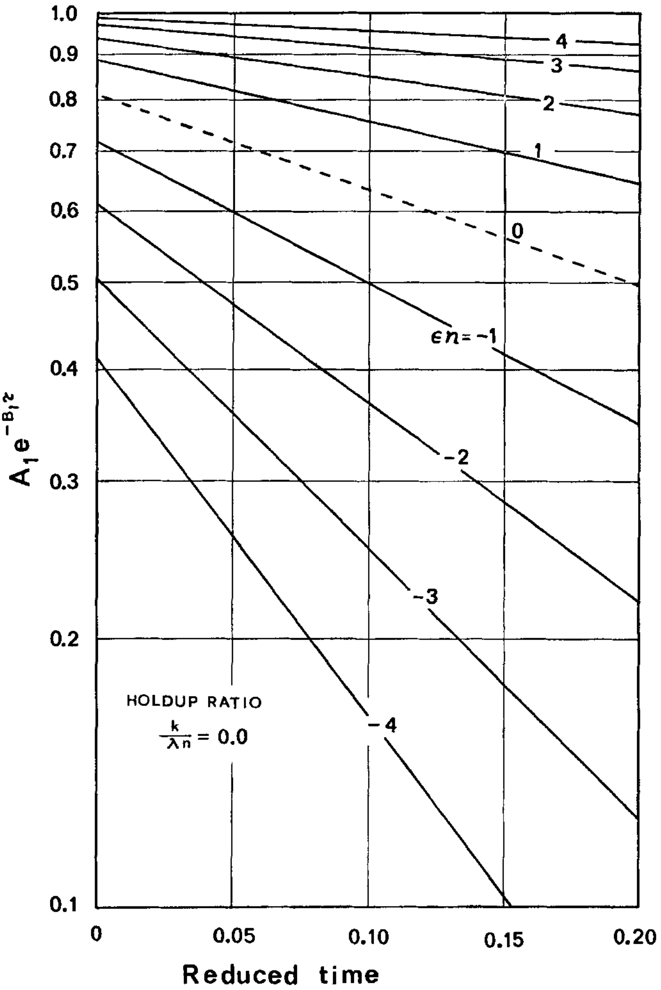

FIG. 4. The first transient term as a function of reduced time τ.

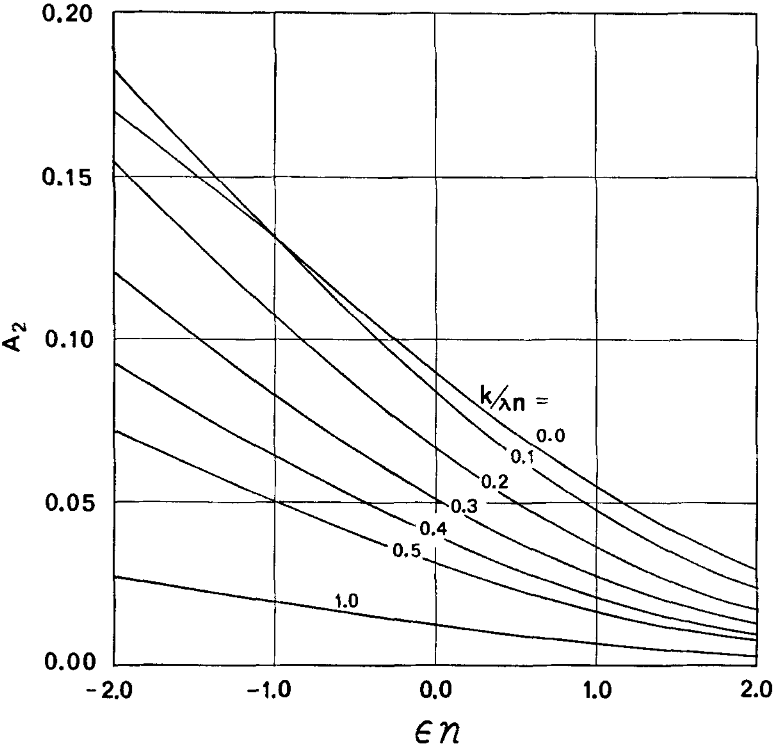

FIG. 5. Preexponential factor A_2 of second transient term.

nificant. It is thus evident that the limitation of $\tau > 0.10$ that Cohen placed for the validity of his solution, Eq. (3), was well founded as far as the enriching section is concerned. In the stripping section and/or at a shorter time, however, the second transient term is significant.

