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LIQUID THERMAL DIFFUSION

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H.W. OTTENSTROER

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INTRODUCTION

The discovery of uranium fission opened up vast new possibilities for useful applications. Among these was the energy-yielding chain reaction. In employing uranium for this purpose only one isotope U-235 takes part. Hence it was thought likely that it might be necessary to obtain some separation of the isotopes of uranium in order to liberate this energy. Representatives of the Navy were interested in the possible application of atomic energy to submarine propulsion. For this purpose the use of an energy source built up of either separated uranium or of uranium plus heavy water seemed essential in order to attain the small weights and small volume necessary for submarine installations. Accordingly, as early as May 1939, the Naval Research Laboratory gave support to a number of researches aimed at separating uranium isotopes. This volume undertakes to discuss some of the aspects of work carried out by the Navy on the Liquid Thermal Diffusion method of isotope separation. In this first chapter the subject of liquid thermal diffusion is considered briefly from four points of view: The role of the method in the production of the atomic bomb, scientific applications of the process, an elementary picture of thermal diffusion, and an outline of some of the more simple theory governing the phenomena.

I. Role of Liquid Thermal Diffusion in the Production of the Atomic Bomb

Preliminary studies of liquid thermal diffusion carried on at the Carnegie Institution of Washington showed promise in 1940. Hence a program of study of this method of isotope separation was supported by the Navy through a contract with the Institution. The work was ultimately expanded and later transferred to the Naval Research Laboratory. When emphasis was shifted from energy aspect to the bomb aspect and the Manhattan District was created, isotope studies were still continued at the Naval Research Laboratory, looking toward useful energy production. The separation method was brought to a state of practical usefulness early in 1943.

Principal research and development work on the method was carried out at the Naval Research Laboratory in Washington, D.C., by a group of men which ranged from one to six in number. In addition to investigating liquid thermal diffusion, this group developed the first practical method of producing uranium hexafluoride, invented the fluorine conditioning technique, and studied many of the chemical and physical properties of uranium hexafluoride, including corrosion studies, vapor pressure, viscosity, critical phenomena, electrical conductivity, and self diffusion.

In the summer of 1943, a small pilot plant at the

Naval Research Laboratory shipped 236 pounds of uranium hexafluoride possessing partial isotopic separation to the Metallurgical Laboratory in Chicago. This material was of particular value at that time because the electro-magnetic devices then being studied at Berkeley were the only other sources of separated uranium. Later, starting January 1944, a large pilot plant was erected at the Naval Base in Philadelphia.

In June 1944 responsible officials of the Manhattan District concluded that liquid thermal diffusion could be effectively employed in the atomic bomb program. Accordingly, the efforts of the liquid thermal diffusion group were integrated into the common effort that led to the atomic bomb. The resulting S-50 plant was constructed in the extremely short time of four months, largely due to the efforts of Lt.Col. M.C. Fox, Corps of Engineers. In the main, this unit served as a feeder for the electro-magnetic method. For this purpose, optimum over-all results were obtainable when normal uranium containing 0.715% U-235 was enhanced to .86% U-235. The value from this comparatively modest change came from two sources:

1. The output of a given electro-magnetic unit was increased by 20%.
2. Simultaneously, the purity of the output was improved some 20%. The method has been credited with shortening the war by 8 days. This was

accomplished by the expenditure of $20,000,000 for the construction and operation, or about 1% of the total cost of the Manhattan Project.

Among the outstanding characteristics of the equipment was simplicity, leading to relatively low installation cost and speedy construction. Principal drawbacks were the relatively long relaxation times and the high heat consumption of the plant.

II. Scientific Applications of Liquid Thermal Diffusion

The studies herein described were pursued for the purpose of developing a separation method to be used in World War II. Hence, the accuracy obtained and required was only that necessary to give practical answers. Purely by accident there were some results of general scientific interest.

Most of the work is in no sense complete from the scientific point of view. We present it because it is of historic interest and because it serves as a starting point for further work.

While the method has been titled liquid thermal diffusion, it should be noted that in many of the experiments and much of the plant operation, part of the process fluid was at temperatures above critical. Strictly speaking, therefore, the method as employed was on these occasions a mixture of gaseous and liquid diffusion.

The results of our work suggest that studies of other substances in the gaseous state under high pressure might be quite interesting. In other cases a combination of gaseous and liquid diffusion might be likewise proved efficacious.

From the viewpoint of scientific interest in future research, liquid thermal diffusion is of some importance. It is a method applicable to many other elements, and can be used either with pure liquid compounds of the element to be studied or solutions of this compound in water or other solvents.

For instance, a small column could produce sufficient separation of isotopes in aqueous solution to aid in the assignment of neutron cross-sections of the isotopes of a given element. In the case of radioactive isotopes whose mass was not known, the column could be used as a tool in the assignment of mass numbers. Conversely, radioactive isotopes could be used in the study of column properties.

Studies involving liquid thermal diffusion give promise of aiding in the elucidation of the liquid state. The method can be used to separate ions dissolved in water. It can be used to separate mixtures of organic materials. It is probably capable of separating mixtures of proteins and other biological materials which are fragile to chemical methods.

No limitation on hot and cold wall temperatures need

exist. A small useful installation could, for instance, operate with a hot wall at 0°C. and a cold wall at -70°C. Many valuable results could be obtained in runs lasting a few hours on small columns costing only several cents an hour to run.

Equipment which can be used for some of the studies indicated above can be built for a few hundred dollars. Once built, it is extremely simple to operate, requiring no delicate adjustments or specialized knowledge.

III. Thermal Diffusion

We have been discussing the present and future uses of liquid thermal diffusion. Some of the readers may wonder what this phenomenon of thermal diffusion is.

Let us suppose we have a substance, in the form of a liquid or a gas, consisting of two different kinds of molecules. This could be, for example, an aqueous solution of a salt, a mixture of two different gases, or a liquid consisting of a given chemical compound in which one of the elements is present as two different isotopes. Suppose that this substance is put into a box-shaped container which has a pair of opposite walls kept at different temperatures: perhaps one wall is heated while the other is cooled. It is found that the substance, which at the beginning is a homogeneous mixture of the two kinds of molecules, after a time becomes in general somewhat inhomogeneous. In the material close to the hotter wall there is an excess of

one kind of molecule, while near the cold wall the other kind of molecule is present in excess. We may think then of thermal diffusion as a process in which one kind of molecule tends to move in the direction of rising temperature, the other in the direction of falling temperature.

It must be remembered, however, that the extent of the separation brought about by the thermal diffusion process is very limited. This is due to the fact that the molecules of the substance are in a continuous state of chaotic motion (associated with their thermal energy), so that the two kinds of molecules tend to mix. This is the phenomenon of ordinary diffusion (as distinct from the thermal diffusion previously mentioned), and it acts to bring about uniformity in the composition of the substance. The greater the inhomogeneity in the distribution of the molecular species, the more rapidly does the ordinary diffusion take place. It follows then that, as one kind of molecule collects near the hot wall and the other near the cold wall, the rate of remixing of the molecules increases until finally a condition of equilibrium is reached at which the separation process due to thermal diffusion is just balanced by the remixing process due to ordinary diffusion.

It turns out that, at equilibrium, the separation produced is in general quite small: the composition of the substance near the hot wall differs but very little from

that near the cold wall. It is therefore not practical to try to separate isotopes in a mixture by the simple process of thermal diffusion described above. The method which is actually used, while based on the phenomenon of thermal diffusion, involves an additional phenomenon. The walls of the container which are kept at the two different temperatures are vertical and close together. The density of the fluid near the hot wall is decreased, that near the cold wall is increased, and convection sets in, in the course of which the fluid near the hot wall rises, while that near the cold wall descends. In this way a situation is brought about where two streams of fluid flow past each other and at the same time exchange molecules of the two species because of the thermal diffusion. The stream near the hot wall catches the molecules moving toward that wall by thermal diffusion and carries them upward, while near the cold wall molecules of the other kind are carried down by the convection flow there. The result is that one kind of molecule accumulates near the top of the container while the other kind collects near the bottom. It turns out that this method of counter-currents under suitable conditions may be much more effective in bringing about separation of the constituents of the fluid than the unaided phenomenon of thermal diffusion. It is this combination of thermal diffusion and convection that is utilized in the apparatus to be described.

While this process can be carried out both in liquids and in gases, it has been found that for the separation of the uranium isotopes in uranium hexafluoride, the liquid or gas under high pressure is much more satisfactory from the standpoint of the yield obtained and hence this combination will be dealt with exclusively in the present work.

IV. Introductory Theory of the Column

The apparatus used in the work, to be referred to hereafter as a "column" was in the form of three long vertical coaxial cylinders, two of which bounded the space in which the working fluid was kept. The length of the column used varied in different experiments from 12 to 48 feet, the latter being the length finally adopted. The annular space between the cylinders in which the working fluid was kept had a diameter of about 4.25 cms, with the spacing between the walls of the order of 0.025 cm. The inner or hot wall was maintained at a temperature which varied in different experiments from about 150° to about 320°C., while the outer or cold wall was kept at a temperature near 70°. It is found that when a column is filled with the uranium hexafluoride, the process or working fluid, and kept at the conditions described, isotope separation actually takes place. The fluid at the top of the column gradually becomes richer in the light isotope U-235, while that at the bottom acquires relatively more U-238.

The separation process can be described quantitatively by introducing the concept of the separation factor. Let us denote by c the concentration of the light isotope, i.e., the fraction of the molecules containing atoms of U-235. Then $1-c$ is the concentration of the heavy isotope. If we let c_T denote the value of c at the top of the column and c_B that at the bottom of the column, then we define the separation factor S by the relation

$$S = \frac{\dfrac{c_T}{1 - c_T}}{\dfrac{c_B}{1 - c_B}} = \frac{c_T\,(1 - c_B)}{c_B\,(1 - c_T)} \qquad (1)$$

It turns out that this separation factor plays a fundamental role in the theory of the behavior of the column. To give some idea of the orders of magnitude involved, it might be mentioned that in a typical case a separation factor $S = 1.4$ was obtained in 5 days, while the limiting or equilibrium value obtained after the column had been run for a much longer period was $S_e = 1.6$. In a few columns separation factors were much higher going up to $S_e = 2.5$.

It was previously pointed out that in the column one constituent, in this case the lighter one, moves toward the hot wall, while the other, the heavier one, moves toward the cold wall, due to thermal diffusion, and that

at the same time the fluid near the hot wall moves upward while that near the cold wall moves downward, due to convection. This results in an accumulation of the light constituent near the top and of the heavy one near the bottom. However, there are factors working to bring about a remixing. The ordinary diffusion process is active: as the concentration up the column begins to vary with the height, ordinary diffusion in the vertical direction sets in, tending to make the concentration more uniform. Besides this, mixing takes place between the two streams because of the ordinary diffusion in a horizontal direction from one to the other. Then too, there are other causes of mixing such as local irregularities in the temperature and flow distribution, known as parasitic convection, agitation of the fluid by mechanical vibrations, etc.

By taking into account these various effects, one finds that the behavior of the column may be described approximately by the following differential equation:

$$\frac{M}{L} \frac{\partial c}{\partial t} = - \frac{\partial \tau}{\partial z} \qquad (2)$$

where c, as before is the concentration of the light constituent, t is the time, z is the distance measured up the column, M is the hold-up mass, i.e., the mass of the material in the column, and L is the length of the column,

so that M/L is the hold-up mass per unit length. The quantity τ is the net rate of transport of the light constituent and is given by

$$\tau = Pc + Hc\,(1-c) - K\frac{\partial c}{\partial z} \tag{3}$$

where P is the product rate, i.e., the rate at which material is being withdrawn from the top of the column, Pc being the corresponding rate for the light constituent, and H and K are constants. The constant H is associated with the separative process in the column, while K is associated with the remixing processes.

For the case of small concentrations ($c \ll 1$) it is not too difficult to investigate the problem involving dependence on the time, as, for example, when the column is set into operation and approaches equilibrium. If $c \ll 1$, the differential equation obtained by substituting Eq. (3), with P = 0 in Eq. (2), is found to be

$$X\alpha^2\,\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha\,\frac{\partial c}{\partial z}\ , \tag{4}$$

where X, the "time constant" of the column, is given by

$$X = \frac{M}{HY}\ , \tag{5}$$

with

$$Y = \alpha L \ , \tag{6}$$

and

$$\alpha = \frac{H}{K} \ . \tag{7}$$

If the column is in a steady state, so that no changes take place with time, then we have

$$\tau = \text{constant} = P \ c_T \tag{8}$$

since in that case the upward rate of transport of the light constituent must equal the rate at which it is removed from the column. In particular, if no product is being removed ($P = 0$), we get the case of equilibrium for which, if we define S as before, i.e.,

$$S = \frac{c_T \ (1 - c_B)}{c_B \ (1 - c_T)} \ , \tag{9}$$

it follows that (using the symbol S_e to denote the value at equilibrium)

$$S_e = e^Y \ . \tag{10}$$

If product is being removed ($P > 0$), we shall simplify

matters here by considering the case in which α is very small compared to unity, which is the case of greatest interest at present. One finds then that

$$S = \frac{1 + \nu}{\nu + e^{-(1 + \nu)Y}} , \tag{11}$$

where

$$\nu = P/H . \tag{12}$$

In the problem of approach to equilibrium, with the column either closed at both ends, or attached to a storage chamber at one end or the other, or both, the solution of the equation is expressible in the form: S is a certain function of t/X and certain constants associated with the column and the storage chamber. In a number of cases the function can be represented in the form:

$$S = S_e - \sum_{n=1}^{\infty} A_n e^{-k_n(t/X)} , \tag{13}$$

where the A_n and k_n are constant coefficients and S_e is the equilibrium value of the separation factor. After a sufficiently long time, all but the first term can be neglected in the series and one can write it

$$S = S_e - A_1 e^{-k_1 t/X} \tag{14}$$

which is of a convenient form.

This equation states that separation in a column approaches an equilibrium value in familiar exponential manner.

A SURVEY OF THE LITERATURE RELEVANT TO LIQUID THERMAL DIFFUSION

H.M. Moseley

To provide the background for the liquid thermal diffusion method of isotope separation, this present chapter surveys the status of experiment and theory as it existed in early 1940. While this volume is devoted primarily to the liquid case, we will describe experimental work on both gaseous and liquid thermal diffusion because of the similarities existing between the two processes. Since much less is known about liquids than about gases, analogies to the gas case are of value in planning liquid experiments. The basic process in thermal diffusion is the separation which occurs when a mixture is subjected simultaneously to two different temperatures. The diffusion column merely magnifies the simple effect. If one is to understand thermal diffusion, he must understand first the basic process. In the gas case, this simple process appears to be understood. For a review of gaseous thermal diffusion the reader is referred to the work of R.C. Jones and W.H. Furry[1]. The basic process in the case of liquids is not understood. For the case of pure substances, almost nothing is known. However, a considerable amount of experimental work and theoretical study has been devoted to a special case of liquid thermal diffusion -- the Soret Effect.

I. The Soret Effect

If a temperature gradient is maintained in an originally homogeneous salt solution, it is found that, after a time, a concentration gradient will also exist in the solution. This phenomenon was first observed by Ludwig[2]; however, it became customary to refer to it as the Soret[3,4,5] effect, after its second discoverer.

Ludwig placed a solution of NA_2SO_4 in a U-tube, one limb of which was kept at 100°C, the other at 0°C. After two days, he observed solid crystals in the cold limb, while the concentration in the hot limb had decreased by a factor of 1/2.

The technique used by Soret was slightly different. A vertical tube of 30 cm. length and 2 cm. diameter was filled with the solution to be investigated, copper sulphate, for example. The upper end was then heated to and maintained at 80°C, whereas the lower end was held at 20°C. After a few months small samples of the solution taken from both ends were analyzed, yielding a typical result:

	A	B
% copper sulphate at cold end:	17.33%	29.87%
% copper sulphate at hot end:	14.03%	23.82%

Soret studied solution of KNO_3, KCl, NaCl, LiCl, and $CuSO_4$ in this manner, obtaining a small change in

concentration in all cases.

No theoretical explanation of the phenomenon was offered until 1887, at which time Van't Hoff[6] attempted to account for it on the basis of his theory of dilute solutions. According to the view taken by Van't Hoff, equilibrium is obtained when the osmotic pressure is everywhere the same, and since, according to his well-known theory, the osmotic pressure is given by

$$p = cRT \tag{1}$$

where c is the molar concentration, R the universal gas constant, and T the absolute temperature, this view leads to the equation cT = a constant, or

$$c_1/c_2 = T_2/T_1 \tag{2}$$

as the criterion for equilibrium. Applying this equation to the data given by Soret, we find that the ratio of the concentrations should equal 1.205. In the two examples quoted above, the values found are (A) 1.235, and (B) 1.254, which are of the correct order of magnitude. Eq. (2) proved to be approximately true for $CuSO_4$, NaCl, KCl, and LiCl.

Using apparatus similar to that employed by Soret,

Berchem[7] investigated aqueous solutions of HCl and NH_3. Shortly thereafter, Arrhenius[8,9] extended the investigation to more dilute solutions, employing a tube of 15 cm length, the top maintained at 67°C, the bottom at 27°C. According to the Van't Hoff theory, the equilibrium ratio of the concentrations should equal 1.133. Typical of Arrhenius' data are the results (for times of 89 - 90 days):

Solution	c_{27}/c_{67}
0.02 n NaOH	1.087
0.1 n NaOH	1.123
1.0 n NaOH	1.167
0.1 n $1/2CuSO_4$	1.088
1.0 n $1/2CuSO_4$	1.456
1.0 n NaCl	1.049

in which concentration ratios both below and above the theoretical value were obtained. The data of Arrhenius served to indicate that the Soret Effect is not completely accounted for by Eq. (2). Since they indicate that the effect depends on the substance being investigated and its concentration as well as the temperature difference, these data not only demonstrated the incorrectness of the theory, but also made desirable more experimental work.

Abegg[10], in a paper dealing for the most part with

demonstration experiments, discussed the effect of the shape of the apparatus on the time required to obtain substantially equilibrium separation. In his apparatus, in which (a) the interfacial area of hot and cold surfaces was as large as practical, and (b) the volume of the cold mass was small in comparison with that of the hot, Abegg obtained crystals of $CuSO_4$ in the cold side after 2 hours, which can be compared with Arrhenius' experimental time of 90 days.

For the most part, however, little additional experimental work was reported until almost twenty years after the publication of Arrhenius' results. In 1914, Wereide[11,12] reported results on NaCl, NaOH, and $CuSO_4$; in addition, he extended the investigation to solutions of organic compounds (antiprine, glycerine, acetic acid, acetone, alcohol) and non-electrolytes. Using a small cell of rectangular cross-section and 1.5 cm in height in place of the long tube, and obtaining his analyses by means of refractive index measurements, he was also able to obtain approach-to-equilibrium data without disturbing the system. Wereide proposed a theory based on the change in the rate of ordinary diffusion with the temperature, but admitted his results were not in accord with his theory.

Chipman[13], by utilizing the changes in electrical conductivity of solutions with change in concentration, was also able to follow the approach to equilibrium. His

investigations were, for the most part, concerned with 0.1 normal solutions of about 40 different salts. With his hot temperature at 30°C, cold at 20°C, he obtained values of the ratio c_{20}/c_{30} randomly distributed between 1 for NH_4Cl and 3 times the theoretical value for $Ba(OH)_2$. No explanation of the discrepancy was offered.

In addition, Chipman investigated 26 solutions of HCl of concentrations varying from 0.00002 normal to 13.6 normal. He found that the percentage separation increased steadily as the concentration increased, reaching a maximum at about 0.1 normal, then fell off for higher concentrations.

The latest report of experimental work on the Soret Effect is that of Tanner[14] who, like Wereide, employed an optical method of analysis. Tanner's investigations covered solutions of some 35 compounds. Porter[15] attempted to explain some of the results obtained by Tanner by theoretical reasoning different from that employed by Van't Hoff. By considering a plane being bombarded from opposite direction perpendicular to the plane, he finds that the net number of particles passing through the plane is $1/6d(cu)$ where c is the concentration of the solvent and u the average velocity of the particles. Assuming u proportional to the square root of the temperature, this yields, at equilibrium

$$cT^{1/2} = \text{a constant.} \tag{3}$$

Like the equation cT = const., Eq. (3) agrees with some experimental results and not with others. Consequently, Porter introduces a factor i, depending on the ionization, and states that

$$icT^{1/2} = \text{const.} \tag{4}$$

the presence of the factor i causing the difference of the Soret Effect in different cases. No further discussion of the i is given; its introduction must be regarded as an ad hoc assumption.

It should also be noted that Eastman[16], in applying the first and second laws of thermodynamics to the deduction of equilibrium conditions in non-isothermal systems, has treated the Soret Effect, arriving at the conclusion that in perfect solutions it is entirely the result of irreversible processes and does not represent a thermodynamic equilibrium. In imperfect solutions his work indicates the Soret Effect to consist in part of a reversible effect.

In summary, although considerable experimental results are available in the literature, a satisfactory explanation of the Soret Effect has not yet been advanced.

II. The Thermal Diffusion (Clusius-Dickel) Column

(a) Note on Theory

The theory of the thermal diffusion column is covered in detail elsewhere in this report, references to previous work being given where due. It suffices here to mention those theoretical investigators who were most active in developing the theory during the year 1939. These include Furry, Jones and Onsager[17], Waldmann[18,19], van der Grinten[20], Debye[21], and Wirtz[22]. For the most part, these men dealt with equilibrium conditions and with approximate solutions of the time dependent differential equation. The exact solution of the time dependent equation, under various set of boundary conditions, for the case in which the concentration of one component is small compared to unity, was later given by Bardeen[23].

(b) Experimental Work

In 1938 Clusius and Dickel[24] ingeniously used convection currents to enhance the normal thermal diffusion process considerably. Their discovery of the fact that the substitution of a horizontal temperature gradient in place of the vertical gradient increased the separation to an enormous extent, made thermal diffusion a method of practical utility for isotope separation.

Soon after the appearance of Clusius and Dickel's initial paper on this subject, describing the "Trennrohr"

only sketchily, a number of investigators, both in this country and in Europe, began work on the utilization of the thermal diffusion column. In spite of the appearance of other investigators, however, the most comprehensive report on the usefulness of the thermal diffusion column and the empirically found laws governing its operation is contained in later papers by Clusius and Dickel[25-28]

The column employed by Clusius and Dickel in their preliminary experiments consisted of a glass tube about one meter long and of about 1 cm internal diameter, surmounted by a sphere of about 1 liter capacity. This tube was enclosed in a second tube through which cooling water could be run. A Cr-Ni wire stretched down the center of the tube served as the hot wall, it being heated electrically.

A mixture containing 42.5% CO_2 and 57.5% H_2 was employed to test the operation. The current was adjusted to give a wire temperature of about 500°C. After one hour, 20 cm^3 of gas were drawn off the bottom, analysis of which indicated practically pure CO_2. This result was encouraging enough to lead Clusius and Dickel to a further investigation of their "Trennrohr".

Their next experiment was with dry air, for which they used a tube of 0.84 cm radius and 260 cm length. After five hours operation at a wire temperature of 650°C,

12 cm^3 of gas were withdrawn from the bottom of the column, this sample analyzing as 43.0% oxygen. Similar results were obtained in various other experiments.

As a final preliminary test to determine whether the method could be used for the separation of isotopes, the 260 cm tube was employed for the separation of the neon isotopes. After an eight-day run, with the wire at 600°C, a 10 cm^3 sample yielded the following analysis:

	Ne^{20}	Ne^{21}	Ne^{22}
Normal Neon	90.0%	0.3%	9.7%
Sample	68.4%	0.6%	31.0%

With these promising preliminary results proving the usefulness of the method, Clusius and Dickel began a lengthy investigation of the laws governing the operation of the thermal diffusion column, their purpose being to determine the dependence of the equilibrium separation and the transport on:

(a) the radius
(b) the length
(c) the pressure
(d) the mixing ratio of the two species
(e) the temperature difference, and
(f) the time.

Dry CO_2-free air was used rather than an isotope mixture for ease of analysis.

Rather than quote numerical results, we give their conclusions in brief outline form:

A. Equilibrium separation:

1. Varies approximately as the inverse fourth power of the difference of the radius of the tube and that of the wire in the range (0.4 - 1.0 mm) investigated.
2. Rises to a maximum at a pressure depending, of course, on the values of the other variables, falling off from this maximum at higher pressures approximately as the inverse square of the pressure.

B. Transport:

1. Proportional to the square of the pressure.
2. Proportional to the fourth power of the tube radius.
3. Proportional to the square of the temperature difference, as long as this value is small.
4. Independent of the length of the tube.

C. Approach to Equilibrium:

1. Separation proportional to the square root of the time for comparatively small times.

Finally, using a group of columns connected in series, Clusius and Dickel were able to realize a practically complete separation of the isotopes of chlorine. The product at the heavy end analyzed 99.4% HCl^{37}, while that at the light end analyzed 99.6% HCl^{35}. With one exception, all tubes had a radius of 0.84 cm, the radius of the other column being 1.28 cm; the hot temperature was around 700°C.

As mentioned above, shortly after the appearance of Clusius and Dickel's original note on the thermal diffusion column, several others undertook investigations with it. In most cases the later workers modified the column along lines introduced by Brewer and Bramley, i.e., the hot wire was replaced by an inner tube, so that the material being investigated was contained in the annular space between two concentric cylinders.

Brewer and Bramley[29-32], employing a column 1 meter long and using a temperature difference of about 350°C, studied mixtures of CH_4 and NH_3. On varying the wall clearance from 0.13 cm to 2.2 cm, they found that the separation rose sharply with increasing wall spacing, reached a broad maximum at around 0.7 cm, and then fell off for larger spacings. The variation of separation with pressure was also studied, and for the 0.7 cm wall spacing a rather broad maximum occurred at about 20 cm Hg.

Brewer and Bramley state that the mechanism of energy flow from the hot to the cold surface consists of a series of swirls in the gas between these surfaces, rather than by an overall convection current up the hot wall and down the cold, as assumed by other investigators.

Groth[33], using a hot wire apparatus of 250 cm length and 0.5 cm wall clearance, studied the separation of the Xenon isotopes. His results were positive, but do not show the quantitative separations, since he reports only the difference in atomic weight of samples from the ends of the column. Normal Xenon exists as a mixture of nine isotopes. His equilibrium values for the difference in atomic weight of the samples taken from the top and bottom were:

for hot temp. = 1650°C. At.wt. = 0.96 units

for hot temp. = 1200°C. At.wt. = 0.65 units.

In addition Groth found a shift in the atomic weight of mercury after a 60 hour run with an apparatus of 2.2 meter length and 0.7 cm wall clearance.

Taylor and Glockler[34,35] constructed a 40-foot concentric tube column with an annular space of 0.9 cm, employing it to study the possible separation of the carbon isotopes, using CH_4. Watson[36] also studied the separation of the carbon isotopes, obtaining a separation factor of about 2.4.

Nier and Bardeen[37], from a unit 74 feet long, obtained every 48 hours 308 m.g. of CH_4 in which the C^{13}/C^{12} ratio had been increased 11.5 times.

Korsching and Wirtz[38-41] investigated the separation of liquid mixtures, for example, hexane and carbon tetrachloride, and aqueous salt solutions. Using an apparatus of 90 mm length and of 0.25 mm wall clearance with a temperature difference of 50°C, and starting with a 50-50 mixture of hexane and carbon tetrachloride, they obtain results for a run of one day, and, on extrapolating these results, arrived at the conclusion that their apparatus would yield an equilibrium separation factor of about 50, with a relaxation time somewhere between 500 and 1000 days.

With the same apparatus, the following results are typical salt solutions:

Exp. No.	Substance	conc. Mole/liter	Time	C_{bottom}/C_{top}
1	$ZnCl_2$	0.1	60 hrs.	1.5
2	$ZnCl_2$	0.1	72 hrs.	1.75
3	$ZnSO_4$	0.1	48 hrs.	4.4
4	$ZnSO_4$	0.4	48 hrs.	7.3
5	$ZnSO_4$	0.6	48 hrs.	9.5

The samples from experiment No. 4 above were analyzed spectroscopically by examining the hyperfine structure of the ZnII line λ = 7479 A° for possible separation of the

zinc isotopes. A summary of results is as follows:

	Normal		Sample	
	Mass Spectr. analysis	Spectro. analysis	Top	Bottom
$\frac{64\ Zn}{68\ Zn}$	2.84	2.93	3.2	2.7
$\frac{64\ Zn}{66\ Zn}$	1.85	1.89	1.95	1.7
$\frac{66\ Zn}{68\ Zn}$	1.53	1.56	1.65	1.56

Clusius and Dickel[27] report the experiments described below, carried out in a sheetiron box of dimensions 20 mm x 1 mm x 150 cm. The top side of the box was heated with steam or hot water, while the lower side was held at a lower temperature with cold water. Convection was obtained by inclining the box to the vertical, the inclination being adjusted to make the separation a maximum.

(c) Liquid Mixtures: An acetone-water mixture, originally 42.2 mole-% acetone, yielded a sample at the bottom or "heavy" end containing 6.2 mole-% acetone after operation for 6 hours with a temperature difference of 40°. It is noteworthy that water, in spite of its small or molecular weight in the monomolecular form, concentrates at the "heavy" end. This result agrees with the conception of the polymeric structure of water.

Isotope Separation: After a run of 8 hours at a temperature difference of 80°C, an H_2O - D_2O mixture yielded 62.9% D_2O at the top or "light" end, and 64.5% D_2O at the opposite end. The thermal diffusion effect in liquid mixtures of isotopes is here demonstrated for the first time. That the effect is small is not surprising since the polymerization of water leads to a small value of the ratio $\frac{m_2 - m_1}{m_2 + m_1}$.

A Survey of the Literature Relevant to Liquid Thermal Diffusion

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HISTORY

In June 1940 the desirability of separating uranium isotopes was very apparent. While there was some doubt as to whether a nuclear chain reaction might be made to proceed using unseparated uranium, it appeared quite probable that energy could be obtained from separated isotopes of uranium. The task was clearly enormous. It was certain that some kilograms of highly separated material would be necessary or that tons of uranium possessing a small separation would be required for a chain reaction. The previous scale of separations of light elements was of the order of a fraction of a gram per day. For a heavy element like uranium, the problem of isotope separation would certainly be far more difficult. Of all the methods known at that time none was understood sufficiently well to permit an immediate engineering development. It was therefore desirable to investigate any method which showed some promise. Liquid thermal diffusion seemed to be such a method.

I. Preliminary Survey of Liquid Thermal Diffusion

It should be clear from the previous chapter that the state of knowledge regarding liquid thermal diffusion was far from complete in 1940. A few experiments had been conducted with water solutions and with mixtures of organic

liquids. A simple experiment had been conducted with a pure liquid -- water, which had given a separation factor of 1.025. No experiments had been conducted employing heavy elements, and no tests had been made involving uranium in any form. No dependable theory had been evolved covering the phenomena, and the dependence of separation on apparatus constants had not even been surveyed. Very little was known regarding behavior as a function of temperature conditions.

Accordingly, in July 1940 an exploratory program was initiated at the Department of Terrestrial Magnetism of the Carnegie Institution of Washington. Work was conducted by P.H. Abelson under the general direction of M.A. Tuve and of John A. Fleming, Director of the Department of Terrestrial Magnetism. Principal effort was devoted to verification of the work of Korsching and Wirtz[1], plus an investigation of the effect of apparatus constants and temperature on separation. The general correctness of the German work was verified, and the striking dependence of column behavior on spacing was demonstrated. Temperature conditions and column length were shown to play an important role. Work on a series of potassium salts, KCl, KBr, K_2SO_4, $K_2CR_2O_7$, showed that the isotope separation obtainable in potassium did not vary much with the molecular weight of the substance used. In the case of solutions it was clear that the primary effect occurring was a separation

of solute and solvent. In one case where a separation factor of 1.2 was obtained in K^{39} versus K^{41}, a simultaneous change in solute concentration of a factor of 14 also occurred.

Extrapolating this effect to larger isotope separation, one would predict that the solute concentration would rapidly approach zero at the top, when higher isotope separations were carried out in an aqueous solution. Studies on aqueous uranium solutions showed further that the compounds employed tended to hydrolyze in the column, probably due to changes in p_h occurring during operation of the column. The obvious answer to these difficulties lay in the use of a pure single compound of uranium. Uranium hexafluoride was the only substance then known which might possibly be employed. Unfortunately, this substance had been previously prepared only in quantities of the order of grams. Its physical properties were not well known and its corrosion characteristics had not been determined.

By September 1940 the work on aqueous solutions had been completed. It seemed worthwhile to expand the research with emphasis on the possible use of uranium hexafluoride. Ross Gunn of the Naval Research Laboratory was interested in the work as was Lyman J. Briggs, Director of the Bureau of Standards. Both men were then members of the Uranium Committee, Briggs serving as chairman. An arrangement was made under which the Naval Research Laboratory made $2,500

available to the Carnegie Institution of Washington for further studies. It was understood that the Institution would use the money for the payment of expenses for equipment while itself paying Abelson's salary. Due to the existence of special facilities at the Bureau of Standards, the research work was moved there.

II. Production of UF_6

The first problem to be solved was the production of UF_6. A survey of the possibilities showed that the best method was the fluorination of metallic uranium. The metal was expensive and fluorine was not commercially available. A method of production was devised employing fluorination of UF_4. This substance could be prepared by ordinary wet chemical methods easily and cheaply. To obtain uranium hexafluoride from the compound required addition of two rather than six fluorine atoms. The method was first tried using a fluorine generator at the Naval Research Laboratory in October 1940. Facilities were then installed in the Chemistry Division at the Bureau of Standards permitting production of as high as 800 grams of uranium hexafluoride per day. At that time this installation was the only one in the country capable of producing such amounts. During the major portion of 1941 this equipment, together with a similar installation later made at the Naval Research Laboratory, supplied the research requirements of the

various organizations employing uranium hexafluoride on isotope separation.

Corrosion studies were made on a number of metals including nickel and some of its alloys, copper, iron, silver solder, and stainless steel. It was learned that the ability of these substances to withstand attack by uranium hexafluoride was enhanced by a conditioning process involving pre-treatment with fluorine gas.

III. Initial Uranium Isotope Separation

With the chemical properties of uranium hexafluoride investigated, it was possible with some confidence to build a liquid thermal diffusion column, knowing that the process fluid would not decompose in the column and that the fluid could be handled successfully. Accordingly, a 12 foot long column was built and operated with uranium hexafluoride. Runs on this column were made in April 1941. The results showed a small separation about equal to the probable error of the measurement. The decision was then made to build a longer column and employ higher temperature differences in an effort to verify the effect. Due to the special facilities existing at the Naval Research Laboratory, the work was moved to that site in June 1941. There the work was conducted under the general scientific supervision of Ross Gunn, with Rear Admiral H.G. Bowen, USN, Director of the Laboratory. In September 1941 P.H. Abelson was joined by John I. Hoover

who was second in command of the experimental work throughout the course of study both at Anacostia and later at Philadelphia.

Ultimately a high-pressure boiler was obtained and a 36 foot column built and installed in January 1942. This column had a space of 0.053 cm and gave a separation of 1.02. The half-time for the column was about a day. A second column having a space of 0.068 cm gave a separation of 1.014 with a half-time of about a day. These results indicated the need for narrower spacing. A column possessing a spacing of 0.038 cm was installed in June 1942, which gave a separation factor of 1.11 with a half-time of about 12 hours. With these encouraging results it was a simple matter to pursue successfully the question of optimum spacing and establish that the best value lay close to 0.025 cm.

While this optimum value was being established, considerable experience was gained in the operation of liquid thermal diffusion columns employing uranium hexafluoride. It was found that the equipment was easy to operate. By cutting columns apart, it was determined that no great corrosion difficulties were involved. These favorable circumstances led to a decision to increase the scope of the work by building at the Naval Research Laboratory a 14-column pilot plant. It was hoped with this equipment to separate small quantities of uranium for experimental

purposes and to acquire experience in running a number of columns in series and parallel combinations. It was further felt that by running a number of columns simultaneously, information might be acquired at a speedier rate. Work on this plant was authorized in July 1942, and the plant was substantially complete by November 15th of that year. It was placed in successful operation and in the course of the subsequent 6 months fulfilled its purpose. During this period William N. Blatt, Robert E. Ruskin, Edward Drott, Jr., and Waldo E. Whybrew were added to the experimental group. The services of Nathan Rosen were obtained to take care of theoretical studies.

IV. Visits of Manhattan District Reviewing Committees

It was the policy of the Naval Research Laboratory to communicate results to the S-1 Committee and later to the Manhattan District as soon as any information was established. Accordingly, in August 1942, Lyman J. Briggs was informed of the new developments regarding the process. This led ultimately to a visit in October by General L.R. Groves, together with Admiral W.R. Purnell. Later, in January 1943, the installation was inspected by a special committee assembled by the Manhattan District. This group consisted of Lyman J. Briggs, Harold Urey and E.V. Murphree, with Karl Cohen and W.I. Thompson as advisers. The Committee was impressed by the simplicity of the equipment and commented favorably. No action was taken.

In a Naval Research Laboratory report submitted in January 1943 the advantages of an enriched chain reactor were pointed out and it was shown that a purely nominally sized thermal diffusion plant (1 - 2 million dollars) would be necessary to provide the necessary separated isotopes.

During the next 6 months improvements were made in column construction. The small pilot plant produced some 236 pounds of uranium hexafluoride possessing isotope separation. The quantity and the isotope separation were greater than had been obtained from the gaseous diffusion method up to that time.

In August 1943 another committee was appointed, consisting of Lyman J. Briggs, Harold C. Urey, E.V. Murphree, and W.K. Lewis, with Karl Cohen and W.I. Thompson serving as technical advisers. On September 8, 1943, the committee submitted a report to James B. Conant emphasizing the large steam consumption involved in the process were the goal to be 1 kg 90% U-235 per day. The magnitude of the proposed steam installation can be judged from the cost ($70,000,000). The thermal diffusion plant itself was estimated to cost $55,000,000.

They were also concerned with the long equilibrium time to produce 90% U-235. In discussing the use of partially enriched feed for another process, the statement was made, "The possibility of using liquid thermal diffusion for the production of an enriched product such as 3.5% for

feed to another type of unit for final enrichment seems inadvisable in view of the large steam consumption and the considerable addition to the time required to reach equilibrium operating conditions". The Committee favored "Support from the S-1 Committee and the Manhattan District on work directed toward improving the efficiency of the liquid thermal diffusion process".

V. Philadelphia Pilot Plant

The Naval Research Laboratory decided to continue its isotope studies with the object of providing an alternate method in the event that the magnetic or gaseous diffusion methods failed. Our further work therefore was in the nature of an insurance against unforeseen events. A survey of Naval establishments indicated that the Naval Boiler and Turbine Laboratory at the Philadelphia Naval Base possessed a number of unique facilities. Building space was available, cooling water could easily be obtained, and the engineers at that Laboratory had considerable experience in high-pressure steam and in large-scale heavy construction. Authorization to build a 300-unit pilot plant at Philadelphia was obtained on November 17, 1943 under a project order signed by Rear Admiral Earle Mills, USN, Assistant Chief of the Bureau of Ships. Construction of the installation began about January 1, 1944. The Naval Boiler and Turbine Laboratory operated under the general direction of Captain C.A. Bonvillian, USN, and Samuel Wier was assigned by the Naval Boiler and Turbine Laboratory to cooperate with the Naval Research Laboratory on the

construction of the plant. The Naval Boiler and Turbine Laboratory undertook to design, construct, and operate the equipment necessary to supply steam and cooling water for the installation. The Naval Research Laboratory undertook to design the columns and subsidiary equipment necessary for operation of the columns, and to operate them. In much of the design they were assisted by Samuel Wier.

In building the Philadelphia plant, a primary consideration was to build something which might serve as a model should the Manhattan District find it desirable to utilize liquid thermal diffusion in their atomic bomb program. Accordingly, a basic unit of a rack consisting of 102 columns was chosen with the thought that, were a large expansion to occur, it would be possible to duplicate the basic unit a large number of times.

VI. The Thermal Diffusion Plant at Oak Ridge (S-50)

In June 1944 the Philadelphia plant was approaching completion. J.R. Oppenheimer learned of our progress and recognized the value that partially separated uranium would have when used in conjunction with the electromagnetic plant. At that time the electromagnetic plant was the only unit in operation, and it was highly desirable that its production should be increased. The matter of the potentialities of liquid thermal diffusion as a method of accomplishing this objective was brought to the attention of General I.R. Groves

by J.R. Oppenheimer. Accordingly, a reviewing committee consisting of Richard Tolman, W.R. Lewis, E.V. Murphree, Karl Cohen, and William Thompson visited the Philadelphia installation about June 15, 1944. Their report to General Groves was favorable. The decision was made to build a liquid thermal diffusion plant at Oak Ridge employing steam from a power house built for the gaseous diffusion process. Work on the power house had been completed ahead of the gaseous diffusion plant so that steam was available. On June 26, 1944, General L.R. Groves, accompanied by Richard Tolman, W.I. Thompson of the Ferguson Corporation, and Lt.Col. M.C. Fox arrived at the Naval Research Laboratory for the purpose of obtaining such information as was available concerning work on the thermal diffusion process. Blueprints of the Philadelphia installation were turned over to them. General Groves issued instructions that the Oak Ridge installation was to be built as a "Chinese Copy" of the Philadelphia plant.

Speed of construction of the Oak Ridge installation was phenomenal. Ground was broken for the S-50 plant on July 6, 1944, and the first columns were available for conditioning on September 15th. The plant was substantially complete 2 months later, with the first product being removed October 31, 1944. Considering the magnitude of the task, the war-time conditions prevailing, this accomplishment was certainly record-shattering. It stemmed from perfect

teamwork of extremely competent people. Lt.Col. M.C. Fox as Unit Chief coordinated activities and supervised the expediting of materials which was the crux of the problem. Major Thomas E. Evans, construction officer, smoothed the way for C.W. Roberts, Project Manager, and associates George Lindquist, General Superintendent, and G.R. Byrd, Mechanical Superintendent. Key top personnel of the Ferguson Company included W.N. Thompson, Chief Engineer, Frank Buck, Chief Mechanical Engineer, and W.K. Mitchell, General Manager.

VII. Operation at Philadelphia

Besides fulfilling the functions of a pilot plant, the Philadelphia installation shipped to Oak Ridge more than 5000 pounds of UF_6 possessing .86% U-235. The plant served as a source of a number of process improvement schemes, among them being the first automatic product withdrawal system. Studies of individual column performance, as well as pyramid feasibility, were likewise made.

Organization at Philadelphia was unique. The Project Officer was then Captain T.A. Solberg, USN, Bureau of Ships. The plant itself was divided into two parts. Operation of steam and water facilities was provided for by enlisted personnel at the Naval Boiler and Turbine Laboratory under the direction of Captain C.A. Bonvillian, USN, with Captain J.K. McCue, USN, executive officer. The process area was the

responsibility of the Naval Research Laboratory. During this period the Laboratory was first under Rear Admiral A.H. Van Keuren, USN, and later Commodore H.A. Schade, USN. Project Officers were Captain R.H. Gibbs, USN, and Captain J.B. Cochran, USN. Since emphasis there was largely on experimental work, it was staffed mainly by technical people. Most of the men were Naval personnel, both officers and enlisted men. These worked under technical direction of civilian supervisors -- P.H. Abelson and John I. Hoover.

Perhaps one of the most important contributions of the Philadelphia plant was its safety program. Following a serious accident on September 2, 1944, Captain George Lyon (MC) USNR, was assigned to the installation. Through his leadership, an extremely successful safety program was initiated. As a result no accident involving loss of personnel time was suffered during more than a year of operation. In addition, thorough physical examinations and blood studies were made at frequent intervals. This work demonstrated that the occasional breathing of UF_6 fumes produced no permanent changes. Many of his recommendations were adopted at S-50 which suffered no fatal accident.

VIII. Operation of S-50

To operate S-50 the Fercleve Corporation was formed. This organization was completely owned by the H.K. Ferguson Company and was established for the purpose of avoiding

labor difficulties in operation. The procedure of using the Ferguson Company in this way was adopted to avoid bringing another company into the Clinton Engineer Works. This was desirable for security reasons and to eliminate friction between construction and operations. Being a totally new organization, the Fercleve Corporation was faced with the task of accumulating a staff at a time when very few persons of any competence were to be hired. The task of establishing an efficient operating organization fell to C.W. Roberts who built up a very fine organization. The Fercleve Corporation was aided in its task by the assignment of twelve Navy men from the Philadelphia plant during the first two crucial months of operation. In addition, the Manhattan District assigned some 120 technically trained young men of the Special Engineer Detachment to the plant. The Fercleve Corporation was fortunate in securing the services of Malcolm Dole and later B.F. Dodge who headed a Technical Division. This group contributed much to the establishment of an ever-increasing plant efficiency.

Representing the Manhattan District as Unit Chief until April 1, 1945, Lt.Col. M.C. Fox contributed greatly to the initiation of successful operation. He was succeeded by Major Thomas E. Evans who contributed a relentless enthusiasm for improved operating efficiency.

As K-25 came into operation, less steam was available for S-50. Normal operation was terminated September 4, 1945.

History

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WATER SOLUTION WORK

The early work at the Carnegie Institution and the Bureau of Standards produced some interesting results on the behavior of water solutions in thermal diffusion columns. This is a field which has been little investigated and which has considerable promise of future interest. It is indeed remarkable, for instance, that Korsching and Wirtz[1] could produce in a column 100 centimeters long a separation of S = 1.18 in the Z_n64, Z_n68 isotopes, a result which was essentially verified and extended in our early work using potassium salts. There appear to be obvious ways in which small laboratory-size thermal diffusion columns can be used in research. Hence it is felt that some description of the early thermal diffusion work would be worthwhile to future investigators in the field. In addition, this early work was of some interest because of the fact that it pointed out cogent variables to be investigated when uranium hexafluoride was employed in the columns. While it is true that the behavior with water solutions did not appear exactly to parallel the uranium compound behavior, nevertheless those variables that were of greatest importance in the water solution case were also found to be similarly important in the latter studies. Later it was also found that the functional dependence between

separation, temperature and relaxation time is extremely complex depending on what spacing is being employed.

I. Apparatus

The columns employed consisted of three concentric tubes; in general, the inner tubing served as the hot wall and was heated by radiant energy from an electrical element; the second tube served as a cold wall and was enclosed by a third jacketing tube; cold water flowed between the second and third tubes. The tubes were rigidly soldered together at one end, while at the other end, the bottom, a section of sylphon bellows was employed to take up differential expansion. As a result of this construction, the bottom of the column possessed added hold-up. In the following table a list of the columns constructed is given:

Table 1

Column No.	Method of Heating	Wall Spacing	Hot Wall Diameter	Length
1	Radiation from electrical resistance.	0.20 cm	1-3/64"	20"
2	"	0.080 cm	1-3/64"	20"
3	"	0.080 cm	1-9/16"	5'
4	"	0.0355 cm	1-3/8"	20"
5	"	0.0584 cm	1-1/2"	20"
6	"	0.11 cm	1-1/2"	20"
7	Calrod	0.080 cm	1-1/2"	24"
8	Steam	0.080 cm	1-1/2"	11' 6"
9	Steam	0.057 cm	1-5/8"	6'
10	Steam	0.11 cm	1-1/4"	11' 6"
11	Steam	0.076 cm	1-1/2"	11' 6"

II. Relation Between Salt Concentration and Isotope Separation

One of the first things learned about the thermal diffusion of salt solutions was the fact that the salt tends to be concentrated at the bottom of the column and that the solution tends to become more diluted at the top. Later on it was found that there is a relation between this change in concentration of a given salt and the isotope separations accompanying the changes in concentration. This is illustrated in the following table where solutions of potassium bromide were involved. Here C_B and C_T are the salt concentrations at the bottom and top of the column, respectively, while S is the separation factor of K_{39} with respect to K_{41}.

Table II

Initial Conc.	C_B	C_T	C_B/C_T	S
2.0 moles/liter	2.08	1.60	1.3	1.015 ± .005
2.0	2.21	1.05	2.1	1.045 ± .005
2.0	4.13	.187	22.0	1.218 ± .005

The values fit the relation $k \log S = \log C_B/C_T$, but this may be merely fortuitous.

It was convenient in the early studies to use this concentration change to determine performance of columns, since analysis of the thermal diffusion effects merely required measurement of the densities of sample solutions taken from the columns.

III. Effect of Length

One of the first relations that was determined was the dependence of equilibrium separation on column length. The results are summarized in the following table where C_B refers to the concentration of the solution at the bottom of the apparatus, and C_T that at the top of the apparatus after the column had been run to equilibrium.

Table III

Apparatus	L	C_B/C_T
No. 2	20"	1.43
No. 3	5'	3.01
No. 8	11' 6"	12.5

These figures agree very well with $C_B/C_T = e^{kL}$.

IV. Effect of Temperature

Another study was made on the role that temperature difference plays in the salt solution thermal diffusion. The effect of the higher ΔT is indeed remarkable.

Table IV

Salt	Length	Spacing	ΔT	C_B/C_T
.5 mole/liter				
K_2SO_4	5'	0.08 cm	9°C.	1.023
"	5'	0.08 cm	18°C.	1.10
"	5'	0.08 cm	30°C.	1.31
"	5'	0.08 cm	39°C.	1.52
"	5'	0.08 cm	51°C.	2.15
"	5'	0.08 cm	78°C.	5.5

These figures fit the relation $\log C_B/C_T \sim (\Delta T)^2$, for constant spacing.

V. Effect of Spacing

Another study which was made demonstrated the crucial dependence of the phenomenon of thermal diffusion on the spacing employed between the hot and cold walls.

Table V

l	a	Gradient	ΔT	Equilibrium C_B/C_T
20"	0.2 cm	375°C/cm	75°C	1.04
20"	0.11 cm	"	40.5	1.15
20"	0.08 cm	"	30	1.3
20"	0.0584 cm	"	21.8	1.6

These figures fit the relation $\log C_B/C_T \sim (1/a^2)$ for temperature gradient constant. Since it has already been shown that $\log C_B/C_T \sim \Delta T^2$, by combining the two relations it can be seen that $\log C_B/C_T \sim \frac{\Delta T^2}{a^4}$. It is interesting to note that, in their studies of gaseous thermal diffusion, Clusius and Dickel found similar relations to hold in a gas.

Our theoretical studies show that the $1/a^4$ relation holds in a region where $a > (a \text{ optimum})$ corresponding to maximum Y. Hence it is inferred that spacings employed in our water studies were considerably wider than optimum. That being the case, the dependence on ΔT^2 found above is rather surprising from the theoretical standpoint. It could

be due to the presence of complicating factors such as a rapid variation of the hydration of the salt or of the association of the water molecules with temperature, etc. Furthermore, it does not follow that the same dependence on temperature difference would be obtained with other salts.

VI. Effect of Salt Employed

Some interesting results were obtained when salts of differing weight were used. Here S, of course, refers to isotope separation of K^{41} and K^{39}.

Table VI

Salt	Mol.Wt.	C_B/C_T	S
KCl	74.56	2.0	1.045 ± .005
KBr	119.02	2.1	1.045 ± .005
K_2SO_4	174.26	5.5	1.034 ± .005
$K_2CR_2O_7$	294.22	2.5	1.035 ± .005

These results were obtained with apparatus No. 3 employing the following conditions:

Power Input	Gradient
1600 cals/sec	625°C/cm

It is to be remembered that the molecular weight of these salts in solution is probably much greater due to an unknown degree of hydration.

VII. Equilibrium Time

It will be shown later that theory predicts an approach to equilibrium in liquid diffusion that is exponential in character. This holds true when the separation has arisen more than halfway to the equilibrium value. Studies of water solutions also showed these statements to apply. Typical data employing a K_2SO_4 solution are given in the following table:

Table VII

l	a	T_1	T_2	t	C_B/C_T
20"	0.08 cm	87°C	24.5°C	10 mins.	1.15
"	"	"	"	20 mins.	1.28
"	"	"	"	30 mins.	1.37
"	"	"	"	120 mins.	1.43
"	"	"	"	240 mins.	1.43

These data fit the relation:

$$\log C_B/C_T = (\log C_B/C_T)\ \text{equil}\ (1 - e^{-Bt})$$

For purposes of this section, it is convenient to use the equation to define τ, relaxation time. The quantity $\tau = 1/B$. It was found that τ is sensitive both to spacing and to ΔT.

Typical values are as follows:

Table VIII

l	a	τ	Gradient
20"	0.11 cm	7 mins.	375°C/cm
"	0.08 cm	20 mins.	"
"	0.0584 cm	120 mins.	"

These values of T are quite different from the much larger values quoted by Korsching and Wirtz[1], but this is not surprising in view of the sharp dependence of T on the spacing. Most of the German work was done with narrower spacing.

VIII. Parasitic Effect of Azimuthal Gradients

In order to obtain any desired temperature of the hot wall, the use of calrod (heater element for electric ranges) recommends itself. This material can be silver-soldered to an outer casing which can be soft-soldered to the hot wall. It was soon found, however, that this means of heating leads to a serious parasitic convection effect, which limits the useful temperature difference between the two walls.

Experiments were carried out using K_2SO_4 solution in apparatus No. 7. Results are summarized in the following table. In the first three experiments the heat was applied by means of four calrods spaced 90° apart. In the last four experiments the heat was applied at eight 45° intervals.

Table IX

Azimuthal Gradient	Transverse Gradient	Equilibrium C_B/C_T	Equilibrium C_B/C_T Az. Gradient approaches zero
3.7°C/cm	625°C/cm	1.42	1.54
4.1°C/cm	700°C/cm	1.44	1.75
6.0°C/cm	900°C/cm	1.47	2.42
1.0°C/cm	625°C/cm	1.53	1.54
1.15°C/cm	700°C/cm	1.73	1.75
1.45°C/cm	900°C/cm	2.23	2.30
1.6°C/cm	1000°C/cm	1.93	2.96

It is apparent that small azimuthal gradients can have serious effects. Furthermore, this effect becomes most pronounced as the transverse gradient is increased.

As a result of these experiments, efforts to use calrod were abandoned and steam used as a source of heat. With this method of heating, parasitic effects were greatly reduced.

Water Solution Work

Reference

[1] H. Korsching and K. Wirtz, Naturwiss. 27, 110 and 27, 367 (1939).

THE COLUMN

The key to the liquid thermal diffusion process is the individual column. In this chapter the principal factors bearing on the construction, operation, and analysis of samples from this basic unit will be discussed.

I. Properties of Process Fluid

The design of equipment and indeed most of the problems of developing the liquid thermal diffusion process hinged upon the physical and the chemical properties of the process fluid, uranium hexafluoride. This substance is a crystalline solid at room temperature, possessing a density of about 4.60. It melts at 64.1°C under a pressure of about 1-1/2 atmospheres. The process of melting is accompanied by an increase in volume of nearly a third. The liquid has a density of 3.7 at the melting point which diminishes to a density of 1.4 at the critical temperature (232°C). In the Appendix, curves are given showing the variation of density of the substance with temperature, and also the dependence of the vapor pressure on temperature. Uranium hexafluoride has a thermal conductivity of about 0.00038 cals/cm sec and does not conduct electricity.

Uranium hexafluoride is chemically quite reactive. It is instantly hydrolyzed by water, being converted into solid UO_2F_2. Since UO_2F_2 occupies more volume than UF_6, this hydrolysis process can lead to difficulty when it occurs inside a limited space. Uranium hexafluoride reacts with

most organic materials at a rate depending on temperature, with the production of UF_4, HF and C. It also reacts with most metals to form UF_4 plus the metallic fluoride. With a few metals such as nickel, an extremely thin coating of fluoride serves to protect the metal from further action. Very early in the development of the process, a technique was evolved in which equipment was "conditioned" by exposing it to fluorine gas. At 300°C "conditioned" nickel reacts with uranium hexafluoride at a rate of less than 2 mg/sq.ft. per day. Nickel is by far the best substance with respect to corrosion and hence it was chosen for use wherever hot process fluid might be found. For temperatures below 100°C copper may be employed, though not as satisfactorily as nickel.

II. Structure of Column

The basic requirements of the thermal diffusion process for UF_6 are a hot wall (200° - 300°C) and a cold wall (approx. 64°C). The typical 48-foot column consumes 200 BTU/sec. The area through which this heat must be transmitted is close to 20 square feet. To maintain column stability in the process fluid it is desirable that any gradient of density in the column be such that the process fluid is less dense at the top. Consideration of the heat quantities and thermal coefficients involved dictates that the heat be supplied by condensing steam, and that heat be removed from the cold wall by cooling water.

Accordingly, the thermal diffusion column consisted of

three concentric tubes. The central tube made of nickel was heated by condensing steam (introduced at the top) on its interior wall. The outside of the nickel tube and the inside of the second tube (copper) formed an annular space about 0.025 cm thick which was filled with process fluid. The copper was cooled by circulating water flowing upward between it and the outer iron pipe.

For the most part the nickel tubing used was commercial grade, in 12-foot lengths, selected for accuracy. Nickel spacer buttons 1/16-inch - 1/8-inch diameter were spot-welded to the surface of this tubing 90° apart at 6-inch intervals. They were finished to the proper height, with due allowance for expansion, to an accuracy of ± 0.001 cm. Four lengths were acetylene-welded together to give the desired 48-foot length. The copper tubing employed was commercial grade, processed in the mill with special care. The copper was slipped over the nickel and joined together by a silver soldering technique employing a collar also of copper. At the ends of the column a short length of nickel of the same diameter as the copper was spliced to the copper again by silver soldering. This permitted junction of the hot and cold walls by making a nickel-nickel weld.

One of the factors to be considered in the design of a column is thermal expansion. If a copper tube and a nickel tube are 48 feet long at room temperature, they would, if unconstrained, differ in length by over an inch under

operating conditions in the column. In early column design this expansion was taken up in sylphon bellows.

These had the disadvantage of possessing excessive hold-up. Due to the high pressures involved, it was necessary to employ a 4-ply bellows which proved difficult to silver-solder in a leak-free manner. It was further learned that the nickel and copper tubings tended to become "hung up" on each other, thus minimizing the value of the expansion joint. Accordingly, it was decided to fasten rigidly the hot and cold walls together at the ends of the column. To introduce minimum stress, this welding was performed with a temperature difference half that of operational. Thus at room temperature the nickel was under a tension of 14,000 lbs./sq.in. while at operating conditions it was under a compressive force of 14,000 lbs./sq.in. The copper was subjected to a force equal in magnitude but opposite in direction to that in the nickel. Both of the metals are annealed during welding and silver-soldering processes. Hence, it is necessary to work-harden them to prevent deformation when excessive stress is applied.

Provision for expansion of the nickel-copper ensemble with respect to the outer jacket was made with a packed slip joint. Coincident with the longitudinal expansion was a change in relative diameters of the hot and cold walls. In a typical instance, the hot nickel expanded 0.010 cm in diameter with respect to the copper. This factor was

taken into account when choosing pairs of tubings to form the hot and cold walls.

The crucial column variable is the spacing between the hot and cold walls. A typical value employed was 0.025 cm (.010-inch). It was assumed and later demonstrated that the magnitude and accuracy of the spacing are extremely important.

In practice it proved difficult to maintain proper spacing in the column. This was partly due to the quality of tubing employed, faults in construction, and to various types of damage occurring during operation. These factors will be considered next.

III. Column Imperfections

While typical commercial tubing is for most purposes surprisingly accurate, careful examination reveals, however, deviations from perfection. One of the common faults is ovality; that is, the tubing is found to be elliptical rather than circular. It is not uncommon to find a difference of 0.010 cm in the major and minor axis of 2-inch diameter copper tubing, whereas nickel is more nearly circular. A second deviation from perfection is a variation in diameter along the length of the tube. This discrepancy occurs to a more pronounced extent in nickel than in copper and may amount to as much as 0.08 cm. A third imperfection is the fact that the inside circle and the outside circle are eccentric. As a result, tubing possessing a nominal .150

inch wall will be found to measure from .140 inch to .160 inch. This effect is more pronounced in the nickel than in copper. Of the three, ovality seemed most serious and most common. Studies showed that ovality could be removed by honing.

Very few serious discrepancies from perfect spacing arose as a result of constructing the column. Use of Precisionaire gauges and sufficient inspection assured accurate measurement of sizes and choice of the best lengths of tubing. Height gauges made it possible to obtain an accuracy of 0.0010 cm in spacer height.

The obvious imperfection introduced in construction came from joining the copper and nickel 12-foot lengths. Much of this was eliminated by obtaining 24-foot lengths of nickel and ultimately 48-foot lengths of copper. Imperfection in the nickel weld consisted mainly in an offset at the junction. A similar remark holds for the copper. In both cases annealing occurred during the joining process. This was most serious in the case of copper. Indeed the metal became so thoroughly annealed that it was necessary to work-harden it in order to restore at least partially its elastic limit. The hardening process introduced imperfections in the spacing near the joints.

The most serious deviations in column spacing were those which were introduced during operation of the column. These were largely associated with the stresses set up when

a column was brought from ambient temperature to operating temperature.

In some cases where the copper tubing was not sufficiently hardened, tension resulting from operating temperatures caused this tubing to yield, resulting in an increase in length and a decrease in diameter. Often the 0.025 cm spacing was reduced to practically zero. On other occasions excessive fluid pressure in the column caused the copper tubing at the joints to bulge out. In some cases the annular space was increased by a factor of ten.

Similarly in the case of the inner nickel tubing, the compressive force was in some cases sufficient to exceed the elastic limit leading to a simultaneous local shortening and bulging of the nickel at the welds.

Imperfect conditioning of columns prior to the introduction of process fluid caused serious difficulty. In particular, incomplete removal of moisture resulted in the formation of UO_2F_2 near the copper splices. In some instances sufficient decomposition occurred to restrict almost completely flow of fluid in the column.

Another source of imperfection in spacing came as a result of the compressive force on the nickel tubing tending to cause buckling. Resistance to this tendency was the function of the spacer buttons. Often the forces involved proved sufficient to press the spacer into the copper. This was particularly true when 1/16-inch diameter buttons were employed.

IV. Column Operation

The columns were hung vertically, being supported on a steel framework. Steam was introduced at the top of the column, condensate being removed at the bottom. A cooling water inlet was located at the bottom of the column, with the outlet at the top. Since the desired cooling temperature was about 64°C, water was circulated through the column by means of a pump. To maintain the desired temperature, some hot water was bled off at the top of the column while sufficient fresh water was added to the ingoing stream to lower the circulating stream to the desired temperature.

In addition to steam and water, columns required process fluid. Hence, it seems desirable to mention a few of the techniques employed to handle the substance. Suitable packing materials were not developed for uranium hexafluoride till late in the project. Our efforts were accordingly directed toward development of packless devices. Valve action was obtained through freezing the process fluid. This was easy because most of the connecting lines carrying hexafluoride were of small-bore and the melting point of the substance is 64.1°C.

Transfer of fluid from one container to another was obtained by taking advantage of the vapor pressure of hexafluoride. Thus one could distill out of the top of a container into a colder one or the pressure could be used to force liquid out of the bottom of a container into another.

Differential pressure in a closed fluid system was obtained by use of the thermal syphon effect. By making the two arms of the syphon 48' long, it was possible to obtain differentials of as much as 10 p.s.i.

After a column was mounted in position and connected to steam and water lines, it was given a treatment designed to prepare it for the process fluid. It was degreased, washed with acid and water, then thoroughly dried by a combination of passing air through the equipment and evacuating. Final preparatory step was to "condition" with fluorine gas at operating temperatures for half an hour. With the conditioning procedure completed, the column was ready for process fluid. The average 48-foot column had a hold-up of 2000 grams when operating with a hot wall temperature of 188°C. (160 lbs. steam) and a hold-up of 1600 grams when operating with a hot wall of 286°C. (1000 lbs. steam). To supply this fluid, an auxiliary chamber (termed a reservoir) was connected to the column. These chambers possessed from 3 kilograms to 170 kilograms of uranium hexafluoride. With the cooling water for the columns heated to 64°C and the hot wall at a temperature midway between the cold wall and operating temperature, the reservoir was heated. As the temperature rose in the storage chamber, the process material was first liquefied; then, as the temperature increased, the vapor pressure in the storage chamber drove the process fluid into the column. In principle, by this means one can develop

almost any pressure simply by regulating the amount of fluid in the reservoir and by choosing a proper temperature. Reflection will show that it is necessary to subject the column to a pressure greater than the vapor pressure of uranium hexafluoride at the temperature of the hot wall. If such a pressure is not applied, process fluid boils at the hot wall and violent motions of fluid in the column occur which have a mixing effect far greater than the separating effect of the thermal diffusion process.

Another reason for having a reservoir connected to a column was for the purpose of taking up changes in operating conditions. This was especially true when the hot wall operating temperature was low (188°C). Under these circumstances the process fluid was fairly incompressible. Were a sudden temperature increase to occur, the process fluid would expand. If there were no possibility of pressure relief, very large pressures could be developed. The converse is also true: were the operating temperatures suddenly to drop, the density of the process fluid would increase, its volume decrease, and hence the fluid would no longer occupy the full volume of the column. As a result, boiling would occur at the hot wall and the separative work which had previously been accomplished would be destroyed. The presence of a reservoir operating at a suitable pressure removed these difficulties.

It can be seen, however, that there would occur a

certain interchange of fluid between the reservoir and the end of the column to which it was attached. This interchange would be variable if it were not controlled. The obvious way of controlling this was deliberately to establish a continuous circulation between the reservoir and the column. To establish such a circulation, some pressure differential was required. The method chosen was that using a thermal syphon. Actually, with single columns, it was necessary to have thermal syphons with members only a few feet long in order to obtain sufficient pressure differential and hence velocity of circulation.

When the column was full, the temperature in the reservoir was regulated to secure desired pressure. The column temperatures were then brought to the desired operating condition. The action of the convective loop was checked by a calorimetric-type flow meter to determine that fluid was actually flowing.

Most of the runs were without event. However, occasionally a sudden shutdown would occur. This introduced a problem. If the shutdown were due to failure of power or the steam supply, the column, as it cooled, increased in hold-up for two reasons: (1) the actual spacing in the column increased by about 20%, and (2) the density of the process fluid increased by about 15%. Indeed, if the power supply failed for a long enough period of time that the steam pressure fell to zero and the cooling water dropped below 64°C, the column became filled

with solid uranium hexafluoride. In this case, the hold-up of the column was increased some 70% over that of normal. In the event that the reservoir were located at the bottom of the column, this led to considerable difficulty. Since the steam was introduced at the top of the column, the fluid at that point would melt first. Since the process fluid, on melting, increased in volume by a third, while at the same time, the volume available for the fluid diminished as the temperature difference between the hot wall and cold wall increased, pressures of the order of 100,000 p.s.i. could be developed, causing stresses in the column greatly in excess of the elastic limits of the walls. As a result, either rupture or permanent deformation occurred. Two remedies existed. The first was to prevent flow of additional fluid into the column when a power failure occurred. This was accomplished by isolating the reservoir from the column. In this event when the process fluid solidified in the column, it would solidify in the lower two-thirds of the unit, leaving the upper third empty and available as space for the expanding melting fluid when the column was again put into operation. The second alternative was to remove process fluid from the top of the column. This procedure was obviously inconvenient.

In order to study the operation of the column, it was necessary to remove samples of process fluid from time to time. This was necessarily performed while the column was in operation and under pressures of from 500 to 1500 p.s.i. By

freezing a small section, 5 centimeters, of the process fluid using dry ice, it was possible to establish a plug in a 1/8-inch I.D. tubing which would not fail under the action of 1500 p.s.i. pressure. This tubing could then be uncapped and a sampling tube attached. When the frozen portion was warmed to above the melting point of the process fluid, liquid flowed into the sampling tube. At first the samples taken were as large as 50 grams; later, they were reduced to 10 grams, and finally, as a result of the intervention of the theoretical physicists, they were diminished to 1 gram.

V. Sample Analysis

One of the principal problems in any isotope research is measurement of the isotope separation. This is especially true when the separation factors are small, as was the case early in our research. The effects obtained with water solutions of potassium salts were measured by A.K. Brewer using a mass spectrograph. Practically all the analytical work with uranium was performed on Nier mass spectrographs, the earliest analyses being made at the University of Minnesota by Nier himself. Later, some 750 samples were measured by E.P. Ney, F.C. Armistead, and J.H. McQueen using a Nier type instrument at the University of Virginia. Later still, a mass spectrograph was constructed by Ney and McQueen for use in the pilot plant at Philadelphia, and this instrument handled analytical problems for the Philadelphia installation. During the early phase of the research, some measurements were made

by L.H. Curtiss at the Bureau of Standards by means of an alpha counting technique.

Measurement of the isotope separation of uranium is complicated when the compound employed is uranium hexafluoride. This is due to an unlooked-for phenomenon which has been called "memory effect". When UF_6 is introduced into the mass spectrograph source, a stream of electrons ionizes it. Part of the ionized molecules pass through the slit system and arrive at the cooling electrode. However, a very large majority of the molecules which are ionized do not follow this path but are instead deposited upon the walls of the ion source. In chemical composition these molecules are in general UF_4 or UF_5. The UF_5 molecules are essentially a combination of UF_6. UF_4 and indeed at room temperature UF_5 has a vapor pressure of UF_6 of about 1 millimeter. Under high vacuum conditions, therefore, UF_6 volatilizes out of the compound, leaving UF_4 behind. If new UF_6 is introduced into the instrument, some of it reacts with UF_4 to form UF_5. When this UF_5 is reconverted back into UF_4 plus UF_6, it has been found that an exchange process occurs between the deposited UF_4 and the new UF_6; i.e., the isotopic concentration of the UF_6 coming off the wall is not the same as that which struck the wall. Hence, after an ion source has come to possess a thin layer of UF_4, results obtained from the mass spectrograph are a function of the materials that have previously been analyzed in the instrument and which have

been deposited on the walls of the ion source. For instance, if a large number of samples possessing an isotopic concentration about equal to normal uranium have been analyzed in the machine and then a sample possessing an enhanced quantity of U-235 is analyzed, the result obtained for the enhanced sample is a value less than that actually present. The error introduced by memory effect can be such as to introduce an error of 10 to 20% in the observed isotope separation. In considering the results obtainable in column studies, all errors that have so far been considered tend to lower the observed results obtainable rather than to enhance it. One of the principal reasons why memory effect was important in our study was the fact that the sample to be measured was always compared to normal uranium. Thus, the memory effect always tended toward normal uranium whether the sample to be measured was enhanced in U-235 or impoverished in U-235.

One of the best solutions to the difficulty was to employ sub-standards which were established immediately after a fresh ion source had been installed in the instrument and before appreciable quantities of UF_4 could collect in the source. In making measurements, comparison was then made of sample to a sub-standard possessing an isotope abundance about equal to that predicted for the sample. Even so, some memory effect was found to be present.

Experience in the analytical laboratory at S-50 pointed to another alternative. There, instruments were installed

both for mass spectrograph measurements and for measurements by the alpha counting technique. The alpha counting technique in the end proved to be the most reliable. Obviously, this method was not confronted with the memory effect.

EXPERIMENTAL COLUMN STUDIES

In this chapter we discuss some of the experimental results obtained from studies of the thermal diffusion column. The principal questions to be considered are: determination of column constants, approach to equilibrium, product rate vs. concentration, column performance as a function of spacing, length, temperature and fluid pressure. In addition, observations will be presented on columns supposedly identical in construction.

I. The Column Constants

The characteristics of a uniform column can be described by the quantities X, Y, M, H. M is the fluid hold-up mass of the column, X is the time constant, Y is the logarithm of the separation factor at equilibrium, and H is the separative constant of the column. These constants will be discussed more fully in the theoretical part of this work. For the present it will suffice to point out that they satisfy the relation

$$X = \frac{M}{HY} , \tag{1}$$

and that they play the following roles in the experimental work.

The equilibrium separation factor is given, of course, by e^Y. The constant H determines the product rate during steady operation; the greater H, the greater the product

rate, for a given value of Y, at a given separation factor.

The relation between half-time, product withdrawal rate, figure of merit and pyramid performance is extremely complicated. In contrast, it has been found that the quantity X, which has the dimensions of time, is simply related to the performance qualities of the column. Furthermore, it is easy to determine X experimentally. Therefore, we describe the time performance of the column in terms of X. Later we shall describe how this quantity can be measured. For the case of an infinite reservoir, column closed at the top end, a few numerical values are given in Table I with a typical value of X to give some idea of the relation between these quantities. "Half-time" may be conveniently defined in two ways: (1) the time required for S to go half-way to its equilibrium value, $S = 1/2\ (S_e + 1)$; and (2) the time required for $\ln S$ to go half-way to its equilibrium value, $\ln S = 1/2\ Y$ or $S = e^{Y/2}$.

Table I

Y	S_e	t/X $S = 1/2\ (S_e + 1)$	Half-time (X = 40 days)	t/X $S = e^{Y/2}$	Half-time (X = 40 days)
.1	1.11	.002	0.08 day	.002	0.08 day
.2	1.22	.009	0.36	.009	0.36
.3	1.35	.022	0.88	.018	0.72
.4	1.49	.040	1.60	.033	1.32
.5	1.65	.066	2.64	.052	2.08
.6	1.82	.102	4.08	.075	3.00
.7	2.01	.146	5.84	.104	4.16
.8	2.23	.202	8.08	.138	5.44
.9	2.46	.273	10.92	.157	6.28
1.0	2.72	.356	14.24	.220	8.80

It will be shown in the theoretical section that the figure of merit of a column, a quantity to serve as a measure of the usefulness of the column, can be defined as

$$\phi = HY = \frac{M}{X} \qquad (2)$$

In view of the relation among these quantities it is only necessary to know X, Y and M in order to predict the behavior of a column at any product rate or to predict approach to equilibrium when run either as an individual or as part of a pyramid. The problem of measuring the

hold-up is trivial and needs no elaboration. Measurement of X and Y are accordingly the principal problems in liquid thermal diffusion work. Theoretical work has shown how these quantities may be measured by studying the behavior of a column during its approach to equilibrium.

II. Approach to Equilibrium

In the theoretical section the equations governing approach to equilibrium for a column closed at the top are derived and discussed. The solutions are of the form:

$$S = 1 + \frac{2}{\sqrt{\pi}} \sqrt{\frac{t}{X}} + \frac{1}{2} \frac{t}{X} + \cdots\cdots \left(\frac{t}{X} \ll 1 \right) \tag{3}$$

$$S = e^{Y} \sum_{n=1}^{\infty} A_n \, e^{-k_n t/X} \quad (t \text{ arbitrary}) \tag{4}$$

It should be noted that the general form of these equations will be the same for various substances and that they are valid to the extent that the concentration of the rare isotopes is small compared to unity. The constants will, of course, vary from substance to substance.

The general characteristics of this equation are shown in Fig. 1. The solid line represents the theoretical curve. The points are experimental.

Let us consider further the nature of Eqs. (3) and (4). The two variables appearing are X and Y. At very short times, the separation increases very rapidly, as $t^{1/2}$. At longer times the separation increases as t. At still longer times it follows an exponential approach toward a limiting value.

It will be seen that the time t appears only in the combination t/X, as might have been anticipated from the form of Eq. (3) and the boundary conditions. Hence it is convenient to plot S as a function of t/X, different curves being obtained for different values of Y. If one has such a family of curves, a comparison of the curve of S vs. t obtained experimentally for the given column with the calculated curves serves to determine the values of X and Y for which best agreement is obtained.

A difficulty in such a comparison arises from the fact that different values of X correspond to different time scales in the graph of S vs. t, and it is not easy to determine simultaneously the appropriate time scale as well as the appropriate member of the calculated family of curves. This difficulty has been largely overcome in Fig. 2, in which graphs of S vs. t/X are presented, with a logarithmic scale for t/X. In this case a change of X corresponds simply to a displacement of the curves horizontally without any change of shape. The procedure

for using the curves of Fig. 2 is as follows:

One plots the experimental values for S on a thin sheet of graph paper with the same ruling as that in Fig. 2, with the same scale of ordinates and with the time expressed in any convenient units. One superimposes this sheet on Fig. 2 so that corresponding ordinates coincide, and one slides it horizontally until the best fit between the experimental points and one of the calculated curves is obtained. From this curve (or, possibly, by interpolation) one gets Y and, from a corresponding pair of values of t on the experimental graph and t/X on the theoretical one, X is obtained.

As has already been pointed out, for small values of t/X, S is independent of Y, so that all the curves of Fig. 2 nearly coincide. This makes the curve fitting particularly simple: fitting the experimental points for small values of t to the (nearly unique) curve serves to determine X; the experimental points for larger values of t enable one to determine Y.

Fig. 3 presents a family of curves for S as a function of t/X, for various values of Y, for a stripper column. They are intended to be used for the determination of the constants of a stripper in the same way as those of Fig. 2 for the rectifier. Columns have been run both as rectifiers and strippers. If the column is uniform, the column

constants should be the same in both cases. As might be expected, it was found that the value of Y was the same. In general, the value obtained for X was somewhat larger (10%) in the case of the stripper. This is attributed to the less satisfactory heat transfer conditions which exist at the bottom of the column resulting in a lower hot wall temperature. In some other cases it was found that X for a stripper was quite different from the value determined as a rectifier. On examining the curve of approach to equilibrium it was noted that the value of X at different portions of the curve was not constant. The source of the discrepancy was traced to gross non-uniformities in the column such as a restriction at one end.

III. Product Rate vs. Concentration

In the preceding section a convenient method of determining column constants has been discussed. It was stated that knowledge of these quantities permitted prediction of the behavior of a uniform column at any given withdrawal rate. We now examine the question of product removal from a single stage rectifier. For the case of an element where concentration C of the sought species is small,

$$S = \frac{1 + \nu}{\nu + e^{-(1 + \nu)Y}} \tag{5}$$

$\nu = \frac{P}{H}$ where P is the product rate and H is a column

constant. Both quantities are, of course, expressed in grams per unit time.

The relation has been verified in a number of experiments. In particular, results were obtained from several columns shown to be reasonably uniform by runs both as strippers and rectifiers and by examination of the curve for approach to equilibrium. The value taken for X was the average from the two types of run. Results are given in the following table:

Table II

M	X	Y	H	P	ν	S Calculated	S Observed
1980 g	153 da	.48	27.0 g/d	87.4 g/d	3.24	1.26	1.27
1980	152	.43	30.4	47.2	1.55	1.35	1.35
1980	181	.4	27.4	22.8	.83	1.40	1.39
1500	34	.65	68	22.6	3.32	1.28	1.27

It is seen that the agreement is very good.

IV. Reproducibility of Results

Observations on reproducibility of results have been made. When a given column was studied it was found that results were reproducible even when the studies were made at intervals of several months. However, the situation was not so bright when an attempt was made to build a number of columns all alike. Even with care and close inspection,

employing selected tubing, a variation in results was found. An experiment at the Naval Research Laboratory was conducted on seven columns under particularly satisfactory conditions. The following results were obtained:

Table III

	Spacing	T_1	T_2	X	Y
1	0.026 cm	185°C	63°C	166	.53
2	"	"	"	153	.48
3	"	"	"	160	.53
4	"	"	"	153	.43
5	"	"	"	210	.40
6	"	"	"	181	.40
7	"	"	"	153	.50

Examination of the data in Table III makes it clear that there were relatively large variations in the most carefully built columns. In Table IV are shown data covering constants of a group of Philadelphia columns. Several extremely poor columns that were in the group originally have been eliminated. These were shown to possess restrictions which reduced the spacing at some point in the column to nearly zero. It is clear from the data that rather large variations in performance are to be found in the run-of-the-mill column.

While several explanations have been offered for the variation, no adequate proof has been demonstrated. The variation in performance of columns supposedly of identical construction is perhaps not surprising in view of the small spacing normally employed in the columns. An error of .001" amounts to 10% in the spacing. Whatever the source of the variation, its existence makes the study of liquid thermal diffusion a most difficult one.

Table IV

Serial No.	X	Y	H
307	46	.56	61
308	51	.67	46
310	51	.58	53
231	81	.39	49
26	40	.80	49
230	110	.42	35
225	68	.38	61
311	82	.55	35
20	160	.40	25
312	53	.66	45
159	63	.28	90
315	70	.68	33
158	150	.45	24
316	31	.52	98
319	44	.74	49

V. Spacing

Spacing is the most crucial column variable. Both X and Y vary as spacing is changed. The general features are: a maximum value of Y is observed in the vicinity of .020 cm. At large spacings Y diminishes as $1/a^4$. At narrower spaces, depending on accuracy of column construction, Y again diminishes. The quantity X is also affected by column spacing with a minimum occurring at about .025 cm.

Before examining in more detail the effect of spacing, a few words should be said concerning two other column variables -- temperature and fluid pressure. Both of these affect the properties of the working substance, thus affecting the value of both X and Y. For instance, the effect of higher ΔT is to move the optimum spacing toward smaller values. In addition for a given column, spacing itself is a function of both pressure and temperature.

In an early series of experiments employing 36-foot units the effect of spacing was surveyed. For purposes of the test, independent facilities for a single column were constructed. Each column was in turn tested under identical conditions. Steam temperature was held at 170°C, cooling water at 65°C. In the experiments the storage chamber was connected through one line to the bottom of the column. Thus each of the group of columns ran essentially as a

combination of rectifier and stripper with the point of unchanged concentration essentially at the middle of the column. Each column had a set of sylphon expansion bellows at the top which had a process fluid hold-up of about 200 grams. In the experiment the quantity measured was the change in concentration at the top of the column. The results are shown in Fig. 4.

The solid line represents a curve given by $Y = \frac{a^2}{b + k\,a^6}$ which has been normalized at 0.02 cm and at 0.053 cm. The agreement between the curve and the data may or may not be significant.

At the same time some observations were made on the value of the half-time. These were necessarily rather rough since the separations observed are small and probable errors in analysis of a magnitude not much smaller than the effect itself.

Table V

	Half Time	
0.068 cm	~	1 day
0.053 cm	~	1 day
0.038 cm	~	.5 day
0.021 cm	~	1.5 days
0.014 cm	~	3.0 days

It appears that an optimum spacing exists. The portion

of the curve corresponding to the wider spacing shows an $1/a^4$ relation which is in agreement with a theoretical deduction. The region of narrow spacing is less clear.

A theoretical prediction by K. Cohen places optimum spacing at a much smaller value. Two factors enter. The first is the fact that imperfections in spacing become relatively more pronounced at the narrower values. The second factor is due to temperature drop in the walls and water films of the column. As smaller spacings are employed, the temperature drop between the hot and cold walls diminishes for a given set of operating conditions. It is accordingly felt that the optimum obtained is a "practical" optimum. Thus if a column employing more perfect spacing were employed, it is probable that the optimum spacing would be smaller and the observed isotope separation larger.

It is not surprising that optimum spacing varies with temperature conditions. Indeed, the spacing of a given column is a function of temperature. Therefore, before completing our remarks on spacing it seems desirable to discuss the temperature dependence of column behavior.

VI. Temperature Dependence of Column Behavior

Theoretical analysis has indicated that the relationship between performance and temperatures in a column is very complicated. Indeed, it is not possible to predict

behavior when comparatively large temperature differences, ΔT, are employed as was the case in these studies. In a general way one would predict that an increase in temperature difference between the hot and cold walls would be beneficial. Studies involving water solution and small values of temperature difference showed that $Y \sim \Delta T^2$. This relation did not apply in the case of our uranium hexafluoride studies.

There are two factors to be taken into account when making temperature studies on the columns. The first has to do with the fact that the temperatures at the hot and cold surfaces of the hexafluoride are different from those of the steam supply or cooling water. The second factor is the variation in column spacing which occurs when temperatures are changed.

When heat travels from the steam to the cooling water it passes through the following layers:

1. A thin film of condensate at the inner surface of the nickel.
2. The nickel wall.
3. The process fluid.
4. The copper wall.
5. A film of water on the surface of the copper.

Principal uncertainty is in the first named item. Examination of standard works on heat transfer shows that

this factor is variable and that condensate may be on the surface in the form of a film or as drops. Some measurements have been made on the temperature drop in this film under conditions of column operation. Temperature drops in the nickel, copper and cooling water film can be calculated. As a result one obtains the following results for a typical temperature distribution in a column (0.025 cm spacing).

Table VI

Steam Temp.	Inner Nickel	Hot Surface of UF_6	Cold Surface of UF_6	Cold Surface outside of copper	
286°C	252°C	244°C	69°C	68°C	63°C
188°C	169°C	164.6°C	66.6°C	66°C	63°C

The second factor is the variation in spacing with temperature. This is demonstrated in the following table. The spacings are calculated at the actual temperatures existing in the metals.

Table VII

Steam Temp.	Water Temp.	Spacing
20°C	20°C	0.030 cm
188°C	63°C	0.0273 cm
286°C	63°C	0.0249 cm

Hence, one cannot determine the effect of temperature variations on a given column without simultaneously varying

the spacing of the column.

Results are presented in Table VIII on studies of three carefully constructed columns which were run as individuals, and given special attention during their operation. The values under T_1 and T_2 are those for temperature of the steam and the cooling water respectively.

Table VIII

Steam p.s.i.	T_1	T_2	Q cals/sec	Spacing	M	X	Y	ϕ	ϕ/Q
160	188°c	63°c	26,000	0.0273	2040 gms	150	.50	13.6	5.2
600	254°c	63°c	41,200	0.0256	1720 gms	63	.53	27.3	6.6
1000	286°c	63°c	48,000	0.0248	1600 gms	32	.6	50	10.4
160	188°c	63°c	28,000	0.0253	1860 gms	140	.6	13.3	4.8
800	271°c	63°c	51,000	0.023	1500 gms	34	.65	44.1	8.6
160	188°c	63°c	31,400	0.225	1600 gms	260	> .7	6.2	2.0
750	267°c	63°c	51,500	0.200	1320 gms	50	.8	26.4	5.1

It appears that at this particular spacing value, the main effect of increased ΔT is to diminish X; that is, to speed up the processes in the column. It is interesting how little the value of Y is changed by an increase in ΔT. Indeed, by comparing columns possessing a different ΔT but the same spacing, one finds that in this particular region of spacing the separation is quite insensitive to ΔT.

The value of ϕ/Q is of practical importance. It is a number which is proportional to the output per unit heat consumed. At the S-50 plant it was particularly important to get maximum output from a limited steam supply. Hence, we wished to have ϕ/Q a maximum. Experience at the Naval Research Laboratory, later confirmed at Philadelphia, showed that ϕ/Q diminished at values above 0.025 cm and below 0.020 cm. Hence, it is felt that the spacing for optimum ϕ/Q lies between 0.023 cm and 0.025 cm.

VII. Effect of Pressure on Performance

One series of observations throws some light on the role of pressure in column performance. The experiments were made employing 0.025 cm spaced column operating at 1000 p.s.i. steam.

Table IX

Fluid Pressure	Q	X	Y	M	ϕ	ϕ/Q
1000 psi	48,500 cals/sec	36	.60	1600 gms	44.4	9.2
1490 "	47,300 "	54	.77	1700 "	31.5	6.6
3000 "	45,000 "	58	--	1810 "	31.2	6.-

The effect of pressure is to increase viscosity of the fluid and to diminish the difference in density between the hot and cold regions of the column. Both these effects tend to slow action in the column. Performance suffers accordingly.

These results were obtained on a column which showed no instability. It is quite possible that the dependence of performance on pressure would be quite different were an unstable column used (see following section).

No value of Y is quoted in the 3000 p.s.i. run because the experiment was interrupted. The value of X, of course, being obtained early in the run was not affected. When a pressure of 3000 p.s.i. is employed, calculations show that an appreciable increase in spacing occurs due to elastic deformation of the copper.

VIII. Fluctuations in Column Pressure

It seems worthwhile to describe some observations on the behavior of columns when pressure is varied.

A column was operated at a steam pressure of 480 p.s.i. and a cold water temperature of 65°C. Allowing for the temperature drop in the condensate film and in the nickel wall, one arrives at a value of 210°C for the temperature of the hot wall at the liquid hexafluoride surface. The reservoir was initially maintained at a temperature of 260°C. Reservoir pressure was 1250 p.s.i. The reservoir was then cooled. When the temperature in the reservoir dropped below the critical point, the pressure in the reservoir became simply the vapor pressure of uranium hexafluoride. Power consumption in the column remained essentially constant, increasing a few per cent until the reservoir reached 210°C. At this point the reservoir temperature and the wall temperature were approximately equal and therefore the pressure at the hot wall was approximately equal to that of the reservoir. Actually, hydro-static head must be taken into account. The reservoir was at the top of the column. Hence, pressures at the top were equal while at points lower in the column the total pressure exceeded that of the reservoir.

Suddenly, as the reservoir cooled a little further, there were loud sharp crackling noises in the column. Power consumption immediately rose by a factor of two. Clearly a new mechanism of heat transfer had been called into action. Our terminology for the phenomenon is "pitching". It seems appropriate to use a word other than

boiling because it later appears that the same effect also occurs at pressures greater than the critical. Through numerous observations it was determined that "pitching" causes a profound mixing effect. If separation exists in a column when the phenomenon occurs, a mixing takes place. If a column is started with fresh material, almost no separation will occur until "pitching" ceases.

Another experiment was conducted using a column heated with 800 p.s.i. steam. Initial pressure in the reservoir was 1300 p.s.i. When the reservoir temperature and hence pressure were dropped, the "pitching" phenomenon occurred at a pressure of 720 p.s.i. This corresponds to a temperature of 231°C. It is not far from our estimates of the inner hot wall temperature.

A similar experiment was performed at a steam pressure of 1000 p.s.i. The reservoir was held at a pressure of 1300 p.s.i. As the fluid pressure was reduced, power remained constant. At 950 p.s.i. a pressure gauge began to indicate a slight instability in the column. The indicating needle jumped from time to time with an amplitude of a few p.s.i. As pressure was lowered further, the amplitude of the variations became greater and more rhythmic at about 5 cycles/sec. However, power consumption remained unchanged. As pressure was lowered further, amplitude increased to 25 p.s.i. At 770 p.s.i. the pressure at the

column suddenly dropped to about 100 p.s.i., power increased by a factor of two, and the sharp crackling noises were heard.

Later, further studies on other columns were made when the steam pressure was 1000 p.s.i. With less accurately constructed columns, instability set in at pressures as high as 2000 p.s.i. In the plant at Philadelphia, data were collected on a group of columns. Below are tabulated results for a group of ten columns all having a common steam and water supply.

Table X

Pressure	P	Pressure	Δ P
1500 psi	0 psi	1200 psi	5 psi
1510	40	1200	100
1490	30	1210	60
1500	10	1200	25
1510	35	1190	60
1510	0	1210	0
1500	0	1200	2
1490	50	1200	130
1500	20	1210	40
1500	10	1200	20

The outstanding features in these data are the variations among the columns and the trend to greater instability at

lower pressures. Attempts were made to relate performance of the various columns to magnitude of the instability. These studies showed that on the average the less stable columns performed less satisfactorily than the stable units. It is perhaps not surprising that no exact correlation between ΔP and performance exists. If the source of the disturbance happened to be some distance from the end of a column where measurements were made, the value observed would obviously be much diminished due to damping.

The observations further showed that the wide-spaced columns had the most instability. At a pressure of 1200 p.s.i. five columns of each of the indicated spacings gave the following average variations:

Table XI

Spacing	ΔP
.011	80 psi
.010	25
.009	6

Coincident with variability in stability was a variation in the pressure at which the various columns began to "pitch". This ranged up to 1200 p.s.i. which is far above the critical pressure of 740 p.s.i. In much of the production work up to twenty-six columns were operated in parallel. It was found that "pitching" in one column

tended to be communicated to neighboring units. Furthermore, disturbances such as product removal tended to initiate "pitching". As a result it was necessary to operate the twenty-six column circuits at 1500 - 1700 p.s.i.

The earlier columns at the Naval Research Laboratory were constructed with individual attention and care. It is not surprising that these should show much less instability than the columns in the pilot plant at Philadelphia or at S-50.

IX. Effect of Column Length

Experiments have been performed leading to evidence of the role played by column length. The results are only in fair agreement with theoretical predictions. According to theory, for a simple column, if one varies the length L, keeping other factors constant, then Y, the logarithm of the equilibrium separation factor, will vary in proportion,

$$Y = \alpha L ,$$

where α is a constant. On the other hand, the time constant X remains constant, independent of length.

The following table gives some experimental results to indicate the extent to which these theoretical predictions are borne out:

Table XII

Nominal Length	Working Length	Exp. Y	Exp. X	Spacing	T_1	T_2
12'	10.7'	0.08	230 days	0.025 cm	61°C	185°C
48'	46.7'	.50	170	0.025 cm	61°C	185°C
12'	10.7'	.10	73	0.025 cm	61°C	254°C
48'	46.7'	.53	63	0.025 cm	61°C	254°C

The "working length" refers to that portion of the column within the water jacket. On this basis, the ratio of the working lengths is 4.36 while for the first two columns the ratio of the Y's is 6.25, and for the last two the ratio is 5.3. It appears that the separation is smaller in the short column than theory would predict. A reasonable explanation for this can be found in the fact that the cooling water enters the jacket through an opening at one side, so that in that region there is an asymmetry in the cooling action of the water with reference to the column axis. This results in an asymmetrical temperature distribution at the cold wall of the process fluid which leads to parasitic convection or mixing; hence, that portion of the column contributes very little to the separative action. A similar effect can be expected to take place at the top near the cold water outlet. If one subtracts about 2 ft. from the working length for each column to allow for

the disturbance in the cooling water, one obtains good agreement with the theoretical prediction for the behavior of Y, particularly if one notes that the percentage errors in the experimental values for the first and third columns are rather large.

As regards the behavior of X, it is to be noted that here again the presence of dead spaces (regions which do not contribute to the separative action) can be thought of as contributing to the mass M without contributing to the value of Y, so that the dead spaces would increase X (since $X = M/HY$). In this way one can understand why the X is larger for the smaller column in the case of each of the two pairs, instead of being the same for both. However, such considerations have to be regarded as having only qualitative significance in view of the fact that the definition of H originally referred only to a uniform column without dead spaces. It might be pointed out that the largest variation in X occurs in that case where the discrepancy in Y is the greatest.

CAPTIONS

Experimental Studies

Figure 1

Approach to equilibrium of a single column with a large reservoir, and no hold-up at the top. Initial buildup of separation goes as $\left(\frac{t}{X}\right)^{1/2}$. At times greater than the half-time, the behavior follows the familiar exponential approach to equilibrium.

Figure 2

Family of curves for rectifiers for various values of Y showing approach to equilibrium. Plotted on a logarithmic scale these curves permit easy determination of column constants. These curves apply to the case where the concentration of the desired isotope is small.

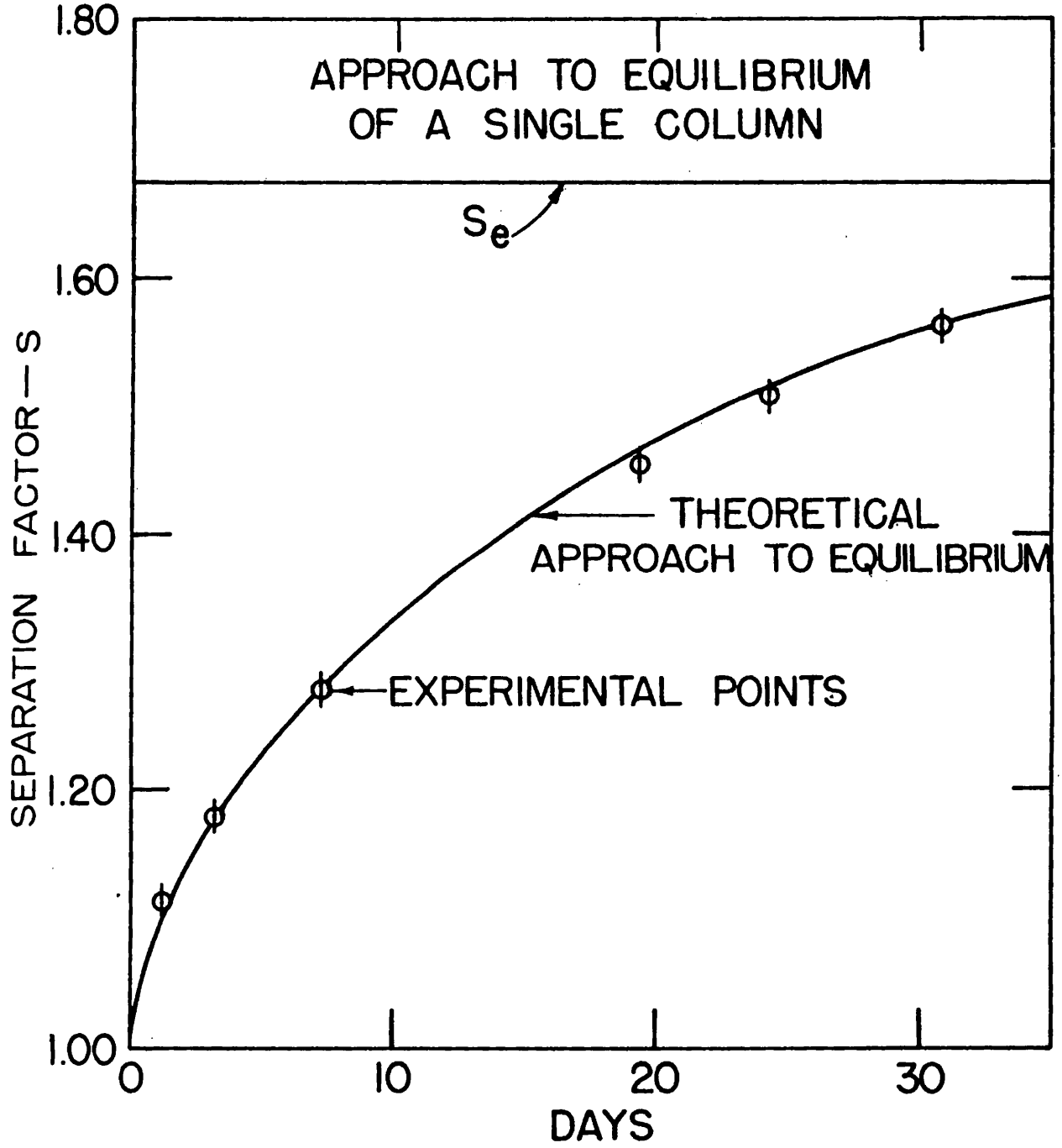
Figure 3

Family of curves for strippers with various values of Y showing approach to equilibrium. Plotted on logarithmic scale these curves permit easy determination of column constants. These curves apply to the case where the concentration of the desired isotope is small.

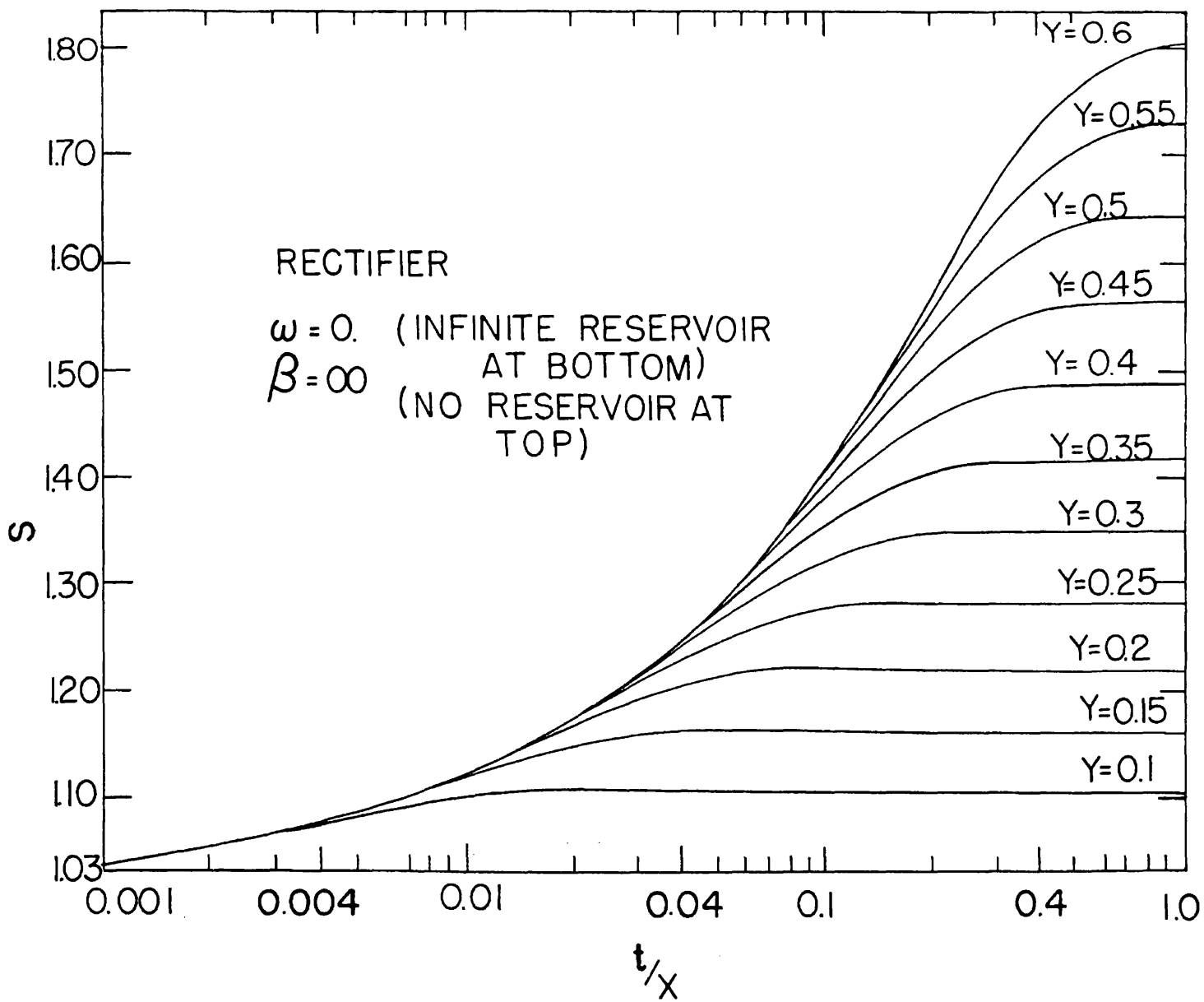
Figure 4

Equilibrium separation factor as a function of spacing. Survey experiments to establish the region of optimum spacing. The separation shown was for an approximate 18 feet of rectifier. The solid line represents a curve given by

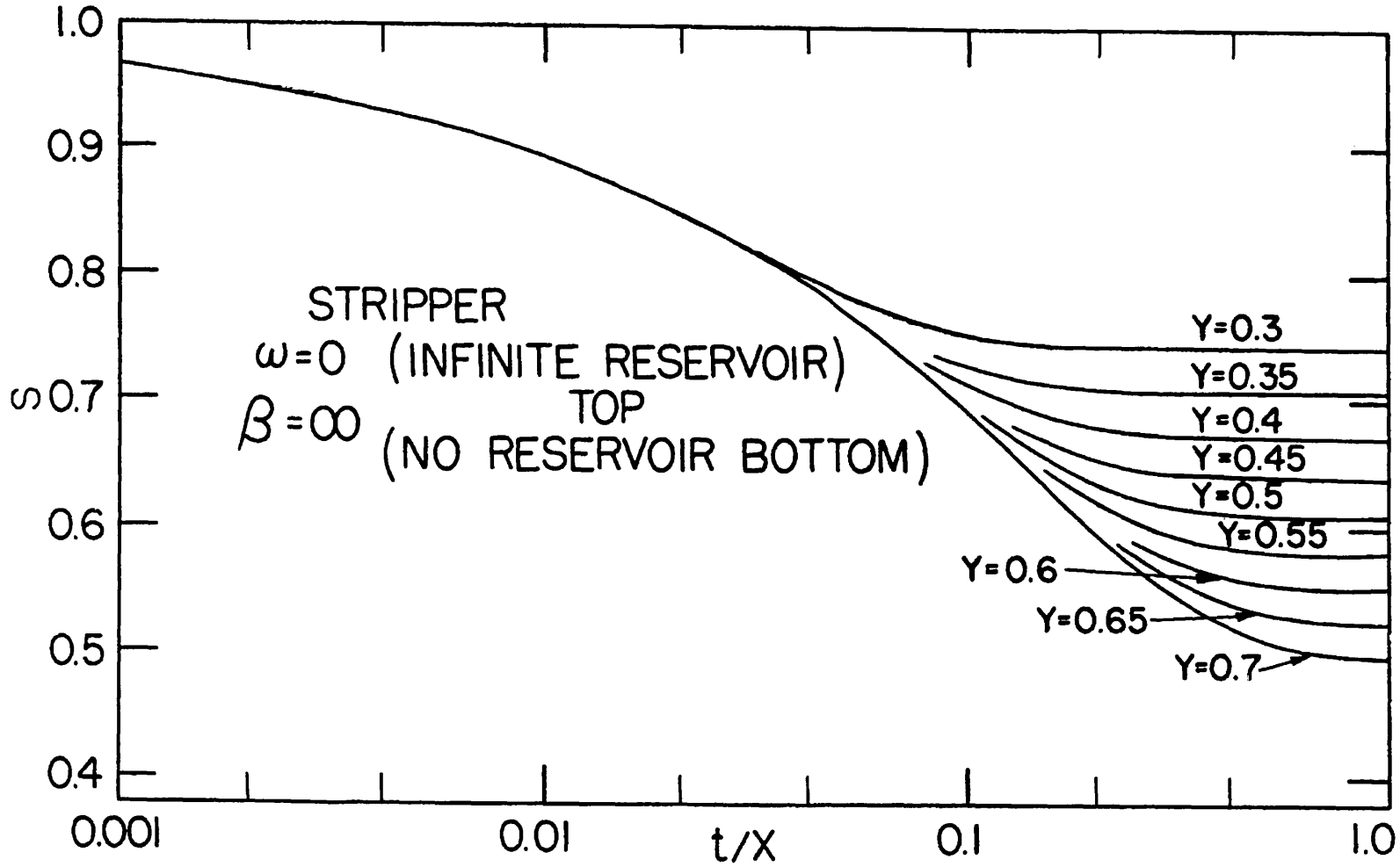
$$Y = \frac{a^2}{b + Ka^6} .$$



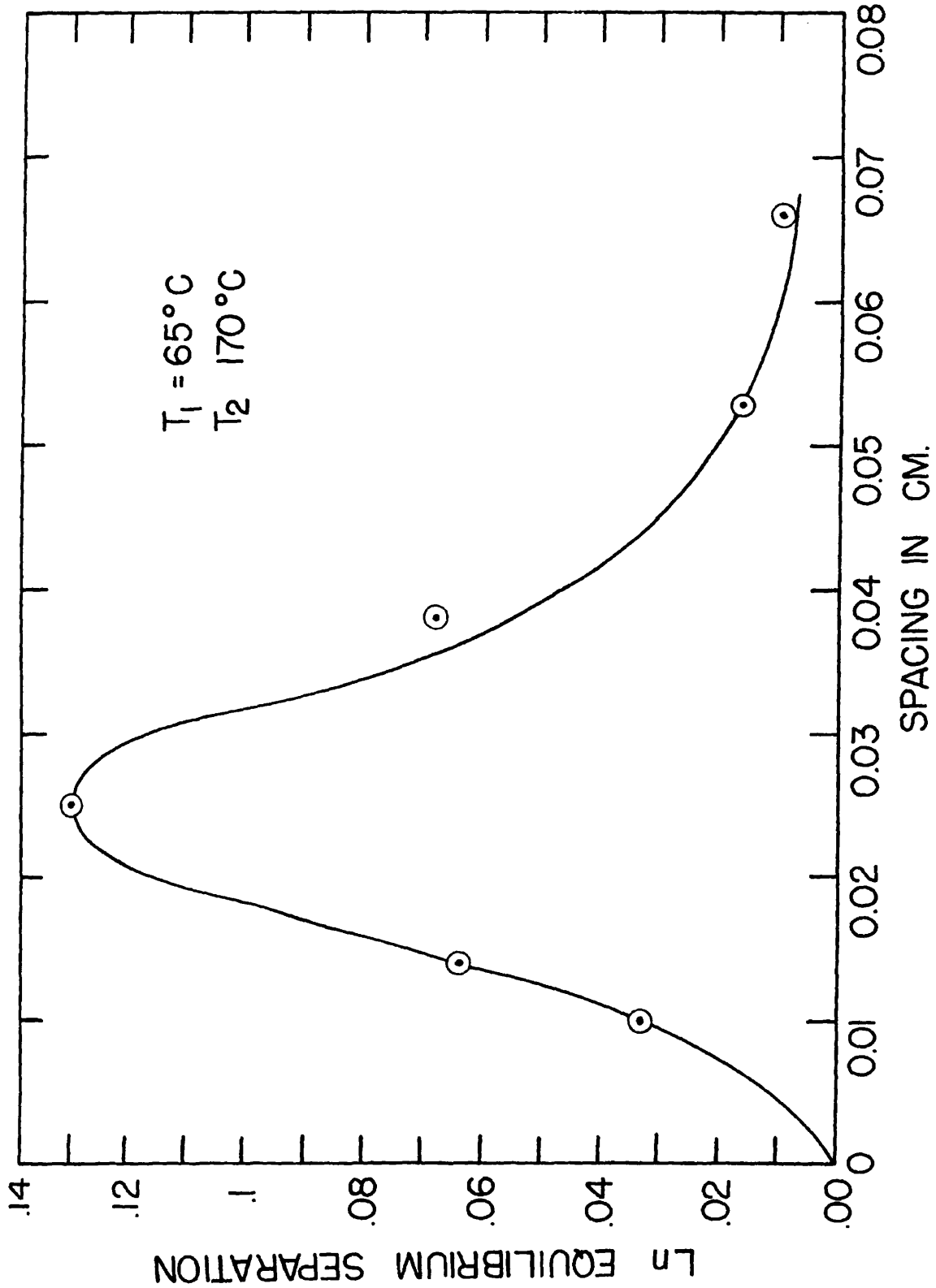
Experiment / Calc. Stab. E. 1



Experimental Column Studies Fig. 2



Experimental Column Studies Fig 3



Experimental Column Studies Fig 4

ENGINEERING AND OPERATION

R.E. Ruskin, E. Drott, H.M. Moseley, J.B. Bidwell

In this chapter we discuss some of the features of liquid thermal diffusion plant design and operation. The attempt is made to emphasize crucial and novel considerations rather than results. In addition, a minimum space is given to design involving conventional engineering practice. In order to give a clearer picture of design, we first present a brief treatment of plant operation.

I. Plant Operation

As mentioned in the Introduction, the principal use of the liquid thermal diffusion process was as a source of feed for other plants. It was determined that best overall results would be obtained by feeding in normal uranium hexafluoride (.715% U-235), withdrawing product at .858% and rejecting waste at .679. This objective was accomplished in a rather simple manner. Columns were connected in parallel in groups of 25 - 26. Feed from a reservoir (capacity 400 pounds) was circulated through the bottoms of the columns. Product was removed from the tops of the columns.

Feed was delivered to the plant in cylinders holding 450 pounds. The cylinder was placed in a steam jacket and the contents were transferred to the reservoirs by distillation. The reservoirs were steam-heated with steam pressure adjusted to give the desired 1550 p.s.i. uranium hexafluoride pressure. Circulation through the reservoir

and the bottoms of the columns was maintained by a thermo-syphon pump described earlier at a flow rate of 6 - 10 pounds per hour.

The process of product removal was carried out in the following way: at periodic intervals the columns were isolated from one another at the bottom by freezing the connecting links. A similar set of intercolumn connectors at the top was then unfrozen. Fluid from the columns was allowed to flow into a common metering device. Due to the compressibility of the process fluid, an appropriate quantity could be withdrawn without excessive lowering of pressure in the column. Once the product had been removed, the top inter-column connectors were frozen and circulation was re-established through the bottoms of the columns. The process of product withdrawal was carried on at 2 - 4 hour intervals. This is a type of procedure easily made automatic by employing a cam timer and solenoid valves. Operations at Philadelphia were carried on exclusively in this automatic way.

When the reservoir became depleted so that the light constituent concentration was down to 0.68%, it was dumped and refilled with fresh feed. Depending on the number of columns connected to a given reservoir, its contents, and their productivity, the waste was dumped from a reservoir every 8 - 16 days. While this process was carried out, the

columns were isolated. Because of the compressibility of the process fluid, this was a satisfactory procedure. Difficulties arose only in the event of steam supply failure.

The remaining operational problems in the liquid thermal diffusion plant were maintenance of a reliable supply of heat in the form of steam and a steady supply of cooling water.

II. S-50

The S-50 plant[1], Fig. 1, was located on the banks of the Clinch River adjacent to the K-25 steam power plant of the Clinton Engineer Works. A building 525 feet long, 82 feet wide, and 75 feet high housed 2,142 columns assembled on 21 steel racks.

Principal steam source was the K-25 power house which produced steam at about 1,275 p.s.i. and 925°F. Steam was desuperheated and reduced in pressure to 1,000 p.s.i. Part of the condensate from the columns was sent back to the power house; the remainder was boosted in pressure and used for the desuperheating. The Clinch River served as a source of the 40,000 g.p.m. cooling-water make-up.

An oil-fired 450 p.s.i. steam plant of capacity 400,000 pounds per hour was completed about July 1, 1945. It served to supplement the K-25 power house supply which at that time was increasingly being devoted to supplying power for the K-25 plant.

The basic unit of the S-50 plant was the 102 column

rack. This unit was almost exactly a copy of those existing in the Philadelphia installation. Hence, in discussing design features in more detail, we shall describe the salient features of the pilot plant.

III. Process Area Design (Philadelphia)

This section covers the principal mechanical engineering aspects involved in the building of the Philadelphia "Reflux Test" pilot plant. The main design work, done between June and October 1943, was based on the 14-column pilot plant at the Naval Research Laboratory, Washington, D.C. The principal objective was the erection of a unit which, by simple multiplication, could be expanded to a production plant of any desired size. In addition, provisions had to be incorporated to allow the continuation of development work begun in Washington, D.C.

The column (Fig. 2) was essentially a central tube of nickel through which steam was passed, surrounded by a small annular space (G) in which the process material was confined by a larger tube of copper (E to F). Around the copper was a larger annular space for circulating hot water, enclosed by a casing of 4-inch i.p.s. pipe. Suitable adaptors were provided at the ends of each unit to admit steam, process material, and water simultaneously, each under considerable pressure, and at the same time permitting differential expansions due to temperature changes.

The basic problem was simply that of maintaining the

inside nickel tubing of a heat exchanger at as high a temperature as practicable, at the same time keeping the temperature of the outer copper just above the melting point of the material being processed. In order to accomplish this, water was recirculated through the water jacket with enough make-up being added to keep the temperature constant while steam entered the inner nickel tube at the top, was condensed over a 48-foot length, and the condensate removed at the bottom.

The size and physical dimensions of individual columns were determined during the operation of the pilot plant at the Naval Research Laboratory, where 25,000 lb./hr. of saturated steam at 165 p.s.i. and 1,000 lb./hr. of saturated steam at 1,000 p.s.i. were available. Experimentation showed that the columns giving the best performance were those with a spacing (G) of .010 inch. Consequently the design of the plant was based on the requirements of such a column -- 1,088 pounds per hour of 1,000 p.s.i. saturated steam.

The design of rack, pipe sizes, and weights was determined on the basis of standard engineering practice. Pipe sizes were based on economy as calculated on the basis of power consumption cost for two years operation.

1. Site

After due study of possible locations, the Naval Boiler and Turbine Laboratory was chosen as the operation site, Fig. 3. Half of a building originally designed for turbine

testing was made available to house three racks plus the necessary steam generating equipment. The approximate dimensions of the plant were 164 feet by 81 feet with half of this area at a level 10 feet below grade so that while the clear height of the upper level was only 46 feet, the distance from the pit floor to the bottom of the roof truss was 56 feet, which was the minimum height to accommodate the columns. All of the boilers and auxiliaries with the exception of the condenser were installed in the remaining space at ground level. Besides the plant proper, about 7,200 sq.ft. were occupied by auxiliary buildings.

2. Rack

Considerations taken into account in arriving at the number of columns per unit were as follows: (1) the cost of erection and availability of materials capable of feeding the necessary amounts of steam and water to and from various numbers of columns; (2) the cost of operating for a two-year period; (3) the length of process-material transfer lines; and (4) the layout of the steel frame. The resultant design was a 102-column unit 50 feet long, 7 feet wide, 54 feet high with two sides of three divisions each and each division containing 17 columns.

Standard structural sections made up the rack, which was constructed in two parts to allow the use of the crane, located in the building, for erecting the heavier structural members of the base and for assembling the condenser and

larger pieces of machinery in the pit. The base, Fig. 4, 41 feet high, supported the weight of the columns, the two 24-inch recirculating water heaters, and the condensate piping. Carried by the superstructure, 13 feet high, were the upper operational deck, the steam piping, and the one-ton capacity monorail hoise used for hanging columns in place.

The top working platform was built with 2 by 8 foot trapdoors around the columns, Fig. 5, to facilitate their installation in the rack. The lower deck was sloped toward floor drains to carry away the considerable amounts of water used at times in operations.

Experience had shown that it was desirable to have approximately 200 g.p.m. of water recirculated through each column. In order to hold the temperature of the inner copper wall of a refluxer above 156°F, the melting point of the material at the operating pressure, the recirculating water entered the unit at 150°F, allowing for film and conductance losses of 6°F for clean copper. In passing the length of the column, the water was heated 7°F to an outlet temperature of 157°F. On this basis, a maximum per rack of 2,200 g.p.m. of river water at a summer temperature of 85°F was needed for make-up. Severe fouling of the metal surface caused by river impurities made a greater temperature drop from copper to water in operation so that the final temperature of the overboard water had to be lowered below

157°F with the consequence that more make-up had to be added.

The path of the recirculating water through the system can be traced on the flow-diagram, Fig. 6. Water was pumped from the river through a 72-inch main by one of two 50,000 g.p.m. circulators which were part of the permanent test equipment of the Turbine Laboratory. This line primarily fed the condensers, a maximum of 6,000 g.p.m. going to the reflux racks through the booster pumps which added enough head to force the water out of the overboard line and maintain a water level above the column tops. A steady temperature was maintained on all three racks by the automatic valve on the No. 2 pump with the control bulb located in the inlet header to rack 1.

The recirculators pumped the water from the pump suction header into the lower 24-inch inlet manifolds by way of the pump discharge header. Gate valves on inlet and outlet headers permitted one rack to be secured while others continued to operate. The water travelled down the connecting piping into the bottom of the column, up the unit, down the 4-inch upper connecting piping, and into the top 24-inch outlet header. Overboard water equal in amount to make up was removed at one end through a line whose highest point passed above that of the columns, so that the units remained full of water. The consideration here was that if the copper of the columns were exposed to air, the steam

would heat it above 400°F, the annealing temperature of the metal, and ruin the worth of all units so affected. The bulk of the water circulated out of the other end of the manifold down the outlet piping, Fig. 7, and back into the pump suction header.

Each of the two boosters had a capacity of 5,000 g.p.m. while an auxiliary line from the Yard fire main, Fig. 6, could put 1,400 g.p.m. into the booster pump header; therefore, in the event of failure of either unit, the other unit plus the fire main supply could keep the plant operating at full load. Should the circulating pumps stop, this source of water would keep the temperature below 212°F for 5 minutes and thereafter supply enough water to make up that boiled off. If both sources of supply failed during normal operation, the quantity in the system was such that a period of 3-1/2 minutes would elapse before boiling occurred.

Two recirculators were employed so that if one were secured for repairs or breakdown, the other allowed operations to continue. It will be readily seen that the pumps supplied only enough head to overcome pipe and velocity head losses in the water circuit -- that they provided no static lift.

Part of the pump capacity was motor driven and part turbine driven so that in the event of either an electric or auxiliary steam power failure, some water would be pushed

through the racks, giving 3-1/2 minutes to secure the steam valve before the water began to boil rather than one minute which would be the time interval to heat the water in a column to boiling if none were being recirculated.

Air-vent headers and piping served the purpose of preventing air from accumulating at the top of the column and then going over into the upper 24-inch manifold in slugs, and also served as an inlet for low pressure steam into the water jacket for conditioning of units.

Inlet and outlet stops on each column were necessary for experimental uses to allow individual regulation of recirculating water and also to secure single units for inspection while the others in the rack continued in operation. In addition, these valves were useful in column conditioning.

3. Steam

The essential path of steam flow is shown in Fig. 6. Superheated steam, 850°F at 1,000 p.s.i. was generated in the two main boilers passed through the superheater headers and later desuperheated to 548°F before going into one of the three rack feeders. The branch from the number one line going to the 1,000 to 600 p.s.i. reducing station was an emergency measure to feed steam auxiliaries if the boiler provided for that purpose should fail. Steam entered at the center of the 6-inch steam manifolds and passed through them to the upper expansion loops, past the 1-inch steam

stop and into the columns where it was condensed.

The condensate followed a path out of the bottom of the column, past the 3/4-inch stops, through the bottom expansion loops, into the condensate manifold to the condensate blow-down station where one-third of the hot (530°F) water was flashed to steam at atmospheric pressure, condensed, and sub-cooled along with the unflashed portion to 180°F, at which temperature the condensate pumps could handle the liquid.

The level of the condensed steam was kept somewhat below the lowest point of the process fluid in the columns on the first rack by manual adjustment of the condensate blow-down valves, the height being indicated by a water level indicator connected across the steam and condensate headers. The level in the other two racks was maintained by slowly closing down the valves on the connecting piping from the lower 4-inch manifolds until the temperature of the condensate in them began to drop off, indicating that live steam was no longer present.

From the condenser back to the boilers, the piping followed conventional practice, the condensate going first through the de-aerating tank to remove most of the air and to heat the water to 240°F with exhaust steam from boiler auxiliaries. The hot wall of the tank discharged into the suction of the feed boosters which supplied suction head

to the main feed pumps. In addition to feeding the boilers, these units also supplied water to the desuperheaters.

4. Equipment

Two Foster-Wheeler oil-burning marine-type steam generators were assigned to supply heat to the column units, and a 600 p.s.i. 156,000 lb./hr. Alaska-type marine boiler from the Naval Boiler and Turbine Laboratory was set up for boiler and plant auxiliaries. Each of the main boilers was rated at 180,000 lbs. of steam per hour at 1,500 p.s.i. and 850°F. With desuperheating, the capacity was 225,000 pounds of saturated steam per hour at 1,500 p.s.i. Since 306 columns consumed 336,000 pounds per hour, the total steam capacity of 450,000 pounds per hour was high enough to take care of plant overloading caused by a column disturbance (pitching) which increased the consumption by 25%. Although it appears at a glance that using the boiler superheaters increases the output by 25%, they actually raised it 40% by virtue of the fact that the hot gases from the superheater bank passed through the saturated side of the boiler so that some steam was generated by these hot gases. The original boiler contracts had called for automatic controls, but because of their untested nature, the Naval Boiler and Turbine Laboratory deemed it advisable to dispense with them for the sake of continuous reliable operation, although this meant the use of more manpower. The boilers were served by

enough auxiliary equipment to insure plant operation in spite of the failure of any single unit.

In running the original experiments at the Naval Research Laboratory with 1,000 lb. steam, a gravity return system was used for a single column so that the hot condensate was fed directly back to the boiler, thus requiring the boiler to supply only the heat of vaporization plus a few BTU lost in subcooling the liquid 10 to 20°F. When the expanded program was laid out, the plan was to use the same system, using a high pressure, high temperature pump to return the feed water to the boilers. An alternative scheme was to use part of the hot condensate for desuperheating and cool down the rest in a condenser. Both of these proposals were discarded when investigation showed that although such pumps were being developed, none had been thoroughly proven to be capable of handling the hot water at 1,000 p.s.i. pressure and producing a differential head of 250 p.s.i. or greater. Consequently, in the interest of moving the plant completion date as far forward as possible and also in having a dependable source of steam when the plant was completed, the system of cooling down all the condensate in a condenser was used.

It will be seen that a tremendous amount of heat was being wasted in this arrangment: the total heat of 1,000 p.s.i. saturated steam was 1,191 BTU/lb. as it went into the columns. At the bottom, after condensation and a slight

sub-cooling, the heat of the liquid was 530 BTU/lb. If this hot condensate had been returned directly to the boiler only 661 BTU/lb. would have had to be added; however, if the liquid was sub-cooled to 180°F, 1,011 BTU/lb. had to be supplied. Based on one rack, the actual steam consumption was 39,400,000 BTU per hour, or 50% in fuel costs higher than would be required if hot condensate were returned. In view of this fact, the acquisition and use of suitable pumps and of boilers designed to operate with hot feed water is imperative to the economical operation of a liquid thermal diffusion plant.

5. Process Fluid Piping

In a thermal diffusion plant there are many miles of process fluid piping. In the interest of safety the size of the nickel tubing employed for the purpose was held as small as possible. In general, 3/16-inch, 1/8-inch, 3/32-inch, and 1/16-inch I.D. sizes were employed. Due to the melting point of the process material (70°C at 1,550 p.s.i.), it was necessary to keep fluid lines above this temperature to prevent solidification. For pipes of long length this was accomplished by jacketing and heating with 5 p.s.i. steam. As many as 32 nickel lines were included in one jacket.

An alternative method of maintaining fluidity was to keep the tubing at a sufficiently high temperature in a heated enclosed space.

Thermo-syphon pumps were located at frequent intervals

along the rack. One leg of the pump was jacketed with 5 p.s.i. steam, the other with 150 p.s.i. steam.

6. Duct System

The ducts around the tops and bottoms of the heat exchangers provided a heated space for link lines carrying process fluid from one unit to another and carried away fumes caused by a break in the material system, if that occurred.

As laid out, the front heating ducts were divided into units of two columns each, with one connecting duct to the collection duct behind each column, Fig. 8. The purpose of the division plates was to prevent cooling the links between more than two columns when an operator had a door open. After operation showed that the columns could be run in larger groups than was at first thought feasible, these dividers were removed so that the number of connecting ducts could be reduced to three or four per group of 17 columns as long as their size was increased appropriately.

The front half of the top of the lower duct and bottom of the upper duct were made removable to aid in installing columns. One hundred-pound steam lines, Fig. 8, were laid in the ducts to enable a temperature of about 212°F to be maintained therein. Back collection ducts were connected through a stack to blowers located on the roof of the plant. Gravity dampers had to be installed in these stacks between the lower and upper heating ducts and before the exhaust

fan to prevent the chimney effect from forcing cold air into the system.

In a properly run plant the number and size of process material leaks can be held down so low that the collection system can be dispensed within a building properly designed with natural convection currents if the process material is of low U-235 concentration.

Even though all steam piping and the columns themselves were insulated, the amount of heat passed to the air was large enough to make operations on the rack very uncomfortable. Louvers were installed in the lower portion of the building and vents were cut in the roof.

IV. Plant Instrumentation

For the most part, the instrumentation served one of two purposes: either (1) to minimize manpower requirements by providing automatic control of operation, or (2) minimize loss of time, or equipment, by providing an automatic alarm system actuated by controls at points where trouble might occur. In order to illustrate use of the control system, a typical one-stage circuit is described in detail.

1. The Product Circuit

Fig. 9 illustrates a typical product circuit. Any two adjacent columns in the circuit were connected together both at top and at bottom, connections at the bottom being made by 1/8-inch nickel tubing attached to the end column

adapters, connections at the top being made through a manifold. Copper tubing was silver-soldered to these "intercolumn connectors" at the indicated points, the copper tubing being connected to a source of water and compressed air. During normal operation, water flowed through the copper line at the tops of the columns (Line No. 2) and through the pre-meter freezer (No. 3). The cold water froze the material in the attached nickel lines. The water was then turned off water lines Nos. 1 and 4, allowing the material in the nickel tubes attached to these lines to melt, since the bottoms and tops of the columns and the intercolumn connectors were all contained in a steam-heated duct maintained at 100° - 130°C. Thus, raw material circulated from the reservoir, through the convector pump, through the bottoms of the columns, and back to the reservoir. Also, if there were any material in the meter chamber (which was maintained at a higher temperature than the product pot) this material distilled into the product pot. This condition existed until it became desirable to draw off product, at which time water was turned into lines Nos. 1 and 4. The water was next turned off line No. 2 and compressed air blown through this line for a period of time sufficient to purge it of water. The material in the manifold then melted; whereupon, water was turned off line No. 3, allowing the UF_6 to melt at this

point, so that the meter chamber filled from the tops of the columns. It was necessary to allow the material in the manifold to melt before the pre-meter freezer, No. 3, was thawed; otherwise it would be possible for the meter to be filled by UF_6 from only one or a few columns. Water was then turned back on lines 2 and 3, blown out of 1 and 4, and fluid circulation through the bottom resumed.

2. TIMER, SOLENOID VALVES AND RELATED APPARATUS

In order to provide continuous, automatic operation of the described cycle, a system of solenoid valves was used to control the flow of water and air through the copper lines. The periodic opening and closing of the various solenoid valves was controlled by an electrical timer which made and broke the electrical circuits to the solenoid valves at pre-set intervals of time.

A schematic diagram of the timer circuit is found in Fig. 10. It is seen that power to the solenoid valves was supplied through the timer and through a contactor. In series with the coil of the contactor were several stop buttons and a normally closed contact of relay CR2. The coil of relay CR2 was connected in series with a pressure switch communicating with the main steam supply and set such that the pressure switch made contact at about 900 p.s.i. (with process steam at 1,000 p.s.i.), opening the contact in the contactor coil circuit and thus breaking

the circuit which supplied power to operate the solenoid valves. The purpose of this device was as follows: if, for some reason, the main steam pressure were to fail and the columns were left to communicate with the reservoir as they cooled down, about two additional pounds of UF_6 would flow into each column from the storage chamber. If the steam were then turned back into the columns containing this excess material, it would be possible for the rapid expansion of the extra material to generate pressures sufficiently high to cause rupture of the columns. The inclusion of the relay CR2 prevented this possibility, since interruption of the power supply to the timer opened all water valves and closed all air valves, isolating the columns from the reservoir. A short-circuiting switch was placed around this contact for use during start-up.

Stop buttons were located at various strategic points in the plant, making it possible for an operator immediately to isolate all units from one another (by freezing) and from the reservoir.

The toggle switch T_{s1} was a selector switch located inside the timer. T_{1a} and T_{1b} represented one cam of the timer; the selector switch T_{s1} was thrown to T_{1a} if contact were desired for a percentage 0 to 50% of a cycle. If no contact was desired for a percentage 0 to 50% of a cycle, this switch was thrown to T_{1b}. SV was the solenoid valve controlled by this cam, while the circled G represented

a green light mounted on the panel, allowing one to tell at a glance whether the corresponding valve was actuated or not. T_{1c}, when closed, formed a short circuit around the cam, allowing one to operate the valves independent of the timer, should occasion arise to make this desirable. The inclusion of T_{1c} was, of course, optional; it was found to be time-saving during start-up and experimental runs, but of no use once steady production had been obtained. Other cams in the timer were connected paralleling that shown.

3. SIGNAL SYSTEM

The main signal system consisted of an annunciator and the necessary normally open switches, located at the various control points. The drops of the annunciator were actuated by such factors as failure of 440-volt power, failure of 110-volt power, low main steam pressure, high circulating water temperature, low freeze-off water pressure, low circulating water pressure, etc. An independent power supply was used for the annunciator (a bank of d-c storage batteries). In series with the individual drops of the annunciator was either a 6-volt bell and/or a relay whose output contacts were in series with a 110-volt bell.

One control, in particular, requires some detailed description, with regard to purpose. It has been found that the best solenoid valves commercially available were not 100% foolproof; i.e., (1) they had a limited life and

(2) they occasionally stuck in either an open or closed position. Reference to Fig. 9 shows that all columns were connected together both at top and bottom, but, as was stated above, at all times either the tops or the bottoms were "frozen" so that at no time could the individual columns communicate with each other both at top and at bottom. However, should a water solenoid valve burn out, or stick closed, then, during part of the cycle, the columns would communicate with each other at both top and bottom. This condition was found to be very detrimental to the process, even though it might exist for as small a time as 5 - 10% of the total cycle period. The reason for such a behavior lies in the inherent variations of structure of columns, temperature, etc., that will exist in any plant. Small though these variations from column to column might be, they result in different average densities of the process material in two adjacent columns, so that, if the columns communicate with each other both at top and bottom, a circulating flow of material will exist, resulting in a general mixing of material. This mixing has been found to be very effective in cutting down the separation factor; hence, it was desirable to have an alarm which would annunicate whenever both upper and lower freeze-off lines were simultaneously without cooling water.

It should be emphasized that a freeze-off water alarm system is a near must in any pyramid arrangement. A

multi-stage pyramid will require, in general, over a month to come up to product concentration. A half-hour of intercolumn circulation will usually nullify over half of the elapsed time.

4. PROCESS FLUID FLOW INDICATORS

For proper operation of the circuit, the process fluid must flow through the circulation loop for as large a fraction of the total cycle time as possible. Since it is quite easy for a "plug" of some sort to form in this line, some type of flow indicator was employed. This was most easily done by attaching thermocouples to two adapters of a column and recording their readings by use of a recording potentiometer calibrated to read temperature when employed with the thermocouples in use. When flow occurred, the fluid flowing out of one adapter of the column was about 100°C hotter than that flowing into the column. If no flow occurred, the two temperatures were about the same. Thus, simultaneous reading of the temperatures of the ingoing and outgoing adapters served as an indication of whether UF_6 flow existed.

One could also merely attach two thermometers to a line through which UF_6 was flowing, one of them being near an adapter through which fluid flowed as it left the column, the other being a foot or so down the line.

V. TRANSFER ROOM

Uranium hexafluoride is a poison of the same general level of toxicity as chlorine. One of the features of a liquid thermal diffusion plant is the high process fluid pressures which must be employed (1550 p.s.i.) Large quantities of process fluid must be maintained in reservoirs at these pressures. Transfers of fluid must be routinely made from shipping cylinders to reservoirs.

It is clear that rather serious operational hazards existed. To minimize these it was felt desirable to perform all tasks relating to bulk handling of uranium hexafluoride in a separate building especially designed to minimize potential hazards. This building was termed the "transfer room", Fig. 11. Functions of the transfer room are listed below:

(1) Transfer of uranium hexafluoride from shipping cylinders to reservoirs.

(2) Control point for keeping all process equipment at proper fluid pressure.

(3) Product metering point.

(4) Product removal point.

(5) Product dumping.

(6) Waste dumping.

(7) Routine transfer of process fluid.

1. General Considerations

The arrangement of instruments allowed convenient

and constant observation of all gauges and meters. A sprinkler system was provided in both main and product scale rooms to protect against bursting hexafluoride containers in case of extreme heat during a fire.

A great deal of piping for gas, water, and steam was needed to handle the requirements for these services in the transfer room. In order to avoid crowding of these lines around the room, the majority of them were placed in trenches running under the reservoir and product ducts along with condensate returns and water drain lines.

2. RESERVOIRS

The twelve reservoirs were the most important items of equipment in the transfer room, and the most dangerous due to the large amount (approximately 450 pounds) of material at 1550 p.s.i. Each of these tanks was a cylinder 8-1/2 ft. long and 8 inches inside diameter made of 1/2-inch nickel plate. The ends were elliptical in form and were somewhat thicker than the walls. The cylinder was made in two halves and welded along the axis with pure nickel rod. The ends were formed and attached with a circumferential weld. A coiled nickel heating pipe was constructed along the axis on the inside of the reservoir for heating the UF_6. A steel heating jacket surrounded the full length of the cylinder. This jacket served both for low temperature heating when starting up and for rapid

cooling of the contents of the chamber in an emergency. Near the bottom of the tank five nickel adapters projected outward for use in filling and connecting the reservoirs into the process fluid circuits. At the same level a thermometer well was welded into the tank. Additional adapters projected out from the top and bottom for cleaning. Blow-off diaphragm flanges were welded into the chamber at the top.

Each tank was mounted vertically upon a framework on a scale platform. The scale dial was turned so that it faced inside the transfer room and had 1000# range (see Fig. 12). The tare weight of tanks and associated equipment was balanced out so that the scale read the weight of UF_6 in the reservoir. The scale beam and dial were actually in the wall of the transfer room and were separated from the tanks by a steel plate. The suspension of the tank and scales of course necessitated generous loops or coils in all steam and water pipe attached thereto in order to eliminate extraneous support. This was well accomplished as tests with weights indicated.

The inner coiled nickel heating tube was attached to a steam loop above the top of the reservoir. This loop received steam from a line in the transfer room wall which was supplied, through a reducing valve, from a 600 p.s.i. steam line in the trench, but faulty operation caused their removal and replacement with 1/2-inch globe valves.

Regulation of the steam pressure provided temperature control at the temperature of condensing steam. The bottom of the coil fed into a steam trap and thence into a condensate return line located in a trench behind the chambers.

The outer jacket was supplied also from 5# steam and water lines in the trench along the front of the chambers. These lines were arranged with suitable checks and valves low on the walls of the transfer room so that either low-pressure steam or water could be routed into the jacket. This also was finally fed through a steam trap and into the rear trench.

Due to the installation of the reservoirs outside of the transfer room, the nickel adapters on them were quite long and had to be heated to prevent freezing. Therefore, a small jacket surrounded them from the point where they left the tank to where they entered the ducts in the transfer room wall. One could either heat these jackets with steam or run cold water through them to freeze-off the adapters in case of a break. These were connected to an automatic freezer valve. In addition, each tit had a copper "freeze-off" line silver-soldered to it inside the duct. Cold water could be run through any one of these lines to freeze it off by opening a cock just above the duct.

A remote indicating dial thermometer was placed just

above the scale dial and the element was located in a nickel well in the reservoir. Steam pressure gauges were located beneath the duct and measured the pressure in the steam heating coil. The UF_6 pressure gauges were connected through an adapter to the interiors of the tanks. These gauges were located just above the duct and were individually steam-heated. The gauges were standard 3000 p.s.i. bourdon tube design with beryllium-copper tubes and all silver-soldered joints.

To prevent the possibility of burst reservoirs and the attendant damage, several precautions were taken. The tanks were placed outside of the room and were completely surrounded by steel plate. Channel sections were used to isolate one tank from another. The plates were supported on channels set into the concrete scale footing. The tanks were then tested hydrostatically to 4000 p.s.i. before installation. Finally each chamber was fitted with a blow-off diaphragm mounted between flanges which would rupture at about 2200 p.s.i. The effective size of the disk was kept to 1/2-inch diameter in order that the jet effect of the blow would not be sufficient to cause damage to the scale mechanism, while still being large enough for reliability and non-plugging. In order to prevent loss of UF_6 after a blow, the diaphragm communicated with a blow-off tank mounted on the back of the steel shield. These tanks were made large enough so that under the worst possible

conditions of weight of material and temperature in the reservoir, the pressure would be dropped to a safe level after blow-off. A well was provided in the blow-off tanks into which the sensitive element of a thermal relay was inserted which operated an alarm bell when hot material entered the tank. When blow-off occurred, the scale indicator increased momentarily but rapidly dropped off as material went over to the blow-off tank; the process fluid pressure dropped off immediately.

All of the connections between the reservoirs and the process piping leading to the racks were made in a duct which was mounted on the wall in front of the reservoirs below the scale dials. This duct contained the transfer manifolds and terminal boxes for all of the lines leading to the columns on racks in addition to the adapters of the reservoirs. The duct was heated by means of steam lines and was well insulated. A blower system was arranged to clear the duct in the even of a break inside it. The air was drawn out of the ducts through circular conduits to a header mounted on the plate in back of the storage chambers. This fed to a blower mounted up on the wall of an adjacent building which forced the air through a washer to remove all UF_6. In addition, blowers were located in ventilators in the roof of the transfer room which cleared out smoke and discharged it at some height above the roof.

3. FILLING OF RESERVOIRS

Provisions were made for simultaneous operation of two transfer pots at the end of the line of reservoirs. These transfer pots were arranged on wheels with a removable top to allow insertion of the shipping containers. The pots were simply steam jackets used to heat the uranium hexafluoride sufficiently to distill it into the reservoirs. The pot was designed with sufficient volume and wall thickness so that in event of failure of the shipping containers, the pot would hold the material liberated. Though the pots were heavy, they were easily handled on their wheels. The head was placed on the shipping tanks and sealed with a neoprene ring and then the assembly was lowered into the jacket with an electric hoist. The pots could then be wheeled onto the scales used to measure the amount transferred. The steam and drain lines were attached to the pots and the heated material flowed through a heated line to the reservoir. Steam pressure regulating valves located on the adjacent wall, along with pressure gauges, allowed temperature control. Water valves operating through checks allowed rapid cooling of the pots in an emergency. The steam-heated process fluid line connected to a manifold inside the duct in front of the reservoirs to allow filling or draining any reservoir from either pot.

4. PRODUCT METERING AND REMOVAL

The product withdrawal operations were carried on in

a duct on the wall separating the two rooms of the transfer building and in the smaller of these two rooms. A large duct, with access doors on both sides of the wall, extended the full width of the transfer room. All metering operations were carried out in there.

Each circuit had its individual metering chamber which was essentially a capsule with a freezer valve at each end. The capsule was enclosed in a steam jacket and communicated with a pressure gauge. This gauge indicated whether the capsule was metering properly. Originally this gauge was steam-heated but later it was found easier to install all but the fact in the duct. In operation, an automatic timer first froze the capsule outlet and unfroze the inlet which communicated with the columns. This allowed UF_6 to enter the capsule at full system pressure which was indicated on the gauge. The inlet was then frozen and the outlet opened, allowing the volume of the capsule to pass out into the product pots. All of these operations were automatic and were carried out by a cam timer operating solenoid valves mounted on the wall above the product duct.

After metering, each of the product lines continued through a steam jacket conduit to its individual product pot. These containers were arranged in units of four on a scale with an air jack arrangement making possible the

individual weighing of these containers and yet conserving space. This product removal system was duplicated by a waste material withdrawal system in the case of the pyramid circuit which utilized similar equipment.

Engineering and Operation

Reference

[1] M.C. Fox, Chem.Metall.Eng. 52, 102 (1945).

CAPTIONS

Engineering and Operation

Figure 1

View of S-50 plant at Oak Ridge, Tennessee.

Figure 2

The liquid thermal diffusion column.

Figure 3

Aerial view of Philadelphia pilot plant located in Philadelphia Naval Base showing (1) boiler room, (2) main pilot plant, (3) transfer room, (4) laboratory building, (5) office and column construction building, (6) pump building, and (7) oil tank farm.

Figure 4

End view of the three racksat Philadelphia. Each rack carried 102 columns spaced 11" apart.

Figure 5

View between two racks (top), showing (1) heating duct, (2) trap door, (3) hoist and mono-rail, and (4) 6" steam headers.

Figure 6

Schematic layout of main steam and water piping for Philadelphia plant.

Figure 7

View across ends of racks showing (1) booster pumps, (2) automatic temperature control valves, (3) booster pump

header, (4) recirculating water pumps, (5) recirculating water discharge piping from 24" top header, and (6) ventilating air ducts.

Figure 8

View at bottom of columns showing (1) duct steam heating lines, (2) bottom of columns, (3) piping to column condensate expansion loop, (4) connecting openings to collection duct, (5) flow meter for process fluid, (6) process fluid adapter, (7) inter-column connectors, (8) freezer, and (9) hot air duct.

Figure 9

Schematic diagram of typical one stage product circuit. Valve action on flow of UF_6 was obtained by freezing the substance. Automatic operation was attained by controlling freezer water flow by solenoid valves and a cam timer.

Figure 10

Schematic diagram of cam timer and associated controls. In the event of any accident leading to loss of process fluid, all columns could be isolated from each other by pressing stop buttons located at strategic spots around the plant.

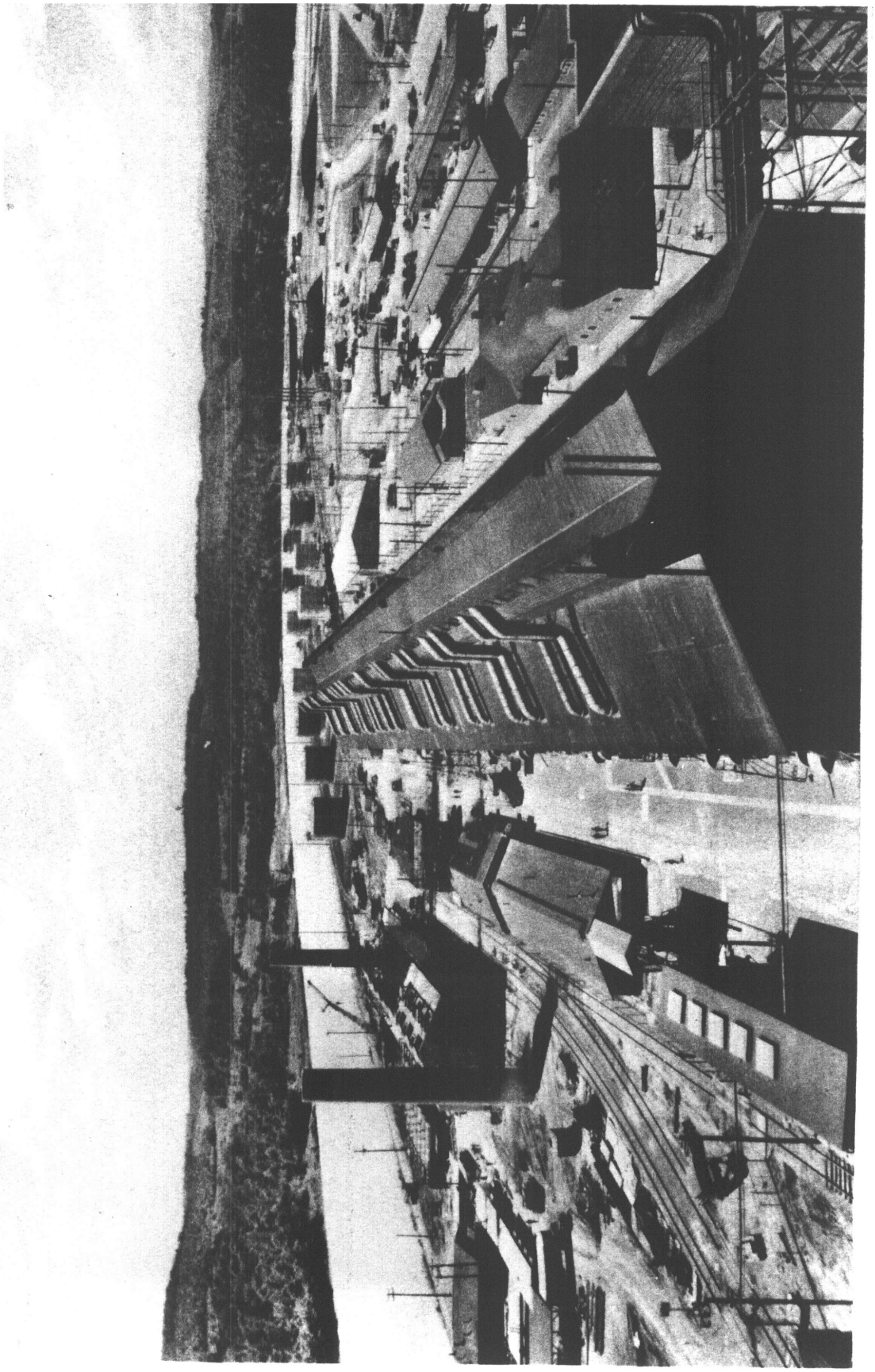
Figure 11

View of transfer room showing (1) scales for the twelve reservoirs, (2) hot air duct to maintain fluidity of UF_6, (3) terminal box -- terminus for 1/8" O.D. nickel piping

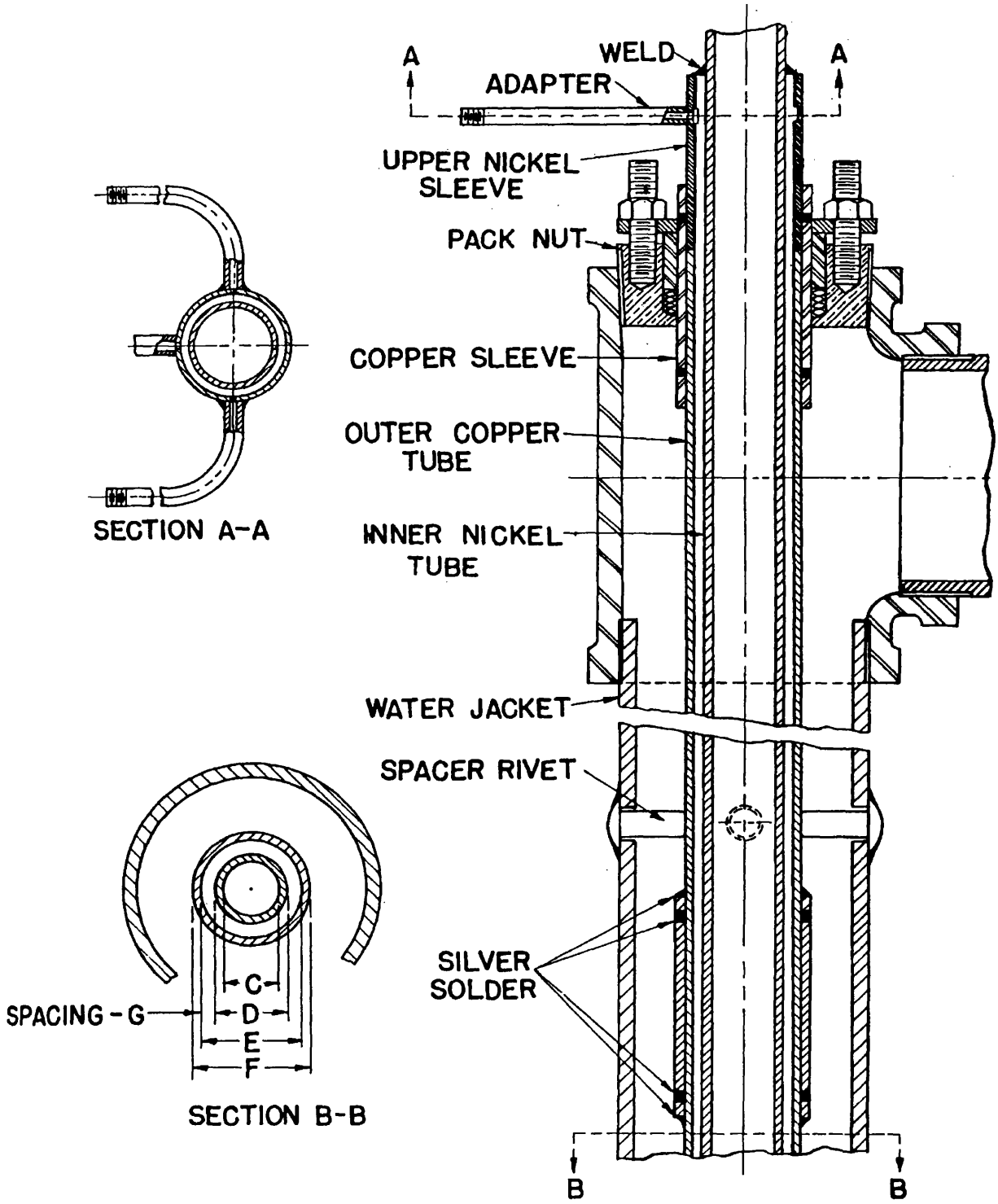
connecting transfer room and main process area, (4) product meter duct, (5) product weighing scales, and (6) steam jacket for rapid distillation of UF_6 from shipping containers.

Figure 12

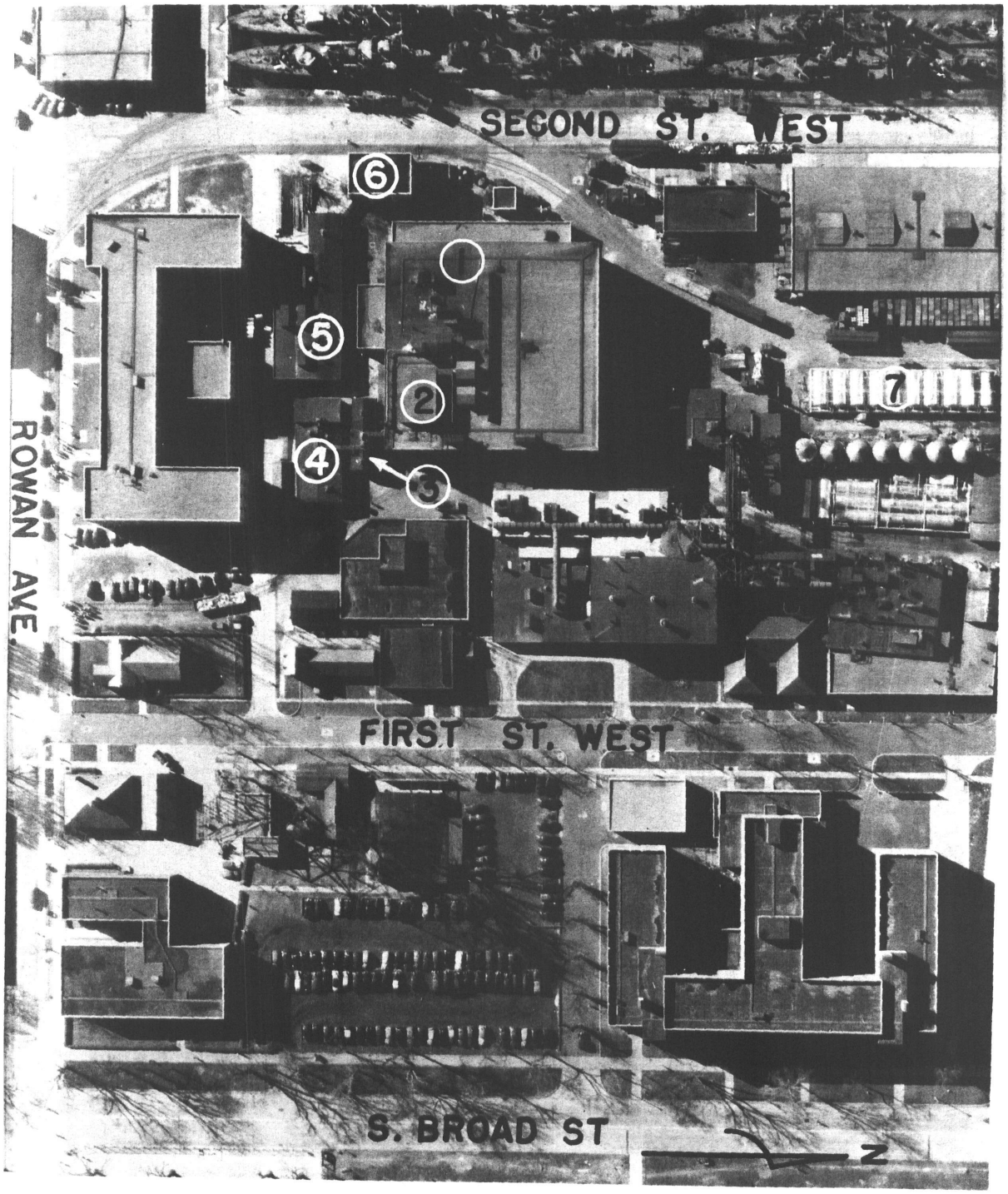
Detail of reservoir mounting and piping.



Engineering and Operation Fig 1



Engineering and Operation Fig. 2



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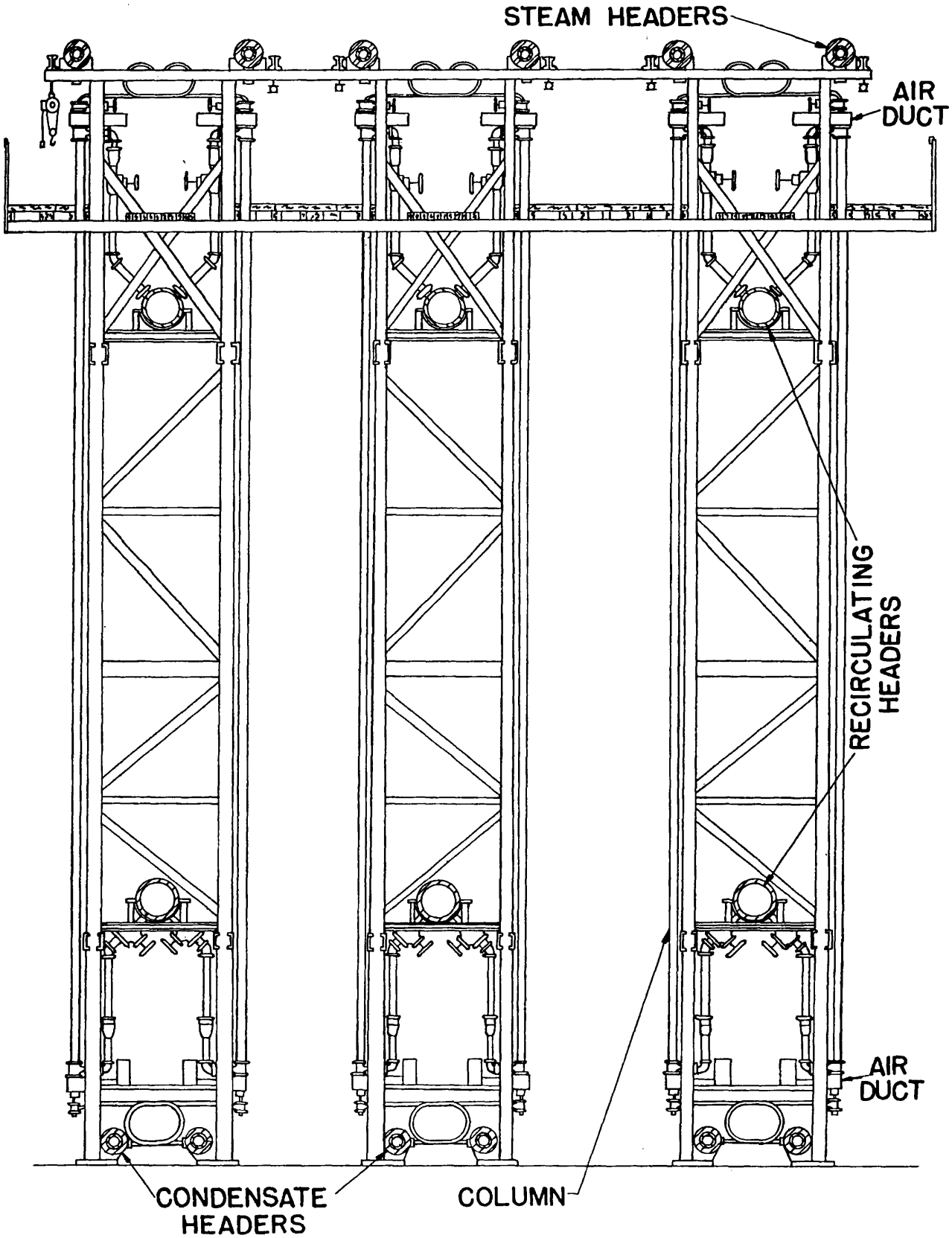

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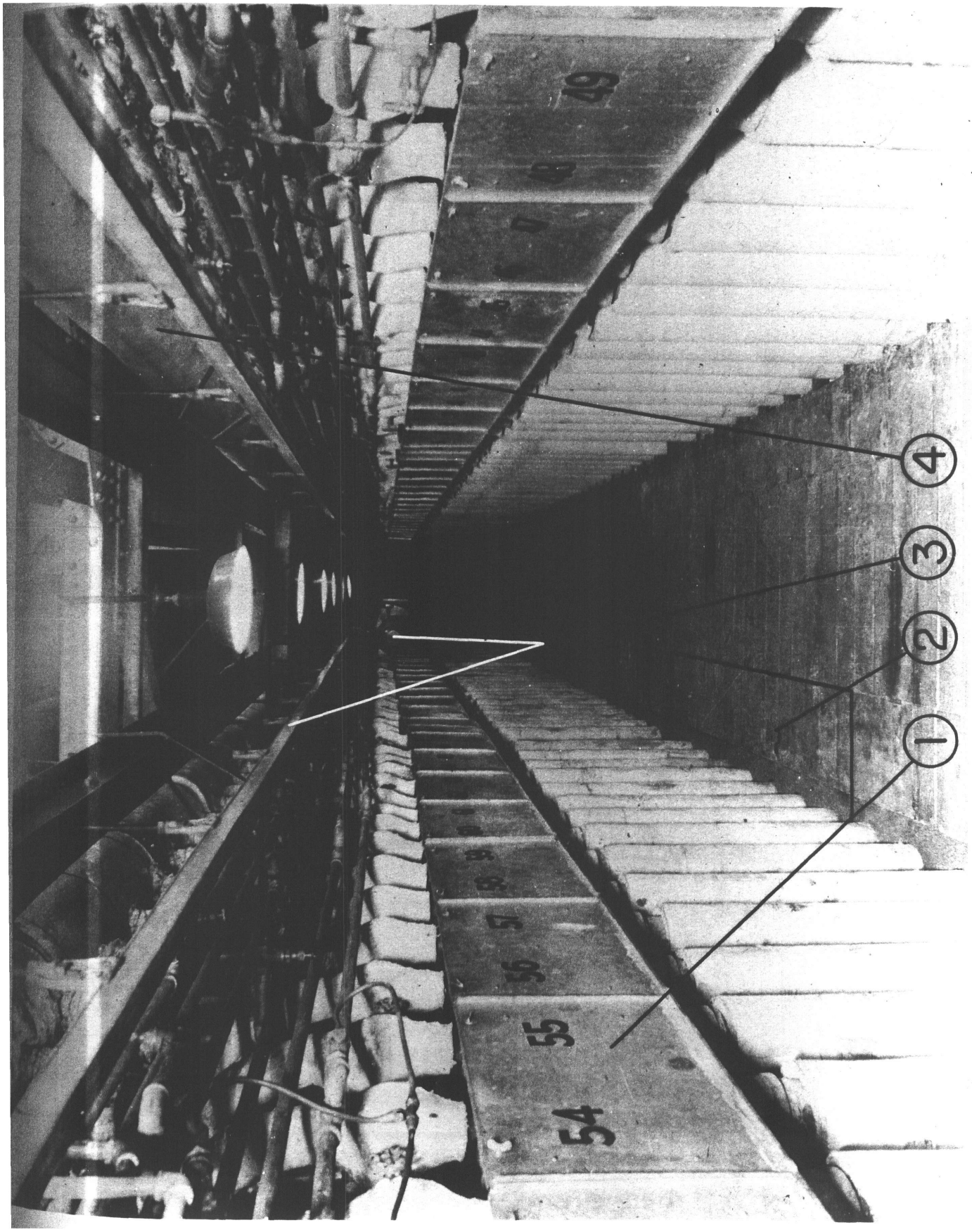
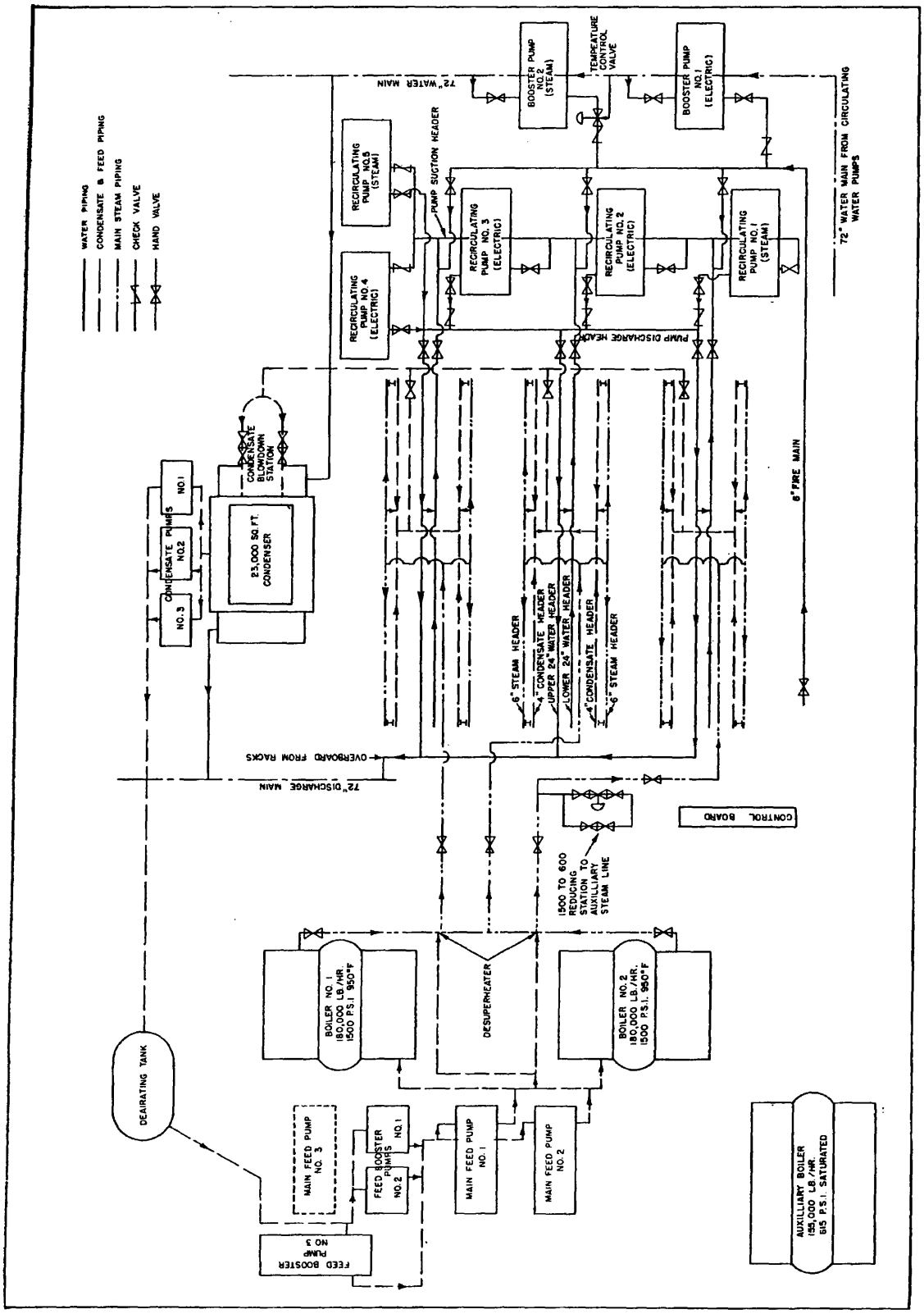
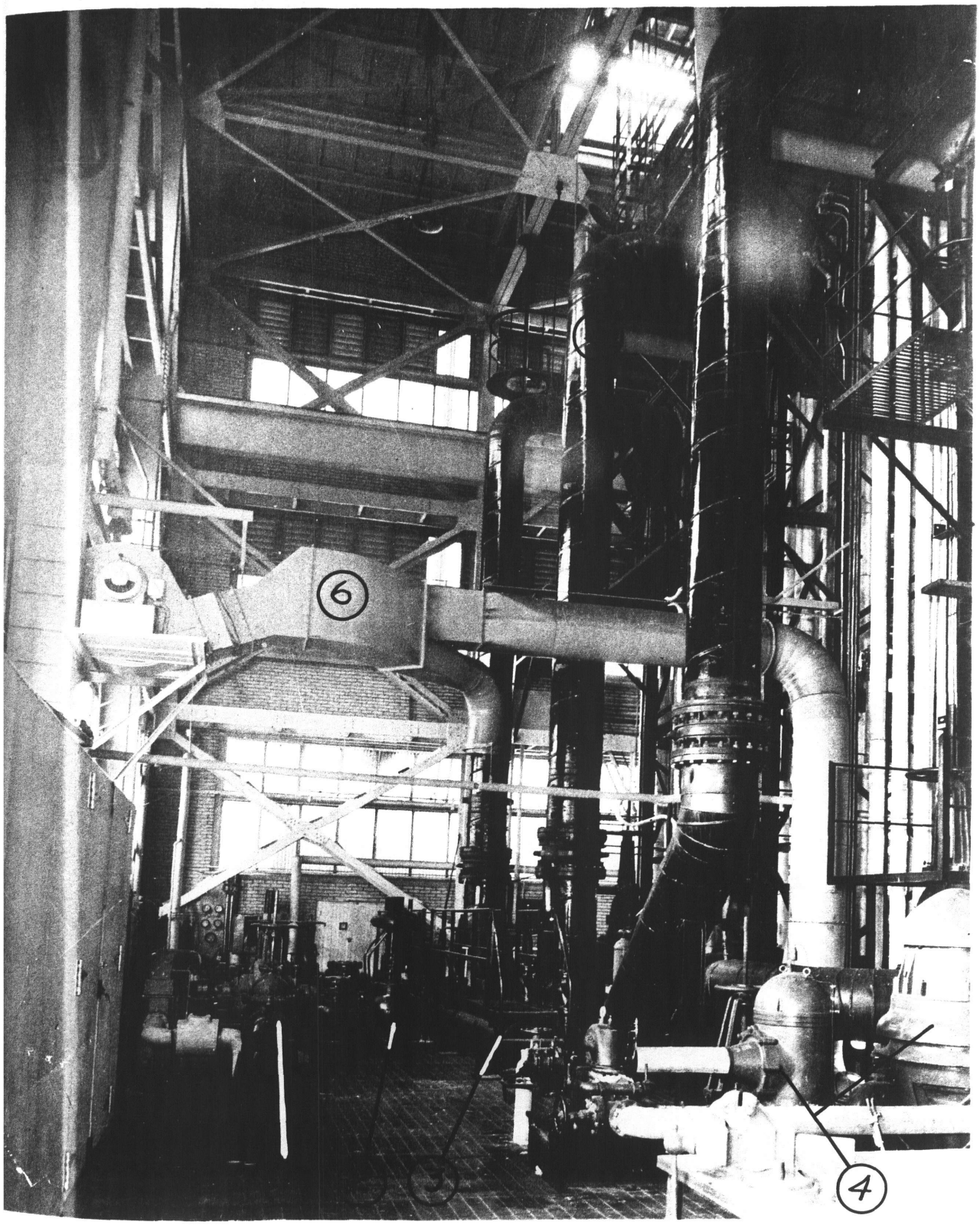