On the other hand, the third transient term in general contributes insignificantly to $(N - N_0)/(N_\infty - N_0)$ at the reduced time much smaller than 0.1. Based on analyses of the upper and lower limits of the third smallest root of Eq. (6), it has been found that the upper limits of the third term is of the order of 10^{-2} or smaller, even at $\tau = 0.01$ for $\epsilon n = -3$ and $K/\lambda n = 0$, the condition under which the contribution would be the greatest. Typically, for $\epsilon n = -3$ and $K/\lambda n = 0$, the upper limit is 0.05, 0.03, and 0.0002 at $\tau = 0.01$, 0.02, and 0.10, respectively. For $\epsilon n = +1$ and $K/\lambda n = 0$, the limit is 0.01, 0.06, and 0.0002 at $\tau = 0.01$, 0.02, and

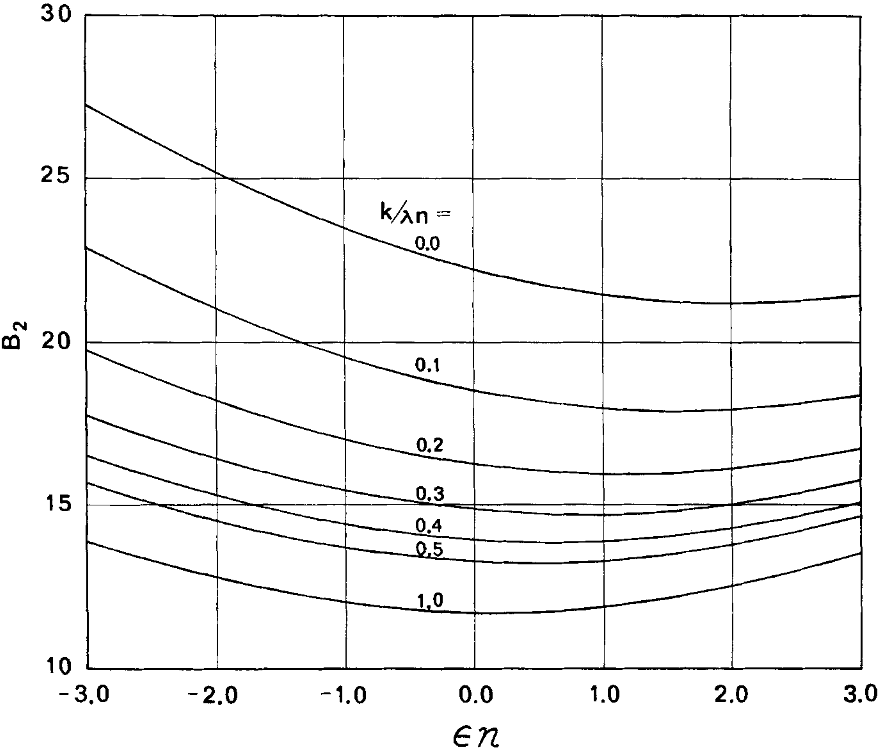

FIG. 6. Exponent factor B_2 of second transient term.

0.10, respectively. It is thus fair to conclude that the inclusion of the second transient term extends the lower limit of applicability of the solution to $\tau = 0.01$ for any enriching section, and the uncertainty at this τ is at most 0.01. For the stripping section, the error may be as high as 0.05 at $\tau = 0.01$ under extreme conditions.