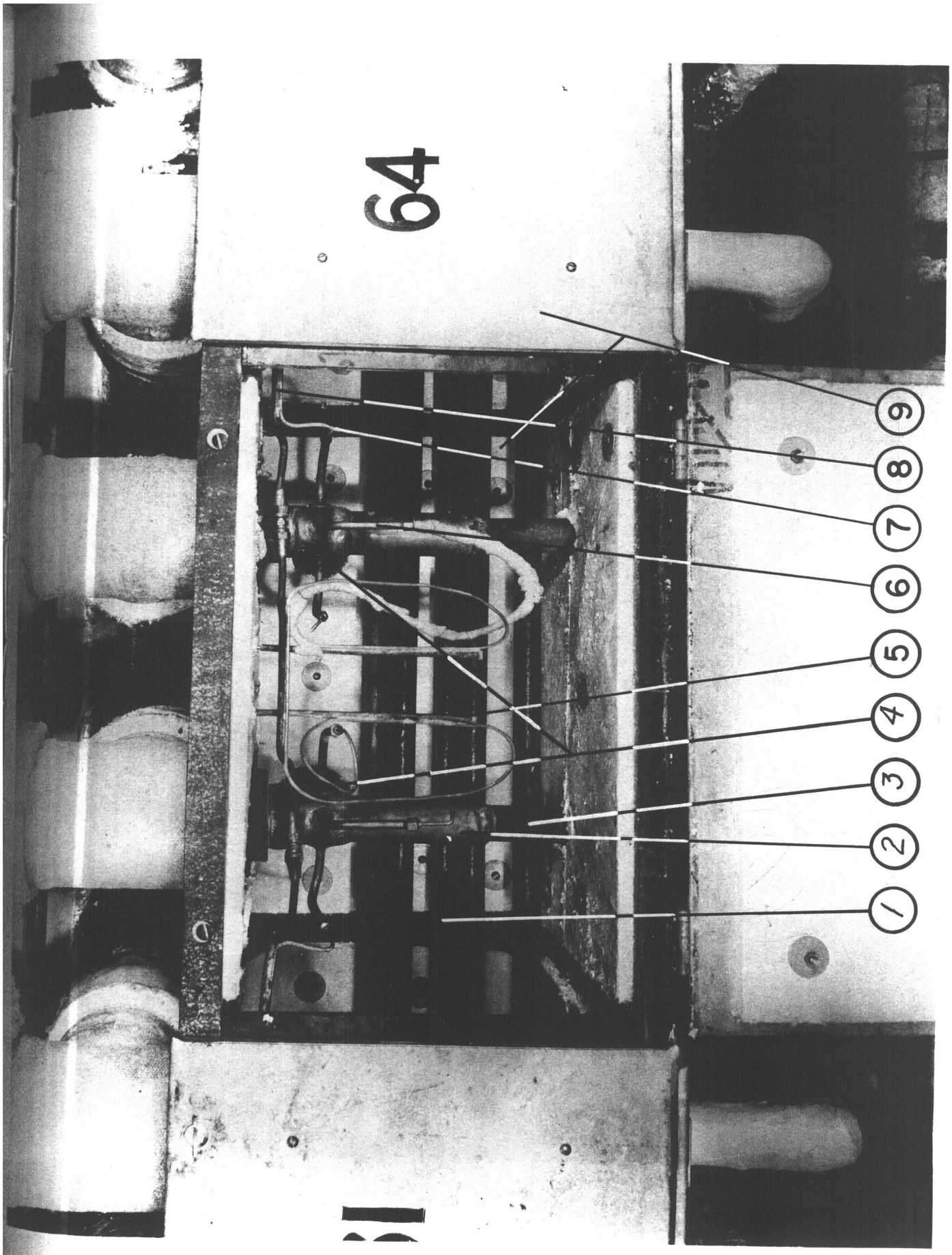
Engineering and Operation Fig 5



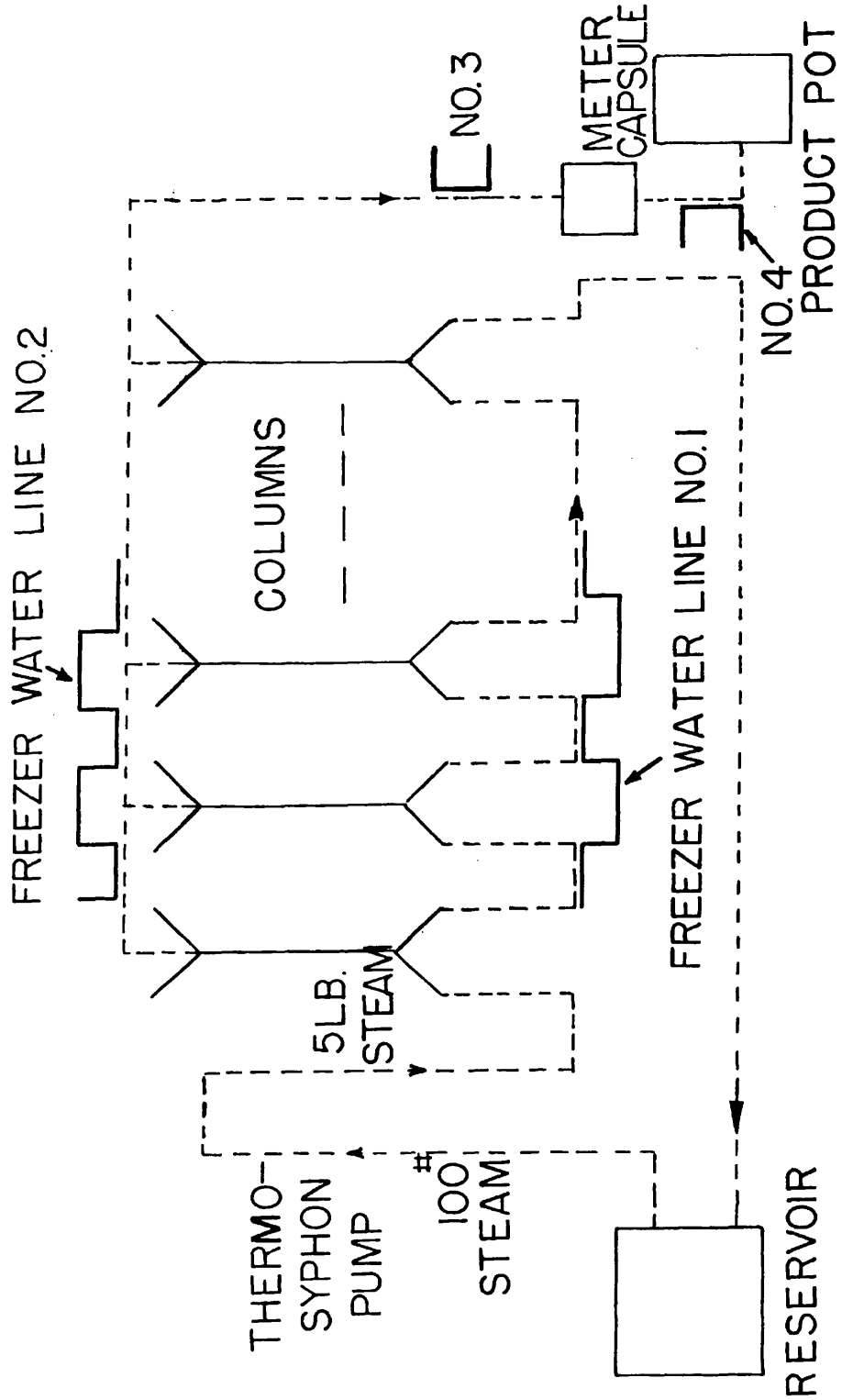
Engineering and Operation Fig. 6



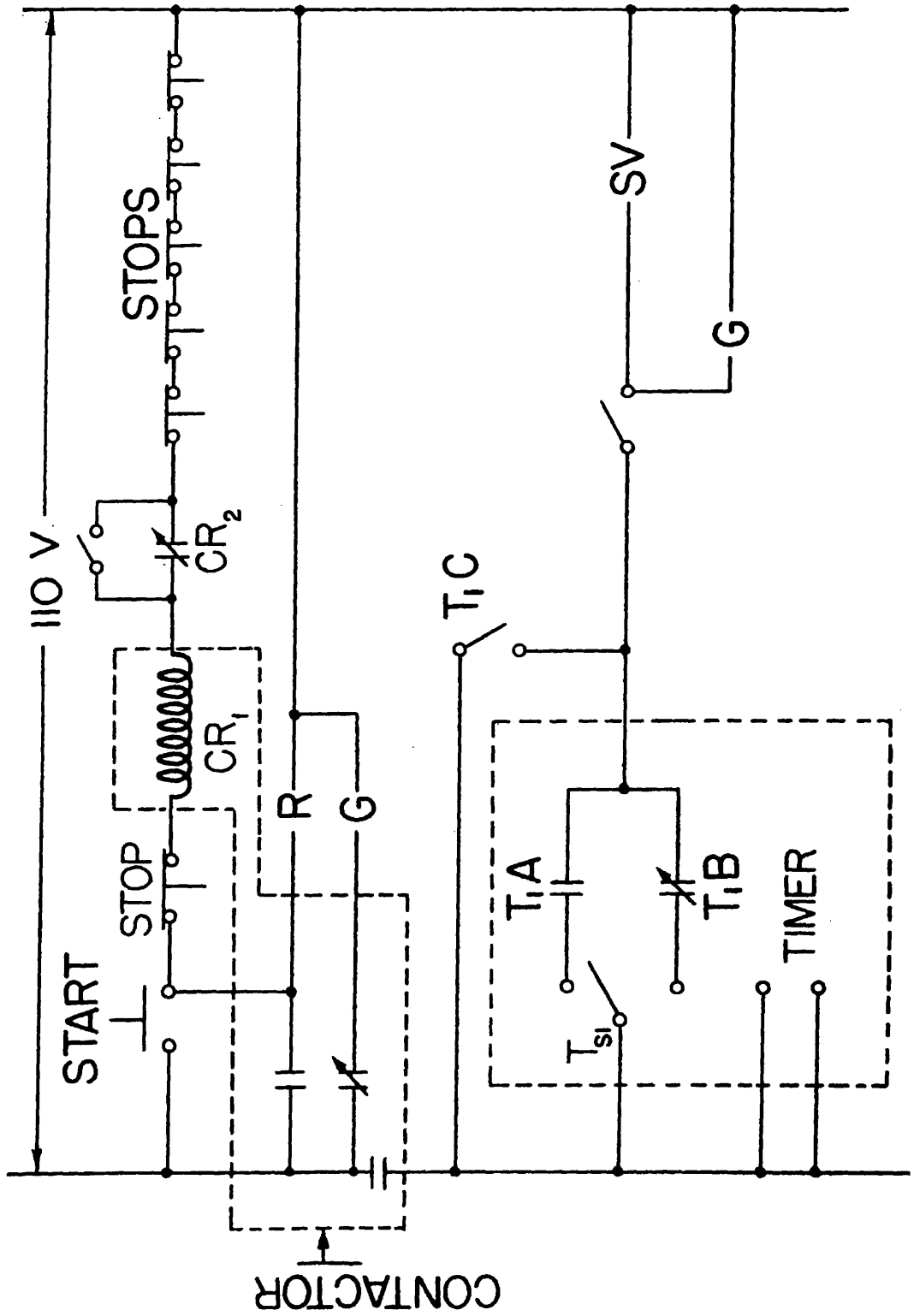
Engineering and operation Fig. 7



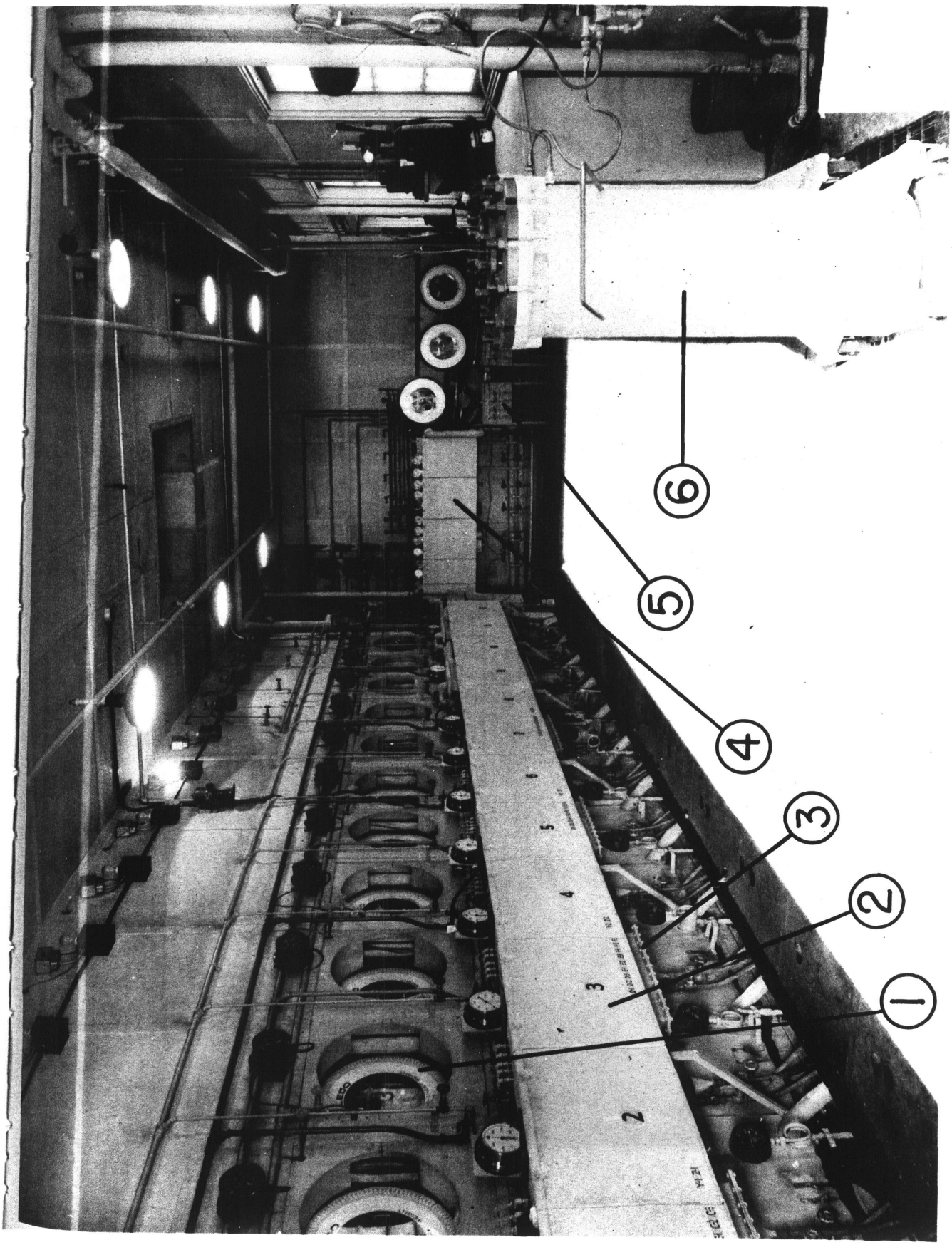
Engineering and Operation Fig. 8



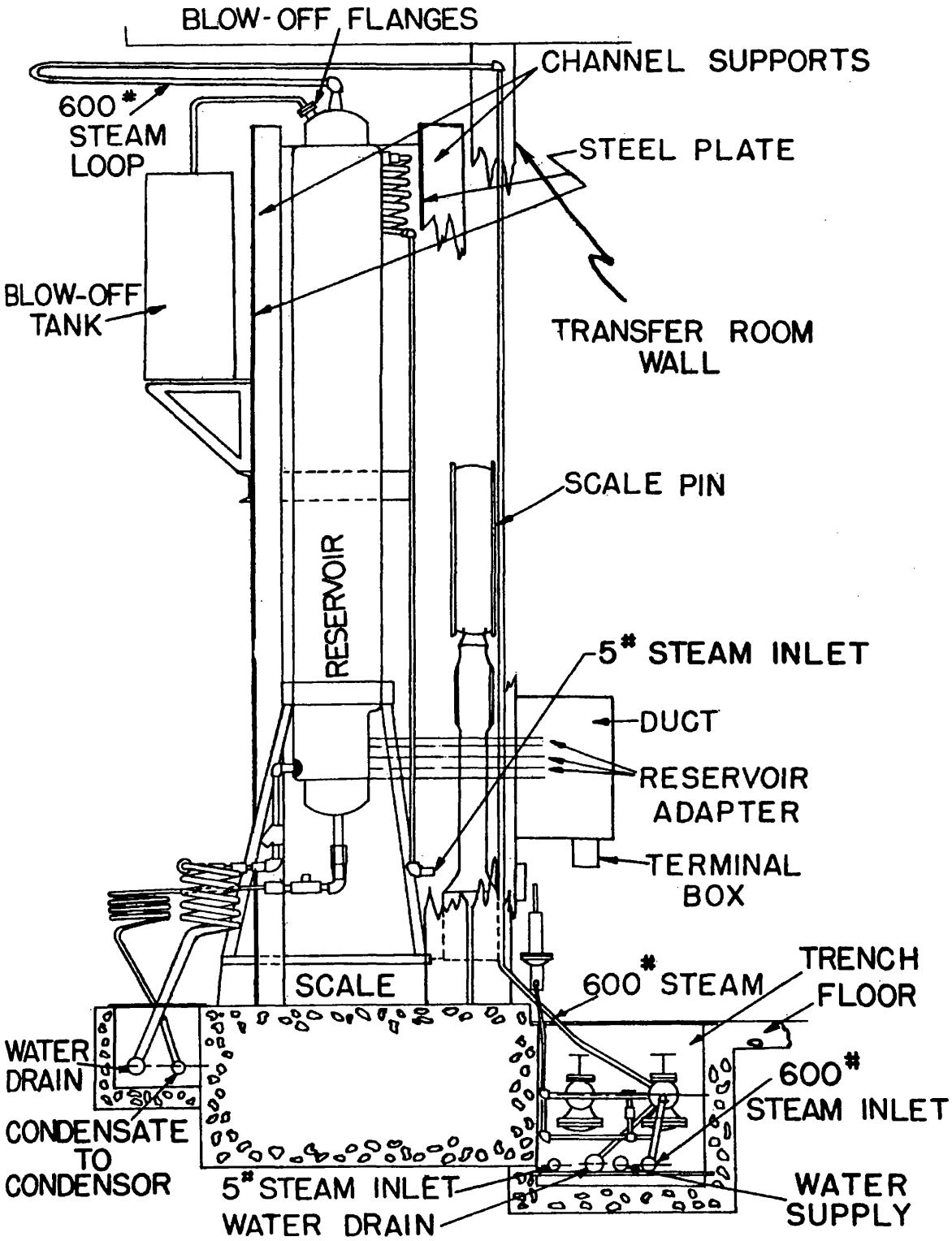
Engineering and Operation Fig.9



Engineering and Operation Fig 10



Engineering and Operation Fig 11



Engineering and Operation Fig. 12

THE PYRAMID

F.J. Gradishar

In principal, one could attain any desired degree of isotope separation from a column by sufficiently increasing its length. In practice, such a procedure is impractical for at least two reasons. The first is the obvious one of the awkwardness of such equipment. The second is more subtle and is best illustrated by the results of the following experiment:

Three columns were connected in series as shown in Fig. 1. Samples were removed from time to time and results were observed which are listed in Table I.

Table I

Sampling Point	Per cent Enrichment A	B	C	D
2.67 days	1.131	.998	.998	.864
6.75 days	1.239	.994	.993	.799
10.67 days	1.273	.984	.995	---

These figures show that only columns 1 and 3 are performing separative work. The remain column could have been out of operation as far as affecting the result during the initial days of operation. These results are in agreement with theoretical studies which show that if columns are to

be in series, a tapering number of columns should be employed for each stage.

To accomplish enhanced enrichment of U-235 beyond that produced by a single stage of optimum length columns, requires a system of cascading. A batchwise process in which the product from one bank or stage is collected in a reservoir and used as feed material for another leads to excessive handling. It is evident that this disadvantage is eliminated in a process in which the product from one stage is fed up to the next stage, and waste is fed downward. Such a system is approximated in our "pyramid", which deviates from the ideal in that the transportation of material is effected at frequent intervals rather than continuously.

The purpose of this investigation was to devise pyramids consisting of several stages and to demonstrate the practicability of operating them.

I. Physical Make-up

To test the feasibility of pyramiding in a practical set-up, two units totally rectifying in character were assembled, one a two-stage unit (designated pyramid 5) and the other a four-stage (designated pyramid 7). A set of 24 columns previously used as parallel rectifiers in production circuit 5 was incorporated into pyramid 5, and 47 columns comprising production circuits 7 and 8 were

combined into pyramid 7. The columns in circuit 5 had been tested while used as producers, and two obviously "bad" columns were replaced by new columns.

Data taken on circuit 5 during production over a period of a month gave the data shown in Table II. The concentration given is taken relative to ordinary uranium.

Table II

Av. Feed Conc.	Grams per col. per day	Prod. Conc.	Separation
.975	132.3	1.184	1.214
.975	156.9	1.163	1.193

The columns making up circuit 5 were somewhat variable in their characteristics. Values of Y ranged from 0.35 to 0.45. If one takes, for simplicity, an effective value of Y = 0.4, it later becomes possible to make a comparison of experimental results to theory. On the basis of Y = .4 and M = 1600 grams/col., the withdrawal data given in Table II are fitted by the value H = 34.8 grams/day. This leads to an average value of X = 115 days. The columns comprising pyramid 7 were never tested as such and must be considered as a combination of a random choice of columns.

During production, circuit 7 (23 columns at bottom of pyramid 7) averaged 2040 gms/day of product at 1.199.

Circuit 8 (24 columns at top of pyramid 7) produced 2508 gms/day at 1.226. The data are summarized in Table III.

Table III

	Av. Feed Conc.	Grams per col. per day	Prod. Conc.	Separation
Circuit 7	.975	88.7	1.199	1.230
Circuit 8	.975	104.5	1.226	1.257

The distribution of the columns into the respective stages followed a plan developed from theoretical considerations. This plan proposed the following ratios: two stage pyramid: 2.5 : 1; three stage: 4.5 : 2.5 : 1; four stage: 7 : 4.5 : 2.5 : 1; five stage: 10 : 7 : 4.5 : 2.5 : 1. Corresponding to these ratios, pyramid 5 consisted of 17 columns in the first stage and 7 columns in the second, while the 47 columns in the 4 stage pyramid 7 were proportioned 22 : 14 : 8 : 3, respectively.

The physical arrangements of the pyramids 5 and 7 are represented schematically in Fig. 2 and Fig. 3, respectively. In the arrangement shown, "circulation loops" powered by "convector pumps" connect the top of one stage to the bottom of the next stage for the purpose of interchanging material. Obviously the most efficient system would be one where continuous motion of material between adjacent stages occurs. However, this arrangment would

result in thermo-syphon effects between adjacent columns and adjacent stages, nullifying the separation process. As a consequence, the expedient of arresting alternate loops on alternate hours was adopted; that is, the number 1 circuits were "frozen" when the number 2 loops circulated and vice versa. A cam timer controlled the process by alternately actuating every hour the appropriate solenoid valves. Auxiliary valves permitting freeze water to be manually introduced at will into any link were installed in parallel with the automatic valves. Nickel lines of 1/16-inch I.D. interconnected various other units of the pyramid. Freezer stop-valves were installed to permit isolating any part of the circuits.

II. Operational Procedure

Since most of the columns had been in operation for some time previous to assembly in pyramids, it was necessary only to drain out the process fluid to ready them for pyramid assembly. In the case of new columns the accepted procedure for conditioning the material space was followed; i.e., a carbon tetrachloride degreasing wash, a water wash, blowing with heated nitorgen until the columns were dry, and a final flushing with gaseous fluorine. The system was ready for introduction of the process material, uranium hexafluoride, upon assembly of component links and testing the system for pressure tightness. When the system was

completely filled and all obstructions to normal operation (plugs) were removed, the system was placed under the control of the automatic cam timer which operated alternately every hour the number 1 and the number 2 circuits.

As with any exploratory experiment, numerous operational difficulties were encountered. Plugs or restrictions to flow of material in the relatively small interlink lines were the principal nuisance; detection and elimination were aggravated by the increased complexity of the system. For example, a plug in the fourth stage loop could be detected best by following the pressure changes from the storage chamber to the loop concerned. This involved leading the pressure-induced flow through selected channels of the first three stages to the stage in question and observing the point at which flow terminated as observed by the "flow meters". Care was exercised to reverse the flow in an identical manner in order not to produce any ultimate disturbance in the relative position of process fluid.

Excessive leaks in the steam system caused several shut-downs during the term of operation. Securing the system and resuming operation at a later date had a disturbing effect on the system as it caused "pitching", a boiling action which stirred up the material within the columns.

At such times the various stages were completely

isolated from one another. While there was some mixing within a stage, only a small amount of separative work was lost.

The method of removing product from the top stage of the pyramid was similar to that of the single stage circuits. At two hour intervals the line connecting the top of the last stage to the product receiver was cleared. A metering cylinder of appropriate size was allowed to fill. The contents of the metering cylinder was later automatically released into a product receiver. The reservoir was of such a large capacity compared to the system that it showed appreciable impoverishment of the light material only after a considerable length of time. In any case when the assay reached 0.67% U-235, the reservoir was replaced with fresh material. A group of columns set up as "stripper" could be utilized further to impoverish the waste were this considered desirable.

III. Results of Pyramid 5

The most successful studies were those pursued on pyramid 5. One run was made to follow the approach to equilibrium. Samples were taken from each stage at a representative point at regular intervals.

Two mishaps occurred to mar the continuity of the experiment. On the eighth day of the run, three pounds of UF_6 were lost by accident from the top of the first

stage. Shortly thereafter the circuit was secured due to lack of adequate steam supply. Upon resumption of operation, seven days passed before a parasitic circulation loop in the top stage was discovered and removed. Thereafter, smooth and uninterrupted operation was experienced until the end of the run.

Fig. 4 shows the approach to equilibrium curves. The solid curves represent the theoretical curves for a pyramid possessing columns all alike, Y = 0.4, X = 115, H = 34.8 gms/day. The dotted curves show the actual values observed. The dip in the upper curve is the result of the parasitic circulation.

The interruption caused by the parasitic convective loop affected mainly the seven columns comprising the top stage. The bottom stage continued performing separative work during the seven-day interval. The principal result of the interruptions, therefore, was the loss of the separative work of seven columns for seven days. In addition, the efficiency of the bottom seventeen columns suffered slightly during this period due to the fact that the concentration at the top of the first stage was higher than it should have been. Hence there was more back diffusion. The net effect of the interruption was, therefore, the loss of 2 - 3 days of separative work for the pyramid taken as a whole.

One other complication in interpretation of the experiment is the fact that the reservoir concentration diminished during the course of the run. The theoretical curve given is calculated on the basis of a constant reservoir concentration held at that of normal uranium. In view of these factors, it is felt that pyramid 5 performed in fairly good agreement with the theoretically expected behavior.

A run was made to determine the separation during product withdrawal. The result of this run is shown in Table IV.

Table IV

Product Rate	Av. Conc. bottom	Conc. top	Conc. top	Sep. Factor	Sep. Factor
	Stage 1	Stage 1	Stage 2	Stage 1	Stage 2
760 g/d	.975	1.19	1.56	1.220	1.31

These results represent a steady withdrawal over a period of 25 days. The result is the average of five samples taken after steady state conditions had been established. The overall separation factor of the final product is 1.60 against an expected value of 1.54 obtained on the basis that all columns are alike and possess M = 1600, Y = .4, X = 115 and H = 34.8 gms/day.

IV. Results of Pyramid 7

The performance curve of pyramid 7, a four stage 47 column unit, is given in Fig. 5. Operation was sluggish for the first few weeks with numerous restrictions and plugs in the 1/8-inch link lines. For 32 days the system was allowed to build up toward equilibrium before the product withdrawal mechanism was set in operation. A run of 40 days established the terminal concentrations in the various stages and the product at this rate. These values are listed in Table V.

Table V

Bottom Stage 1	Bottom Stage 2	Bottom Stage 3	Bottom Stage 4	Top Stage 4	Withdrawal Rate
.975	1.155	1.354	1.523	1.80	536.1 gms/day

These results show the following separations for each stage:

Table VI

Stage 1	Stage 2	Stage 3	Stage 4
1.182	1.172	1.117	1.182

From the table it is clear that stage 3 performed very poorly. This was probably due to one or more very poor columns in the stage. However, the remaining stages show a behavior not much different from theoretical. Taking an effective Y = .4, the results from single stage operation

of circuit 8 gave: H = 36.0 gms/day, X = 111 days. From these figures one predicts for the top stage of the pyramid a separation factor of 1.18.

From our studies of pyramid behavior the following observations are made:

1. The pyramid was easy to operate automatically once proper fluid flow was obtained.
2. Principal difficulties were plugs which it was possible to eliminate.
3. It was found especially important that "freezer" mechanism for alternate circulation be completely dependable.
4. A program of elimination of poor performing columns was found to be essential.
5. With uniform columns it was possible to approach the theoretically predicted performance.

CAPTIONS

Pyramid

Figure 1

Three columns connected in series. Samples were removed from points A, B, C, D with results shown in Table I.

Figure 2

Schematic process fluid flow diagram of two stage pyramid.

Figure 3

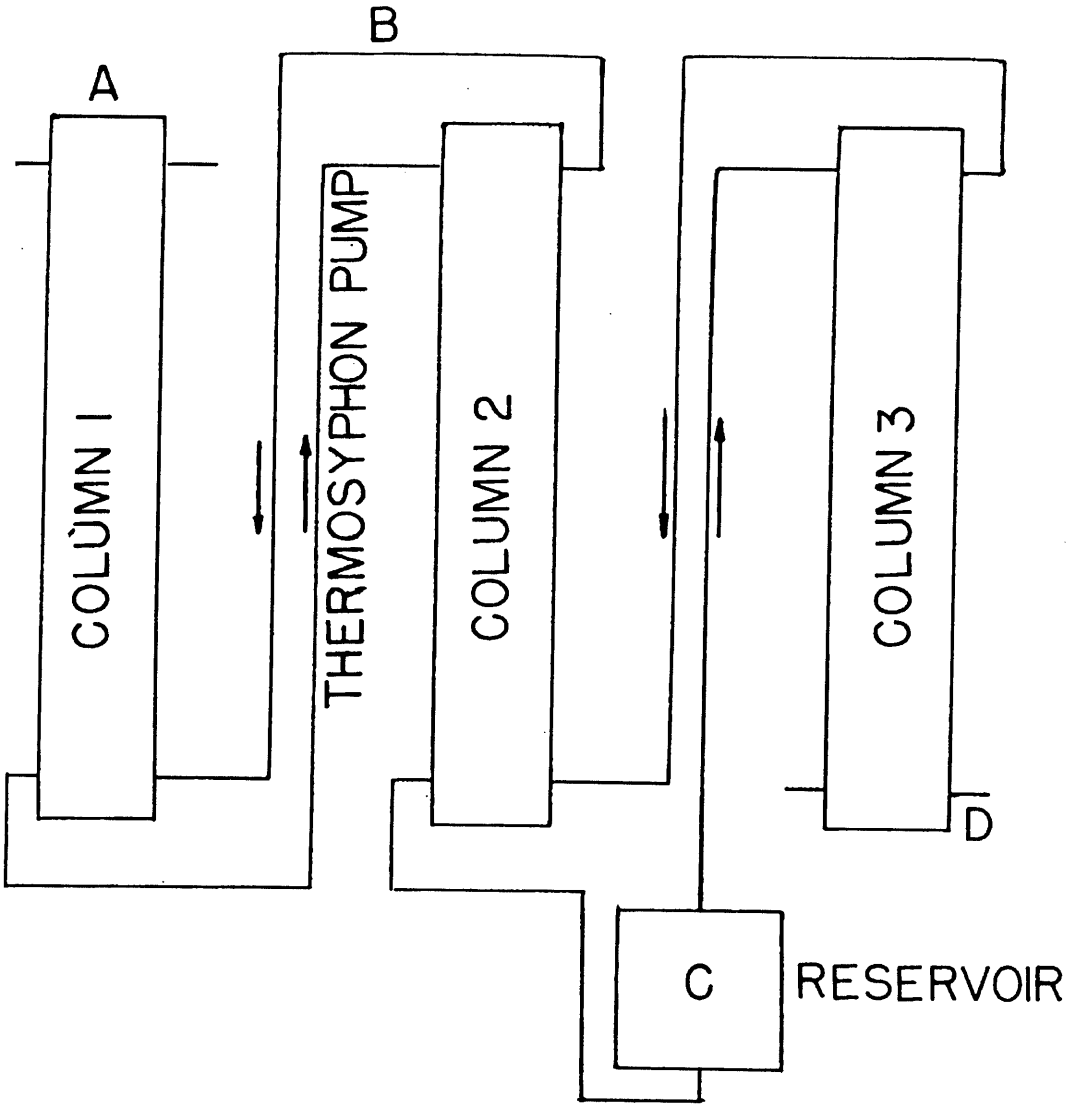
Schematic process fluid flow diagram of four stage pyramid.

Figure 4

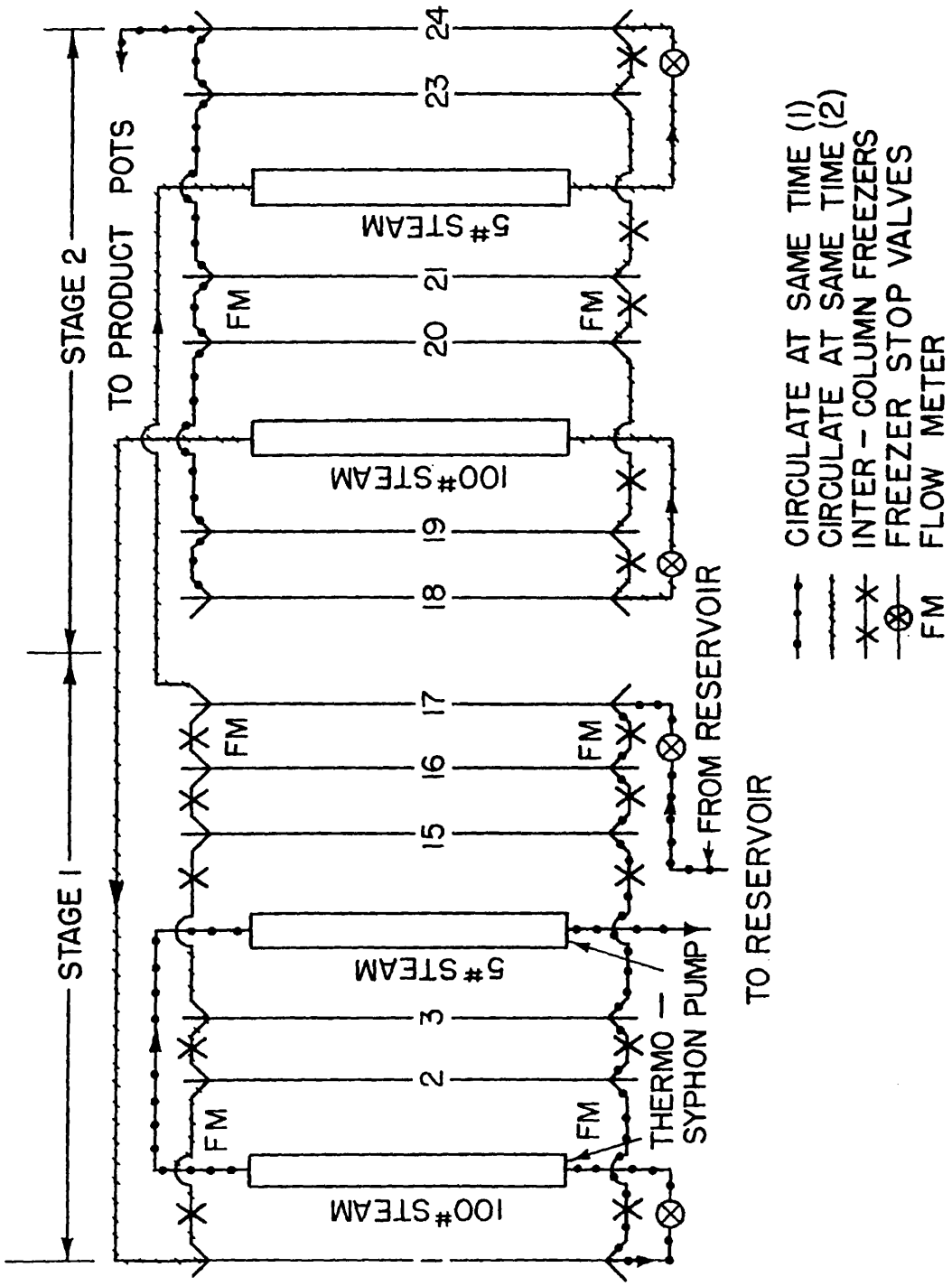
Approach to equilibrium of a two stage rectifying pyramid. The dip beginning at 8 days was due to a parasitic convective loop.

Figure 5

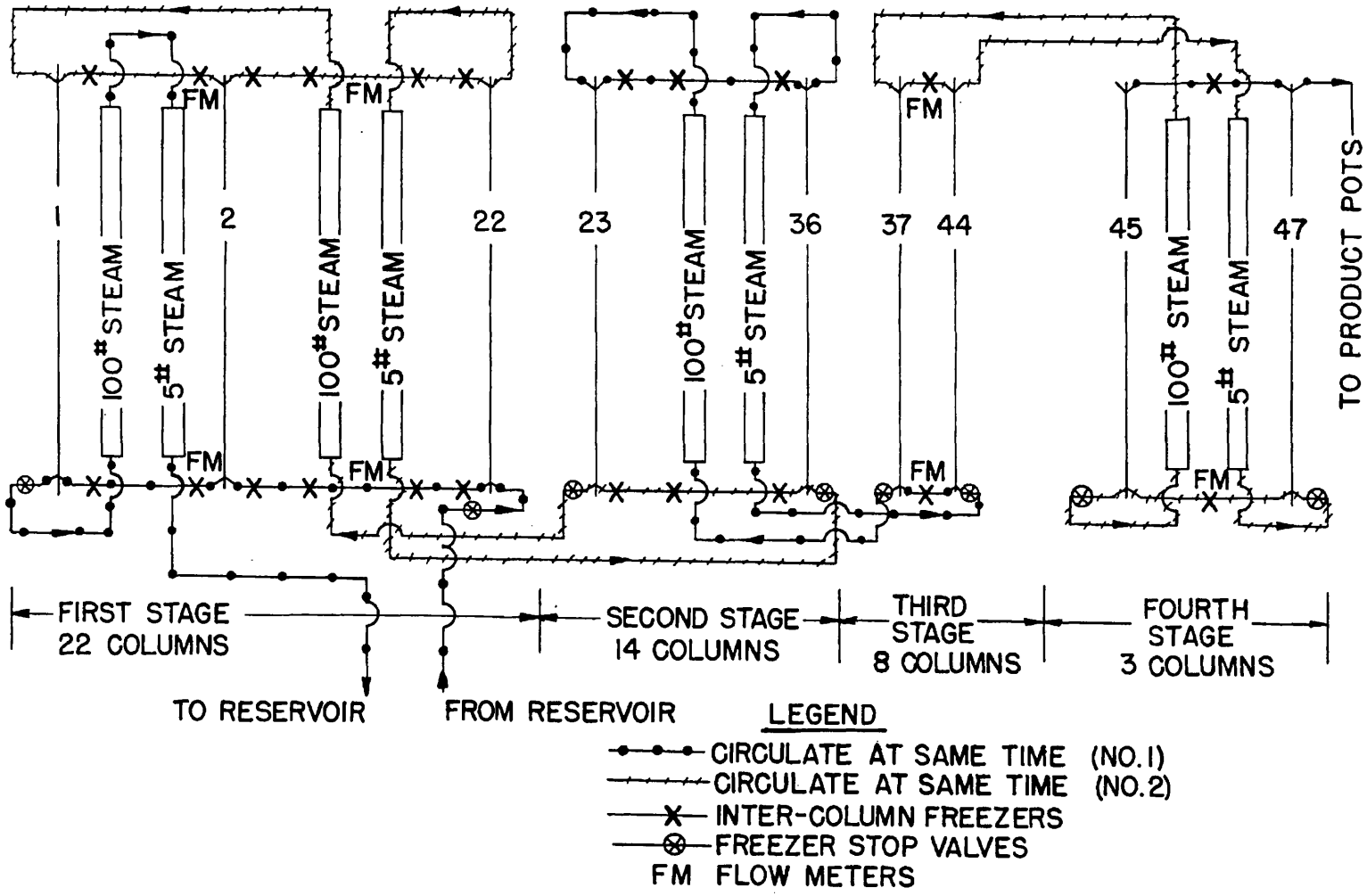
Performance curve for a four stage pyramid. No product was removed during the first 32 days. Product was removed at the rate of 536.1 gms/day during the remainder of the run.



The Pyramid Fig. 1



The Prrn. mid Fig. 2


FM
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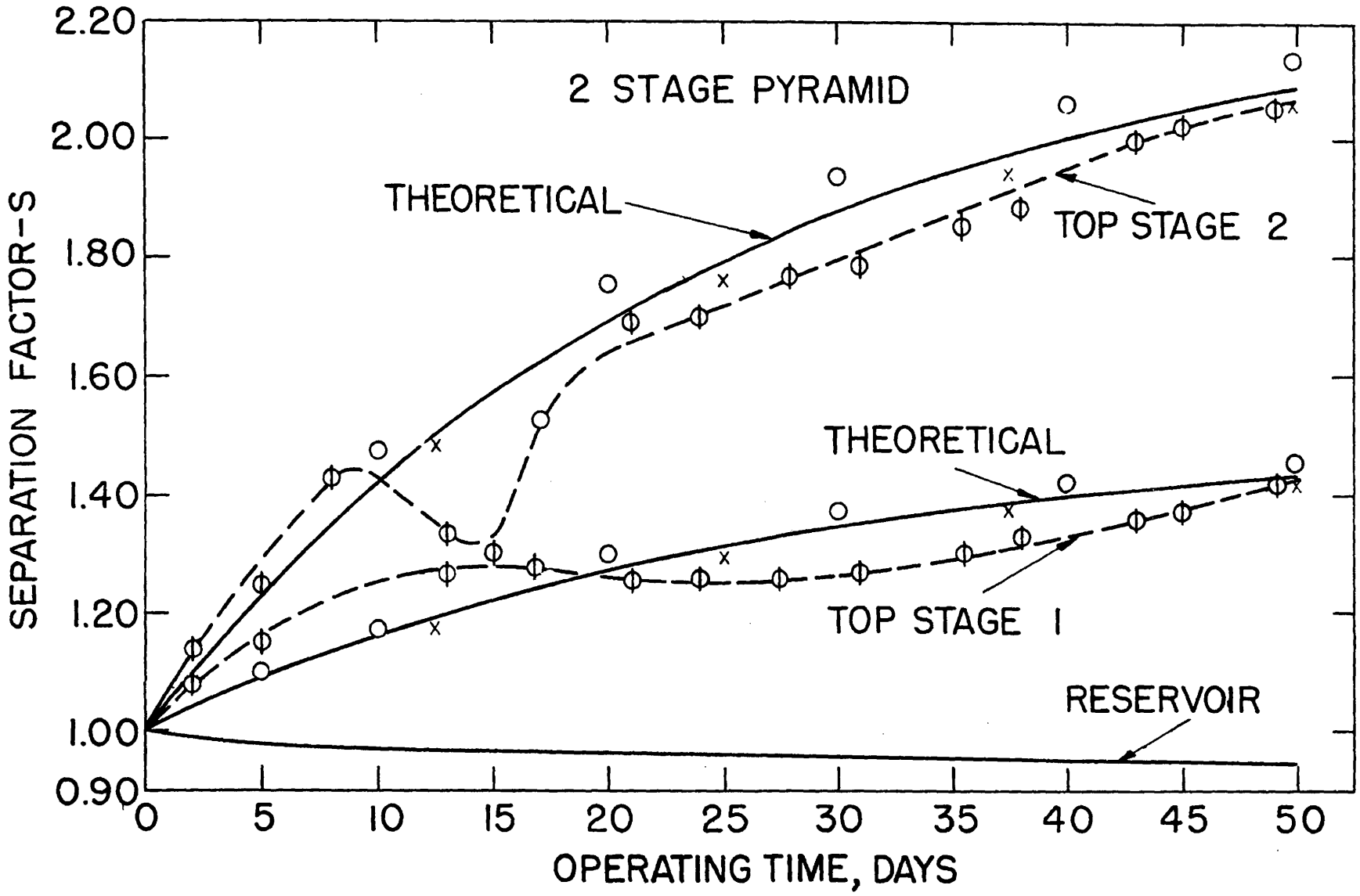
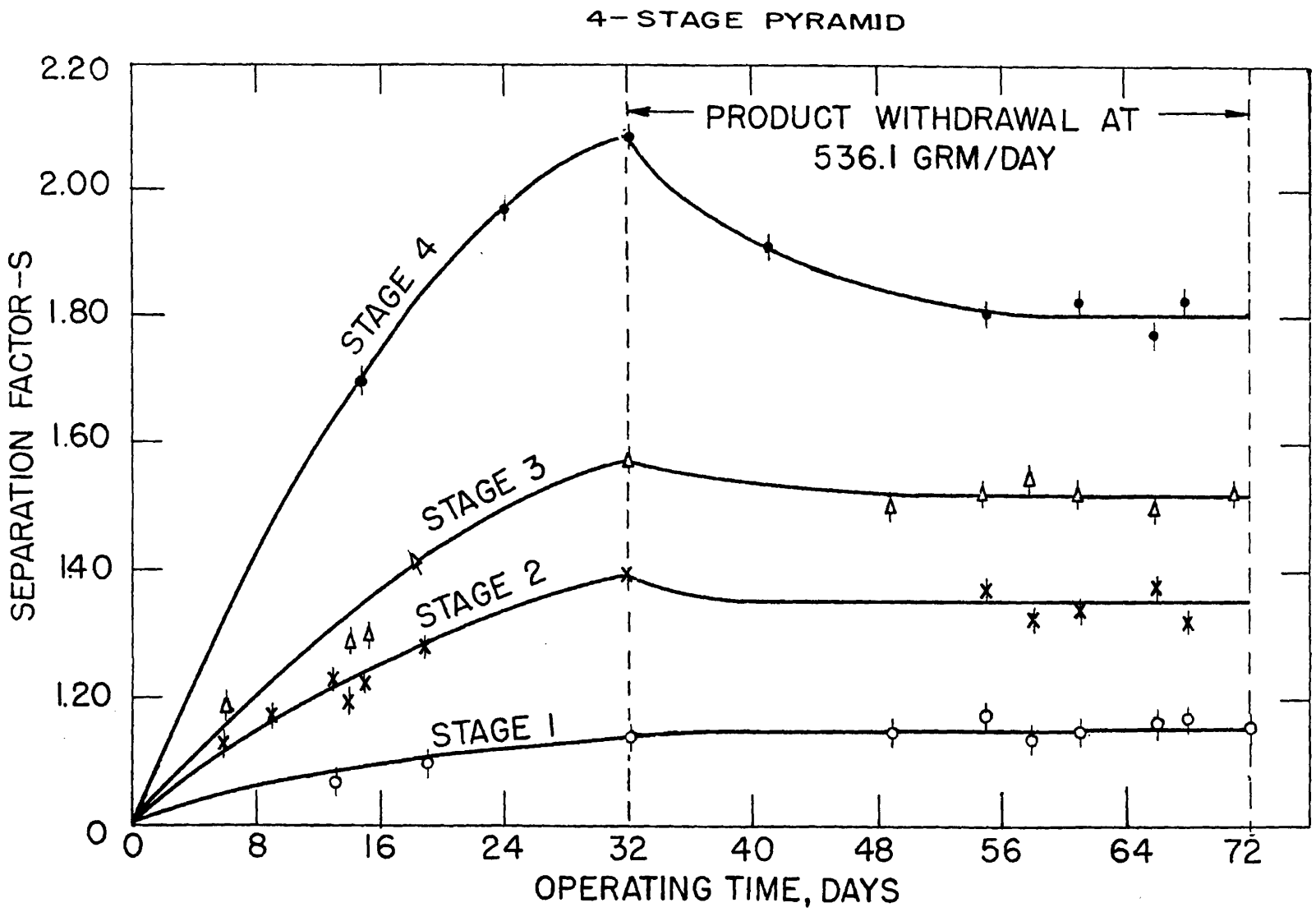
37
44
45
47
100# STEAM
5# STEAM
100# STEAM
5# STEAM
100# STEAM
5# STEAM
100# STEAM
5# STEAM
TO PRODUCT POTS
FIRST STAGE
22 COLUMNS
SECOND STAGE
14 COLUMNS
THIRD
STAGE
8 COLUMNS
FOURTH
STAGE
3 COLUMNS
TO RESERVOIR
FROM RESERVOIR
LEGEND
CIRCULATE AT SAME TIME (NO. 1)
CIRCULATE AT SAME TIME (NO. 2)
INTER-COLUMN FREEZERS
FREEZER STOP VALVES
FM FLOW METERS

Fig. 10



The Pyramid Fig. 4



The Pyramid Fig. 5

CONTRIBUTIONS BY THE TECHNICAL DIVISION, FERCLEVE CORPORATION

The Ferclave Corporation Technical Division was directed by B.F. Dodge. Under him as project directors were O.E. Dwyer and C.A. Todaro with Forrest Western head of the Mass Spectrograph Analytical Laboratory. Technical effort was directed principally toward process improvement and a considerable degree of success along that line was attained. More than two score projects were undertaken, many of which were completed. Others were only partially finished at the time of plant shut-down. A two-volume final report edited by O.E. Dwyer issued October 1945 served to summarize the work of the Technical Division. Abstracts of the reports on the various projects are reproduced here. They have been edited to a slight extent to conform to the notation of this volume.

Summaries of All Projects Undertaken by the Technical Division

Project No. 1 - Individual Column Performance.

by: John D. Hoffman
Mark D. Snyder

All columns in the S-50 plant have been tested by withdrawing 100 grams per column per day for seven days and averaging the assay of the product withdrawn for the last four days.

Columns were classified by a letter or number, and a summary of the per cent in the various categories is as follows:

Class	Assay Range at 100 g.c.d.	Per Cent in this Range
A	Above 1.32	1.4
B	1.29 to 1.32	3.1
C	1.26 to 1.29	7.8
D	1.23 to 1.26	20.2
E	1.20 to 1.23	35.1
I	1.17 to 1.20	24.8
II	1.14 to 1.17	4.7
III	1.11 to 1.14	2.6
IV	1.08 to 1.11	0.9
V	Below - 12	0.4

Thus the search for poor columns revealed a great deal of information concerning columns in the plant. Based on the results obtained, the plant, as a whole, was capable of averaging about 130 gms/col/day at "par" (1.20) assay using 1000 lbs. steam. However, it was believed that the data gave slightly low results (about 10%), and the average maximum production was believed to be nearer 145 gms/col/day at par assay.

Project No. 2 - Comparison of Individual Column Performance Using Continuous Project Withdrawal and the Intermittent Method.

by: Daniel Frishman

In developing the method of product removal by top circulation (see Project No. 12), it became necessary to compare product removal by top circulation to the intermittent method on an individual column. In this fashion, it would be easier to control all variables and a decision as to which was the better method could be more easily reached.

Two columns were selected on a rack that were similar in performance; each column had product removed by one of the above methods. After the first run, the two methods were interchanged on the two columns and the tests repeated. Check runs were made on two columns on another rack.

With continuous top and bottom circulation (which was feasible on an individual column, but not on a circuit) product removal by top circulation gave approximately the same results as product removal by the intermittent method with continuous bottom circulation. Later it was hoped a comparison of the two methods could be made, limiting top and/or bottom circulation time. This was begun in order to determine just exactly which factors contributed to the lower production rates obtained on entire circuits that operated with product removal by top circulation.

Project No. 3 - Measurement of the Rate of Flow of Process Fluid.

by: J.D. Hoffman
M.D. Snyder

A method of measuring the rate of flow of process fluid was needed to determine whether circulation rates across the bottom of the circuits were sufficient for good plant operation. Since no instrument was available (except the "Flow Indicator"), it was necessary to develop one. The Thermal or Thomas type meter was adopted to this type of fluid with an accuracy of 5 per cent for flow rates ranging from 3 to 15 lbs. per hour. Later, by varying the heating unit of the thermal meter, flow rates from 15 to 50 pounds per hour could be measured, but its accuracy has not yet been determined.

Flow rates throughout the plant were measured periodically and found to average about 7 lbs. per hour. It was also found that a convector heated by 1000 p.s.i. steam increased the rate of flow 2.2 times over the 145 p.s.i. convector. Three ordinary convectors (145 p.s.i.) in series approximately tripled the flow rate in a circuit, showing that the convector loops offered very little resistance to flow.

Project No. 4 - Equilibrium Studies on Isolated Columns.

by: William B. Daly, Jr.

The original purpose of this project was to obtain

data for theoretical studies. Later, it was attempted to find out whether the same performance characteristics would be obtained for a column whether it was isolated at both ends or only isolated on the top. Also, a few exceptionally good columns were tested by the rate-of-rise method to see how well the predicted product rates based on such data checked with actual product rates.

Rate-of-rise-to-equilibrium data were obtained on fifteen columns. They can be divided into the following categories: four exceptionally good columns, seven newly-installed columns, and four columns picked at random in the plant. It was found that the seven new columns, on the average, performed better than the supposedly exceptional ones giving data which indicated an average production rate well above 200 grams per day at par assay. On the other hand, the columns which were picked at random gave predicted product rates roughly only about half as great. This may mean that the newly-installed columns are better constructed and/or better conditioned than the original columns. Of course, the number of columns tested was not sufficient to definitely conclude that the newly-installed columns are very much better than the originally-installed columns.

Only two columns were tested by both the isolated-top-only and isolated-both-ends methods and the agreement between the

two methods is not good. However, the issue is clouded due to certain operating difficulties at the time of testing.

These were three columns for which product rate data were available. In each of the three cases the actual rates and those predicted from rate-of-rise data were in excellent agreement.

Project No. 5 - Production Rate vs. Assay Studies on Whole Circuits, Using Intermittent Method of Product Withdrawal.

by: O.E. Dwyer

This project was begun last February for the purpose of determining the assay-production rate relationship for S-50, based upon normally operating circuits composed of 20-25 columns. A final report was issued on April 25, 1945 as Report No. M-2354 by O.E. Dwyer. A supplement to this report was issued in the Monthly Report for June 1945 under this project. The relation between product assay and production rate, to give a few figures, was found to be as follows:

Product Assay	Production Rate grams/column/day
1.25	55
1.23	74
1.21	96
1.20	108
1.19	120
1.17	148
1.15	178
1.13	210

The above assay values are based upon an average bottom assay of 0.975.

It should be mentioned that due to equipment, process, and personnel improvements during the last few months of operation, the above figures do not accurately represent plant performance at the time of shut-down. For example, it is estimated that for the month of August the entire plant, including all abnormal operation, produced at a rate of about 110 gms/col/day based on par (or 1.20) assay. This figure is based on data supplied by the Material Accounting Office.

Project No. 6 - Cross-Check on Shipment Samples between M.S. and "Counting Method" Laboratories at Ferroleve and Carbide and Carbon, Using Special "Double-end" Sample Tubes.

by: O.E. Dwyer

This project was conducted in March 1945 for the purpose of checking the accuracy of the Ferroleve Laboratories when, in certain instances, they showed unsatisfactory agreement on shipment samples from the same container. However, this cross-check showed very satisfactory agreement between the two Ferroleve Laboratories and also with those of the Carbide and Carbon Corporation. A report by O.E. Dwyer was issued on this project on March 28, 1945. It was Report No. 1 of the Technical Division.

Project No. 7 - Storage Chamber Depletion Studies

Investigation was largely confined to a comparison of the material balance versus the laboratory assay method of determining when a storage chamber contents should be changed. Since the assay of the feed material dropped only from 1.00 to 0.95 during a complete cycle, and since laboratory assays were estimated to be no better than 0.005, it was concluded that the material balance method was preferred for predicting when to change storage chambers. It was found that, within the limits of their accuracy, laboratory assays checked fairly well with calculated values.

Project No. 8 - Sampling Methods

The purpose of this project was to determine the most satisfactory method for taking samples -- primarily from columns. The following three sampling methods were compared by withdrawing samples from isolated columns which were initially filled throughout with material of uniform concentration:

1. "Regular" Method. This was the method commonly used in the plant; namely, adapter was frozen, sample tube was attached, adapter was thawed to fill tube, and then the adapter was frozen again to remove the tube.

2. "Freeze-and-Thaw" Method. This method was the same as that described above, except the adapter was frozen and thawed twice before the adapter was finally frozen for attaching the tube.

3. "Duplex Tube" Method. For this method a removable double-end sample tube was contained in a small convector loop attached to the two opposite adapters on the column. Circulation of material through the loop would make the material in the sample tube, at any moment, the same as that in the end of the column.

The results of the investigation showed that there were no significant differences between the three different methods of sampling. Column samples taken in the "regular" manner were considered to be quite satisfactory for both plant control and experimental work.

Project No. 9 - Preparation of a Technical Operating Manual.

by: Ralph T. Overman

Preliminary draft of an operating manual was prepared and a few copies printed in June 1945. This manual was quite comprehensive and required about three months for its preparation. Due to its urgent need for training purposes, a few preliminary copies were issued, and further revisions were to be made in the future.

Project No. 10 - Assembly of PVT Data and Thermal Data on Process Fluid in Form for Convenient Use.

by: O.E. Dwyer

In February 1945 the Division undertook the assembly of the most reliable physical, thermal, and chemical properties of the process material. Ralph Overman summarized these data in a report dated March 20, 1945, which can be found in the files of the Technical Division under Project No. 10.

Project No. 11 - Stress Corrosion of Nickel Welds.

by: H. Tilp

Six nickel vessels were built by the Youngstown Welding and Engineering Company. Each of these vessels was to contain six welded test specimens for stress corrosion tests of the welds in the presence of UF_6. Ten other control samples were to be run under identical conditions, but without exposure to process material. Since this project was not completed, best evidence is to be found in the reservoirs themselves. After nearly one year of exposure to process material, no reservoir has failed at the welds and no welds have been found which showed appreciable corrosion.

Project No. 12 - Development of Method of Product Removal by Top Circulation.

by: Daniel Frishman

Product removal by the top circulation method was

inaugurated by Malcolm Dole in February 1945. The advantages expected were: (1) simplification of product removal, (2) reduction in material handling, and (3) possible improvement in rack performance. The first two of these advantages were soon realized on an experimental unit and this method of product removal was subsequently installed on a total of four racks. However, by May 1945 the technical division recommended discontinuance of the method of product removal. This was based on the fact that the above four racks consistently produced about 20% less than the average plant rack having the intermittent-monorail product removal method.

Project No. 13 - Plotting Daily and Accumulative Production Rates vs. Time for Six Selected Racks.

This project was abandoned shortly after it was begun. The purpose was to obtain a running record of plant performance for certain "good", "average", and "poor" racks in order to follow plant progress. It was found later that the Material Accounting Office and laboratory together were doing essentially the same thing, so in order to avoid duplication of effort this project was discontinued before a significant amount of data were obtained.

Project No. 14 - Pressure Measurements.

by: R. Van Winkle
W.W. Binger

For some time, erratic and non-uniform column performance

was thought to be due to steam pressure and condensate level fluctuations. Study of steam and material pressures would reveal the magnitude of those variations.

Steam and material pressure recorders were installed at various convenient places on Rack No. 1 and Transfer Room No. 1. After two months of continuous recordings, it was found that the largest variations in material pressures were caused by product withdrawal and poor control of steam pressure on the storage chambers. It was also found that rack steam pressure variations, for all practical purposes, did not exist.

Project No. 15 - Variations in Top Assay Among Columns in a Circuit and Effect of Product Removal on It.

The final report for this project was written in the May report. However, a little additional information was included in the June report. For "Product Withdrawal Technique" see Project 39-II.

In general, product withdrawal from the individual columns by the monorail method was found to be fairly uniform, provided no obstructions were present in the top inter-column connectors.

Project No. 16 - Service Test of Fittings for Use on Process Fluid.

by: Harry Tilp

This project was originally set up for the purpose of

following plant tests on a certain type of Parker appliance flared tubing, and also a needle valve supplied by the same firm. The project was soon expanded to include all new gadgets and devices used on process fluid systems. Three new types of inter-column connectors, an individual column product meter, and use of high pressure pots for product removal were developed on this project.

When the needle valve supplied by Parker applicance failed to operate properly, many changes were made in its design.

For details and drawings of the items developed, see the June, July and August Ferclave reports.

Project No. 17 - Study of Accuracy of Assay Results from the Two Laboratories.

by: May Farber

In order to obtain a rigorous comparison of the precision of the assay results from the two laboratories, a large number of samples of the same material were sent to each laboratory for analysis. The samples were disguised so that the laboratory personnel were not aware of the special nature of the samples. Two sets of samples were submitted.

In the first set, Laboratory 1 (mass spectrograph) reported an average assay of 1.180 for 70 determinations with an average deviation of 0.012, whereas Laboratory 2 (alpha counting) reported an average assay of 1.180 for 41 determinations with an average deviation of 0.006. These results

for Laboratory 2 are on a two-film plating basis. On a one-film basis, the average assay would have been 1.181 with an average deviation of 0.008. The one-film assay results were based on the first film data of the two-film runs.

In the second set, Laboratory 1 reported an average assay of 1.190 for 99 samples with an average deviation of 0.015. The corresponding figures for Laboratory 2 were 1.185, 103, and 0.006, respectively, for two-film results; and 1.185, 103, and 0.008 for single-film results.

On the basis of the above results, it is seen that the precision of Laboratory 2 results are considered quite satisfactory for plant control purposes. It was the practice to submit the great majority of Technical Division samples and shipment samples to Laboratory 2. The cross-check results showed that the averaged assays from the two laboratories were in good agreement. A report covering this study is given in the appendix.

For a comparison of the precision of the assay results from the two laboratories during the past months, as indicated by shipment assays, see past monthly reports on this project.

Project No. 18 - Production of a Standard of Product for Comparison of Assays of the Ferroleve Laboratories and Outside Laboratories.

This project was started in April 1945 for the purpose of comparing the accuracy of the Ferroleve laboratories with

certain outside laboratories. For a summary of the test results obtained, see the Summary of this project in the monthly report for July 1945. In general, the agreement between all Mass Spectrograph and Alpha Counting laboratories, including those at Ferolevo, was very good.

Project No. 19-I - Test of Uniformity of Columns in a Circuit.

by: L. Davidson
C.J. Raseman

This project was initiated last March when the question of non-uniformity of columns first arose. Forty-four columns in two different circuits were tested by the rate-of-rise method, and the results showed that there were very great differences in the performance characteristics of individual columns. The detailed procedures used and the test results were presented in the Technical Division Report No. 6 by L. Davidson and Ensign C.J. Raseman issued on April 28, 1945, as Report No. M-2356 of the U.S.E.D. series.

This project, showing that there were great differences in columns, opened the way for much later work regarding the production capacities of individual columns and the effect of this factor on plant output.

Project No. 19-II - Correlation Between Annular Spacing and Column Performance.

by: Walter J. Clossey
William R. Casto

When it was known that there were great differences

in the quality of individual columns, this project was undertaken for the purpose of determining the extent to which column differences were due to variation in size of annular spacing. A large number of columns were measured for their average annular spacings. For details of the methods employed and the accuracy of the test results, see Project No. 21.

A total of 38 columns, on which average annular measurements were available, were eventually tested by the rate-of-rise method. Although the results are not absolutely clear-cut due to some uncertainty about the accuracy of both the rate-of-rise and the column measurement data, nevertheless the results indicated that, in general, there were no significant correlation between observed column performance and the average annular spacing measurements which were obtained. For details, see report on this project in the appendix.

Project No. 19-III - Effect of Material Pressure on Column Performance Using 450 lb. Steam Pressure.

by: William B. Daly, Jr.

The purpose of this project was to determine the best material pressure at which it would be feasible to operate these racks using 450 lb. steam. Rate-of-rise data were obtained on five average columns in each of four circuits at material pressures ranging from 750 to 1900 lbs/sq.in.

The data cannot be considered as fully complete, but in general it can be concluded that the production rate increases with material pressure. This increase is of the order of 7 gms/col/day for each 100 lbs. increase in process fluid pressure.

Project No. 19-IV - Rate-of-Rise Tests on Reclaimed and Reconditioned Columns.

by: Walter J. Clossey
William R. Casto

When reclaimed and reconditioned columns were placed back in service, they were tested for their performance characteristics by the rate-of-rise method. This work was covered under this project. The results show that reclaimed columns test essentially the same as run-of-the-mill columns.

Project No. 20 - Effect of Scale Formation on the Copper Tube on the Performance of a Column.

The purpose of this project was to determine whether there was appreciable scale formation occurring on the water side of the copper tubes in the columns. Such scale formation would necessarily reduce the rate of heat transfer through the copper tube and consequently adversely affect the efficiency of the columns.

During the three months period from 1 April to 1 July 1945, steam consumption and cooling water measurements on Rack 21 showed that there was no significant build-up of

scale on the copper tubes. This was confirmed by thermocouple measurements of the copper wall and water temperatures on two individual columns. It was concluded that water fouling of the copper tubes in S-50 columns was no matter for concern.

Project No. 21 - Measurement of Annular Space in Columns.

This project has been divided into three parts.

Part A - Measurement of Annulus by Nitrogen Flow and Volumetric Methods; Testing of Columns for Flaws.

by: John D. Hoffman
Mark D. Snyder
Ralph A. Hill

A need for measuring the average annulus of a column had been of importance since the first columns were built. If a correlation could be found between average annulus and column performance, new columns to be installed could be screened and the poor ones discarded.

A calibrated orifice meter was supplied by the Naval Research Laboratory. By measuring the rate of flow of nitrogen through the column annulus under known conditions, the average annular spacing could be determined. The technique was quite poor at the beginning, but after a few months, fairly good results were obtained. The average maximum deviation for triplicate runs on 36 columns for the month of August was 1.0%.

Each column tested by the above procedure was checked by the volumetric method. This consisted of filling the

column with a liquid, such as carbon tetrachloride, from a graduated burette and calculating the average annulus from the volume necessary to fill the column. The average deviation for duplicate runs by this method was about 0.2%.

On the average, the two methods agreed to within 2%. Exact agreement was not to be expected in all cases, since an accentric annulus would give high results by the nitrogen flow method. Also, a constriction would give low results by the nitrogen flow method. It was also found that a hot column (steam and circulating water on) had an annulus about 80% that of a cold column (65°F). The average annulus on 36 cold columns measured by the nitrogen flow method in August ranged from 12.48×10^{-3} inches to 14.55 to 10^{-3} inches; the volume method gave results ranging from 12.98 to 13.86×10^{-3} inches on the same columns.

Before any measurements were made on a column, the columns were tested for mechanical flaws. About 10% were rejected because of defects, but many of these columns were repaired and put into service.

<u>Part B</u> - Measurement of Annulus Variation by the Increment Method.

by: John D. Hoffman
William S. Farmer
Mark D. Snyder

When no satisfactory relationship was found between column performance and average annulus (see Project 19-II),

a means of measuring variations in annulus at various heights of a column was desired. The first attempt was made by injecting a definite quantity (5 cc) of a liquid from a burette with nitrogen pressure behind it, and then measuring the hydrostatic head produced on an inclined manometer. The average annulus for the small increment (5 cc) was then calculated. In this fashion, approximately 100 increments per column would probably determine the position and size of restrictions or bulges.

Part C - The Effect of Conditioning on Column Performance.

by: John D. Hoffman
Mark D. Snyder

There has been some evidence in the past pointing to the fact that plugs or partial plugs existed part way up the columns. Obviously this would be detrimental to column performance. This project was, therefore, begun to determine whether reconditioning poor columns that had been in operation would improve their performance.

Three poor columns and one good column were chosen, and the normal production test (assay at 100 g.c.d.) run on them. The columns were then drained, conditioned thoroughly, and the production test was to be repeated. However, the shut-down interrupted the last test and no conclusions could be drawn.

Project No. 22 - Examination of Steam and Condensate for Foreign Material, Particularly Hydrogen and Soluble Salts.

by: J.H. Goldstein

With the aid of the standard A.S.T.M. sampling nozzles and non-ferrous sampling lines, it was determined that the actual hydrogen content of S-50 condensate returns in the K-25 power plant was of the same order as the values obtained in the S-50 plant. Peripheral sampling using iron sampling lines, on the other hand, yielded much higher values, a result to be ascribed to inhomogeneity or to localized corrosion in the long iron pipes. For a quantitative comparison of the two methods and the respective ranges of values obtained, the Appendix to the August 1945 report of Project No. 22 should be consulted.

Preliminary trials of a micro degassing technique on S-50 condensate gave extremely low values, approximately 5 liters of hydrogen per million pounds of condensate. The method shows considerable promise, but its efficiency and the validity of the results so obtained are as yet unproved.

Project No. 23 - Theoretical Investigations.

by: O.E. Dwyer

This project was set up to include all miscellaneous calculations and theoretical investigations related to S-50 operations. Reports on several of these sub-projects can be found in past monthly reports. Calculations on certain

minor topics can be found in the Technical Division files under this project. A separate report entitled "Application of Theory to S-50 Plant Practice" by O.E. Dwyer was issued as Report No. 10 of the Technical Division on September 5, 1945. This report was No. 2360 in the U.S.E.D. series.

Project No. 24 - Freeze-Off Studies.

by: W.W. Binger
R. Van Winkle

During June and July 1945 a number of freeze-off coils were designed, built, and tested. All of these coils were inadequate due to the fact that purging too quickly with steam would fracture the nickel lines. A satisfactory design was found which consisted of two concentric pipes with a nickel coil for the process fluid in the inner pipe. The process fluid was "frozen" by running water into the inner pipe; steam was allowed to flow through the outer jacket for "thawing" the coil. The effect produced by the steam in the outer jacket was to heat the residual water in the inner jacket slow enough to prevent the nickel coil from rupturing.

Project No. 25 - Effect of Circulation Rate on the Performance of a Circuit.

by: J.D. Hoffman
M.D. Snyder

The purpose of the project was to obtain actual plant

data in an attempt to determine the effect of circulation rate on circuit performance. On the basis of the data obtained, it was concluded that a circulation rate of about 7 lbs. per hour for a 25-column circuit was sufficient for good plant operation. This rate is based upon a total circulation time of about 18-20 hours per day. For rates above 7 lbs. per hour, the data showed no significant improvement in circuit performance. For further information on this project, see monthly reports for June and July 1945. For a theoretical treatment of the effect of circulation rate on circuit performance, see "Application of Theory to S-50 Plant Practice" Report No. 2360 U.S.E.D. series by O.D. Dwyer issued on September 5, 1945.

Project No. 26 - Tests of Columns of Non-Standard Design.

No work was ever done on this project. This was, in part, due to the fact that a contract with Mehring and Hanson Company for construction of 75 columns of larger than standard size was cancelled.

Project No. 27 - Identification and Removal of Plug-Forming Materials.

by: Bernard Selikson

Stoppage of circulation across the bottom of the circuits due to "plugs" in the system has been one of the most serious operating problems at S-50, particularly during "starting-up" periods. However, due to a number of factors,

the situation showed considerable improvement during the final months of operation. Chief among these factors were believed to be: (1) improved skill on the part of the operators when opening or making connections to a circulation system, (2) more thorough conditioning, (3) gradual elimination of plug-forming materials from the system by removal of plugged columns, inter-column connectors, and link lines, and (4) removal of plug-forming materials from the circulation systems by means of traps.

The original objectives of this project were: (1) to identify the plug-forming materials in order to eliminate them at their source if possible, and (2) to seek effective means of removing such material from the plant circulation systems.

Analyses of sediment collected from several circulation statems indicated that it consisted most of copper and nickel chips and the green insoluble uranium tetrfluoride. There was probably a small amount of the hydrolyzed material present as well as traces of metallic fluorides. The metal chips resulted from column fabrication, while the tetrafluoride compound is the result of reduction reactions with process fluid. Installation of sediment traps seemed to improve the circulation on these circuits where they were tried. These traps hold about a pound of material and, when in the system for about 2-3 weeks, yielded an amount of sediment ranging from 0.1 to 0.5 grams.

Although sediment traps do remove some plug-forming material, it is felt that the most effective means of solving the problem of "plugs" is to prevent the material from forming initially. For the most part, this can be accomplished by proper conditioning techniques and intelligent operation of the racks. However, as a safety precaution the use of sediment traps on all circuits is recommended.

Project No. 28 - Examination of Broken Columns.

by: Roy W. Greenlee

Broken columns which were taken out of operation and removed from the plant were sent to the Continental Gin Company for dismantling and inspection. A study was made of the causes of failures. It was found that the nickel tube never failed; but the copper tube either split, bulged, or caused a constriction a short distance from one or both ends of a copper sleeve joint.

A Rockwell "F" hardness test on several pieces of copper from a column which had failed revealed that the copper tube was annealed at the joints. Yield strength tests verified that annealing of the joints had occurred, which caused weakening of copper and consequent failure.

Project No. 29-I - Analysis of Production Data on Apparently High-Producing Circuits.

by: J.C. Blackwood

The Operations Division observed that production was considerably increased when the columns in a rack were divided into six circuits instead of four. This meant that there were about 15-17 operating columns in a circuit instead of 22-25. This project consisted of an analysis of the plant production data both before and after conversion of a number of racks to six circuits. In all, 77 short circuits were studied. The data showed that on reducing the size of the circuits from 22-25 to 15-17, column production was increased about 30%. It was believed that this improvement was due primarily to more uniform withdrawal of product from the individual columns in the case of the shorter circuits.

Project No. 29-II - Study of Twelve-Column Circuits.

by: W.R. Casto

When the results of Project 29-I showed that there was considerable improvement in production when the columns in a rack were split up into six circuits instead of four, it was proposed to determine what further improvement could be realized if a rack were split up into eight circuits. This was the purpose of this project. Unfortunately, due to rack shut-downs there were not sufficient data obtained to draw definite conclusions. However, on the basis of preliminary results, it was concluded that there was only slight improvement in productive capacity when the number

of milking circuits in a rack was increased from six to eight.

Project No. 30 - Production Rate vs. Assay on Circuits Composed of Selected Columns.

by: R. Van Winkle

The purpose of this project was to see what production rate could be realized if the plant contained all "good" columns. Accordingly, all the columns in a typical circuit were individually tested and arbitrarily re-grouped into two circuits of "good" and "poor" columns, respectively. There were 9 columns in the "good" circuit and 13 columns in the "poor" circuit. The results showed that, whereas the original circuit was capable of producing at the rate of 89 gms/col/day at a par assay, the "good" circuit could produce at a rate of 170 and the "poor" circuit could only produce at the rate of about 30, operating conditions remaining the same. These figures showed that with selected columns, plant production could be very greatly increased for the same steam consumption.

Project No. 31 - Two-Stage Operation for Increased Production.

by: Daniel Frishman

When product removal by top circulation began to show signs of producing less than the intermittent-monorail milking method (see Project No. 12), it was felt that a two-stage system with top-circulation method of product

removal would show increased production rate.

This was thought to be true since the pots were enhanced quickly in the low assay range and very slowly as the assay of the pot approached par. Furthermore, a study of the assay vs. production curve (see April report, Project No. 29, Figure 3) showed that for 20% enhancement, production for an average column was 103 g.c.d.; at 10% enhancement, production of 250 g.c.d. could be expected. If two columns were operated in series, an increase in production rate might be obtained.

The two-stage system of product removal was tried on one side of Rack No. 9, with 28 columns in the first stage and 12 columns in the second stage. The production rate remained the same as the one-stage system with product removal by top circulation, namely, 90 g.c.d. at par assay. The second stage was then changed to monorail milking and 99 g.c.d. at par were obtained as an average for one month. This was a 10% improvement and 6% less than was expected on the basis of the individual column tests (see Project No. 1). During August the plant gave approximately 10% less production than that predicted by the individual column capacities.

In August, the ratio of columns in each stage was changed to 20 columns in each stage. Essentially the same results were obtained.

In view of the fact that many operational difficulties

were experienced, such as inter-column circulation, some hope had been expressed for this type of operation. If both systems (single-stage and two-stage) give equal performance, the two-stage system has several operational advantages that might make a definite contribution. These are: (1) greater simplification of product removal, (2) lower labor requirements, and (3) better adaptability to automatic control.

Project No. 32 - Testing Columns by Separating Systems Other than Uranium Hexafluoride.

by: L. Silver
S.J. Green

The purpose of this project was to determine whether there is a correlation between the performance of a column when separating process fluid and when separating the constituents of some other two-component system. If such a correlation did exist, it would be possible to test columns before they were installed in the plant, possibly at the point of manufacture.

Attempts to separate oxygen and nitrogen in air were unsuccessful due to disappearance of oxygen -- apparently as a result of some oxidation reaction. However, very good separation was obtained with a 40-60 (by volume) helium-carbon dioxide mixture. A considerable number of runs were made using this system, in an attempt to determine optimum operating pressure and also to develop satisfactory sampling

and analytical techniques. This gaseous system was very sensitive to pressure changes, so much so that the drop in pressure caused by the removal of samples materially influenced the results. Separation factors of He-CO_2 as high as 100 were obtained.

The separative capacities of a number of columns were determined with the helium-CO_2 system, but the project was terminated before these same columns could be tested with UF_6. Consequently, the question as to whether or not there is a correlation between the separative capacities of a column when using UF_6 and when using a mixture of carbon dioxide and helium still remains unanswered. Since the helium-carbon dioxide system did show considerable differences in columns, there is reason to believe that some correlation may exist between the performance of a particular column when using the two separative systems.

Project No. 33 - Gas Formation from Process Material.

by: W.J. Clossey

At one time, there were frequent instances of accidentally filling the collecting containers during product removal. This meant that the freezer valve on the removal system failed to form a plug either after the previous withdrawal or during the present cycle as the product was flowing from the metering capsule into the collecting capsule. It was believed that failure to form a plug in the freeze-off coil, in many cases, was due to the presence of

non-condensable gases in the product. The original purpose of this project was to determine whether this was so, and if so, to determine the source of the gases, and to make recommendations for remedying the difficulty.

Considerable evidence was found to indicate that these difficulties were often caused by the presence of non-condensible gases in the product removal system. The work of Project No. 24 showed that such accidents could be prevented with the use of freeze-off coil long enough to form a plug while UF_6 was flowing through it. As a result, 8-foot freeze-off coils made with 1/16" I.D. nickel tubing were installed on the plant circuits. With this type of coil replacing the original No. 2 freeze-off coil, the trouble was practically eliminated.

Analyses of non-condensible gas collected from several plant systems showed that it was mainly oxygen and nitrogen with lesser amounts of hydrogen fluoride. The oxygen and nitrogen were present in essentially the same ratio as they exist in air, indicating that these constituents came from the air. It is believed that the two sources of hydrogen fluoride were the original UF_6 and the reaction of water with this substance. The amount of hydrogen fluoride found in S-50 product and in fluid taken from the plant systems was found to be no greater than that in fresh feed, namely, about 0.005 to 0.010%.

Project No. 34 - Investigation of the Methods of Transferring Process Material.

by: W.W. Binger
R. Van Winkle

Due to the non-uniformity of the methods of emptying and refilling reservoirs used in the plant, the Technical Division was asked in May 1945 to suggest the best means of transferring process material. The main points covered were: (1) safety of operators, (2) transfer rate, (3) simplicity of operation, and (4) amount of labor required. After many modifications, a highly satisfactory method was proposed in the July 1945 report. This was tried in August with great success. However, the shut-down of the S-50 project prevented its installation in all transfer rooms.

Project No. 35 - Effect of Short and Long Non-Circulation Periods on Circuit Performance.

by: Leonard Silver

This project was undertaken for the purpose of determining the effect of various length periods of non-circulation uniformity distributed throughout the day on the production capacity of a circuit. The experimental results indicated that the production capacity of a circuit was not appreciably affected by a total non-circulation time of up to 15 hours per day, where the maximum length of a single non-circulation period is no greater than five hours. Apparently, any less circulation time adversely affected capacity; for

example, three six-hour periods of non-circulation per day resulted in a 20-25% decrease in production capacity. With the exception of the circulation changes, all other operating conditions were normal, and all tests were made on the same circuit.

Project No. 36 - Sample Requirements at S-50 in Relation to Laboratories' Capacities.

by: O.E. Dwyer

At one time, the number of samples sent to the laboratories was considerably in excess of their capacities. Consequently, this study was undertaken to see what changes could be made to remedy the situation. As a result, a new procedure for dumping product capsules was recommended which required assay results on only 60% of the capsules. This change, combined with the fact that during the summer months the plant operated at only partial capacity, eased the load on the laboratories so that they could conveniently take care of the sample needs of both the Production and Technical Divisions.

Project No. 37 - Effect of Cooling Water Temperature on Column Performance.

In June, warmer river water temperatures and larger requirements of river water by the Carbide and Carbon powerhouse made the pumping capacity a limiting factor in supplying the 21 racks with sufficient cooling water. By increasing the circulating water temperature in the unit, it was

believed the pumping requirements would be reduced to the point where all 21 units could be operated.

This project was proposed to determine the effect of increasing the circulating water temperature on column performance. However, about a week later, the steam supply became the limiting factor controlling the number of racks which could be operated. Hence, this project was no longer of much concern and was discontinued before any data were obtained.

Project No. 38 - Material Balance.

by: J.C. Blackwood
C.A. Todaro

For many months, the Material Accounting Section had reported a considerable loss of material that could not be accounted for. At times, this amounted to as much as 3000 lbs. per month. A great deal of time had been spent in the expectation of locating part of this material in the condensate of circulating water, to no avail.

In June and July, a determined effort was made to determine the material lost in the Material Ship and Plant. Many discrepancies were found in scales, inventories, and failure to empty containers. By the end of July, the total unaccounted material losses dropped to 100 lbs. for the month. The project was then discontinued, since the losses were believed to be, for the most part, "book" losses.

Project 39-I - Varying Product Removal Time with Different Restrictor Coils.

by: William B. Daly, Jr.

The purpose of this project was to see whether the productivity of 25-column circuits could be increased by product removal through restrictor coils which would give increased time of withdrawal. It was thought that slow removal of product would give more uniform withdrawal from the individual columns. Unfortunately, the data obtained on this project were not sufficient to warrant a definite conclusion, but they indicate that no appreciable improvement in circuit performance was obtained by increasing the withdrawal time.

Project No. 39-II - Improvement of Product Removal Technique.

by: J.D. Hoffman
M.D. Snyder

Automatic and semi-automatic product withdrawal were installed on the operating racks in the early days of the S-50 plant. These were installed for the purpose of removing product from an entire circuit (25 columns), and eliminating the laborious individual removal. During the succeeding months, this project was concerned with improving the automatic systems and developing methods for improving its operating technique.

Project No. 40 - Best Operating Conditions with 450 Pound Steam.

by: Daniel Frishman

In order more reliably to establish the effect of UF_6 pressure on production rate when using 450 lbs. steam, a rate-of-rise study on columns using 450 p.s.i. steam pressures was begun. This study was made under Project No. 19-III. The most efficient material pressure at which to operate was to be determined by the rate-of-rise method.

Project No. 40 was discontinued the first week of August until new problems arose concerning operation with 450 lbs. steam.

It has been definitely established that production increased with increase in material pressure using 450 p.s.i. steam. The data showed a minimum production rate existing at about 1200 p.s.i. material pressure, but this was not considered to be real.

Project No. 41 - Column Construction at Continental Gin Company.

by: Roy W. Greenlee

Examination of defective columns taken from the S-50 plant had shown that silver soldering the copper joints had resulted in annealing and critically weakening the copper tube in the region of the joints (see Project No. 28). Soldering by induction heating, cooling the copper tube with a stream of water up to the end of the sleeve

proved more satisfactory, but annealing of the joint area itself still occurred. An attempt was then made to construct a joint by rolling out swaged ends of copper tubes into a grooved monel sleeve by use of a boiler tube type rolling tool. This proved very satisfactory, and was immediately applied to the end joint, in which case the nickel stub was welded into the monel sleeve prior to rolling the copper tube.

Neither of these improved sleeve designs was used in the actual column construction which followed, the center joint being eliminated by procurement of a single-piece 46' copper tubing, and the end joint (with the stub welded into the monel sleeve) being superseded by a special double rolled joint. This joint, used in the fabrication of about fifteen columns before curtailment of the construction program, consisted of a long monel tube drilled and grooved in one end to accommodate the rolling of the copper tube joint, the remainder of the sleeve length having the same inside diameter as the copper tube. After assembling the concentric tubes, the nickel tube was rolled out into grooves in the last 3" of the monel sleeve, completing the annulus closure. The tits were welded directly to the sleeve, which extended 7-1/2" outside the stuffing box at both ends of the column.

Individual tests on samples of all the joints described have shown that their yield strength is equivalent to that

of the copper tube, and hydrostatic pressures greater than 5000 p.s.i. occasion no failures.

A special 8' test column with a rolled type joint tested under normal plant operating conditions gave satisfactory results for one week. At the end of the time, raising the material pressure suddenly to 7000 p.s.i. had no effect on the copper tubing or the joints at either end. (See Project No. 41-A).

Since the construction of these new columns no longer included the troublesome center joint of the copper tube, and has substituted considerable work-hardening for the annealing which previously weakened the copper tube near the end joints, it can be seen that the major causes for column failure have apparently been eliminated.

Project No. 42 - Comparison of Actual Production Rates with those Predicted from Rate-of-Rise Data.

by: William B. Daly, Jr.

There are two ways of determining the production capacity of a particular column: (1) by actually removing product from the column at different rates and determining the product assay corresponding to these rates, and (2) by determining rate-of-rise data and then calculating the production rate for a particular product assay by means of theoretical considerations. The rate-of-rise method has the advantage of being much quicker but has the disadvantage of not yielding product during the period of test.

Of the 16 columns tested, all but two showed fairly good agreement between the actual and predicted separation factors for a given product rate. There were two columns which, on the basis of their rate-of-rise data, should have produced about 180 grams per day each at a separation factor of 1.30. Actually, however, at the same milking rate of 180 grams per day, they showed separation factors of only 1.26 and 1.27 respectively.

There may be some reason why the predicted and actual milking rates for exceptionally good columns do not agree at very high milking rates. Perhaps the removal of so much material has a disturbing influence on the operation of the column. However, in general, it can be said that there is fairly good agreement between actual column capacity and that predicted from rate-of-rise data.

Project No. 43 - Investigation of Solenoid Valve Performance.

by: R. Van Winkle
W.W. Binger

Operations had been thoroughly discussed during the past few months with the use of solenoid valves. A number of failures had been reported, and these failures kept multiplying as time went on. Hence, this project was undertaken to find the reasons for solenoid valve failures, and to recommend remedial measures. Three solenoid valves were operated at an accelerated rate of 190 times per 24 hours. (The valvesused were reconditioned ones.) They

operated for 22 consecutive days without failure, and were then shut down and inspected.

It was found that the rubber gasket was still in good condition, but the lever mechanism showed signs of corrosion which started to make its action sluggish. It was suggested that a maintenance procedure be developed for keeping the valve mechanism in good operating condition.

Project 44 - Investigation of the Reasons for Differences in the Performance of Individual Columns.

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Great differences in the performance of supposedly identical columns has been found in Project 1, 4 and 19. This difference became of great practical importance, since all "good" columns could at least double and conceivably a good column should be controlled in the fabrication or conditioning of columns. Hence, this project was undertaken in the hope of determining those factors. The project was, however, interrupted by the shut-down before any significant information was obtained.

Project No. 45 - Effect of Frequency of Product Withdrawal on Column Performance.

Very recently a number of columns were found throughout the S-50 plant that should, according to predictions from

the column study of Project No. 1 and also from Projects No. 19-II and No. 42 produce considerably more than had been obtained from them. For instance, Circuit No. 1 of Rack No. 5 was predicted to produce 350-390 gms/col/day. The maximum amount produced had been 167 g.c.d. at par for the month of June. Other columns, from rate-of-rise study, were predicted to produce as high as 490 gms/col/day, but only actually produced 250 gms/col/day.

This project was started late in August 1945 to determine the effect of frequency of withdrawal on production for these high producing columns. It was conceivable that columns as capable as those mentioned above would not produce the expected amount due to disturbances in the column caused by withdrawal. By removing product from a few columns (having similar characteristics) at various frequencies but at the same rate in gms/col/day, it was hoped that the effect of disturbances could be observed.

Miscellaneous

During August 1945, considerable progress was made in the development of a gear pump for transfer of process fluid. If a suitable pump could be developed it would have very definite advantages over the thermal convector loop circulation system.

This special pump was being built by the Research Engineering Corporation of New Haven, Connecticut, when,

due to cessation of activities, Ferolevo terminated its contract. This pump had an external magnetic drive with a variable drive motor, which was to be furnished by the General Electric Company, Schenectady, New York. Beryllium copper and monel were used as the materials of construction, the latter being used for all moving parts. As an exception, the magnetic drive rotor had 0.005 inches of nickel plating directly on steel. The pumping unit and magnetic drive were submerged in an oil bath. This was to provide means of supplying heat with the use of electric heaters and also to lubricate the external moving parts.

THEORETICAL ASPECTS

CHAPTER I. THE COLUMN

1. Processes in Column

As was pointed out in the preliminary discussion, the functioning of a liquid thermal diffusion column involves three basic processes: convection, thermal diffusion, and ordinary diffusion. The liquid near the hot wall is carried upward by convection, while that near the cold wall is carried downward. At the same time the process of thermal diffusion takes place, involving generally a transfer of molecules of the light isotope from the cold to the hot wall. The combination of these two processes results in the accumulation of the lighter isotope near the top of the column, while the heavier molecules collect near the bottom. However, ordinary diffusion also sets in as soon as any appreciable concentration gradient develops and acts so as to reduce such a gradient. The first theoretical treatment of the liquid thermal diffusion column was given by Debye[1]. However, his calculation applies only to the case of small temperature differences. We shall use here what is essentially the method of Furry, Jones and Onsager[2], which they developed for gases, but which with some modifications can be applied to liquids.

The behavior of each of these processes can be described by writing the expression for the corresponding mass current density of the light isotope. Let c denote the concentration of the light constituent, i.e., its molecular fraction.

Since the two isotopes under consideration are so nearly equal in atomic weight, this can also be taken as the mass fraction. Let ρ be the density and $\underset{\sim}{v}$ the velocity of the liquid due to convection. It will be assumed, as is usually the case in practice, that the flow of the liquid is lamellar in character, so that the velocity is a smoothly varying function of position. If we denote by i_H the hydrodynamical mass current density, i.e., the rate of flow per unit cross-section of the light component associated with the convection, then we have

$$i_H = \rho c \underline{v} \tag{1}$$

In the case of ordinary diffusion, the corresponding current density associated with the transfer of light molecules by diffusion is given by

$$i_D = -\rho D \nabla c \tag{2}$$

where the ordinary diffusion coefficient $\underline{D}$ will be a function of the temperature but will be very nearly independent of the concentration $\underline{c}$ because of the great similarity in the properties of the two isotopes.

The current density associated with thermal diffusion i_T can be written

$$i_T = F \nabla T \tag{3}$$

where T is the temperature, and F is a coefficient depending in general both on the temperature and the concentration. Since there is no thermal diffusion if either species of molecule is present alone, one can assume F to contain a factor $c(1 - c)$. We shall write therefore

$$i_T = Dq\, c(1 - c)\, \nabla T \tag{4}$$

where D is the ordinary diffusion coefficient previously defined, and q is what will be referred to as the thermal diffusion coefficient.

One can expect that q will depend on T and that it will be, in general, a slowly varying function of the concentrations. In fact, since we are dealing with isotopes, that is, with molecules of very similar physical properties, it is reasonable to believe that q will be very nearly independent of the concentration c. This is borne out by the fact that such is the case for thermal diffusion in gases[3]. We shall therefore assume that q in Eq.(4) is a function only of the temperature. The nature of this function is not known at present. In the case of gases it has been found to be of the form α/T, where T is the absolute temperature and α is nearly a constant; this is the function used by Furry, Jones and Onsager[2]. For liquids, very rough theoretical arguments[4] have led to either α/T or α/T^2, depending on the model assumed.

If all three processes take place simultaneously, then the resultant light-constituent current density is given by

$$\underline{i} = i_H + i_T + i_D \tag{5}$$

The equation of continuity, representing the condition for the conservation of the light constituent is then

$$\frac{\partial}{\partial t} (\rho c) = - \nabla \cdot \underset{\sim}{i} \tag{6}$$

2. Differential Equation of the Column

A column will be considered as consisting of two vertical coaxial tubes, spaced a distance a apart, each of length L, between which the working liquid is contained in the annular space of mean circumference b. The inner surface of the outer tube, the "cold wall" is maintained at a low temperature T_1 by means of some cooling agent (water). The outer surface of the inner tube, the "hot wall" is maintained at a high temperature T_2 by some heating agent in this tube (steam).

Since in practice the spacing a is very small compared to the mean circumference b, the curvature of the walls can be neglected, so that one can treat them as plane surfaces. Furthermore, because the spacing a is extremely small compared to the length L, one can neglect "end effects" at the ends of the column where the temperature

distributions vary from that prevailing elsewhere and where the convection streams curve back to reverse their directions.

In order to obtain the differential equation for the column, we shall begin by investigating first the process of convection, since this will not be affected appreciably by the other two processes, because of the similarity of the two species of molecules. Let us suppose that we have the liquid between two parallel vertical walls a distance a apart, of breadth b and height L. Let us take a cartesian coordinate system with the X-axis at right angles to the plates and the Z-axis vertical so that in the working space $o \leqslant x \leqslant a$, $o \leqslant z \leqslant L$. For the present we shall consider the ideal case in which none of the quantities to be discussed varies in the direction of the third (Y) coordinate. Let us take the cold wall at $x = 0$ as having the temperature T_1 and the hot wall at $x = a$ as having the temperature T_2, so that $\Delta T = T_2 - T_1 > 0$.

Let p be the pressure and g the acceleration of gravity. Furthermore, let ρ and μ denote, respectively, the density and viscosity of the liquid; these will in general be functions of the temperature T, but will be practically independent of the concentration c because of the similarity of the molecules being separated. For the present we shall assume that the temperature and hence these quantities are independent of the coordinate z.

Following Furry, Jones and Onsager[2], we calculate the convection velocity by solving the hydrodynamical equation for the steady flow of a viscous fluid in the form

$$\nabla \cdot (\mu \nabla \underset{\sim}{v}) = \nabla p - \rho \underset{\sim}{g}, \tag{7}$$

where $\underset{\sim}{v}$, the velocity vector, is taken to have only a component in the z-direction, but is independent of z, and $\underset{\sim}{g}$ is the gravitational acceleration vector with the magnitude $\underline{g}$ and direction (-z). From Eq. (7) we get for the x-component

$$\frac{\partial p}{\partial x} = 0 \tag{8}$$

so that $p = p(z)$, and for the z-component

$$\frac{d}{dx} \left(\mu \frac{dv}{dx} \right) = \frac{dp}{dz} + \rho g. \tag{9}$$

Since in (9) all terms except $\frac{dp}{dz}$ depend only on x, we see that

$$\frac{dp}{dz} = B \tag{10}$$

where B is a constant, and the equation can be written

$$\frac{d}{dx}\left(\mu\frac{dv}{dx}\right) = B + \rho g. \tag{11}$$

This equation is to be solved subject to the boundary conditions:

$$v(o) = v(a) = 0, \tag{12}$$

the layers of fluid in contact with the walls being taken to be at rest. The constant B, the pressure gradient along the column, is to be determined from the condition

$$b \int_o^a \rho\, v\, dx = P \tag{13}$$

where P is the product rate, i.e., the mass of material removed from the top of the column per unit time. Ordinarily, in experiments on approach to equilibrium, one has $P = 0$.

Integrating Eq. (11), we get

$$v = g\int_o^x \frac{1}{\mu}\, dx \int_o^x \rho\, dx + B\int_o^x \frac{x}{\mu}\, dx + C\int_o^x \frac{1}{\mu}\, dx, \tag{14}$$

with μ and ρ functions of $\underline{x}$, and $\underline{C}$ a constant of integration. The constants $\underline{B}$ and $\underline{C}$ can be determined from the two relations

$$v(a) = g\int_o^a \frac{dx}{\mu}\int_o^x \rho\, dx + B\int_o^a \frac{x}{\mu}\, dx + C\int_o^a \frac{dx}{\mu} = 0, \tag{15}$$

and

$$g\int_0^a \rho\, dx \int_0^x \frac{dx}{\mu} \int_0^x \rho\, dx + B\int_0^a \rho\, dx \int_0^x \frac{x\,dx}{\mu} + C\int_0^a \rho\, dx \int_0^x \frac{dx}{\mu} = \frac{P}{b}. \quad (16)$$

In order to carry out the integrations it is necessary to have the relation between x and the temperature T, since μ and ρ are actually known as functions of T rather than of x. In the case of steady heat flow (except near the edges of the plates) one can write

$$Q = \lambda \frac{dT}{dx} \quad (17)$$

where λ is the thermal conductivity of the material (in general a function of T) and Q is the rate of heat flow per unit area of plate. Integrating this, we obtain

$$x = \frac{1}{Q} \int_{T_1}^{T} \lambda\, dT, \quad (18)$$

and

$$Q = \frac{1}{a} \int_{T_1}^{T_2} \lambda\, dT. \quad (19)$$

Knowing Q, one can express dx in terms of dT in the preceding integrals by means of Eq. (17).

Having obtained the convection velocity v, we can now consider the other processes in the column. The equation of continuity in the present case takes the form

$$\frac{\partial}{\partial t}(\rho c) = -\frac{\partial}{\partial x}\left[-\rho D\frac{\partial c}{\partial x} + \rho D q c (1-c)\frac{dT}{dx}\right] -$$

$$-\left(\rho v \frac{\partial c}{\partial z} - \rho D \frac{\partial^2 c}{\partial z^2}\right). \tag{20}$$

Integrating with respect to x and making use of the fact that at $x = 0$ the expression in the brackets vanishes, we get

$$\frac{\partial}{\partial t}\int_0^x \rho c\,dx = \rho D\frac{\partial c}{\partial x} - \rho D q c (1-c)\frac{dT}{dx} -$$

$$-\int_0^x \left(\rho v \frac{\partial c}{\partial z} - \rho D \frac{\partial^2 c}{\partial z^2}\right) dx, \tag{21}$$

from which we find

$$\frac{\partial c}{\partial x} = \frac{1}{\rho D}\frac{\partial}{\partial t}\int_0^x \rho c\,dx + qc(1-c)\frac{dT}{dx} +$$

$$+\frac{1}{\rho D}\int_0^x \left(\rho v \frac{\partial c}{\partial z} - \rho D \frac{\partial^2 c}{\partial z^2}\right) dx. \tag{22}$$

Now let τ denote the net rate of transport of the light constituent up the column. Then

$$\tau = b\int_0^a \rho\, cv dx = b\int_0^a \rho D \frac{\partial c}{\partial x}\, dx \tag{23}$$

Let us define a function

$$G(x) = b\int_0^x \rho\, v dx\,, \tag{24}$$

so that

$$G(o) = 0, \qquad G(a) = P. \tag{25}$$

It follows then that the first term in the expression for τ is given by

$$b\int_0^a \rho\, cv\, dx = \int_0^a c\frac{dG}{dx}\, dx = \Big[cG\Big]_0^a -$$

$$-\int_0^a G\frac{\partial c}{\partial x}\, dx = Pc - \int_0^a G\frac{\partial c}{\partial x}\, dx \tag{26}$$

where in the first term c represents the value of $\underline{c}$ for $x = a$; however, since c varies only slightly across the section $(o \leqslant x \leqslant a)$ it is not important what value $\underline{x}$ is given. If we now substitute Eq. (22) into Eq. (26) and then use the latter in Eq. (23), we get

$$\tau = Pc - \int_0^a \frac{G}{\rho D}\, dx \int_0^x \rho \frac{\partial c}{\partial t}\, dx - \int_0^a Gqc\,(1 - c)\, \frac{dT}{dx}\, dx -$$

$$- \int_0^a \frac{G}{\rho D}\, dx \int_0^x \rho v \frac{\partial c}{\partial z}\, dx + \int_0^a \frac{G}{\rho D}\, dx \int_0^x \rho D \frac{\partial^2 c}{\partial z^2}\, dx -$$

$$- b \int_0^a \rho D \frac{\partial c}{\partial z}\, dx \,. \qquad (27)$$

Making use of the fact that c varies only slightly with x and noting that none of the integrals in Eq. (27) is critically dependent on the variation of c with x, we can write

$$\tau = Pc + W \frac{\partial c}{\partial t} + H\, c\,(1-c) - K \frac{\partial c}{\partial z} - N \frac{\partial^2 c}{\partial z^2} \qquad (28)$$

where c is now regarded as a function of z and t only, and the coefficients are given by

$$H = -\int_0^a Gq \frac{dT}{dx}\, dx \,,$$

$$K = K_M + K_D \,,$$

$$K_M = \int_0^a \frac{G}{\rho D}\, dx \int_0^x \rho\, v dx = \frac{1}{b} \int_0^a \frac{G^2}{\rho D}\, dx \,,$$

$$K_D = b\int_0^a \rho D dx ,$$

$$N = \int_0^a \frac{G}{\rho D} dx \int_0^x \rho D dx ,$$

$$W = \int_0^a \frac{G}{\rho D} dx \int_0^x \rho dx . \tag{29}$$

If we go back to Eq. (21) and set $x = a$, noting that the same boundary condition holds as for $x = 0$, we get, on multiplication by b,

$$\frac{M}{L} \frac{\partial \sigma}{\partial t} = - \frac{\partial \tau}{\partial z} , \tag{30}$$

where we have put $\frac{M}{L}$ in place of $b\int_0^a \rho dx$, M being the mass of all the material in the column. Eq. (30), with τ given by Eq. (28), describes the behavior of the column as an isotope separator.

In order to get some idea of the magnitudes of the various integrals encountered thus far, let us carry out an approximate calculation by assuming that the temperature difference ΔT between the hot and cold walls is small so that we can treat all the quantities associated with the liquid as constant, except the density where it is necessary to take account of its variation in order to get convection. (Another way of expressing this is to say

that we shall replace all these quantities, which are functions of the temperature, by suitable mean values.)
In this way we find that the convection velocity is given by

$$v = \left[\frac{g\Delta\rho}{6\mu} a^2 \left(\frac{x}{a} - \frac{1}{2}\right) + \frac{6P}{ab\rho}\right] \frac{x}{a} \left(1 - \frac{x}{a}\right) \tag{31}$$

where $\Delta\rho$ is the difference between the density of the fluid at the cold wall and that at the hot wall. From this function one finds

$$G = \left(\frac{x}{a}\right)^2 \left[-\frac{g\rho\Delta\rho b a^3}{24\mu} \left(1 - \frac{x}{a}\right)^2 + P\left(3 - 2\frac{x}{a}\right)\right] \tag{32}$$

The integrals are given in this case by the following expressions:

$$H = \left[\frac{g\rho\Delta\rho b a^3}{720\mu} - \frac{1}{2} P\right] q\Delta T ,$$

$$K_M = \frac{g^2\rho(\Delta\rho)^2 b a^7}{362880\mu^2 D} - \frac{g\Delta\rho a^4 P}{720\mu D} + \frac{13}{35}\frac{P^2 a}{\rho D b} ,$$

$$K_D = \rho D a b ,$$

$$N = \frac{g\rho\Delta\rho b a^5}{1440\mu} - \frac{7}{20} P a^2 , \tag{33}$$

$$W = \frac{N}{D} .$$

First let us investigate the importance of the terms involving the product rate P. As an example, let us consider the expression for H. One can write

$$H = H_o (1 - \xi) \tag{34}$$

where

$$H_o = \frac{g \rho \Delta \rho b a^3 q \Delta T}{720 \mu} \tag{35}$$

is the value of H for P = 0, and ξ is a dimensionless quantity

$$\xi = P / \left(\frac{g \rho \Delta \rho b a^3}{360 \mu} \right) \tag{36}$$

To get orders of magnitude in the present and the following cases, let us take: $\rho = 2$ gm/cm^3, $\Delta \rho = 1$ gm/cm^3, $\mu = 6 \times 10^{-3}$ poises, $D = 2 \times 10^{-5}$ cm^2/sec., a = 0.025 cm., b = 13 cm., L = 1500 cm. It follows that $g \rho \Delta \rho b a^3 / 360 \mu$ is of the order of 0.2 gm/sec. On the other hand, P is something of the order of 100 gm/day in practice or of the order of 10^{-3} gm/sec. Hence ξ is of the order of 0.005, so that it can be neglected under ordinary circumstances. This means that we can replace H by H_o, a constant with respect to variation of the product rate. In the same way one finds that the other integrals likewise depend on ξ,

so that if ξ is small compared to unity the terms involving P can be neglected. It follows then that one can calculate all the integrals for zero product rate and use them for product rates occurring in practice. While we see this on the basis of the approximate values of the integrals given above, we can expect that the results, insofar as orders of magnitude are concerned, will agree with those obtainable by the use of more exact values for the integrals. Hereafter we shall treat the integrals of Eq. (29) as independent of P.

Next let us note the orders of magnitude of the expressions in Eq. (33) (with P = 0). One finds for the case being considered that, in c.g.s. units,

$$H \sim \frac{1}{10} q \Delta T$$

$$K_M \sim 0.6$$

$$K_D \sim 10^{-5}$$

$$N \sim 3 \times 10^{-5}$$

$$W \sim 1$$

Actually, experimental values of H are of the order of 60 gm/day, or 10^{-3} gm/sec.

Since it is found that it takes several days to build up an appreciable increase in concentration, the term $W \frac{\partial c}{\partial t}$ in Eq. (28) is in general of the order of 10^{-5} c.

The term $K \frac{\partial c}{\partial z}$ is of the order of 10^{-3} c if we suppose that the variation of c over the length of the column is of the order of c itself. The term $N \frac{\partial^2 c}{\partial z^2}$ is of the order of 10^{-11} on this assumption. The term $Hc\ (1 - c)$, with $c \ll 1$ is of the order of 10^{-3} c. On the basis of such rough estimates it appears plausible to neglect the terms $W \frac{\partial c}{\partial t}$ and $N \frac{\partial^2 c}{\partial z^2}$ in Eq. (28)[5]. This we shall do hereafter.

Accordingly we shall write

$$\tau = Pc + Hc\ (1 - c) - K \frac{\partial c}{\partial z} \tag{37}$$

for the net transport rate of the light constituent up the column.

If we are dealing with a steady state of operation, then τ is constant and is equal to Pc_T where c_T is the concentration at the top of the column at the point where the product is removed. Eq. (37) then becomes

$$K \frac{\partial c}{\partial z} = Hc\ (1 - c) - P\ (c_T - c)\ . \tag{38}$$

If we are dealing with a process of approach to equilibrium, then the expression (37) must be substituted into Eq. (30) to get the equation for the column. Usually in a process of this sort one has $P = 0$. If furthermore,

$c \ll 1$, as is the case of interest in practice, then one can write

$$\tau = Hc - K \frac{\partial c}{\partial z} , \tag{39}$$

and if this is substituted into Eq. (30) we get

$$X \alpha^2 \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha \frac{\partial c}{\partial z} , \tag{40}$$

where

$$\alpha = \frac{H}{K} \tag{41}$$

and

$$X = \frac{MK}{H^2 L} = \frac{M}{HY} , \tag{42}$$

if we set

$$Y = \alpha L. \tag{43}$$

3. <u>Column In Steady State</u>

The simplest case to treat is the one in which the column has reached equilibrium and no product is being removed. In this case we have $\tau = 0$ and the equation determining the concentration is of the form

$$Hc\,(1 - c) - K \frac{dc}{dz} = 0 \tag{44}$$

If we let c_B denote the concentration at the bottom of the column, the solution of this equation can be written

$$\frac{c}{1-c} = \frac{c_B}{1 - c_B} e^{\alpha Z} , \tag{45}$$

where, as before, $\alpha = H/K$. If we let c_T denote the concentration at the top of the column and define the separation factor S by the relation

$$S = \left(\frac{c_T}{1 - c_T}\right) \Big/ \left(\frac{c_B}{1 - c_B}\right) , \tag{46}$$

it follows that, at equilibrium, S has the value

$$S_e = e^Y \tag{47}$$

where, as before, $Y = \alpha L$.

If the column is operated with continuous product removal so that it remains in a steady state, then the transport rate up the column is constant and is equal to the rate at which the light constituent is withdrawn in the product, Pc_T. The equation for this case, Eq. (38), can be written

$$\frac{dc}{dz} = \alpha c (1 - c) - \alpha \nu (c_T - c) , \tag{48}$$

where

$$\nu = \frac{P}{H} . \tag{49}$$

This equation can be integrated[2]. If we let

$$\omega = \sqrt{(1+\nu)^2 - 4\nu c_T} , \tag{50}$$

then the solution can be written:

$$\ln \frac{2c - 1 - \nu + \omega}{2c - 1 - \nu - \omega} = \omega\alpha z + \text{const.} \tag{51}$$

It follows from this that the separation factor for the column is given by

$$S = \frac{(\omega + \nu + 1)\, e^{\omega Y} + \omega - \nu - 1}{(\omega + \nu - 1)\, e^{\omega Y} + \omega - \nu + 1} , \tag{52}$$

The concentration c along the column can be obtained from the relation

$$\frac{c}{c_T} = \frac{(\omega + \nu - 1)\, e^{\omega\alpha(L-z)} + \omega - \nu + 1}{(\omega + \nu + 1 - 2\, c_T)\, e^{\omega\alpha(L-z)} + \omega - \nu - 1 + 2\, c_T} , \tag{53}$$

which is convenient if c_T is known. Frequently it happens that one knows c_B rather than c_T. In that case one can calculate c_T either numerically or graphically by means of Eqs. (52) and (46), and then use Eq. (53).

The calculations can be simplified considerably if one can take $c \ll 1$, which is usually the case. Then Eq. (48) can be approximated by

$$\frac{dc}{dz} = \alpha(1 + \nu)\, c - \nu\, c_T \,, \tag{54}$$

and the solution of this equation is given by

$$\frac{c}{c_T} = \frac{\nu + e^{\alpha(1 + \nu)(z - L)}}{\nu + 1} \,. \tag{55}$$

If $c \ll 1$, then the separation factor S is given by

$$S = \frac{c_T}{c_B} \,, \tag{56}$$

and from Eq. (55) one gets

$$S = \frac{\nu + 1}{\nu + e^{-Y}(1 + \nu)} \,. \tag{57}$$

From Eqs. (55) and (57) one can also write

$$\frac{c}{c_B} = \frac{\nu + e^{\alpha(1 + \nu)(z - L)}}{\nu + e^{-Y}(1 + \nu)} \tag{58}$$

4. Irregularities

The equations derived earlier in this chapter referred to an ideal column in which the hot and cold walls were assumed to be perfectly plane and parallel and the

temperature of each perfectly uniform, with the fluid in a state of lamellar flow. In the case of any practical column these assumptions are fulfilled only approximately at best, and it is therefore to be expected that there will be deviations from the behavior predicted on the basis of the preceding equations. The discrepancies arising in practice are associated with factors that can be classified roughly under three headings:

(1) Geometrical irregularities

(2) Temperature irregularities

(3) Vibrations and turbulence.

(1) By geometrical irregularities are meant such things as variations in the spacing between the walls, producing variations in the convection current, or the presence of spacers in the working space, representing obstacles around which the current must flow. Obviously in the presence of such irregularities the flow of the process material will not be as simple as was assumed.

(2) Temperature irregularities produce parasitic convection, that is, local convection, the effect of which is to bring about mixing of the fluid and thus reduce the separative action of the column. It is clear that geometrical irregularities will always be accompanied by temperature irregularities. However, it is possible to have temperature irregularities in the working space without the presence of geometrical irregularities there. This can

occur if there are variations in the thickness of the walls, or if there are spatial or temporal changes present in the steam or cooling water.

(3) Turbulence may set in, in which case the particles of the fluid will no longer move along smooth stream-lines, but will move in an erratic way, so that mixing will take place, resulting in a reduction or cessation of separative action. Such turbulence will arise if the convection velocity exceeds some critical value. In this connection, it is well known that the critical velocity in the case of a body of fluid having two streams flowing side by side in opposite directions is very much lower than in the case of a single stream. Furthermore, the presence of mechanical vibrations -- and in plant operation such vibrations are inevitable -- lowers the critical velocity. Turbulence or oscillations may also set in under certain conditions of temperature and pressure due to boiling or density fluctuations in the fluid near the hot wall.

It appears that one can adjust the operating conditions so as to make the effect of turbulence relatively unimportant. However, with columns constructed by the usual methods from commercial tubing it is impossible to eliminate parasitic convection.

One can calculate the parasitic convection for some simple temperature distributions and determine the effect of this convection on the performance of the column[2].

However, for the irregularities of temperature that are present in practical cases, the calculations would be very difficult to carry out. A study of the equations shows that the general effect of such convection is essentially equivalent to an increase in the column constant K. That is, in the differential equation for column behavior and in the expression for τ, one should replace K by

$$K' = K + K_p \tag{59}$$

where K_p is the contribution due to parasitic convection. The extra term K_p may be appreciably larger than K. In particular, as the spacing a is made smaller and smaller, the geometrical irregularities become relatively more and more important and K_p/K becomes very large. As pointed out by Cohen[6], the effect of parasitic convection will cause the curve of $\ln S_e$ vs a to have its maximum lowered and displaced to a larger value of a than would otherwise be the case.

A point to note in this matter is that if the parasitic convection is distributed nearly uniformly down the column -- which will be the case if the irregularities are randomly distributed or if, for example, the two tubes surrounding the working space are parallel but not coaxial, then the K' introduced above will be constant. The behavior of the column will be qualitatively similar to that of the ideal

column. However, if the distribution of the irregularities varies along the length of the column, so that K' is a function of z then one will find marked differences between the observed behavior and that predicted by the simple theory.

5. Variation of Conditions

The next question to consider is how the behavior of a column will vary if its dimensions or the conditions under which it is operated are varied.

If we assume, for the present, the validity of the results obtained in Section 2, it follows that if the temperatures at the two walls and the pressure are kept fixed, the constants H, K_M and K_D (for $P = 0$) can be written

$$H = C_1 \, ba^3 \, , \tag{60}$$

$$K_M = C_2 \, ba^7 \, , \tag{61}$$

$$K_D = C_3 \, ba \, , \tag{62}$$

where the C's are constants. It follows that

$$Y = \ln S_e = \frac{C_1 \, a^2 L}{C_2 \, a^6 + C_3} \tag{63}$$

This means that for a fixed spacing $\underline{a}$, $\ln S_e$ should be

proportional to the length of the column L, and that for a fixed value of L it should vary as $1/a^4$ for large values of a and as a^2 for small values of a, with a maximum value for some point in between.

The position of the maximum can be obtained by setting the derivative of the right hand member of Eq. (63) with respect to a equal to zero. One gets for the corresponding value for a, denoted by a_s:

$$a_s = \sqrt[6]{\frac{c_3}{2\,c_2}}\,, \tag{64}$$

and for this value of a one has for Y

$$(Y)_{max} = \frac{2\,c_1\,L}{3 \cdot 2^{\frac{1}{3}}\,c_2^{\frac{1}{3}}\,c_3^{\frac{2}{3}}}\,. \tag{65}$$

For the conditions assumed above we can also write

$$M = c_4\,abL \tag{66}$$

and, by Eq. (42),

$$X = \frac{c_4\,(c_2\,a^6 + c_3)}{c_1^2\,a^4}\,. \tag{67}$$

The value of a for which X is a minimum, denoted by a_x, is found to be given by

$$a_x = \sqrt[6]{\frac{2\,c_3}{c_2}} = 1.26\ a_s \tag{68}$$

and the corresponding value of X

$$(X)_{min} = \frac{3\ c_2^{\frac{2}{3}}\ c_3^{\frac{1}{3}}\ c_4}{2^{\frac{2}{3}}\ c_1^{\ 2}} \ . \tag{69}$$

It will be convenient later on to introduce a function, the figure of merit, Φ , defined by the relation

$$\Phi = HY \ . \tag{70}$$

With the present assumptions we can write

$$\Phi = \frac{c_1^{\ 2}\ a^5\ bL}{c_2\ a^6 + c_3} \ . \tag{71}$$

It follows that the value of <u>a</u> at which this function has a maximum, is given by

$$a_\Phi = \sqrt[6]{\frac{5\ c_3}{c_2}} = 1.47\ a_s \tag{72}$$

and the corresponding value of Φ by

$$(\Phi)_{max} = \frac{5^{\frac{5}{6}}\ c_1^{\ 2}\ bL}{6\ c_2^{\frac{5}{6}}\ c_3^{\frac{1}{6}}} \tag{73}$$

The preceding results, obtained for an ideal case, will differ from those for a practical case for several reasons. Thus, we have assumed that the temperature is kept fixed while the spacing is varied. Actually, with given steam and cooling-water temperatures, if the spacing is varied, the temperatures of the hot and cold walls will also vary because of the variation of the heat flow.

A more important cause of discrepancy between the above theoretical results and experiment is the presence of parasitic convection, discussed in the preceding section. As Cohen[6] pointed out, this will become increasingly important at smaller spacings and will cause $(Y)_{max}$ to decrease and a_s to increase. It does not mean very much to try to calculate $\underline{Y}$ as a function of $\underline{a}$ in this case, since the parasitic convection, being associated with irregularities, will vary from column to column in an unpredictable way, giving rise to statistical variations. For large values of $\underline{a}$, the above calculations should still be applicable and Y should vary as $1/a^4$.

As regards the effect of varying the temperature and pressure, it is difficult to make any accurate predictions because of our lack of knowledge of the dependence of some of the properties of the process fluid on these variables. In particular, the thermal diffusion coefficient is at present known only as far as order of magnitude is concerned, and there is no reliable information as to how it varies

with temperature. Some calculations were carried out by Cohen[6] on these questions, but he had to make a number of speculative assumptions (because of the lack of data) and it is not clear how valid the results are.

6. Quasi-Continuous Product Removal

In practice it is difficult to arrange to have continuous product removal. The nearest one usually comes to it is in withdrawing small fixed quantities at regular, short intervals, a procedure that will be referred to as quasi-continuous withdrawal. The question comes up: how is this process related to the continuous one which is the one considered in Section 2 and used to derive the differential equations for the behavior of the column?

In the case of continuous product removal ($P \neq 0$), the differential equation governing the process at small concentrations corresponding to Eq. (40) for $P = 0$, is given by

$$X\alpha^2 \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha(1+\nu)\frac{\partial c}{\partial z} \tag{74}$$

where c is the concentration, t the time, z the distance up the column, X is the time constant, $\alpha = H/K$, and $\nu = P/H$, with H and K the column constants and P the rate of product withdrawal. To simplify the calculations without affecting the essentials of the problem, let us suppose that the column is connected at the bottom to

an infinite reservoir. Then, as one boundary condition, we have

$$z = 0 : \qquad c = c_o , \tag{75}$$

where c_o is a constant. At the top of the column, on the other hand, the boundary condition expresses the fact that there the transport of light constituent, aside from that due to flow, vanishes. If L is the length of the column, then

$$z = L : \qquad \frac{\partial c}{\partial z} - \alpha c = 0 . \tag{76}$$

If we are dealing with a steady process, $\frac{\partial c}{\partial t} = 0$, and Eq. (74) becomes

$$\frac{d^2 c}{dz^2} - \alpha (1 + \nu) \frac{dc}{dz} = 0 . \tag{77}$$

The solution of this equation, satisfying the boundary conditions, is found to be

$$c = \frac{c_o \nu e^{(1+\nu)Y}}{1 + \nu e^{(1+\nu)Y}} + \frac{c_o e^{(1+\nu)\alpha z}}{1 + \nu e^{(1+\nu)Y}} , \tag{78}$$

where $Y = \alpha L$. If we put $z = L$, and let $S = c/c_o$, we get

$$S = \frac{(1+\nu) e^{(1+\nu)Y}}{1 + \nu e^{(1+\nu)Y}} . \tag{79}$$

In the case of quasi-continuous product removal, during the time between withdrawals the appropriate differential equation is the one obtained by putting $\nu = 0$ in Eq. (74):

$$X\alpha^2 \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha \frac{\partial c}{\partial z} , \tag{80}$$

with the same boundary conditions as above. However, at regular intervals, say at $t = nT$ ($n = 1, 2, 3, \ldots$), where T is the period, product is removed and the conditions altered. The time of product withdrawal is quite short in practice and can be neglected. During one cycle, a mass $\underline{m}$ of product is removed, so that the average product rate $\overline{\sigma} = m/T$. Let $\overline{\nu} = \overline{\sigma}/H$. The mass $\underline{m}$ is equal to the mass of a portion of the column of length $L' = mL/M$, where M is the column hold-up.

Let ε denote the time during which product is removed, and let us assume that it is so small that during this time no appreciable change in the concentration occurs because of separation. The only change occurs because of the flow in the column accompanying product removal. One can expect to get a reasonable approximation to what actually takes place by supposing that during the product removal process there is an upward displacement of all the material in the column through the distance L'. After the product withdrawal has been carried out a number of times, the

concentration c will become a periodic function of t with a period T. We can represent this periodic behavior in the following way:

For t in the range $0 \leq t \leq T - \epsilon$, c satisfies Eq. (80). For t in the range $T - \epsilon < t < T$, the product removal takes place, so that

$$c\,(T,z) = c\,(T - \epsilon,\ z - L') , \tag{81}$$

where, for $z \leq L'$, we shall take $c = c_0$. At the end one has regained the initial distribution,

$$c\,(T,z) = c\,(0,z). \tag{82}$$

It is possible to solve rigorously the problem formulated in this way. However, since the calculations involved are somewhat tedious, this will not be done here; instead, some of the properties of the solution will be investigated. We can regard the present case as one which can be treated by Eq. (74), provided we consider ν, not as a constant, but as a function of t which differs from zero only in the range $T - \epsilon < t < T$ (during the first cycle). Let us integrate both sides of Eq. (74) over a complete period of the time. On the left-hand side of the equation we obtain zero, because of the periodicity of the function c, as expressed by Eq. (82). Hence we have

$$\int_0^T \frac{\partial^2 c}{\partial z^2}\, dt - \alpha \int_0^T \frac{\partial c}{\partial z}\, dt - \alpha \int_0^T \nu \frac{\partial c}{\partial z}\, dt = 0 \,, \tag{83}$$

or

$$\frac{d^2}{dz^2}\int_0^T c(t,z)\, dt - \alpha \frac{d}{dz}\int_0^T c(t,z)\, dt - \alpha \int_{T-\epsilon}^T \nu \frac{\partial c}{\partial z}\, dt = 0. \tag{84}$$

Let us investigate the last integral more closely. If we think of the material as being carried up the column during product removal without any mixing taking place, then, if the distance through which it has moved be denoted by ξ , we can write

$$\nu = \frac{\sigma}{H} = \frac{M}{L}\,\frac{v}{H} = \frac{M}{HL}\,\frac{d\xi}{dt} \,, \tag{85}$$

where $\underline{v}$ is the velocity of the material in the column due to product removal. Hence

$$\int_{T-\epsilon}^T \nu \frac{\partial c(t,z)}{\partial z}\, dt = \int_{T-\epsilon}^T \frac{M}{HL}\,\frac{d\xi}{dt}\,\frac{\partial c(t,z)}{\partial z}\, dt = \frac{M}{HL}\int_0^{L'} \frac{\partial c(T-\epsilon, z-\xi)}{\partial z}\, d\xi,$$

$$= -\frac{M}{HL}\int_0^{L'} \frac{\partial c(T-\epsilon, z-\xi)}{\partial \xi}\, d\xi = \frac{M}{HL}\Big\{c(T-\epsilon,z) - c(T-\epsilon, z-L')\Big\},$$

$$= \overline{\nu}\, T \cdot \frac{1}{L'}\Big\{c(T-\epsilon,z) - c(T-\epsilon,z-L')\Big\}. \tag{86}$$

Let us define

$$\tilde{\sigma}(z) = \frac{1}{L'} \int_{z-L'}^{z} \sigma(T-\epsilon, x)\, dx \tag{87}$$

Then we can write

$$\int_{T-\epsilon}^{T} \nu \frac{\partial}{\partial z} \sigma(t,z)\, dt = \bar{\nu}\, T \frac{d\tilde{\sigma}}{dz} \tag{88}$$

If we substitute this into Eq. (84), divide by T, and introduce

$$\bar{\sigma}(z) = \frac{1}{T} \int_{0}^{T} \sigma(t,z)\, dt, \tag{89}$$

we see that (84) becomes

$$\frac{d^2\bar{\sigma}}{dz^2} - \alpha \frac{d\bar{\sigma}}{dz} - \alpha\bar{\nu} \frac{d\tilde{\sigma}}{dz} = 0. \tag{90}$$

Now if we can write

$$\tilde{\sigma}(z) = \bar{\sigma}(z) \tag{91}$$

then Eq. (90) becomes

$$\frac{d^2\bar{c}}{dz^2} - \alpha (1 + \bar{\nu}) \frac{d\bar{c}}{dz} = 0 , \tag{92}$$

which is of the same form as Eq. (77), but with $\bar{\nu}$ instead of ν . Since the boundary conditions (75) and (76) hold at all times for $\underline{c}$ they must also hold for $\bar{c}$. Hence it is clear that, to the extent that Eq. (91) is valid, the quasi-continuous process is equivalent to a continuous process having the same average product rate. This will be the case if T/X and L'/L are sufficiently small, for then the variations of the concentrations over the time 0 to $T-\epsilon$ and the distance L' will be nearly linear, and one can write

$$\bar{c}(z) \doteq \frac{1}{2}\left\{c(0,z) + c(T-\epsilon, z)\right\} = \frac{1}{2}\left\{c(T-\epsilon, z) + c(T-\epsilon, z-L')\right\} = \tilde{c}(z) , \tag{93}$$

to a good approximation.

To get a rough estimate of the errors involved in this approximation, let us suppose that at a certain time ($t = 0$) the column is in a state described in Eq. (78), so that the separation factor is given by Eq. (79). Let us identify the ν in Eqs. (78) and (79) with $\bar{\nu}$, and let us denote the corresponding value of S by S_0. One can solve Eq. (80) with the boundary conditions (75) and (76) for this case to get the subsequent behavior of the column.

A calculation, based on the Laplace transformation, leads to the result that for $t \ll X$ the separation factor is given by

$$S = S_0 \left[1 + \nu\left(\frac{t}{X}\right) - \frac{4\nu^2}{3\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{3}{2}} + \cdots \right] . \qquad (94)$$

We see that the fractional deviation from linearity during a time of the order T is of the order of $\frac{4\nu^2}{3\sqrt{\pi}} \left(\frac{T}{X}\right)^{\frac{3}{2}}$.

For example, with $T/X \sim 0.002$, $\nu \sim 2$, this is about 3×10^{-4}.

On the other hand, to get some idea of the variation with height near the top of the column, we note that if we let ξ represent the distance down from the top of the column, then from Eqs. (78) and (79) we get

$$S = S_0 \left[1 - \alpha \xi + \frac{1}{2} (1 + \nu) \alpha^2 \xi^2 - \cdots \right] . \qquad (95)$$

If we take $\xi = L'$, the fractional deviation from linearity is of the order of $\frac{1}{2} (1 + \nu) Y^2 \left(\frac{L'}{L}\right)^2$. For example, if $L'/L = 0.01$, $Y = 0.5$, $\nu = 2$, this is of the order of 10^{-4}.

Since the actual function will not be very different from the one used in the preceding calculations, one can expect the order of magnitude of the deviations from linearity to be about as given above. Hence Eqs. (93), and therefore (92), should be valid in the usual cases.

One might raise the question of the effect of the short region near the bottom of the column, where the behavior is somewhat exceptional because of the arrival of material of concentration C_o during the product removal. However, the variation in concentration during a cycle is small in this region, and its reaction on the behavior of the other end of the column during a short time T can be expected to be unimportant.

Finally, on the basis of the preceding calculations, one can estimate the variation in product concentration during the course of its removal. By any of several lines of reasoning one finds quite readily that the maximum variation in the separation factor is of the order of

$$\Delta S = (\alpha L') S_o = Y\left(\frac{L'}{L}\right) S_o = \frac{\bar{\nu} T}{X} S_o , \qquad (96)$$

where S_o is the mean separation factor or that for continuous operation, as given by Eq. (79).

Footnotes

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CHAPTER II. APPROACH TO EQUILIBRIUM BY A SINGLE COLUMN

1. Introduction

The question of the approach to equilibrium by a column is of interest for, at least, two reasons. Sometimes the time required for a column to come up to a concentration at which one can begin continuous operation is appreciable and is important to know. More frequently, however, one is interested in this question because, by studying the behavior of a column as it approaches equilibrium, one can get information about it to predict its performance in continuous operation. The present chapter will be concerned mainly with the latter standpoint.

We have seen in the preceding chapter that, for a column approaching equilibrium without any product being removed, the differential equation is given by[1]

$$X \alpha^2 \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha \frac{\partial c}{\partial z} , \qquad (1)$$

where

$$\alpha = \frac{H}{K} , \qquad X = \frac{M}{HY} , \qquad Y = \alpha L , \qquad (2)$$

for a column of length L, hold-up mass M and characteristic constants H and K, provided the concentration $c \ll 1$.

Eq. (1), with appropriate initial and boundary conditions, determines the concentration of the light constituent $c(z,t)$ as a function of the distance up the column z and the time t, during the approach to equilibrium. If one starts with a concentration c_o, that of normal material, one can define the separation factors

$$S_T = \frac{c(L,t)}{c_o}, \quad S_B = \frac{c(0,t)}{c_o}, \quad S = \frac{S_T}{S_B}. \tag{3}$$

From a knowledge of one of these, say S_T as a function of the time under a given set of conditions, it is possible to determine X and Y for the column under consideration. From them one gets

$$S_e = \ln Y \tag{4}$$

where S_e is the value of S at equilibrium, and

$$H = \frac{M}{XY}, \qquad K = \frac{ML}{XY^2}. \tag{5}$$

The constants H and Y are useful in predicting the behavior of a column under continuous operation, as was seen in the preceding chapter, Eq. (57).

To assist in such prediction, Fig. 1 presents a family of curves, showing S vs. $\nu = P/H$ for various values of Y, on the basis of Eq. (57) of Chapter I.

We see then that it is desirable to be able to determine

the constants of a column from the observation of its behavior during this process. In the following sections calculations and graphs are given for this purpose for several typical cases.

2. Column with Infinite Reservoir

In practice, the most common procedure for testing a column is to let it approach equilibrium while it is attached at one end to a large reservoir, its other end being closed. Depending on whether the lower end or the upper end is the one connected to the reservoir, one has a rectifier or a stripper. Frequently one has occasion to deal with the case in which M_R, the hold-up of the reservoir, is large compared to M, the hold-up of the column, so that $\omega = \frac{M}{M_R}$ is small. In that case one can get a good approximation by considering the reservoir to be infinite, i.e., $\omega = 0$. Since this case is somewhat simpler to treat than the more general one, it will be taken up first.

In the case of a rectifier with an infinite reservoir, the boundary and initial conditions are

$$c = c_0 \quad (z = 0, \quad t \geqslant 0), \tag{6}$$

$$\tau = 0 \quad (z = L, \quad t \geqslant 0), \tag{7}$$

$$c = c_0 \quad (0 \leqslant z \leqslant L, \ t = 0), \tag{8}$$

if we suppose that the reservoir and the column, initially, are filled with material of concentration c_o.

The solution can be readily obtained by the use of operational calculus. Multiply the differential equation (1) by e^{-pt} and integrate over $\underline{t}$ from 0 to ∞. Let the Laplace transform be given by

$$f = \int_0^\infty c\, e^{-pt}\, dt\,. \tag{9}$$

Then the equation becomes, after an integration by parts,

$$X\alpha^2 (pf - c_o) = \frac{d^2f}{dz^2} - \alpha \frac{df}{dz}\,. \tag{10}$$

In terms of f, the boundary conditions are

$$\left.\begin{aligned} f &= \frac{c_o}{p} \qquad (z = 0)\,, \\ \frac{df}{dz} - \alpha f &= 0 \quad (z = L). \end{aligned}\right\} \tag{11}$$

The solution of (10) satisfying the boundary conditions (11) is

$$f = \frac{c_o}{p} + \frac{2c_o}{p} \cdot \frac{e^{\frac{1}{2}(1+\lambda)\alpha z} - e^{\frac{1}{2}(1-\lambda)\alpha z}}{(\lambda-1)e^{\frac{1}{2}(1+\lambda)Y} + (\lambda+1)e^{\frac{1}{2}(1-\lambda)Y}}\,, \tag{12}$$

where

$$\lambda = \sqrt{1 + 4 X p}, \tag{13}$$

or, in terms of hyperbolic functions,

$$f = \frac{c_0}{p} + \frac{2c_0}{p} e^{\frac{1}{2}(\alpha z - Y)} \frac{\sinh \frac{\lambda \alpha z}{2}}{\lambda \cosh \frac{\lambda Y}{2} - \sinh \frac{\lambda Y}{2}}. \tag{14}$$

Having obtained f, one must apply the inverse Laplace transformation to get c. This can be done by means of a line integral in the complex plane:

$$c = \frac{1}{2\pi i} \int_{\beta - i\infty}^{\beta + i\infty} e^{pt} f \, dp \tag{15}$$

where β is an arbitrary real number, sufficiently large so that all the poles of the integrand are on the left of the path of integration. The integral can be evaluated by summing over the residues at the poles of the integrand. At $p = 0$, the residue is $c_0 e^{\alpha z}$. The other poles are at the values of p for which

$$\lambda \cosh \frac{\lambda Y}{2} - \sinh \frac{\lambda Y}{2} = 0. \tag{16}$$

At each of these poles, the residue is

$$\frac{2\, c_0\, e^{\frac{1}{2}(\alpha z - Y)} \sinh \frac{\lambda \alpha z}{2}\, e^{pt}}{p\left[\cosh \frac{\lambda Y}{2} + \frac{\lambda Y}{2} \sinh \frac{\lambda Y}{2} - \frac{Y}{2} \cosh \frac{\lambda Y}{2}\right] \frac{d\lambda}{dp}} =$$

$$= \frac{4\, c_0 \lambda\, e^{\frac{1}{2}(\alpha z - Y)} \sinh \frac{\lambda \alpha z}{2}\, e^{pt}}{(\lambda^2 - 1)\left[(1 - \frac{Y}{2}) \cosh \frac{\lambda Y}{2} + \frac{\lambda Y}{2} \sinh \frac{\lambda Y}{2}\right]} . \tag{17}$$

If $Y < 2$, one can show that the roots of (16) are all pure imaginary. Hence it is convenient to set $\lambda = i \frac{2\theta}{Y}$. Eq. (16) then becomes

$$\tan \theta = \frac{2\theta}{Y} , \tag{18}$$

and, if we express the residue in terms of θ, we get for the solution

$$c = c_0 e^{\alpha z} - 4\, c_0 e^{-\frac{\alpha}{2}(L-z)} \sum_{n=1}^{\infty} \frac{\sin \theta_n \sin 2\theta_n}{2\theta_n - \sin 2\theta_n} \sin \frac{\theta_n z}{L}\, e^{-k_n t/X} , \tag{19}$$

where θ_n is the n'th positive root of (18), omitting $\theta = 0$, and k_n is given by

$$k_n = \frac{\theta_n^2}{Y^2} + \frac{1}{4} = \frac{1}{4 \cos^2 \theta_n} . \tag{20}$$

For $z = L$, we find $S = S_T$,

$$S = e^{Y} - 4 \sum_{h=1}^{\infty} \frac{\sin^2 \theta_n \sin 2\theta_n}{2\theta_n - \sin 2\theta_n} \; e^{-k_n t/X} . \tag{21}$$

From (19) one obtains by integration the mean value of c, $\bar{c}$:

$$\bar{c} = \frac{1}{L} \int_0^L c \, dz . \tag{22}$$

One finds

$$\bar{S} = \frac{\bar{c}}{c_o} = \frac{1}{Y} \left\{ e^{Y} - 1 - 4e^{-\frac{Y}{2}} \sum_{n=1}^{\infty} \frac{\sin \theta_n \sin^2 2\theta_n}{2\theta_n - \sin 2\theta_n} \, e^{-k_n t/X} \right\}, \tag{23}$$

with the increase in the light-constituent mass $\underline{m}$ given by

$$m = M \, (\bar{c} - c_o) = M \, c_o \, (\bar{S} - 1). \tag{24}$$

From (19) one also gets for the light-constituent transport

$$\tau = \frac{4c_o K}{L} \; e^{-\frac{\alpha}{2}(L-z)} \sum_{h=1}^{\infty} \frac{\sin \theta_n \sin 2\theta_n}{2\theta_n - \sin 2\theta_n} \quad x$$

$$\left[\theta_n \cos \frac{\theta_n Z}{L} - \frac{Y}{2} \sin \frac{\theta_n Z}{L} \right] e^{-k_n t/X} , \tag{25}$$

which, for $z = 0$, gives the transport from the reservoir to the column

$$\tau_o = 4\, Hc_o\, e^{-\frac{Y}{2}} \sum_{h=1}^{\infty} \frac{\sin^3 \theta_n}{2\theta_n - \sin 2\theta_n}\, e^{-k_n t/X} . \tag{26}$$

It follows from the preceding equations that

$$\tau_o = \frac{dm}{dt} , \tag{27}$$

as was to be expected.

We see that we have obtained a number of results as series expansions. For sufficiently large values of t/X, these series converge very rapidly so that only the first one or two terms are needed. However, for small values of t/X, a large number of terms may be required, in which case the above expansions become inconvenient. It is therefore desirable to have some other form of solution which is more appropriate for this case.

Let us go back to the solution in the form of Eq. (12). For sufficiently large (positive, real) values of λ, f can be expanded as follows:

$$f = \frac{c_o}{p} + \frac{2c_o}{p(\lambda - 1)}\, e^{\frac{1}{2}\alpha(z-L)} \left[e^{\frac{1}{2}\lambda\alpha(z-L)} - e^{-\frac{1}{2}\lambda\alpha(z+L)} \right]$$

$$\left\{ 1 - \frac{\lambda + 1}{\lambda - 1}\, e^{-\lambda Y} + \left(\frac{\lambda + 1}{\lambda - 1}\right)^2 e^{-2\lambda Y} + \ldots \right\} . \tag{28}$$

If z is not very much smaller than L, we can neglect the second term in the square brackets. Let us further neglect all but the first term in the series. If we also expand λ,

$$\lambda = \sqrt{1 + 4\,Xp} = 2\sqrt{Xp}\left(1 + \frac{1}{8\,Xp} + \ldots\right),$$

then we can write f approximately

$$f = \frac{c_0}{p} + c_0 e^{\alpha(z-L)\left[\frac{1}{2} + \sqrt{Xp}\right]}\left\{\frac{1}{X^{\frac{1}{2}}p^{\frac{3}{2}}} + \frac{1}{2\,Xp^2} + \ldots\right\}. \quad (29)$$

On carrying out the inverse Laplace transformation, one gets

$$c = c_0 + c_0 e^{\frac{1}{2}\alpha(z-L)}\left\{2\sqrt{\frac{t}{\pi X}}\; e^{-\frac{\alpha^2(L-z)^2 X}{4\,t}} - \right.$$

$$\left. -\alpha(L-z)\,\mathrm{erfc}\left[\frac{\alpha(L-z)\sqrt{X}}{2\sqrt{t}}\right] + \frac{1}{2X}\int_0^t \mathrm{erfc}\left[\frac{\alpha(L-z)\sqrt{X}}{2\sqrt{t}}\right] d\tau + \ldots\right., \quad (30)$$

where

$$\mathrm{erfc}\,(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-u^2}\,du\,. \quad (31)$$

If we set $z = L$, we get through such a procedure

$$S = 1 + \frac{2}{\sqrt{\pi}} \frac{t}{X} + \frac{1}{2} \frac{t}{X} + \frac{1}{6\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{3}{2}} + \dots , \qquad (32)$$

which is an expansion appropriate for small values of t/X. It should be noted that, to the approximation to which (32) is valid, S depends only on t/X and does not depend on Y.

By a similar procedure one finds that for small values of t, the light constituent hold-up $\underline{m}$ is given by

$$m = Hc_o t . \qquad (33)$$

If we examine (30), we see that, for very small values of t, c differs appreciably from c_o only for z nearly equal to L. This means that the $\underline{m}$ given by (33) is accumulated early in the process only in a thin layer close to the top of the column.

To give some idea of the general behavior of a column approaching equilibrium under the conditions being considered, Fig. 2 shows, by means of the solid curve, the dependence of S on t/X for the case of $Y = 0.6$, according to Eq. (21). The dotted curve in this figure describes the dependence obtained from Eq. (21) by neglecting in the series all but the first term. It will be seen that in this case the two curves practically coincide for $t/X \geqslant 0.05$.

One can investigate the relation between the time-constant X and the half-time of approach to equilibrium. The half-time can be defined in either of two ways: (1) the time for S to go half-way to equilibrium, i.e.,

$$S = \frac{1}{2}(1 + S_e) = \frac{1}{2}(1 + e^Y) ,$$

or (2) the time for $\ln S$ to go half-way to equilibrium, i.e.,

$$\ln S = \frac{Y}{2}$$

Fig. 3 shows curves for $T_{\frac{1}{2}}/X$ as a function of Y, with the half-time $T_{\frac{1}{2}}$ defined in each of the preceding ways.

Fig. 4 shows the distribution of concentration along the column at various times. It should be noted that for small values of $\underline{t}$, the concentration is very small everywhere except at the top, near which the concentration increases rather abruptly. As time goes on, the concentration increases lower down, and the gradient becomes more nearly uniform throughout the column.

The results obtained in this section can be used to study the properties of a given column. It will be seen that the time t appears only in the combination t/X, as might have been anticipated from the form of Eq. (1) and the boundary conditions. Hence it is convenient to plot S

as a function of t/X, different curves being obtained for different values of Y. If one has such a family of curves, a comparison of the curve of S vs. t obtained experimentally for the given column with the calculated curves serves to determine the values of X and Y for which best agreement is obtained.

A difficulty in such a comparison arises from the fact that different values of X correspond to different time scales in the graph of S vs. t, and it is necessary to determine simultaneously the appropriate time scale as well as the appropriate member of the calculated family of curves. This difficulty has been largely overcome in Fig. 5, in which graphs of S vs. t/X are presented, with a logarithmic scale for t/X. Since in this case a change of X corresponds simply to a displacement of the curves horizontally without any change of shape, it becomes quite easy to fit the experimental data to the theoretical curves.

It has already been pointed out that for small values of t/X, S is independent of Y, so that all the curves of Fig. 5 nearly coincide. This makes the curve fitting particularly simple: fitting the experimental points for small values of t to the (nearly unique) curve serves to determine X; the experimental points for larger values of t enable one to determine Y.

Thus far we have been considering the column to be operated as a rectifier. At times it is desirable to

experiment with the column operated as a stripper. For one thing, the column approaches equilibrium more rapidly when it is run as a stripper. Then, too, one is sometimes interested in comparing the column constants as obtained for the same column in the two different kinds of operation, since an appreciable discrepancy might indicate the presence of some source of disturbance somewhere in the system.

For a column run as a stripper, some modifications in the formulas given above are required. If we now take $z = 0$ at the top of the column where the reservoir is connected, then we must take $z = -L$ at the bottom, so that Y has to be replaced by $-Y$ in the formulas. It is convenient in this case to replace z by $-z$, so that z now represents the distance measured down from the top of the column, and $z = L$ at the bottom. However, in that case certain other changes have to be made: H must be replaced by $-H$, and, hence, α by $-\alpha$. In place of (18) we now have

$$\tan \theta = - \frac{2\theta}{Y} , \tag{34}$$

the roots of which, θ_n, are to be put into the equation

$$c = c_0 e^{-\alpha z} - 4\, c_0 e^{\frac{\alpha}{2}(L-z)} \sum_{h=1}^{\infty} \frac{\sin\theta_n \sin 2\theta_n}{2\theta_n - \sin 2\theta_n} \sin \frac{\theta_n z}{L}\, e^{-k_n t/X} , \tag{35}$$

k_n being given by the same formula as before, but with the

new roots θ_n. For $z = L$, we get $S = c_p/c_o$ from the equation

$$S = e^{-Y} - 4\sum \frac{\sin^2 \theta_n \sin 2\theta_n}{2\theta_n - \sin 2\theta_n} e^{-k_n t/X} . \qquad (36)$$

If one repeats the calculation for small values of t, one finds that the results obtained for the rectifier can be carried over to the stripper provided the signs of some of the constants are changed as described above and, in addition, $\sqrt{X}$ is replaced by $-\sqrt{X}$. In particular one gets, for $t/X \ll 1$,

$$S = 1 - \frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{X}} + \frac{1}{2}\frac{t}{X} - \frac{1}{6\sqrt{\pi}}\left(\frac{t}{X}\right)^{\frac{3}{2}} + \dots . \qquad (37)$$

Fig. 6 presents a family of curves for S as a function of t/X, for various values of Y. They are intended to be used for the determination of the constants of a stripper in the same way as those of Fig. 2 for the rectifier.

3. <u>Column with Finite Reservoir</u>

If the column approaching equilibrium is connected to a reservoir having a hold-up which is not very large compared to that of the column, the concentration in the reservoir will change during the process and some of the results of the preceding section will no longer be applicable. This case is to be found in the literature as a special case of a more general one worked out by Bardeen[2].

Let us begin with the rectifier. If we have a finite reservoir of hold-up M_R, the boundary conditions are now:

$$\tau = M_R \frac{\partial c}{\partial t} \qquad (z = 0, \quad t \geqslant 0), \tag{38}$$

$$\tau = 0 \qquad (z = L, \quad t \geqslant 0), \tag{39}$$

with the initial condition

$$c = c_0 \qquad (0 \leqslant z \leqslant L, \ t = 0), \tag{40}$$

if we suppose the system initially filled with normal material.

Using the method of operational calculus, or the Laplace transform, one finds, for the range of values of constants encountered in practice, that the solution is given by

$$c = \frac{c_0 (1 + \omega) e^{\alpha z}}{1 + \frac{\omega}{Y} (e^{Y} - 1)} - \frac{8\omega}{Y} e^{\frac{\alpha z}{2}} \sum_{n=1}^{\infty} \frac{A_n - B_n}{D_n} e^{-k_n t/X}, \tag{41}$$

where

$$A_n = \varkappa_n \sin \frac{\theta_n (z-L)}{L} + \varkappa_n^2 \cos \frac{\theta_n (z-L)}{L}, \tag{42}$$

$$B_n = \varkappa_n e^{-\frac{Y}{2}} \left[\left(1 - \frac{Y}{2\omega} (1+\varkappa_n^2)\right) \sin \frac{\theta_n z}{L} + \varkappa_n \cos \frac{\theta_n z}{L} \right], \tag{43}$$

and

$$D_n = (1 + \mu_n^2)^2 \left[\frac{\theta_n}{\sin \theta_n} - \cos \theta_n \right] , \tag{44}$$

where θ_n is the n'th positive root of the equation

$$\tan \theta = \frac{\theta}{\frac{Y}{2} - \omega} , \tag{45}$$

and

$$\omega = \frac{M}{M_R} , \quad \mu_n = \frac{2\,\theta_n}{Y} , \quad k_n = \frac{1}{4} (\mu_n^2 + 1) . \tag{46}$$

From (41, putting $z = L$, we get

$$S_T = \frac{(1 + \omega)\, e^Y}{1 + \frac{\omega}{Y} (e^Y - 1)} - \frac{8\omega}{Y} \times$$

$$\sum_{h=1}^{\infty} \frac{\mu_n^2 \left[e^{\frac{Y}{2}} + \mu_n \sin \theta_n + \frac{1}{2\omega} (1 + \mu_n^2)\, Y - 1) \cos \theta_n \right] e^{-k_n t/X}}{(1 + \mu_n^2)^2 \left[\frac{\theta_n}{\sin \theta_n} - \cos \theta_n \right]} , \tag{47}$$

and, for $z = 0$,

$$S_B = \frac{1 + \omega}{1 + \frac{\omega}{Y}(e^Y - 1)} + \frac{8\omega}{Y} \quad \times$$

$$\sum_{n=1}^{\infty} \frac{\left[\mu_n^2 e^{-\frac{Y}{2}} + \mu_n \sin\theta_n - \mu_n^2 \cos\theta_n\right] e^{-k_n t/X}}{(1 + \mu_n^2)^2 \left[\frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right]} . \qquad (48)$$

In addition to the above results, we also need expressions useful for small values of t. By the method used in the previous section one finds that, for $t/X \ll 1$,

$$S_T = 1 + \frac{2}{\sqrt{\pi}}\left(\frac{t}{X}\right)^{\frac{1}{2}} + \frac{1}{2}\left(\frac{t}{X}\right) + \frac{1}{6\sqrt{\pi}}\left(\frac{t}{X}\right)^{\frac{3}{2}} + \ldots \quad , \qquad (49)$$

$$S_B = 1 - \frac{\omega}{Y}\left(\frac{t}{X}\right) + \frac{4}{3\sqrt{\pi}} \quad \frac{\omega^2}{Y^2}\left(\frac{t}{X}\right)^{\frac{3}{2}} + \ldots \quad , \qquad (50)$$

Fig. 7 shows a family of curves for S_T and S_B as functions of t/X, for $\omega = \frac{M}{M_R} = 1.0$. It will be noted that the general character of S_T is the same as that of S for $\omega = 0$, and the curves can be used in the same way as those of Fig. 5 to determine the constants of the column.

The formulas for the stripper can be obtained from those for the rectifier by introducing the same changes as were made in the previous section. Letting now z denote the distance from the top, we must change the sign of H, α, Y and $\sqrt{X}$. Fig. 8 presents graphs of S_T and S_B for a stripper with $\omega = 1.0$, for various values of Y.

4. Isolated Column

The simplest case to treat mathematically is that of a column closed at both ends. From the experimental standpoint this case has several advantages. The column approaches equilibrium much more rapidly than for any other case, so that the least amount of time is required for the experiment. Furthermore, the column is less likely to experience disturbances than when it is connected to a reservoir or storage chamber to which other columns are also connected. On the other hand, this arrangement has the disadvantage that, if one removes samples of appreciable size for analysis, the material pressure gradually drops in the course of the experiment, thereby altering conditions and, if the pressure change is sufficiently great, producing instability. It is possible to use a method of sample withdrawal in which the material removed is almost completely replaced, but the procedure is then more complicated.

The isolated column is described by Eq. (1) with the boundary conditions,

$$\tau = 0 \qquad (z = 0,\ L)\ . \tag{51}$$

If the column is filled with material of normal concentration at the beginning of the experiment, then we have for the initial condition,

$$c = c_0 \qquad (t = 0)\ . \tag{52}$$

The solution of Eq. (1) with the above conditions has been given by Bardeen[2] in the form of an infinite series expansion in characteristic functions. In the present notation, it can be written

$$\frac{c}{c_0} = \frac{Y e^{\alpha z}}{e^{Y} - 1} + 16\pi Y e^{\frac{1}{2}\alpha z} \times$$

$$\sum_{n=1}^{\infty} \frac{\left[1 - (-1)^n e^{-\frac{Y}{2}}\right]\left[nY \sin\frac{n\pi z}{L} + 2n^2\pi \cos\frac{n\pi z}{L}\right] e^{-\left(\frac{n^2\pi^2}{Y^2} + \frac{1}{4}\right)\frac{t}{X}}}{(Y^2 + 4n^2\pi^2)^2}\ . \tag{53}$$

From this one gets, for $z = L$,

$$S_T = \frac{Ye^{Y}}{e^{Y}-1} + 8Y \sum_{n=1}^{\infty} \frac{4n^2\pi^2}{(Y^2 + 4n^2\pi^2)^2}\left[(-1)^n e^{\frac{Y}{2}} - 1\right] e^{-\left(\frac{n^2\pi^2}{Y^2} + \frac{1}{4}\right)\frac{t}{X}} \tag{54}$$

and, for $s = 0$,

$$S_B = \frac{Y}{e^Y - 1} + 8Y \sum_{h=1}^{\infty} \frac{4n^2\pi^2}{(Y^2 + 4n^2\pi^2)^2} \left[1 - (-1)^n e^{-\frac{Y}{2}} \right] e^{-\left(\frac{n^2\pi^2}{Y^2} + \frac{1}{4}\right) \frac{t}{X}}. \tag{55}$$

In place of the expansion method of obtaining the solution, one can use the operational calculus, or the Laplace transform, method. This gives a solution in the same form as above (this solution being the limiting form of that obtained in the previous section, for $\omega = \infty$). However, as we have seen, it can also be used to obtain a solution in the form of a power series in t/X, which converges rapidly for small values of this variable. One finds in this way that, for t/X sufficiently small,

$$S_T = 1 + \frac{2}{\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{1}{2}} + \frac{1}{2} \left(\frac{t}{X}\right) + \frac{1}{6\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{3}{2}} + \dots \quad , \tag{56}$$

$$S_B = 1 - \frac{2}{\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{1}{2}} + \frac{1}{2} \left(\frac{t}{X}\right) - \frac{1}{6\sqrt{\pi}} \left(\frac{t}{X}\right)^{\frac{3}{2}} + \dots \quad . \tag{57}$$

Fig. 9 presents families of curves for S_T and S_B as functions of t/X, for various values of Y. Like the curves given in the preceding two sections it uses a logarithmic time scale to facilitate the determination of X for a given column.

5. Column with Infinite Reservoir and Finite Storage Chamber

Thus far we have been considering the behavior of columns which were closed at one end, the other end being either also closed or else connected to a reservoir. Now we consider the case of a column which has one end connected to a reservoir while the other end is connected to a small storage chamber. The presence of the storage chamber lengthens the time of approach to equilibrium. However, it is sometimes used because, among other things, it reduces the disturbance due to sample removal.

Let us first simplify the problem by supposing the reservoir to be infinitely large. This case has been treated by Cohen[3]. Let M_s be the hold-up of the storage chamber. The boundary and initial conditions (if the system is filled throughout with normal material) are given by

$$\left.\begin{array}{lll} z = 0, & t \geqslant 0 : & c = c_o , \\ z = L, & t \geqslant 0 : & M_s \dfrac{\partial c}{\partial t} = \tau , \\ t = 0, & 0 \leqslant z \leqslant L : & c = c_o . \end{array}\right\} \qquad (58)$$

By the use of operational calculus, as before, one finds for the solution

$$\frac{c}{c_o} = e^{\alpha z} - 4\, e^{\frac{\alpha}{2}(z-L)} \times \sum_{n=1}^{\infty} \frac{\mu_n \sin \frac{\theta_n z}{L}\; e^{-k_n t/X}}{(1+\mu_n^2)\left[\frac{2\theta_n}{\beta}\sin\theta_n + \frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right]} , \qquad (59)$$

where

$$\beta = \frac{M}{M_s}, \quad \varkappa_n = \frac{2\theta_n}{Y}, \quad k_n = \frac{1}{4}(\varkappa_n^2 + 1), \tag{60}$$

and θ_n is the n'th positive root of the equation

$$\tan\theta = \frac{\theta}{\frac{Y}{2} + \frac{1}{\beta}\left(\theta^2 + \frac{Y^2}{4}\right)}. \tag{61}$$

Setting $z = L$, we get for $S = S_T$,

$$S = e^Y - 4\sum_{h=1}^{\infty} \frac{\varkappa_n \sin\theta_n \, e^{-k_n t/X}}{(1+\varkappa_n^2)\left[\frac{2\theta_n}{\beta}\sin\theta_n + \frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right]}. \tag{62}$$

Certain other functions are of interest. From (62) one can get the light constituent hold-up in the storage chamber m_s by means of the relation

$$m_s = \frac{MSc_o}{\beta}, \tag{63}$$

while the total light constituent hold-up in the column and storage chamber is found, after some calculation, to be

$$m + m_B = Mc_0 \left\{ \frac{(e^Y - 1)(1 + \frac{Y}{\beta}) - Y}{Y} - \right.$$

$$\left. - \frac{8e^{-\frac{Y}{2}}}{Y} \sum_{n=1}^{\infty} \frac{\kappa_n^2 \, e^{-k_n t/X}}{(1+\kappa_n^2)^2 \left[\frac{2\theta_n \sin \theta_n}{\beta} + \frac{\theta_n}{\sin \theta_n} - \cos \theta_n \right]} \right\} \quad (64)$$

For small values of t/X, by the method used in Sect. 2, one finds

$$S = 1 + \frac{\beta t}{YX} - \frac{4}{3\sqrt{\pi}} \frac{\beta^2}{Y^2} \left(\frac{t}{X}\right)^{3/2} + \ldots \quad (65)$$

If the column is being operated as a stripper rather than as a rectifier, i.e., if the small storage chamber is at the bottom and the large reservoir at the top, the same changes have to be made in the results obtained above as were described in the preceding sections.

If one plots S as a function of t/X for a given value of β, the family of curves obtained for various values of Y is unsatisfactory because the different members of the family cross one another, which makes curve fitting difficult. Hence it is better to take, in place of t/X, the variable $\frac{\beta t}{XY}$, for in that case for small values of this variable all the curves come together (as can be seen from Eq. (65), while for larger values the curves of a particular family spread apart without intersecting.

Fig. 10 presents graphs of S vs. $\frac{\beta t}{XY}$, for various values of Y for the case of a rectifier with $\beta = 1$. As before, a logarithmic scale of abscissas is used to facilitate fitting the calculated curves to experimental points. Fig. 11 presents the corresponding curves for the case of the column run as a stripper.

6. General Case

Finally we consider the general case of a column of hold-up M connected at the bottom to a reservoir of hold-up M_R and at the top to a storage chamber of hold-up M_S. The differential equation is the same as before. The boundary and initial conditions are now given by

$$\begin{aligned} z = 0, \quad & t \geqslant 0 : \quad M_R \frac{\partial c}{\partial t} = - \\ z = L, \quad & t \geqslant 0 : \quad M_S \frac{\partial c}{\partial t} = \\ t = 0, \quad & 0 \leqslant z \leqslant L : \quad c = c_o \end{aligned} \tag{66}$$

The solution for this case, obtained by the use of operational calculus, is found to be

$$c = c_o \frac{Y(\beta\omega + \beta + \omega)e^{\alpha z}}{\beta(Y - \omega) + \omega(Y + \beta)e^{Y}} + \frac{c_o \beta\omega e^{\alpha z/2}}{2Y} \times$$

$$\sum_n \frac{\left[(1 + \frac{2Yk_n}{\beta})\sin\theta_n + \mu_n(e^{-\frac{Y}{2}} - \cos\theta_n)\right]\left[\mu_n \cos\frac{\theta_n z}{L} + (1 - \frac{2Yk_n}{\omega})\sin\theta_n \frac{z}{L}\right]e^{-k_n t/X}}{k_n^2\left[2\theta_n \sin\theta_n + (\beta + \omega)(\frac{\theta_n}{\sin\theta_n} - \cos\theta_n)\right]} \tag{67}$$

where

$$\beta = \frac{M}{M_S}, \quad \omega = \frac{M}{M_R}, \quad \alpha = \frac{H}{K}, \quad Y = \alpha L,$$

$$X = \frac{M}{HY}, \quad \mu_n = \frac{2\theta_n}{Y}, \quad k_n = \frac{1}{4}(1 + \mu_n^2),$$

and θ_n is the n'th positive root of the equation

$$\left[\left(\beta + \frac{Y}{2}\right)\left(\omega - \frac{Y}{2}\right) - \theta^2\right] \sin\theta + \theta\,(\beta + \omega)\cos\theta = 0. \qquad (68)$$

It follows that for $z = L$ one can write

$$S_T = \frac{Y\,(\beta\omega + \beta + \omega)}{\omega\,(Y + \beta) + \beta\,(Y - \omega)e^{-Y}} - \frac{\beta\omega}{2Y} \quad x$$

$$\sum_n \frac{\left[\mu_n^2\left(e^{\frac{Y}{2}} - \cos\theta_n\right) + \mu_n\left(\frac{2Yk_n}{\omega} - 1\right)\sin\theta_n\right] e^{-k_n t/X}}{k_n^2\left[2\theta_n \sin\theta_n + (\beta + \omega)\left(\frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right)\right]}, \qquad (69)$$

while for $z = 0$ one has

$$S_B = \frac{Y\,(\beta\omega + \beta + \omega)}{\beta\,(Y - \omega) + \omega\,(Y + \beta)e^{Y}} + \frac{\beta\omega}{2Y} \quad x$$

$$\sum_n \frac{\left[\mu_n^2\left(e^{-\frac{Y}{2}} - \cos\theta_n\right) + \mu_n\left(\frac{2Yk_n}{\beta} + 1\right)\sin\theta_n\right. e^{-k_n t/X}}{k_n^2\left[2\theta_n \sin\theta_n + (\beta + \omega)\left(\frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right)\right]}. \qquad (70)$$

For small values of $\underline{t}$, one can get power series

expansions of the form:

$$S_T = 1 + \frac{\beta}{Y}\left(\frac{t}{X}\right) - \frac{4}{3\sqrt{\pi}}\,\frac{\beta^2}{Y^2}\left(\frac{t}{X}\right)^{\frac{3}{2}} + \frac{1}{2}\left(\frac{\beta^3}{Y^3} + \frac{\beta^2}{2Y^2}\right)\left(\frac{t}{X}\right)^2 -$$

$$- \frac{8}{15\sqrt{\pi}}\left(\frac{\beta^4}{Y^4} + \frac{\beta^3}{Y^3} + \frac{\beta^2}{8Y^2}\right)\left(\frac{t}{X}\right)^{\frac{5}{2}} + \cdots \quad , \tag{71}$$

$$S_B = 1 - \frac{\omega}{Y}\left(\frac{t}{X}\right) + \frac{4}{3\sqrt{\pi}}\,\frac{\omega^2}{Y^2}\left(\frac{t}{X}\right)^{\frac{3}{2}} + \frac{1}{2}\left(-\frac{\omega^3}{Y^3} + \frac{\omega^2}{2Y^2}\right)\left(\frac{t}{X}\right)^2 +$$

$$+ \frac{8}{15\sqrt{\pi}}\left(\frac{\omega^4}{Y^4} - \frac{\omega^3}{Y^3} + \frac{\omega^2}{8Y^2}\right)\left(\frac{t}{X}\right)^{\frac{5}{2}} + \cdots \quad . \tag{72}$$

Because of the large number of parameters involved, no systematic numerical calculations have been carried out for the general case discussed in this section. However, for given values of the constants it is not difficult to obtain numerical results by the use of equations (68) to (72).

Footnotes

[1]Furry, Jones and Onsager, Phys.Rev. 55, 1083 (1939)

[2]J. Bardeen, Phys.Rev. 57, 35 (1940) and 58, 94 (1940)

[3]Karl Cohen, Columbia University Report No. A-530, Feb.4,1943

CAPTIONS FOR FIGURES IN THEORETICAL CHAPTERS

Chapter 2

Figure 1

The steady state separation factor as a function of the product withdrawal rate for columns possessing various values of P/H.

Figure 2

The solid curve shows the dependence of the separation factor on time for the case of Y = 0.6 calculated on the basis of Eq. (19). The dotted curve shows the approximate dependence obtained from Eq. (19) by neglecting all but the first term in the series.

Figure 3

On the basis of two different definitions of half time, this figure shows how the ratio of the half time to the time constant X depends on Y.

Figure 4

This shows the distribution of concentration along the column at various times.

Figure 5

A family of curves for separation factor as a function of $\frac{t}{X}$ for various values of Y. This for the case of a rectifier operating from an infinite reservoir and with no storage chamber.

Figure 6

A family of curves for separation factor as a function of $\frac{t}{X}$. This is the case of an infinite reservoir located at the top of the column and no storage chamber.

Figure 7

A family of curves for separation factor as a function of $\frac{t}{X}$ for various values of Y. This is for the case of a reservoir at the bottom of the column possessing a hold-up equal to that of the column with no storage chamber.

Figure 8

A family of curves for separation factor as a function of $\frac{t}{X}$ for various values of Y. This is for the case of a stripper having a reservoir of capacity equal to the hold-up of the column and no storage chamber.

Figure 9

A family of curves for separation factor as a function of $\frac{t}{X}$ for various values of Y. This is the case of an isolated column, closed at both ends.

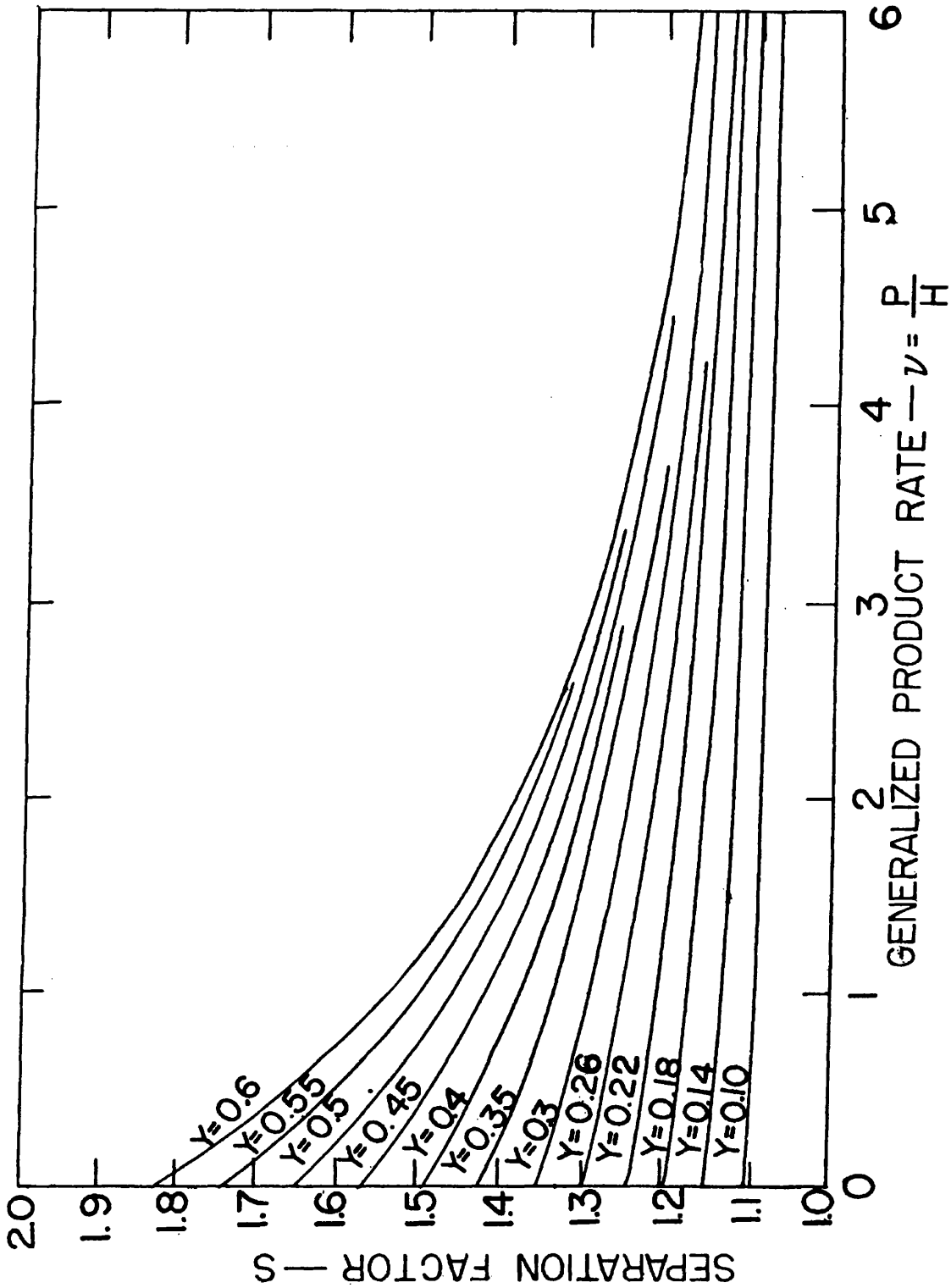
Figure 10

A family of curves for separation factor as a function of $\frac{t}{X}$ for various values of Y. This is the case of a rectifier having an infinite reservoir and a storage chamber at the top possessing a hold-up equal to that of the column.

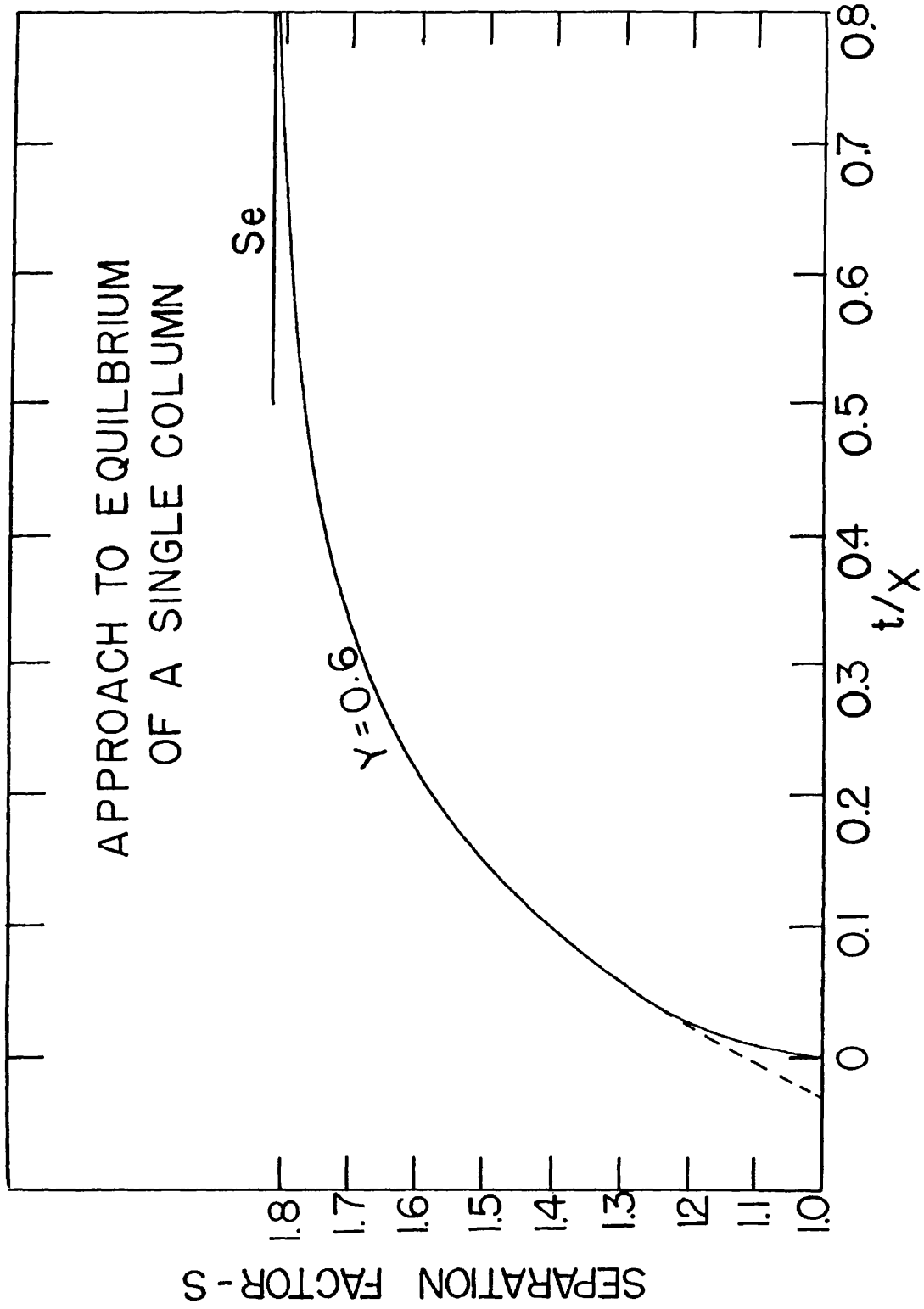
Figure 11

A family of curves for separation factor as a function of

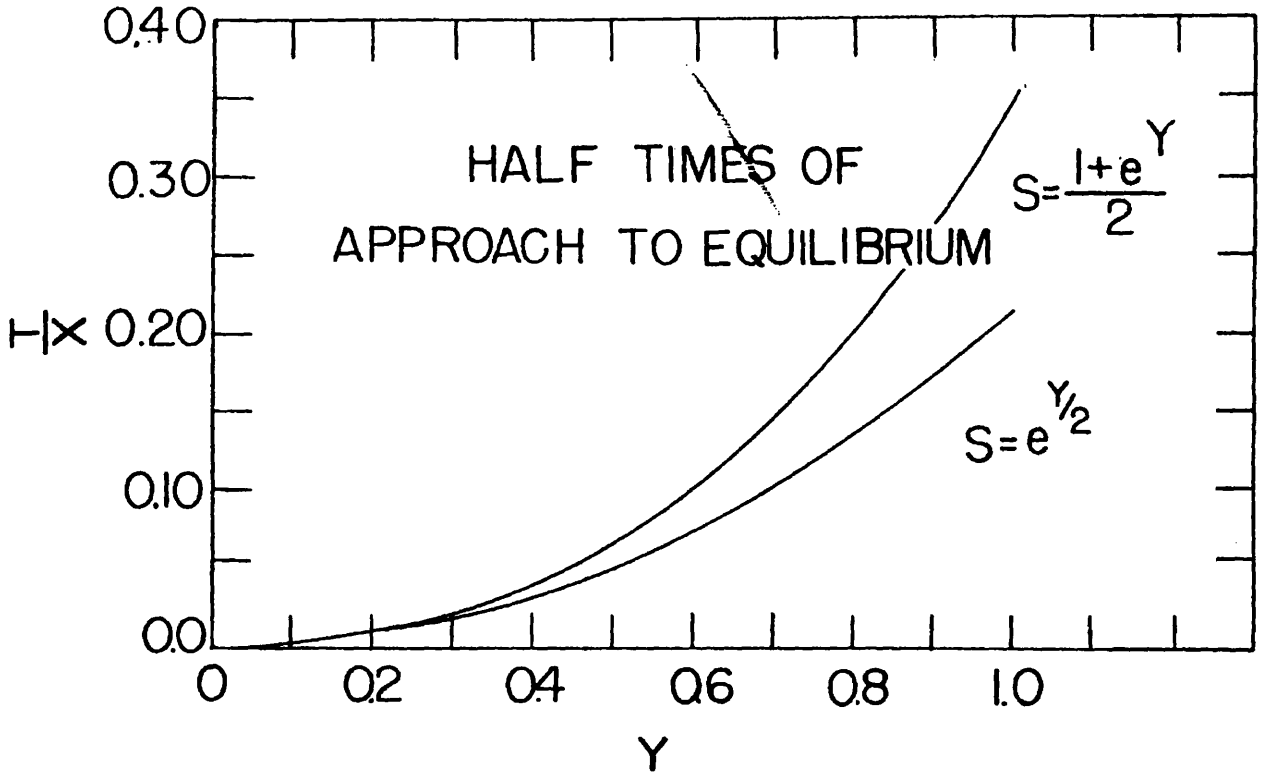
$\frac{t}{X}$ for various values of Y. This is the case of a stripper having an infinite reservoir and a storage chamber at the bottom possessing a hold-up equal to that of the column.