As an application of the subroutine programs written for calculations of A_1, B_1, A_2, and B_2, the reduced time, $\tau_{0.95}$, required for the achievement of 95% of the steady-state value was calculated at various values of εn and $K/\lambda n$. The problem is that of solving Eq. (4) for τ, with the left-hand side equated to 0.95. It involves an iterative procedure. Results of these calculations have been plotted in Fig. 9. The graph clearly shows an increasing trend in the enriching section of equilibrium time with increasing holdup in product refluxer, $K/\lambda n$, and overall separation εn. It should

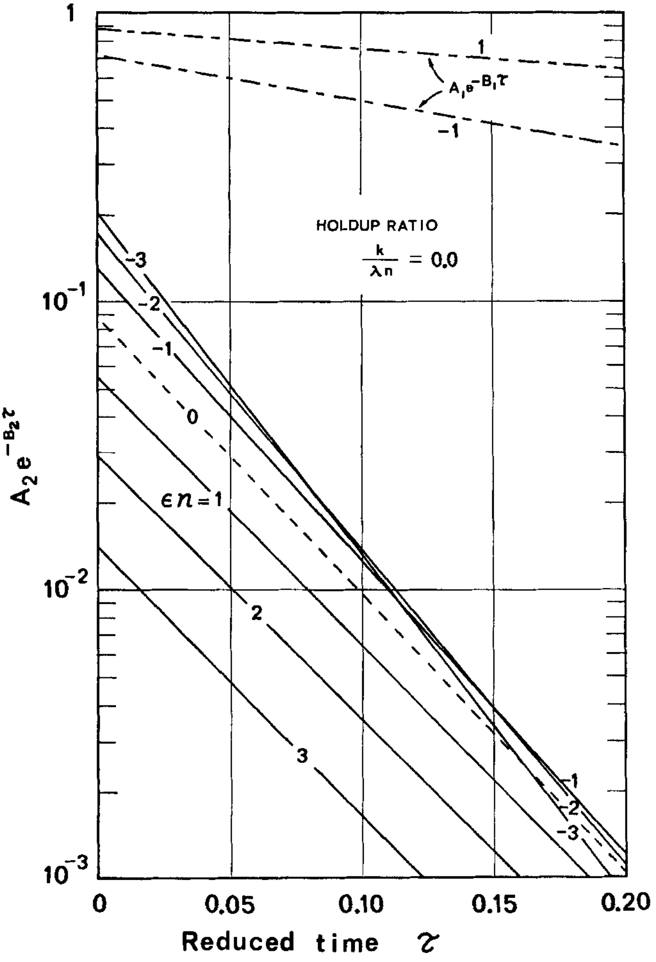

FIG. 7. The second transient term as a function of reduced time τ.