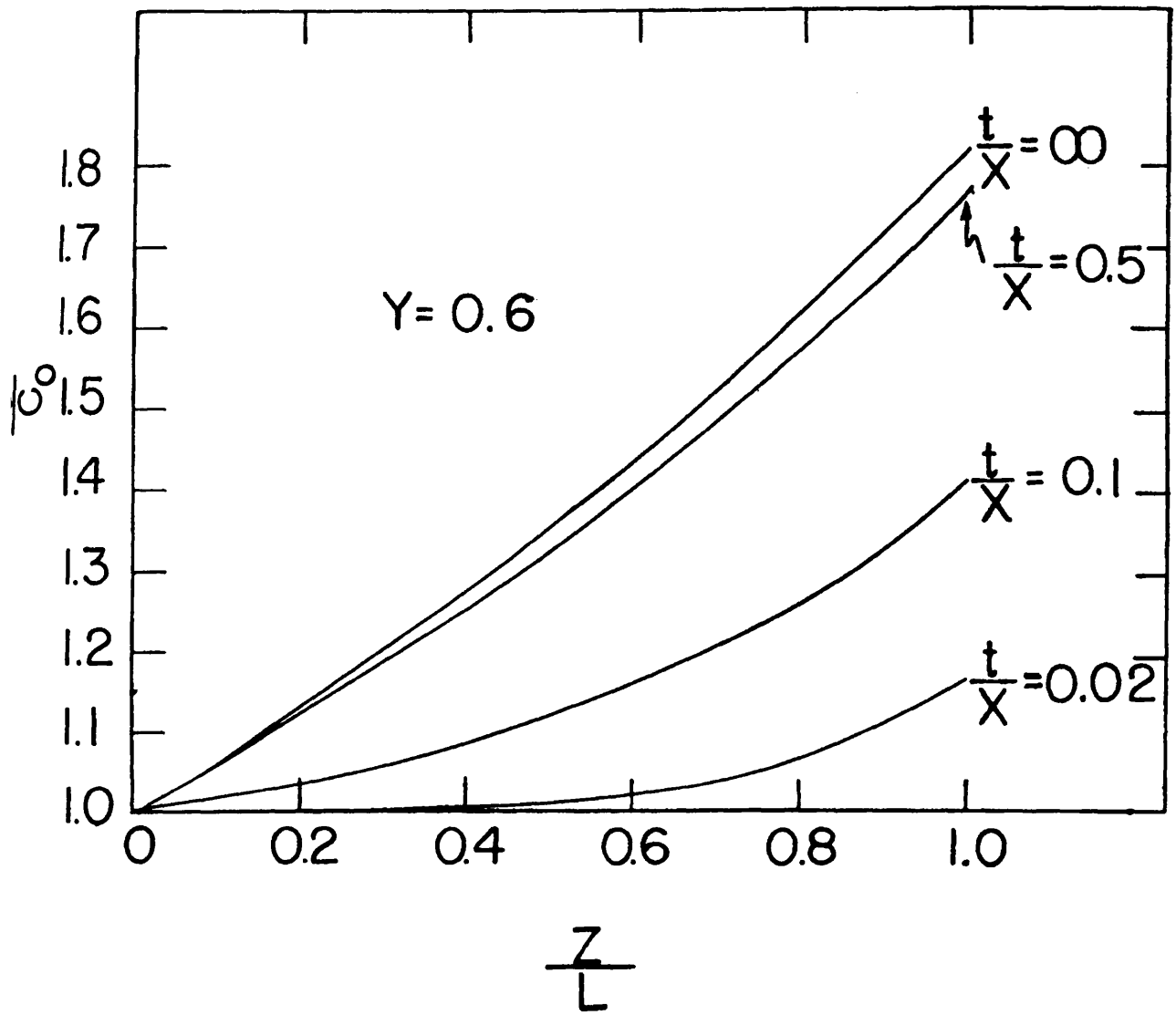
Theoretical Chap. 2 Fig. 1



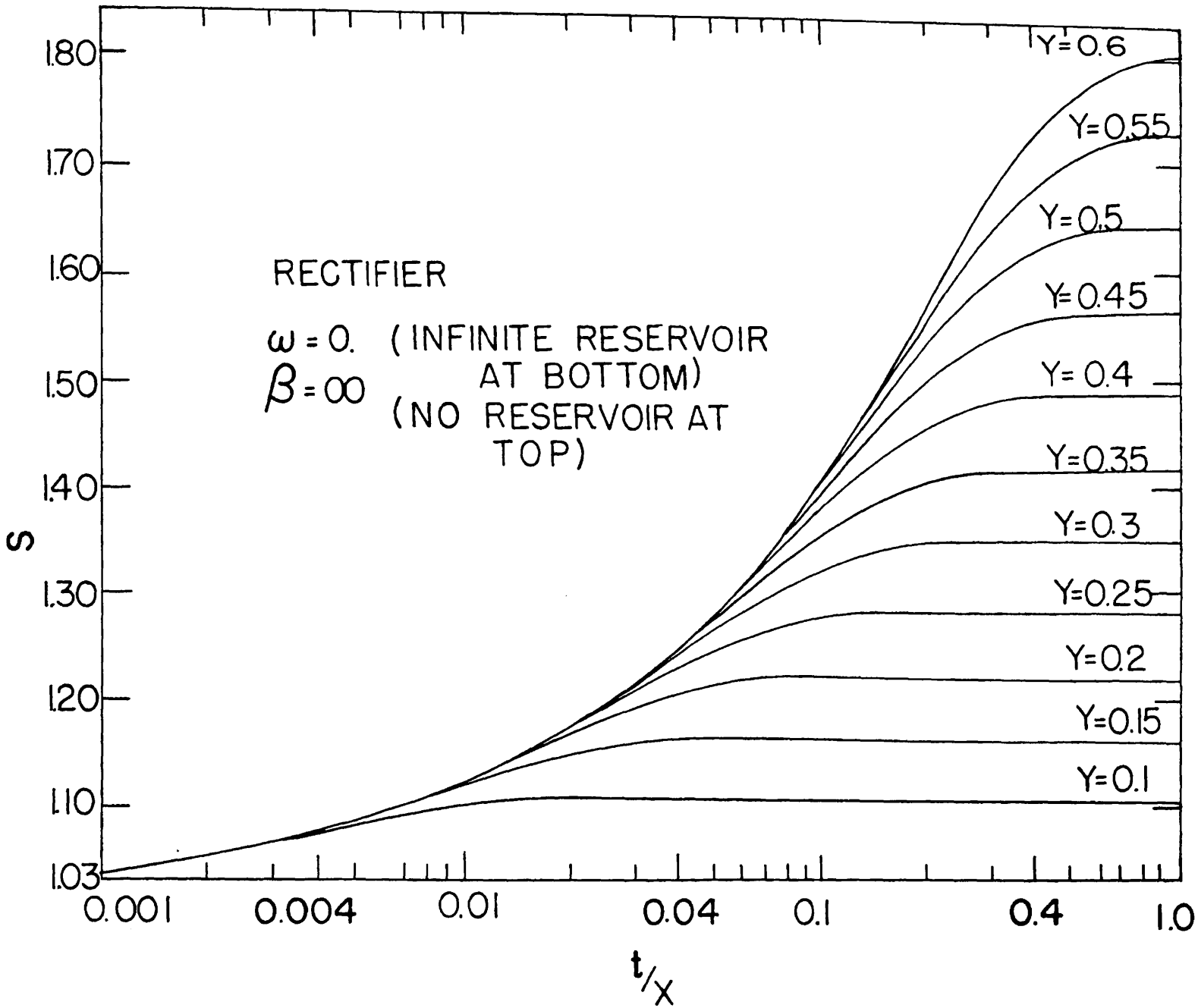
Theoretical Chap. 2 Fig. 2



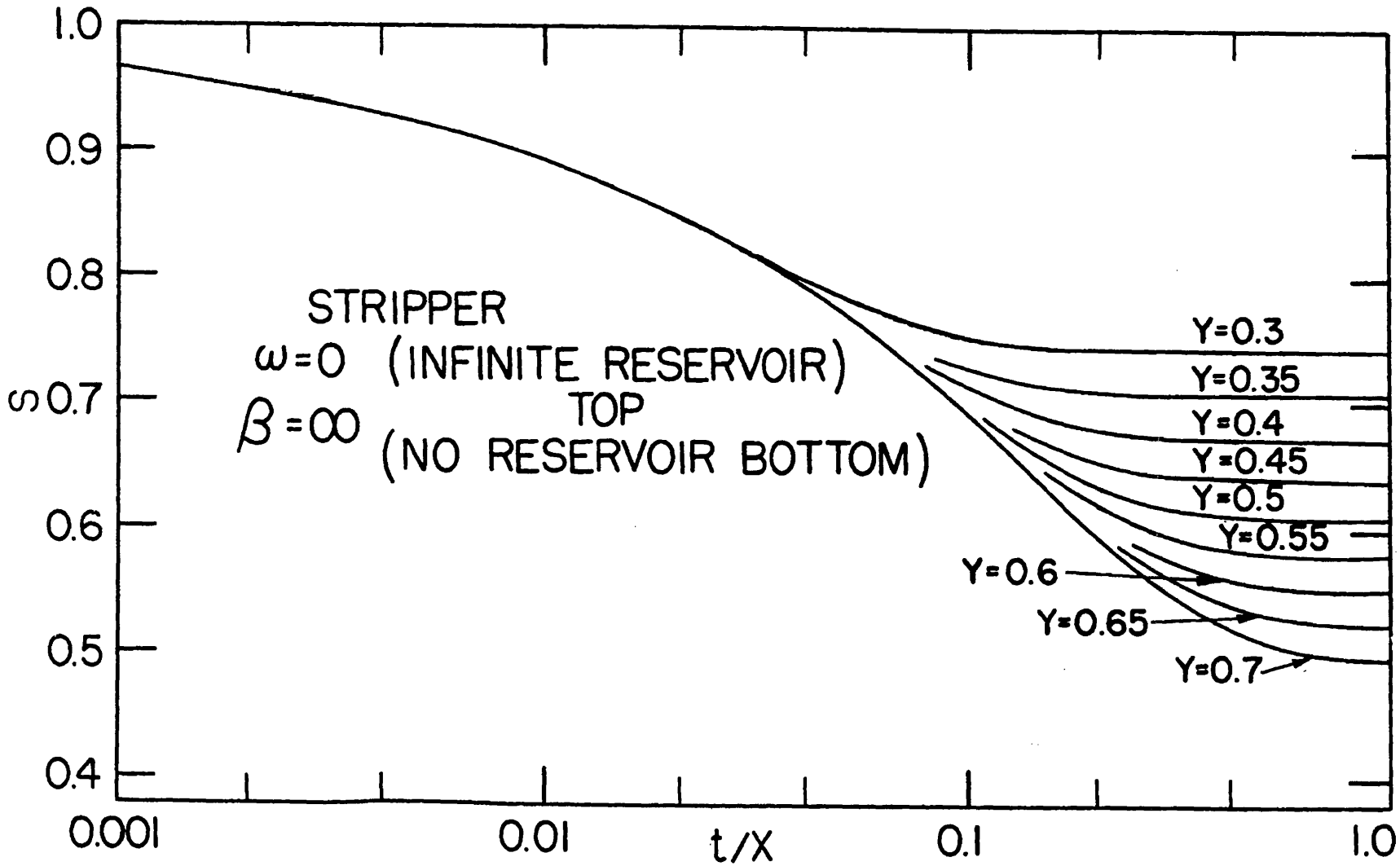
Theoretical Chap. 2 Fig. 3



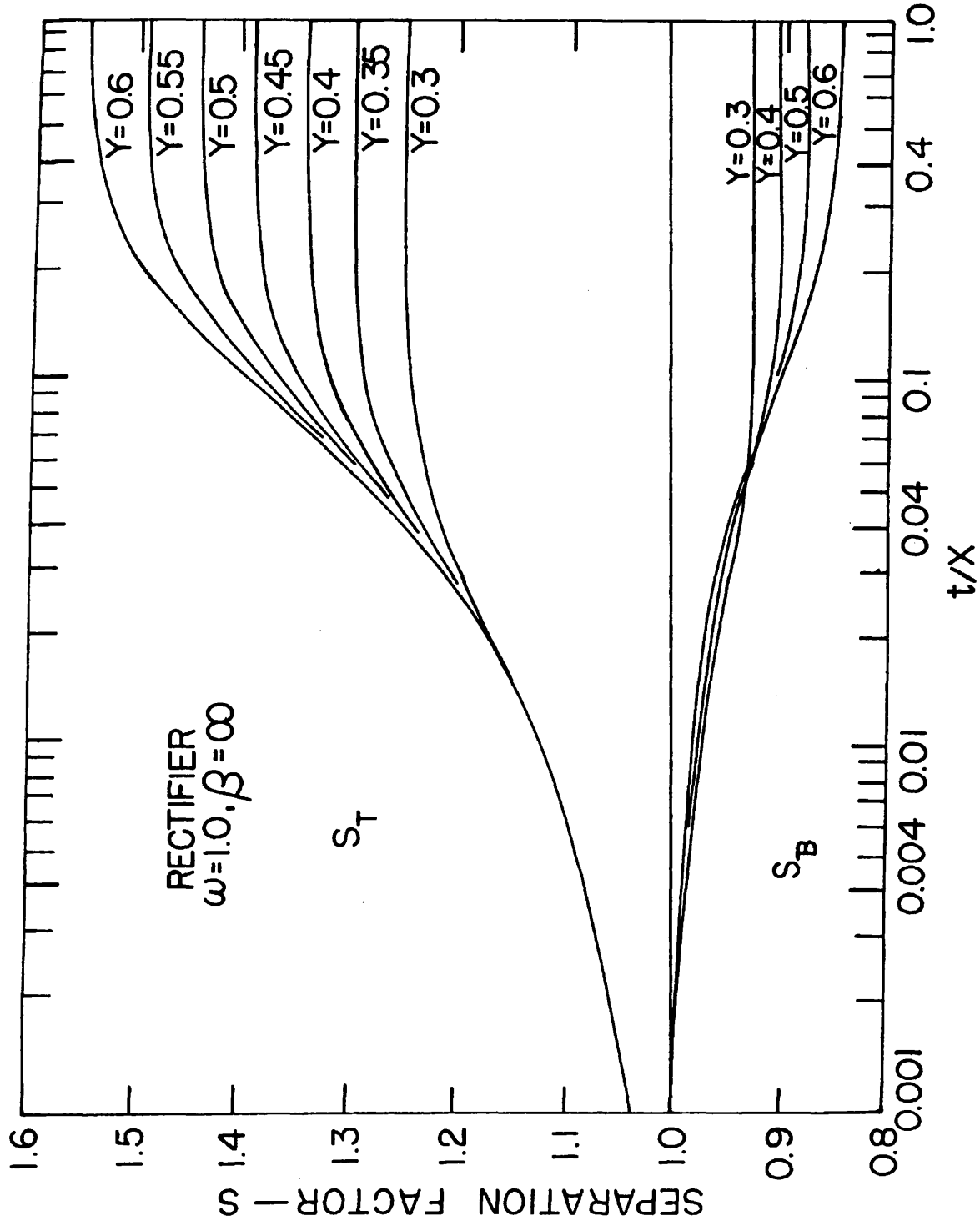
Theoretical Chap. 2 Fig. 4



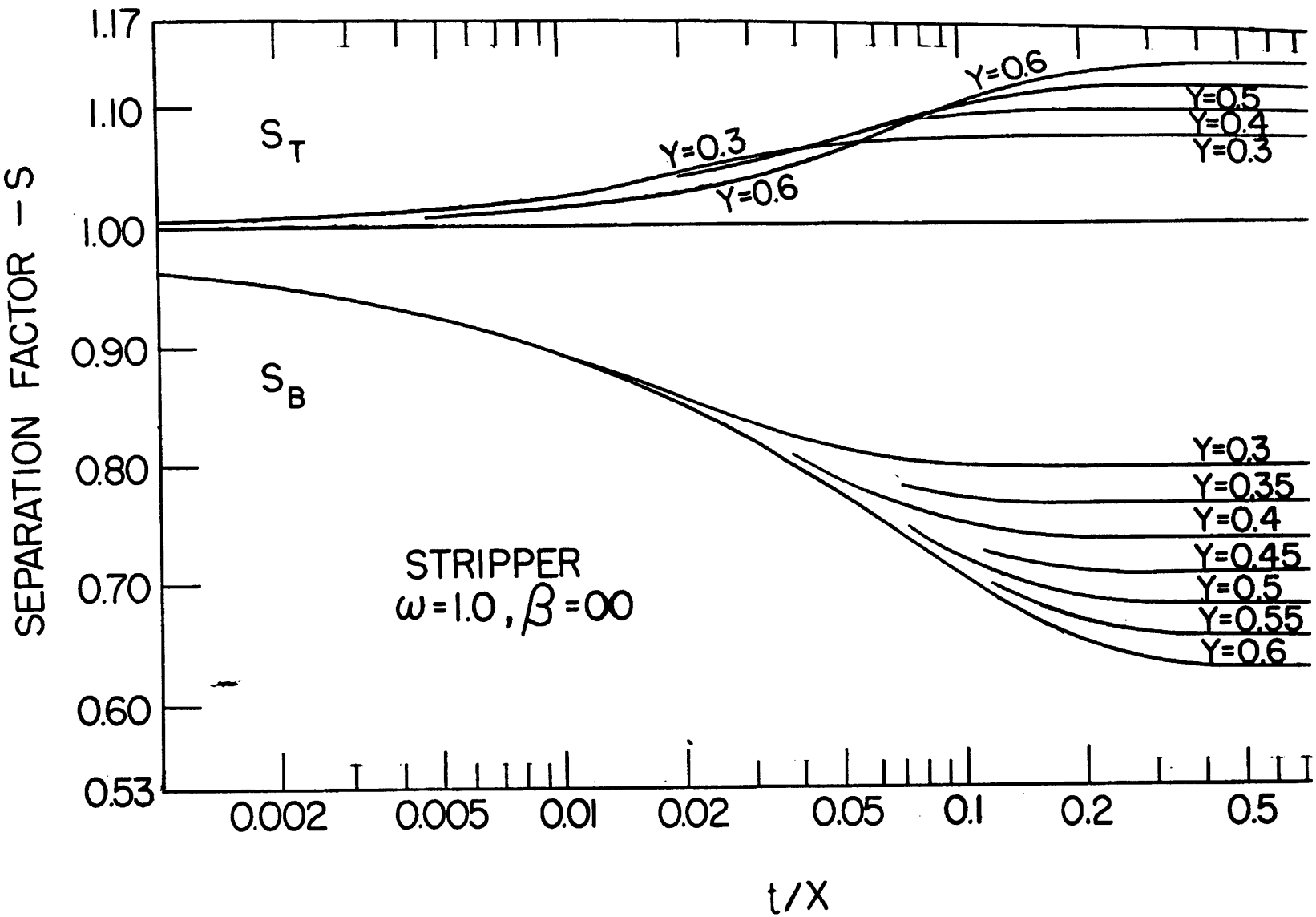
Theoretical Chart Fig. 5



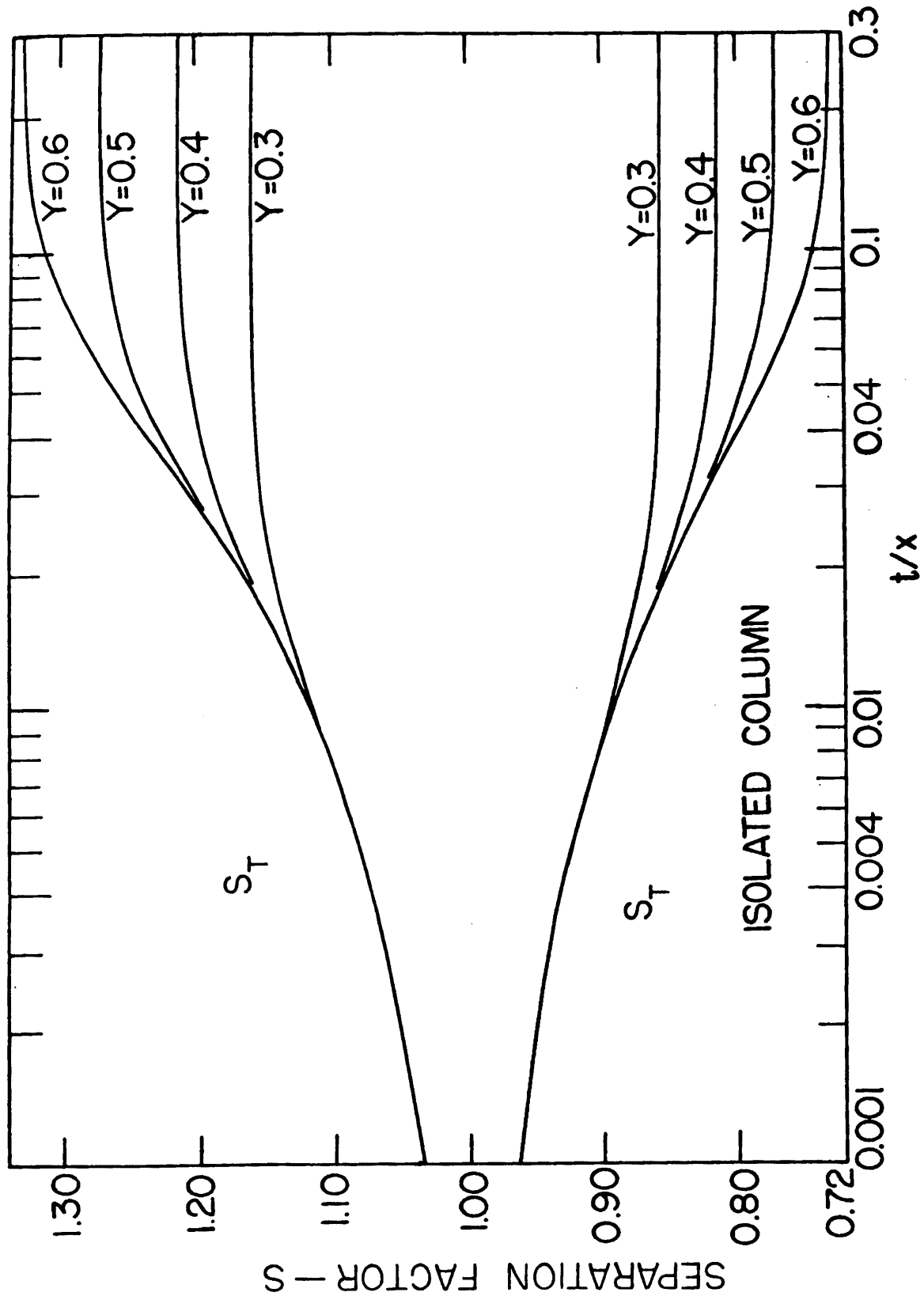
Theoretical Chart Fig. 6



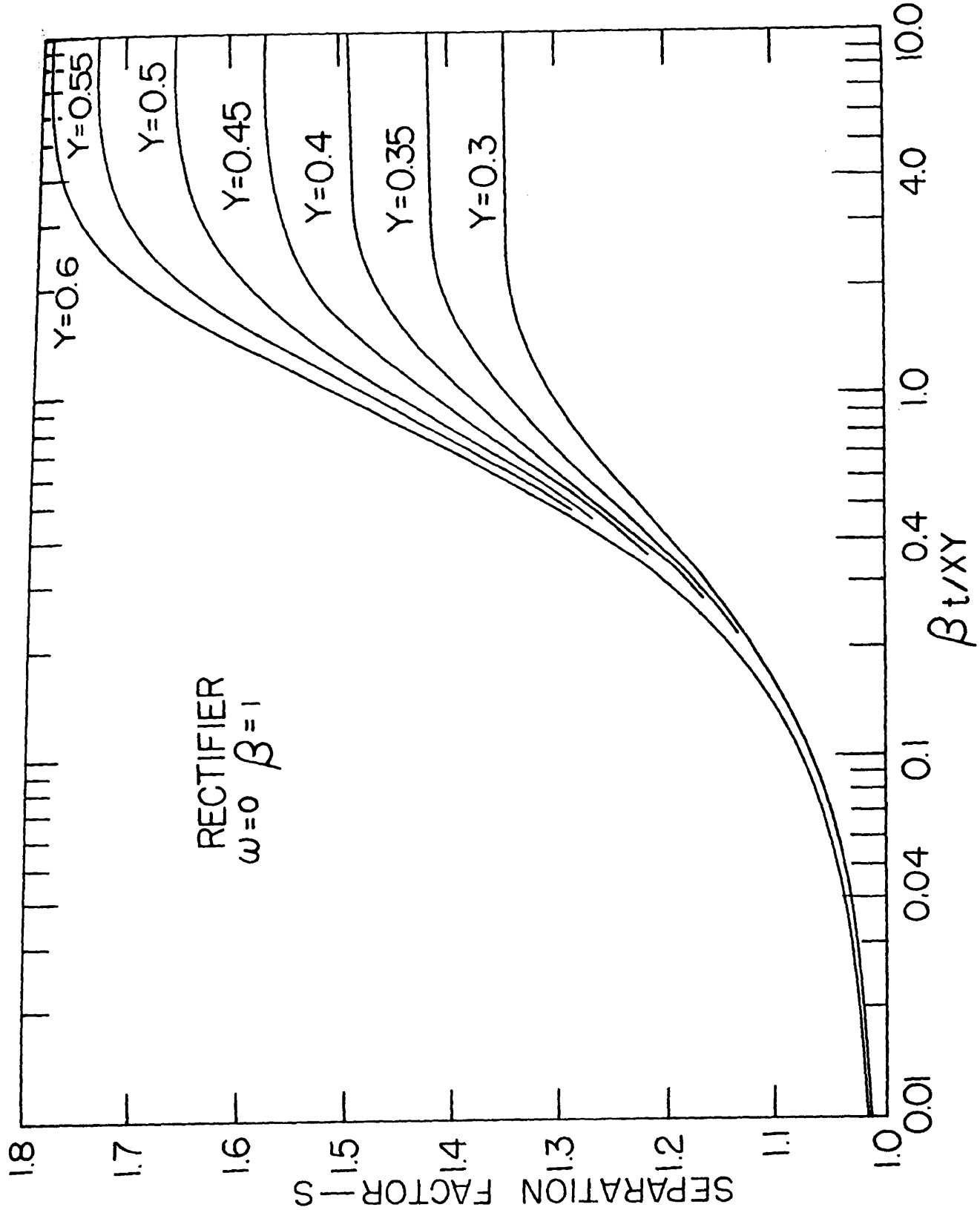
Theoretical Chap 2 Fig. 7



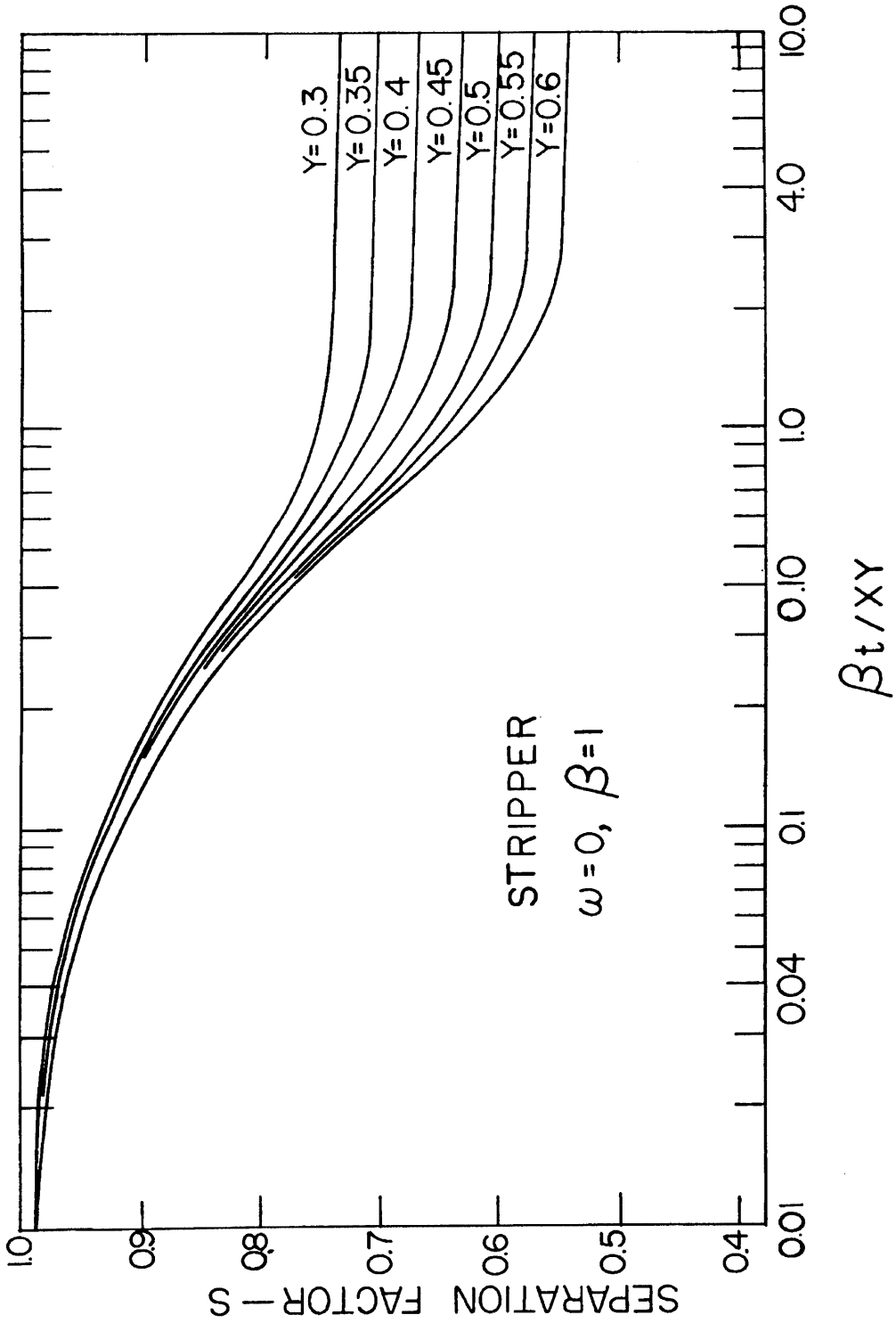
Theoretical Chart Fig. 8



Theoretical Chap 2 Fig. 9



Theoretical Chap 2 Fig. 10



Theoretical Chap.2 Fig.11

CHAPTER III. EFFECT OF CIRCULATION

1. Boundary Conditions

In previous calculations on the approach to equilibrium by a single column, it was assumed that the column was connected to a reservoir or storage chamber so that the concentration at the bottom of the column was the same as that in the reservoir, while the concentration at the top was the same as in the storage chamber. In practice, however, the reservoir, or storage chamber, is connected to the column by means of two tubes through which a continuous circulation of material is maintained by the presence in the circuit of a "convection loop" consisting of two lengths of vertical tubing maintained at different temperatures and connected in series. In such a case there may be an appreciable difference in concentration between the bottom of the column and the reservoir. In the present chapter the effect of this circulation on the behavior of the column during the approach to equilibrium is investigated.

Let us begin by considering the case of the reservoir attached to the bottom of the column, as indicated schematically in Fig. 1. The reservoir has a hold-up M_r and is connected by two tubes to the column, tube No. 1 carrying material from the column to the reservoir and

tube No. 2 carrying material in the reverse direction. Using subscripts 1 and 2 to denote the tube considered, let L be the length, A the cross-sectional area, v the velocity of the material and ρ the density (determined by the temperature). For simplicity we shall assume A, v and ρ to be constant over the entire length of each tube, although possibly different for the two tubes. The generalization to the case where these quantities vary along each tube will be apparent later. If we consider a steady state of circulatory flow then

$$A_1 \rho_1 v_1 = A_2 \rho_2 v_2 = U , \qquad (1)$$

where U is the mass of material circulated per unit time.

Let c_1 be the light-constituent concentration at the bottom of the column at a given time t, and let us suppose that the material, in passing through the bottom of the column, acquires this concentration, so that c_1 is the concentration at the column-end of tube No. 1 at this instant. Let c_2 be the concentration in the reservoir at time t, and again let us assume that this is the concentration at the reservoir-end of tube No. 2. In general, the concentrations will vary along the tubes. Let c_3 be that at the reservoir-end of tube No. 1, and c_4 that of the column-end of tube No. 2, at the time t. At the bottom of the column there will be an upward rate of

transport of light constituent, τ , given by

$$\tau = Hc_1 - K \frac{\partial c_1}{\partial z} \tag{2}$$

where H and K are the column constants. This rate of transport must be equal to the net rate at which light constituent is brought into the column by circulation, or

$$\tau = U (c_4 - c_1) . \tag{3}$$

Correspondingly, for the reservoir we can write the relation

$$M_r \frac{dc_2}{dt} = U (c_3 - c_2) . \tag{4}$$

If we let v denote the fluid velocity in either one of the tubes then we can say that, at a given point in the tube, the concentration c will ordinarily satisfy the equation

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = 0 , \tag{5}$$

where x is the distance along the tube in the direction of flow, the equation expressing the fact that the concentration in a given column element carried along with

the fluid remains constant in time. The solution of Eq. (5) is, of course,

$$\sigma = f\left(t - \frac{x}{v}\right) , \tag{6}$$

where f is an arbitrary function.

Let us set

$$\sigma_1 = f(t) , \qquad \sigma_2 = g(t), \tag{7}$$

where f and g are functions to be determined. Then it follows from the preceding considerations that

$$\sigma_3 = f\left(t - \frac{L_1}{v_1}\right), \qquad \sigma_4 = g\left(t - \frac{L_2}{v_2}\right) . \tag{8}$$

Eqs. (3) and (4) can be written, respectively,

$$g\left(t - \frac{L_2}{v_2}\right) = f(t) + \frac{1}{U} \tau(t) , \tag{9}$$

$$f\left(t - \frac{L_1}{v_1}\right) = g(t) + \frac{M_r}{U} g'(t) , \tag{10}$$

where the prime denotes the derivative with respect to t.

From Eq. (10) we can write

$$f(t - \frac{L_1}{v_1} - \frac{L_2}{v_2}) = g(t - \frac{L_2}{v_2}) + \frac{M_r}{U} g'(t - \frac{L_2}{v_2}) , \qquad (11)$$

and, if we substitute for the terms on the right-hand side the values as obtained from Eq. (9), we get

$$f(t - \frac{L_1}{v_1} - \frac{L_2}{v_2}) = f(t) + \frac{1}{U}\tau(t) + \frac{M_r}{U}\left[f'(t) + \frac{1}{U}\tau'(t)\right] . \qquad (12)$$

If we write

$$T_c = \frac{L_1}{v_1} + \frac{L_2}{v_2} , \qquad T_r = \frac{M_r}{U} \qquad (13)$$

so that T_c, the circulation time, is essentially the time required for a particle of the fluid to go around the circulation loop, while T_r, the replacement time, is the time that would be required to fill the reservoir if material were brought to it at the rate U, then we can put (12) into the form

$$M_r f'(t) + U\left[f(t) - f(t - T_c)\right] = -\tau(t) - T_r \tau'(t). \qquad (14)$$

If we now replace $f(t)$ by $c(t)$, which is to represent the concentration at the bottom of the column, previously denoted by c_1, we obtain the boundary condition that is to hold at the bottom of the column during approach to equilibrium,

$$M_r \frac{dc(t)}{dt} + U \left[c(t) - c\ (t - T_c) \right] = - \tau(t) - T_r \frac{d\tau(t)}{dt}, \quad (15)$$

where τ is given by

$$\tau = Hc - K \frac{\partial c}{\partial z}.$$

It is readily seen that Eq. (15) will remain valid in the case where A, v and ρ are different at different points along the tubes provided we retain for T_c and T_r the meanings assigned above.

In the cases encountered in practice the circulating time T_c is generally negligibly small compared to the time during which the concentration at the bottom of the column changes by an appreciable amount. Usually the replacement time T_r is too large to be neglected. Under these conditions, Eq. (15) can be replaced by

$$M_r \frac{dc}{dt} = - \tau - T_r \frac{d\tau}{dt}, \quad (16)$$

where all the quantities refer to the same moment of time. As a boundary condition, Eq. (16) leads to much simpler calculations than those connected with Eq. (15), and will be used in the subsequent work. Hereafter T_r will be denoted simply by T.

The discussion given above can be carried over to the

case of a storage chamber connected to the top of a column if we replace M_r by M_s, the hold-up of the storage chamber, and change the signs of the terms involving τ and $\frac{d\tau}{dt}$ in Eqs. (15) and (16).

2. Circulation to Reservoir

Let us suppose that we have a column of hold-up M, length L and constants H and K attached at the bottom to a reservoir of hold-up M_r by a circuit with replacement time T and negligible hold-up, and closed at the top. The concentration c in the column, if small compared to unity, satisfies the equation

$$X\alpha^2 \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial z^2} - \alpha \frac{\partial c}{\partial z} , \tag{17}$$

where

$$\alpha = H/K , \qquad X = M/HY , \qquad Y = \alpha L , \tag{18}$$

and z is the distance up the column measured from the bottom. The boundary conditions are:

$$z = 0, \quad M_r \frac{\partial c}{\partial t} = - (Hc - K \frac{\partial c}{\partial z}) - T \frac{\partial}{\partial t} (Hc - K \frac{\partial c}{\partial z}) \tag{19}$$

$$z = L, \quad Hc - K \frac{\partial c}{\partial z} = 0 , \tag{20}$$

while the initial condition is

$$t = 0 , \qquad c = c_0 \tag{21}$$

where c_0 is the normal concentration.

To solve this problem, let us use the method of the Laplace transformation. Let us take

$$h = \int_0^\infty c\, e^{-pt}\, dt . \tag{22}$$

Going over to this variable by carrying out a similar integration of the preceding equations, one gets, corresponding to Eq. (17), if a prime denotes differentiation with respect to z,

$$h'' - \alpha h' - X\alpha^2 p\, h = - X\alpha^2 c_0 . \tag{23}$$

Similarly, (19) gives

$$z = 0, \quad M_r (ph - c_0) = - (Hh - Kh') - pT(Hh - Kh') + \tau_0, \tag{24}$$

where τ_0 is the initial value of τ, which we take to be <u>zero</u> in the present case. Eq. (20) goes over into

$$z = L, \qquad Hh - Kh' = 0 . \tag{25}$$

These equations can be solved for h by letting $\lambda = \sqrt{1 + 4\, Xp}$ and setting

$$h = \frac{c_o}{p} + A\, e^{\frac{\alpha z}{2}} \sinh \frac{\alpha\lambda}{2}(L-z) + B\, e^{\frac{\alpha z}{2}} \cosh \frac{\alpha\lambda}{2}(L-z), \quad (26)$$

which satisfies Eq. (23) for arbitrary values of A and B, then determining these constants so as to satisfy the boundary conditions, Eqs. (24) and (25). Having obtained an expression for h, one can then invert the transformation (22) to obtain c. The final result is found to be

$$\frac{c}{c_o} = \frac{(1+\omega)e^{\alpha z}}{1 + \frac{\omega}{Y}(e^{Y} - 1)} -$$

$$- e^{\frac{\alpha z}{2}} \sum_{n=1}^{\infty} \frac{P_n}{Q_n k_n^2} \left\{ \mu_n \cos \theta_n\left(1-\frac{z}{L}\right) - \sin \theta_n\left(1-\frac{z}{L}\right) \right\} e^{-k_n t/X}, \quad (27)$$

where

$$\omega = \frac{M}{M_r}, \qquad \mu_n = \frac{Y}{2}\theta_n, \qquad k_n = \frac{1}{4}(1 + \mu_n^2), \quad (28)$$

with θ_n the n'th positive root of the equation

$$\tan \theta = \frac{\theta}{\frac{Y}{2} - \omega\left[1 - \frac{T}{X}\left(\frac{\theta^2}{Y^2} + \frac{1}{4}\right)\right]}, \quad (29)$$

while P_n and Q_n are given by

$$P_n = \frac{1}{2}\,\omega\kappa_n\left[1 - \frac{T\,k_n}{X}\right] \times$$

$$\left[1 + e^{-\frac{Y}{2}}\left(\kappa_n \sin\theta_n - \cos\theta_n\right) + Y\kappa_n k_n\, e^{-\frac{Y}{2}}\cos\theta_n\right]; \quad (30)$$

$$Q_n = Y\left(\frac{\theta_n}{\sin\theta_n} - \cos\theta_n\right) + \frac{\omega T}{X}\,\kappa_n \sin\theta_n\,. \quad (31)$$

If we let c_B denote the concentration at the bottom of the column ($z = 0$) and c_T that at the top ($z = L$), then it follows from (27) that

$$S_B \equiv \frac{c_B}{c_o} = \frac{1+\omega}{1 + \frac{\omega}{Y}\left(e^{Y} - 1\right)} -$$

$$- \sum_{n=1}^{\infty} \frac{P_n}{Q_n k_n^2}\left[\kappa_n' \cos\theta_n - \sin\theta_n\right] e^{-k_n t/X}\,, \quad (32)$$

$$S_T \equiv \frac{c_T}{c_o} = \frac{(1+\omega)e^{Y}}{1 + \frac{\omega}{Y}\left(e^{Y}-1\right)} - e^{\frac{Y}{2}} \sum_{n=1}^{\infty} \frac{P_n \kappa_n}{Q_n k_n^2}\, e^{-k_n t/X}\,. \quad (33)$$

From (27) one also finds that, for $z = 0$

$$\tau = 2\,Hc_o \sum_{n=1}^{\infty} \frac{P_n}{Q_n k_n} \sin\theta_n \, e^{-k_n t/X} . \tag{34}$$

Now, if we let c_R denote the concentration in the reservoir and U the rate of circulation in the connecting tubes, then (if we can neglect the circulation time) from Eq. (3) we have

$$c_R = c_B + \frac{\tau}{U} . \tag{35}$$

Using (32) and (34) one gets

$$\frac{c_R - c_B}{c_o} = \frac{2\omega T}{XY} \sum_{n=1}^{\infty} \frac{P_n}{k_n Q_n} \sin\theta_n \, e^{-k_n t/X} . \tag{36}$$

By way of illustration, Fig. 2 presents graphs of S_T, S_B and $S_R = \frac{c_R}{c_o}$ as functions of t/X for the case $Y = 0.35$, $\omega = 0.6$ with $T/X = 0$ and 0.2. It can be seen that for a sufficiently large value of T/X the behavior of the concentration can differ markedly from that in the case of T/X negligible.

3. <u>Circulation to Storage Chamber</u>

In the present section we consider the case of a column attached at the bottom to a very large storage chamber so that the concentration there remains constant, while at

the top it is attached to a storage chamber by means of a circulating system, as previously described. Let M_s be the hold-up mass of the storage chamber and let T be the replacement time. The differential equation satisfied by the concentration c is the same as in the preceding section, i.e., Eq. (17), but the boundary conditions are now different. We now have

$$z = 0, \qquad c = c_0 \tag{37}$$

$$z = L, \qquad M_s \frac{\partial c}{\partial t} = Hc - K \frac{\partial c}{\partial z} + T \frac{\partial}{\partial t} \left(Hc - K \frac{\partial c}{\partial z}\right). \tag{38}$$

The initial conditions are given by:

$$\left.\begin{array}{lll} t = 0, & c = c_0 & (0 \leqslant z \leqslant L), \\ & \tau = 0 & (z = L). \end{array}\right\} \tag{39}$$

The solution in this case can be obtained again by the use of the Laplace transformation and is found to be:

$$\frac{c}{c_0} = e^{\alpha z} - e^{\frac{\alpha}{2}(z-L)} \sum_{n=1}^{\infty} \frac{\mu_n \left(1 - Tk_n/X\right) \sin \frac{\theta_n z}{L} e^{-k_n t/X}}{R_n k_n}, \tag{40}$$

where

$$R_n = \left(\frac{Y}{\beta} - \frac{T}{2X}\right)\varkappa_n \sin\theta_n +$$

$$+ \left(1 - \frac{Tk_n}{X}\right)\frac{\theta_n}{\sin\theta_n} - \left[1 - \frac{T}{X}\left(k_n + \frac{1}{2}\varkappa_n^2\right)\right]\cos\theta_n, \qquad (41)$$

with

$$\beta = \frac{M}{M_s} \qquad (42)$$

and θ_n the n'th root of the equation

$$\tan\theta = \frac{\theta}{\frac{Y}{2} + \frac{Y^2}{\beta}\,\frac{k}{1 - Tk/X}}, \qquad (43)$$

where

$$k = \frac{1}{4}(1 + \varkappa^2) = \frac{\theta^2}{Y^2} + \frac{1}{4}. \qquad (44)$$

From Eq. (40) one gets

$$S_T = \frac{c_T}{c_o} = e^Y - \sum_{n=1}^{\infty}\frac{\varkappa_n}{k_n R_n}(1 - Tk_n/X)\sin\theta_n\, e^{-k_n t/X}, \qquad (45)$$

where c_T is the concentration at the top of the column ($z = L$).

If we let c_s denote the concentration in the storage chamber then we can write

$$c_s = c_T - \frac{\beta T}{M} \tau_{(z=L)} . \tag{46}$$

It follows that

$$\frac{c_T - c_s}{c_o} = \frac{\beta T}{2XY} \sum_{n=1}^{\infty} \frac{\kappa_n}{k_n R_n} \left(1 - \frac{T k_n}{X}\right) (\kappa_n \cos \theta_n - \sin \theta_n) e^{-k_n t/X} . \tag{47}$$

As an example, Fig. 3 gives S_T and $S_S \equiv \frac{c_s}{c_o}$ for the case $Y = 0.35$, $\beta = 2.7$ and $\frac{T}{X} = 0.01$ and also, for comparison, $S_T = S_S$ for $\frac{T}{X} = 0$.

Chapter 3

Figure 1

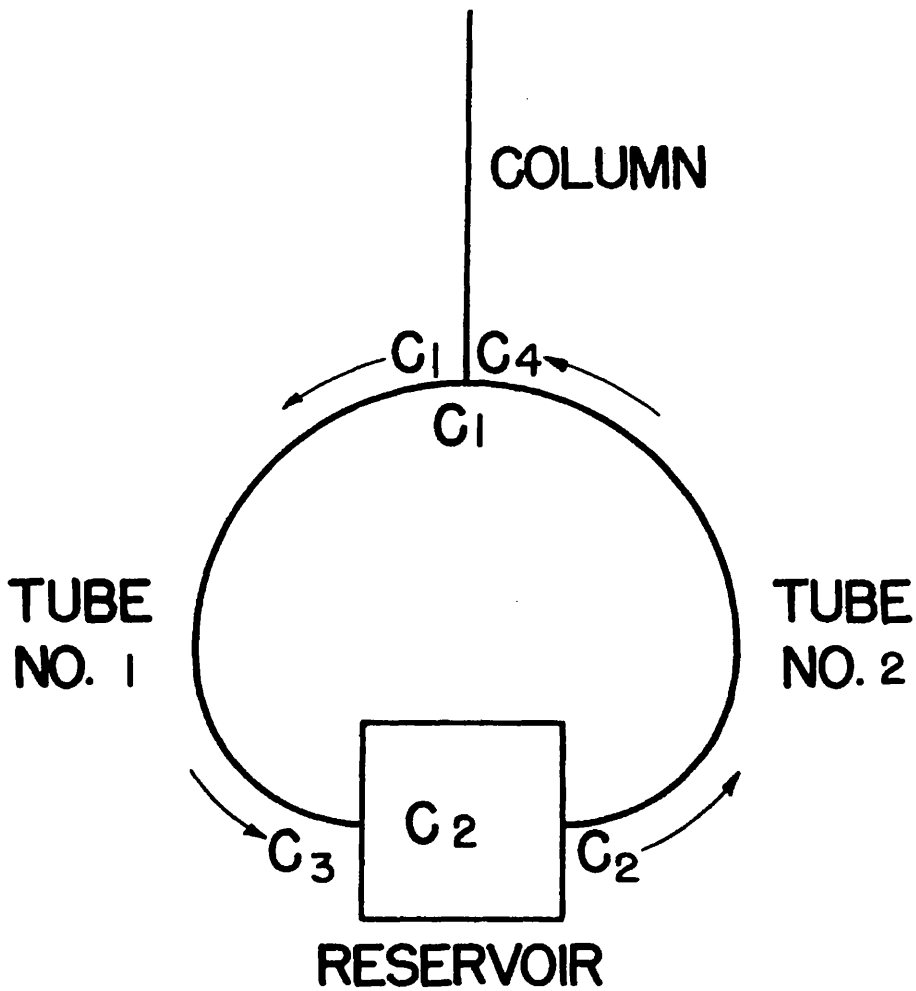
Schematic diagram showing column, reservoir, and circulating system.

Figure 2

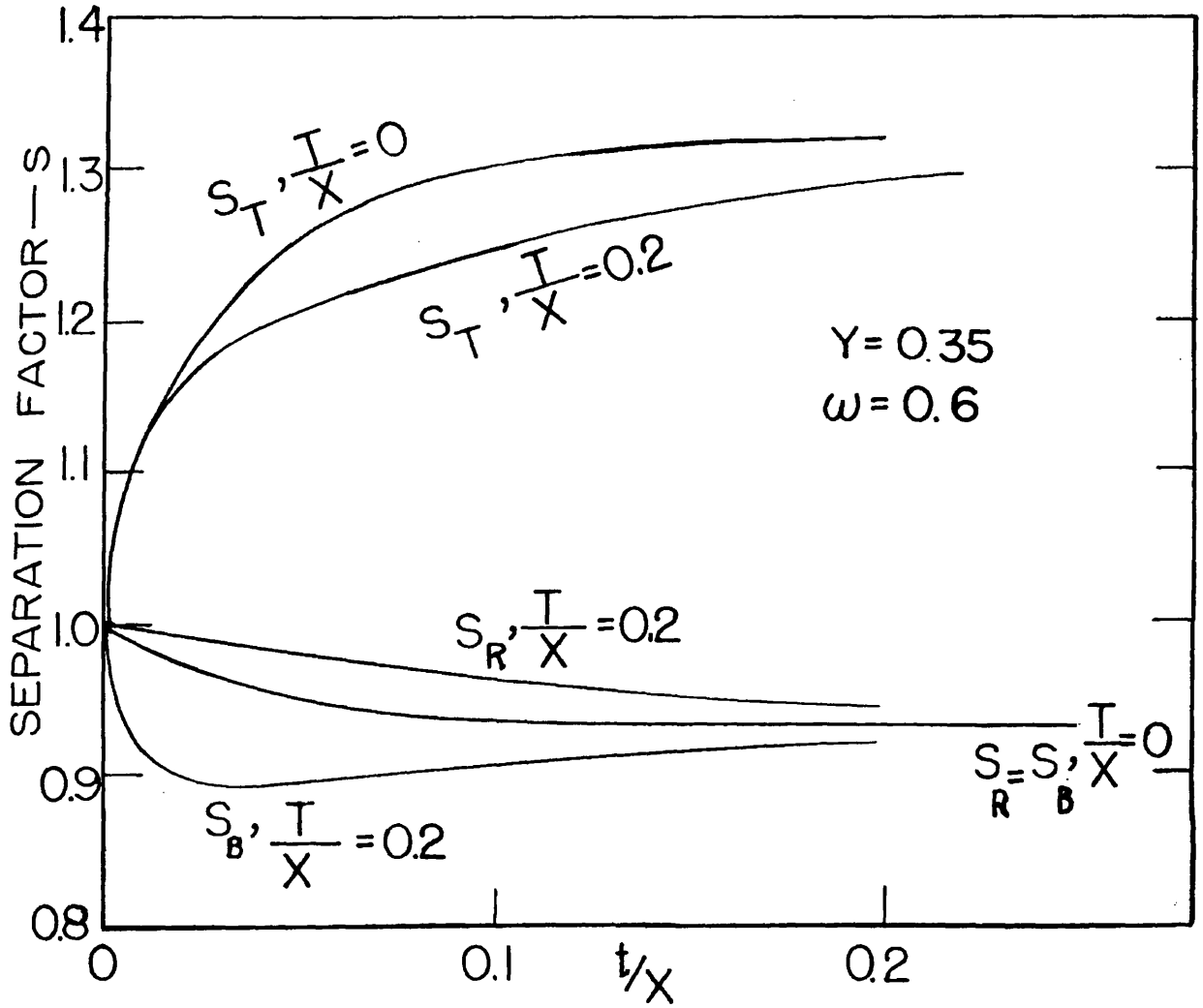
Comparison of effect of good circulation (T/X = 0) with that of slow circulation (T/X = .2). The result of poor circulation is to slow down the approach to equilibrium. This is for the case of a rectifier with an infinite reservoir and a finite storage chamber at the top, connected by a circulating system, T being the replacement time.

Figure 3

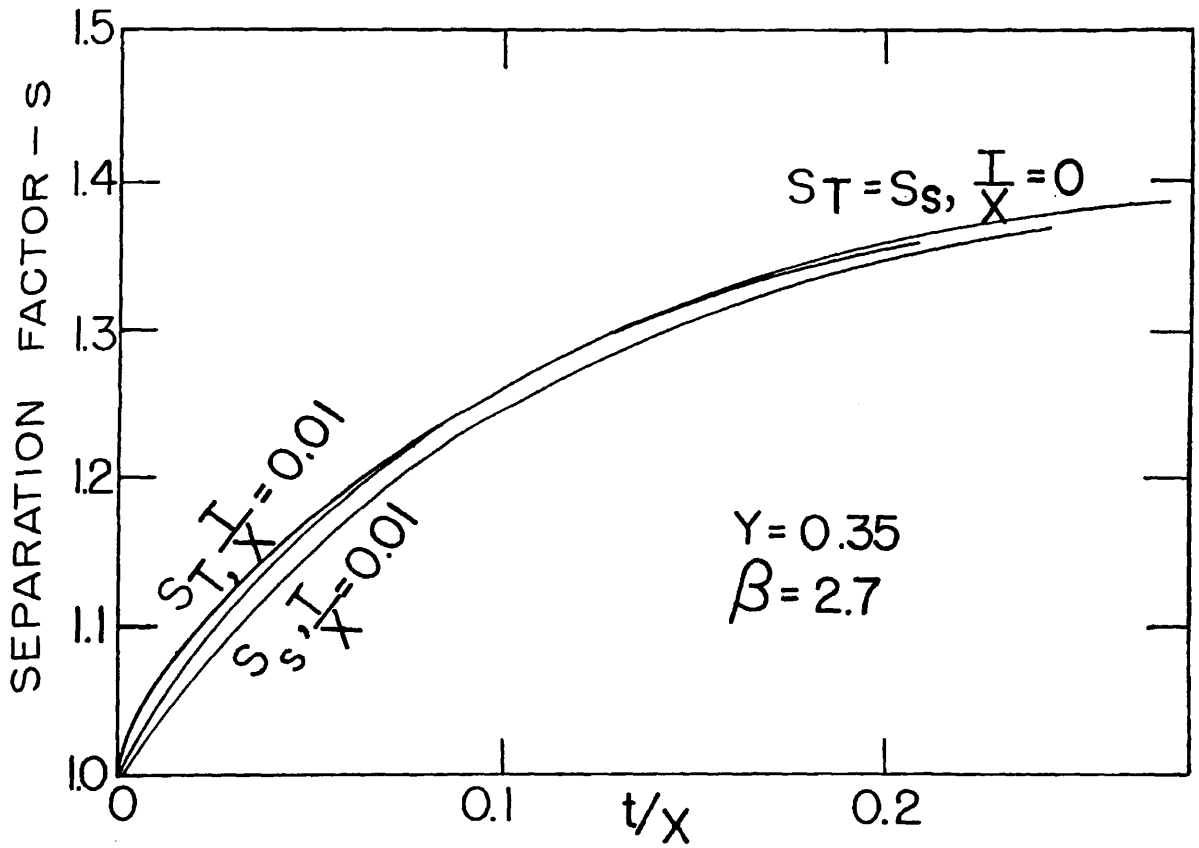
Comparison of effect of fast circulation (T/X = 0) to slow circulation (T/X = 0.01) on approach to equilibrium. This is for the case of a rectifier with an infinite reservoir and a finite storage chamber at the top, connected by a circulating system, T being the replacement time.



Theoretical Chap. 3 Fig. 1



Theoretical Chap. 3 Fig. 2



Theoretical Chap. 3 Fig. 3

CHAPTER IV. THE CONTINUOUS PYRAMID

1. Equations

In the case of a pyramid containing a large number of stages, it is often possible to obtain a good approximation by supposing the actual pyramid to be replaced by a single column having a continuously varying cross-section, the latter at any height being nearly proportional to the number of parallel columns in the pyramid at the corresponding stage. Such a continuous pyramid, or pyramid with infinitesimal steps, has been discussed by Jones and Furry[1] and by Cohen[2].

Let us consider the case of steady flow. We have seen that the process in a single column is described approximately by the equation

$$\tau = Pc + Hc\,(1-c) - K\frac{dc}{dz}\ , \qquad (1)$$

where τ is the net upward rate of transport of the light constituent, P is the rate of upward flow of the fluid, or rate of withdrawal, $\underline{c}$ the concentration of the light constituent, $\underline{z}$ the distance up the column measured from the bottom, and $\underline{H}$ and $\underline{K}$ are the "column constants". The column constants H and K are proportional to the cross-sectional area of the column. Hence if, instead of a single column, we have $\underline{n}$ columns in parallel, then for the equivalent column one can write

$$H = nH_1 \ , \qquad\qquad K = nK_1 \tag{2}$$

where H_1 and K_1 are the corresponding constants for a single column. It should be pointed out that Eq. (1) was originally derived for the case in which H and K are constant, while we shall be considering them as functions of z. However, if $\underline{n}$ in (2) is a function of $\underline{z}$ that varies sufficiently slowly, one can expect that the equation can still be used.

In the case of steady flow, τ is constant and is given by

$$\tau = Pc^* \tag{3}$$

where c^* is the value of $\underline{c}$ at the top of the pyramid where the liquid is withdrawn. Let us define

$$\alpha = \frac{H}{K} = \frac{H_1}{K_1} \tag{4}$$

and

$$\nu = \frac{P}{H} = \frac{P}{nH_1} \ . \tag{5}$$

Then (1) can be written

$$\frac{dc}{dz} = \alpha c\,(1-c) - \alpha\nu\,(c^* - c) \ . \tag{6}$$

2. Optimum Performance

(a) The problem of the optimum design of a continuous pyramid can be formulated in various ways. One possibility is to require n as a function of z so that the pyramid will yield a fixed product rate P of material of fixed concentration c^*, when the input concentration is c_o, with the smallest possible number of columns.

If we let L_1 be the length of a single column, then the number of columns in an element of length dz will be ndz/L_1 and the total number of columns in the pyramid, N, by Eqs. (4), (5) and (6), will be

$$N = \frac{K_1}{L_1} \int_{c_o}^{c^*} \frac{n^2 dc}{H_1 nc(1-c) - P(c^*-c)} . \tag{7}$$

Let us introduce a small arbitrary variation in n, δn. The corresponding variation δN of N is then

$$\delta N = \frac{K_1}{L_1} \int_{c_o}^{c^*} \frac{H_1 n^2 c(1-c) - 2nP(c^*-c)}{\left[H_1 nc(1-c) - P(c^*-c)\right]^2} \, ndc . \tag{8}$$

The necessary condition that N be a minimum is that δN vanish for arbitrary δn. The latter will be the case if

$$n = \frac{2P\,(c^* - c)}{H_1\, c(1 - c)} = \frac{2P}{H_1} \left\{ \frac{c^*}{c} - \frac{1 - c^*}{1 - c} \right\} , \tag{9}$$

or

$$\nu = \frac{c\,(1 - c)}{2\,(c^* - c)} . \tag{10}$$

It follows from (6) that in this case

$$\frac{dc}{dz} = \frac{\alpha}{2}\, c\,(1 - c) . \tag{11}$$

This integrates to give

$$S = e^{\frac{\alpha z}{2}} , \tag{12}$$

where

$$S = \frac{c\,(1 - c_o)}{c_o\,(1 - c)} . \tag{13}$$

For the whole pyramid we get ($c = c^*$)

$$S^* = e^{\frac{\alpha L}{2}} \tag{14}$$

If one solves (12) and (13) for $\underline{c}$ and substitutes into (9) one gets $\underline{n}$ as a function of $\underline{z}$. This will be considered below in greater detail.

It will be noticed that in the equilibrium case, in which $\sigma = 0$, integration of (6) gives, corresponding to (12),

$$s_e = e^{\alpha z} \tag{15}$$

so that one has

$$s = \sqrt{s_e} \tag{16}$$

for optimum performance. This relation holds for any part of the pyramid, as well as for the pyramid as a whole.

(b) An alternative formulation of the optimum-design problem is to require $\underline{n}$ as a function of $\underline{z}$ so that the pyramid will contain a fixed number of columns, N, will give a fixed product rate P, and, for a given input concentration c_o, will have a maximum withdrawal concentration c^*.

In this case the number of columns, N, as given by (7) is fixed, so that δN vanishes. If we carry out a small variation δn, we must take into account a possible variation, δc^* of c^*, since the latter is not fixed. We get, letting n^* be the value of n for $c = c^*$,

$$\left\{ \frac{n^*}{H_1\, c^*\, (1 - c^*)} + P \int_{c_0}^{c^*} \frac{n^2\, dc}{\left[H_1\, nc\, (1 - c) - P\, (c^* - c)\right]^2} \right\} \delta c^* +$$

$$+ \int_{c_0}^{c^*} \left\{ \frac{2n}{H_1\, nc\, (1 - c) - P\, (c^* - c)} - \right.$$

$$\left. - \frac{n^2\, H_1\, c\, (1 - c)}{\left[H_1\, nc\, (1 - c) - P\, (c^* - c)\right]^2} \right\} \delta n dc = 0. \qquad (17)$$

However, if c^* has its maximum value, then δc^* vanishes for arbitrary δn. This will occur only if the coefficient of δn vanishes, in which case we find that we get Eq. (9) once more.

The continuous pyramid for which (9) holds will be referred to as the ideal pyramid.

3. <u>Structure of the Pyramid</u>

From the equations in the preceding sections we can find the number of columns in parallel at any height $\underline{z}$ in the ideal pyramid. If we define the complementary separation factor S^c by the equation

$$S^c = S^*/S = e^{\frac{\alpha}{2}(L-z)} \qquad (18)$$

then we find that

$$\sigma = \frac{\sigma^*}{\sigma^* + S^{\sigma}(1 - \sigma^*)} \quad , \tag{19}$$

and, putting this into Eq. (9) we get the result

$$n = \frac{2P}{H_1}\left[(1 - \sigma^*)(S^{\sigma} - 1) + \sigma^*\left(1 - \frac{1}{S^{\sigma}}\right)\right] \quad , \tag{20}$$

$$= \frac{2P}{H_1}\left[(1 - \sigma^*)\, e^{\frac{\alpha}{2}(L - z)} - \sigma^*\, e^{-\frac{\alpha}{2}(L - z)} + 2\sigma^* - 1\right] . \tag{21}$$

Let $N(z_1, z_2)$ be the number of columns in the pyramid in the height range between z_1 and z_2, $(z_2 > z_1)$. It is given by

$$N(z_1, z_2) = \frac{1}{L_1}\int_{z_1}^{z_2} n\,dz \quad , \tag{22}$$

and, if we make use of (9) and (11), we can write

$$N(z_1, z_2) = \frac{4P}{\alpha L_1 H_1}\int_{\sigma(1)}^{\sigma(2)} \frac{\sigma^* - \sigma}{\sigma^2(1 - \sigma)^2}\, d\sigma \quad ,$$

$$= \frac{4P}{\alpha L_1 H_1}\left\{(2\sigma^* - 1)\ln\frac{S_{(2)}}{S_{(1)}} + \right.$$

$$\left. + (1 - \sigma^*)\, S^*\left(\frac{1}{S_{(1)}} - \frac{1}{S_{(2)}}\right) - \frac{\sigma^*}{S^*}\left(S_{(2)} - S_{(1)}\right)\right\} , \tag{23}$$

where $o_{(1)} = o(z_1)$, $o_{(2)} = o(z_2)$, $S_{(1)} = S(z_1)$, $S_{(2)} = S(z_2)$. From (23) or by direct integration of (21) one gets

$$N(z_1\ z_2) = \frac{4P}{\alpha L_1 H_1}\left\{(o^* - \frac{1}{2})\ \alpha(z_2 - z_1) + \right.$$

$$\left. + (1 - o^*)\, e^{\frac{\alpha L}{2}}\left(e^{-\frac{\alpha z_1}{2}} - e^{-\frac{\alpha z_2}{2}}\right) - o^*\, e^{-\frac{\alpha L}{2}}\left(e^{\frac{\alpha z_2}{2}} - e^{\frac{\alpha z_1}{2}}\right)\right\}. \quad (24)$$

By means of the relation between S^* and o^*, corresponding to (13), Eq. (23) can be written

$$N\ (z_1, z_2) = \frac{4P}{\alpha L_1 H_1}\left\{o^*\left[\frac{1-o_{(1)}}{o_{(1)}} + \ln\frac{1-o_{(1)}}{o_{(1)}} - \left(\frac{1-o_{(2)}}{o_{(2)}} + \ln\frac{1-o_{(2)}}{o_{(2)}}\right)\right]\right.$$

$$\left. + (1 - o^*)\left[\frac{o_{(1)}}{1-o_{(1)}} + \ln\frac{o_{(1)}}{1-o_{(1)}} - \left(\frac{o_{(2)}}{1-o_{(2)}} + \ln\frac{o_{(2)}}{1-o_{(2)}}\right)\right]\right\}. \quad (25)$$

Now let us suppose that the actual pyramid consists of $\underline{m}$ stages, so that its height L is given by

$$L = mL_1\ . \quad (26)$$

Let o_k and S_k be the values of $\underline{o}$ and $\underline{S}$, respectively, at the top of the $\underline{k}$'th stage, where $k = 1$ for the bottom stage and $k = m$ for the top stage of the pyramid. Then, from (12)

and (13), we have

$$S_k = e^{\frac{\alpha k L_1}{2}} , \tag{27}$$

$$c_k = \frac{c_o S_k}{1 + c_o (S_k - 1)} , \tag{28}$$

$$c^* = c_m = \frac{c_o e^{\frac{\alpha L}{2}}}{1 + c_o (e^{\frac{\alpha L}{2}} - 1)} . \tag{29}$$

To get the total number of columns in the pyramid, $N = N(0,L)$, we make use of some of the formulas given above. We find

$$N = \frac{4P}{\alpha L_1 H_1} \left\{ c^* \left[\frac{1}{S^*} + \ln S^* - 1 \right] + (1-c^*) \left[S^* - \ln S^* - 1 \right] \right\} , \tag{30}$$

$$= \frac{4P}{\alpha L_1 H_1} \left\{ (2c^* - 1) \ln S^* + \frac{c^* - c_o)\ (1 - 2c_o)}{c_o\ (1 - c_o)} \right\} , \tag{31}$$

$$= \frac{2mP}{H_1} \cdot \frac{c_o\ (S^* + 1) + (1 - 2c_o)(S^* - 1)/\ln S^*}{1 + c_o\ (S^* - 1)} . \tag{32}$$

To get the number of columns in the <u>k</u>'th stage, N_k, one can proceed in several different ways. One possibility is to

use the value of $\underline{n}$, as given by (9), for some suitable value of $\underline{z}$, for example $z = (k-1/2)L_1$, corresponding to a point half-way up the $\underline{k}$'th stage. Another possibility is to get $\underline{n}$ from (9) with $c = c_k$ and $c = c_{k-1}$, and then to take the mean of the two values of $\underline{n}$. However, the best procedure is to take $N_k = N((k-1)\,L_1,\ kL_1)$, which is found to be given by

$$N_k = \frac{2P}{H_1}\left\{c^*\left[1 + \frac{2(1-c_k)}{c_k\,\alpha L_1}\left(e^{\frac{\alpha L_1}{2}} - 1\right)\right] - \right.$$

$$\left. - (1-c^*)\left[1 + \frac{2\,c_k}{(1-c_k)\alpha L_1}\left(1 - e^{-\frac{\alpha L_1}{2}}\right)\right]\right\}, \qquad (33)$$

$$N_k = \frac{2P}{H_1}\left\{c^*\left[1 - \frac{2}{\alpha L_1}\left(1 - e^{-\frac{\alpha L_1}{2}}\right) e^{-\frac{1}{2}\alpha L_1(m-k)}\right] + \right.$$

$$\left. + (1-c^*)\left[\frac{2}{\alpha L_1}\left(e^{\frac{\alpha L_1}{2}} - 1\right) e^{\frac{1}{2}\alpha L_1(m-k)} - 1\right]\right\}. \qquad (34)$$

With N_k given by (33) or (34), it is obvious that

$$N = \sum_{k=1}^{m} N_k\,. \qquad (35)$$

From (34) it follows that, in the top stage of the pyramid, the number of columns is given by

$$N_m = \frac{2P}{H_1}\left\{c^* \left[1 - \frac{2}{\alpha L_1}\left(1 - e^{-\frac{\alpha L_1}{2}}\right)\right] + (1-c^*)\left[\frac{2}{\alpha L_1}\left(e^{\alpha L_1} - 1\right) - 1\right]\right\}. \tag{36}$$

For values of αL_1 small compared to unity, this becomes

$$N_m = \frac{P}{2\,H_1}\left\{\alpha L_1 + \frac{1}{6}\,\alpha^2 L_1^{\,2}\,(1 - 2c^*)\right\}. \tag{37}$$

4. <u>Time to Put into Operation</u>

To determine the time required to put the pyramid into operation we use the method used by Jones and Furry[1] and by Cohen[2]. Let U be the holdup of the light constituent in the pyramid in the steady state of flow, and let U_I be the initial holdup. Then the time required is taken as

$$T = \frac{U - U_I}{P\,(c^* - c_o)}, \tag{38}$$

that is, the time for the column to reproduce the increase of its holdup from its initial value. To evaluate this quantity we note that, if we let M_1 be the mass of material (total holdup) in one column, then, provided we can neglect inter-stage holdup,

$$U = \frac{M_1}{L_1} \int_0^L n\sigma dz,$$

$$= \frac{4P\ M_1}{\alpha L_1 H_1} \int_{\sigma_0}^{\sigma^*} \frac{\sigma^* - \sigma}{\sigma(1 - \sigma)^2}\ d\sigma. \tag{39}$$

Carrying out the integration, we get

$$U = \frac{4P\ M_1}{\alpha L_1 H_1} \left\{ \sigma^* \ln S^* - \frac{\sigma^* - \sigma_0}{1 - \sigma_0} \right\}. \tag{40}$$

On the other hand, we have

$$U_I = N\ M_1\ \sigma_0\ , \tag{41}$$

whence, by (31) we find

$$U - U_I = \frac{4P\ M_1}{\alpha L_1 H_1} \left\{ (\sigma^* - 2\ \sigma_0\ \sigma^* + \sigma_0) \ln S^* - 2\ (\sigma^* - \sigma_0) \right\}. \tag{42}$$

Substituting this into (38) we get

$$T = \frac{4\ M_1}{\alpha L_1 H_1} \left\{ \frac{\sigma^* - 2\ \sigma_0\ \sigma^* + \sigma_0}{\sigma^* - \sigma_0} \ln S^* - 2 \right\}. \tag{43}$$

If we define the time constant for a single column, X, by

$$X = \frac{M_1}{\alpha L_1 H_1} = \frac{M_1 K_1}{H_1^2 L_1} , \tag{44}$$

then we finally get[1]

$$T = 4X \left\{ \frac{\sigma^* - 2\,\sigma_o\,\sigma^* + \sigma_o}{\sigma^* - \sigma_o} \ln S^* - 2 \right\} . \tag{45}$$

Footnotes

[1] Jones and Furry, unpublished manuscript.

[2] K. Cohen, Columbia University Report A-530, Feb. 4, 1946.

CHAPTER V. PERFORMANCE CRITERIA

1. Column Constants

It is desirable to have some convention for assigning numbers to columns so as to provide the means for comparing two different columns, as well as the performance of the same column under different conditions.

It will be recalled that, from the theoretical standpoint, the quantities that one first encounters in connection with a single column are the constants H and K that enter into the differential equation for equilibrium separation, H being a measure of the rate of the separating process and K that of the remixing process. Setting

$$\alpha = \frac{H}{K} , \qquad Y = \alpha L , \tag{1}$$

where L is the length of the column, we have for the equilibrium separation factor

$$S_e = e^Y . \tag{2}$$

In the differential equation describing the approach to equilibrium, there occurs the quantity X, the "time constant" of the column, given by

$$X = \frac{ab\,\rho\,K}{H^2} , \tag{3}$$

where $\underline{a}$ is the spacing, $\underline{b}$ the mean wall circumference, and ρ the mean fluid density. Since, for a column having negligible dead space, the total material hold-up M is given by

$$M = \rho\, ab\, L \,, \tag{4}$$

one can write

$$X = \frac{MK}{H^2 L} = \frac{M}{HY} \,. \tag{5}$$

From the experimentally determined values of S_e and X, for a column of given L and M, H and K can be calculated from the preceding equations:

$$H = \frac{M}{X \ln S_e} \,, \qquad K = \frac{ML}{X (\ln S_e)^2} \,. \tag{6}$$

2. <u>Performance Criterion (Q)</u>

We have seen in the preceding chapter that, for a large pyramid which can be treated as consisting of infinitesimal steps (continuous pyramid) and which is designed for optimum performance (ideal pyramid), the number of columns required is given by

$$N = \frac{4P}{HY} \left\{ (1-c^*)\,(S^*-1-\ln S^*) + c^* \left(\frac{1}{S^*} - 1 + \ln S^* \right) \right\} \tag{7}$$

where H and Y refer to a single column, all the columns in

the pyramid being supposed identical, P is the product rate of the pyramid, c^* is the output concentration of the light constituent and S^* is the separation factor developed by the pyramid.

On the basis of Eq. (7) it appears reasonable to take as the <u>figure of merit</u> of a column

$$\Phi = HY = \frac{H^2L}{K} , \tag{8}$$

since the number of columns required in a pyramid operating at a given product rate between given concentrations is inversely proportional to Φ . The figure of merit enables one to make a quantitative comparison of two given columns. It will be noted that, by Eq. (5), one can write

$$\Phi = \frac{M}{X} . \tag{9}$$

Suppose we wish to maintain a column in operation at a given separation factor. Let us define the <u>productivity</u> of the column $\underline{p}$ by

$$p = \frac{P}{\Phi} = \frac{P}{HY} = \frac{\nu}{Y} , \tag{10}$$

where P is the product rate of the column, and

$$\nu = \frac{P}{H} . \tag{11}$$

For columns with the same cross-section, operating under the same conditions, the cost of fuel per unit time is nearly proportional to $\underline{L}$. Hence $\underline{p}$ varies nearly inversely as the operational cost per unit mass of enriched material. If, now, for fixed concentrations at the top and bottom, we vary P (or ν) and at the same time suppose $\underline{L}$ (or $\underline{Y}$) to be varied (to keep the concentrations fixed), there will be a certain value of P for which $\underline{p}$ will be a maximum. This has been taken by some authors (Jones and Furry[1]; Cohen[2]) as the condition for optimum performance: namely, that $\underline{p}$ be a maximum.

One can go farther in this direction. Again let us suppose that we vary ν and at the same time vary Y to keep the concentration at the top of the column fixed, with a given concentration at the bottom. Let p_m denote the maximum value of p and let ν_o denote the value of ν for which it occurs. For any other value of ν we define the <u>productivity quotient</u>

$$Q = \frac{p}{p_m} . \tag{12}$$

This is a measure of how well the column has been chosen (as regards Y or S_e) for the particular task involved. Optimum performance, as defined above, means operating at a Q of 100%.

Suppose we are dealing with a single column (or one at the top of a pyramid). If we write down the relation among

ν, Y, S and c_T, the concentration at the top of the column (= c^*) and then impose the preceding condition for optimum performance we find that, for a fixed value of c_T, the quantities ν (= ν_o) and S(= S_o) are determined for each value of Y. We can thus obtain p_m as a function of any one of the variables: ν, S, or Y. For example, Fig. 1 gives p_m as a function of S, if $c_T \ll 1$.

Let us now suppose that we have a particular column with a given value of Y, and that we operate it at various values of ν. For each value of ν we can determine the corresponding value of S. For example, under the conditions being considered, and with $c_T \ll 1$,

$$S = \frac{\nu + 1}{\nu + e^{-Y(\nu + 1)}} . \tag{13}$$

To get Q as a function of ν for this case, we find p by means of Eq. (10), we obtain p_m from Fig. 1, using the value of S given by Eq. (13), and we substitute into Eq. (12). In this way we compare the actual productivity with the maximum productivity that we might have by a suitable choice of ν and y, but with the same S.

As an example, Fig. 2 gives Q as a function of ν_o/ν for the case $Y = 0.6$, $c_T = c^* \ll 1$, $\nu_o = 1.77$. This independent variable has been chosen because, for the case where a certain product rate is to be maintained, and we have n columns in parallel,

$$\frac{n}{n_o} = \frac{\nu_o}{\nu} , \tag{14}$$

where n is the number of columns so that each has the value ν, while n_o is the number corresponding to ν_o. We see from the graph that the curve is quite flat near the maximum, so that one can decrease the number of columns by 40% or increase them by 80% as compared to the optimum value without bringing down the productivity quotient below 90%. Doubling the optimum number results in a Q of over 87%, while halving the number gives nearly 84%. We see then that there is considerable latitude in the number that one can choose without sacrificing the Q excessively.

By the same general procedure one can determine Q for other cases. Fig. 3 refers to the case of a column which is in a pyramid, far enough below the top so that $c_T = 0.5c^*$, and all the concentrations are small compared to unity. In the last case it will be noted that, if ν is increased to a certain critical value, separation ceases and Q drops to zero, an effect which could have been predicted from the equation for a single column.

The preceding and other examples lead one to conclude that the choice of the number of columns in each stage of a pyramid

is not very critical. Moreover, it appears that it is generally safer to have an excess of a given number rather than a deficit of the same number.

3. <u>Performance Criterion</u> (E)

While the productivity quotient Q, introduced in the previous section, has considerable usefulness, it suffers from the drawback that its calculations may be somewhat lengthy, particularly as regards the determination of p_m. Moreover, it will be noted that it fails to provide any means of comparing directly the performance of a column at two <u>different</u> separation factors.

To be sure, any evaluation of performance involving a comparison at two different separation factors is arbitrary to some extent and depends on the purpose for which the product is intended. However, there is one standpoint from which this question can be treated, which recommends itself because of its plausibility, self-consistency and mathematical simplicity, and that is the one based on a comparison with the ideal pyramid. If we refer back to Eq. (7) for the ideal pyramid, we see that the quantity

$$\Psi = 4P \left\{ (1 - c^*) \left[S^* - 1 - \ln S^* \right] + c^* \left[\frac{1}{S^*} - 1 + \ln S^* \right] \right\} \quad (15)$$

is proportional to the number of columns N being used and is thus a measure of what is being accomplished by the pyramid. Let us define Ψ as the enrichment rate. It is natural to

use this quantity as a measure of what is being accomplished also by a single column or group of columns. Hence, other factors being equal, it is desirable to operate the column or group of columns so that the enrichment rate is as high as possible. It turns out, as we shall see, that in practice the condition for maximum Q as discussed previously is nearly the same as that of maximum Ψ.

We have already defined the <u>figure of merit</u> of a single column by Eq. (8). Let us extend the definition to N columns by the relation

$$\Phi = N H Y . \tag{16}$$

That the Φ's of individual columns combine additively, independently of the method of connecting them, as implied by Eq. (16), can be made plausible from a consideration of two identical columns: if they are connected in series, H is unchanged and Y is doubled; if in parallel, Y is unchanged while H is doubled, so that in either case Φ is doubled.

Let us now define the separative efficiency of a column or system of columns by

$$E = \frac{\Psi}{\Phi} , \tag{17}$$

where Ψ is calculated by Eq. (15), with c* and S* referring to the top of the column or group, and Φ is calculated by

Eq. (16), using for N the number of columns under consideration. From Eq. (7) we see that $E = 1$ for the ideal pyramid. For any single column or finite pyramid, $E < 1$, and the value of E gives a comparison of the performance with that of the ideal pyramid. It is reasonable to use Eq. (17) as a measure of how effectively a column or pyramid is being used.

Up to this point we have been considering a single column or a whole group, or pyramid. From the theory of the ideal pyramid, one can get a generalization of Eq. (15) which can be applied to columns forming a <u>part</u> of a pyramid. One gets as a more general definition of the <u>enrichment rate</u>, in place of Eq. (15),

$$\Psi = 4P\left\{(1 - c^*)\left[S^*\left(\frac{1}{S_1} - \frac{1}{S_2}\right) + \ln\frac{S_1}{S_2}\right] + \right.$$

$$\left. + c^*\left[\frac{1}{S^*}(S_1 - S_2) + \ln\frac{S_2}{S_1}\right]\right\} , \qquad (18)$$

where S_1 and S_2 are the separation factors between the bottom of the pyramid and the bottom and top of the group of columns, respectively.

In the case of low concentrations ($c^* \ll 1$), letting $S = S_2/S_1$, Eq. (18) goes over into

$$\Psi = 4P\left\{\frac{c^*}{c_T}(S - 1) - \ln S\right\} , \qquad (19)$$

while, for a single column or the top column of a pyramid ($c_T = c^*$), Eq. (15) gives

$$\Psi = 4P \left\{ S - 1 - \ln S \right\} . \tag{20}$$

For $\underline{S}$ near unity, Eq. (20) can be approximated by

$$\Psi = 2P \quad (\ln S)^2 . \tag{21}$$

In the case of low concentrations one can show that, as $\underline{Y}$ tends to zero, the separative efficiency of a column approaches 0.814 if the column is operating singly or at the top of a pyramid, while it approaches unity if it is far down in the pyramid.

It is sometimes convenient to split up the enrichment rate into two factors,

$$\Psi = PR , \tag{22}$$

where P is the <u>product rate</u>, and R is the <u>enrichment factor</u> (to be distinguished from the separation factor S):

$$R = 4 \left\{ (1-c^*) \left[S^* \left(\frac{1}{S_1} - \frac{1}{S_2} \right) - \ln S \right] + c^* \left[\frac{1}{S^*} (S_1 - S_2) + \ln S \right] \right\} . \tag{23}$$

It follows that Eq. (17) can be written

$$E = \frac{\nu_a R}{Y} , \tag{24}$$

where ν_a is defined by

$$\nu_a = \frac{P}{NH} . \tag{25}$$

It might be well to remark that, along with the separative efficiency defined above, it is often convenient to define the <u>power efficiency</u> E by the relation

$$E = \frac{\Psi}{\pi} \tag{26}$$

where π is the power supplied to the column or pyramid which is producing the enrichment rate Ψ.

4. <u>Relation between Criteria</u>

In section 2 we discussed what might be referred to as the Q criterion, in section 3, the E criterion. It is of interest to investigate the relation between them. If we have a column forming part of a pyramid with a fixed output concentration, then by Eqs. (11), (23), (24) and (25) it follows that one can write

$$E = \frac{\nu}{Y} R (S). \tag{27}$$

Now S, ν, and Y are connected by a relation which can be written in the general form

$$F (S, \nu , Y) = 0 , \tag{28}$$

and by means of which any one of these can be expressed in terms of the other two.

The Q criterion for optimum performance is given by

$$\left(\frac{\partial p}{\partial \nu}\right)_S = 0 \, . \tag{29}$$

However, by Eq. (10), this is equivalent to

$$\left(\frac{\partial E}{\partial \nu}\right)_S = 0. \tag{30}$$

On the other hand, the E criterion for optimum performance of a given column (with a given value of $\underline{Y}$) is obviously

$$\left(\frac{\partial E}{\partial \nu}\right)_Y = 0. \tag{31}$$

Taking account of the relation (28), we see that in general the conditions (30) and (31) are not the same. However, it turns out that, in the cases of interest the consequences of these conditions are practically equivalent. For example, in Fig. 4 we have a comparison of the curves of Q and E as functions of ν for the case $Y = 0.6$, $c_T = c^* \ll 1$. The ordinates of the two curves are nearly proportional and the maxima are nearly coincident.

In practice, it is found that for a given set of conditions it is generally simpler to calculate E rather than Q. On

the other hand, in determining the conditions for optimum performance, the Q criterion usually leads to simpler calculations than the E criterion.

5. <u>Enrichment Rate and Related Functions</u>

Eq. (18), after some manipulation, can be rewritten in the form

$$\Psi = 4P \left\{ c^* \left[\frac{1 - c_B}{c_B} + \ln \frac{1 - c_B}{c_B} - \frac{1 - c_T}{c_T} - \ln \frac{1 - c_T}{c_T} \right] \right.$$

$$\left. + (1 - c^*) \left[\frac{c_B}{1 - c_B} + \ln \frac{c_B}{1 - c_B} - \frac{c_T}{1 - c_T} - \ln \frac{c_T}{1 - c_T} \right] \right\}, \quad (32)$$

where c_B and c_T are the bottom and top concentrations of the column or group under consideration. Now the rate of transport of the lighter component in the steady state is constant throughout the system and is given by

$$\tau = Pc^* \quad (33)$$

while that of the heavier component is given by

$$\tau' = P(1 - c^*) . \quad (34)$$

If we denote quantities referring to the heavier component by primes ($c' = 1 - c$), then we can write

$$\Psi = -\tau \Delta \textcircled{H} - \tau' \Delta \textcircled{H}' , \quad (35)$$

where

$$\textcircled{H} = 4\left[\frac{1-c}{c} + \ln\frac{1-c}{c}\right] , \tag{36}$$

$$\textcircled{H}' = 4\left[\frac{c}{1-c} + \ln\frac{c}{1-c}\right] \tag{37}$$

and Δ is the change in going from the bottom of the column or group of columns up to the point in question. From (35) and the properties of τ and τ', we see that Ψ is additive: the value for the whole is the sum of the values for the parts of a system. The function $\textcircled{H}$ varies from $+\infty$ to $-\infty$ as c varies from 0 to 1.

If z is the distance up along a column or pyramid, then from (35) we have for the enrichment rate per unit length

$$\frac{d\Psi}{dz} = -\tau\frac{d\textcircled{H}}{dz} - \tau'\frac{d\textcircled{H}'}{dz} . \tag{38}$$

Now, from the theory of a column we have

$$\tau = Pc + Hc\,(1-c) - K\frac{dc}{dz} , \tag{39}$$

$$\tau' = P\,(1-c) - Hc\,(1-c) + K\frac{dc}{dz} , \tag{40}$$

and from (36) and (37),

$$\frac{d\textcircled{H}}{dz} = -\frac{4}{c^2\,(1-c)}\frac{dc}{dz} , \quad \frac{d\textcircled{H}}{dz} = \frac{4}{c(1-c)^2}\frac{dc}{dz} . \tag{41}$$

It follows that

$$\frac{d\Psi}{dz} = 4\left\{H\,\frac{d\ln S}{dz} - K\left(\frac{d\ln S}{dz}\right)^2\right\}, \tag{42}$$

where, as usual,

$$S = \frac{c\,(1 - c_0)}{c_0\,(1 - c)}\,. \tag{43}$$

From (42) we see that for $\frac{d\Psi}{dz}$ to be a maximum one must have

$$\frac{d\ln S}{dz} = \frac{H}{2K} = \frac{1}{2}\,\frac{d\ln S_e}{dz}\,, \tag{44}$$

where S_e is the equilibrium value of S for the case of zero product rate. If (44) holds then

$$\frac{d\Psi}{dz} = \frac{H^2}{K}\,. \tag{45}$$

Eq. (44) is just the condition holding for the ideal continuous pyramid.

Finally, it follows from (35) that, for material of mass $\underline{M}$ and concentration $\underline{c}$ one can define the mixing function, or <u>misceance</u>,

$$\begin{aligned} X &= M\,(c\,\textcircled{H} + c'\,\textcircled{H}') \\ &= 4M\left[1 - \ln c\,(1-c) - 2c\ln c - 2\,(1-c)\ln(1-c)\right], \end{aligned} \tag{46}$$

such that the total enrichment rate of a pyramid is equal to the rate at which X is decreased. Obviously X is determined

only to within an additive constant, so that the unity occurring as the first term in the brackets of (46) can be discarded.

Footnotes

[1] Jones and Furry, unpublished manuscript.

[2] K. Cohen, Columbia University Report A-530, Feb. 4, 1946.

Chapter 5

Figure 1

Maximum productivity of a column as a function of the separation factor for the case of low concentration of the desired isotope.

Figure 2

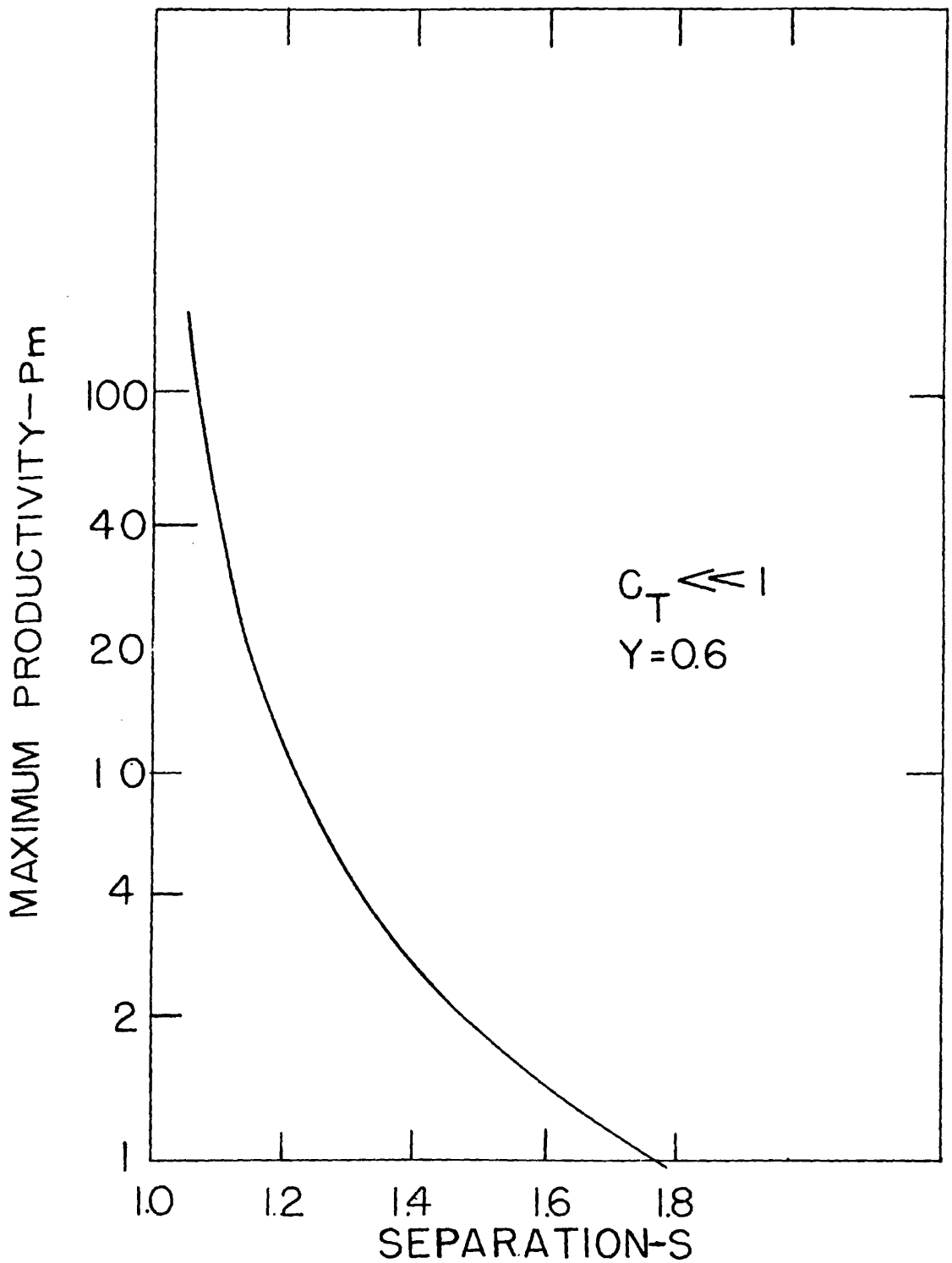
Productivity quotient as a function of the product rate for the case of a single column operating at low concentration of the desired isotope.

Figure 3

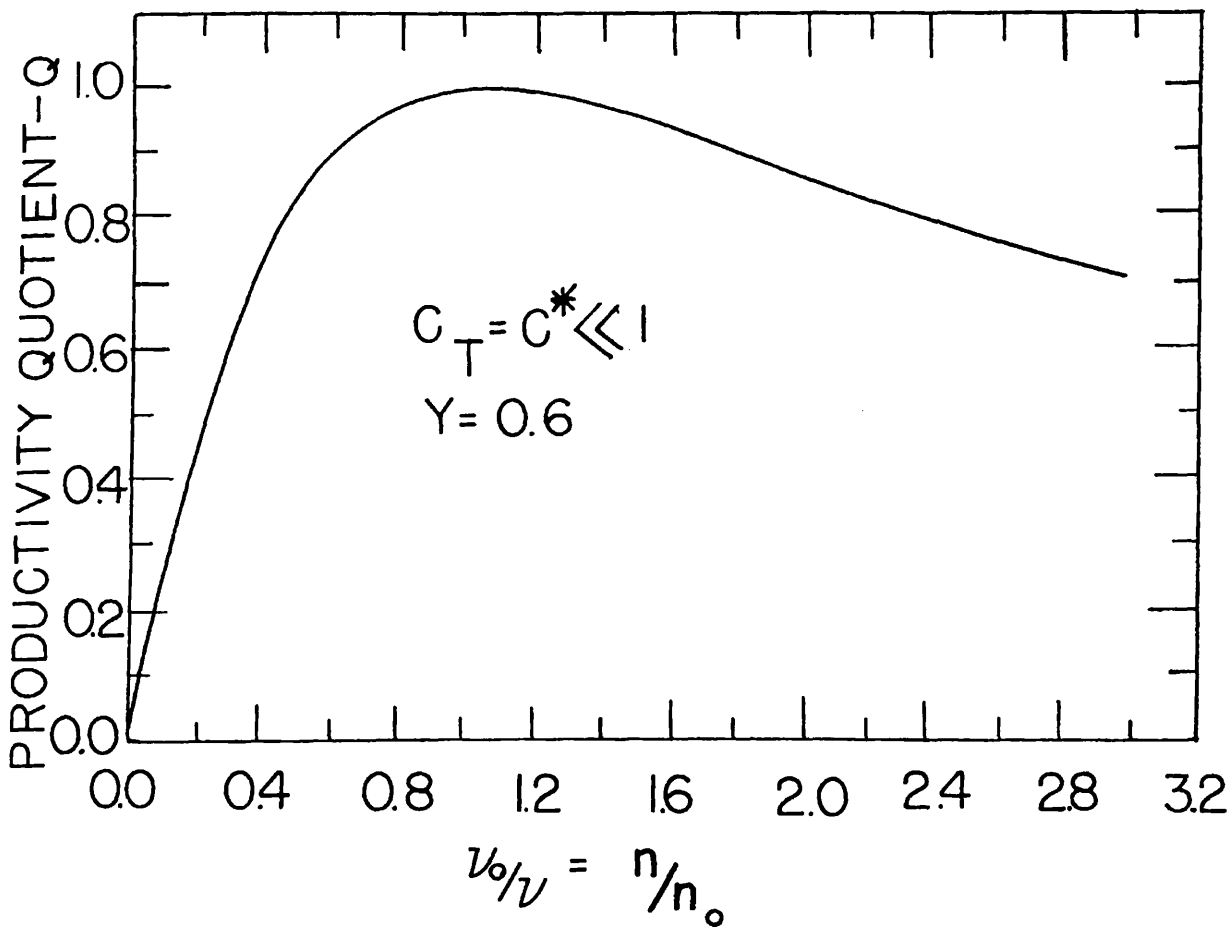
Productivity quotient as a function of product rate for the case of a column in a pyramid at the point where C_T (concentration at the top of this column) equals 0.5 c* (concentration at the top of the pyramid) for the case of low concentration of the desired isotope.

Figure 4

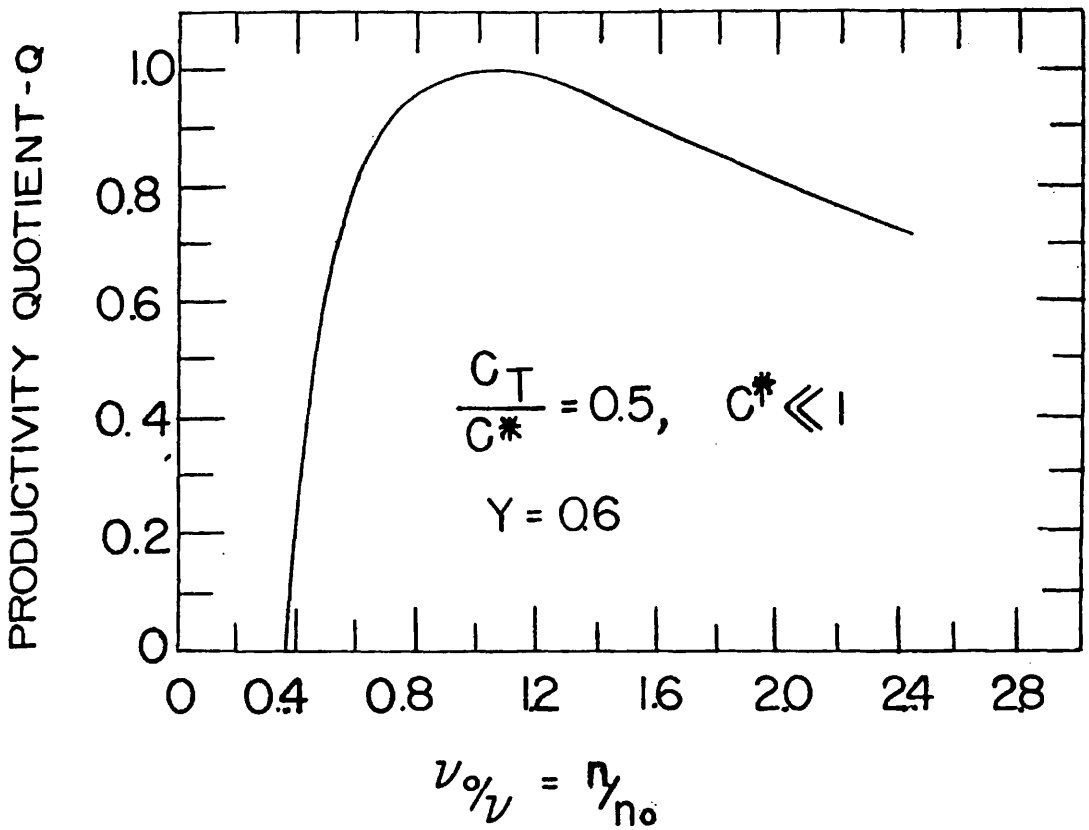
A comparison of the dependence of the productivity quotient and the separative efficiency on the product rate.



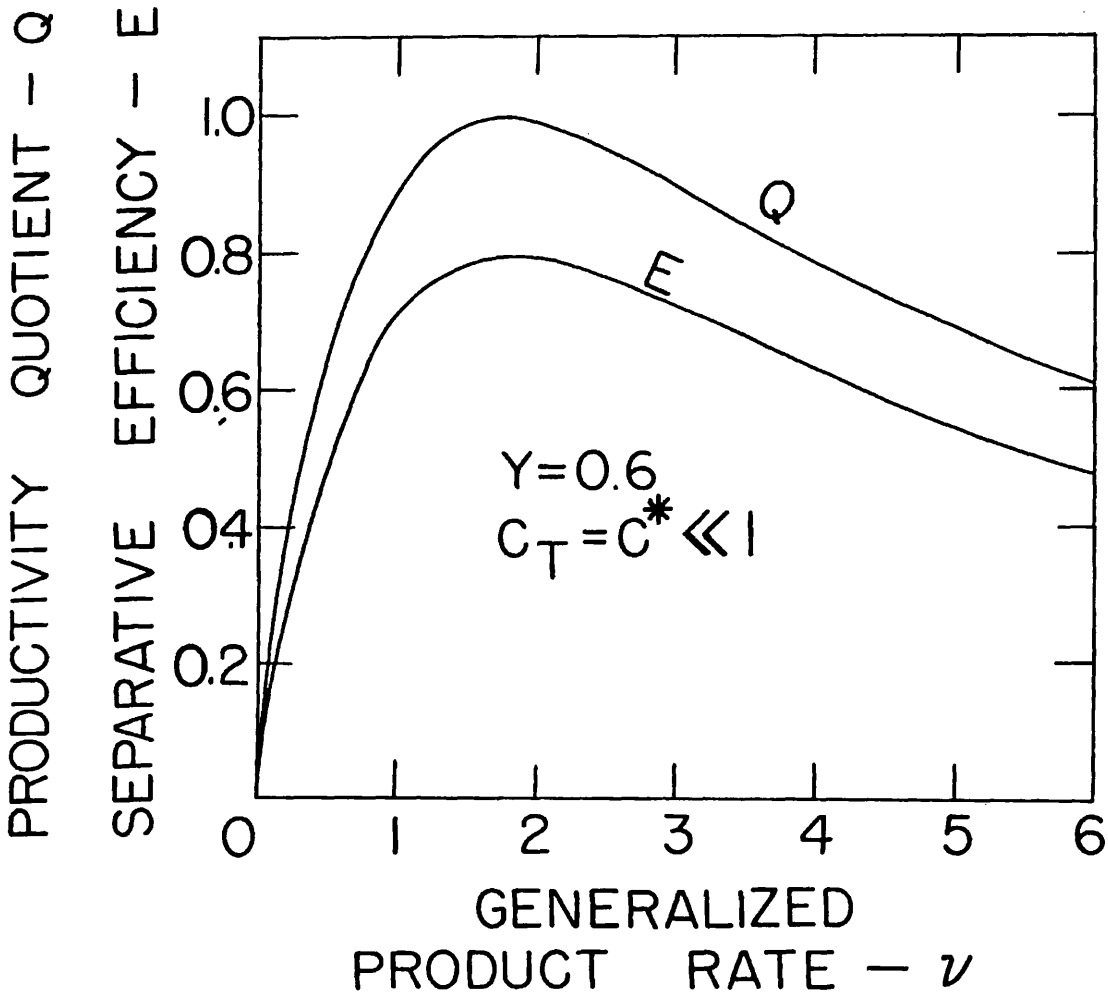
Theoretical Chap. 5 Fig. 1



Theoretical Chap. 5 Fig. 2



Theoretical Chap 5 Fig. 9



Theoretical Chap. 5 Fig. 4

CHAPTER VI. COLUMNS IN A PYRAMID

1. Equations

The differential equation for the light-constituent concentration c in a column under steady operation has the form

$$\frac{dc}{dz} = \alpha c\,(1 - c) - \alpha\nu(c^* - c), \tag{1}$$

where

$$\alpha = \frac{H}{K}, \qquad \nu = \frac{P}{H}, \tag{2}$$

H and K being the column constants, P the product rate, z the distance up the column (measured from the bottom), and c^* the concentration at the top of the pyramid where product is removed.

Eq. (1) can be integrated. Let c_B and c_T be the concentrations at the bottom and top of the column, respectively. The solution of (1) can be written

$$\ln \frac{(2c - 1 - \nu + q)(2c_B - 1 - \nu - q)}{(2c - 1 - \nu - q)(2c_B - 1 - \nu + q)} = q\alpha z \quad , \tag{3}$$

where

$$q = \sqrt{(1 + \nu)^2 - 4\nu c^*} \quad . \tag{4}$$

Solving (3) for c, one gets

$$c = \frac{\left[2\nu c^* - (1+\nu+q)\, c_B\right] e^{q\alpha z} + (1+\nu-q)\, c_B - 2\nu c^*}{\left[1+\nu-q-2\, c_B\right] e^{q\alpha z} + 2\, c_B - (1+\nu+q)} \,. \quad (5)$$

If we set $z = L$, the length of the column, and $c = c_T$, (3) becomes

$$\ln \frac{(2\, c_T - 1 - \nu + q)(2\, c_B - 1 - \nu - q)}{(2\, c_T - 1 - \nu - q)(2\, c_B - 1 - \nu + q)} = q\, Y \,, \quad (6)$$

where $Y = \alpha L$. If we are dealing with a single column or one in the top stage of a pyramid, then $c_T = c^*$.

Let us now consider the case in which $c \ll 1$. Then Eq. (1) can be written to a sufficient accuracy

$$\frac{dc}{dz} = \alpha(1+\nu)\, c - \alpha\nu c_m . \quad (7)$$

The solution of this equation is given by

$$\ln \frac{(1+\nu)\, c - \nu c^*}{(1+\nu)\, c_B - \nu c^*} = \alpha(1+\nu)\, z \,, \quad (8)$$

so that

$$\ln \frac{(1+\nu)\, c_T - \nu c^*}{(1+\nu)\, c_B - \nu c^*} = (1+\nu)\, Y \,. \quad (9)$$

Solving (8) for $\underline{c}$, one gets

$$c = \frac{\nu c^*}{1+\nu} + \left(c_B - \frac{\nu c^*}{1+\nu}\right) e^{\alpha(1+\nu)z} , \tag{10}$$

On the other hand, if we have $c \sim 1$, so that $1 - c \ll 1$, we write

$$c = 1 - c' , \qquad c^* = 1 - c'^* , \tag{11}$$

and get for c' the equation

$$\frac{dc'}{dz} = -\alpha c' + \alpha\nu(c'^* - c') , \tag{12}$$

which takes on the same form as (7) if we replace α and ν by α' and ν',

$$\alpha = -\alpha', \qquad \nu = -\nu'. \tag{13}$$

The separation factor for the column, S, is defined as

$$S = \frac{c_T\,(1 - c_B)}{c_B\,(1 - c_T)} . \tag{14}$$

If $c \ll 1$, one can write

$$S = \frac{c_T}{c_B} , \tag{15}$$

while, if $1 - c \ll 1$,

$$S = \frac{1 - c_B}{1 - c_T} = \frac{c_B'}{c_T'} \tag{16}$$

where

$$c_B' = 1 - c_B , \qquad c_T' = 1 - c_T .$$

2. <u>Column in Top Stage or Single Column</u>

Suppose that we are dealing with a column operated singly or in the top stage of a pyramid, so that $c_T = c^*$, and we consider the question: what is the best rate of flow P in this column or, by (2), what is the best value of ν? We saw in the preceding chapter that a reasonable criterion (the "Q criterion") was that based on maximizing $p = \frac{\nu}{Y}$, or, what is the same thing, minimizing $\frac{1}{p} = \frac{Y}{\nu}$. We take then as the condition for the optimum rate of flow

$$\frac{\partial}{\partial \nu} \left(\frac{Y}{\nu}\right) = 0 \tag{17}$$

where Y is to be expressed by means of Eq. (6), and where c_B and c_T are to be kept constant in the differentiation.

Let

$$\psi = \frac{(\omega + q)(\lambda - q)}{(\omega - q)(\lambda + q)} , \tag{18}$$

where

$$\omega = 1 + \nu - 2\, c_B , \tag{19}$$

$$\lambda = 1 + \nu - 2\, c_T . \tag{20}$$

Then (17) becomes

$$\left(\frac{q}{\nu} + \frac{\lambda}{q}\right) \ln \psi = \frac{\lambda + q}{\omega + q} + \frac{\lambda - q}{\omega - q} - 2 . \tag{21}$$

This is to be solved simultaneously with (6), which can be written

$$q = \frac{\ln \psi}{Y} . \tag{22}$$

From (18) one can write

$$\omega = q \, \frac{\lambda(\psi + 1) + q\,(\psi - 1)}{\lambda(\psi - 1) + q\,(\psi + 1)} , \tag{23}$$

while from (4), with $c^* = c_T$ one finds

$$\lambda = \frac{q^2 + \nu^2 - 1}{2\nu} . \tag{24}$$

Using (22), (23) and (24) to eliminate $\ln \psi$, ω and λ in (21) one gets an equation for ν of the form

$$A\nu^2 - B\nu + C = 0 , \tag{25}$$

where

$$\left.\begin{aligned} A &= 2\,Yq\,\psi + 1 - \psi^2 , \\ B &= 2\,(\psi - 1)^2 q , \\ C &= 6\,Y\psi q^3 - 2\,Y\psi q - (\psi^2 - 1)(q^2 - 1) . \end{aligned}\right\} \tag{26}$$

We now have a procedure for solving the equations numerically. For a given value of Y, the steps are as follows:

(a) Assume some value for φ (or $\ln \varphi$).

(b) Get q from (22).

(c) Set up Eq. (25) and solve for ν.

(d) Get λ from (24) and c_T from (20).

(e) Get ω from (23) and c_B from (19).

In this way, for a given value of Y, we obtain corresponding values of ν, c_B and c_T. If φ has been chosen so that $\nu > 0$, $0 < c_B < c_T < 1$, these values are useable. By taking a number of values of φ one can plot graphs giving ν as a function of c_T, as well as S as a function of c_T, where S is given by Eq. (11). Such graphs are shown in Figs. 1 and 2 for $Y = 0.5, 0.6, 0.7, 0.8$.

It is convenient to have analytical expressions for these functions. It is found that, at least in the range: $-1 \leqslant Y \leqslant 1$, $\ln S$ is nearly a linear function of c_T. Hence one can write

$$\ln S = A' c_T + B' (1 - c_T) + C' c_T (1 - c_T), \qquad (27)$$

where the last term has been added to allow for a small deviation from linearity. The coefficients A' and B' can be determined from the behavior of $\ln S$ for $c_T \to 1$ and $c_T \to 0$, respectively. The latter was investigated by a

method to be described in the next section. The coefficient C' was determined by the deviation from linearity in the cases previously calculated numerically. The result obtained in this way was given by

$$\frac{\ln S}{Y} = 0.5693 + 0.0124\ Y\ (1-2\ c_T) + Y^2 \left[0.0013 + 0.0082\ c_T(1-c_T)\right] . \tag{28}$$

A similar procedure gave

$$\nu Y = 1.256 - 0.339\ Y\ (1-2\ c_T) + Y^2 \left[0.019 - 0.315\ c_T(1-c_T)\right] , \tag{29}$$

a result which was not as accurate as (28).

In terms of c_B the corresponding relations are

$$\frac{\ln S}{Y} = 0.5693 + 0.0124\ Y\ (1-2\ c_B) + Y^2 \left[0.0013 - 0.0059\ c_B(1-c_B)\right] , \tag{30}$$

and

$$\nu Y = 1.256 - 0.339\ Y\ (1-2\ c_B) + Y^2 \left[0.019 + 0.070\ c_B(1-c_B)\right] . \tag{31}$$

3. <u>Column Anywhere in Pyramid</u>

In the preceding section we considered the case of a column

operated single or in the top stage of a pyramid. We now consider the general case of a column anywhere in a pyramid. This general case is characterized by the fact that one may have $c_T \neq c^*$. In the latter case the calculations required to determine the optimum rate of flow become rather tedious. For this reason we limit the discussion to two cases: (a) $c \ll 1$, and (b) $1 - c \ll 1$.

Let us consider first the case $c \ll 1$. Then Eq. (7) is valid, and hence Eq. (9) follows. To determine the optimum value of ν, we again set $\frac{\partial}{\partial \nu}\left(\frac{Y}{\nu}\right) = 0$, expressing Y as a function of ν by means of (9), keeping c^*, c_B and c_T constant. In this way we get the equation

$$\ln \frac{(1+\nu)c_T - \nu c^*}{(1+\nu)c_B - \nu c^*} = \frac{\nu(1+\nu)}{1+2\nu}\left\{\frac{c^* - c_B}{(1+\nu)c_B - \nu c^*} - \frac{c^* - c_T}{(1+\nu)c_T - \nu c^*}\right\}, \tag{32}$$

which must be satisfied together with Eq. (9).

For a given value of Y these two equations can be solved parametrically by taking as a variable

$$\psi = \ln \frac{(1+\nu)c_T - \nu c^*}{(1+\nu)c_B - \nu c^*} . \tag{33}$$

We have then from (9)

$$\nu = \frac{\psi}{Y} - 1, \tag{34}$$

while from (32) and (33) we find that

$$\frac{c_T}{c^*} = \frac{\nu}{1+\nu} \cdot \frac{1+\xi}{\xi} ,$$

$$\frac{c_B}{c^*} = \frac{\nu}{1+\nu} \cdot \frac{1+\zeta}{\zeta} , \tag{35}$$

$$\frac{c_T}{c_B} = \frac{1+\xi}{\xi} \cdot \frac{\zeta}{1+\zeta} ,$$

where

$$\xi = \frac{\psi\left(\frac{2\psi}{Y} - 1\right)}{e^{\psi} - 1} , \qquad \zeta = \xi e^{\psi} . \tag{36}$$

By assigning various values to ψ , one can find sets of related values of $\frac{c_T}{c^*}$, $S = \frac{c_T}{c_B}$ and ν for a fixed value of Y.

On the basis of such calculations, Fig. 3 presents curves of S as a function of $\frac{c_T}{c^*}$ for a number of values of Y, while Fig. 4 gives curves of ν as a function of the same variable.

Certain limiting values are of interest. For the case $c_T = c^*$ one finds that the results can be represented in the range $0 \leq Y \leq 1$ by

$$\frac{\ln S}{Y} = 0.5693 + 0.0124\ Y + 0.0013\ Y^2 \tag{37}$$

and

$$\nu Y = 1.2564 - 0.3392\ Y + 0.0189\ Y^2 + 0.0015\ Y^3. \tag{38}$$

In particular, one finds

$$\lim_{Y \to 0} \left(\frac{\ln S}{Y} \right) = \frac{2}{\gamma}\ , \quad \lim_{Y \to 0} (\nu Y) = \ln \gamma \tag{39}$$

where

$$2 \ln \gamma = \gamma - 1 \tag{40}$$

which has a solution $\gamma = 3.5129$, $\ln \gamma = 1.2564$, so that $\frac{2}{\gamma} = 0.5693$. Eqs. (37) and (38) are plotted in the right-hand half of Fig. 5.

For the case $\sigma_T \ll \sigma^*$ one finds

$$S = \frac{e^Y + Y - 1}{1 + Y - e^{-Y}}\ , \tag{41}$$

which can be replaced in the range $0 \leqslant Y \leqslant 1$ by the more convenient expression

$$\frac{\ln S}{Y} = 0.5000 + 0.0102\ Y^2\ , \tag{42}$$

and also

$$\nu = \frac{\sigma_T}{\sigma^*} \quad \frac{Y}{e^Y + Y - 1}\ . \tag{43}$$

We see that in this case we get $\frac{\ln 3}{Y}$ very nearly equal to $\frac{1}{2}$, as was the case in the ideal pyramid. The ratio $\nu/\left(\frac{c_T}{c^*}\right)$ is plotted in Fig. 6 as a function of Y.

By means of the information presented graphically in Figs. 3 and 4 one can determine the optimum concentration and value of ν for each stage of a pyramid, starting from the top and working down stage by stage. For the case in which all the stages consist of columns with the same value of Y the results of such calculations are given in Fig. 7. In this figure curves will be found giving the ratio of the concentration <u>at the bottom</u> of each stage to the concentration at the top of the highest stage, taken as stage #1. Using this ratio for the lowest stage and the concentration of material fed in at the bottom of this stage one can find the concentration at the top of the pyramid and from this the actual concentrations at the various stages.

Since the total upward flow of fluid must be the same at every stage of the pyramid, the number of columns per stage varies inversely as ν, if we take all the columns to have the same value of H. On this basis, Fig. 8 gives the number of columns at various stages corresponding to one column in the top stage (#1).

To get the optimum product rate from each column of the top stage, let X be the time constant of the column

$$X = \frac{M}{HY}, \tag{44}$$

where M is the material hold-up in the column. Then

$$P = H\nu = \frac{M}{X} \cdot \frac{\nu}{Y} \quad . \tag{45}$$

Fig. 9 gives $\frac{\nu}{Y}$ as a function of Y for the top stage ($c_T = c^*$). From this function, together with a knowledge of M and X, or from ν of Fig. 5 and a knowledge of H, the product rate per top-stage column can be obtained.

The preceding calculations and the accompanying graphs enable one to determine the design and operating conditions for small pyramids provided one is dealing with small concentrations so that the linear equation, Eq. (7), is valid. If the concentration is small but too large for (7) to be valid, and if the separation factor is sufficiently small, one can make Eq. (1) effectively linear by replacing the slowly varying factor $1 - c$ by some mean value, and then introducing new coefficients in place of α and ν to give the equation the same form as (7).

If one is dealing with very high concentrations so that $1 - c \ll 1$ then one makes use of Eqs. (11), (12) and (13), whereby one is led to calculations of the same kind as for low concentrations, but with negative values of α and ν. In this way results were obtained as shown in Figs. 10 and 11. Fig. 10 gives $S = \frac{1 - c_B}{1 - c_T}$ as a function of $\frac{1 - c^*}{1 - c_T}$ for various values of Y, and Fig. 11 gives ν as a function of the same variable. From these curves one can determine

operating conditions near the top of a pyramid which is used for material of high concentration. As we shall see later, these results are also applicable to strippers.

If we are dealing with the top stage ($c_T = c^*$) then we find that ($0 \leqslant Y \leqslant 1$)

$$\frac{\ln S}{Y} = 0.5693 - 0.0124\,Y + 0.0013\,Y^2 \tag{46}$$

and

$$\nu Y = 1.2564 + 0.3392\,Y + 0.0189\,Y^2 - 0.0015\,Y^3\,, \tag{47}$$

corresponding to (37) and (38). These functions are shown in the left-hand half of Fig. 5.

For the case: $1 - c_T \gg 1 - c^*$ one finds

$$S = e^{\frac{Y}{2}}\,, \tag{48}$$

and

$$\nu = \frac{1}{2}\,. \tag{49}$$

Chapter 6

Figure 1

Graphs of generalized product rate ν as a function of the concentration at the top of the column, C_T for optimum performance. This applies to a column being operated singly or as the top stage of a pyramid.

Figure 2

Separation factor at optimum withdrawal rate for a column operated singly or as the top stage of a pyramid. C_T is the concentration of the desired isotope at the top of the column.

Figure 3

These curves refer to the case of a column operating at optimum performance as part of a pyramid at low concentration of the desired isotope. Here C_T, C_B and C^* are the concentrations at the top of the column, the bottom of the column and the top of the pyramid respectively.

Figure 4

These curves refer to the optimum performance in a column operating as part of a pyramid at low concentrations of the desired isotope. Here ν is the generalized product rate, C_T, C^* are the concentrations at the top of the column and at the top of the pyramid respectively.

Figure 5

Curves of ln S/Y and ν Y as functions of $C_T = C^*$ for

optimum performance in the case of a single column or the top stage of a pyramid. On the left are shown curves for high concentrations of the desired isotope, on the right curves for low concentrations are given.

Figure 6

These curves are for optimum performance in the case of a column near the bottom of a pyramid where $C_T \ll C^* \ll 1$, C_T being the desired isotope concentration at the top of the column, C^* that at the top of the pyramid.

Figure 7

The ratio of the concentration (C_B) at the bottom of a stage to that (C^*) at the top of the pyramid as a function of Y. The various stages are numbered down from the top. This is for the case of low concentrations of the desired isotope with the pyramid operating at optimum performance.

Figure 8

These curves show the number of columns in each stage of pyramid per column in the top stage as a function of Y. The stages are numbered down from top stage which is number one. This for the case of low concentrations of the desired isotope and optimum performance of the pyramid.

Figure 9

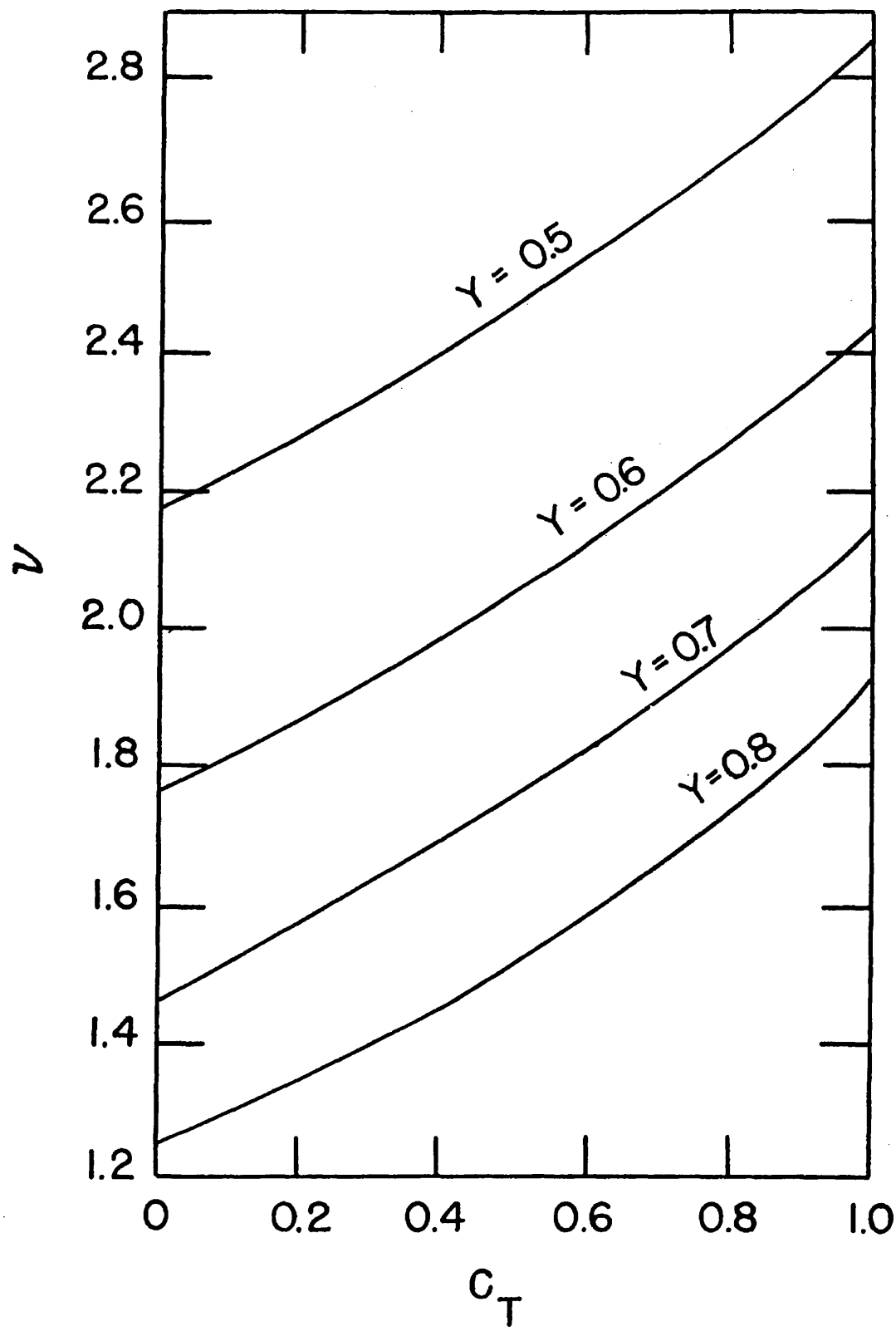
This shows the dependence of ν/Y on Y for the top stage of a pyramid operating at optimum performance and employing low concentrations of the desired isotope.

Figure 10

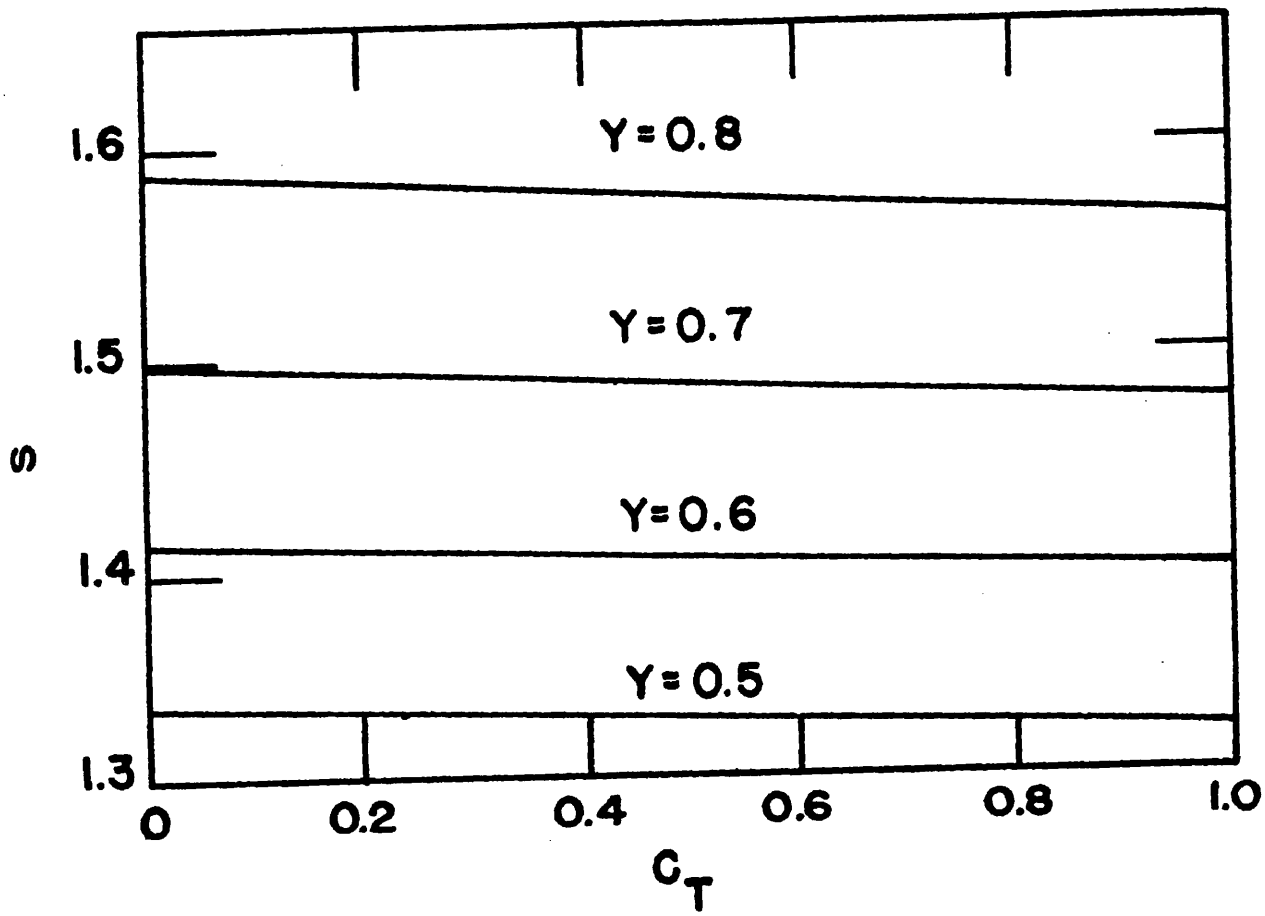
Dependence of separation factor on concentration. These curves refer to a column operating at optimum performance as part of a pyramid. C_B, C_T and C^* the concentrations of the desired isotope at the bottom of a column, at the top of the column and at the top of the pyramid are nearly equal to unity. Large values of the abscissa indicate the column is near the top of the pyramid.

Figure 11

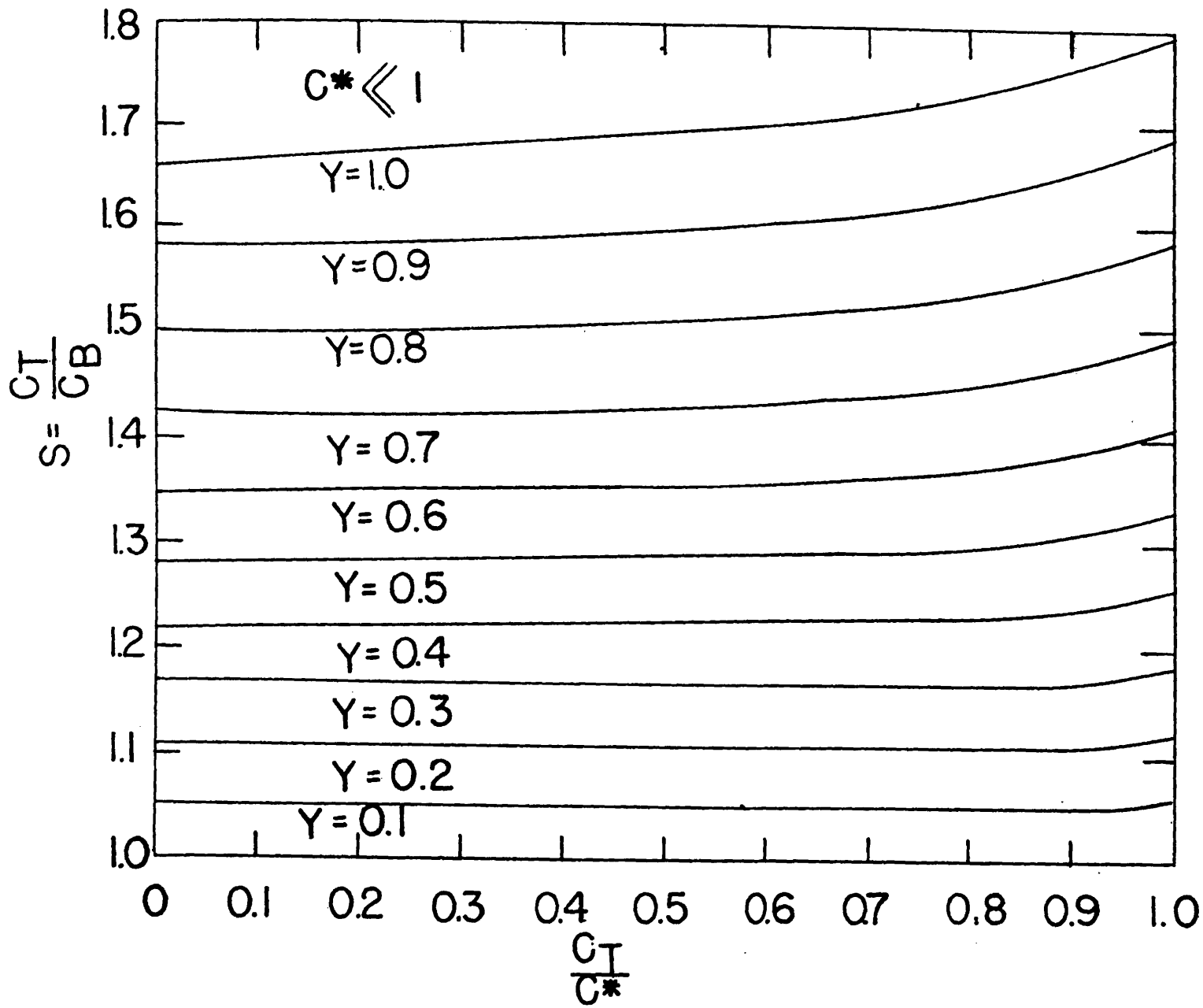
Curves showing the generalized product rate as a function of the concentrations for a column operating at optimum performance as part of pyramid. This is for the case where the concentration of the desired isotope is close to unity. High values of the abscissa indicate that column is near to the top of the pyramid.



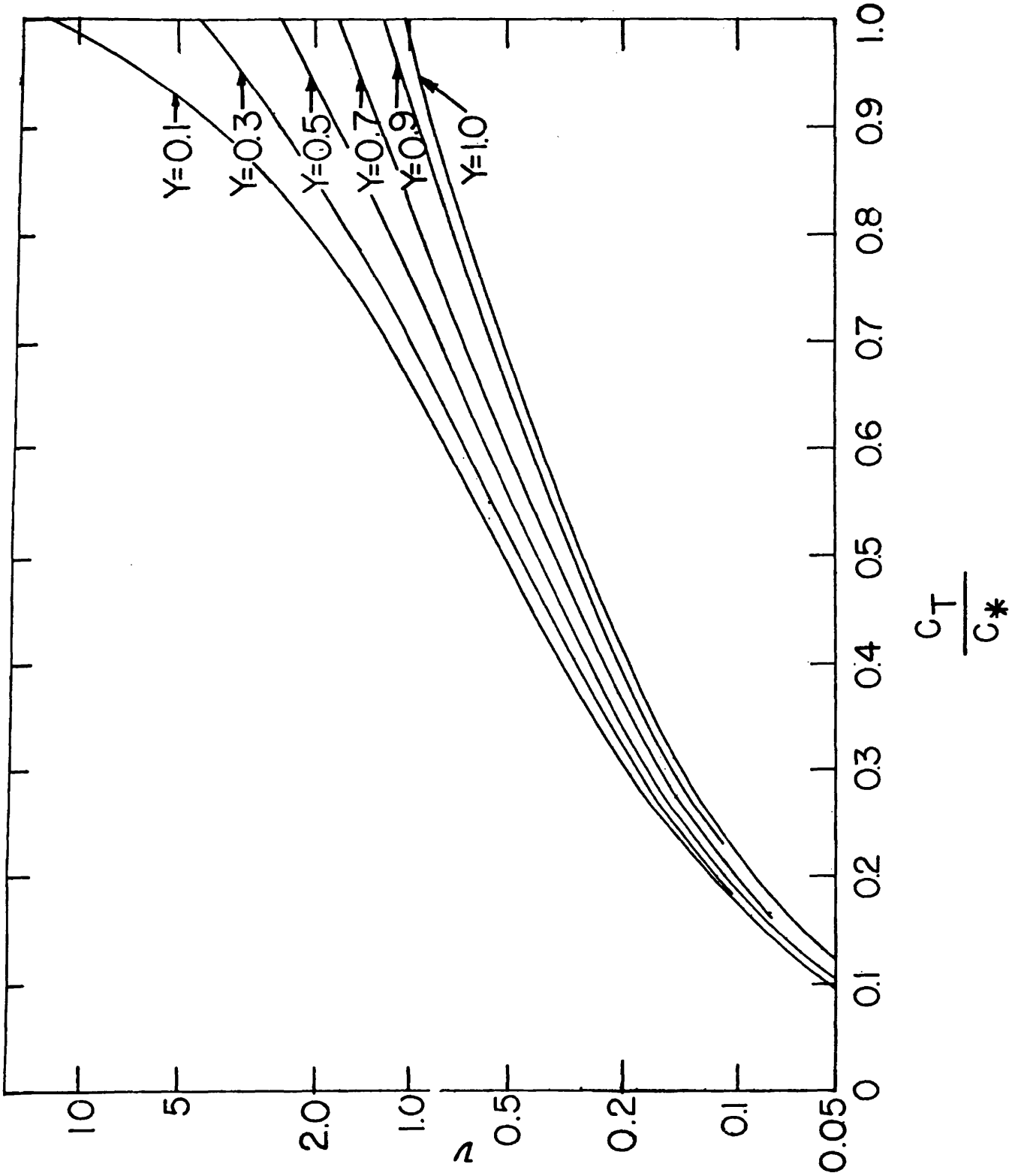
Theoretical Chap. 6 Fig. 1



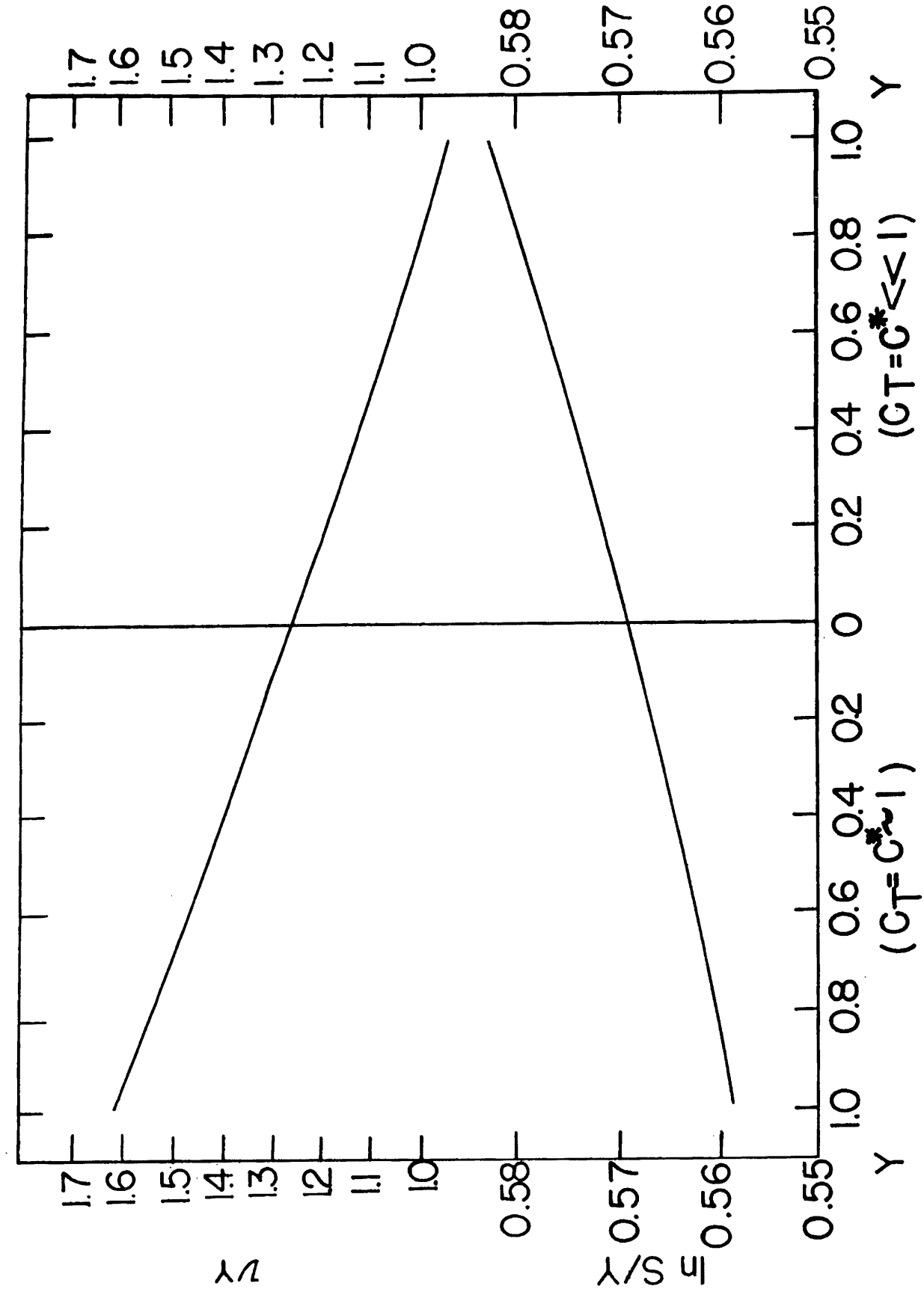
Theoretical Chap. 6 Fig. 2



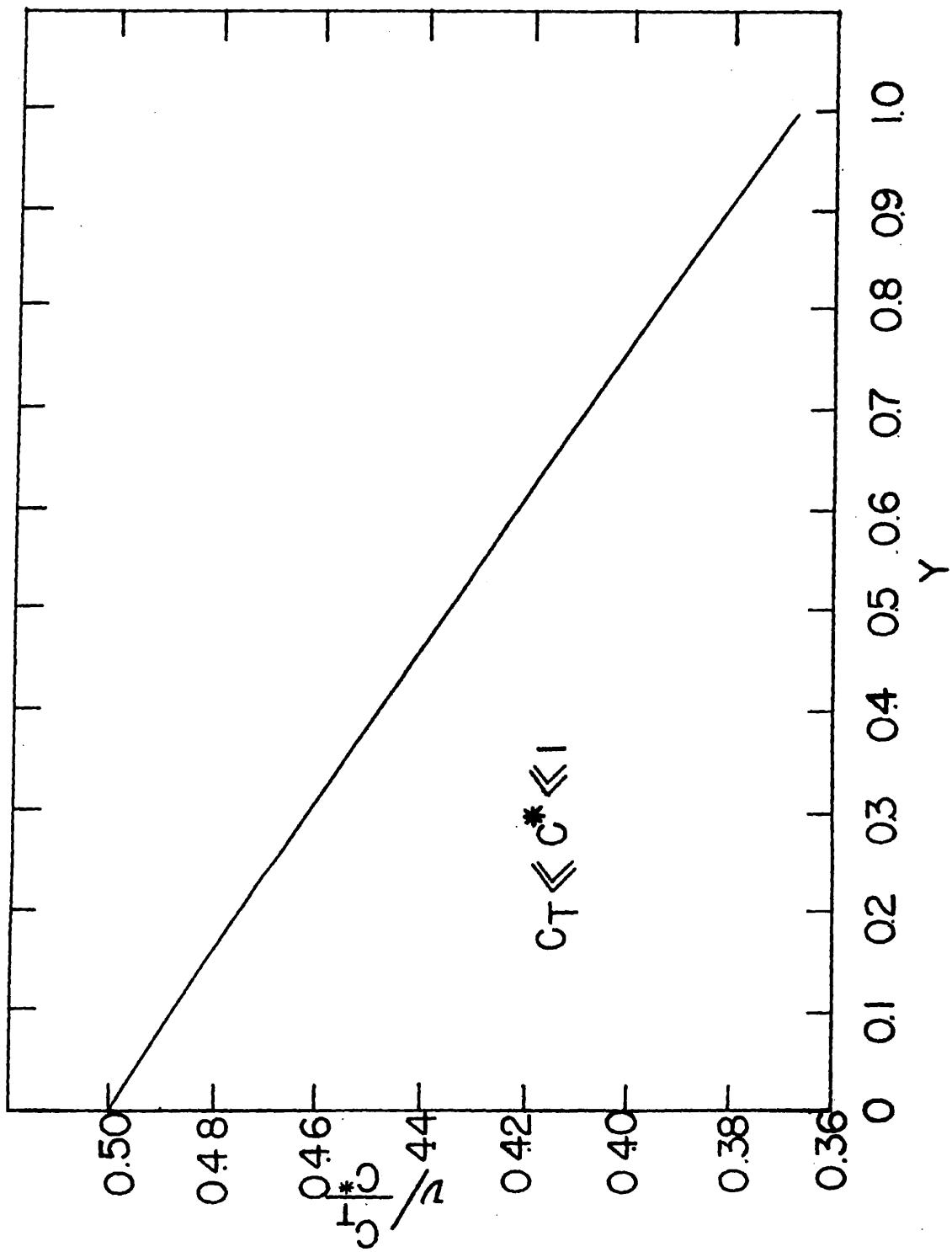
Theoretical Chart 6 Fig. 3



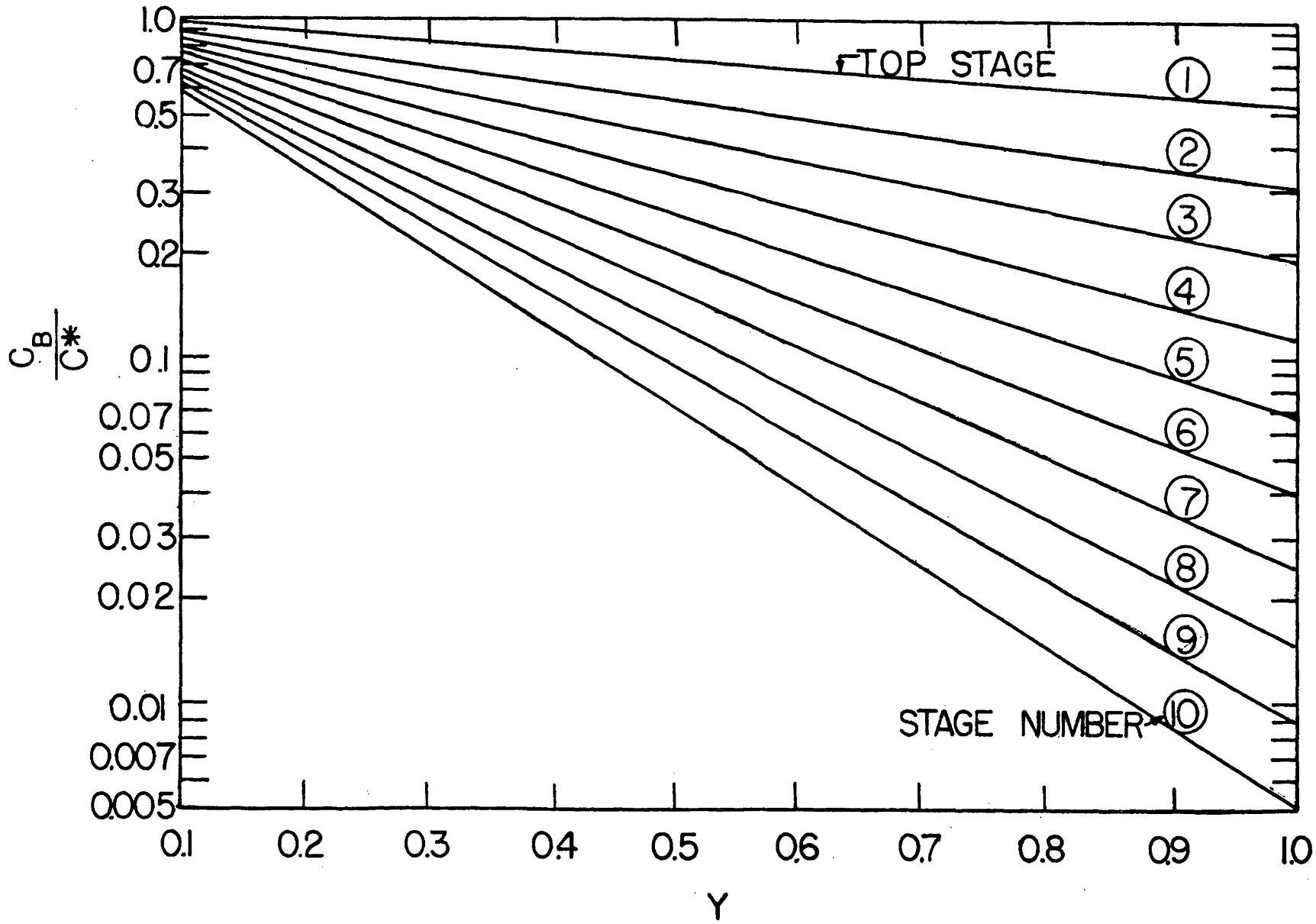
Theoretical Chap. 6 Fig. 4



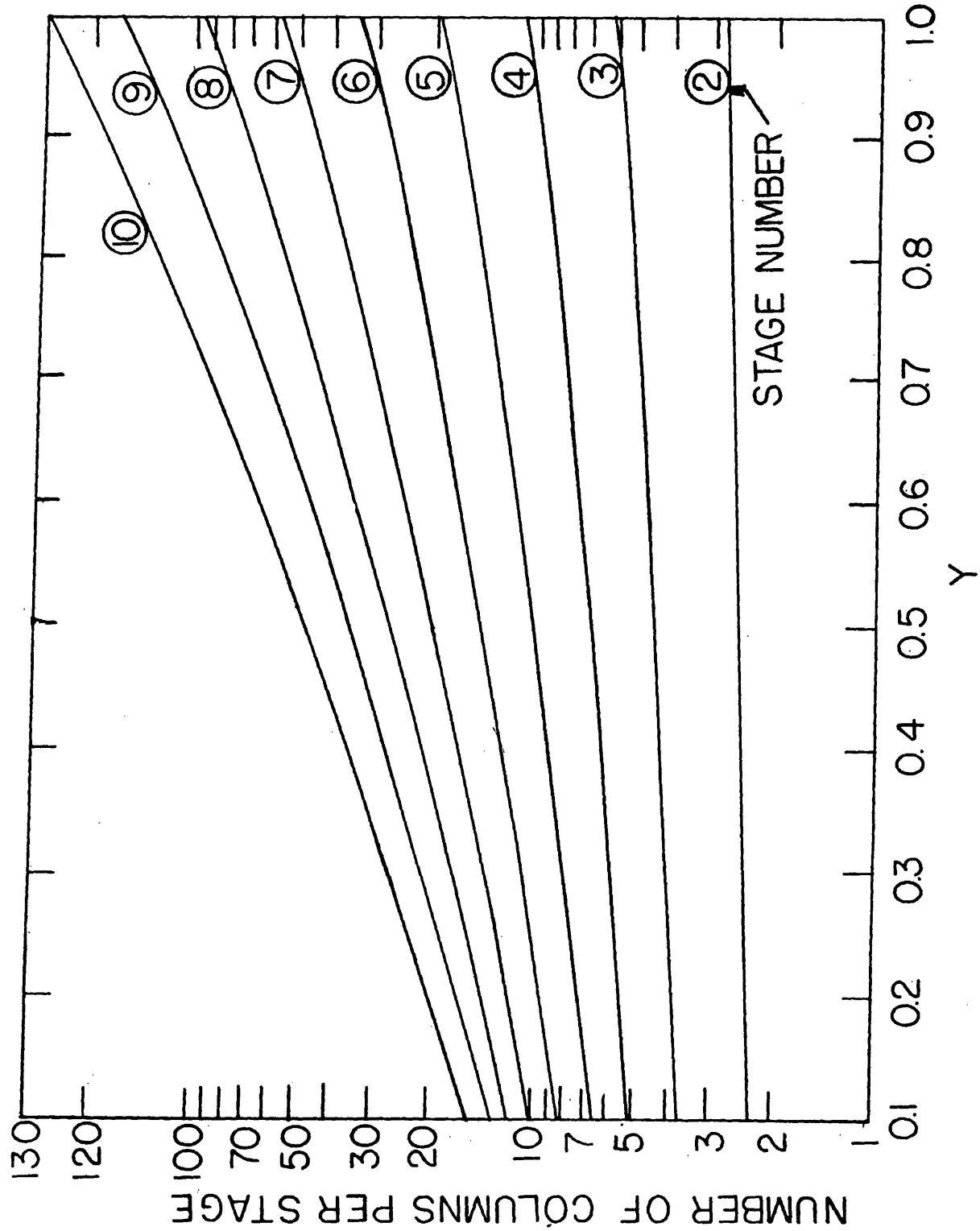
Theoretical Chap. 6 Fig. 5



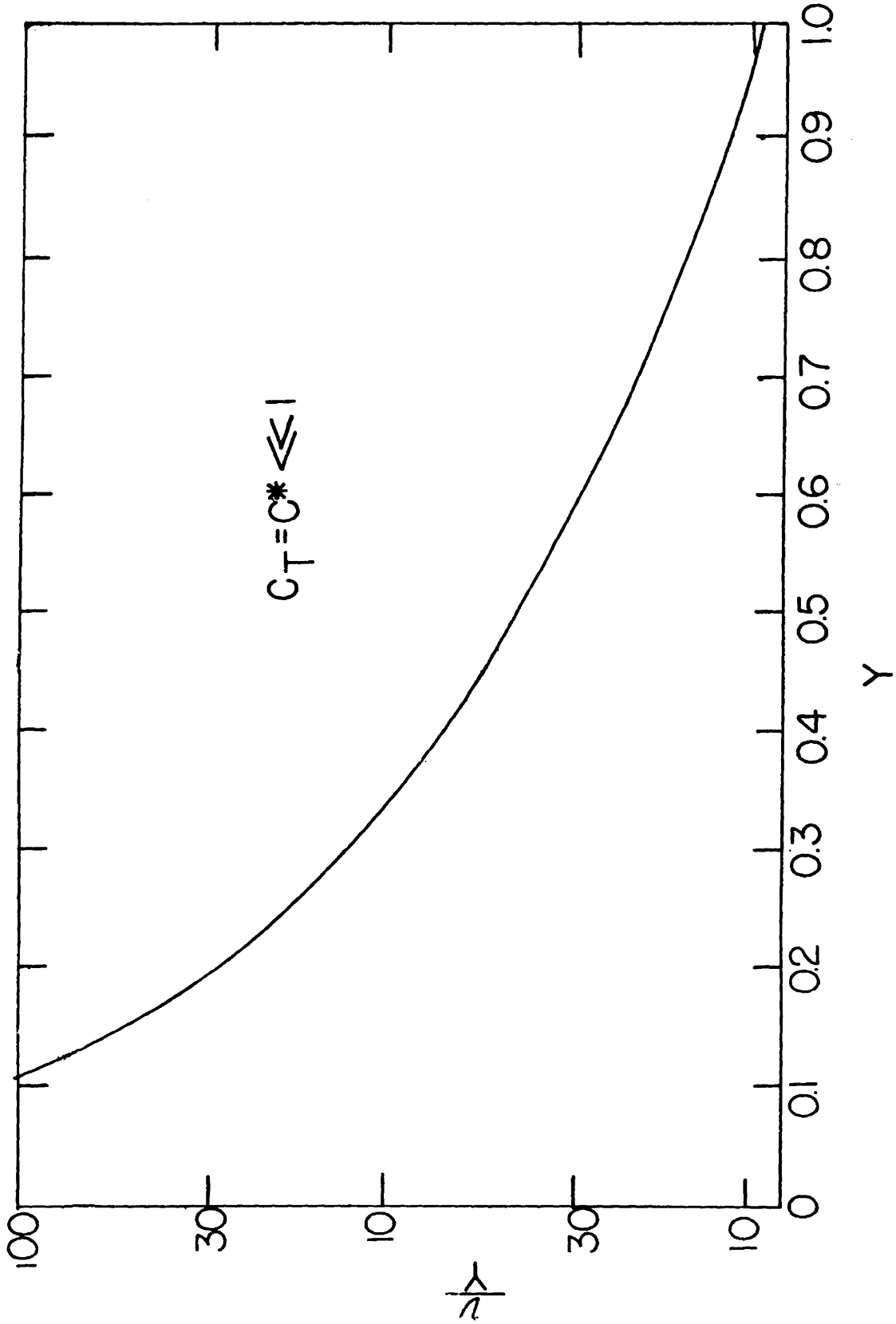
Theoretical Chap 6 Fig 6



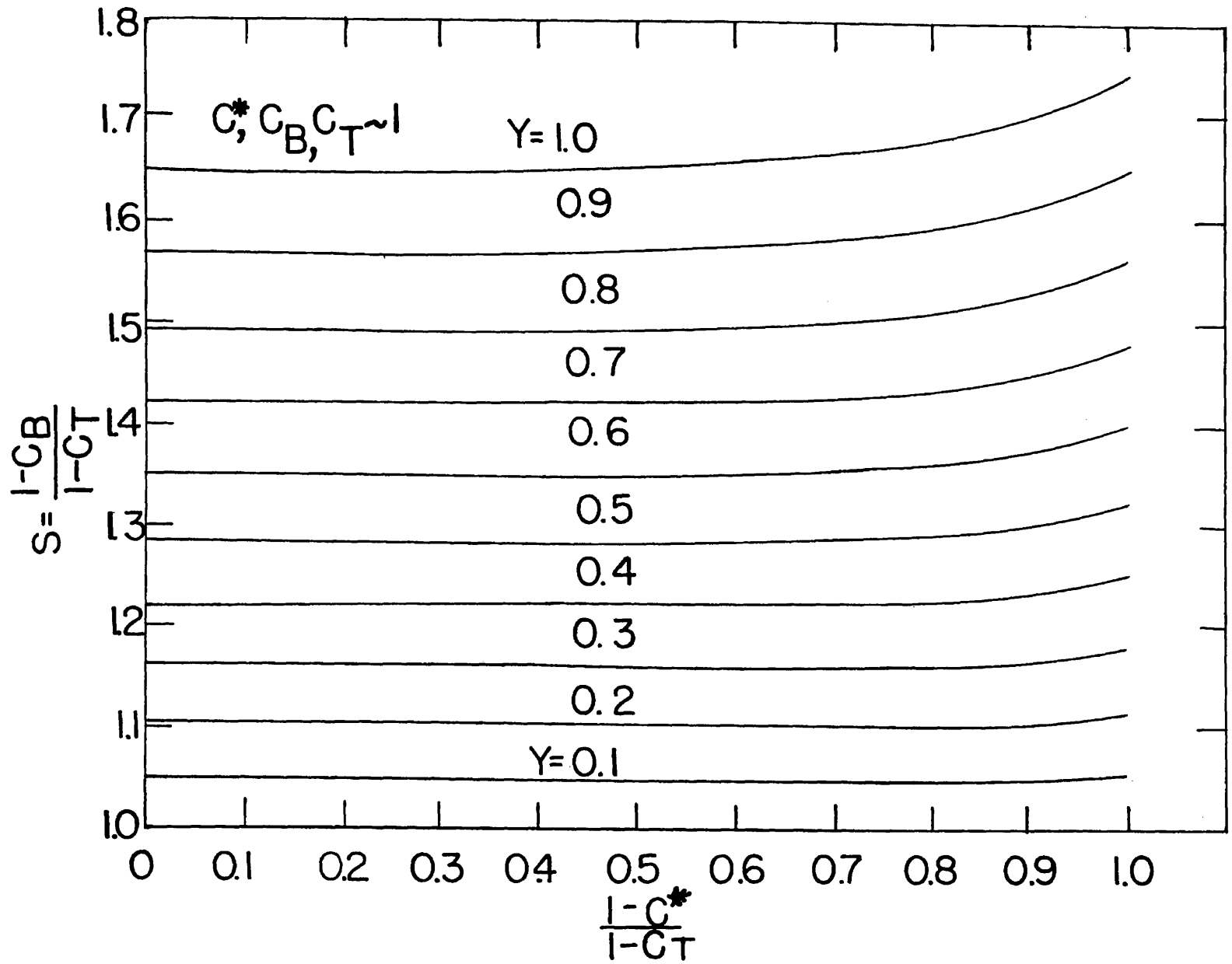
Theoretical Chap. 6 Fig. 7



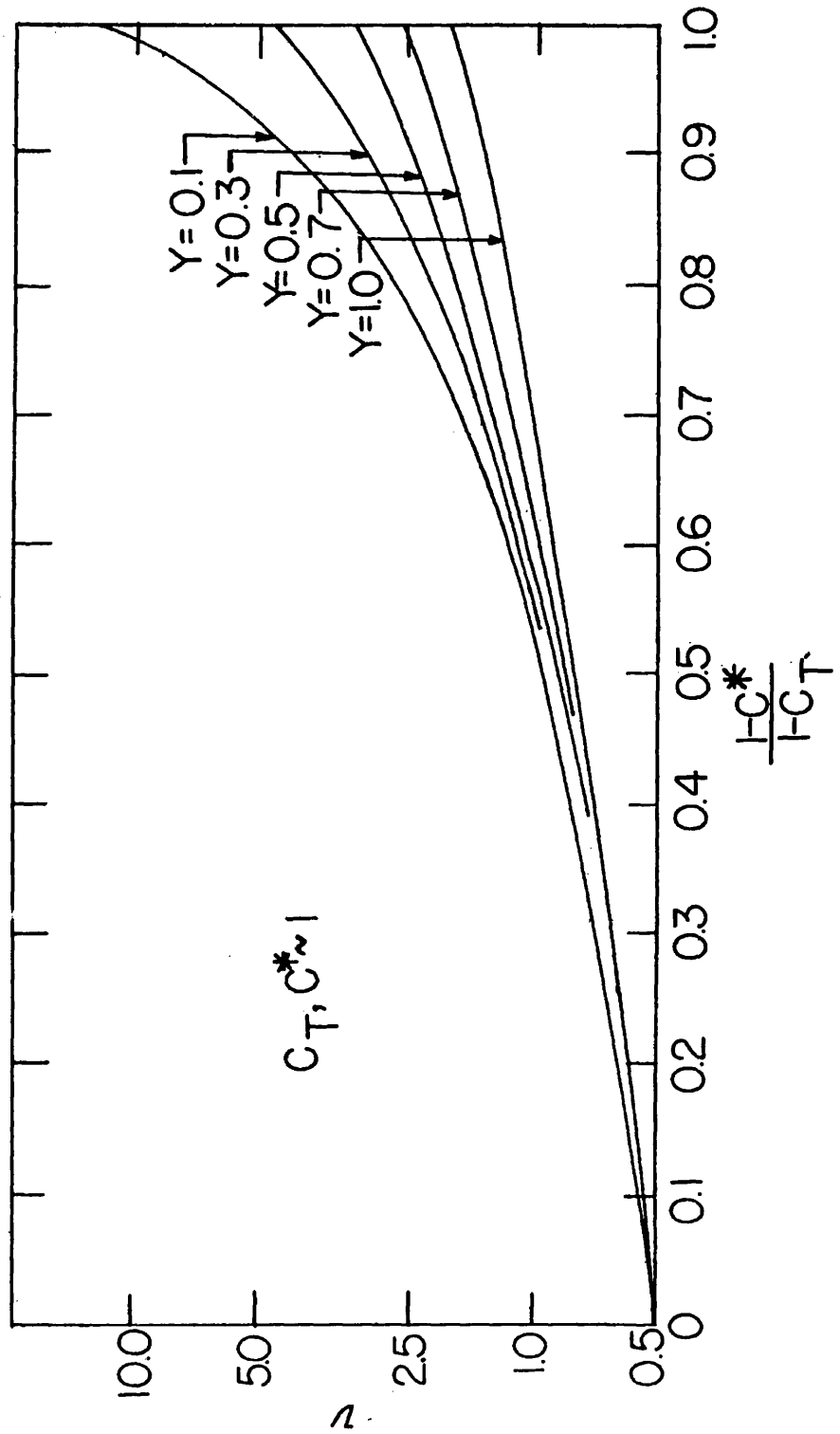
Theoretical Chap. 6 Fig. 8



Theoretical Chap. 6 Fig. 9



Theoretical Chap. 6 Fig. 10



Theoretical Chap. 6 Fig. 11

CHAPTER VII. DESIGN AND PERFORMANCE OF SMALL PYRAMIDS

1. Separation Factors

In the preceding chapter calculations were carried out and graphs were given to enable one to design and operate a small pyramid for optimum performance. Sometimes, however, the design and operation of the pyramid are limited by the necessity of fulfilling some additional condition. For example, it may be that, with a given number of columns in the pyramid, a prescribed product rate is to be maintained, and that this product rate is not the one that would have been arrived at on the basis of the criterion of optimum performance. Or it may be that the over-all separation factor for the pyramid is pre-assigned and is not the same as that based on the optimum performance criterion. Such problems frequently arise in practice and it is desirable to have a systematic procedure for solving them.

We shall treat here the case of low concentrations and hence shall use the linear approximation. Let us number the stages counting down from the top. Let S_k denote the separation factor for the k'th stage, and let S^*_k denote the separation factor between the bottom of the k'th stage and the top of the pyramid, so that

$$S^*_k = S_1 \, S_2 \cdots S_k \, . \tag{1}$$

From the theory of the single column, we have

$$\frac{1}{S_k} = \frac{\nu_k}{1+\nu_k} S^*_{k-1} + \left[1 - \frac{\nu_k}{1+\nu_k} S^*_{k-1}\right] \Big/ \beta_k \ , \quad (k = 2, \cdots n)$$

$$\frac{1}{S_1} = \frac{\nu_1}{1+\nu_1} + \frac{1}{(1+\nu_1)\beta_1} \ , \qquad (k = 1) \tag{2}$$

where

$$\nu_k = \frac{P}{H\,N_k} \ , \ \beta_k = e^{Y(1+\nu_k)} \ , \tag{3}$$

<u>n</u> is the total number of stages, N_k is the number of columns in the k'th stage, P is the product rate of the pyramid and <u>H</u> and <u>Y</u> are the column constants, as previously defined. From Eq. (2) one gets

$$\frac{1}{S^*_k} = \frac{\nu_k}{1+\nu_k} + \left[\frac{1}{S^*_{k-1}} - \frac{\nu_k}{1+\nu_k}\right] \Big/ \beta_k \ . \quad (k = 2, \cdots n) \ . \tag{4}$$

The total number of columns is given by

$$N = \sum_{k=1}^{n} N_k = \frac{P}{H\,\nu_{an}} \ , \tag{5}$$

where ν_{an} is defined by

$$\frac{1}{\nu_{an}} = \sum_{k=1}^{n} \frac{1}{\nu_k} \tag{6}$$

2. Optimum Performance Design

A problem encountered in practice in the following: given a fixed number of columns N and a prescribed product P, to design the pyramid so that the over-all separation factor shall be a maximum. In this case we have, on the basis of Eq. (5), that

$$\nu_{an} = \text{constant}, \tag{7}$$

or if we introduce infinitesimal changes $d\nu_k$ in the ν_k, we must keep

$$\sum_{k=1}^{n} \frac{d\nu_k}{\nu_k^2} = 0 . \tag{8}$$

On the other hand, the necessary condition that $S^* = S^*_n$ be a maximum is that

$$d\, S^*_n = 0 \tag{9}$$

for arbitrary $d\nu_k$ subject only to the restriction (8). If we express Eq. (9) in terms of the $d\nu_k$, then we can eliminate one of the latter, say $d\nu_1$ between this equation and Eq. (8) and thus obtain an equation in which there is no longer any restriction on any of the remaining $d\nu_k$, so that, if the whole expression is to vanish, the coefficient of each $d\nu_k$

must vanish.

Another formulation of the optimum-design problem is as follows: for a given value of N and a prescribed separation factor $S_n^* = S^*$, to make the product rate a maximum. This means: to keep S^*_n fixed and make $\frac{1}{\nu_{an}}$ a minimum. If we introduce infinitesimal changes $d\nu_k$, they must now satisfy the restriction (9) corresponding to S^*_n constant, but for all such changes Eq. (8) must hold, as the condition that $\frac{1}{\nu_a}$ be a minimum. We are thus led to the same equations as in the previous formulation of the problem (although their interpretations are different), and can use the same procedure for treating them as above, obtaining the same results.

Let us carry out the procedure mentioned above. For convenience we write Eq. (9) in the form

$$d\left(\frac{1}{S^*_n}\right) = 0 \tag{9a}$$

and, eliminating $d\nu_1$ between this equation and (8), we get

$$\sum_{k=2}^{n}\left[\frac{\partial}{\partial\nu_k}\left(\frac{1}{S^*_n}\right) - \frac{\nu_1^2}{\nu_k^2}\frac{\partial}{\partial\nu_1}\left(\frac{1}{S^*_n}\right)\right] d\nu_k = 0 \ . \tag{10}$$

Since we can take $d\nu_2 \cdots d\nu_k$ arbitrarily, we get as our system of equations

$$\frac{\partial}{\partial \nu_k}\left(\frac{1}{S^*_n}\right) - \frac{\nu_1^2}{\nu_k^2}\frac{\partial}{\partial \nu_1}\left(\frac{1}{S^*_n}\right) = 0. \quad (k = 2,\cdots n) \tag{11}$$

Now, from (4) we have

$$\frac{\partial}{\partial \nu_k}\left(\frac{1}{S^*_k}\right) = \frac{1}{(1+\nu_k)^2}\left(1 - \frac{1}{\beta_k}\right) - \frac{Y}{\beta_k}\left(\frac{1}{S^*_{k-1}} - \frac{\nu_k}{1+\nu_k}\right), \quad (k>1) \tag{12a}$$

$$\frac{\partial}{\partial \nu_j}\left(\frac{1}{S^*_k}\right) = 0, \quad (j>k) \tag{12b}$$

$$\frac{\partial}{\partial \nu_j}\left(\frac{1}{S^*_k}\right) = \frac{1}{\beta_{j+1}\cdots\beta_k}\frac{\partial}{\partial \nu_j}\left(\frac{1}{S^*_j}\right), \quad (j<k) \tag{12c}$$

$$\frac{\partial}{\partial \nu_1}\left(\frac{1}{S^*_k}\right) = \frac{1}{\beta_2\cdots\beta_k}\left\{\frac{1}{(1+\nu_1)^2}\left(1 - \frac{1}{\beta_1}\right) - \frac{Y}{\beta_1(1+\nu_1)}\right\}. \tag{12d}$$

Making use of (12c), we find that (11) can be written

$$\frac{\partial}{\partial \nu_k}\left(\frac{1}{S^*_k}\right) - \frac{\nu_1^2}{\nu_k^2}\frac{\partial}{\partial \nu_1}\left(\frac{1}{S^*_k}\right) = 0. \quad (k = 2,\cdots n) \tag{13}$$

From this it is evident that the condition to be satisfied at each stage is independent of the stages below it. This is convenient since it enables one to carry out the calculations by starting from the top and working down step by step as far as desired.

By using (12a) and (12d) in (13), we get equations which can be put into the form

$$\beta_k - 1 = Y\left\{\frac{(1+\nu_k)^2}{S^*_{k-1}} - \nu_k\,(1+\nu_k) - \frac{\nu_1^2(1+\nu_k)^2}{\nu_k^2\,(1+\nu_1)}\cdot\frac{1}{\beta_1\cdots\beta_{k-1}}\right\} +$$

$$+\frac{\nu_1^2(1+\nu_k)^2}{\nu_k^2(1+\nu_1)^2}\quad\frac{\beta_1 - 1}{\beta_1\cdots\beta_{k-1}}\qquad (k>2)\ , \tag{14}$$

and

$$\beta_2 - 1 = \left[\frac{\nu_1(1+\nu_2)}{\nu_2(1+\nu_1)}\right]^2 (1-\frac{1}{\beta_1}) - \frac{Y(1+\nu_2)(\nu_1-\nu_2)}{1+\nu_1}\left[\frac{(1+\nu_2)(\nu_1+\nu_2)}{\beta_1\quad\nu_2^2} - 1\right]\ . \tag{15}$$

The limiting cases are of interest. If we let $\nu_1 \to 0$, then all the $\nu_k \to 0$, and if we set $q_k = \frac{\nu_1}{\nu_k}$, we get in the limit

$$q_k^{\ 2} = \frac{e^{kY} - e^{(k-1)Y} - Y}{e^Y - Y - 1}\ . \tag{16}$$

For k = 2 we have

$$q_2^{\ 2} = \frac{e^{2Y} - e^Y - Y}{e^Y - Y - 1}\ . \tag{17}$$

On the other hand, if we let $\nu_1 \to \infty$ we find that the other ν_k remain finite, and equation (14) gives over into

$$\beta_k - 1 = Y\left\{\frac{(1+\nu_k)^2}{S^*_{k-1}} - \nu_k\,(1+\nu_k)\right\} + \left(\frac{1+\nu_k}{\nu_k}\right)^2 \Big/ \beta_2 \cdots \beta_{k-1} \quad (k > 2), \tag{18}$$

while for k = 2 we get

$$\beta_2 - 1 = Y\,(1+\nu_2) + \left(\frac{1+\nu_2}{\nu_2}\right)^2 . \tag{19}$$

Some calculations have been carried out based on the preceding equations. Various values of ν_1 were taken, and the equations were solved numerically for ν_2 and ν_3. From these $S^*_1 = S_1$, S^*_2, S^*_3, ν_{a2} and ν_{a3} were calculated. Figs. 1-5 show S^* as a function of ν_{an} for 1, 2 and 3 stages, each figure referring to a different value of Y from 0.4 to 0.8. The x's represent the endpoints of the curves for 2 and 3 stages and correspond to $\nu_1 = \infty$. It will be seen that the curves meet tangentially. Figs. 6 and 7 show $\frac{1}{\nu_1}$ and $\frac{1}{\nu_2}$ as functions of $\frac{1}{\nu_{a2}}$ for the 2-stage pyramid for various values of Y. Figs. 8, 9 and 10 show $\frac{1}{\nu_1}$, $\frac{1}{\nu_2}$ and $\frac{1}{\nu_3}$ as functions of $\frac{1}{\nu_{a3}}$ for the three stage pyramid. It will be recalled that ν_{an} is given by Eq. (5) in terms of N, P and H, and N_k is given by Eq. (3) in terms of ν_k, P and H.

3. <u>Comparison of Performance</u>

For a given value of ν_{an}, as determined by the given values of N, P and H, the procedure of the previous section gives

the best distribution of the columns among the various stages. With this "best" distribution, the separative efficiency will be a function of ν_{an}. Since we are restricting ourselves here to the linear approximation, we write for the separative efficiency

$$E = \frac{4P}{NHY}(S^* - 1 - \ln S^*) = \frac{4\nu_a}{Y}(S^* - 1 - \ln S^*) \qquad (20)$$

Fig. 11 shows E as a function of ν_a for 1, 2 and 3 stages and for $Y = 0.6$, as a typical case. For a given number of stages, E as a function of ν_a has a maximum. An interesting feature of the curves is the fact that the point at which the curves for different numbers of stages meet lies close to the maximum of the curve with the smaller number of stages. In other words, if one starts out with a pyramid of a certain number of stages and gradually increases the number of columns (keeping the ratios of the numbers in the various stages so as to conform to the criterion for optimum performance developed here) one reaches a point at which the separative efficiency is a maximum. Increasing the number of columns further then results in a lowering of separative efficiency unless one adds another stage to the pyramid. If one adds another stage (and one continues to satisfy the optimum-performance criterion) then the new curve for E starts out at a value very slightly lower than the previous maximum,

but rises rapidly to a new, and appreciably higher, maximum.

It will be seen that there is a definite advantage in having more than one stage. For the range of values of Y considered here (0.4 - 0.8) the separative efficiency is about 80% for a single stage, while for two stages it is over 90%. Going from two to three stages leads to a further, although smaller, improvement. Above three stages, the improvement due to the addition of a stage will be still smaller.

4. Operating Time

A question of practical importance is that of the time required for the pyramid, initially filled with low-concentration material, to reach the distribution of concentration at which the pyramid can be put into operation, i.e., the steady-state product can be withdrawn.

To get this time accurately involves lengthy calculations. An approximate value can be obtained fairly readily, however, by the method used in the discussion of the continuous pyramid (Chap. I): We find the time required for the pyramid to reproduce its hold-up of excess light constituent.