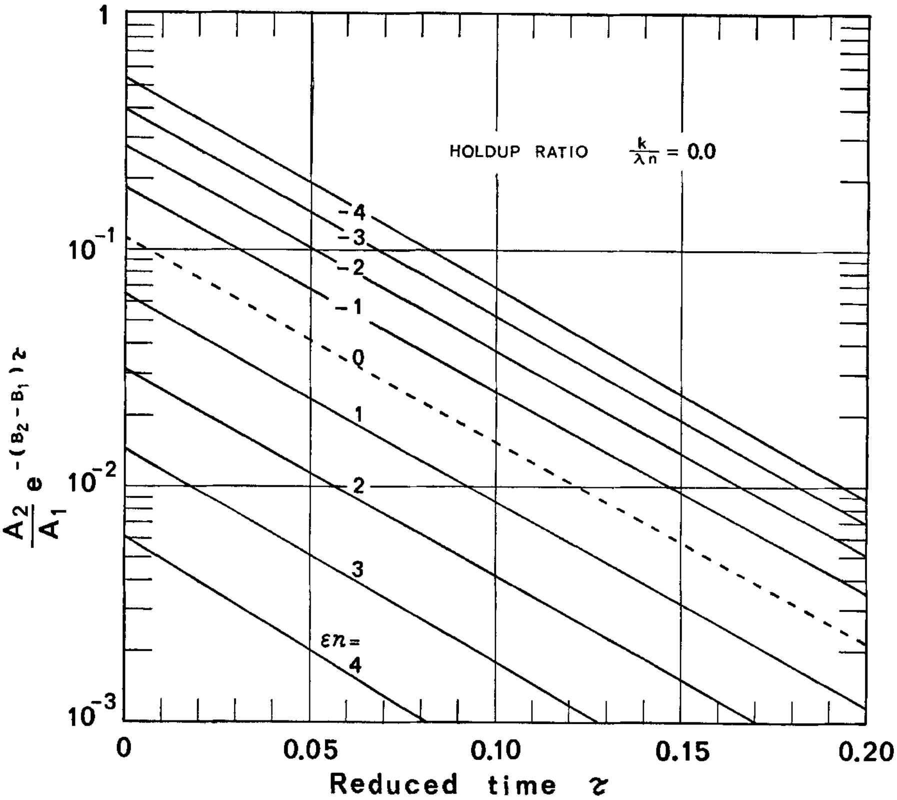

FIG. 8. Relative importance of the first and second terms.

also be noted that the actual equilibrium time $t_{0.95}$ is equal to $\lambda n^2 \times \tau_{0.95}$, which in fact also increases with the length of the stripping section.

One feature in Fig. 9 worth noting is the fact that the equilibrium time increases sharply with an increasing holdup ratio. This is due to the fact that, for a large holdup in the product refluxer, a large inventory of the desired isotope must be built up at the product end. The desired isotope is, by definition (cf. Eqs. 1 and 2), the minor component, i.e., $N \ll 1$. When the minor component enriches in the liquid phase, the material holdup in the product refluxer is necessarily large. This is the case existing in most isotope separation plants. For example, in the distillation of carbon

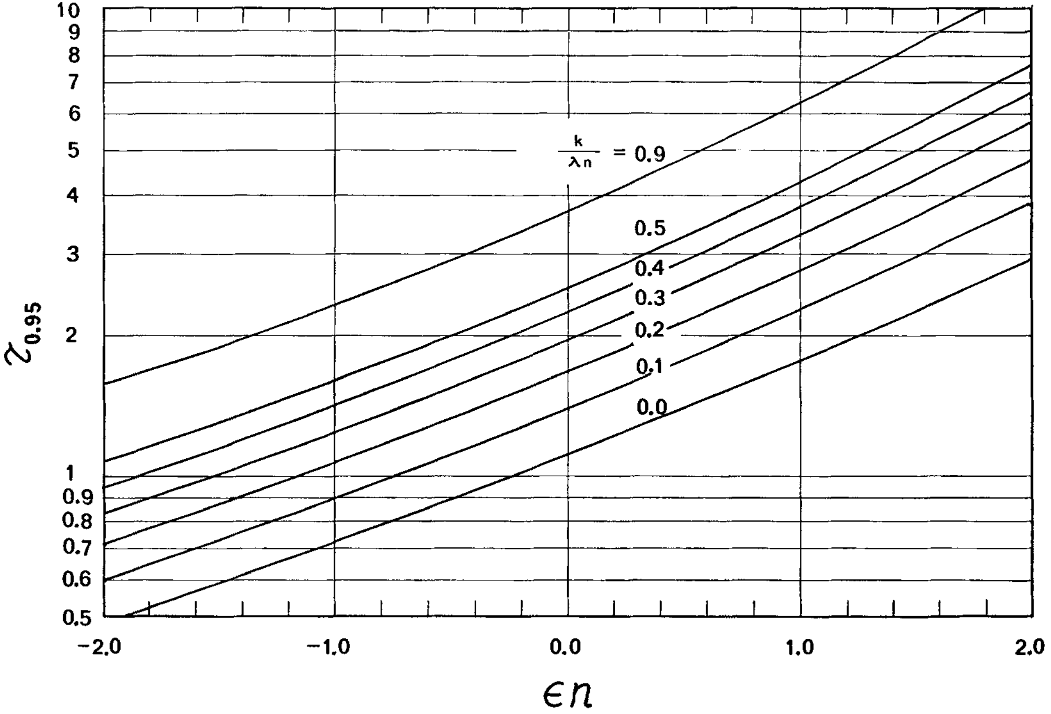

FIG. 9. The 95% equilibrium time.