For the k'th stage, the concentration c_k a distance z up from the bottom of a column is given by

$$c_k = \frac{\nu_k c^*}{1+\nu_k} + \left[c_{Bk} - \frac{\nu_k c^*}{1+\nu_k} \right] e^{(1+\nu_k)\alpha z} , \qquad (21)$$

where c^* is the concentration at the top of the pyramid, and c_{Bk} is the concentration at the bottom of the k'th stage. The average value $\bar{c}_k$, for a column of length L, is given by

$$\bar{c}_k = \frac{1}{L} \int_0^L c_k \, dz \ , \tag{22}$$

and on the basis of (21), this is found to be

$$\bar{c}_k = \frac{\nu_k \, c^*}{1+\nu_k} + \left[c_{Bk} - \frac{\nu_k \, c^*}{1+\nu_k} \right] \frac{e^{(1+\nu_k) \, Y} - 1}{(1+\nu_k) \, Y} \tag{23}$$

The net light material hold-up is given by

$$M \sum_k^n N_k \, (\bar{c}_k - c_o) \ ,$$

where M is the total hold-up of material in one column, n is the number of stages and c_o is the impart concentration. The excess light material in the product per unit time is $P(c^* - c_o)$. Hence the operating time (or relaxation time) T_n is given by

$$T_n = \frac{M \sum_{k=1}^n N_k \, (\bar{c}_k - c_o)}{P \, (c^* - c_o)} \tag{24}$$

If we make use of (23) and write $N_k = \frac{P}{H\nu_k}$, we get

$$T_n = \frac{M}{H(c^* - c_o)} \sum_{k=1}^{n} \left\{ \frac{c^*}{1+\nu_k} - \frac{c_o}{\nu_k} + \left(\frac{c_{Bk}}{\nu_k} - \frac{c^*}{1+\nu_k} \right) \frac{\beta_k - 1}{(1+\nu_k)} \right\}. \qquad (25)$$

Setting

$$\frac{c^*}{c_o} = S^*_n , \qquad \frac{c_{Bk}}{c_o} = \frac{S^*_n}{S^*_k} \qquad (26)$$

we get

$$T_n = \frac{M\, S^*_n}{H(S^*_n - 1)} \sum_{k=1}^{n} \left\{ \frac{1}{1+\nu_k} - \frac{1}{S^*_n \nu_k} + \left(\frac{1}{S^*_k \nu_k} - \frac{1}{1+\nu_k} \right) \frac{\beta_k - 1}{(1+\nu_k)\, Y} \right\}, \qquad (27)$$

making use of the time constant X given by

$$X = \frac{M}{HY} ,$$

this can be written finally as

$$\frac{T_n}{X} = \frac{S^*_n}{S^*_n - 1} \sum_{k=1}^{k} \left\{ Y \left[\frac{1}{1+\nu_k} - \frac{1}{S^*_n \nu_k} \right] + \left[\frac{1}{S^*_k \nu_k} - \frac{1}{1+\nu_k} \right] \frac{\beta_k - 1}{1+\nu_k} \right\} \qquad (29)$$

For the case $n = 1$, this expression can be reduced to the form

$$\frac{T_1}{X} = \frac{1}{\nu_1} \left[\frac{1}{1+\nu_1} - \frac{Y}{\beta_1 - 1} \right] . \tag{30}$$

For pyramids designed for optimum performance, as in Section 2, calculations have been carried out for one, two and three stages, and the results are presented as graphs in Figs. 12, 13 and 14, where T/X is given as a function of ν_a, for values of Y from 0.4 to 0.8.

Chapter 7

Figure 1

Optimum design of a small pyramid for columns possessing Y = .4. If a separation factor less than 1.26 is desired a single stage is best. If a separation factor between 1.26 and 1.57 is desired two stages should be employed.

Figure 2

Optimum design of a small pyramid for columns possessing Y = .5. If a separation factor less than 1.34 is desired a single stage is best. If a separation factor between 1.34 and 1.75 is desired two stages should be employed.

Figure 3

Optimum design of a small pyramid for columns possessing Y = .6. If a separation factor less than 1.42 is desired a single stage is best. If a separation factor between 1.42 and 1.95 is desired two stages should be employed.

Figure 4

Optimum design of a small pyramid for columns possessing Y = .7. If a separation factor less than 1.50 is desired a single stage is best. If a separation factor between 1.50 and 2.17 is desired two stages should be employed.

Figure 5

Optimum design of a small pyramid for columns possessing Y = .8. If a separation factor less than 1.58 is desired a single stage is best. If a separation factor between

1.58 and 2.43 is desired two stages should be employed.

Figure 6

Optimum design of a two stage pyramid. The curves assist in choice of the proper number of columns for each stage (see text).

Figure 7

Optimum design of a two stage pyramid. The curves assist in choice of the proper number of columns for each stage (see text).

Figure 8

Optimum design of three stage pyramid. The curves assist in choice of the proper number of columns for each stage (see text).

Figure 9

Optimum design of three stage pyramid. The curves assist in choice of the proper number of columns for each stage (see text).

Figure 10

Optimum design of three stage pyramid. The curves assist in choice of the proper number of columns for each stage (see text).

Figure 11

Separative efficiency as a function of the generalized pyramid product rate for the optimum designs presented in the previous figures of the present chapter.

Figure 12

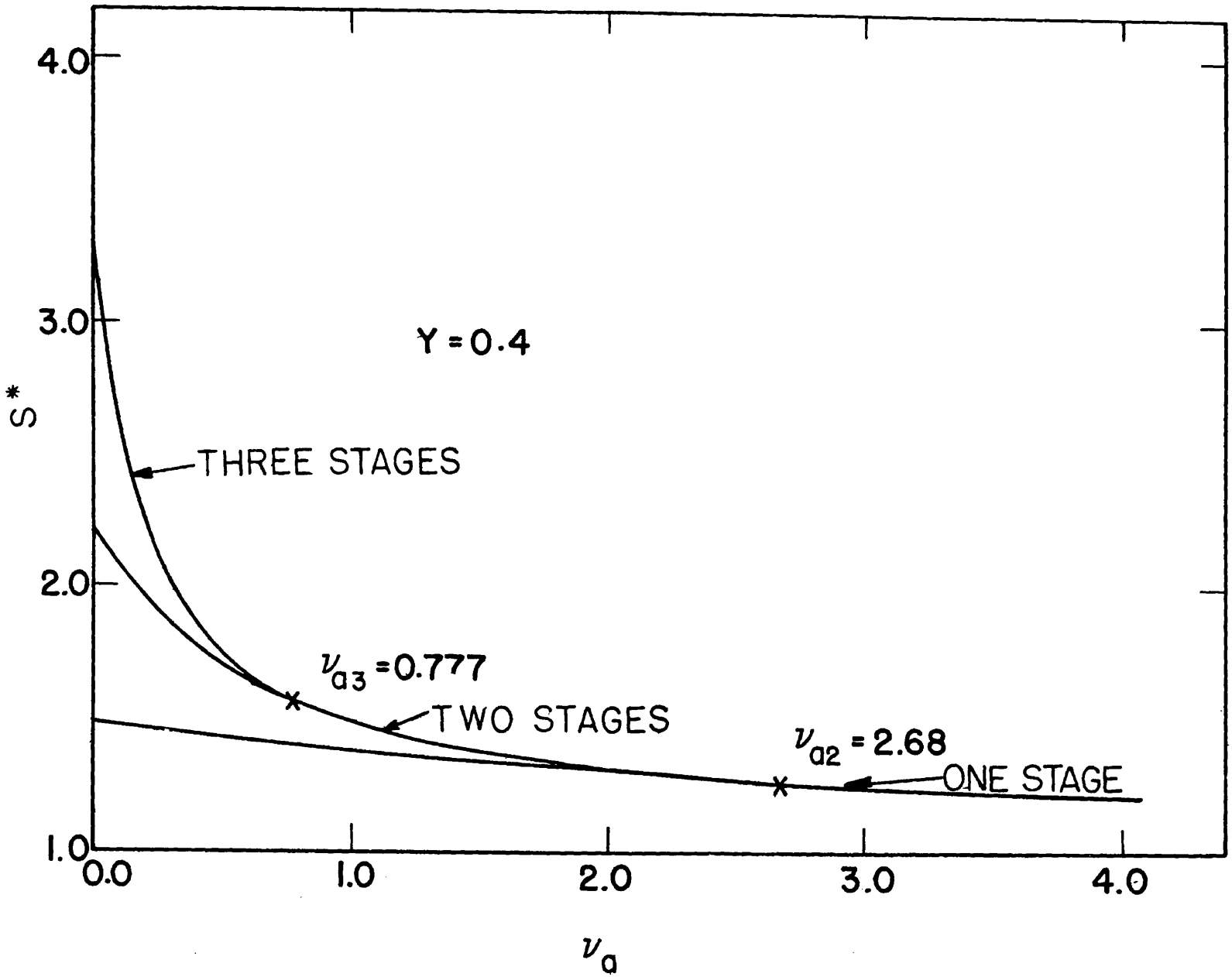
Time (T_1) necessary to reach steady state operating conditions for a one stage pyramid as a function of the reciprocal of the generalized product rate.

Figure 13

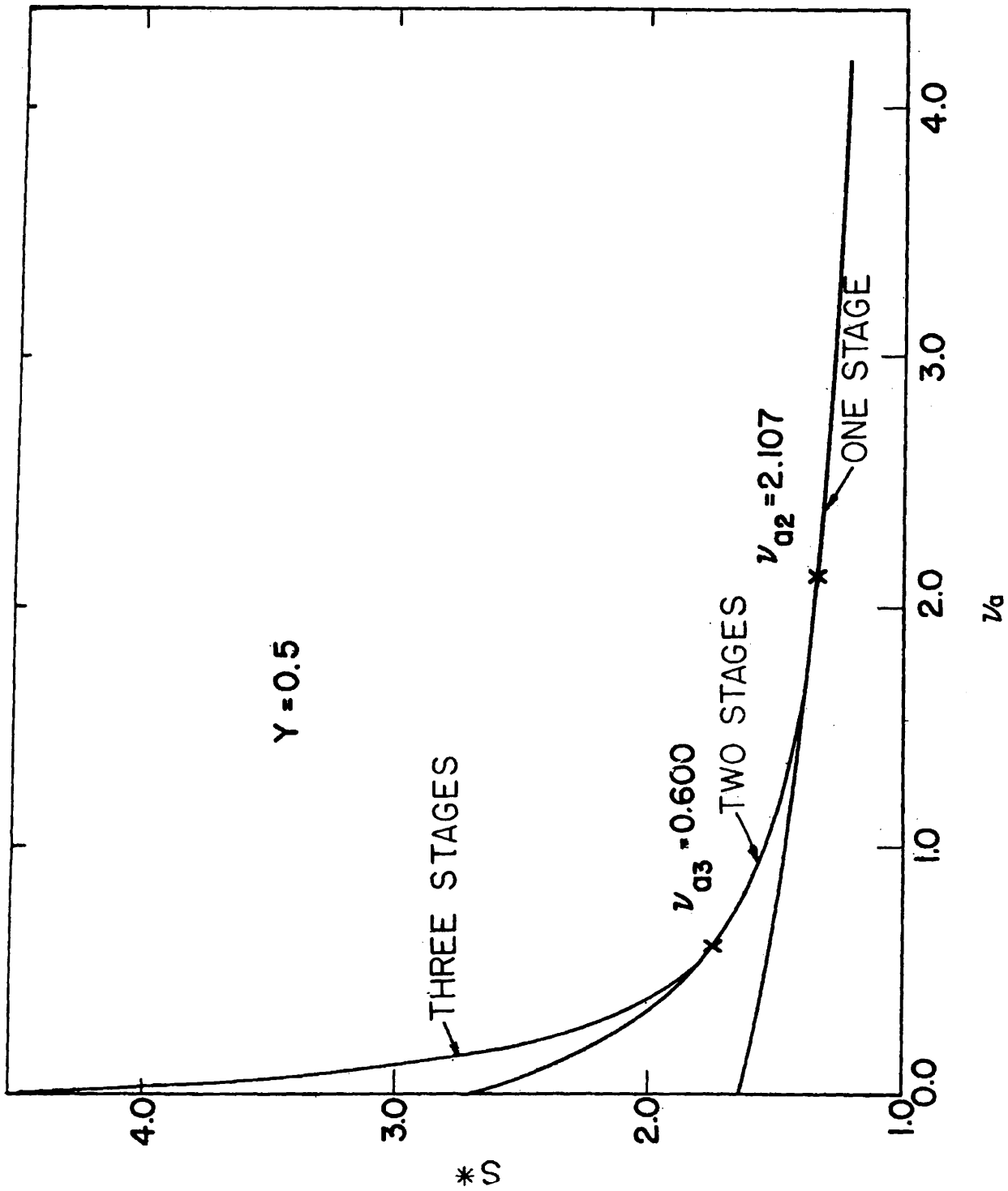
Time (T_2) necessary to reach steady state operating conditions for a two stage pyramid as a function of the reciprocal of the generalized product rate.

Figure 14

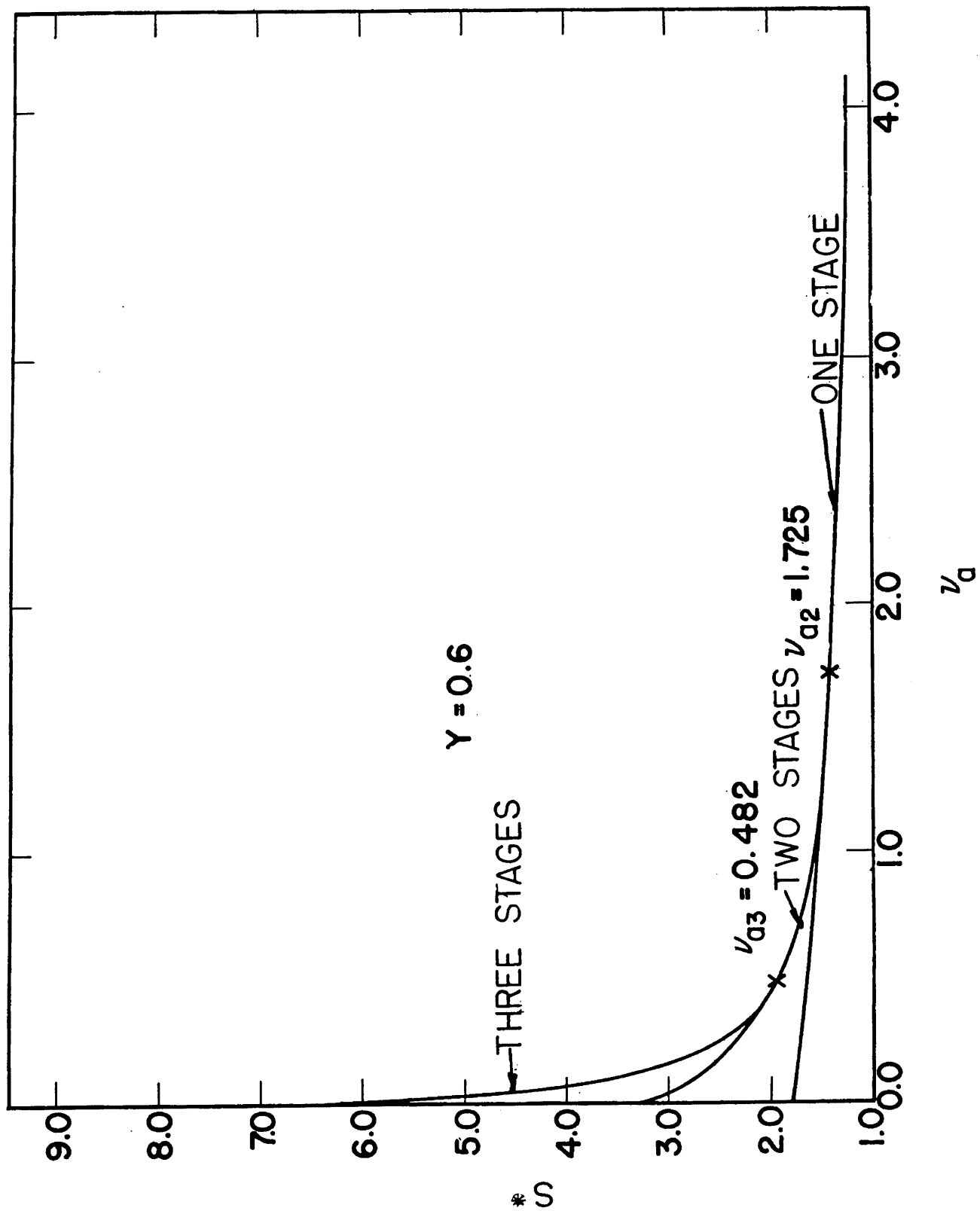
Time (T_3) to reach steady state operating conditions for a three stage pyramid as a function of the reciprocal of the generalized product rate.



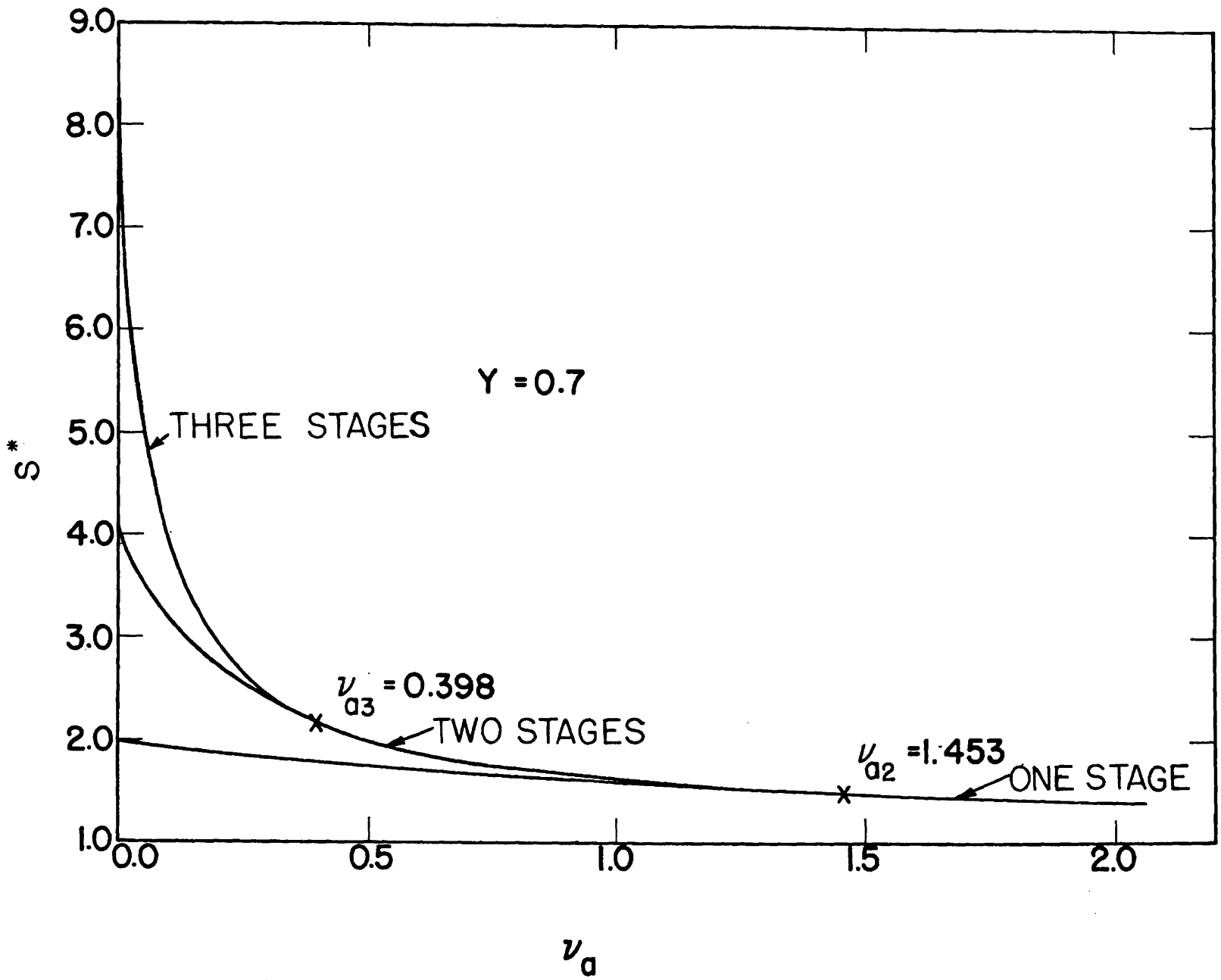
Theoretical Phase 7 Fig 1



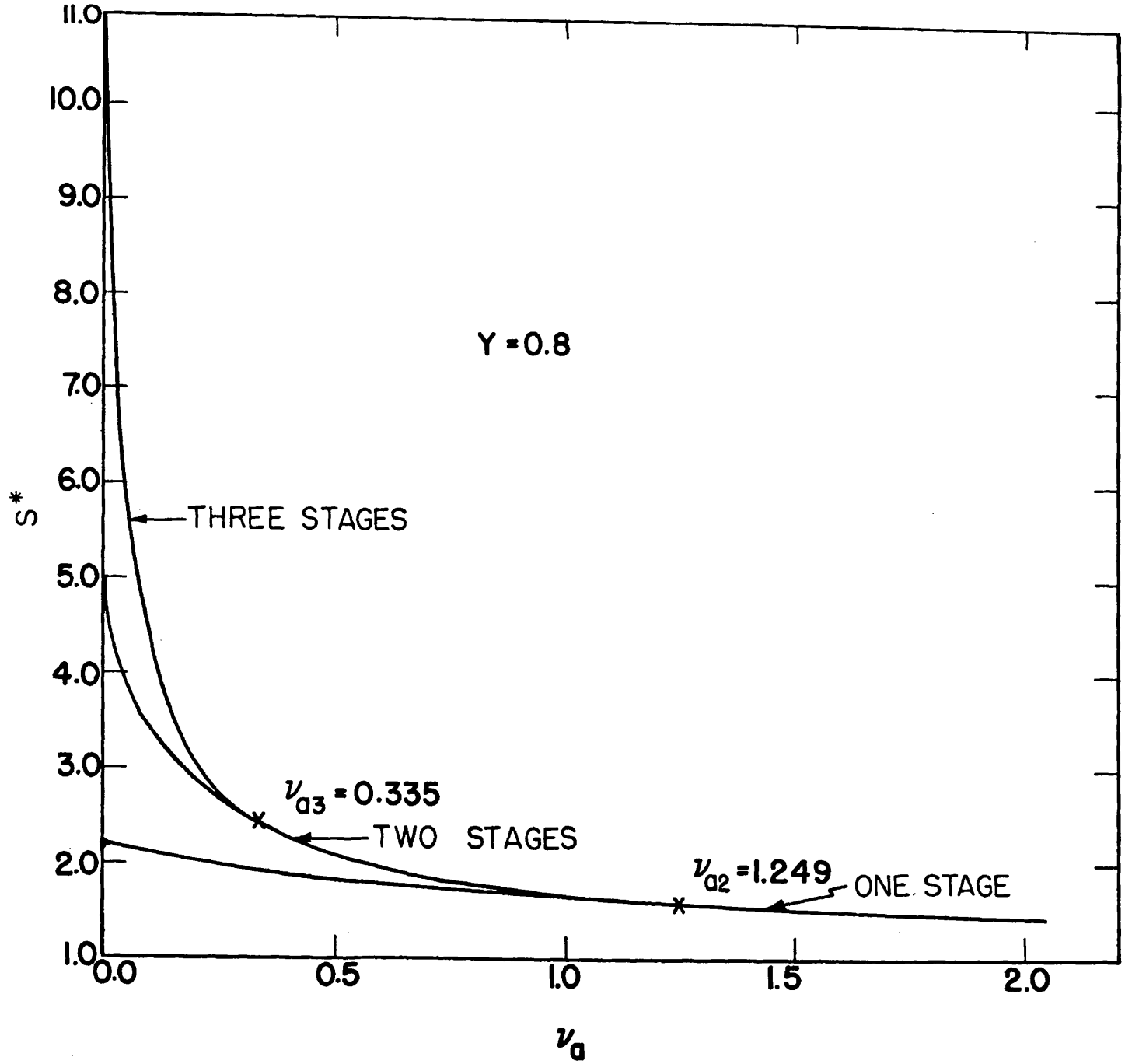
Theoretical Chap. 7 Fig. 2



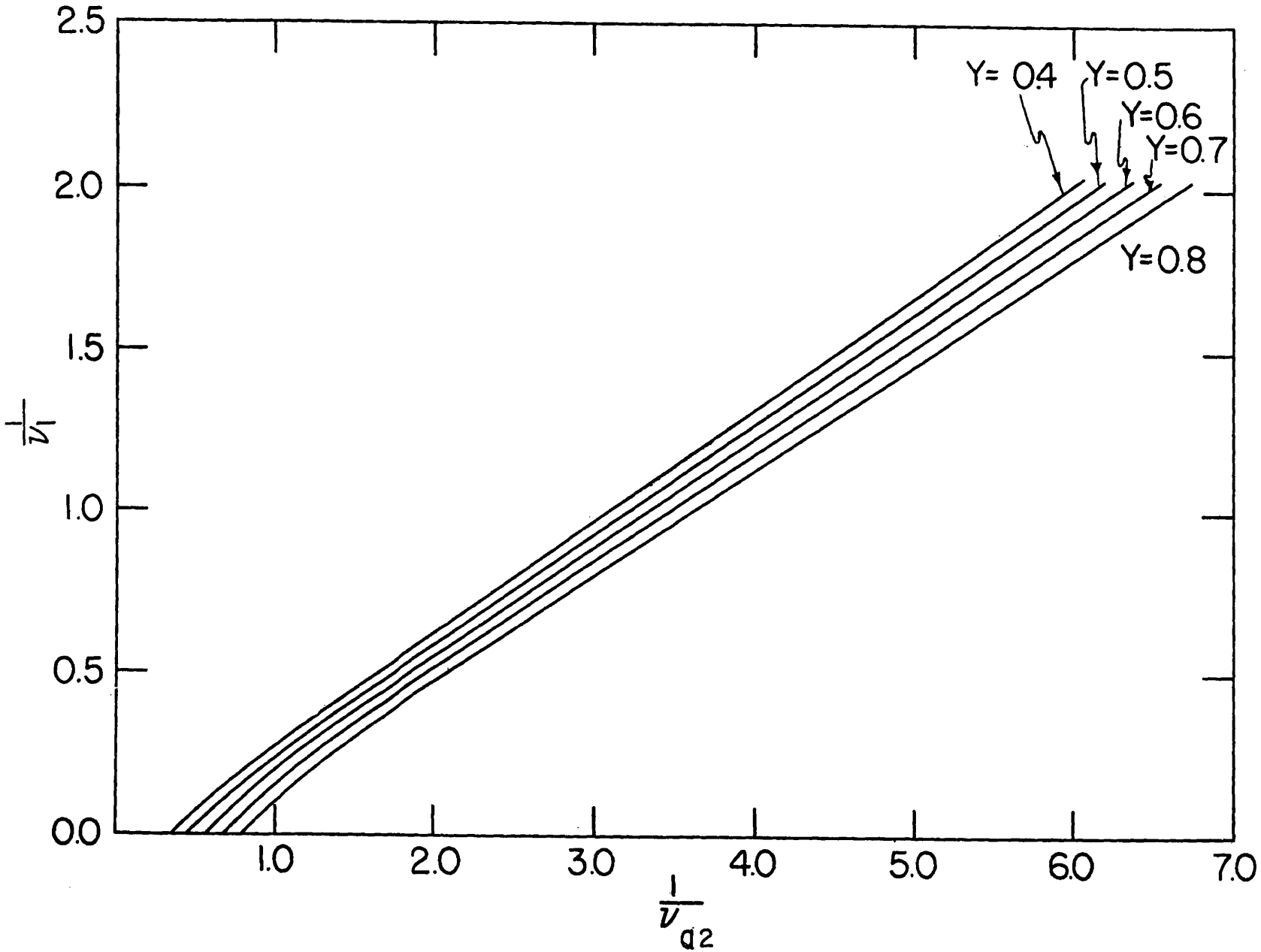
Theoretical Chap. 7 Fig. 3



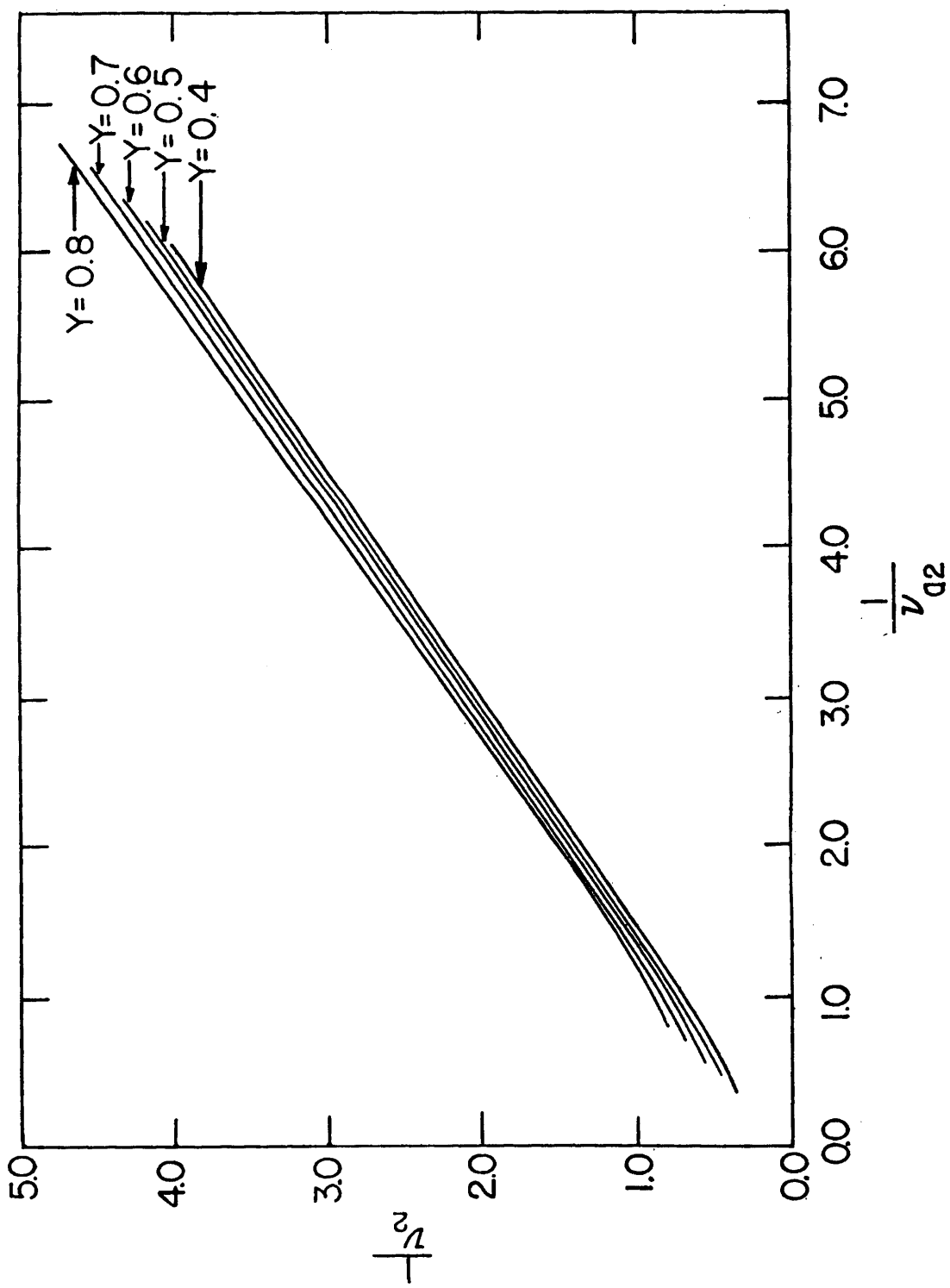
Theoretical Char. 7 Fig. 4



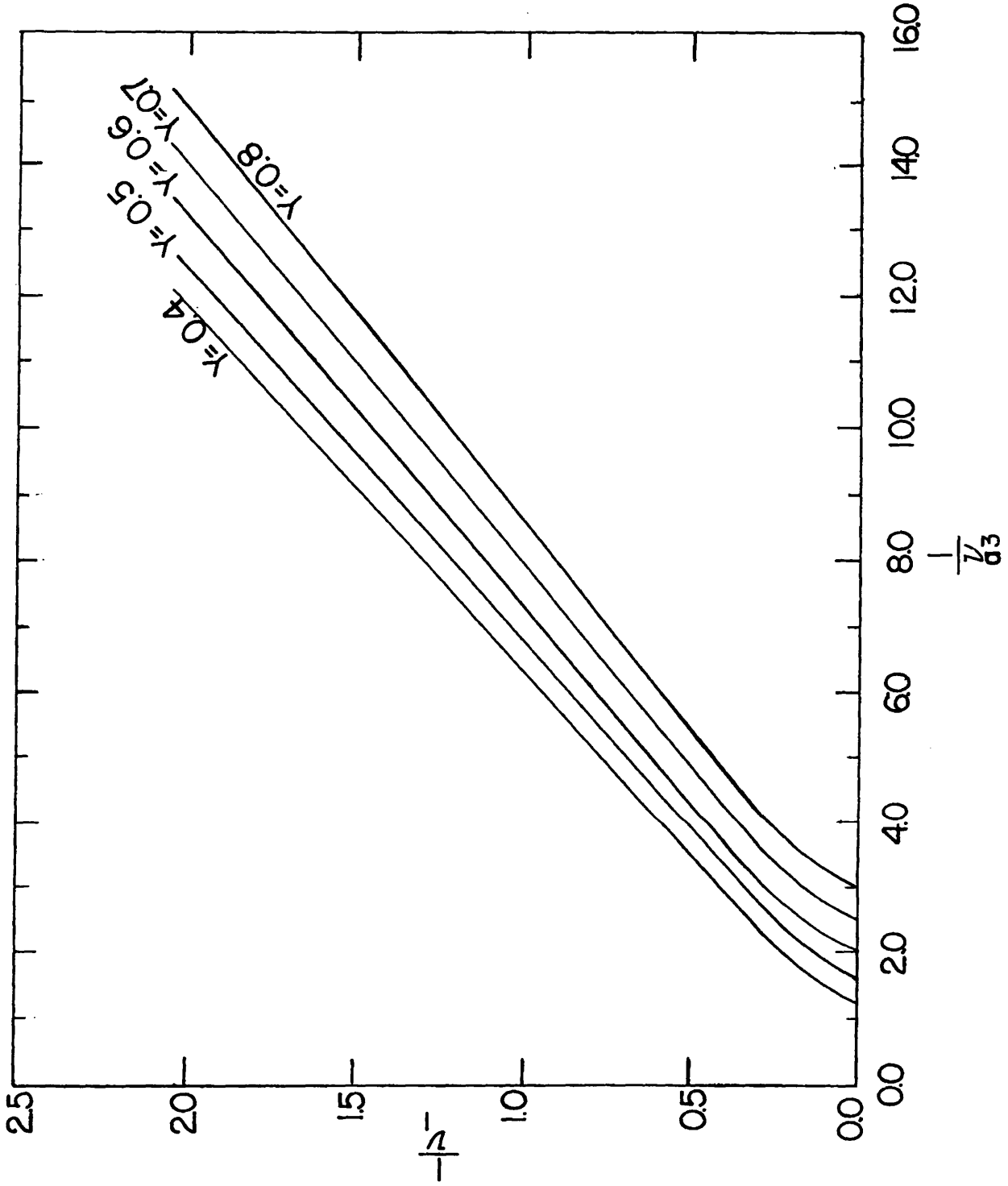
Theoretical Chap. 7 Fig. 5



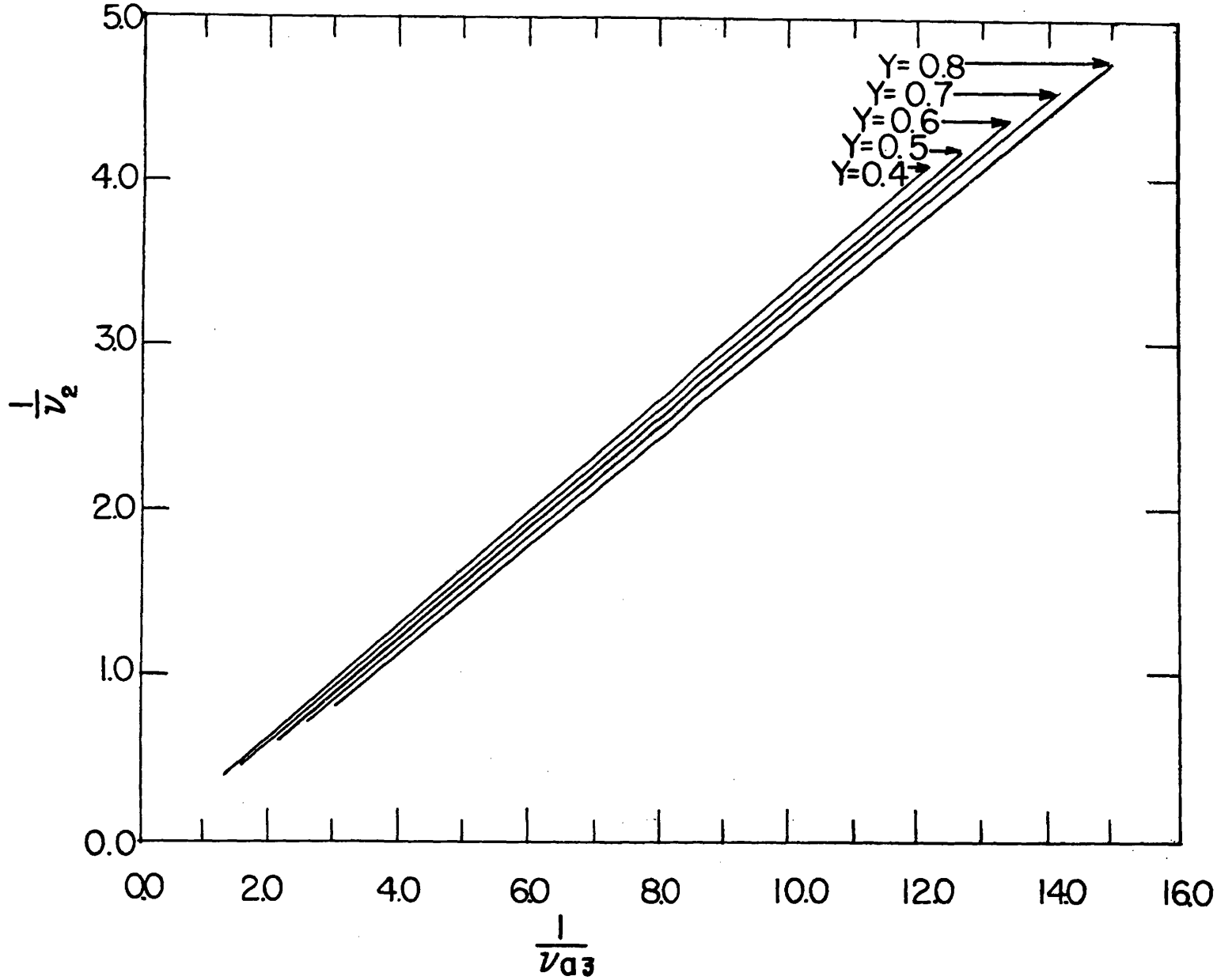
Theoretical Chart Fig 6



Theoretical Chap 7 Fig 7



Theoretical Chap. 7 Fig 8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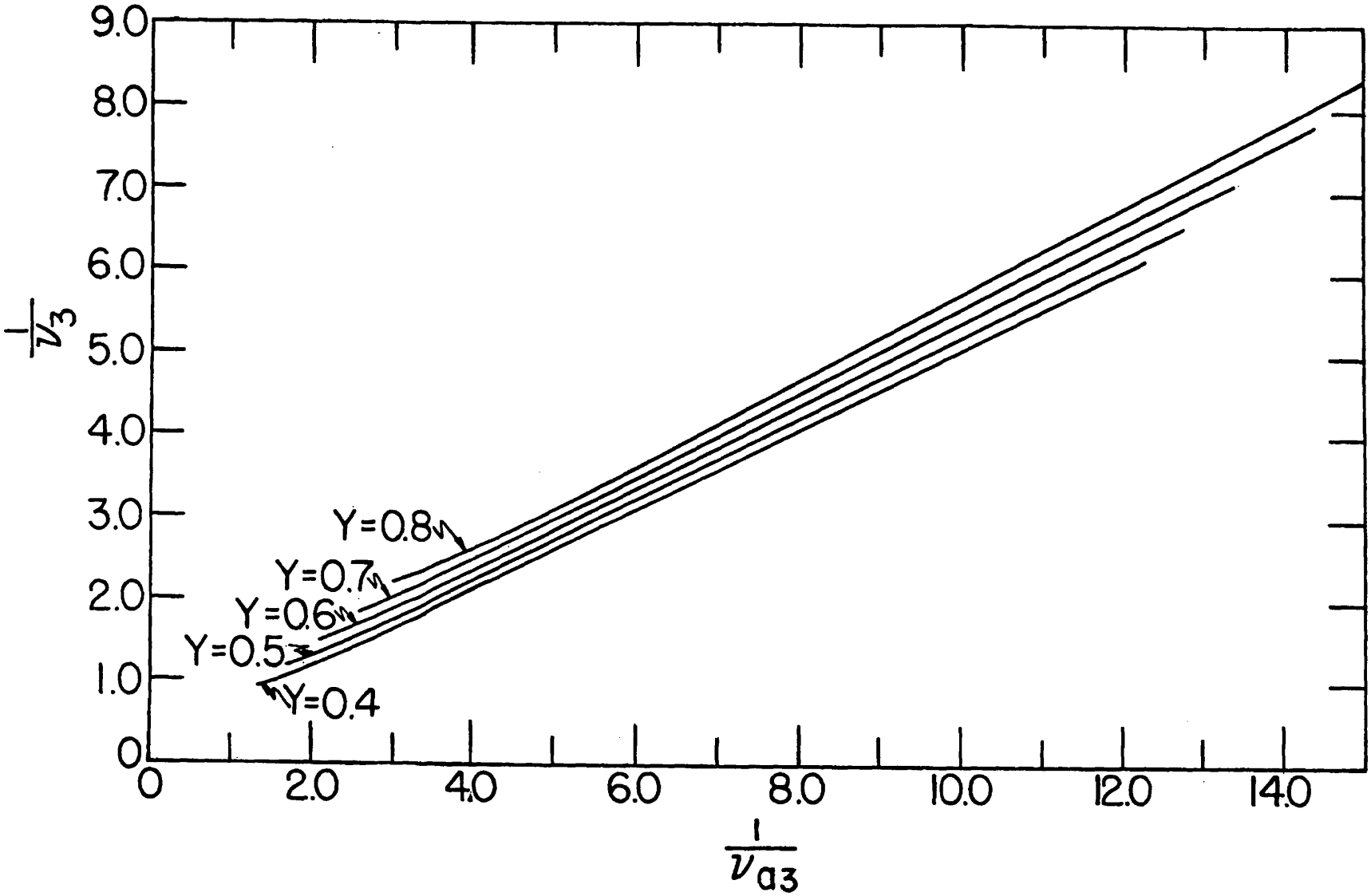
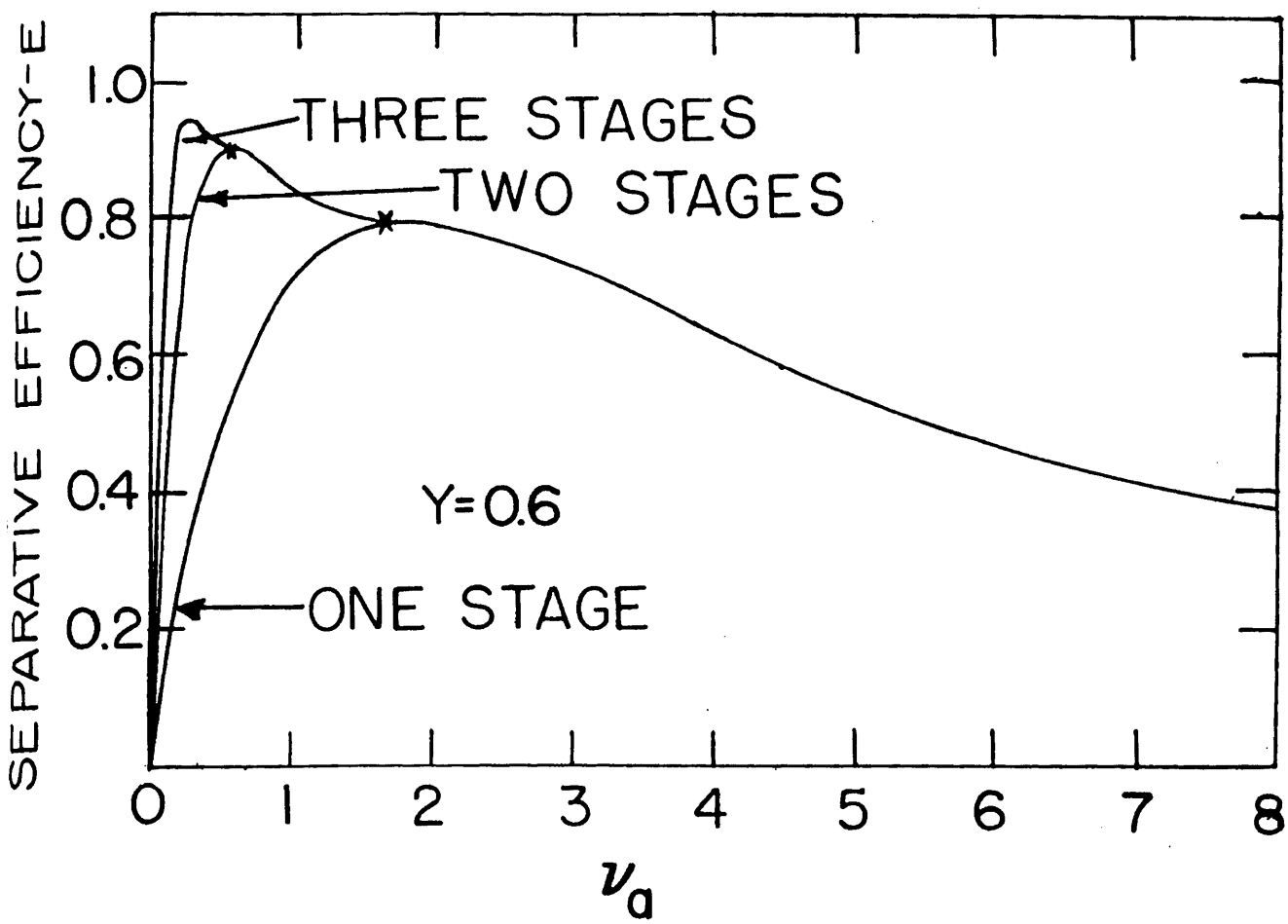
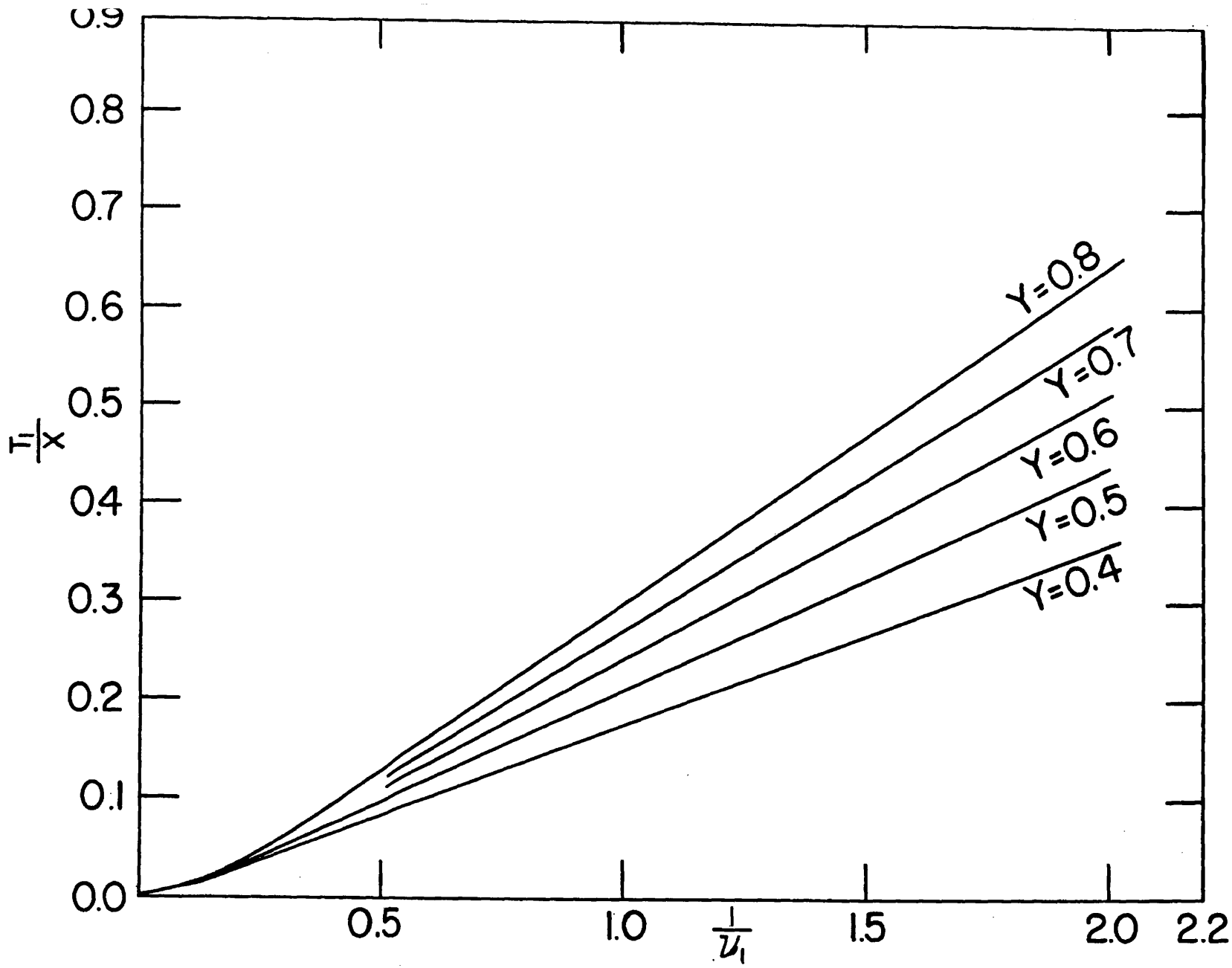
Y= 0.7
Y= 0.6
Y= 0.5
Y=0.4
5.0
4.0
3.0
2.0
1.0
0.0
$-\frac{1}{\nu_2}$
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
$\frac{1}{\nu_{a3}}$



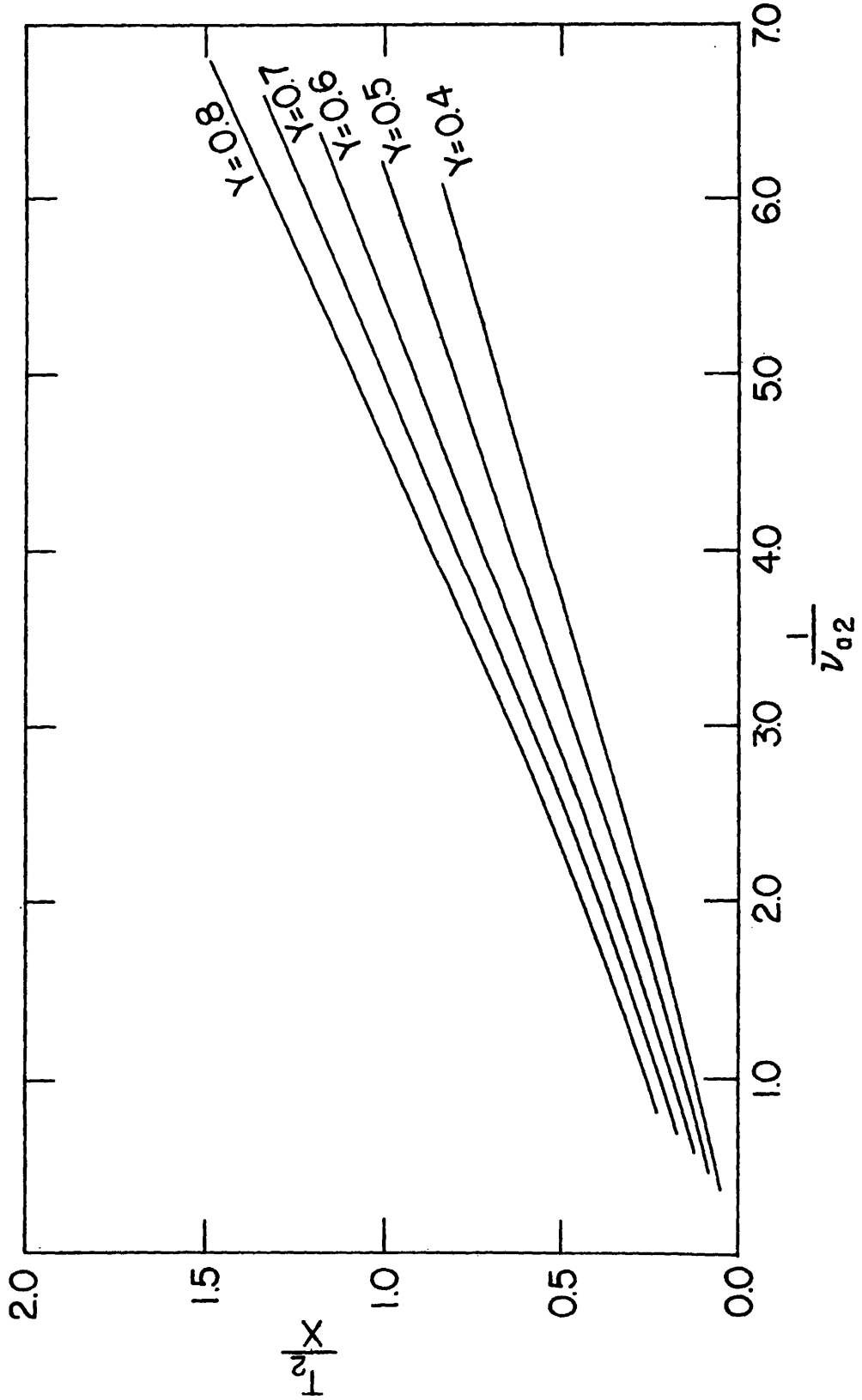
Theoretical Chap 7 Fig 10



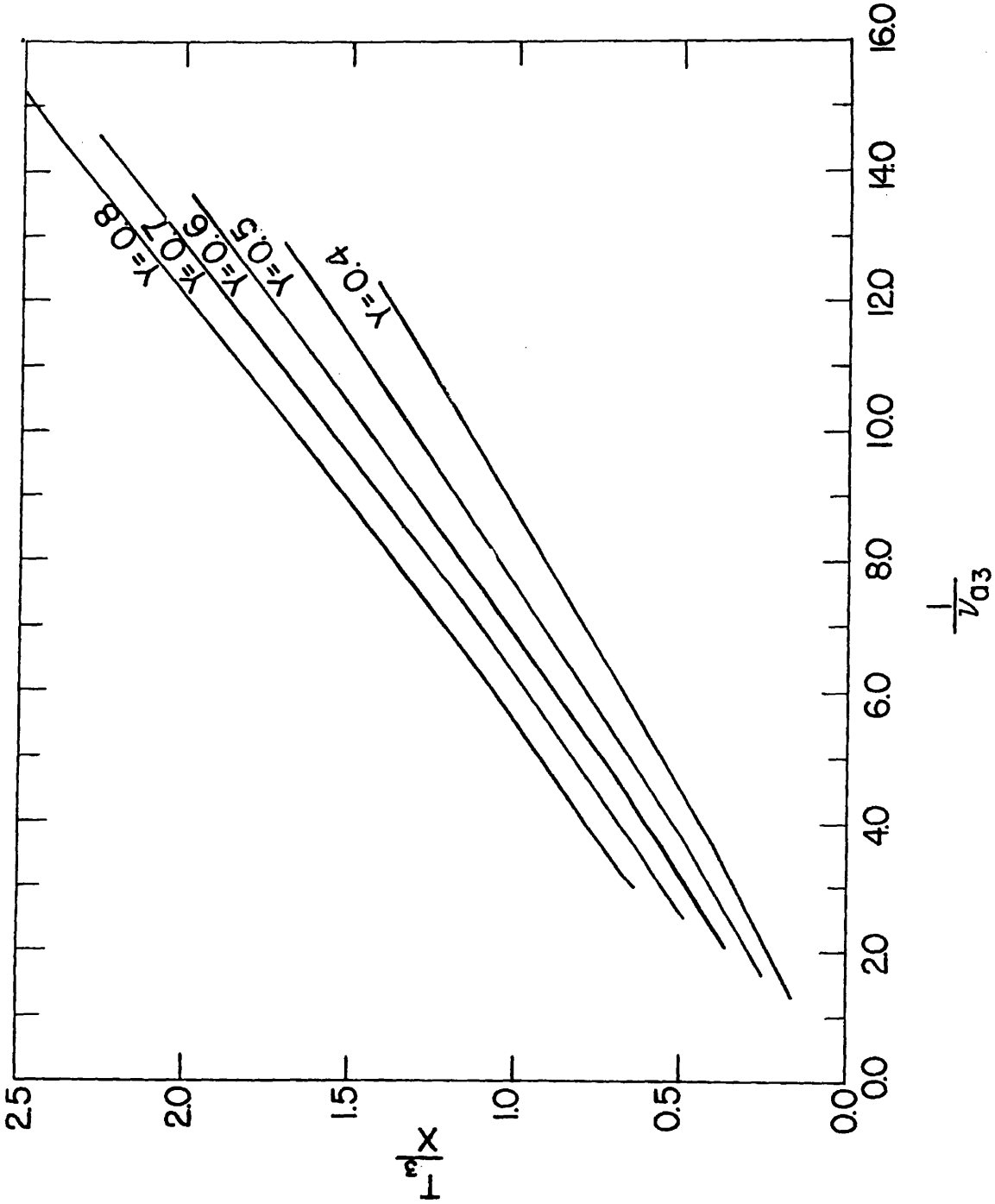
Theoretical Chap. 7 Fig. 11



Theoretical Chap. 7 Fig. 12



Theoretical Chart 7 Fig. 13



Theoretical Chap 7 Fig 14

CHAPTER VIII. APPROXIMATE TREATMENT OF SMALL PYRAMIDS APPROACHING EQUILIBRIUM

1. Method

The case of a single column approaching equilibrium can be treated by setting up and solving a partial differential equation with suitable boundary conditions. If the concentrations involved are small, the equation is linear and can usually be solved by standard methods. If, however, one tries to treat the corresponding case of a pyramid with several stages, one encounters a much more difficult problem, for one now has a number of partial differential equations with interrelated boundary conditions. To solve such a problem is, in general, a very laborious task. Frequently, however, one is interested in getting an approximate result without lengthy calculations. The present note discusses one method of accomplishing this.

The method is based on the idea of simplifying the calculations by assuming that within each column, at all times, the concentration varies linearly with the distance up the column. By means of this assumption one obtains a system of ordinary differential equations instead of the partial differential equations of the more exact treatment, and this results in a substantial reduction in the work of obtaining a solution.

Let us consider the case of a pyramid of m stages, with the bottom connected to a large reservoir, so that the

concentration there remains constant in the course of time. Let the number of parallel columns in the k'th stage ($k = 1, 2, \ldots, m$), counting up from the bottom, be N_k. Let all the columns in the system be identical, and let H and K be the constants of a single column. Let L be the length and M the hold-up of a column, and let MU_k be the inter-stage hold-up above the k'th stage. Let c_0 be the concentration at the bottom of the first stage (this being a constant in the present case), and c_k the concentration at the top of the k'th stage. Finally, let us suppose that, as the pyramid approaches equilibrium from an initial concentration c_0, a constant product rate P is removed.

The net upward transport of light constituent at the middle of the k'th column is, if the concentration is sufficiently small,

$$\tau_k = \frac{1}{2}(N_k H + P)(c_k + c_{k-1}) - \frac{N_k K}{L}(c_k - c_{k-1}) \qquad (1)$$

since, on the basis of the assumption of linearity, the concentration there is $(c_k + c_{k-1})/2$, while the gradient of the concentration is $(c_k - c_{k-1})/L$. In the same way, for the next stage up we have

$$\tau_{k+1} = \frac{1}{2}(N_{k+1} H + P)(c_k + c_{k+1}) - \frac{N_{k+1} K}{L}(c_{k+1} - c_k). \qquad (2)$$

The difference between these two, $\tau_k - \tau_{k+1}$, equals the

rate at which the light constituent accumulates in the region between the middle of the k'th and the middle of the (k+1)'th stage. The mass of light constituent present in this region is given by

$$W_k = N_k \left(\frac{M}{2}\right)\left(\frac{1}{4} c_{k-1} + \frac{3}{4} c_k\right) + N_{k+1} \left(\frac{M}{2}\right)\left(\frac{3}{4} c_k + \frac{1}{4} c_{k+1}\right) + M U_k c_k$$

$$= \frac{M}{8}\left[N_k c_{k-1} + (3N_k + 3N_{k+1} + 8U_k) c_k + N_{k+1} c_{k+1}\right] . \qquad (3)$$

Hence we can write

$$\frac{d W_k}{dt} = \tau_k - \tau_{k+1} , \qquad (4)$$

or

$$\frac{M}{8}\left[N_k \frac{dc_{k-1}}{dt} + (3N_k + 3N_{k+1} + 8U_k) \frac{dc_k}{dt} + N_{k+1} \frac{dc_{k+1}}{dt}\right] =$$

$$\left[N_k \left(\frac{K}{L} + \frac{H}{2}\right) + \frac{P}{2}\right] c_{k-1} + \left[N_k \left(-\frac{K}{L} + \frac{H}{2}\right) - N_{k+1} \left(\frac{K}{L} + \frac{H}{2}\right)\right] c_k$$

$$+ \left[N_{k+1} \left(\frac{K}{L} - \frac{H}{2}\right) - \frac{P}{2}\right] c_{k+1} , \qquad (5)$$

for k = 1, 2, ..., m - 1.

In the case of the top stage ($k = m$), some modification is necessary. In place of (4) we must have

$$\frac{d\,W_m}{dt} = \tau_m - P\,c_m \tag{6}$$

where now

$$W_m = N_m\,\left(\frac{M}{2}\right)\left(\frac{1}{4}\,c_{m-1} + \frac{3}{4}\,c_m\right) + M\,U_m c_m$$

$$= \frac{M}{8}\left[N_m\,c_{m-1} + (3\,N_m + 8\,U_m)\,c_m\right], \tag{7}$$

so that the equation for this case is

$$\frac{M}{8}\left[N_m\,\frac{dc_{m-1}}{dt} + (3\,N_m + 8\,U_m)\,\frac{dc_m}{dt}\right] = \left[N_m\left(\frac{K}{L} + \frac{H}{2}\right) + \frac{P}{2}\right]c_{m-1} +$$

$$+ \left[N_m\left(-\frac{K}{L} + \frac{H}{2}\right) - \frac{P}{2}\right]c_m\,. \tag{8}$$

Finally, let us introduce the constants $Y = \frac{HL}{K}$, $X = \frac{MK}{H^2L}$ and $\nu = \frac{P}{H}$. Then (5) can be written, using a dot to denote a time derivative,

$$XY^2 \left[N_k \dot{c}_{k-1} + (3N_k + 3N_{k+1} + 8U_k) \dot{c}_k + N_{k+1} \dot{c}_{k+1} \right] -$$

$$- \left[N_k (8 + 4Y) + 4\nu Y \right] c_{k-1} - \left[N_k (-8 + 4Y) - N_{k+1}(8 + 4Y) \right] c_k -$$

$$- \left[N_{k+1} (8 - 4Y) - 4\nu Y \right] c_{k+1} = 0 , \qquad (9)$$

and (8),

$$XY^2 \left[N_m \dot{c}_{m-1} + (3N_m + 8 U_m) \dot{c}_m \right] - \left[N_m(8 + 4Y) + 4\nu Y \right] c_{m-1} -$$

$$- \left[N_m (-8 + 4Y) - 4\nu Y \right] c_m = 0. \qquad (10)$$

To solve this system of equations, we first get the steady-state solution by setting all derivatives equal to zero. This solution can be obtained from (1) by setting $\tau_k = Pc_m$. One finds

$$S_j' \equiv \frac{c_j}{c_{j-1}} = \frac{1 + \frac{1}{2} Y (1 + \nu_j)}{1 + \frac{1}{2} Y \left[(2 S_j^{c} - 1) \nu_j - 1 \right]} , \quad (j = 1, 2, \cdots m) \qquad (11)$$

where we have set

$$\nu_j = \frac{\nu}{N_j} , \qquad S_j^{c} = \frac{c_m}{c_j} . \qquad (12)$$

From (11), working down the pyramid from the top, one can express all the c_j in terms of c_m, and, by getting also a relation between c_o and c_m, one can then express all the c_j in terms of c_o.

Next we get the solutions of the homogeneous equations obtained by omitting from (9) and (10) all terms containing c_o. To do this we write

$$c_j = A_j \, e^{\beta t/XY^2} , \qquad (j = 1, 2, \ldots, m \tag{13}$$

and substitute back into the homogeneous equations. The latter now become a set of linear homogeneous equations for the A_j with an unknown parameter β. Putting the determinant of the coefficients of the A_j equal to zero, as the condition for the existence of a non-trivial solution, one gets a secular equation to determine β. In general, this equation, being of the m'th degree, will have m roots: $\beta_1, \beta_2, \ldots, \beta_m$. If one puts the i'th root β_i back into the equation one gets a solution for the A's

$$A_j = A_j^{(i)} \qquad (i = 1, 2, \cdots, m) , \tag{14}$$

determined to within a common factor. If all the m roots are different, m such independent solutions will be obtained. If some of the roots are repeated, it is possible to construct m independent solutions; however, this case is not likely

to arise and will not be discussed any further.

The general solution of Eqs. (9) and (10) can now be written

$$c_j = c_j^o + \sum_{i=1}^{m} B_i A_j^{(i)} e^{\beta_i t/XY^2} , \tag{15}$$

where the c_j^o are the steady-state solutions, and the B_i are a set of $\underline{m}$ arbitrary constants. These constants are to be chosen so as to satisfy the initial conditions, which in the present case are given by

$$t = 0: \qquad c_j = c_o \qquad (j = 1,\cdots,m) . \tag{16}$$

In this way one obtains the solution to the problem.

Other situations involving pyramids can be treated in the same way, but with appropriate modifications in the details.

2. <u>Examples</u>

(a) By way of illustration, we first apply the above method to the case of a single column, for which we can make a comparison with the results of a more accurate calculation.

For a single column, we have only one equation, that corresponding to (10). Let $U_m = 0$. Setting $c_{m-1} = c_o = 0$ and dropping subscripts, except in the case of c_o, we get for (10)

$$3\,XY^2\,\dot{c} + (8 - 4Y + 4\nu Y)\,c = (8 + 4Y + 4\nu Y)\,c_o\,, \tag{17}$$

where $\underline{c}$ refers to the top of the column.

The steady-state solution is given by

$$S \equiv \frac{c}{c_o} = \frac{1 + \frac{1}{2}\,Y\,(\nu + 1)}{1 + \frac{1}{2}\,Y\,(\nu - 1)}\,. \tag{18}$$

Fig. 1 shows a graph of S vs. ν, as given by (18) with $Y = 0.4$, and also a corresponding graph for the more accurate value

$$S_a = \frac{\nu + 1}{\nu + e^{-Y(\nu + 1)}}\,. \tag{19}$$

It will be seen that the two agree best for small values of ν.

Let us now determine the behavior of the column as it approaches equilibrium. Omitting in (17) the term with c_o and writing

$$c = Ae^{\beta t/XY^2}\,, \tag{20}$$

we get

$$3\beta A + \left[8 + 4Y\,(\nu - 1)\right]\,A = 0 \tag{21}$$

whence

$$\beta = -\frac{8}{3}\left[1 + \frac{1}{2}Y(\nu - 1)\right] \tag{22}$$

and the general solution for $\underline{c}$ is

$$c = c_o\left\{\frac{1 + \frac{1}{2}Y(\nu + 1)}{1 + \frac{1}{2}Y(\nu - 1)} + B\, e^{-\frac{8}{3}\,\frac{1 + \frac{1}{2}Y(\nu - 1)}{XY^2}\,t}\right\}. \tag{23}$$

Putting $t = 0$, $c = c_o$, one determines B, getting finally

$$c = c_o\left\{\frac{1 + \frac{1}{2}Y(\nu + 1)}{1 + \frac{1}{2}Y(\nu - 1)} - \frac{Y}{1 + \frac{1}{2}Y(\nu - 1)}\, e^{-\frac{8}{3}\,\frac{1 + \frac{1}{2}Y(\nu - 1)}{XY^2}\,t}\right\}. \tag{24}$$

In the case in which no product is removed during the process ($\nu = 0$), this becomes

$$S = \frac{1 + \frac{1}{2}Y}{1 - \frac{1}{2}Y} - \frac{Y}{1 - \frac{1}{2}Y}\, e^{-\frac{8}{3}\,\frac{1 - \frac{1}{2}Y}{XY^2}\,t}. \tag{25}$$

Fig. 2 shows a graph of S vs. t/X for the case $Y = 0.4$ and also a corresponding graph for the more accurate function S_a as determined by solving the partial differential equation for the single column. It will be seen that the agreement is best for the larger values of t/X.

It appears from the preceding results that the present

method is better suited to the problem of the approach to equilibrium without product removal than to the case in which there is a finite product rate. It should be noted that it is reasonable to expect that the discrepancy between the approximate and accurate calculations will be greatest for a single column and will decrease with an increase in the number of stages in the pyramid; for, as the number of stages is increased, the role of any one stage becomes relatively less important and the pyramid tends toward the continuous, or infinitesimal-step, pyramid for which the approximate calculation becomes exact.

It might be mentioned parenthetically that, if one wishes to apply the method discussed here to the case of a single column but yet one wants greater accuracy than that obtained in the above example, one can do this by treating each half of the column as a separate stage with its $\underline{Y}$ having a value half that of the column. Thus, if we take $N_1 = N_2 = 1$, and $Y = 0.2$, we find for the solution

$$S = 1.494 - 0.436\, e^{-13.2\, t/X} - 0.058\, e^{-144\, t/X},$$

which is to be compared with the expansion obtained by solving the partial differential equation for a single column

$$S_a = 1.492 - 0.415\, e^{-13.1\, t/X} - 0.037\, e^{-137\, t/X} - \ldots$$

Obviously, one can attain any degree of accuracy by subdividing the column sufficiently.

(b) As another example, let us take the case of a 3-stage pyramid approaching equilibrium with zero product rate and attached at the bottom to an infinite reservoir. For the sake of simplicity let us suppose that the interstage hold-ups are negligible. The equations for this case can be written

$$\left.\begin{aligned}
&XY^2\left[(3N_1+3N_2)\,\dot{c}_1+N_2\dot{c}_2\right]-N_1\,(8+4Y)\,c_o+\\
&\qquad+\left[N_1\,(8-4Y)+N_2\,(8+4Y)\right]c_1-N_2\,(8-4Y)\,c_2=0,\\
&XY^2\left[N_2\dot{c}_1+(3N_2+3N_3)\,\dot{c}_2+N_3\dot{c}_3\right]-N_2\,(8+4Y)\,c_1+\\
&\qquad+\left[N_2\,(8-4Y)+N_3\,(8+4Y)\right]c_2-N_3\,(8-4Y)\,c_3=0,\\
&XY^2\left[N_3\dot{c}_2+3N_3\dot{c}_3\right]-N_3\,(8+4Y)\,c_2+N_3\,(8-4Y)\,c_3=0.
\end{aligned}\right\}\quad(26)$$

To make the problem specific, let us take $N_1 = 9$, $N_2 = 5$, $N_3 = 2$. Then the preceding equations become

$$\left.\begin{aligned}
&XY^2\left[42\dot{c}_1+5\dot{c}_2\right]-(72+36Y)\,c_o+(112-16Y)\,c_1-(40-20Y)\,c_2=0,\\
&XY^2\left[5\dot{c}_1+21\dot{c}_2+2\dot{c}_3\right]-(40+20Y)\,c_1+(56-12Y)\,c_2-(16-8Y)\,c_3=0,\\
&XY^2\left[2\dot{c}_2+6\dot{c}_3\right]-(16+8Y)\,c_2+(16-8Y)\,c_3=0.
\end{aligned}\right\}\quad(27)$$

If we let $s_j = c_j/c_o$, it follows from the above that at equilibrium

$$s_1 = \frac{1 + \frac{Y}{2}}{1 - \frac{Y}{2}}, \qquad s_2 = s_1^2, \qquad s_3 = s_1^3 . \tag{28}$$

To get the "transient terms" in the solution, we delete the terms in the equations containing c_o and write temporarily

$$c_1 = A_1 e^{\beta t/XY^2}, \qquad c_2 = A_2 e^{\beta t/XY^2}, \qquad c_3 = A_3 e^{\beta t/XY^2}. \tag{29}$$

The equations become

$$\left.\begin{aligned} (42\beta+112-16Y)\ A_1 + (5\beta-40+20Y)\ A_2 &= 0 \\ (5\beta-40-20Y)\ A_1 + (21\beta+56-12Y)\ A_2 + (2\beta-16+8Y)\ A_3 &= 0 \\ (2\beta-16-8Y)\ A_2 + (6\beta+16-8Y)\ A_3 &= 0 \end{aligned}\right\} \tag{30}$$

Hence the secular equation for β is

$$\begin{vmatrix} 42\beta + 112 - 16Y & 5\beta - 40 + 20Y & 0 \\ 5\beta - 40 - 20Y & 21\beta + 56 - 12Y & 2\beta - 16 + 8Y \\ 0 & 2\beta - 16 - 8Y & 6\beta + 16 - 8Y \end{vmatrix} = 0. \tag{31}$$

This represents a cubic equation for β. If one takes $Y = 0.4$, one finds that the roots are

$$\beta_1 = 0.3549, \qquad \beta_2 = 2.335, \qquad \beta_3 = 5.722. \tag{32}$$

Substituting these three values successively into the system of equations (30), we get three independent solutions for the A's:

$$\left.\begin{array}{lll} \beta = \beta_1: & A_2 = 2.685\ A_1, & A_3 = 5.011\ A_1, \\ \beta = \beta_2: & A_2 = 0.1722\ A_1, & A_3 = 3.395\ A_1, \\ \beta = \beta_3: & A_2 = 2.223\ A_1, & A_3 = 3.164\ A_1. \end{array}\right\} \tag{33}$$

Hence the general solution, with appropriate equilibrium values, is given by

$$\left.\begin{array}{l} S_1 = 1.5 + B_1 e^{\beta_1 t/XY^2} + B_2 e^{\beta_2 t/XY^2} + B_3 e^{\beta_3 t/XY^2}, \\ S_2 = 2.25 + 2.685\ B_1 e^{\beta_1 t/XY^2} + 0.1722\ B_2 e^{\beta_2 t/XY^2} - 2.223\ B_3 e^{\beta_3 t/XY^2}, \\ S_3 = 3.375 + 5.011\ B_1 e^{\beta_1 t/XY^2} - 3.395\ B_2 e^{\beta_2 t/XY^2} + 3.164\ B_3 e^{\beta_3 t/XY^2}, \end{array}\right\} \tag{34}$$

where B_1, B_2, B_3 are arbitrary constants. To get the solution which has $S_1 = S_2 = S_3 = 1$ for $t = 0$, we determine B_1, B_2, and B_3 from the relations

$$\left.\begin{aligned} B_1 + B_2 + B_3 &= -0.5, \\ 2.685\, B_1 + 0.1722\, B_2 - 2.223\, B_3 &= -1.25, \\ 5.011\, B_1 - 3.395\, B_2 + 3.164\, B_3 &= -2.375, \end{aligned}\right\} \qquad (35)$$

and find

$$B_1 = -0.475, \quad B_2 = -0.0128, \quad B_3 = -0.0123, \qquad (36)$$

so that, finally, the solution of our problem is given by

$$\left.\begin{aligned} S_1 &= 1.5 - 0.475\, e^{-2.22\, t/X} - 0.013\, e^{-14.6\, t/X} - 0.012\, e^{-35.8\, t/X}, \\ S_2 &= 2.25 - 1.275\, e^{-2.22\, t/X} - 0.002\, e^{-14.6\, t/X} + 0.027\, e^{-35.8\, t/X}, \\ S_3 &= 3.375 - 2.380\, e^{-2.22\, t/X} + 0.044\, e^{-14.6\, t/X} - 0.039\, e^{-35.8\, t/X}. \end{aligned}\right\} \qquad (37)$$

Graphs of S_1, S_2, and S_3 as functions of t/X are given in Fig. 4.

In addition to the preceding, Fig. 3 presents corresponding graphs for a pyramid of 2 stages, and Fig. 5 for one of 4 stages.

Chapter 8

Figure 1

Comparison of separation factor (S) calculated by an approximate method with the accurate value (S_a). The case considered is steady state operation of a single column at low concentrations of the desired isotope.

Figure 2

Comparison of separation factor (S) calculated by an approximate method with the accurate value (S_a). This refers to approach to equilibrium of a single column with a reservoir at the bottom and closed at the top.

Figure 3

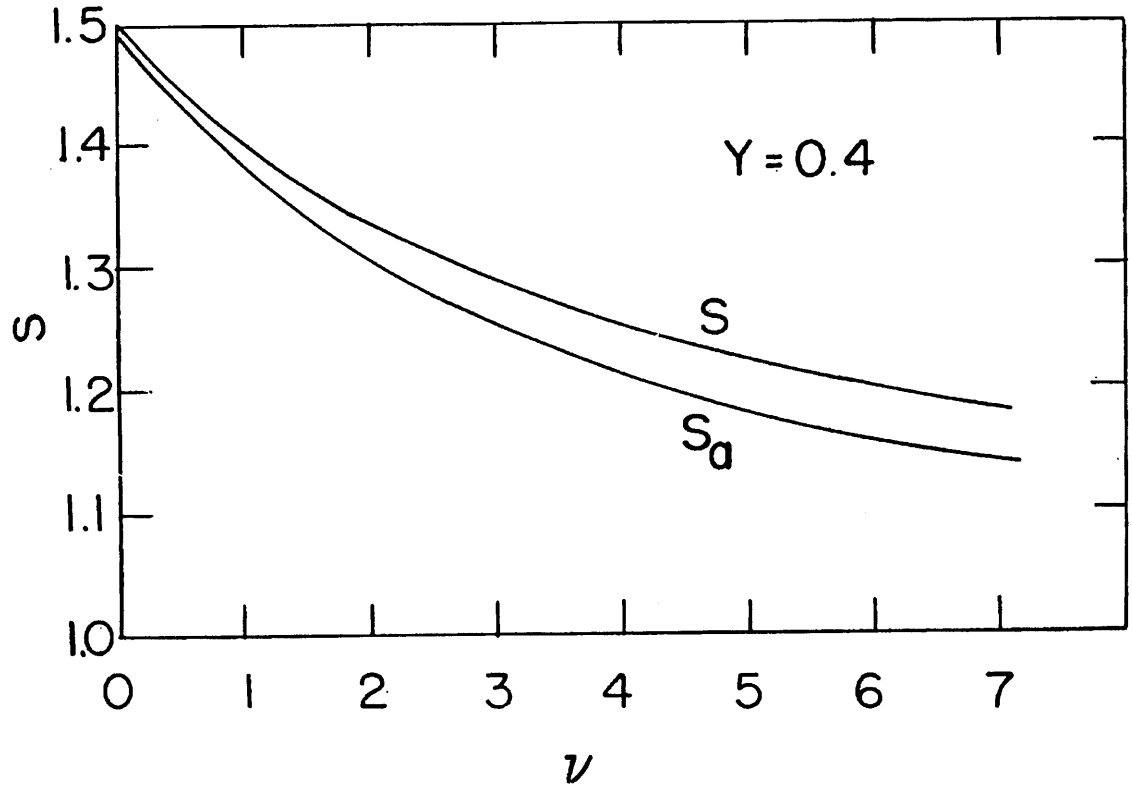
Approach to equilibrium of two stage pyramid as calculated by the approximate method.

Figure 4

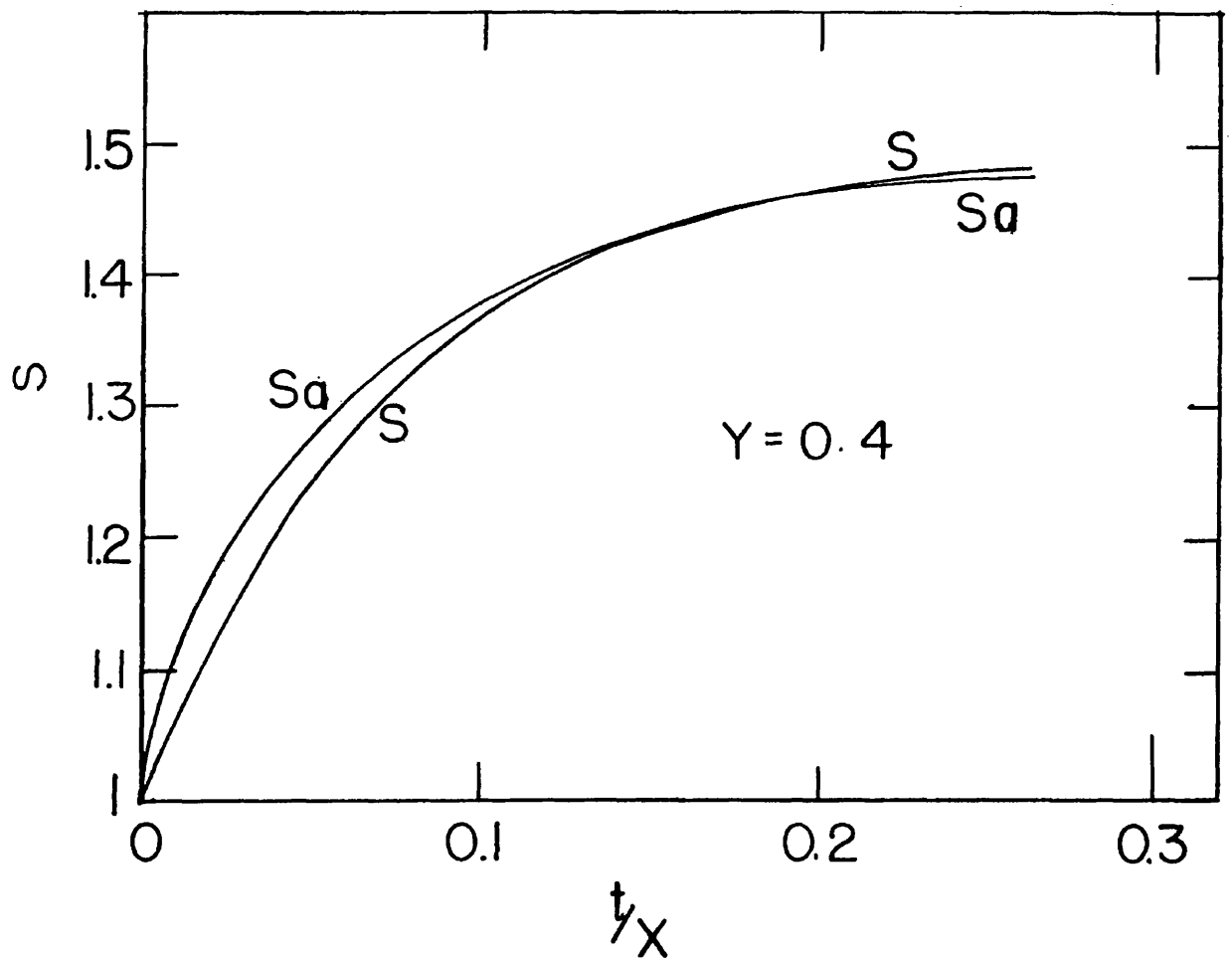
Approach to equilibrium of a three stage pyramid as calculated by the approximate method.

Figure 5

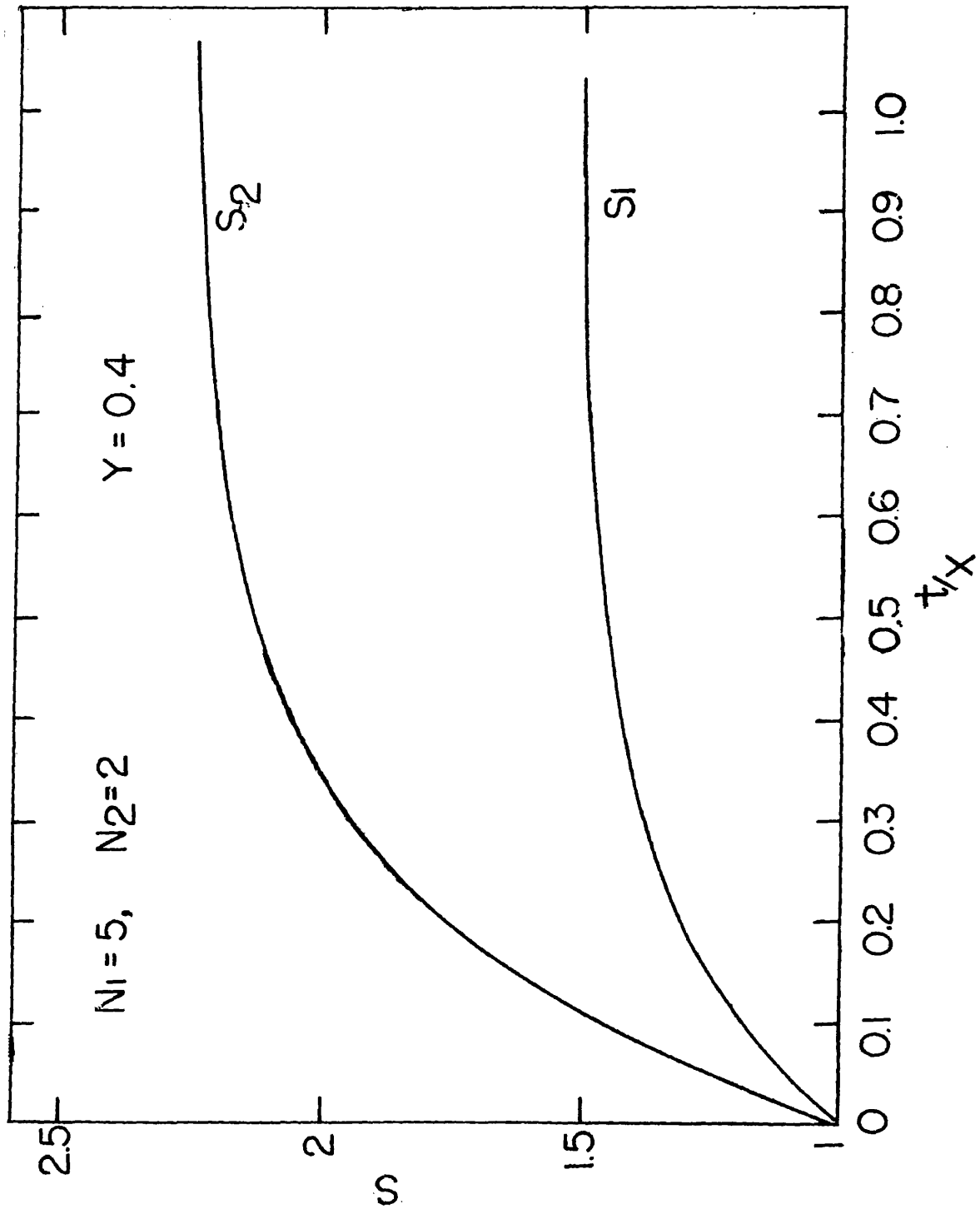
Approach to equilibrium of a four stage pyramid as calculated by the approximate method.



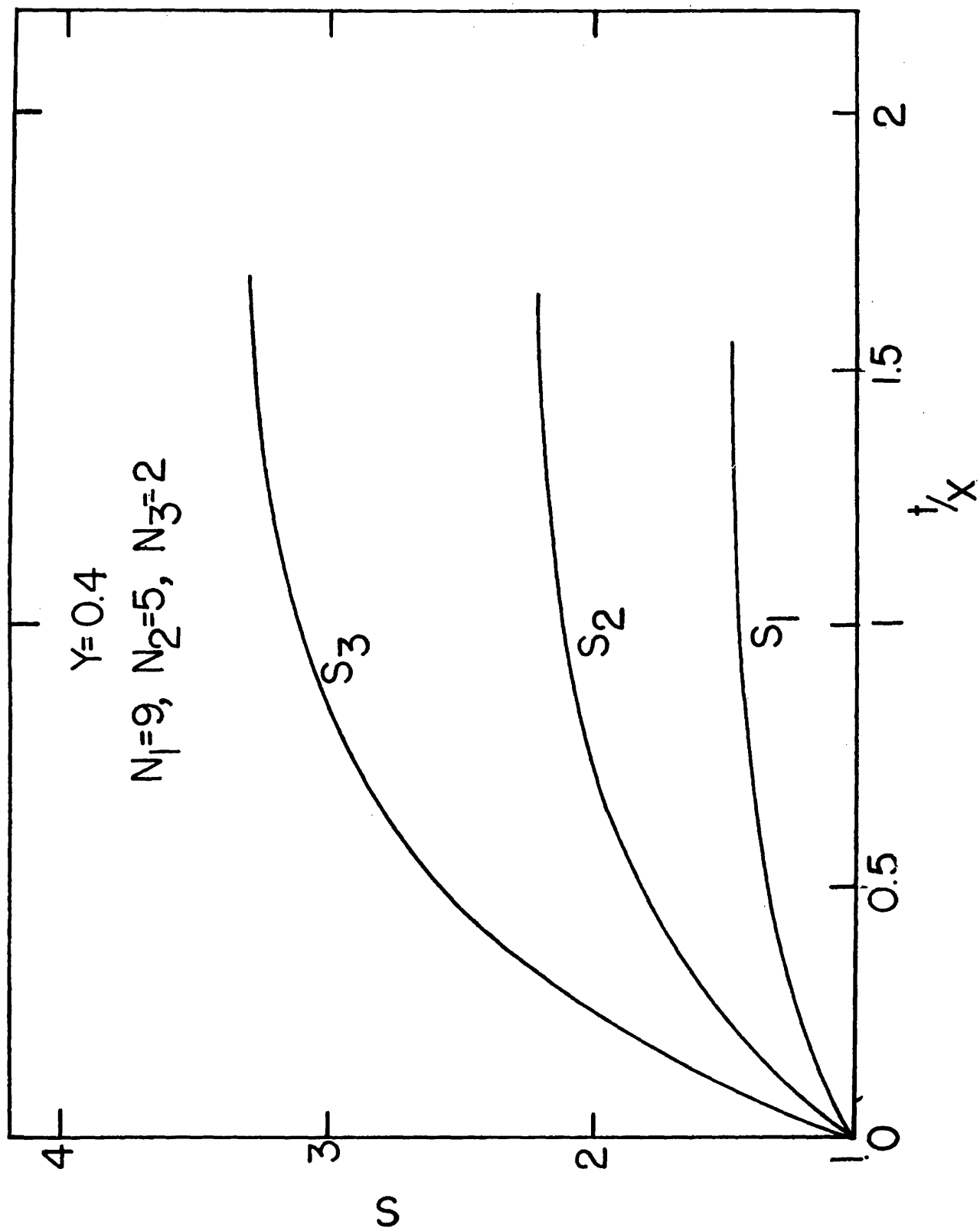
Theoretical Chap 8 Fig 1



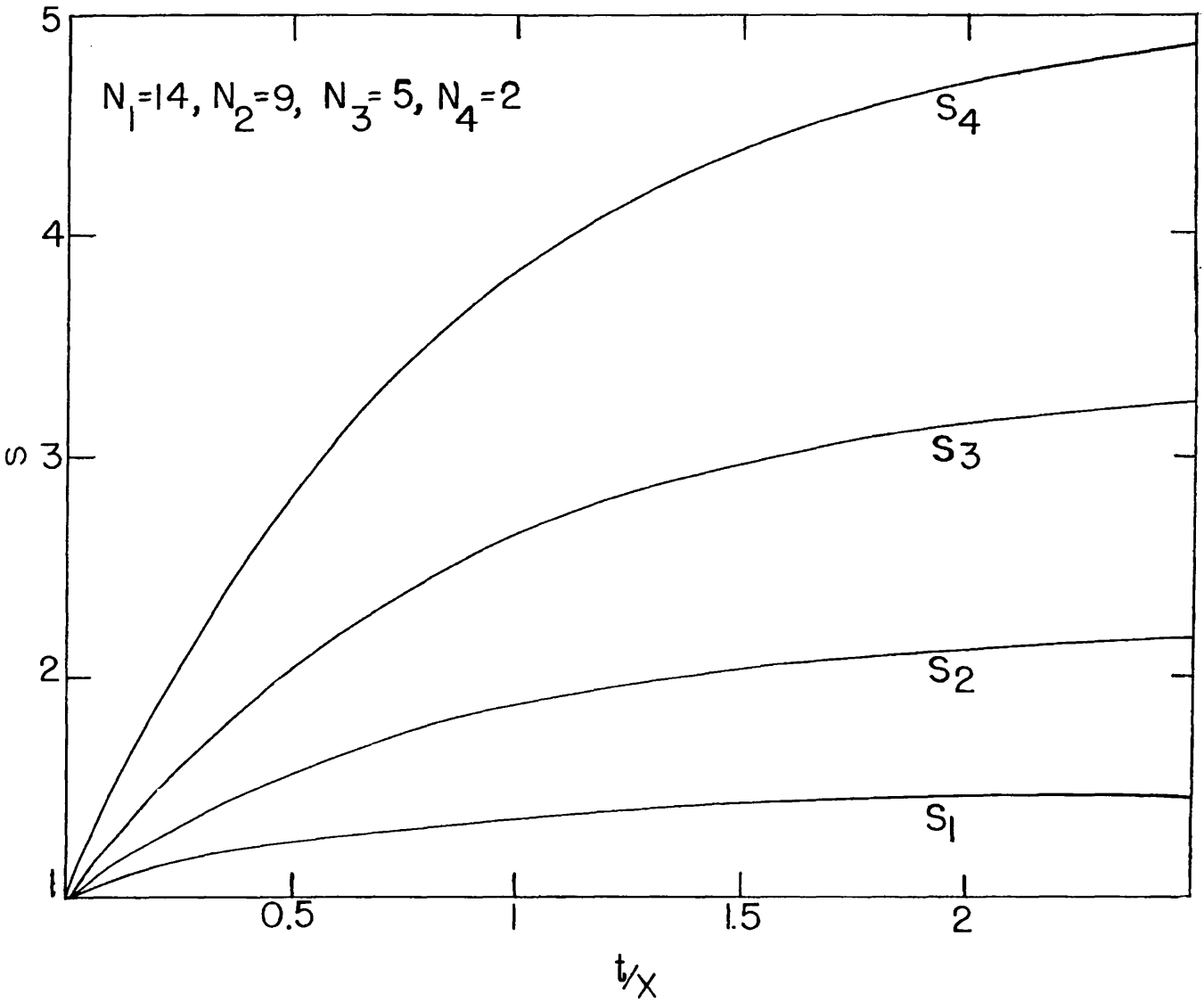
Theoretical Chap. 8 Fig 2



Theoretical Chap 8 Fig 3



Theoretical Chap 8 Fig 4



Theoretical Chap 8 Fig. 5

CHAPTER IX. THE STRIPPER SECTION

1. General

Thusfar in our discussion of pyramids we have been concerned with rectifiers, or enrichers. Frequently, however, it is desirable to have a stripper section connected to the bottom of the rectifying pyramid. This stripper can be thought of as a pyramid or a single stage of columns operated at a negative $\underline{Y}$, i.e., with the input at the top and the output, or product, removed from the bottom. The purpose of using the stripper may be two-fold: (1) to remove a certain fraction of the light constituent from the working substance before the latter is discarded, and (2) to maintain the "neutral point", i.e., the point where the concentration is the same as that of normal material, at a fixed place, namely, at the point of input to the pyramid.

Let us use the subscript $\underline{r}$ to denote quantities referring to the rectifier, $\underline{s}$ to denote those referring to the stripper. Let c_r denote the output concentration of the rectifier (we omit here the previously used asterisk for the sake of convenience), c_o the input concentration, and c_s the concentration of the stripper output, or rejected material. Similarly, let P_r denote the product rate, P_o the rate of input of normal material, and P_s the rate of output of the stripped material. Then, at steady operation, we can write two equations representing the conservation of the working

substance and of the light constituent, respectively:

$$P_o = P_r + P_s \ , \tag{1}$$

$$P_o c_o = P_r c_r + P_s c_s \ . \tag{2}$$

If the concentrations are all prescribed, then one can solve these equations for P_o and P_s:

$$P_o = \frac{c_r - c_s}{c_o - c_s} P_r \ , \tag{3}$$

$$P_s = \frac{c_r - c_o}{c_o - c_s} P_r \ . \tag{4}$$

If only c_o, c_r and P_r are fixed, then P_o and P_s will depend on the choice of c_s, the concentration of the waste material. The latter will generally be determined by economic considerations.

To treat the stripper mathematically, we can proceed in either of two ways:

(1) We can treat each column in the same way as we have done in the preceding chapters, but we suppose P to be negative, so that raw material is supplied at the top of the column or group of columns and product is removed at the bottom. It is convenient in this case to measure $\underline{z}$ down

from the top, rather than up from the bottom of a column, i.e., we replace z by $-z$ and L by $-L$ in the various formulas. Likewise we replace P by $-P$, and τ by $-\tau$, so as to deal with positive quantities.

(2) We think of each stripper column simply as a column with a negative value for the column constant H, so that we replace H by $-H$. This amounts to looking at the column "upside down" and leads to the same results as the first standpoint.

It can be readily verified that the same expression is obtained by either of the above methods for the net rate of transport of light constituent,

$$\tau = Pc - Hc\,(1-c) - K\frac{\partial c}{\partial z}\,. \tag{5}$$

It will be recalled that one can write

$$\tau = Pc^* \,, \tag{6}$$

where c^* is the concentration of the product (in this case that which is rejected) and, as usual, P is the product rate per column in a given stage. If we consider the case where $c \ll 1$, which is certainly appropriate for the stripper, then (5) can be written as a differential equation for c; if we let $\alpha = \frac{H}{K}$, $\nu = \frac{P}{H}$:

$$\frac{dc}{dz} + \alpha (1 - \nu) c + \alpha \nu c^* = 0. \tag{7}$$

Letting $c(0) = c_T$, $c(L) = c_B$, we get for the solution of this equation

$$c = \frac{\nu c^*}{\nu - 1} + \left(c_T - \frac{\nu c^*}{\nu - 1}\right) e^{\alpha(\nu - 1) z} , \tag{8}$$

so that

$$c_B = \frac{\nu c^*}{\nu - 1} + \left(c_T - \frac{\nu c^*}{\nu - 1}\right) e^{(\nu - 1) Y} , \tag{9}$$

with $Y = \alpha L$. If we let

$$S = \frac{c_T}{c_B} , \qquad S^c = \frac{c_B}{c^*} , \tag{10}$$

then we get from (8)

$$S = \frac{1}{(\nu - 1) S^c} \left\{ \nu + \left[(\nu - 1) S^c - \nu \right] e^{-(\nu - 1) Y} \right\} , \tag{11}$$

so that, in a pyramid with a given distribution of columns, it is possible to get the separation factor by starting from the output stage and applying (11) to each stage in succession. In particular, for the output stage ($S^c = 1$), we have

$$S = \frac{\nu - e^{-(\nu - 1) Y}}{\nu - 1} . \tag{12}$$

In addition to Eqs. (11) and (12), involving quantities referring to the individual columns of the stripper section (we have omitted the subscript $\underline{s}$ for simplicity), we also have to satisfy Eqs. (1) and (2). The concentration c_s occurring in these equations is given by

$$c_s = \frac{c_o}{S_s^*} , \tag{13}$$

where S_s^* is the product of all the separation factors of the stripper stages, while P_s is given by the product of νH and the number of columns in any one stage of the stripper. Now, if we replace (1) and (2) by (3) and (4), we see that one condition determines P_o, the rate at which raw material is to be fed into the system at the neutral point, while the other condition fixes P_s.

The method of solution will depend on the way the problem is formulated. In some cases it may be necessary to solve simultaneously Eq. (4) and the set of equations represented by (11) and (12), which can be done by graphical methods in complicated cases.

Usually only a small fraction of the total number of columns will be used for the stripper, so that the question of design for optimum performance is not so important in this case. However, if it is desired to design a stripper for optimum performance, that can be done on the basis of

the ideas discussed in the preceding chapters. For example, Figs. 10 and 11 of Chap. VI which were calculated for a rectifier working at very high concentrations also apply to a stripper at low concentrations (if one interchanges c and $c' = 1 - c$). Just as in the case of a rectifier one can use these graphs to work stage by stage, starting from the output stage, so as to get the optimum separation factor for each stage and the corresponding value of ν. Eq. (4) can then be satisfied by choosing the proper number of columns for each stage, i.e., we take in the k'th stage N_k columns given by

$$N_k = \frac{P_s}{H \nu_k} \tag{14}$$

where ν_k is the value of ν for the k'th stage as obtained from considerations of optimum performance and P_s is given by (4), with c_s determined by (13).

2. Single-Stage Stripper

An interesting case to consider is the one in which the stripper consists of only a single stage. Such an arrangement is likely to be used where one is more concerned about maintaining a fixed neutral point than about the degree to which the material is stripped before being discarded. If we denote the value of S^* for the rectifier by S_r and that for the stripper by S_s, then Eq. (4) can be written

$$P_s = \frac{S_r - 1}{1 - \frac{1}{S_s}} P_r , \tag{15}$$

so that

$$1 - \frac{1}{S_s} = (S_r - 1) P_r / H \nu_s N_s \tag{16}$$

where ν_s is the value of ν for each stripper column and N_s is the total number of such columns.

On the other hand from (12), if we add subscripts s, we get

$$S_s = \frac{\nu_s - e^{-(\nu_s - 1) Y}}{\nu_s - 1} . \tag{17}$$

Hence, eliminating S_s between (16) and (17), we obtain

$$\frac{(S_r - 1) P_r}{H N_s} = \frac{\nu_s \left[1 - e^{-(\nu_s - 1) Y}\right]}{\nu_s - e^{-(\nu_s - 1) Y}} . \tag{18}$$

If we denote the right-hand side of (18) by W, then W as a function of ν_s for a given value of Y is a function which vanishes for $\nu_s = 0$ and then increases monotonically to unity as ν_s tends to infinity. We see from this that

$$N_s \geqslant (S_r - 1) P_r / H , \tag{19}$$

so that there is a lower limit to the number of columns

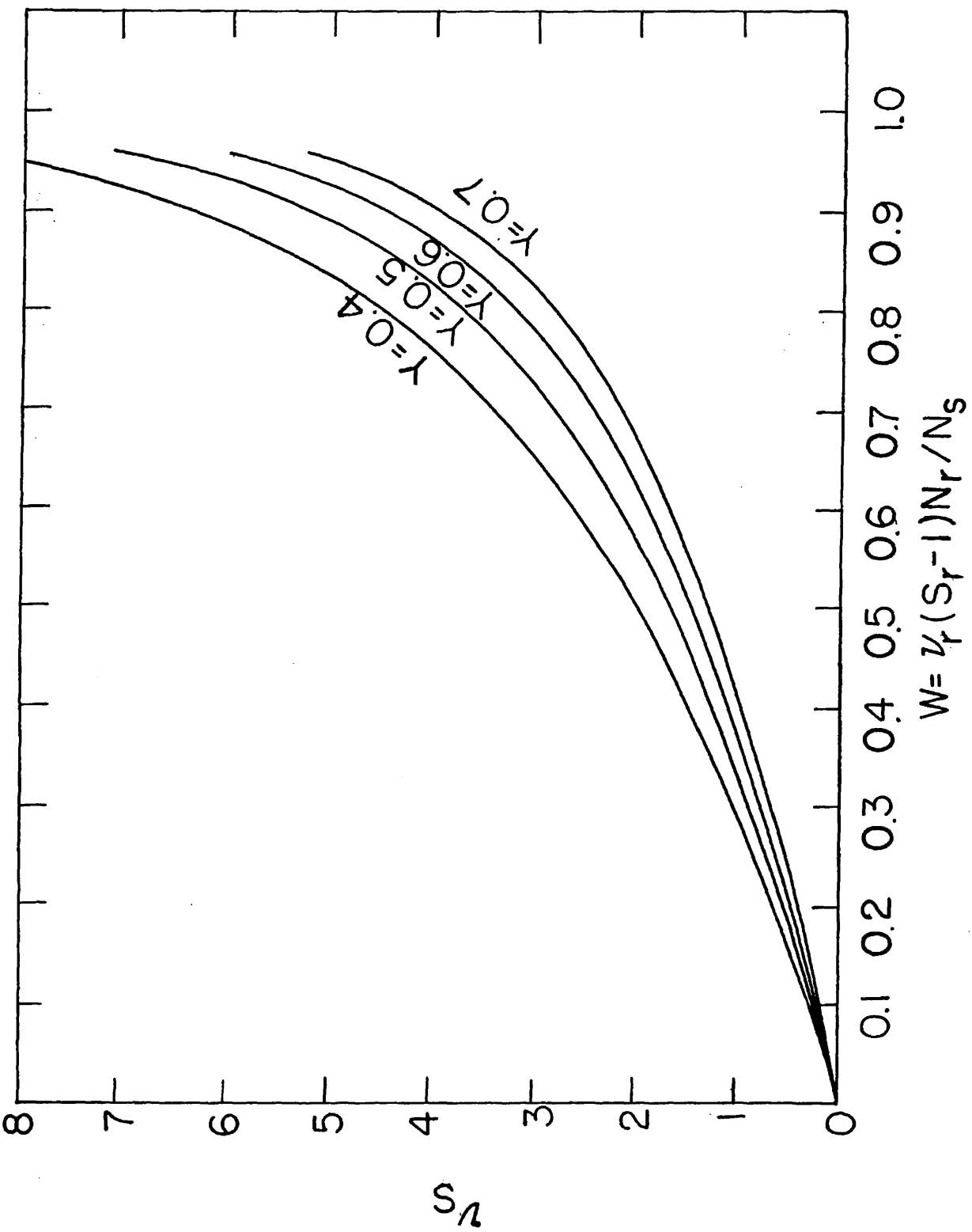
Chapter 9

Figure 1

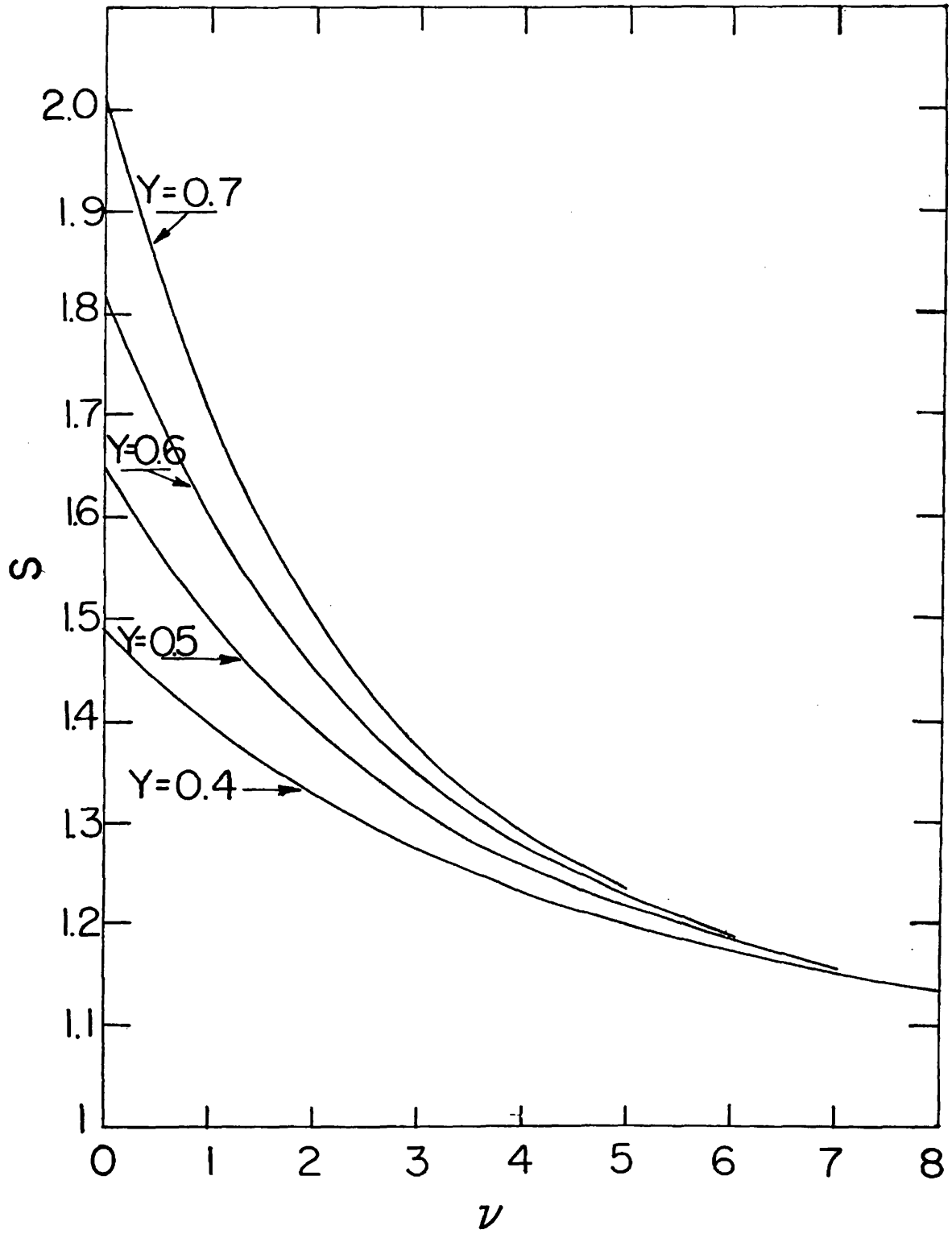
Stripper withdrawal rate (ν_s) necessary to maintain steady state operation when product withdrawal rate is ν_r and separation factor of rectifier section is S_r. The number of columns in the rectifier and stripper stage is given by N_r and N_s respectively.

Figure 2

Dependence of separation factor S on generalized product rate ν for single stage stripper with various values of Y.



Theoretical Chap 9 Fig 1



Theoretical chap 9 Fig 2

CHAPTER X. NON-UNIFORM COLUMNS IN PARALLEL OPERATION

1. General Treatment

The purpose of this chapter is to consider the behavior of a group of columns operated in parallel, taking into account possible differences in the properties of the columns and their product rates.

Each column is characterized under steady flow by the column constants H and K, its length L and mass M, and the product rate P. The constants H and K can be calculated from measured values of the equilibrium separation factor S_e and the time constant X by the relations

$$H = \frac{M}{X \ln S_e} \tag{1}$$

and

$$K = \frac{ML}{X(\ln S_e)^2} \tag{2}$$

The product rate P, of course, can be made to have any arbitrary value by a suitable choice of auxiliary equipment.

Let us consider the steady operation of a group of n columns in parallel, representing a particular stage of a pyramid, and let us use subscripts to distinguish quantities referring to the various columns in this group. Let τ

denote the total transport of light constituent in one column. Then, for the k'th column, if the concentration is sufficiently low, one can write

$$\tau_k = (H_k + P_k)\, c_k - K_k \frac{dc_k}{dz} \quad (k = 1, \cdots n) \ , \tag{3}$$

where z is the distance measured up the column. If c^* is the concentration at the top of the pyramid, where the product is withdrawn, then there exists the relation

$$\sum_{k=1}^{n} \tau_k = c^* \sum_{k=1}^{n} P_k \ . \tag{4}$$

By "parallel" operation we shall mean that the tops of all the columns are connected, and that their bottoms are all connected. Hence for the k'th column, we have the boundary conditions:

$$c_k = c_B \qquad (z = 0) \ , \tag{5a}$$

$$c_k = c_T \qquad (z = L) \ , \tag{5b}$$

where c_B and c_T are the concentrations at the bottom and

top of the stage, respectively, these quantities being taken to be the same for all the columns.

Integrating (3) so as to satisfy (5a), one gets

$$c_k = c_B e^{\gamma_k z} - \frac{\tau_k}{H_k + P_k} (e^{\gamma z} - 1) \tag{6}$$

where

$$\gamma_k = \frac{H_k + P_k}{K_k} \tag{7}$$

For $z = L_k$, we have

$$c_T = c_B e^{\gamma_k L_k} - \frac{\tau_k}{H_k + P_k} (e^{\gamma_k L_k} - 1) \tag{8}$$

Let

$$\beta_k = e^{\gamma_k L_k}, \qquad \varphi_k = \frac{H_k + P_k}{\beta_k - 1} \tag{9}$$

Then, from (8),

$$\tau_k = \varphi_k (c_B \beta_k - c_T) \tag{10}$$

Substituting this expression into (4), we get

$$c_B \sum_{k=1}^{n} \varphi_k \beta_k = c_T \sum_{k=1}^{n} \varphi_k = c^* \sum_{k=1}^{n} P_k \tag{11}$$

so that

$$c_T = \frac{c_B \sum_{k=1}^{n} \varphi_k \beta_k - c^* \sum_{k=1}^{n} P_k}{\sum_{k=1}^{n} \varphi_k \beta_k} \tag{12a}$$

$$c_B = \frac{c_T \sum_{k=1}^{n} \varphi_k + c^* \sum_{k=1}^{n} P_k}{\sum_{k=1}^{n} \varphi_k \beta_k} \tag{12b}$$

From Eqs. (10) and (12a) or (12b), we get

$$\tau_i = \varphi_i \frac{c_B \sum_{k=1}^{n} \varphi_k (\beta_i - \beta_k) + c^* \sum P_k}{\sum_{k=1}^{n} \varphi_k} \tag{13a}$$

or

$$\tau_i = \varphi_i \frac{c_T \sum_{k=1}^{n} \varphi_k (\beta_i - \beta_k) + c^* \beta_i \sum P_k}{\sum \varphi_k \beta_k} \tag{13b}$$

If we introduce the separation factors

$$S_p = \frac{c_T}{c_B}, \quad S^* = \frac{c^*}{c_B}, \quad S^c = \frac{c^*}{c_T} = \frac{S^*}{S}, \tag{14}$$

then we get from (12a) or (12b)

$$S_p = \frac{\sum_{k=1}^{n} \varphi_k \beta_k - S^* \sum_{k=1}^{n} P_k}{\sum_{k=1}^{n} \varphi_k}, \tag{15a}$$

or

$$S_p = \frac{\sum_{k=1}^{n} \varphi_k \beta_k}{\sum_{k=1}^{n} \varphi_k + S^c \sum_{k=1}^{n} P_k}. \tag{15b}$$

Of these two expressions, that in Eq. (15b) is generally the more useful one, since, if one investigates a pyramid stage by stage, one generally starts at the top and works down, so that at each stage S^c, the separation factor for

all the higher stages is known, and not S^*. Suppose then that we are given a value of S^0. If only the k'th column had been present above, its separation factor would have been S_k, given, according to (15b), by

$$S_k = \frac{(H_k + P_k)\,\beta_k}{H_k + P_k + S^0\,P_k\,(\beta_k - 1)} \quad , \tag{16}$$

or if we let

$$\nu_k = \frac{P_k}{H_k} \, , \tag{17}$$

then

$$S_k = \frac{(1 + \nu_k)\,\beta_k}{1 + \nu_k + S^0\,\nu_k\,(\beta_k - 1)} \quad . \tag{18}$$

From this we find that

$$\beta_k = \frac{1 - (S^0 - 1)\nu_k}{\frac{1}{S_k}\,(1 + \nu_k) - S^0\,\nu_k} \tag{19}$$

and

$$\varphi_k = \frac{\frac{1}{S_k}\,(1 + \nu_k) - S^0\,\nu_k}{1 - \frac{1}{S_k}} \quad . \tag{20}$$

Substituting these expressions into (15b) one finds that

$$S_p = \frac{\sum_{k=1}^{n} H_k \left[1 - (S^0 - 1)\,\nu_k\right] \frac{S_k}{S_k - 1}}{\sum_{k=1}^{n} H_k \left[1 - (S^0 - 1)\,\nu_k\right] \Big/ (S_k - 1)} = \frac{\sum_{k=1}^{n} \varphi_k \beta_k}{\sum_{k=1}^{n} (\varphi_k \beta_k / S_k)} \quad . \tag{21}$$

In particular, if we are dealing with a pyramid consisting of only a single stage, or if the group of columns is the top stage of a pyramid, then $S^0 = 1$ and

$$S_p = \frac{\sum_{k=1}^{n} \frac{H_k\, S_k}{S_k - 1}}{\sum_{k=1}^{n} \frac{H_k}{S_k - 1}} \quad , \tag{22}$$

so that S_p is a mean value of the S's of the individual columns with a weighting factor $H_k/(S_k - 1)$.

Having expressed S_p in a convenient form, let us return to the expression for τ_i given by Eq. (13b) and see whether it too can be simplified. First let us write (13b), or (10), in the form

$$\tau_i = \varphi_i\, c_T \left(\frac{\beta_i}{S_p} - 1\right) \quad . \tag{23}$$

If, now, we make use of (19) and (20), we can write this

$$\tau_i = \frac{c_B\, H_i}{1 - \frac{1}{S_i}} \left\{ (1 + \nu_i)(1 - \frac{S_p}{S_i}) + \nu_i\, S^0\, (S_p - 1) \right\} \quad . \tag{24}$$

One can regard the transport in each column as made up of two parts:

$$\tau_i = \tau_i^{o} + \tau_i^{'} \tag{25}$$

where the first term on the right is the "normal" transport given by

$$\tau_i^{o} = c^* P_i \ , \tag{26}$$

while the second term is the "circulatory" transport, since it follows from Eq. (4) that

$$\sum_{i=1}^{n} \tau_i^{'} = 0 \ . \tag{27}$$

It follows readily from (24) that

$$\tau_i^{'} = \tau_i - c^* P_i = \frac{c_B H_i \ (S_i - S_p) \left[1 - \nu_i (S^o - 1)\right]}{S_i - 1} \ . \tag{28}$$

In the special case $S^o = 1$ (only one stage, or the top stage of a pyramid) one gets

$$\tau_i = c_T \left[P_i + \frac{H_i \ (S_i - S_p)}{S_p \ (S_i - 1)}\right] = c_T \left[P_i + H_i \frac{\frac{1}{S_p} - \frac{1}{S_i}}{1 - \frac{1}{S_i}}\right] \ . \tag{29}$$

Finally, it is instructive to compare (22) with the expression for the separation factor S_m which would be obtained if all the columns were operated independently and their products mixed together. Clearly, one would have

$$S_m = \frac{\sum_{k=1}^{n} S_k P_k}{\sum_{k=1}^{n} P_k} , \tag{30}$$

which involves a weighting factor, $P_k = H_k \nu_k$, that is in in general quite different from the corresponding weighting factor in (22).

2. <u>Average Properties</u>

Let us compare Eq. (15b) with the corresponding equation one would have if all the columns were identical and were operated at the same product rate. In the latter case, if we write the constants of any one column without any subscripts,

$$S = \frac{\varphi \beta}{\varphi + S^0 P} . \tag{31}$$

In making the comparison, one naturally takes

$$P = \frac{1}{n} \sum_{k=1}^{n} P_k . \tag{32}$$

Hence, for (31) and (15b) to be equivalent

$$\varphi = \frac{H + P}{\beta - 1} = \frac{1}{n} \sum_{k=1}^{n} \frac{H_k + P_k}{\beta_k - 1} \tag{33}$$

$$\varphi\beta = \frac{(H + P)}{\beta - 1} = \frac{1}{n} \sum_{k=1}^{n} \frac{(H_k + P_k)\beta_k}{\beta_k - 1} . \tag{34}$$

Subtracting (33) from (34), we get

$$H + P = \frac{1}{n} \sum_{k=1}^{n} (H_k + P_k)$$

whence, on the basis of (32),

$$H = \frac{1}{n} \sum_{k=1}^{n} H_k . \tag{35}$$

We see that the average H is just the arithmetic mean, or in other words, the H's of parallel columns combine additively.

To get K, we use (33) and write

$$\frac{1}{\beta - 1} = \frac{1}{n(H + P)} \sum_{k=1}^{n} \frac{H_k + P_k}{\beta_k - 1} . \tag{36}$$

From this one gets K:

$$K = \frac{(H + P)\,L}{\ln \beta} = \frac{(H + P)\,L}{\ln \left\{ 1 + \dfrac{n\,(H + P)}{\displaystyle\sum_{k=1}^{n} \dfrac{H_k + P_k}{\beta_k - 1}} \right\}} . \tag{37}$$

3. <u>Illustrations</u>

Let us restrict ourselves here to a single-stage system so that $S^{\theta} = 1$, and let us suppose that the group consists of only two columns. If we further suppose that $H_1 = H_2$, then Eq. (22) reduces to

$$S_p = \frac{\dfrac{S_1}{S_1 - 1} + \dfrac{S_2}{S_2 - 1}}{\dfrac{1}{S_1 - 1} \quad \dfrac{1}{S_2 - 1}} . \tag{38}$$

If one has a family of curves of S vs. ν for a single column, one can read off from it the values of S_1 and S_2 for any ν_1 and ν_2 and get S_p from (38).

From (26) and (29) one can get the "circulatory" transport

$$\tau_1' = -\tau_2' = \sigma_T \frac{H_1\,(S_1 - S_p)}{S_p\,(S_1 - 1)} .$$

The equivalent product rate is τ_1' / c_T.

In Fig. 1 are presented graphs for the case considered here: $H_1 = H_2$, with the further simplification $P_1 = P_2$. The two columns are characterized by $Y_1 = \ln S_{e1} = 0.35$, $Y_2 = \ln S_{e2} = 0.15$. Fig. 1 shows S_1, S_2, S_m and S_p as functions of $\nu_1 = \nu_2 = \nu$, so that one can compare the performance of the columns singly and together. Fig. 1 also includes a curve of $\frac{\tau_1'}{H_1 c_T}$ as a function of ν to show the relation between the circulatory transport and the product rate.

It will be seen from Fig. 1 that S_p is less than S_m, as was to be expected from the presence of the weighting factor $\frac{1}{S_k - 1}$ in the former, since this weights the poorer column more heavily. Suppose it is required to find ν for $S = 1.26$. From the graph one finds that it is <u>impossible</u> to obtain this value in parallel operation. In independent operation ($S_m = 1.26$) one finds $\nu = 0.6$. On the other hand for $S_1 = 1.26$, $\nu = 2.3$. It follows then that a single good column ($Y_1 = 0.35$) will produce about twice as much product as the good one and poor one ($Y_2 = 0.15$) together. Suppose next that it is required to find ν for $S = 1.22$. From the graph one gets for parallel operation $\nu = 0.5$, approximately. On the other hand, for $S_1 = 1.22$, $\nu = 3.3$. Hence the good column alone produces more than three times as much product as the good one and poor one in parallel.

We see then in the preceding cases that the presence of

the poor column reduces the efficiency both because of the fuel consumption associated with its operation and because of an actual decrease in the product rate. While it is true that the examples given represent somewhat extreme cases of difference in the properties of two columns, yet they can occur in practice. But even with smaller differences in the column constants the same tendency will be found -- a decrease in efficiency if the two columns are operated together, particularly if they are operated in parallel.

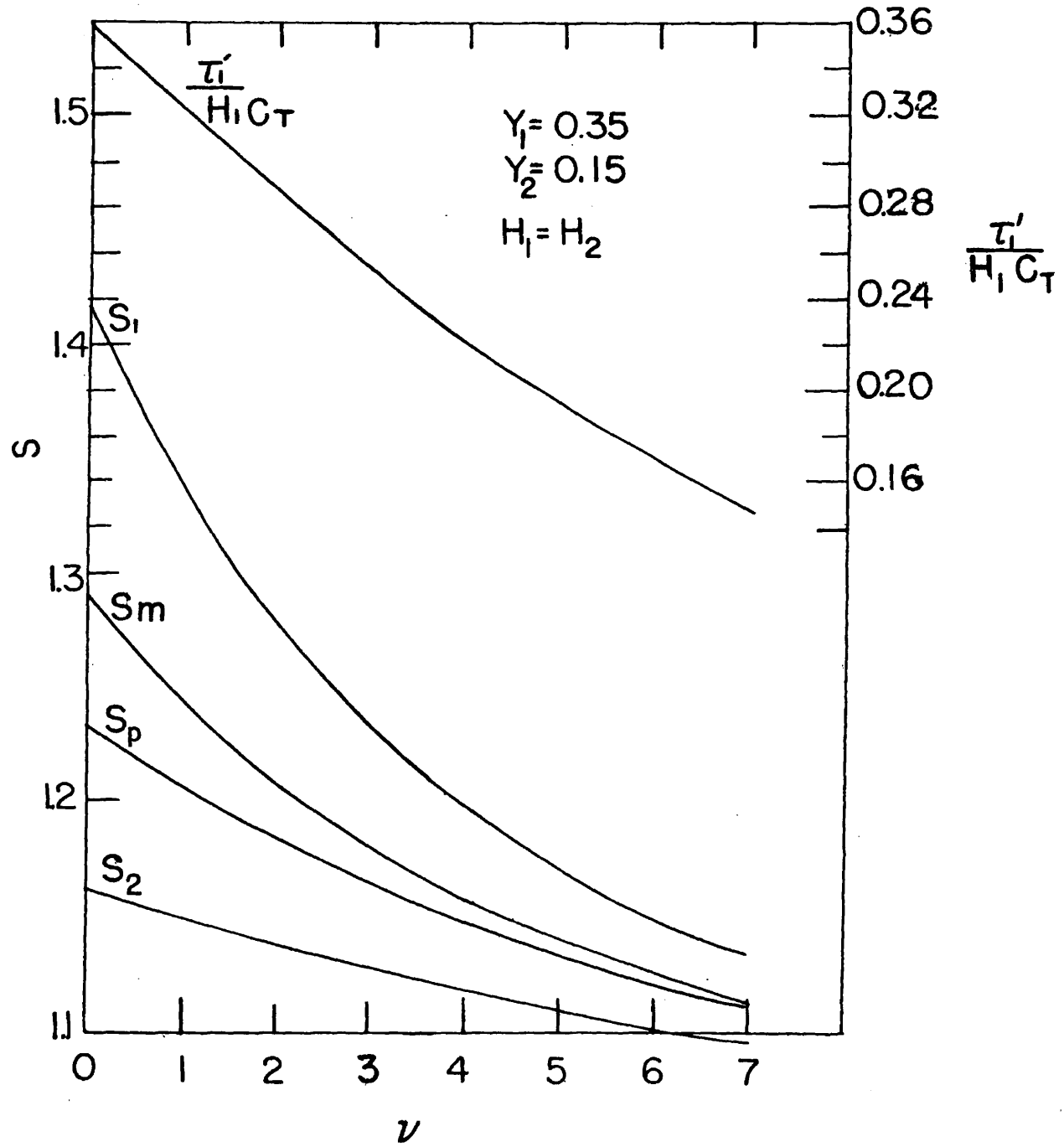
The conclusion to be drawn from the preceding is very clear:

Given a group of columns operating in parallel, it is important to weed out the poor ones, since the efficiency of the group will be increased thereby.

Chapter 10

Figure 1

Effect of using combinations of inhomogeneous columns on separation factor of product. S_1 refers to the performance of the good column ($Y = 0.35$) while S_2 refers to the bad column ($Y = 0.15$). S_m and S_p refer to the products obtained when the columns are connected together for mixed product and for parallel operation. τ_1' represents the circulatory transport rate in the latter case.



Theoretical chap 10 Fig. 1

APPENDIX

I. CRITICAL TEMPERATURE MEASUREMENT OF URANIUM HEXAFLUORIDE

Waldo E. Whybrew
James H. Tayman
Paul N. Kokulis

In determining the critical temperature of many substances, it is possible to use the visual method, observing the phenomenon of the actual disappearance of the meniscus of the liquid - gas demarcation line. This is based on the fact that, as the temperature of a liquid approaches the critical temperature, the density of the liquid approaches that of the saturated vapor. The first successful experiment was conducted on carbon disulfide by Cagniard de la Tour. The principle of this method is simple. A liquid is placed in a sealed tube and the temperature gradually raised above the critical. It may be necessary to try this experiment a number of times to determine the correct amount of material needed to give the critical pressure and temperature with the meniscus about half-way up the tube. When the proper amount has been determined, it is placed in the glass tube and sealed off. The temperature is slowly raised until the area around the meniscus becomes hazy, and the maniscus suddenly disappears, leaving the tube filled with a uniform fog. The pressure at which this occurs is known as the critical pressure.

A second method was devised by P.A. Bond and D.A. Williams (1931), in which a metal container was used, approximately half filled with liquid and supported at a small inclination to the horizontal, on a knife edge. A wire supporting the lower end was attached to the beam of a balance. The tube was placed in a heating jacket and the temperature was raised above the critical point. The balance was adjusted after time had been allowed for the material in the container to become uniform in density. The temperature was then allowed to drop slowly until the fluid separated into two phases. The liquid then ran down the tube, deflecting the beam balance. The temperature at which this happened was the critical temperature.

The method employed by the authors in their first experiments was a variation of the early visual procedure. Since the substance being investigated was corrosive to glass, the visual method was modified by the use of a metal container, viewed by means of an X-ray apparatus and a fluorescent screen. The screen showed the tube and the liquid as a dark shadow, with a lighter shadow for the gas phase.

The tube used was made of copper, 3/8" O.D., 1/32" wall, and about 5" long. Into its lower end was silver-soldered a 3' length of 1/8" O.D. nickel tubing of 0.060" bore. The nickel tubing was attached to a reservoir of

50 ml. capacity, made of nickel with a heavy wall. The reservoir, the 3' length of nickel tubing, and the critical-point tube were wound separately with heating elements of nichrome wire so that the temperature of each could be varied independently. The reservoir was below the critical-point tube and contained an amount of UF_6 in it which was chosen so that by varying the temperature of the reservoir it was possible to introduce into the critical-point tube the proper amount of material over the needed range of temperature and pressure required. An iron-constantan thermocouple was silver-soldered to the center of the critical-point tube, a Type-K potentiometer being used as the temperature indicating instrument. The cold junction was kept at $0^{\circ}C$ by means of crushed ice in a thermos bottle. The thermocouple was calibrated by standard tin, which melts within $1^{\circ}C$ of the critical point being determined.

The apparatus was arranged as follows: The X-ray machine was set up, adequately protected on all sides by lead shields. About 1 ft. in front of the X-ray tube was placed the critical-point tube, in front of a lead plate containing a slit 3/16" wide and 4" long. Next was a fluorescent screen, and then two plates of lead glass to protect the person observing the disappearance of the meniscus. By varying the voltage on the X-ray machine, it was observed that the meniscus could be seen better at

higher voltages. Hence the voltage used was 120 KV., the limit for this machine. The principal limitation on the accuracy of this experiment was that near the critical point where the meniscus disappeared, the contrast between liquid and vapor was exceedingly faint. However, two observers taking turns viewing it could check themselves and each other. The experiment was repeated several times, the critical temperature being approached from both above and below. From the results obtained by this experiment, one arrived at a critical temperature of 232.7°C ± 1.0°C.

In order to increase the accuracy and reliability of the data, a later set of experiments was run. In these experiments a higher voltage X-ray machine was used in order to produce a sharper change in intensity at the meniscus. The apparatus employed was modified somewhat from that used in the visual determinations. A 1/2" O.D., 1/32" wall, copper tube about 5" long was used. The lower reservoir previously used to adjust the amount of UF_6 in the tube was eliminated. Instead, with a few trials the proper amount of UF_6 was found, so that the meniscus would not disappear at the bottom or top before the critical temperature was reached. With a critical-point tube having a measured volume of 15 ml., it was found that 22 gm. of UF_6 was the right amount. Preliminary trials were run using a fluorescent screen; then pictures were made on X-ray film, prints from which are included as Fig. 1 of this section.

The meniscus could be seen at 232.4°C faintly and it could not be seen at 232.8°C. Hence the critical temperature was taken to be the average of these two, which is 232.6°C. This is 0.1°C lower than the value obtained by the visual method. By the amount of UF_6 in the tube and its volume, the critical density should be close to 22/15 = 1.47 gm/ml. The value 232.6°C is considered to be correct within ± 1.0°C.

II. PRESSURE-TEMPERATURE-VOLUME CHARACTERISTICS

George Y. Brokaw

In connection with the experimental and plant procedures it was highly desirable to have accurate data on pressure-volume-temperature characteristics for example, in predicting the pressures that occur during transfer operations, as well as in routine plant operations. Consequently, a set of measurements was carried out to determine the pressure-volume-temperature characteristics. This included measurements to determine the critical constants.

The measurement apparatus employed was as follows:

Two 3000 p.s.i. Be-Cu gauges were calibrated on a dead weight tester and then attached to a 1904 ml. nickel reservoir. This reservoir was 16" long, 3" in diameter with 1/4" thick walls. Variable temperature was provided by a heating element and measured by two thermometers located at the middle and at one end of the reservoir.

After thorough "conditioning", a suitable amount of UF_6 was introduced in the apparatus. The equipment was cooled and air evacuated.

The temperature was then gradually increased with observations of the corresponding pressure. On reaching maximum temperature, the container was cooled with observation

of pressure made during the cooling phase. By removing some UF_6, a similar curve could be obtained at a different density.

The first curve was obtained by permitting the temperature to come to equilibrium for about 2 hours for each point. It was then found that 10-15 minutes per point at a rise of 1 volt on the heater (usually 7-8°C) per point gave a curve which exactly coincided with the first. Therefore, the speed of obtaining points within the limits employed did not alter the characteristics of the results.

A dead weight calibration of the gauges after the experiment showed that a weighted average of the readings would fall within experimental error. Due to the fact that 3000 p.s.i. gauges were used, readings below 200 p.s.i. were not considered sufficiently precise for recording.

The thermometers were calibrated to 250°C, using a Bureau of Standards thermometer. The calibration correction values were small (< 1°C).

Correction to ρ due to change in volume of the storage chamber with temperature and pressure variations amount to 0.005 or less in the vicinity of the critical point, the effect of which is well within experimental error. The correction approaches 0.01 at 1500 p.s.i. and temperatures in excess of 200°C; and it approaches 0.027 at 3000 p.s.i. and 200°C or more. Due to the insignificance of these

corrections with regard to the purpose of the report, the magnitudes of their values are noted only.

Results

The direct results of the measurements are plotted in Fig. 2 in the form of curves showing pressure vs. temperature for various values of the density. For these curves, the points plotted were chosen at random from the experimental data, approximately in the ratio of one point out of every two measured on the straight portions and one out of every 20 on the vapor pressure curve. In all, 447 points were determined from which those shown were selected without discrimination.

By the use of values read off from the preceding graph it was possible to obtain a number of other plots.

Fig. 3 contains curves of the orthobaric densities of liquid and vapor as functions of the temperature. It also includes a curve of the mean of the two, which is found to be very nearly a straight line (law of rectilinear diameters). The critical temperature is at the point where the curves for the liquid and vapor join.

Fig. 4 consists of a family of isotherms, showing the dependence of the density ρ on the pressure P at various temperatures.

On the basis of the earlier measurements of critical temperature by means of X-rays and from the curves in Fig. 3, the critical temperature was taken as 232.5°C. From

the curve of mean density in Fig. 3, one gets at this temperature for the critical density, $\rho c = 1.41$ gm/cm^3, and for the critical molar volume, $V_c = 0.250$ liters.

III. VISCOSITY OF LIQUID URANIUM HEXAFLUORIDE

William N. Blatt

The viscosity was measured by flowing uranium hexafluoride through a tubing of known length and diameter. The pressure to drive the material came from a thermo syphon. The rate of flow was measured by heating the material to a constant temperature and extracting the heat in a calorimeter bath. Variations in pressure could be effected by connecting a container of material to the system and adjusting the temperature of the container.

Following are the values of the viscosity at various temperatures and pressures, calculated on the basis of Poiseuille's formula:

Visc.	Temp.	Pressure
10.35 millipoises	75.8°	3000 p.s.i.
6.89	153.5	3200
5.52	248.0	3000
5.05	250.0	1000
7.88	74.6	374
6.68	153.0	400

Karl Cohen, using an expression for the viscosity μ,

$$\mu = Ae^{\frac{\Delta F^* - P\Delta V^*}{RT}},$$

based on the theory of the liquid state, fitted the constants empirically to the above data and obtained the values:

$$A = 1.67\ 10^{-3} \text{ poises},$$
$$\Delta F^* = 1100 \text{ cal./mole},$$
$$\Delta V^* = 28 \text{ cm}^3,$$

R being the gas constant. It follows that Cohen's formula can be written

$$\mu = 1.67\ 10^{-3}\ e^{\frac{554 - 0.023\,P}{T}}$$

where T is in degrees Kelvin, and P is in lb/in^2.

IV. MEASUREMENT OF DIFFUSION COEFFICIENT OF URANIUM HEXAFLUORIDE

Nathan Rosen
Waldo E. Whybrew

1. Introduction

Since the ordinary diffusion coefficient plays an important role in determining column behavior, an experiment was carried out to measure this coefficient. The idea on which the measurement was based was in itself rather simple: the two halves of a long narrow tube were filled with material having two different concentrations of light constituent, and diffusion was allowed to take for a definite period of time with the tube kept in a constant-temperature bath. From the change in the mean concentration in each half of the tube, as determined by means of a mass spectroscope, one could calculate the diffusion coefficient. However, in carrying out this idea, certain difficulties had to be overcome; in particular, precautions had to be taken to avoid appreciable convection, which, if present, could mask the effect of diffusion.

In addition to the practical value of the measurement described here, it is believed that the work also has a certain amount of scientific interest. The diffusion coefficient measured is the coefficient for the diffusion of one isotope (the lighter one) into the other. However, in

the present case the isotopes concerned differ in mass by such a small percentage that the coefficient is essentially that of self-diffusion.

A. Experimental Work

The tubes used for the diffusion experiment were made from nickel tubing, 1/8" O.D. and 0.06" I.D., cut into 6-inch lengths, narrow tubing being used in order to reduce convection currents. Two such tubes, connected together by means of a close-fitting nickel sleeve, 5/16" O.D. and 1-1/2" long, and Lunkenheimer fittings, formed the "sample tube".

At the beginning of the experiment, the two halves of each sample tube were filled with material having two different concentrations of U-235. In filling a tube with material, it was necessary to prevent air pockets from being left in the tube. The tube to be filled was connected to a small container, in the form of a closed copper tube, 1/4" O.D., 3/16" I.D. and 4" long, containing about 8 gms. of uranium hexafluoride. To get rid of air in the system, the container was heated up until about 3 gms. of material had passed through the tube and escaped from the open end of the latter, whereupon the open end of the tube was quickly crimped and welded. Both tube and container were heated to about 200°C to render the material highly fluid. The tube was then immersed in a water bath having a

temperature of about 70°C and was kept there for about three minutes, after which dry ice was applied to the junction of the tube and the container to freeze the material there. (It was found that, if the tube was disconnected, weighed, connected again to the container, heated up to drive out the material and refilled as before while immersed in the 70°C bath, the weight of material in the tube was substantially the same as after the first filling, so that this method of filling gave essentially reproducible results.)

In the same way, the mate to this tube was filled from another small chamber containing material of a different concentration. When both tubes were ready, they were disconnected from the containers and, after it was verified that the material filling each tube was flush with the opening, the tubes were fitted into the nickel sleeve so that their open ends were in contact, and the Lunkenheimer fittings were made tight. Four sample tubes were made up in this way.

The two ends of each sample tube were bent into arcs of about 4" length and 4" radius, both in the same plane, so as to form a wide U-shaped figure. One purpose of having this shape was to maintain a continuous column of liquid in the sample tube during the diffusion process, the sample tube being kept in the constant-temperature bath in a vertical plane with the nickel sleeve at the bottom, so that

if any vapor formed, it would collect at the ends of the tube. Another reason for having this shape was that, when the sample tube was put into the constant-temperature bath, during the approach to temperature equilibrium the material at the bottom was cooler than that at the top because of the difference in wall thickness, so that convection was kept down. A thin wire was fastened between the two ends of the sample tube to facilitate handling it.

The constant-temperature bath, in which the samples were kept, consisted of a cylindrical copper vessel about 12" in diameter and 10" high, enclosed in a masonite box lined with 3 inches of cork. The vessel was covered with a copper lid suspended by chains from an insulating cover containing a 3" layer of Celotex. The stirrer motor was mounted on a brass plate resting on the insulating cover and separated from it by a 1" layer of sponge rubber to reduce vibration. The stirrer was of the perforated-cylinder type and was attached to the end of a vertical shaft extending down from the motor through suitable openings into the bath. For the bath liquid, Prestone was used because of its comparatively low vapor pressure. The main heating for the bath was provided by a copper coil covering almost the entire lateral surface of the copper vessel and carrying water under forced circulation from a large commercial constant-temperature bath, to be referred to as the auxiliary bath. Additional heating was provided by a

resistance-type heating element, the voltage across which was controlled by a Variac. The temperature was regulated by means of a bi-metallic thermostat in the auxiliary bath, controlling the heater, and a mercury thermostat in the main bath actuating the heating element through a sensitive relay. The temperature of the main bath was measured by means of a Beckmann thermometer, the readings of which could be estimated to 0.001°C; the auxiliary bath had an ordinary mercury-in-glass thermometer, the reading of which could be estimated to 0.01°C.

To hold the sample tubes in the bath, a wooden box was made of 1/2" stock, 8" long, 3" wide and 6" high on the outside, with a hinged cover on top. The box, covered with a protective paint coating, was weighted down with copper plates attached to top and bottom and was lined with sheet copper. The inside of the box was divided into 4 compartments, each about 1/2" wide, by means of vertical sheet-copper partitions extending lengthwise. The design of the box was intended to reduce fluctuations in the temperatures of the sample tubes, since such fluctuations could bring about mixing.

Before the constant-temperature bath was put into service, it underwent extensive observation and adjustment. The purpose was to adjust the temperature of the heating water and the current in the heating elements to obtain a temperature of about 70°C and at the same time reduce the

temperature fluctuations in the bath to a minimum, and also to study the behavior of the bath temperature after adjustments had been made to assure the stability of conditions.

When it appeared that the behavior of the constant-temperature bath was reasonably reliable and that no significant improvement was to be obtained through further adjustment of the bath equipment, the diffusion run was started. The four sample tubes filled with material, as previously described, were put into the four compartments of the wooden box, each sample tube being in a vertical plane, with the nickel sleeve at the bottom and the two ends, or horns, at the top, and with the axis of symmetry in the vertical direction. The box was lowered gently into the bath and allowed to fill with bath liquid. The covers of the box and of the bath were closed, and the bath was allowed to reach temperature equilibrium, which required several hours.

During the diffusion period, there was a temperature oscillation in the bath with an amplitude of the order of 0.01°C and a period of four or five minutes. The corresponding variation in the temperature of the sample tubes in the box could be expected to be considerably less. There was also a slow drift in temperature, of irregular period, with an amplitude of approximately 0.04°C. During the removal of a sample tube, there was a temperature drop of

the order of 0.1°C. Furthermore, on the morning of the 21st day, after all but one sample tube had been removed, it was discovered that during the previous night the thermostat of the auxiliary bath had stuck, resulting in a rise in temperature of the main bath of about 0.45°C. This was corrected over a period of several hours and did not appear to have introduced any irregularity in the final results. The mean value of the bath temperature was about 69.5°C.

The sample tubes were removed from the bath, one at a time, at the end of 4, 12, 20 and 28 days. In removing a sample, the procedure was as follows: With the sample tube kept in its vertical orientation, the middle part, i.e., the nickel sleeve, was at once plunged into a dry ice and alcohol mixture in order to freeze the liquid at the junction of the two halves before any appreciable mixing occurred there.

After all the sample tubes had been taken out of the bath the two halves of each tube were separated. The contents of each half were thoroughly mixed and were analyzed for the light constituent on the mass spectroscope. From the results of the analyses, the diffusion coefficient was calculated, as will be described later.

2. Theory

If a substance diffuses in a long narrow tube of uniform cross-section, the differential equation governing

the diffusion process is given by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (0 \leqslant x \leqslant a) , \tag{1}$$

where c is the concentration of the substance at the time t and at a distance x from one end, D is the diffusion coefficient, and a is the length of the tube. If the tube is closed at both ends, since the diffusion current is proportional to $\frac{\partial c}{\partial x}$, we have as boundary conditions

$$\frac{\partial c}{\partial x} = 0 \quad (x = 0, a) . \tag{2}$$

Let us suppose that initially $(t = 0)$

$$c = c_1^{\,o} \ (0 \leqslant x \leqslant \tfrac{a}{2}), \quad c = c_2^{\,o} \ (\tfrac{a}{2} \leqslant x \leqslant a) , \tag{3}$$

where $c_1^{\,o}$ and $c_2^{\,o}$ are constants, and $c_1^{\,o} > c_2^{\,o}$. Then the solution can be expressed in the form

$$c = \frac{1}{2} (c_1^{\,o} + c_2^{\,o}) +$$

$$+ \frac{2}{\pi} (c_1^{\,o} - c_2^{\,o}) \sum_{n^{odd}} \frac{\sin \frac{n\pi}{2} \cos \frac{n\pi x}{a}}{n} e^{-\frac{n^2 \pi^2 Dt}{a^2}} \tag{4}$$

Let us denote by $\bar{\sigma}_1$ and $\bar{\sigma}_2$ the mean values of $\underline{\sigma}$ over the two halves of the tube,

$$\bar{\sigma}_1 = \frac{2}{a}\int_0^{\frac{a}{2}} \sigma dx \ , \qquad \bar{\sigma}_2 = \frac{2}{a}\int_0^{\frac{a}{2}} \sigma dx \ . \tag{5}$$

By using (4), one finds that

$$\bar{\sigma}_1 = \frac{1}{2}(\sigma_1{}^o + \sigma_2{}^o) +$$

$$+ \frac{4}{\pi^2}(\sigma_1{}^o - \sigma_2{}^o)\sum_{n^{odd}} \frac{1}{n^2} e^{-\frac{n^2\pi^2 Dt}{a^2}} \ , \tag{6a}$$

and

$$\bar{\sigma}_2 = \frac{1}{2}(\sigma_1{}^o + \sigma_2{}^o) +$$

$$+ \frac{4}{\pi^2}(\sigma_2{}^o - \sigma_1{}^o)\sum_{n^{odd}} \frac{1}{n^2} e^{-\frac{n^2\pi^2 Dt}{a^2}} \ , \tag{6b}$$

so that

$$\frac{1}{2}(\bar{\sigma}_1 + \bar{\sigma}_2) = \frac{1}{2}(\sigma_1{}^o + \sigma_2{}^o) = \bar{\sigma} \ . \tag{7}$$

If we write

$$\Delta c = \bar{c}_1 - \bar{c}_2 , \qquad \Delta c^o = c_1^o - c_2^o , \tag{8}$$

it follows that

$$\frac{\Delta c}{\Delta c^o} = \frac{8}{\pi^2} \sum_{n^{odd}} \frac{1}{n^2} e^{-\frac{n^2 \pi^2 Dt}{a^2}} . \tag{9}$$

If $\underline{t}$ is sufficiently large so that one can neglect all but the first term in the series of Eq. (9), which will be the case if, say $\frac{Dt}{a} \sim 0.04$, or larger, then one can solve this equation for $\underline{D}$, obtaining

$$D = \frac{a^2}{\pi^2 t} \ln \left(\frac{8}{\pi^2} \frac{\Delta c^o}{\Delta c}\right) , \tag{10}$$

which will be valid provided $\frac{\Delta c^o}{\Delta c} \sim 2$, or larger.

3. Data and Results

The average effective length of a sample tube (corresponding to $\underline{a}$ in the preceding section) was 24.4 ± 0.5 cm., the estimated uncertainty taking account of the tapering of the bore near the crimped ends. The analyses of the concentrations initially and at various times are given in Table I, in the form of $\frac{\Delta c}{\bar{c}}$. By means of Eq. (10), $\underline{D}$ was calculated for t = 12, 20, and 28 days; this equation

was not valid for the case t = 4 days. The results are included in Table I, which also indicates the uncertainties in various quantities due to uncertainties in the analyses.

The final result is taken as

$$D = (1.90 \pm 0.13) \quad 10^{-5} \text{ cm}^2/\text{sec.} \tag{11}$$

In order to show the relation between the calculated and the measured values, in general, and for the case t = 4 days, which we have thus far not used, in particular, Fig. 1 presents a graph of $\frac{\Delta c}{c}$ vs. $\underline{t}$, as calculated from Eq. (9), using the value (11) for $\underline{D}$, as well as the corresponding experimental points, represented by the $\underline{x}$'s. The agreement between the experimental points and the curve, as calculated with a suitable choice of the one constant $\underline{D}$, appears to be satisfactory.

4. Discussion

It is obvious that the value of the diffusion coefficient as obtained in the present work, if it is in error, is more likely to be too high rather than too low. For if any disturbing factor were present that tended to bring about mixing, its effect on the concentration distribution would be more or less equivalent to that of an increase in the rate of diffusion. To be sure, the experimental conditions were intended to eliminate, or at least reduce, such disturbances, but one cannot be sure to what

extent success in this matter was achieved. However, if such disturbances were present in the experiment, they must have been small, since the value of the coefficient obtained was small, and hence would be expected to depend strongly on the experimental conditions, so that changes in these conditions should lead to marked changes in the final results. Now, before the work described here was carried out, some preliminary experiments had been run, based on the same principle but involving a number of differences in apparatus and procedure. The preliminary experiments will not be described here, but the important fact is that final value for the diffusion coefficient obtained in those experiments turned out to agree with that of the present work to within about the estimated experimental error. This is a good indication that the measured value is that of the true diffusion coefficient.

It is interesting to note that Cohen[2], using an approximate formula for the diffusion coefficient of a liquid given by Powell, Roseveare and Eyring[3], predicted a value of about 5×10^{-5} cm^2/sec. According to the present measurements, the value at 69.5°C turns out to be smaller, but the order of the magnitude is that predicted by Cohen. At the temperatures in the working space of a column, the mean value should be considerably higher.

1. W.J.C. Orr and J.A.V. Butler, J.Chem.Soc., 1273 (1935).
2. Karl Cohen, Columbia Report No. A-531, Feb., 1945.
3. R.E. Powell, W.E. Roseveare, and H. Eyring, Ind.Eng. Chem. 33, 430 (1941).

TABLE I

t (days)	Analysis, $\Delta\sigma/\bar{\sigma}$	$D \cdot 10^5$ (cm^2/sec)
0	0.577 ± .010	
4	0.453 ± .008	
12	0.335 ± .006	1.95 ± .17
20	0.283 ± .004	1.76 ± .11
28	0.211 ± .004	1.99 ± .10

V. CORROSION OF NICKEL BY URANIUM HEXAFLUORIDE AT ELEVATED TEMPERATURES

In order to determine the rate of corrosion by UF_6 at elevated temperatures -- obviously of great importance in column work -- the following experiment was carried out:

Three nickel strips were each washed with carbon tetrachloride, dried, and weighed. The strips were sealed inside a welded nickel container. The container and the strips were then subjected to treatment with fluorine at 375°C for two hours. Uranium hexafluoride of sufficient quantity (1-1/2 lbs.) to give a density of 1 gm/cm^3 was distilled into the container, which was then heated for one hour at 375°C, the pressure in the container being therefore about 1500 lb/in^2. The UF_6 was then distilled out and fluorine was again passed through for an hour at 375°C. The container was cooled and its contents washed with H_2O, NH_4OH, HCl and H_2O. This was done for the purpose of removing uranyl fluoride formed by reaction of UF_6 with nickel oxide produced during the welding process. The container and its contents were dried, and fluorine was again passed through for an hour at 375°C. Sufficient UF_6 was again distilled in to give a density of 1 gm/cm^3. The container and its contents were then maintained at a

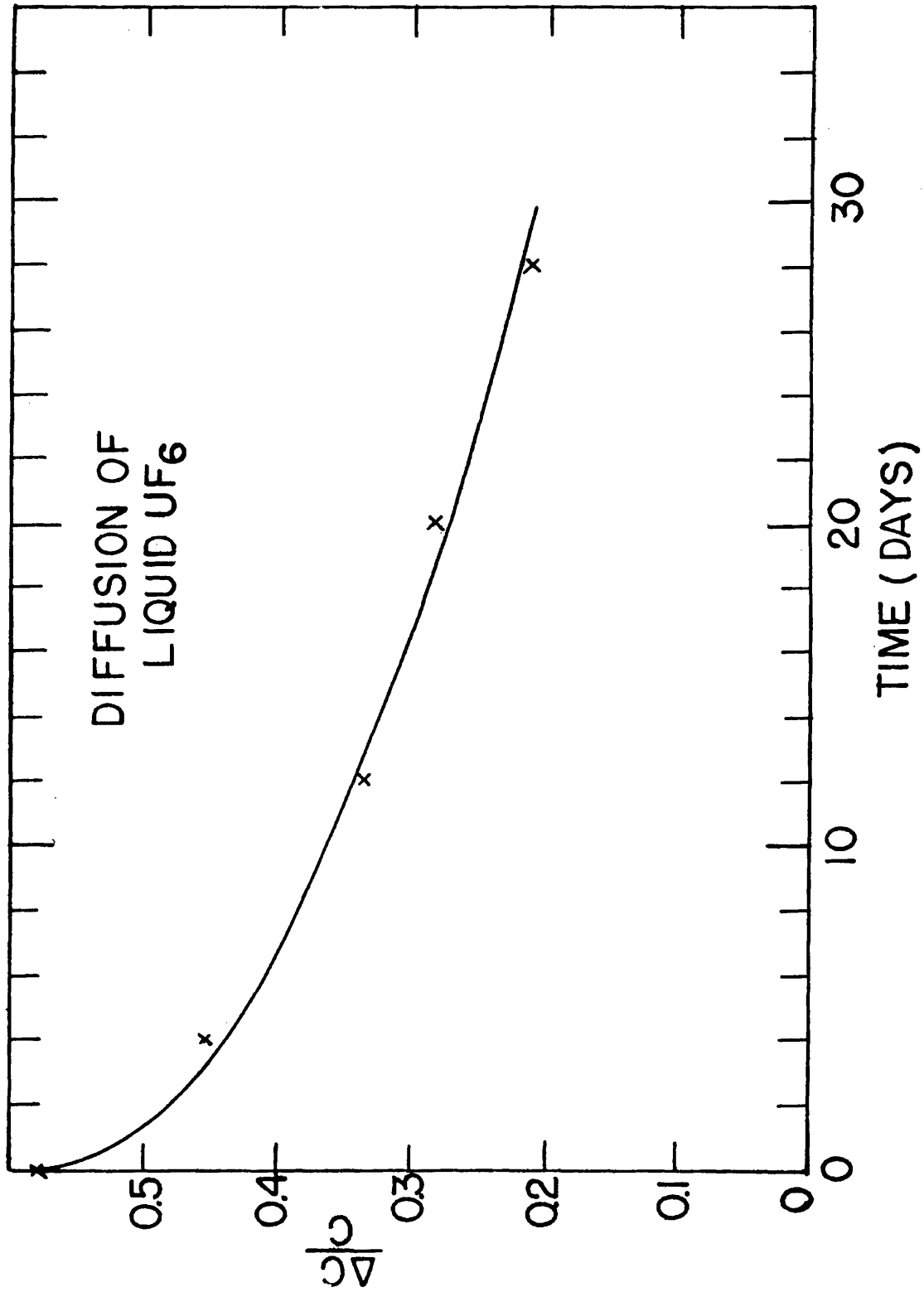
temperature of 350°C for seven days. At the end of that time, the UF_6 was removed by distillation and the nickel container was cut apart. Examination of the container and the strips showed no loose uranium compound of any kind, either on the strips or in the container. The strips were found to show gains in weight of 0 mg, 1 mg, and 4 mg. Three other strips, treated in the same way, except that they were subjected only one day to UF_6 at 350°C showed losses in weight of 15 mg, 12 mg, and 10 mg. On this basis, the effect of running for six days at 350°C is an average increase in weight of 14 mg per strip. Since the exposed surface area of each strip was about 1/3 sq.ft., the observed gain in weight represents 7 mg day sq.ft.

Subsequently the experiment was repeated with other strips, the changes in weights for strips exposed to UF_6 at 350°C for various periods being given in the following table. It should be emphasized that the data refer to different strips cut out of the same piece of nickel sheet

	1 day	2 days	7 days	35 days
	- 9 mg	+ 2 mg	+ 4 mg	- 5 mg
	- 15	0	+ 1.0	- 6
	- 13	- 15	0	+ 13
				+ 12
Average	- 12 mg	- 4.3 mg	+ 1.7 mg	+ 3.5 mg

It appeared from the data that after two days there was little change in weight. Since the area of each strip was about 1/3 sq.ft., the corrosion rate must have been less than 2 mg. sq.ft., and probably less than 1 mg sq.ft. per day.

Since the nickel in the above experiments was exposed to the UF_6 at a temperature appreciably higher than that to be found in a column, it was concluded that the rate of corrosion of nickel in a column would be too small to have any practical significance.



Appendix Fig 5

CAPTIONS

Appendix

Figure 1

X-ray photographs of a tube containing UF_6 at temperatures approaching critical. Near the critical point the density of the gas phase approaches that of the liquid. Critical temperature of UF_6 lies between 232.4°C and 232.8°C.

Figure 2

Pressure temperature curve for UF_6 at various densities. Gauge pressure is plotted against Centigrade temperature.

Figure 3

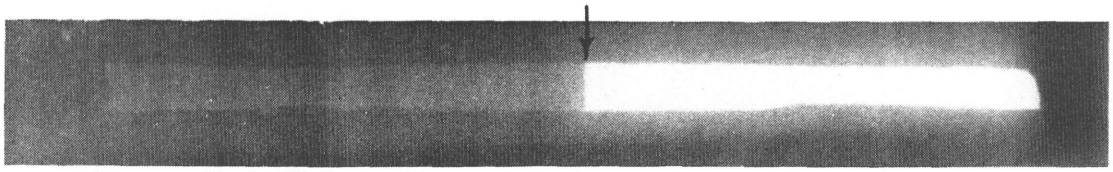
Orthobaric density of UF_6. Straight line represents average of liquid and vapor densities. Intersection of line with curve gives an easy way of determining the critical density.

Figure 4

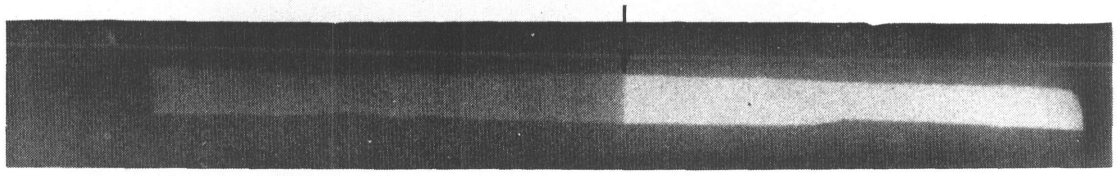
Pressure-density curves for UF_6.

Figure 5

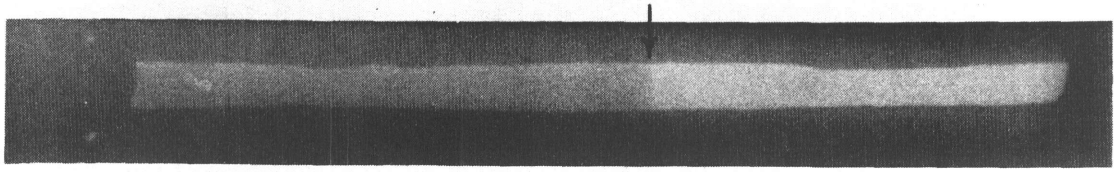
Diffusion which occurs when two liquid UF_6 samples of different U-235 concentration are connected together. Δc is the difference in concentration of the two samples.



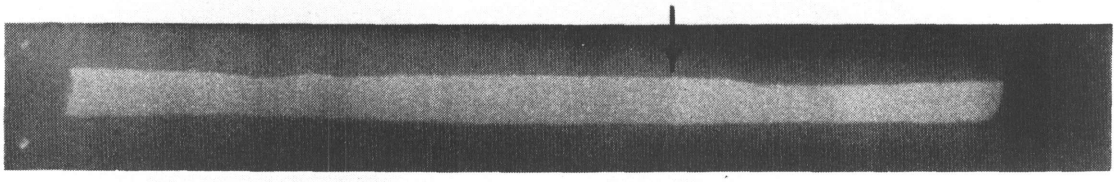
TEMP. 226.6°C



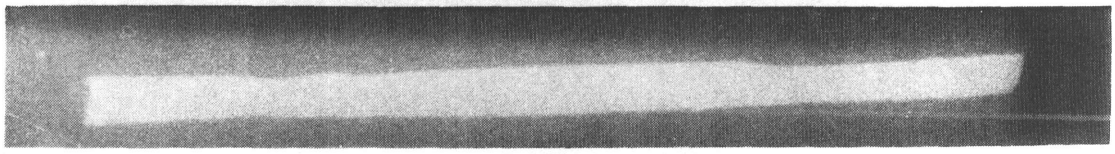
TEMP. 229.9°C



TEMP. 231.4°C

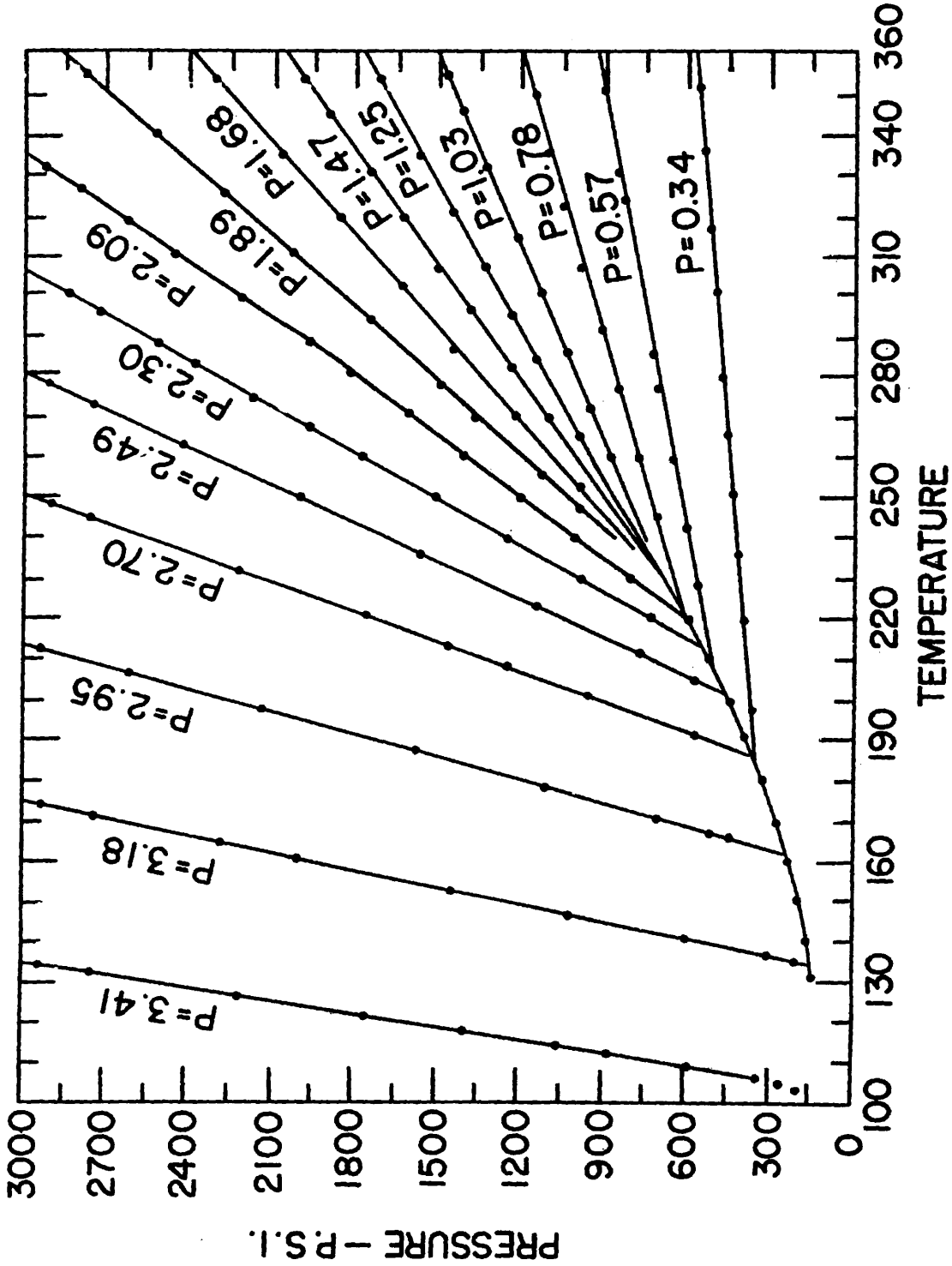


TEMP. 232.4°C

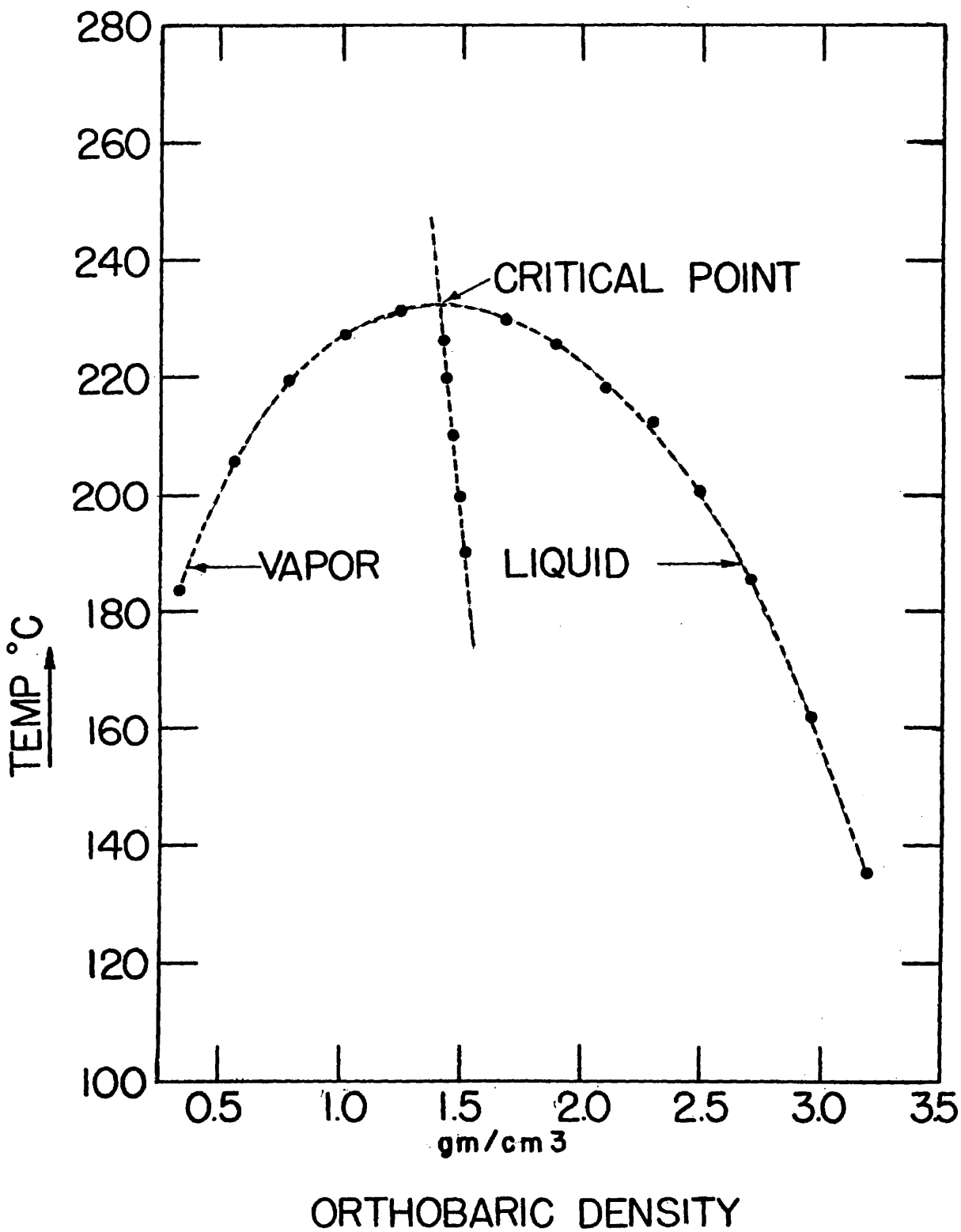


TEMP. 232.8°C

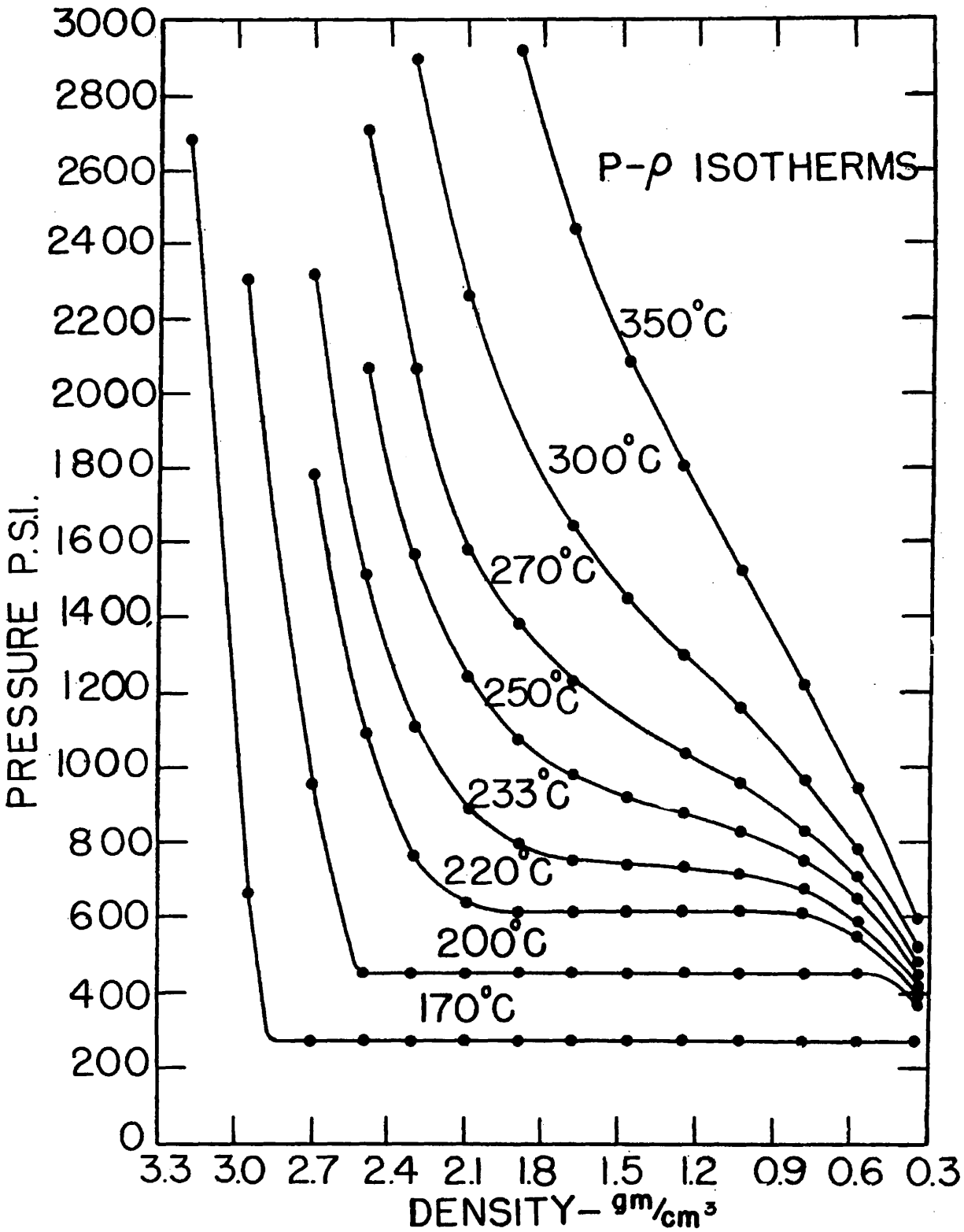
Appendix Fig. 1



Appendix Fig 2



Appendix Fig.3



Appendix Fig.4

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