monoxide, ^{13}C (natural abundance = 1.1 %) enriches in the liquid. In the exchange of nitrogen isotopes between nitric oxide and nitric acid, ^{15}N (0.37 %) concentrates in the aqueous phase (*5*). However, the reverse situation is possible: the minor component may be enriched in the gas phase. For instance, ^{13}C enriches in the gas phase in an exchange between hydrogen cyanide and aqueous cyanide solution (*6*). In a distillation, a heavy isotopic molecule may have a higher vapor pressure than the lighter molecule in a temperature range in which the vapor pressure isotope effect is "inversed." The inverse effect is favored in an isotopic molecular pair which exhibits a large isotope effect in the zero-point energy shifts of internal vibrations upon condensation (*7*). In these cases the heavier isotopic species, which is the minor isotope for most of the light elements, enriches in the gas phase. Here, the holdup in the product refluxer can be made negligibly small. All other considerations being comparable, a system in which the desired isotope enriches in the gas phase has a definite advantage in that it requires a shorter startup period.

For the determination of the separation factor and the number of theoretical plates using the long-time kinetics, one would take up to the first transient term of Eq. (4), and obtain the best straight line through a plot of ln $((N_\infty - N)/(N_\infty - N_0))$ against τ. The intercept and the slope give A_1 and B_1, respectively, both of which are functions of ε and n. This information, combined with experimental data on εn, which is ln N_∞, leads to the first approximation for ε and n. The second transient term in Eq. (4) may then be added to $(N_\infty - N)$ $(N_\infty - N_0)$ to correct for small deviations of experimental points corresponding to small τ from the straight line. The natural logarithm of the resulting quantity would then be plotted against τ, and the second approximation for ε and n would be obtained accordingly.

It is worth noting that, if the desired isotope enriches in the liquid, that which is operated in an ordinary, laboratory scale distillation column, with a large holdup in the boiler, is a stripping section. Due to the nonsymmetry of transient behavior between the enriching and stripping sections, it is incorrect to use the tables of A's and B's of the positive εn when the desired minor component enriches in the liquid. On the other hand, if the minor component enriches in the vapor phase, the proper tables to use are the ones for the positive εn.

Such a distinction is not necessary for consideration of the transient period for an operation of production scale, because such a column is always operated as an enriching column.

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REFERENCES

1. K. Cohen, *The Theory of Isotope Separation as Applied to the Large-Scale Production of U-235*, McGraw-Hill, New York, 1951.
2. J. Bigeleisen and S. V. Ribnikar, *J. Chem. Phys.*, *35*, 1297 (1961). J. Bigeleisen, M. J. Stern, and W. A. VanHook, *Ibid.*, *38*, 497 (1963). J. Bigeleisen, C. B. Cragg, and M. Jeevanandam, *Ibid.*, *47*, 4335 (1967).
3. M. Benedict and T. H. Pigford, *Nuclear Chemical Engineering*, McGraw-Hill, New York, 1957.
4. Tables of (A_1, B_1) and (A_2, B_2) calculated for $K/\lambda n$ from 0.00 to 0.50 in steps of 0.05 and for εn from -3.0 to $+3.0$ in steps of 0.1 are available from the authors by writing directly to them.
5. W. Spindel and T. I. Taylor, *J. Chem. Phys.*, *24*, 626 (1956).
6. C. A. Hutchison, D. W. Stewart, and H. C. Urey, *Ibid.*, *8*, 532 (1940).
7. J. Bigeleisen, *Ibid.*, *34*, 1485 (1961). M. J. Stern, W. A. VanHook and M. Wolfsberg, *Ibid.*, *39*, 3179 (1963). M. Wolfsberg, *J. Chem. Phys.*, *60*, 15 (1963).

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